

**Targeted Synthesis and Characterization of Nanostructured Silicate
Building Block Supports and Heterogeneous Catalysts with
Tungsten(VI) or Zirconium(IV) Centers**

A Dissertation
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Michael Edward Peretich
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DEDICATION

This dissertation is dedicated
to everyone who has supported me over the years

especially

my wife

Amanda Peretich

my parents and in-laws

Ed and Irene Peretich

J.B. and Jill Anderson

my siblings

Melissa and Austin Vigil

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ABSTRACT

Catalysts play a vital role in almost every aspect of our lives and are used in the production of fuels, polymers, chemicals, foods, and pharmaceuticals. One challenge facing the heterogeneous catalysis community is the targeted synthesis of dispersed catalyst ensembles.

The Barnes research group has developed a general methodology for the synthesis of nanostructured silicate building block supports and heterogeneous catalysts. This methodology provides researchers with the ability to control the dispersion of surface functionality, the dispersion of metal cation centers, the number of linkages from the metal cation center to the support, the surface area of the support, and the porosity of the support. This dissertation describes work aimed at synthesizing and characterizing nanostructured silicate building block supports and heterogeneous catalysts.

Nanostructured silicate building block supports were synthesized by reacting SiCl_4py_2 with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The resulting supports contained spatially isolated Me_3Sn groups and the density of Me_3Sn groups was targeted by varying the stoichiometric ratio of reactants. The stoichiometric ratio of reactants also controlled the surface area and porosity of the supports.

Nanostructured heterogeneous catalysts with isolated tungsten(VI) or zirconium(IV) centers were synthesized by reacting a limiting amount of a metal chloride with either $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ or a premade silicate building block support. Two types of catalyst ensembles were targeted: embedded and surface. Embedded ensembles were successfully targeted using WOCl_4 and ZrCl_4 while the reaction between WCl_6 and the building block did not result in the preparation of the targeted ensemble. However the resulting ensemble was thoroughly characterized even though the targeted ensemble was not produced. In all three cases a single type of catalyst ensembles was synthesized and a high surface area silicate support was generated around the embedded ensembles without disrupting the ensemble itself. Surface ensembles were successfully targeted using ZrCl_4 . The reaction between the tungsten chlorides (WOCl_4 and WCl_6) and the premade support did not result in the preparation of the targeted ensembles however the resulting ensembles were thoroughly characterized.

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CHAPTER 1. INTRODUCTION

Importance of Catalysis

Catalysis plays an essential role in almost every facet of our daily lives and its contributions to present day society cannot be overstated. The production of fuels, polymeric materials, nanomaterials, chemicals, foods, and pharmaceuticals all involve catalysis. Catalysis plays an important role in almost all biological reactions (e.g. enzymes) and plays a role in the reduction of harmful pollutants that are present in automobile emissions and the waste streams from fossil fuel power plants.[1]

What is a Catalyst?

A catalyst is a material that increases the rate of a reaction without being consumed during the reaction. A catalyst increases the reaction rate by lowering the activation energy (E_a) of the chemical reaction. Therefore a catalyzed reaction has a lower energy barrier than the same reaction when not catalyzed (Figure 1).

The role of a catalyst during a reaction can be broken up into three unique steps (binding, transformation, and release) and the entire process is commonly referred to as a catalytic cycle. A catalytic reaction begins when the catalyst chemically combines with a reactant (i.e. binding). The catalyst then transforms the bound reactant into an intermediate which can be converted into other intermediates and finally into products (i.e. transformation). The last step of the catalytic cycle involves the catalyst releasing the product and returning to its initial state (i.e. release). Once the catalyst has returned to its initial state it can combine with another reactant and go through the cycle again. Good catalysts can cycle through a catalytic cycle over and over again. Ideally, a catalytic cycle continues without limit, but in reality, undesired changes can render the catalyst less active with continued use, and so many catalysts must be periodically regenerated or replaced.[1]

An example of a well known application of catalysis in everyday life is the catalytic converter found on almost every automobile (Figure 2). Catalytic converters transform harmful emissions (unburned fuel, carbon monoxide, and nitrogen oxides) to less harmful emissions (carbon dioxide, nitrogen, and water). Ideally the catalytic converter on an automobile should never need to be replaced because a catalyst is not consumed as it performs its function even though the amount of exhaust that is treated is many times the weight of the catalyst.

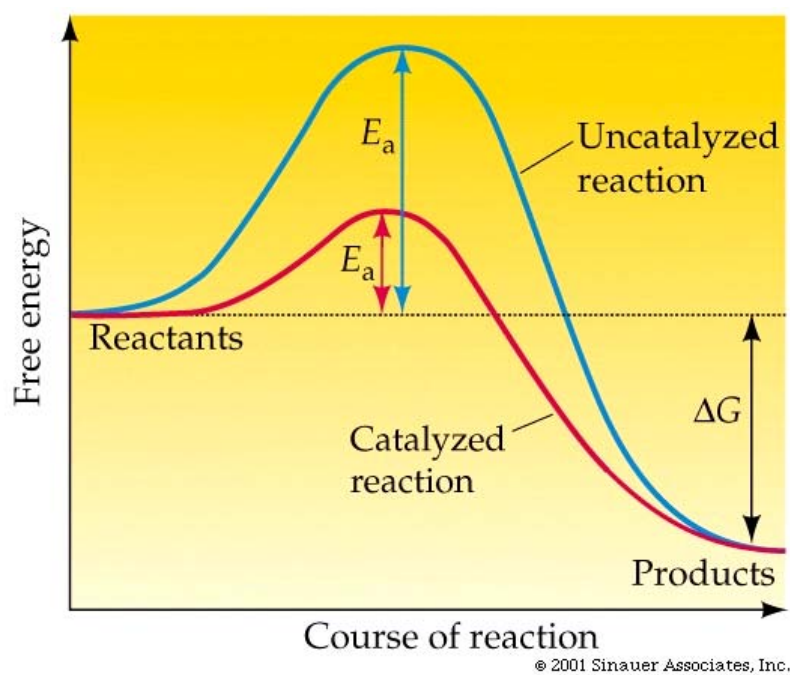


Figure 1: Illustration of the energy diagram of an uncatalyzed (blue) and catalyzed (red) reaction showing that a catalyzed reaction has a lower activation energy (E_a) than the same reaction when not catalyzed (Figure was reproduced from Ref [2]).

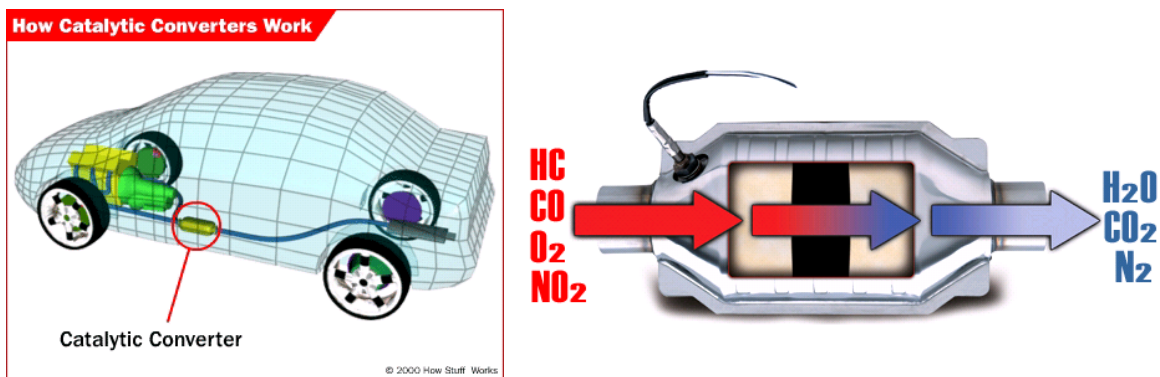


Figure 2: Illustration of the location of a catalytic converter in an automobile (left) (Figure was reproduced from Ref [3]) and a diagram showing the reactants (unburned fuel, carbon monoxide, oxygen, nitrogen oxide) and products (water, carbon dioxide, nitrogen) of a catalytic converter (right) (Figure was reproduced from Ref [4]).

Types of Catalysts

Catalysts can be classified as homogenous, where the catalyst and the substrate are in the same phase (e.g. liquid substrate reacting with a catalyst that is dissolved in solution), or heterogeneous, where the catalyst and the substrate are in different phases (e.g. gaseous or liquid substrate reacting with a solid catalyst).[5]

Homogeneous versus Heterogeneous Catalysts

This section will explore four of the main fundamental differences between homogeneous and heterogeneous catalysts.

First, homogeneous catalysts are in general more well-defined (i.e. better characterized) than heterogeneous analogues, having benefited greatly from the use of several molecular characterization tools (e.g. NMR spectroscopy and X-ray diffraction) that allow scientists to precisely define at least the stable precursors to active species. Researchers typically cannot use only one characterization tool to clearly define heterogeneous catalysts. In fact heterogeneous catalysts generally require the use of several characterization tools to construct a piecewise model of the active species.

Second, heterogeneous catalysts generally exhibit greater thermal stability than homogeneous analogues. Heterogeneous catalysts frequently involve reactions that occur over a broad range of temperatures (room temperature to 1000°C) while most homogeneous catalysts are stable only below 200°C.[6] The use of catalysts at high reaction temperatures leads to high rates of reaction which means increased catalytic activity. Therefore heterogeneous catalysts are better suited than homogeneous catalysts for use in reactions requiring higher temperatures.

Third, a major technological advantage of heterogeneous catalysts is they are easy to recycle and separate from the products.[5,7] This technological advantage results from the catalyst and products being in separate phases while the separation of homogeneous catalysts from the products tends to be a more complicated procedure since the catalysts is in the same phase as the products. The ease of separation from reaction products that is associated with heterogeneous catalysts results in lower processing costs therefore the chemical industry tends to favor heterogeneous catalysts when the expense of separating the catalyst and the products is a large portion of the overall cost of the process.

Finally, the ligands found in homogeneous catalysts can be tailored to a much higher degree than is typically possible in the case of heterogeneous catalysts. Thus, it is possible to vary the steric and electronic features of homogeneous catalysts much easier than heterogeneous catalysts.[5] For example, metallocene complexes are commonly used as homogeneous catalysts and the sterics and electronics of the cyclopentadienyl (Cp) ligands can easily be modified. As shown in Figure 3, pentamethylcyclopentadienyl (Cp*) ligands are sterically larger and donate more electron density to the metal center than Cp ligands. Linking two Cp ligands together producing *ansa*-Cp ligands which allows one to tailor both the sterics and electronics in addition to opening up access to the metal center. The ability to control the sterics and electronics of ligands, as in the case of Cp ligands for homogeneous metallocene catalysts, is a component of heterogeneous catalyst synthesis that is significantly lacking. Therefore heterogeneous catalysts cannot be modified as easily as their homogeneous analogues which impedes the ability of researchers to tailor heterogeneous catalysts to specific reactions. As a result, the pursuit of new synthetic methodologies that can be used to prepare tailored heterogeneous catalysts has been a longstanding challenge for the heterogeneous catalysis community.

The Active Site and the Catalyst Ensemble

To understand how to synthetically tailor heterogeneous catalysts one must first consider the active site of a heterogeneous catalyst, which is the specific entity that needs to be tailored. The active site of a heterogeneous catalyst is more than the catalytically active metal cations in or on the support. In fact everything in the immediate environment of the metal cations can influence the observed catalytic behavior. As shown in Figure 4, typically a metal cation will be bound to a metal oxide support (e.g. SiO₂ or Al₂O₃) by the terminating oxygen ligands on the surface of the support. Three siloxide ligands (M-O-Si) serve to hold the metal cation in place on the surface of a silica support as well as contribute to the overall charge balance between the positive charge on the metal cation and the negative charges on the siloxide groups shown in Figure 4. Furthermore, the spatial arrangement of the metal-to-support linkages will influence the electronic character of the metal cation and thereby its reactivity. To fill out the coordination

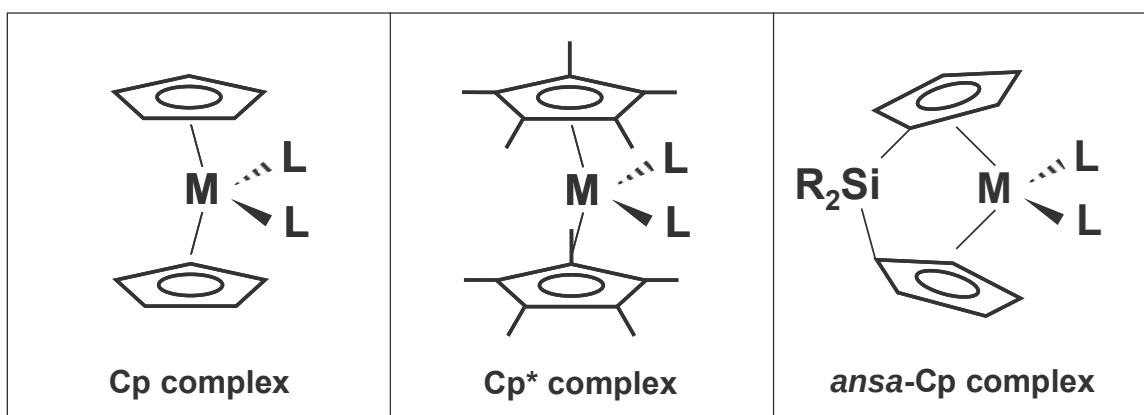


Figure 3: Illustration of metallocene complexes with different Cp ligands.

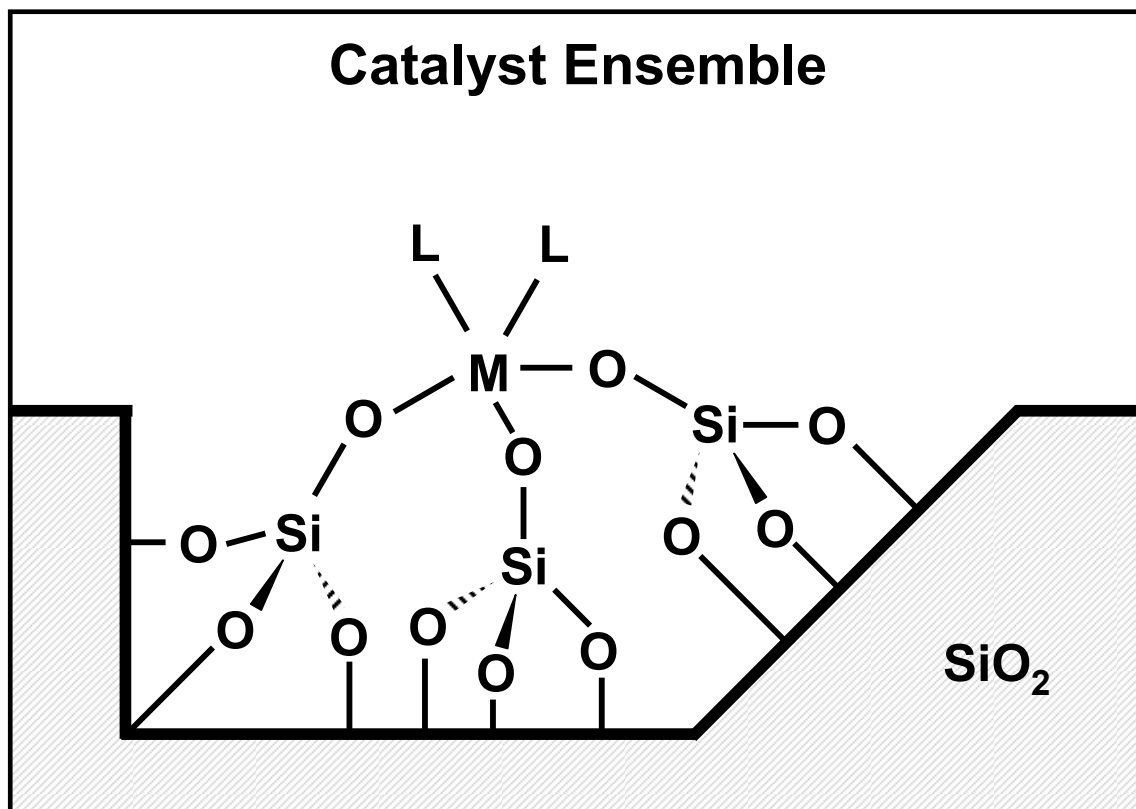


Figure 4: Illustration of a catalyst ensemble showing the ligands (L), metal-to-surface binding interactions (M-O-Si), and the support (SiO_2).

sphere of the metal cation, a number of additional ligands (M-L), which can be charged or neutral, may also be present. The metal cations, ligands, and metal-to-support linkages that are directly associated with the binding and transformation of a substrate into a product will be referred to as the “catalyst ensemble”. ***One of the primary focuses of this dissertation is the preparation of tailored catalyst ensembles where one can control all of the necessary components of the catalyst ensemble (metal cation, ligands, and metal-to-support linkages).***

The Surface Functionality of a Support

To understand how catalytically active metal cations are linked to the support one must first consider the surface functionality initially present. The surface functionalities that are present on the support play a significant role in attachment of metal cations to the support. Metal oxides are some of the simplest supports used to synthesize heterogeneous catalysts and contain some of the simplest surface functionality. The surface of silica, one of the most common metal oxide support materials, consists of siloxane bridges ($\equiv\text{Si-O-Si}\equiv$) and silanol groups ($\equiv\text{Si-OH}$). Three types of silanol groups (isolated, vicinal, or geminal) generally exist on the surface of silica (Figure 5).[8,9] Typical untreated metal oxide supports contain high densities of surface hydroxyl groups and it is well known that the hydroxyl groups tend to cluster together.[10] Thermal protocols are commonly used to remove potential interferences of physisorbed water as well as reduce the number of surface hydroxyl groups via dehydration and reconstruction of the surface.[8,11-13] For example, heating silica to 500°C will cause the dehydration of neighboring hydroxyl groups to form Si-O-Si bonds and reduce the density of silanol groups to ~ 1 per nm^2 . Metal cations can become attached to the support when one or more of its ligands react with the surface functionality (typically a hydroxyl group) of the support. The heterogeneity of the surface of a metal oxide support makes it difficult to know exactly what active site is formed. The pursuit of procedures that can be used to control the surface functionalities present on the support has been a longstanding challenge for the heterogeneous catalysis community. ***Another primary focus of this dissertation is the preparation of tailored supports where one can target specific densities of the surface functionality.***

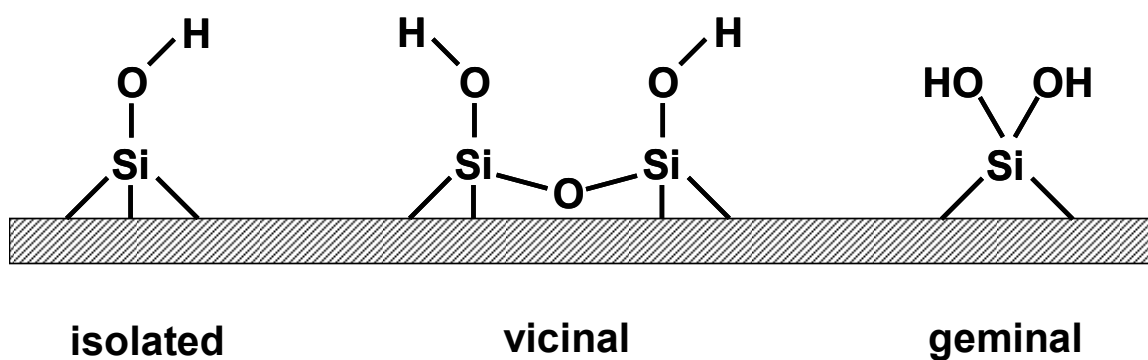


Figure 5: Illustration of the three types of silanol groups.

The Porosity of a Support

Lastly, to understand how to maximize the accessibility of the catalyst ensembles one must be able to control the surface area and porosity of the material. Heterogeneous catalysis is inherently a surface or interfacial phenomena and therefore high surface area porous supports are generally used as heterogeneous catalysts in order to maximize the rate of a catalytic reaction. High surface area porous materials can have hundreds of square meters per gram of material (typically 100-1000 m²/g) meaning that a few grams of the material could have the internal surface area of several football fields (the area of a football field is approximately 5500 m²). The pursuit of procedures that can be used to control the surface area and porosity of supports and heterogeneous catalysts has been a longstanding challenge for the heterogeneous catalysis community. ***Another primary focus of this dissertation is the preparation of tailored supports where one can control the surface area and porosity of the support.***

Traditional synthetic methodologies that are used to prepare heterogeneous catalysts clearly illustrate some of the challenges facing the heterogeneous catalysis community. These challenges include the lack of synthetic control with respect to the catalyst ensemble, the surface functionalities present on a support, the surface area of the support, and the porosity of the support. To understand how to gain synthetic control one must first understand some of the traditional synthetic methodologies and consider the shortcomings of these methodologies.

Traditional Synthetic Methodologies

Traditionally, heterogeneous catalysts have been prepared using a number of synthetic procedures.[5,8,9,14-23] In general, these procedures can be divided into two groups: those in which the deposition of the catalytically active metal cations occurs during the synthesis of the material and those in which the catalytically active metal cations are deposited onto a pre-existing support. Methods that deposit the active metal cations during the synthesis of the material generally produce catalytically active metal cations that are classified as framework or embedded centers. As shown in Figure 6, metal cations that end up occupying framework positions in the support generally have multiple links to the support. Methods that deposit the active metal cations onto a pre-existing support generally produce catalytically active metal

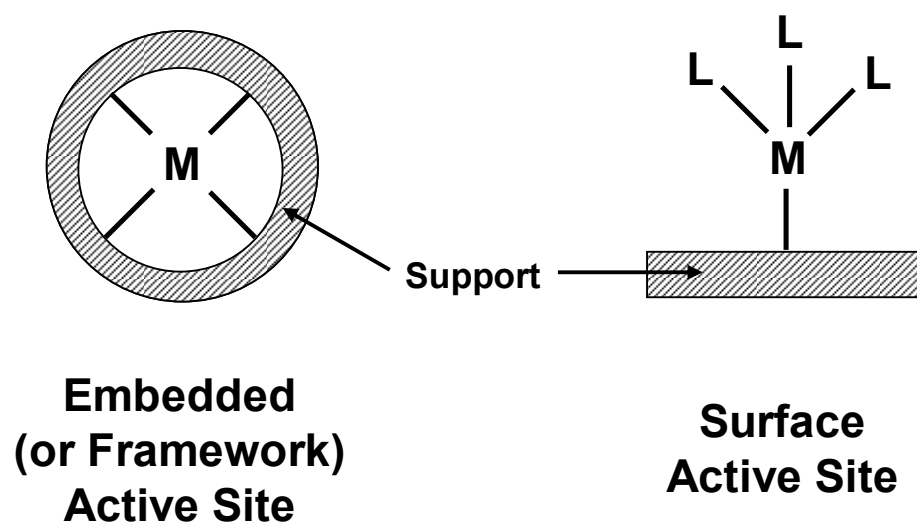


Figure 6: Generic illustration of an embedded and a surface active site.

cations that are classified as surface centers. As shown in Figure 6, metal cations that end up occupying locations on the surface of the support generally have fewer links to the support, and in the extreme, may only have only one link to the support.

The following sections will discuss in more detail some of the traditional synthetic methodologies used to prepare heterogeneous catalysts.

Supports and Heterogeneous Catalysts with Embedded Active Sites

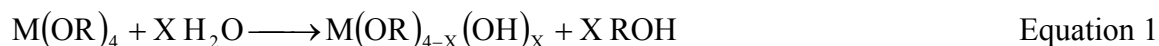
Traditional methods used to prepare embedded active sites include sol-gel, templating, nonhydrolytic sol-gel, and hydrothermal processes which will be discussed in more detail in the following sections.

Sol-Gel Process

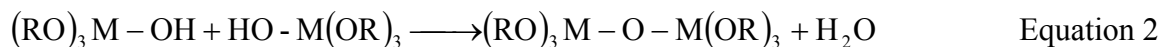
The sol-gel process is probably one of the most common procedures used to prepare supports and heterogeneous catalysts because the materials (chemicals, apparatus, etc) are inexpensive, the reactions are simple, and the required reaction conditions are mild (i.e. temperatures less than 100°C). A sol-gel process can be divided into six steps: preparation of a sol, hydrolysis, condensation, formation of a gel, ageing, and drying.[16,24]

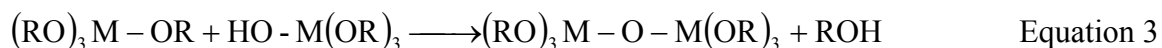
A typical sol-gel process begins with the active site precursor being dissolved in an aqueous solution. Metal alkoxides are generally used as the metal precursors in sol-gel processes because they react readily with water and are relatively inexpensive which helps minimize the cost of the process.[16,24]

In the presence of water, metal alkoxides hydrolyze to form metal hydroxides. Hydrolysis (Equation 1) occurs when at least one of the alkoxide groups is transformed to hydroxide groups.



Two complexes containing hydroxide ligands (Equation 2) or a hydrolyzed molecule and a molecule containing an alkoxide ligand (Equation 3) then link together via a condensation reaction that produces water or an alcohol.[16,24] Hydrolysis and condensation represent a very complicated series of coupled reactions which are difficult to control. Therefore it is difficult to tailor the ligands and metal-to-support linkages (i.e. the catalyst ensemble) using the sol-gel process.



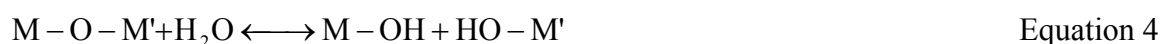


The combination of hydrolysis and condensation reactions will continue to build larger and larger molecules until a gel is formed. Gel formation occurs when a molecule reaches macroscopic dimensions so that it extends throughout the solution.[16,24]

Once a gel forms it can be aged before drying. Ageing is the further cross-linking of unreacted sites after gelation occurs. Ageing can result in a significant increase in the surface area and porosity of the final material.

The final step of the sol-gel process is drying of the gel. Drying is the process by which the solvent is removed from the sol-gel product. If the drying occurs via evaporation under normal conditions the resulting material is classified as a xerogel. This drying process gives rise to capillary pressure that can cause the collapse of the pore structure. An aerogel is produced when a wet gel is placed in an autoclave and dried under supercritical conditions. This drying process does not produce capillary pressure and therefore there is relatively little collapse of the pore structure.[16,24]

Even though the sol-gel process is one of the most common synthetic techniques for making metal oxides there are several disadvantages associated with the process. A drawback is that the condensation step can be reversible which means that even if the desired pattern of linkages is formed initially, it can still be lost as the system anneals itself (Equation 4).



Another drawback arises when using the sol-gel process to prepare mixed metal oxides (e.g. TiO_2/SiO_2 or ZrO_2/SiO_2). In the case of mixed metal oxides, the dispersion of a metal in the final product is influenced by the relative rates of homocondensation (formation of M-O-M or Si-O-Si) versus heterocondensation (formation M-O-Si) for the reactants involved. Controlling the hydrolysis and condensation rates can be rather difficult in the sol-gel process. This is true for mixed metal oxides like TiO_2/SiO_2 and ZrO_2/SiO_2 . Both zirconium and titanium alkoxides are more reactive than silicon alkoxides.[25] Therefore homocondensation, i.e. the formation of Ti-O-Ti, is favored over heterocondensation, specifically the formation of Ti-O-Si, in a mixed metal oxide system like TiO_2/SiO_2 . The degree of homogeneity of the final material will depend on the ability to favor heterocondensation. Several strategies have been reported in the literature to compensate for the differences in reactivity of titanium and silicon alkoxides. One strategy

involves hydrolyzing the silicon alkoxide before adding the titanium alkoxide because silanols are more reactive than silicon alkoxides.[26] Another strategy involves using acetic acid which decreases the reactivity of the titanium alkoxide and acts as a catalyst for the hydrolysis and condensation reactions.[27] A third strategy involves using large bulky titanium alkoxides to decrease the reactivity of the titanium alkoxide.[28] All three strategies are reported to produce amorphous powders containing a homogeneous distribution of titanium sites.

Summary of Sol-Gel Process

The sol-gel process suffers from a lack synthetic control with respect to the active site even though it is probably one of the most common procedures used to prepare supports and heterogeneous catalysts. The number of linkages that a metal cation forms to a support as well as the dispersion of the surface functionality on the support and metal cations throughout the support are not easily controlled using the sol-gel process. Also simple first order sol-gel processes offers little control of the surface area and porosity of the final material. The sol-gel process can be used to prepare amorphous porous materials but it is not ideal for the preparation of tailored supports and heterogeneous catalysts.

Templating Process

Templated mesoporous materials represent a subset of the materials prepared using the sol-gel process. Templated mesoporous materials typically are high surface amorphous materials with ordered pore structures. The amorphous nature of the pore walls makes the hydrothermal stability of these mesoporous materials lower than that of related zeolites.

The templates used to produce these materials can be divided into two groups: hard or soft. Hard templates normally possess well-defined shapes and voids which can be in the form of channels, pores, or connected hollow space. Anodic aluminum oxide membranes and silica are typical examples of hard templates.[29] On the other hand soft templates usually consist of organic surfactants, polymers, and even biological viruses, which are relatively flexible in shape.[29] Figure 7 illustrates the general process that is used to synthesize templated mesoporous silica, typically a soft template approach. Initially a surfactant (the soft template) is added to an aqueous solution where it forms micelles. The micelles then self-assemble into a specific arrangement, which is followed by the addition of the silica precursor. Silica then forms

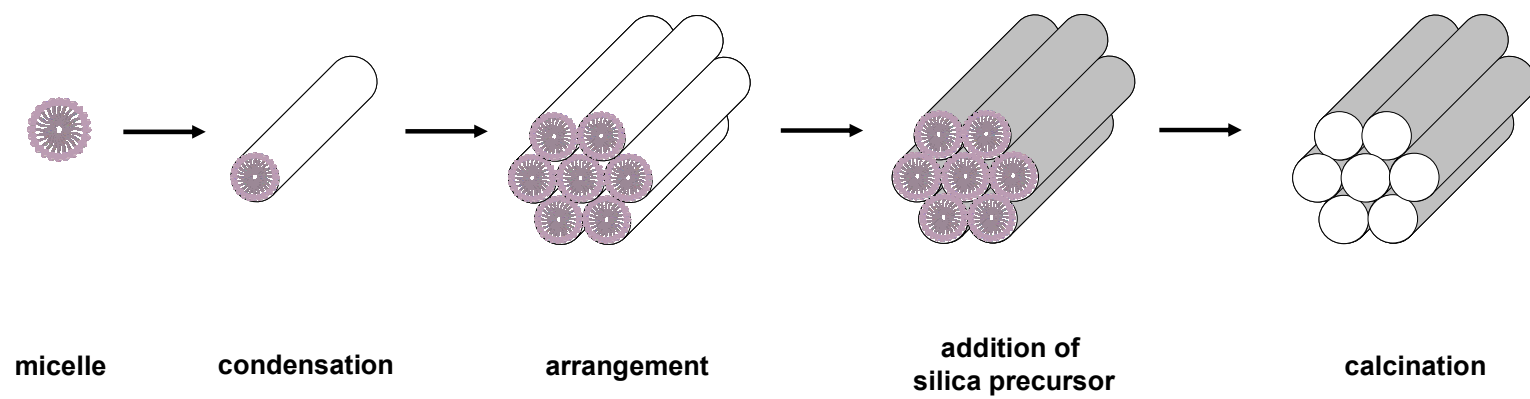


Figure 7: Illustration of a templating process using a soft template.

around the template micelle assemblies. Finally the template is removed either by calcination at high temperature or repeated washing resulting in a high surface area mesoporous silica with ordered porosity.

The two most common examples of templated mesoporous supports are MCM-41 (MCM = Mobil Crystalline Material)[17] and SBA-15 (SBA = Santa Barbara Amorphous).[19] Both supports are synthesized using soft templates. SBA-15 is synthesized using nonionic surfactants, specifically amphiphilic triblock copolymers, while MCM-41 is synthesized using cationic surfactants, specifically quaternary ammonium salts.[17,19]

Three different structures of MCM materials have been identified and are shown in Figure 8.[30] MCM-41 has an ordered hexagonal structure, MCM-48 has an ordered cubic structure, and MCM-50 has an ordered lamellar structure.[31] The ratio of surfactant to silicon precursor influences the structure of the resulting material. MCM-41 is produced when the ratio is less than 1, MCM-48 is produced when the ratio is greater than 1, and MCM-50 is produced at even larger ratios.[32,33]

Similar to MCM materials, several different structures of SBA materials have been identified. SBA-15 has an ordered 2-dimensional hexagonal structure, SBA-2 and SBA-12 have ordered 3-dimensional hexagonal structures, SBA-1, SBA-16 and SBA-11 all have ordered 3-D cubic structures.[34,35]

Metal cations ($M = \text{Ti, V, Zr, Mo, Sn, W, Pt, Au, etc}$) can be incorporated into the framework of templated mesoporous silicas such as SBA-15[36-42] and MCM-41[43-53] during synthesis which is known to result in the production of high surface area heterogeneous catalysts. There is little if any control of the dispersion of the metal cations in these materials which exhibit highly ordered pore structures.

Summary of Templating Process

Templating produces mesoporous materials and enhances the mass transport properties of the materials but it does not provide any benefits with respect to synthetic control of the surface functionality or active site. The number of linkages that a metal cation forms to a support as well as the dispersion of the surface functionality on the support and the metal cations throughout the support are not easily controlled using templating processes, especially when calcination is used

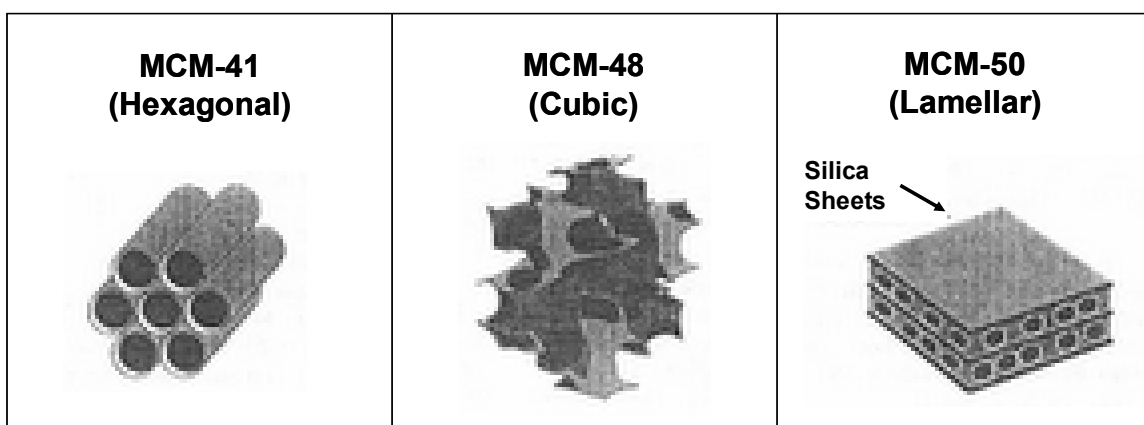


Figure 8: Illustration of the pore structure of three MCM materials (MCM-41, MCM-48, and MCM-50) (Figures obtain from Ref [31] and Ref [54]).

for template removal. Templating processes can be used to prepare high surface area mesoporous supports and heterogeneous catalysts but they are not ideal for the preparation of tailored supports and heterogeneous catalysts.

Nonhydrolytic Sol-Gel Process

A sol-gel process is classified as nonhydrolytic when the oxygen donor is not water and more specifically water is not present at any point during the process. Similar to sol-gel processes both metal oxides (i.e. supports) and mixed metal oxides (i.e. heterogeneous catalysts) can be synthesized using nonhydrolytic sol-gel processes. Metal precursors are typically linked together via a condensation reaction between two different metal precursors bearing two different functional groups (i.e. metal alkoxide, metal halide, metal carboxylate, etc) by eliminating a small organic molecule (i.e. alkyl halide, ether, ester, etc) (Equation 5).



M-OR = metal alkoxide

M-X = metal alkoxide, metal halide, metal carboxylate

RX = alkyl halide, ether, ester

One of the main advantages of nonhydrolytic sol-gel processes is that the condensation reaction is generally considered irreversible. One disadvantage is the necessity for the complete exclusion of water which means moisture-sensitive techniques are required for these syntheses.

Nonhydrolytic sol-gel process may be classified according to the nature of the metal precursor (halide, alkoxide, etc), the nature of the oxygen donor (alkoxide, alcohol, ether, etc) or the nature of the predominant molecule eliminated (alkyl halide, ether, ester, etc). The latter will be used in the brief overview of the three most common nonhydrolytic sol-gel condensation reactions (i.e. alkyl halide, ether, and ester elimination) presented here.

Alkyl Halide Elimination

Alkyl halide elimination, the condensation between metal halides (M-X such as SiCl₄, TiCl₄, ZrCl₄, AlCl₃) and metal alkoxides (M-OR such as Si(OPrⁱ)₄, Ti(OPrⁱ)₄, Zr(OEt)₄, Al(OPrⁱ)₃) produces an alkyl halide (R-X such as ethyl chloride, isopropyl chloride), as shown in Equation 6.[18,55,56] Alkyl halide elimination is probably the most common nonhydrolytic sol-gel condensation reaction even though the activation barrier for this process is larger than the corresponding hydrolytic process.[18]

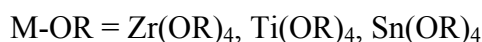
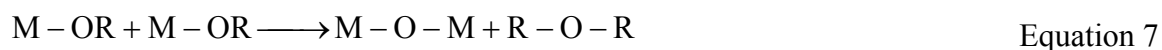


Typically reaction temperatures around 100°C are required for the synthesis of metal oxides and transition metal oxides using alkyl halide elimination.[18] Primary and secondary R groups are not ideal when synthesizing silica because a Lewis acid catalyst, such as FeCl₃, AlCl₃, TiCl₄, ZrCl₄, or BCl₃, is needed to catalyze the condensation reaction.[57,58] Therefore tertiary R groups as well as allyl and benzyl groups appear to be the best candidates because the tertiary carbocations required in the mechanism for condensation are more stable than when primary or secondary R groups are involved.[59]

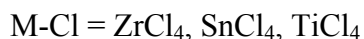
In the case of mixed metal oxides (SiO₂-MO_x), the reactivity of the silicon precursor is increased by the presence of the metal precursor which acts as a Lewis catalyst. Thus mixed metal oxides are possible because the metal precursor serves as both a reagent and a catalyst for the heterocondensation (M-O-Si formation).[56]

Ether Elimination

Ether elimination, the condensation between two metal alkoxides (M = Zr, Ti, Sn; R = methyl, ethyl, isopropyl, n-butyl, benzyl) involving the release of an ether (R-O-R = dimethyl ether, diethyl ether, diisopropyl ether, di-n-butyl ether, dibenzyl ether), is shown in Equation 7.[60,61]



One or both of the metal alkoxides can be generated in situ by reacting the corresponding metal halide (M-Cl such as ZrCl₄, SnCl₄, TiCl₄) with an alcohol (ROH such as MeOH, EtOH, ⁱPrOH, ⁿBuOH, benzyl alcohol) as shown in Equation 8.[60,61] This can be useful if the metal alkoxide is expensive or is not commercially available.

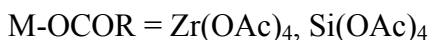
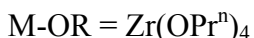


ROH = MeOH, EtOH, ⁱPrOH, ⁿBuOH, benzyl alcohol

When a metal alkoxide is generated in situ there is a chance that alkyl halide elimination could occur before ether elimination (i.e. the metal halide reacts with a metal alkoxide before two metal alkoxides react). Generally alkyl halide elimination occurs at lower temperature than ether elimination. Both alkyl halide and ether elimination produce M-O-M bonds so in the end it may not matter exactly which condensation reaction occurs.

Ester Elimination

Ester elimination, the condensation between metal alkoxides (M-OR such as Zr(OPrⁿ)₄) and metal carboxylates (M-OCOR such as Zr(OAc)₄, Si(OAc)₄) involving the release of an ester, is shown in Equation 9.[18,62] One reason why this is the least common of the three procedures is because this condensation reaction appears to be a slow process requiring several days at refluxing conditions.[62] Another reason this procedure is less common is that few metal carboxylates are commercially available.



Summary of Nonhydrolytic Sol-Gel Process

Nonhydrolytic sol-gel processes provide a variety of condensation reactions that can be used to synthesize porous metal oxides (supports) and mixed metal oxides (heterogeneous catalysts) however nonhydrolytic sol-gel processes suffer from the same problems as sol-gel processes. The number of linkages that a metal cation forms to a support as well as the dispersion of the surface functionality on the support and the metal cations throughout the support are not easily controlled using nonhydrolytic sol-gel processes. Also the nonhydrolytic sol-gel process offers little control of the surface area and porosity of the final material. Nonhydrolytic sol-gel process can be used to prepare amorphous porous materials but they are not ideal for the preparation of tailored heterogeneous catalysts.

Hydrothermally Process

Hydrothermal synthesis refers to high temperature reactions involving water in sealed reaction vessels above ambient temperature and pressure (aqueous media above 100°C and 1 bar).[63] Zeolites are examples of the materials prepared using hydrothermal processes.[15]

Zeolites

Zeolites are among the most important materials in the chemical industry with a multitude of technical applications which includes heterogeneous catalysis. Zeolites are crystalline aluminosilicates built from TO_4 tetrahedra ($\text{T} = \text{Si}, \text{Al}$) that are arranged in such a manner that the pores present in these materials are of molecular dimensions. Typically, the pores found in zeolites have diameters in the range of 4-12 Å. Each zeolite structure type features a unique micropore system with the sizes and shapes of the micropores being determined exclusively by the crystal structure of the zeolite. Currently, more than 170 different zeolite structure types have identified with several new discoveries occurring every year. Figure 9 illustrates the pores and molecular scaffolding in two common zeolite structure types, BEA and MFI.

Zeolites can be used as either supports or heterogeneous catalysts. One major drawback of zeolites is that they are microporous materials. In numerous cases, the sole presence of micropores imposes significant limitations on the range of reactions that are efficiently catalyzed by zeolites.[14] For example, titanium silicalite-1 (TS-1) (Ti in MFI type zeolite, pore diameter = 5.5 Å) readily catalyzes the epoxidation of 1-hexene in aqueous H_2O_2 but does not catalyze the epoxidation of cyclohexene. Cyclohexene is too large to fit into the pores of TS-1 and consequently cannot be epoxidized using TS-1. On the other hand, titanium-zeolite beta (Ti-β) (Ti in BEA type zeolite, pore diameter 7.6 Å) can catalyze the oxidation of both cyclohexene and 1-hexene with aqueous H_2O_2 in methanol. Cyclohexene can fit into the larger pores of Ti-β and therefore can be oxidized by Ti-β.[64]

Single Site Heterogeneous Catalysts

Single site heterogeneous catalysts are a subset of heterogeneous catalysts that have gained much attention over the past few decades. A single site heterogeneous catalyst is a solid where the catalytically active metal sites are well-defined and all are identical.[5]

In a single site catalyst, all the active sites carrying on catalysis are identical. In talking about an active site, it is important to clearly define exactly what is being referenced. The single sites consist of a defined number of atoms (one or more) and should be structurally well-characterized.[5,22,65]. These sites are both spatially and electronically isolated from one

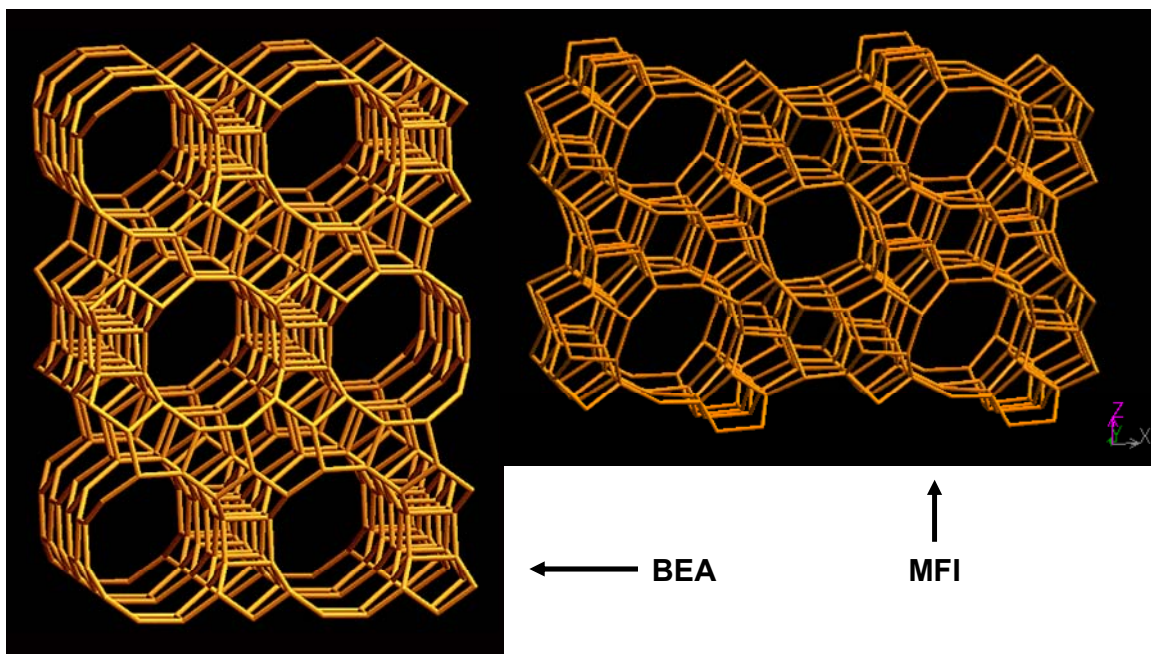


Figure 9: Illustration of two types of zeolite structures (BEA and MFI) (Figure was reproduced from Ref [66]).

another. Each active site has the same energy of interaction between it and a reactant as every other active site.[5,7] Another advantage, a direct consequence of spatial isolation and same energy of interaction, is that such catalysts are readily amenable to almost all of the common characterization techniques (e.g. NMR, IR, XAS, etc).[7] Single site heterogeneous catalysts are similar to homogeneous catalysts since they both are thought to have spatially isolated sites and are “ideal” samples for standard characterization techniques.

Several examples of what are thought to be single site heterogeneous catalysts can be found in the literature with TS-1 and tin-zeolite beta (Sn-β) being two classic examples of such catalysts.[67-71] TS-1 and Sn-β are two different silicate based zeolites in which a small percentage of the tetravalent framework silicon atoms have been replaced with tetravalent titanium or tin. Even though both materials are considered single site heterogeneous catalysts, the substituted metal cations actually occupy more than one framework position in the host zeolite material. In the case of TS-1, Ti^{4+} ions are preferentially substituted into the T8 and T10 sites of the MFI structure (Figure 10).[72] In the case of Sn-β, Sn^{4+} ions are preferentially substituted into the T5 and T6 sites of the BEA structure (Figure 11).[67]

In addition to the substituted metal cations occupying multiple framework positions, it is known that both catalysts contain more than one potential active site. In the case of TS-1, two sites, $\text{Ti}(\text{OSi}\equiv)_4$ and $\text{Ti}(\text{OSi}\equiv)_3(\text{OH})$, are known to coexist in the material (Figure 12).[73] The $\text{Ti}(\text{OSi}\equiv)_4$ active site is generally the more abundant site in the material. In the case of Sn-β, the material initially contains a single Sn site, $\text{Sn}(\text{OSi}\equiv)_4$, but it has been reported that the real active species is produced in-situ when one of the Sn-O-Si linkages is hydrolyzed to produce $\text{Sn}(\text{OSi}\equiv)_3(\text{OH})$ active sites (Figure 12).[74]

In spite of there being more than one type of potential active site in each material and that the metal cations occupy multiple framework positions, both TS-1 and Sn-β are referred to as the stereotypical examples of single site heterogeneous catalysts. Traditional methods that are used to prepare heterogeneous catalysts, and even single site heterogeneous catalysts, really do not provide the necessary synthetic control to produce a single type of active site.

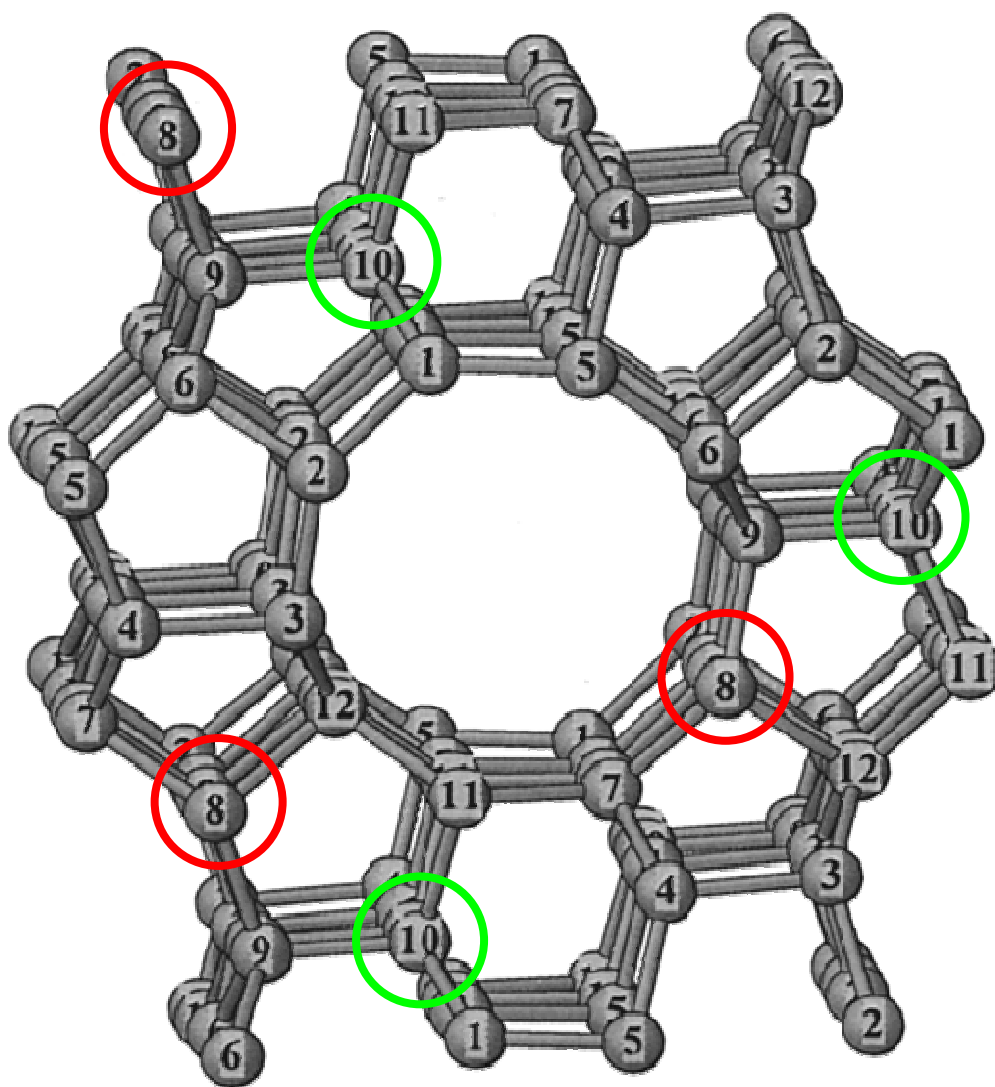


Figure 10: Illustration of the silicalite pore structure and the framework sites (T8 circled in red, T10 circled in green) for titanium substitution in the zeolite scaffolding (Figure was reproduced from Ref [72]).

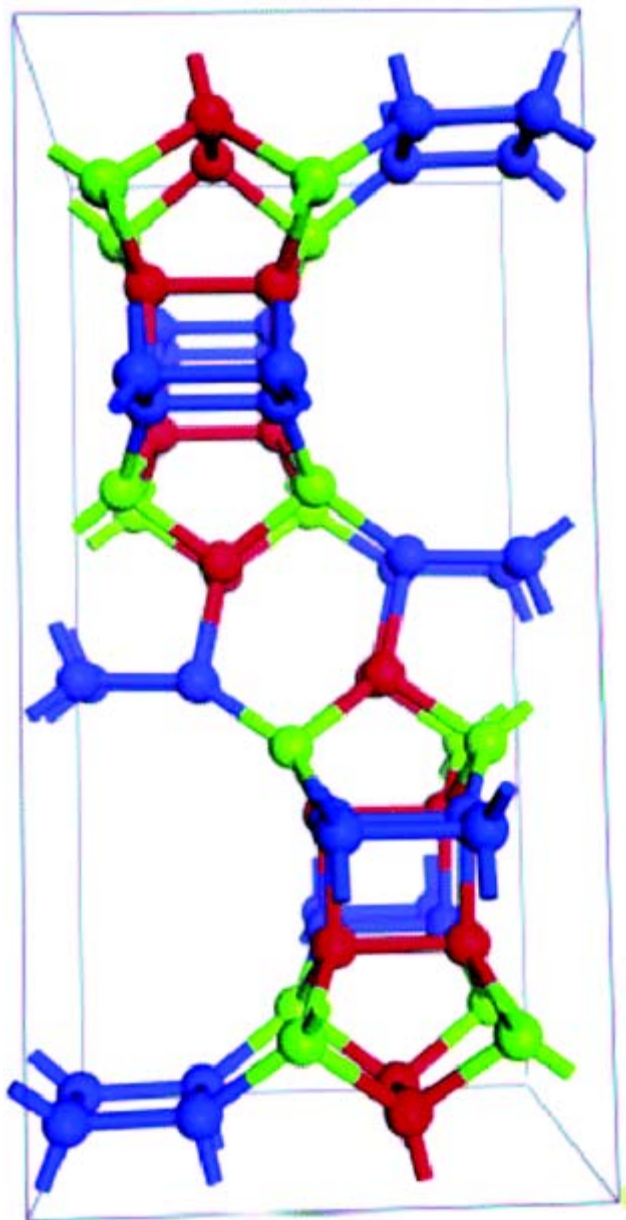


Figure 11: Illustration of a section of the β -zeolite and silicon framework sites (T5 and T6 are colored red) where tin is substituted (Figure was reproduced from Ref [67]).

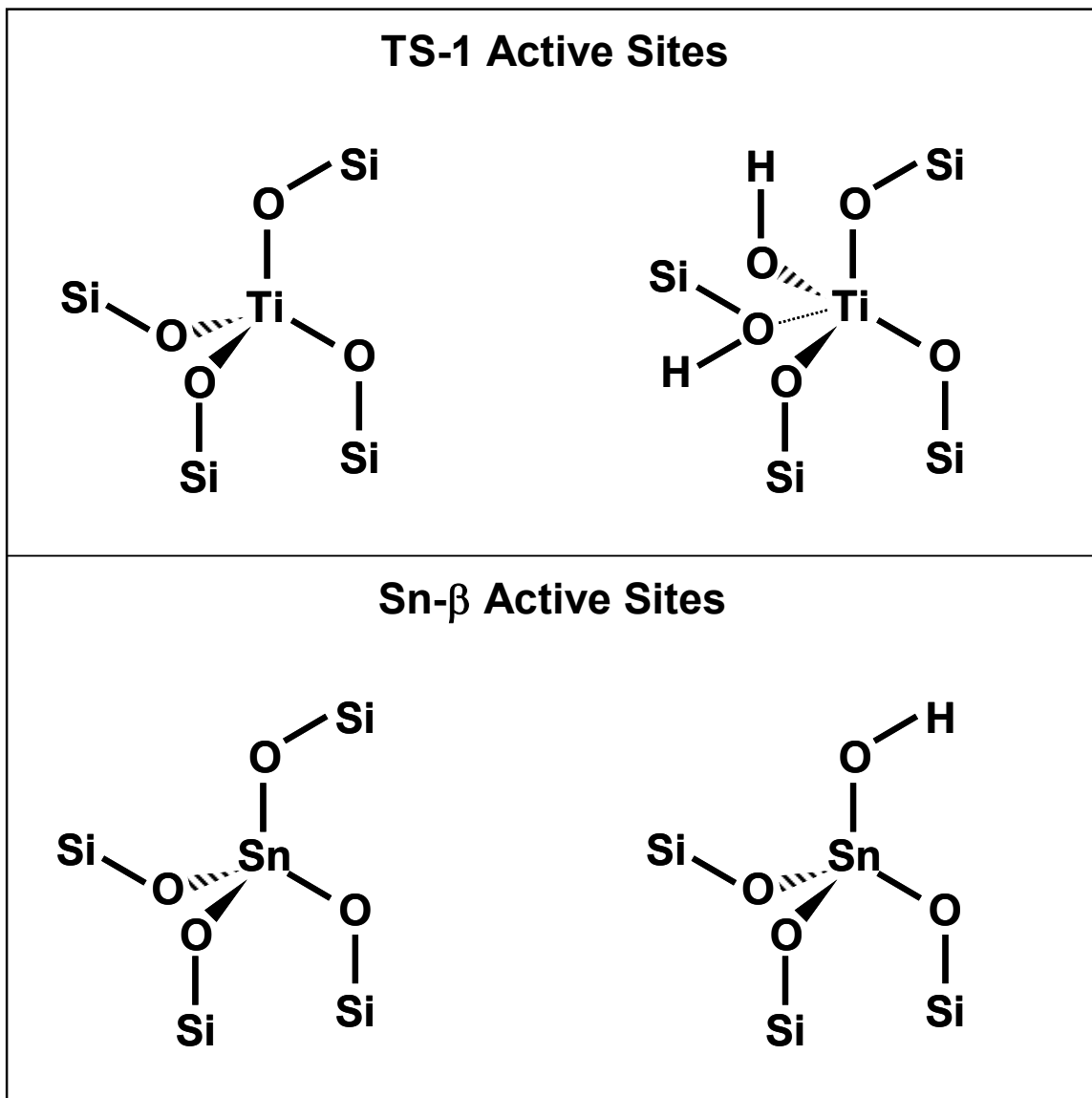


Figure 12: Illustration of the potential active sites present in TS-1[73] and Sn-β[74].

Isomorphous Substitution

Isomorphous substitution is the replacement of one atom (typically silicon) by another atom of similar size without disrupting or changing the crystal structure of the material (Figure 13). Isomorphous substitution of elements such as Be, B, Mg, P, Ti, V, Cr, Fe, Cu, Ga, Zr, Nb, Ce, and W for Si or Al in zeolites[75-77] and silicates[78-84] have previously been reported. Generally the isomorphous substitution of metals into zeolitic frameworks is not thought to be a highly controlled process. In several cases, the silicon or aluminum atoms can be stripped from their framework position under harsh conditions (reaction temperatures around 300°C in the presence of steam or anhydrous SiCl₄). This process is most likely not selective and therefore there is no guarantee that all of the atoms removed are from the same framework position. Therefore the resulting materials may not necessarily contain a single type of active site.

TS-1 and Sn-β are two examples of single site heterogeneous catalysts that exhibit isomorphous substitution (Ti into MFI zeolitic structure and Sn into BEA zeolitic structure).

Summary of Hydrothermally Process

Zeolites are widely used in the chemical industry even though they can suffer significant mass transport problems due to the microporosity of the material. Hydrothermal processes require harsh reaction conditions (high temperature and pressure) which provide little synthetic control. The number of linkages that a metal cation forms to a support as well as the dispersion of the surface functionality on the support and the metal cations throughout the support are not easily controlled using hydrothermal processes. Also hydrothermal processes offer little control of or the ability to target specific surface areas and porosities in the final materials. Therefore hydrothermal processes are not ideal for the preparation of tailored supports and heterogeneous catalysts.

Summary of Supports and Heterogeneous Catalysts with Embedded Active Sites

In order to prepare tailored supports and heterogeneous catalysts with embedded active sites one must first be able to control the dispersion of the surface functionality on supports and the active sites throughout heterogeneous catalysts, the number of linkages from the active site to the support, and the surface area of the support. None of the traditional synthetic methodologies for the preparation of supports and heterogeneous catalysts with embedded active sites presented in this section provide the necessary synthetic control to achieve these goals.

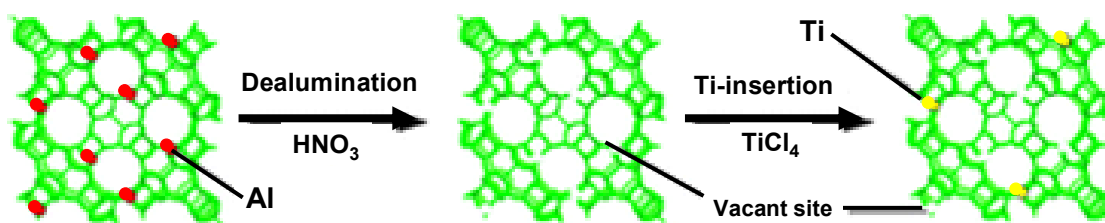


Figure 13: Illustration of isomorphous substitution, the replacement of one atom (in this case aluminum) by another atom (in this case titanium) of similar size without disrupting or changing the crystal structure of the material (Figure was reproduced from [85]).

Heterogeneous Catalysts with Surface Active Sites

Traditional methods used to prepare surface active sites via covalent (incipient wetness, grafting and tethering) and noncovalent (encapsulation) interactions will be discussed in more detail in the following sections.

Incipient Wetness and Grafting

Incipient wetness and grafting procedures are fundamentally equivalent in that both procedures deposit metal cations onto the surface of a pre-existing support.

Incipient wetness is one of the most simple and direct methods for the synthesis of surface active sites. A typical incipient wetness procedure begins with the active site precursor (frequently a water soluble metal salt) being dissolved in an aqueous solution. This solution is then put in contact with a porous support. Capillary action will then draw the solution into the pores. The idea is to add only enough solution to fill the pores of the support which should result in the active site precursor being evenly distributed in the pores of the support.[21] The solvent is allowed to evaporate leaving the active site precursor within the pores of the support. The exact interactions between the active site precursor and the support depend on the metal complex or complexes that are formed in the solution because every complex can interact differently with the surface of the support.[86]

Grafting is just a recent reincarnation of incipient wetness where organometallic precursors are commonly used in which ligands are chosen specifically to react with surface functionality. For example, metal hydrides and alkyls will reaction with surface hydroxyl groups to form molecular hydrogen and alkanes and Si-O-M bonds that are the attachment points of the metal to the support (Figure 14).

The immediate environment around the active site changes during incipient wetness and grafting procedures since at least one ligand on the active site precursor reacts with the surface functionality of the support.

In some cases, after the metal cation is deposited on the surface, the material is calcined, reduced, and possibly calcined again. Calcination can further change the immediate environment around the active site by destroying unreacted ligands on the active site in addition to generating more direct linkages to the support. The grafted active site (both before and after

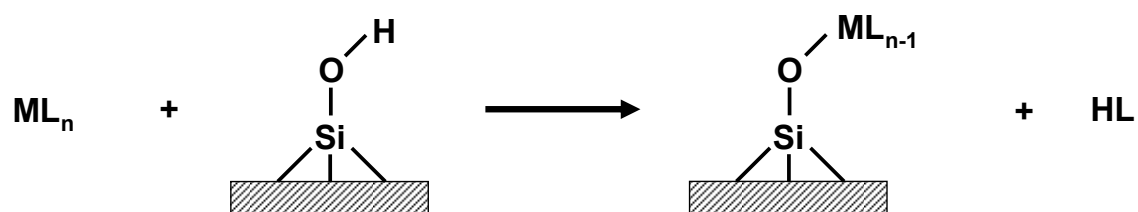


Figure 14: Generic illustration of the grafting of a catalytically active metal center (ML_n , L = hydride, alkyl, amide, halide) onto the surface of a silica support.

calcination) should exhibit different reactivity than is observed by the active site precursor.[5] Also promoters and poisons may be added to adjust reactivity to desired level as in the case of selective oxidation or reduction reactions. These are examples of the empiricism or “art” that permeated the beginnings of heterogeneous catalysis.

A drawback of incipient wetness and grafting procedures (both before and after calcination) is that the generation of multiple types of active sites is possible and even likely in most cases. Those active sites will generally be randomly spread across the surface of the support with little control of dispersion possible.

Several examples of grafted metal cations can be found in the literature. An example of a grafting procedure is when titanium(IV) diethylamide ($\text{Ti}(\text{NEt}_2)_4$) reacts with an isolated silanol to produce the grafted titanium species shown in Figure 15.[87] Another example of grafting is when vanadyl chloride (VOCl_3) reacts with an isolated silanol to produce the grafted vanadyl species shown in Figure 16.[88] A third example of grafting is when vanadyl isopropoxide ($\text{VO}(\text{O}^i\text{Pr})_3$) reacts with an isolated silanol to produce the grafted vanadyl species shown in Figure 16.[88] A fourth example of grafting is when cyclopentadienyl trimethylzirconium ($\text{Zr}(\text{Cp})\text{Me}_3$) reacts with an isolated silanol to produce the grafted zirconium species shown in Figure 17.[89]

Summary of Incipient Wetness and Grafting

Incipient wetness and grafting suffer from a lack of synthetic control with respect to the active site. The heterogeneity of the surface functionalities found on the support leads to little control of the number of linkages that a metal cation forms to a support as well as the dispersion of the metal cations on the support. Therefore incipient wetness and grafting are not ideal for the preparation of tailored supports and heterogeneous catalysts.

Tethering

Tethering is similar to incipient wetness and grafting except for one main difference. Similar to incipient wetness and grafting, the active site is covalently bound to the support. The main difference is that the active site is not directly bound to the support in tethering whereas the active site directly binds to the support in incipient wetness and grafting. In tethering procedures the active site is connected to the support via an ancillary ligand (i.e. a tether) (Figure 18). The

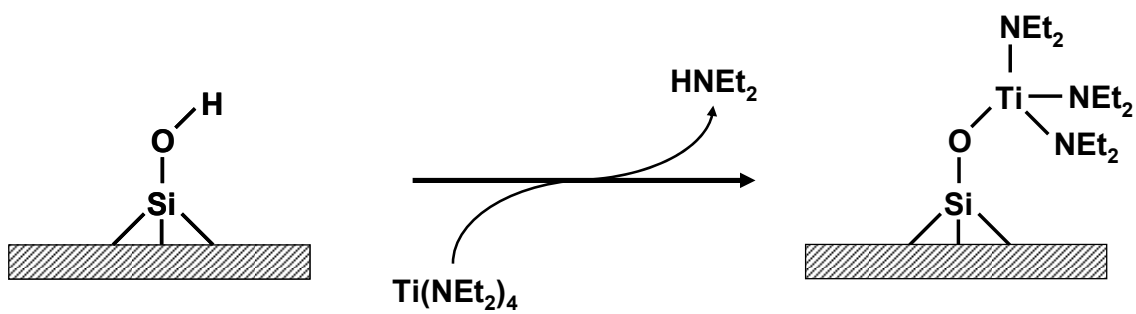


Figure 15: Illustration of the grafting of a titanium amide species.[87]

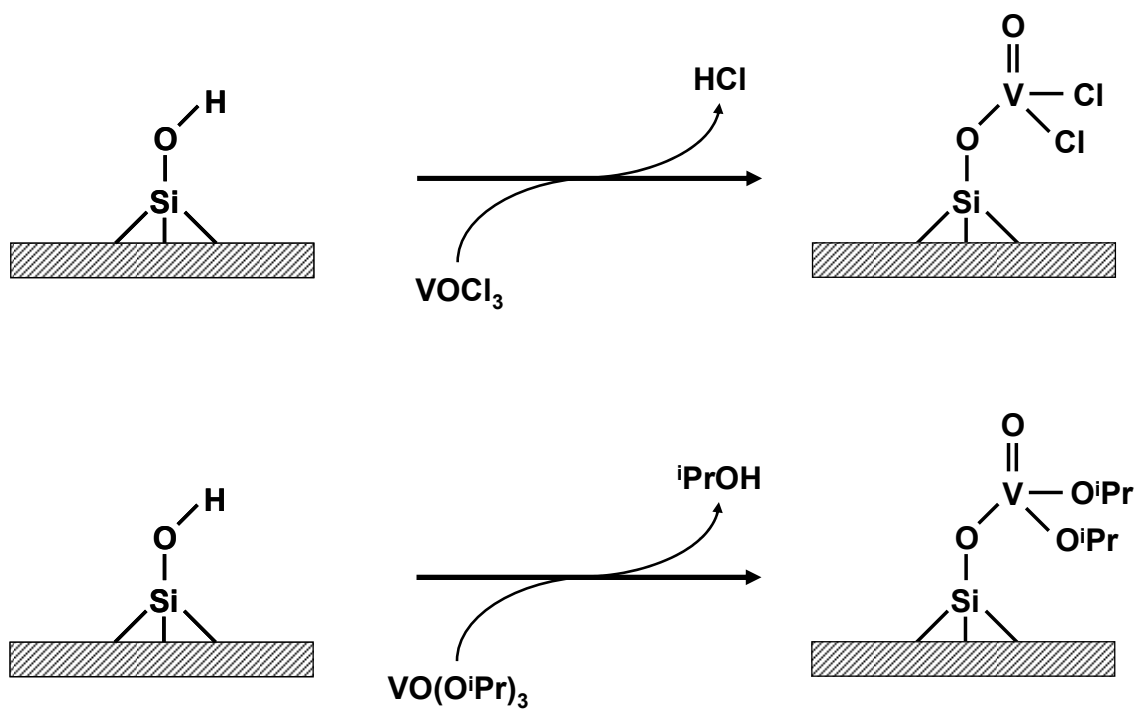


Figure 16: Illustration of the grafting of a vanadyl chloride species (top) and a vanadyl isopropoxide species (bottom).[88]

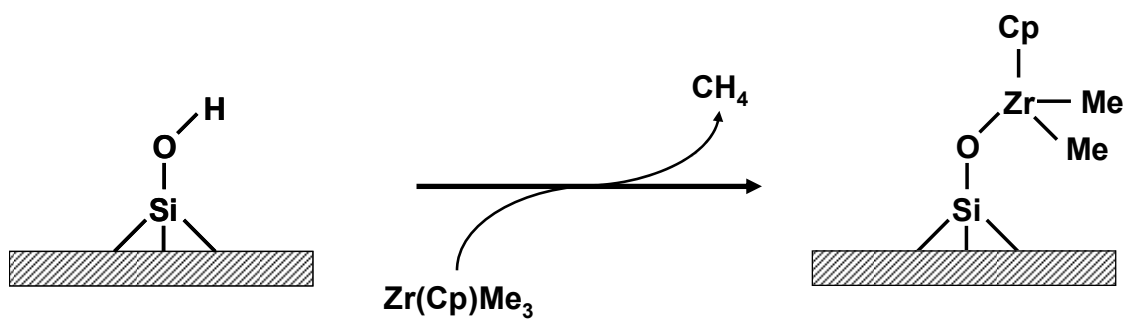


Figure 17: Illustration of the grafting of a zirconium cyclopentadienyl complex.[89]

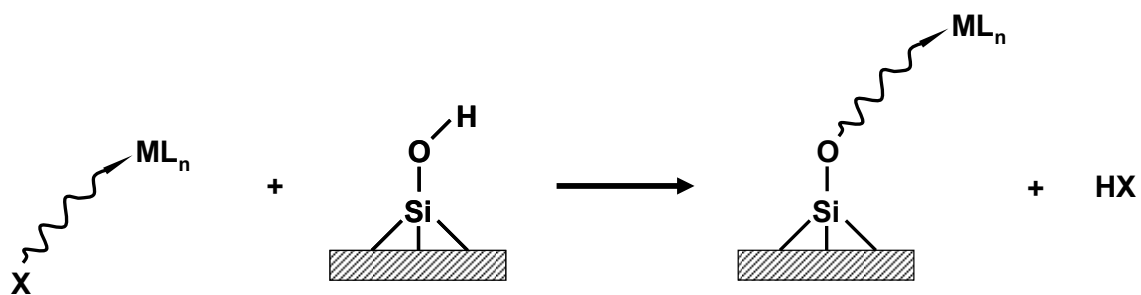


Figure 18: Generic illustration of the tethering of a catalytically active metal center onto the surface of a silica support.

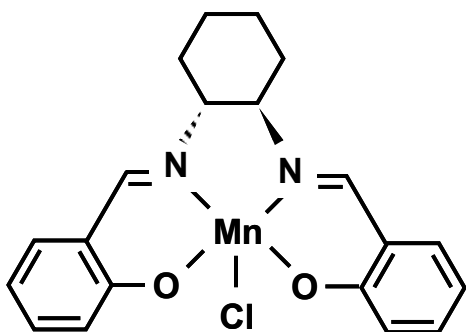
immediate environment around the active site does not change during a tethering procedure because none of the ligands on the metal center react with the surface functionality of the support. There are two parts to a tether: the linking group (frequently a hydrocarbon chain) and a functional group designed to react with specific surface functionality. The end of the tether that is directly attached to the active site should remain unchanged during the tethering process while the opposite end of the tether (i.e. the functional group designed to react with the support) reacts with the surface functionality. In essence, this is a strategy of heterogenizing a homogeneous catalyst and therefore the tethered active site should exhibit similar reactivity to its precursor in addition to having all of the benefits of heterogeneous catalysts.[5]

The active sites generated using tethering procedures must remain firmly anchored to the support at all times in the hope that the catalyst will not leach. Tethers not only serve as the link that binds the active site to the support but also help isolate the active site from the steric and electronic effects of the support.[9]

There are several disadvantages of tethering. First, the addition of a tether typically increases the synthesis time and cost. Second, the tether-to-support (typically Si-C linkage) and tether-to-metal (typically M-X linkage, X = N, C, O, P, S) linkages tend to be weak. Third, the tether which is typically a hydrocarbon chain is vulnerable to attack and decomposition at high temperature. Finally, it is difficult to keep the active sites isolated from one another because the tether is generally flexible enough that the active sites can come in contact with each other if the metal loadings are not kept quite low.

An example of heterogenizing a homogeneous catalyst is shown in Figure 19. The Jacobson-Katsuki catalyst, a chiral Mn(III)-salen catalyst, is a known homogeneous catalyst which has drawn the attention of researchers who are interested in determining a way to prepare a heterogeneous analogue. Researchers believe a heterogeneous analogue should be easier to separate from the reaction mixture in addition to keeping the active sites spatially isolated. As shown in Figure 19, the Jacobson-Katsuki catalyst has been tethered to silica via a propyl chain. The catalyst was tethered to the silica via a sol-gel reaction between an silicon alkoxide functionality on the tether and another silicon alkoxide precursor (tetraethyl orthosilicate).[90]

Homogeneous Catalyst



Tethered Heterogeneous Catalyst

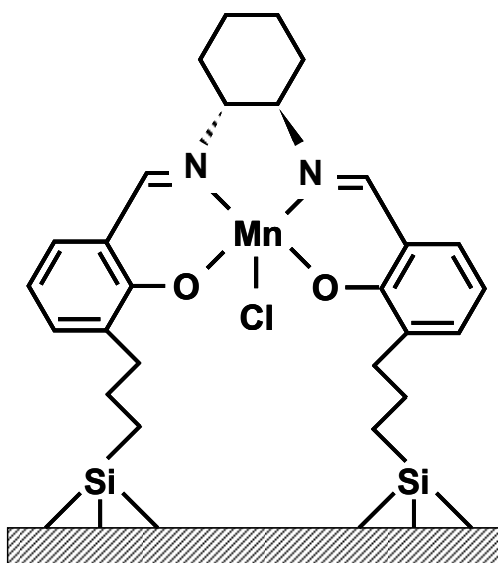


Figure 19: Example of a heterogenized catalyst.[90]

Another example of a tethered catalyst is shown in Figure 20. A titanium-bridged polyhedral oligomeric silsesquioxane (Ti-bridged POSS)[91], a homogeneous model of the active site found in TS-1, was tethered to the surface of dimethylsilyl-functionalized silica via a hydrosilylation reaction using Karstedt's catalyst.[92] This is an example of heterogenizing a homogeneous model of an active site in a heterogeneous catalyst. Unlike studies conducted using TS-1, researchers are able to test the catalytic activity of this tethered catalyst on a variety of reactions. Since the active sites are tethered to the surface of the support researchers do not have to worry if the substrate is too large to diffuse into micropores.

One final example of a tethered catalyst is shown in Figure 21. This catalyst is different than the other two because the tether was initially attached to the surface of the support rather than the traditional approach of having the tether initially attached to the metal center. A carboxylic acid-functionalized support serves two roles in this system (as a tether and a co-catalyst).[93]

These three examples of tethered heterogeneous catalysts illustrate a few of the various approaches used to tether catalyst ensemble to the surface of supports.

Summary of Tethering

Tethering provides researchers another way to anchor catalyst ensembles to supports and can be used as a strategy to heterogenize a homogeneous catalyst. Tethering suffers from a lack synthetic control with respect to the active site. The heterogeneity of the surface functionalities found on the support leads to no control of the number of linkages that a metal cation forms to a support as well as the dispersion of the metal cations on the support.

Encapsulation

Encapsulation is a procedure where the active sites are immobilized within the pores of the support.[5] A subset of catalysts that are synthesized via encapsulation are commonly referred to as “ship-in-a-bottle” complexes. The term “ship-in-a-bottle” refers to the process of building catalytic species inside the pores of a porous material from smaller precursors that are able to diffuse through the pores that connect them to the surface of the support. Once formed, the resulting metal complexes are spatially entrapped in the support, since they are too bulky to diffuse out, whereas reactants and products can freely move through the pores (Figure 22).

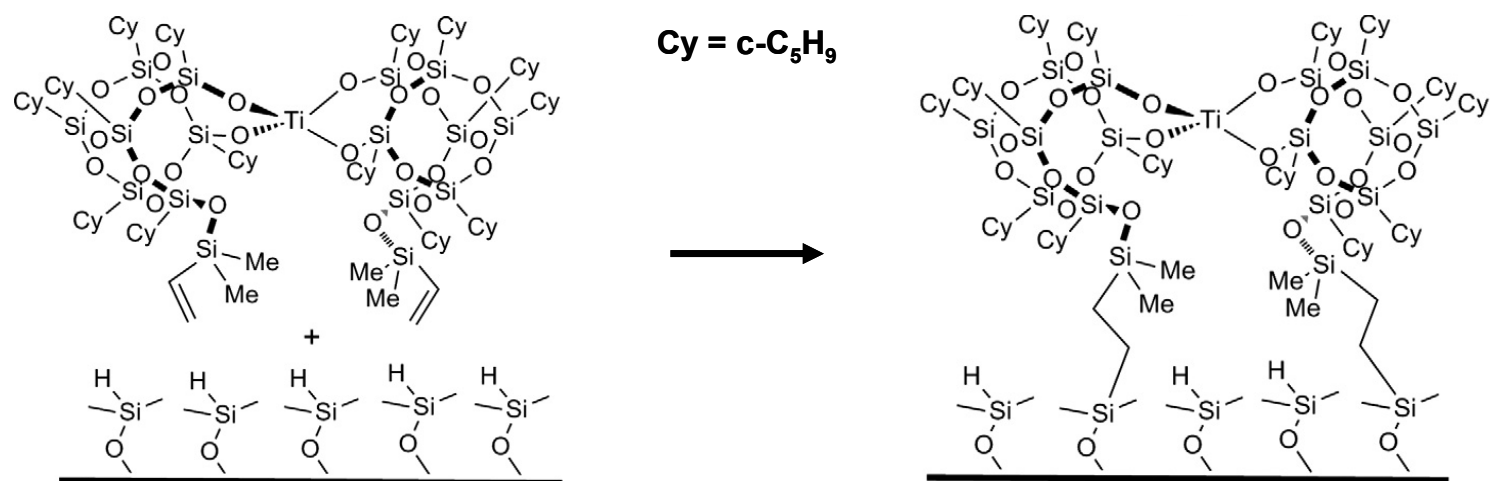


Figure 20: Illustration of the tethering of a titanium-POSS complex to a silica surface (Figure was reproduced from Ref [92]).

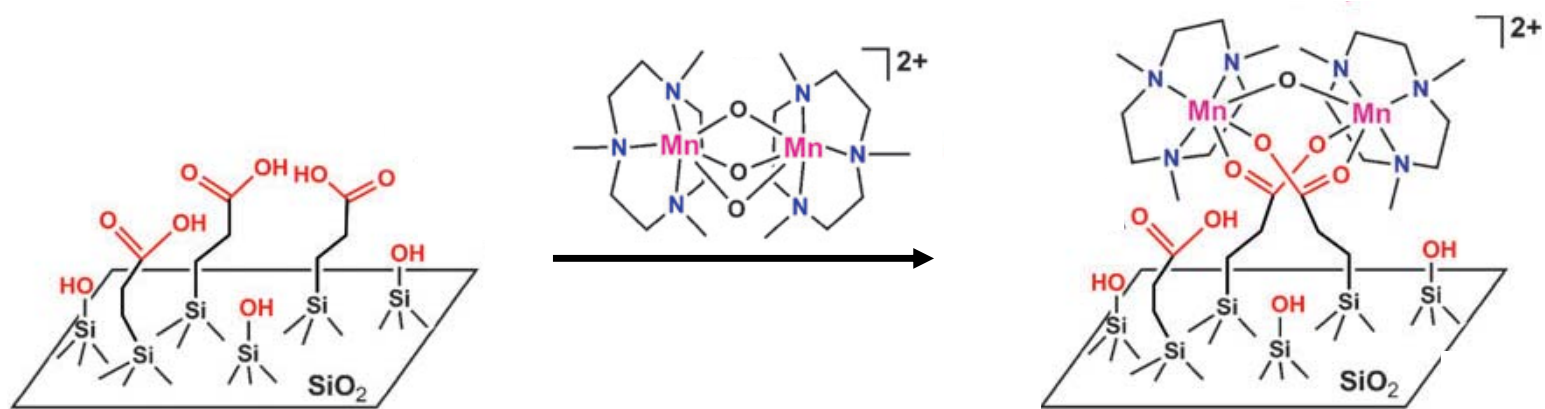


Figure 21: Illustration of the tethering of a manganese complex to a functionalized silica surface (Figure was reproduced from Ref [93]).

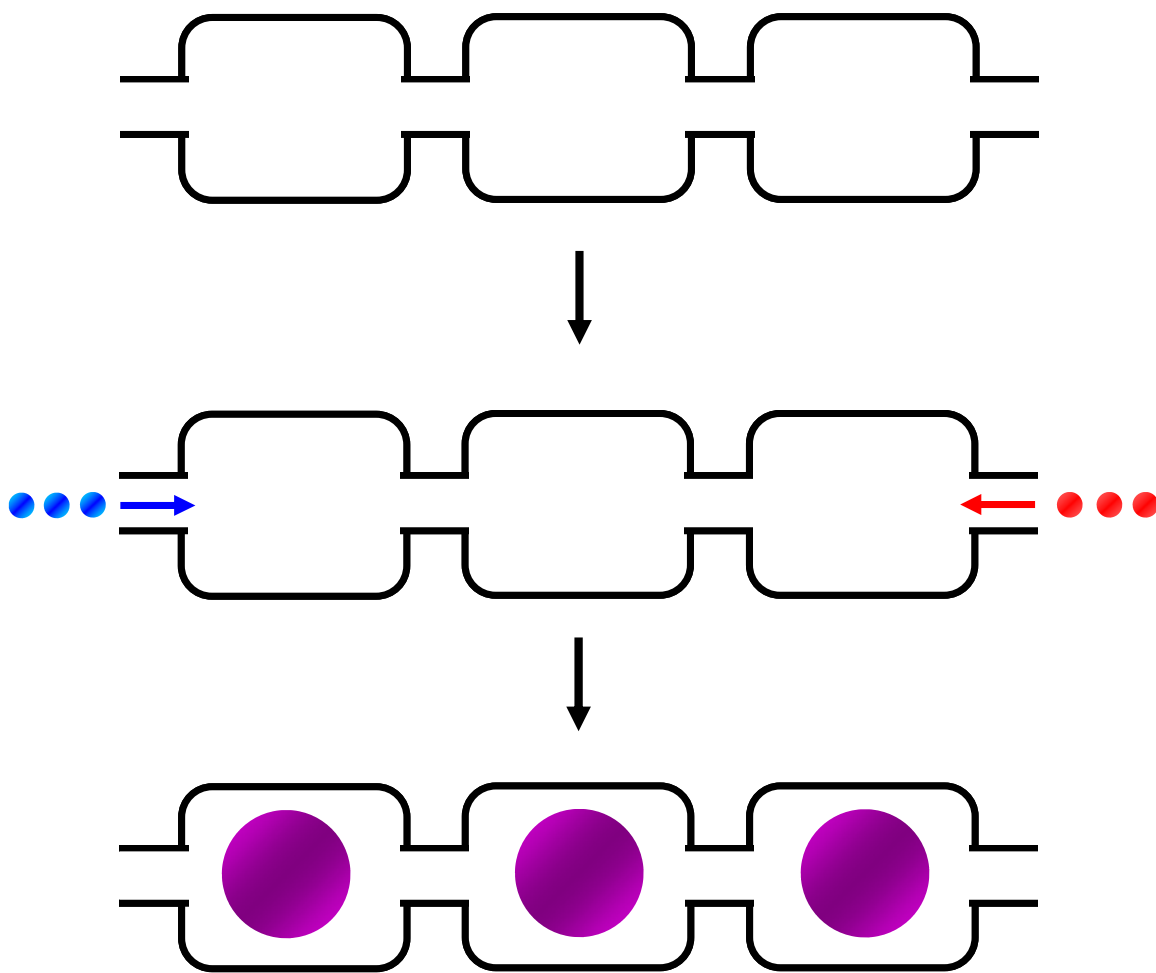


Figure 22: Generic illustration of a porous material (top) which small active site precursors, blue and red circles, diffuse into (middle) forming the trapped active site, purple circles (bottom).

The requirement of small precursors that are small enough diffuse into the pores of the support and build the active site inside the pores limits the application of this technique. One advantage is that encapsulated metal complexes can also easily be separated from the reaction media and reused with no metal leaching.[5]

Cobalt phthalocyanine encapsulated in the pore structure of zeolite-Y is an example of a “ship-in-a-bottle” catalyst, which is shown in Figure 23. The “ship-in-a-bottle” complex was synthesized by diffusing 1,2-dicyanobenzene into the pores of zeolite-Y that already contains Co^{2+} ions. 1,2-dicyanobenzene is small enough to diffuse into the pores and cobalt phthalocyanine is too large to diffuse out of the pores.[94]

Summary of Encapsulation

Encapsulation offers the necessary control of the dispersion of the active sites without the need to worry about the number of linkages that the active site forms to the support. However encapsulated catalysts are limited in two ways. First, they are limited to reactions that use substrates small enough to fit into the pores of the support. Second, they are limited to catalytic species that can be assembled in the pores of the material.

Summary of Surface Active Sites

In order to prepare tailored heterogeneous catalysts with surface active sites one must first be able to control the dispersion of the active sites on the surface of the support and the number of linkages from the active site to the support. The heterogeneity of the surfaces of most “real world” supports makes controlling the dispersion of the active sites and the number of linkages from the active site to the support difficult. Therefore none of the traditional synthetic methodologies for the preparation of heterogeneous catalysts with surface active sites presented in this section provide the necessary synthetic control to reliably and generally achieve the goal of preparing single site catalysts.

Summary of Traditional Synthetic Methodologies

The traditional synthetic methods mentioned in this section all have been used to prepare a variety of productive heterogeneous catalysts. However, all of the traditional methods mentioned above suffer from one main drawback. Every method exhibits a lack of synthetic control with respect to the active site itself.

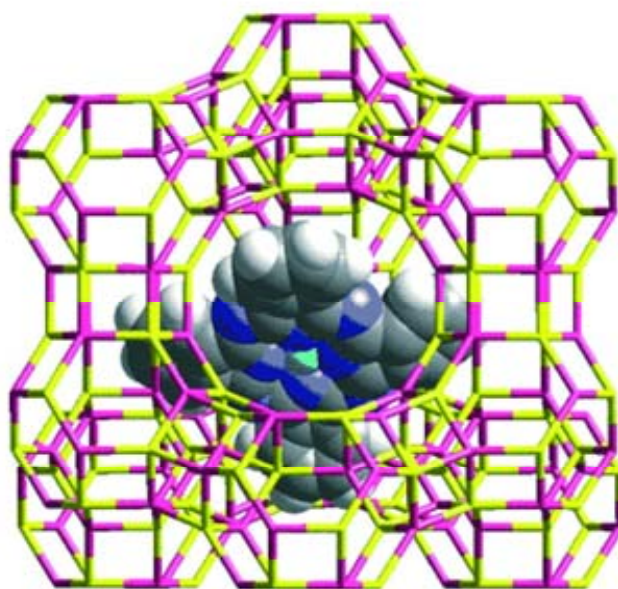


Figure 23: Illustration of a "ship-in-a-bottle" catalyst, cobalt phthalocyanine housed within zeolite Y.[94]
(Figure was reproduced from Ref [22]).

A new synthetic methodology is required to produce tailored supports and heterogeneous catalysts. The dispersion of surface functionalities, the dispersion of the active sites, the number of linkages from the active sites to the support, the surface area, and the porosity must be controlled in the new methodology.

Single Site, Supported Heterogeneous Catalysts – A New Approach

Targeted, Single-Site, Nanostructured Heterogeneous Catalysts

For the past decade, the Barnes research group has investigated a strategy by which targeted, single site, nanostructured heterogeneous catalysts may be synthesized using a building block approach and characterized using a wide variety of characterization techniques.[95,96] The general methodology developed by the Barnes research group focuses on addressing some of the challenges facing the heterogeneous catalysis community which were just discussed. Before one can understand this approach to targeted nanostructuring the three terms used to describe these heterogeneous catalysts need to be clearly defined.

First, the heterogeneous catalysts are described as being targeted. Targeting refers to the controlled synthesis of specific catalyst ensembles. The idea is that researchers target active sites by looking into the scientific literature and finding specific catalyst ensembles that are proposed to be active, inactive, rarely reported, and difficult to synthesize. Once a specific ensemble has been identified, researchers would be able to use a synthetic methodology to generate the specific ensembles and only those ensembles.

Second, the heterogeneous catalysts are described as being single site. Single site heterogeneous catalysts have been discussed earlier however the main points will be reiterated here. Single site refers to the presence of only one type of active catalyst ensemble in the final material. This specific catalyst ensemble is spatially isolated from all others and evenly distributed throughout the support. Every catalyst ensemble must have the same immediate environment (same type of ligands, number of ligands, number of links to the support, and geometry) in order for a catalyst to be considered single site.

Third, these heterogeneous catalysts are described as being nanostructured. Nanostructured, in this context, refers to synthetic control at several different length scales. The first level of synthetic control is at the atomic level, specifically controlling the immediate environment of the catalyst ensemble (i.e. the components and structure) as described above.

The second level of synthetic control deals with the ability to maintain strict site isolation while achieving the maximum loading of catalytically active metal cations. Researchers using the methodology must be able to generate as many identical catalyst ensembles on the surface as possible. The third level of synthetic control focuses on the ability to produce a distribution of different sized pores in the material. High surface area materials with large pore volumes should increase the diffusion of reactants and products to and from active sites (i.e. increased mass transport). The pore network can be thought of as being similar to the transportation network of a city. Cities are not built with only two-lane roads or multiple-lane freeways instead they contain a distribution of different sized roadways.

The new methodology developed by the Barnes research group provides control of the dispersion of surface functionality, the dispersion of the active sites, the number of linkages from the active sites to the support, the surface area, and the porosity.

Benefits of New Methodology

The main benefit of using this new methodology to synthesize targeted, single site, nanostructured heterogeneous catalysts should be the production of “better” catalysts. In a comparison with other catalysts, “better” catalysts will exhibit increased selectivity, activity, and stability. Intuitively the resulting single site catalysts should be more selective than traditional heterogeneous catalysts that contain more than one catalyst ensemble. These “next generation” catalysts should contain higher active site densities than traditional heterogeneous catalysts while still maintaining site isolation. These catalysts having designed pore systems should also have fewer diffusion problems so mass transport rates should be higher than traditional heterogeneous catalysts. Catalysts with higher site density and mass transport rates should exhibit high activities and therefore the nanostructured catalysts should be more active than traditional heterogeneous catalysts. The resulting catalysts should also be more stable (e.g. toward leaching) than traditional heterogeneous catalysts because one component of the nanostructuring (i.e. the synthetic control) mentioned above should produce catalyst ensembles that are more strongly bound to the support than those found in traditional heterogeneous catalyst.

The general methodology developed by the Barnes research group that attempts to address these goals is described in the following sections.

Building Block Approach

A building block approach is used to synthesize well-defined, single site, nanostructured heterogeneous catalysts and supports. In this building block approach, rigid, well defined, chemically robust, molecular building blocks will make up the majority of the matrix rather than using a preexisting support or building the support atom-by-atom. In general, a building block approach requires three components: a building block, linking agents, and a cross-linking reaction. The goal of using a building block approach is to synthesize supports with spatially isolated binding sites (in our work silica) with catalyst ensembles that are atomically dispersed throughout or on the building block support (i.e. isolated tungsten(VI) or zirconium(IV) centers).

Component 1: The Building Block

The selection of an appropriate building block is essential for success in this approach. Building blocks that are nanometer sized or greater will make it easier to ensure that catalytic centers remain chemically isolated from one another and non-interacting. Linking points on the building block that are fixed in space and that are well separated from one another will also help ensure site isolation. The molecular building block that was selected is the structurally well-defined cubooctameric spherosilicate, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. This crystalline octa(trimethyltin) spherosilicate was first described by Walzer and Feher.[18,97,98] Figure 24 illustrates the structure of $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. [99] The Si_8O_{12} core has a cubic structure with silicon atoms on the corners (purple atoms in Figure 24a, blue atoms in Figure 24b) and bridging oxygen atoms along the edges (red atoms in Figure 24). Each silicon atom is connected to four oxygen atoms (three bridging oxygen atoms and one terminal oxygen atom). Each terminal oxygen atom is connected to a trimethyltin group (green atoms in Figure 24a), which will react with high valent metal and main group chlorides. The trimethyltin groups are fixed in space and well separated from each other, which will help ensure site isolation in the final material (Figure 25).[6,99] The geometry and bonds along the edge of a building block effectively isolate the terminal oxygen atoms from one another and prevent a metal center from bridging positions around the building block.

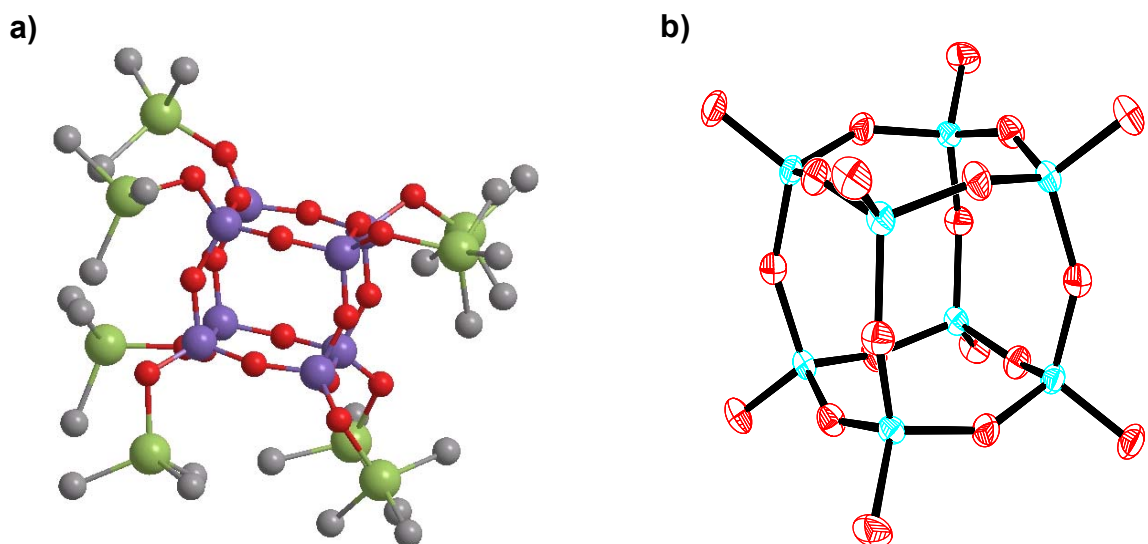


Figure 24: a) Illustration of the structure of the building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. Silicon atoms are purple, oxygen atoms are red, tin atoms are green, and methyl groups are gray. b) Illustration of the core structure of the building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. [99] Silicon atoms are light blue and oxygen atoms are red.

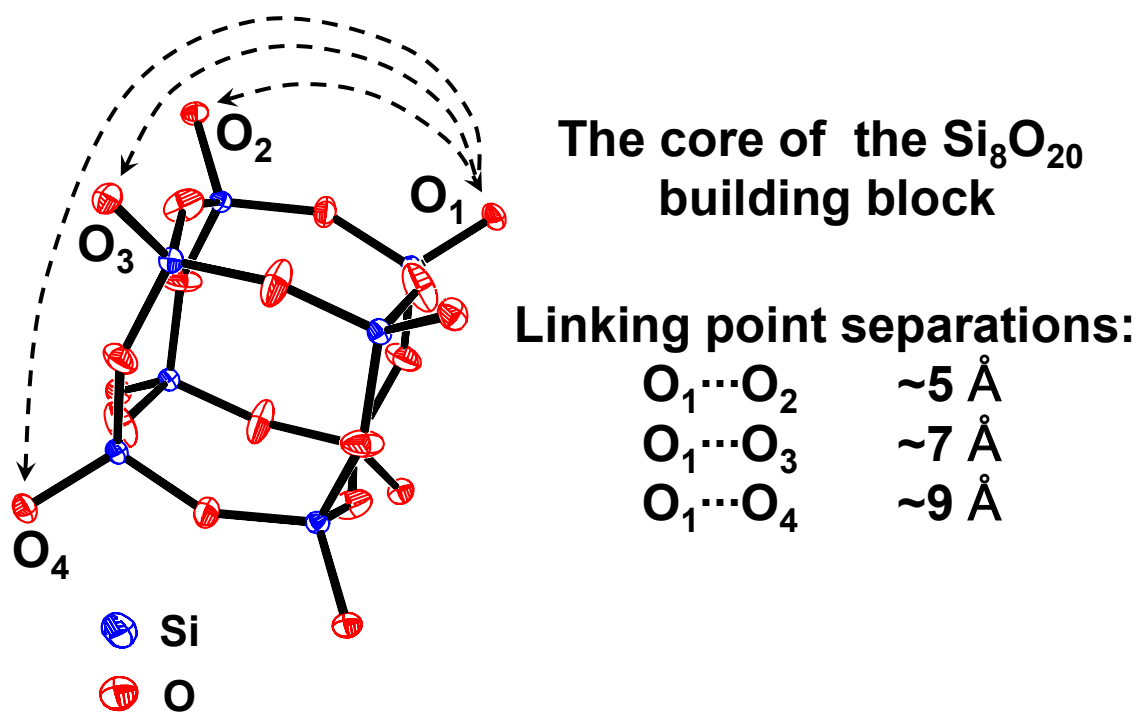


Figure 25: Illustration of separation distances for the terminal oxygen linking points on $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.
 (Figure was reproduced from Ref [6]).

Component 2: The Linking Agents

As mentioned previously, the Me_3Sn groups rapidly react with a variety of high valent metal and main group halides, which naturally are selected as the linking agents. Metal and main group chlorides are convenient linking agents because acceptable quantities of high purity material are commercially available and are generally inexpensive. Care must be taken when handling and storing these materials because of their hydrolytic sensitivity. Standard air sensitive (inert atmosphere glovebox and Schlenk line) techniques are required. The linking agents can be divided into two types: those that insert the catalytic centers into the material (referred to as catalytically active linking agents) and those that insert more silicon into the material (referred to as inert linking agents). Table 1 shows linking agents that have been reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ by the Barnes group to date.

Component 3: Cross-Linking Reaction

With the building block and linking agents in hand, a well-defined linking reaction must be identified. A simple nonhydrolytic sol gel linking reaction was first reported by Feher.[98] This linking reaction is run in anhydrous organic solvents (e.g. hexanes, toluene, ether, THF, etc) at temperatures between 20°C and 80°C for less than 24 hours. In each linking reaction, a linking agent (i.e. metal or silicon chloride) and the building block react to produce a new siloxane linkage (M-O-Si ($\text{M} = \text{metal or Si}$)) and trimethyltin chloride (Me_3SnCl) (Figure 26).

This process will continue until all the chloride ligands on linking agent are consumed or a chloride ligand becomes unreactive as more M-O-Si bonds are formed to a metal center. The first chloride ligand on the linking agent is thought to react upon contact with solutions of the silicate building block. The rate of reaction of each subsequent chloride ligand decreases as more chloride ligands react.[95] Generally it has been found that all of the chloride ligands will react with any accessible Me_3Sn group within 24 hours. Preliminary results also indicate that upon phase separation the reaction is complete however more studies are needed to confirm and quantify this statement.

Under non-aqueous conditions, the Me_3Sn groups and chloride ligands are complementary functional groups which means two building blocks cannot react with each other

Table 1: List of inert and catalytically active linking agents

Inert linking agents	Catalytically active linking agents	
SiCl ₄	W ⁶⁺	WCl ₆ , WOCl ₄ , WO ₂ Cl ₂
SiCl ₄ py ₂	V ⁵⁺	VOCl ₃
HSiCl ₃	Zr ⁴⁺	ZrCl ₄
MeSiCl ₃	Ti ⁴⁺	TiCl ₄
Me ₂ SiCl ₂	V ⁴⁺	VCl ₄
Me ₃ SiCl	Sn ⁴⁺	SnCl ₄ , BuSnCl ₃ , Bu ₂ SnCl ₂
	B ³⁺	BBr ₃
	Al ³⁺	AlCl ₃
	Ga ³⁺	GaCl ₃
	P ³⁺	PCl ₃
	Au ³⁺	AuCl ₃ py

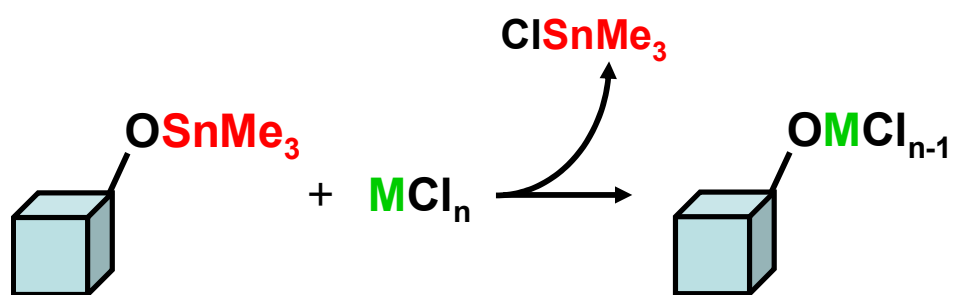


Figure 26: Illustration of the cross-linking reaction.

to produce $(\text{Me}_3\text{Sn})_2\text{O}$ and two linking agents cannot react with each other to produce Cl_2 . Figure 27 illustrates a generic linking reaction where molecular building blocks with type A functionality and a linking agent with type B functionality react to link together the building blocks and produce the linking byproduct AB. Since the A and B functionalities are complementary it ensures that the building blocks do not react with each other therefore the byproducts AA is not produced. The same can be said for the linking agents with type B functionality.

Ideally the building block and linking agents should not be able to exchange functionalities meaning the building blocks never have the B functionality and the linking agents never have the A functionality. If this exchange did occur then the byproduct AB could be produced by the desired reaction (building block + linking agent) and by undesired reactions (building block + building block or linking agent + linking agent). It is important to note that the building block $(\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8)$ and linking agents (metal and main group chlorides) do not exchange ligands. Me_3SnCl is only produced when a building block reacts with a linking agent.

Based on the evidence in hand, we believe the linking reaction is completely random throughout the various stages of cross-linking and growth of these building block matrices (i.e. the probability of any of the eight Me_3Sn groups on the building block reacting is the same). Furthermore the linkages are irreversibly formed which means that the siloxane bond is stable under the reaction conditions employed. This results in the formation of amorphous silicate materials. Based upon previous studies, the building block is thought to remain intact during most cross-linking reactions.[95] There has been no evidence observed in ours or previous work for the formation of products derived from the cleavage or degradation of the Si_8O_{12} core.[98]

In each cross-linking reaction, a linking agent and the building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ are reacted together to produce M-O-Si (M = metal or Si) links and Me_3SnCl (Figure 26). After all the cross-linking reagent is consumed, the solid residue is isolated by removing the solvent and volatile byproduct Me_3SnCl under vacuum. If the linking reaction occurs as expected and no side reactions occur, then the measured weight loss is directly related the amount of Me_3SnCl produced. The amount of Me_3SnCl produced during each cross-linking reaction is related to the connectivity (number of linkages to the support) achieved by the metal or silicon center.

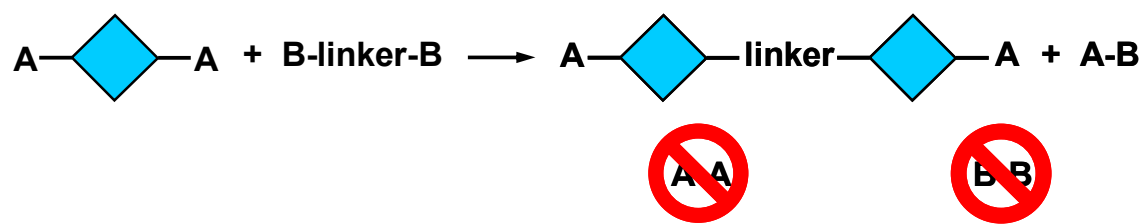


Figure 27: Generic cross-linking reaction between a building block and linking agent with complementary functionalities.

Gravimetric data (measuring the weight change that occurs following the linking reaction) thus provide two types of information about the reaction and resulting material: it directly defines the overall reaction stoichiometry and it indirectly defines the local environment around the metal or silicon center. The exact connectivity is obtained in cases when either one or all of the chloride ligands on the linking agent have reacted with Me₃Sn groups. When gravimetric data indicate that the connectivity achieved by the linking agent is intermediate, between one and the maximum (governed by the total number chloride ligands originally present on the linking agent), then the connectivity number represents the average for the distribution of centers present in the material.

Gravimetric Analysis

The following example illustrates a typical gravimetric analysis for a cross-linking reaction between SiCl₄ and Si₈O₁₂(OSnMe₃)₈ (0.5 SiCl₄ : 1.0 Si₈O₁₂(OSnMe₃)₈).

The mass of Si₈O₁₂(OSnMe₃)₈ used (1.000 g) is determined by the weight difference between the reaction vessel with Si₈O₁₂(OSnMe₃)₈ under vacuum and the empty reaction vessel under vacuum. The mass of SiCl₄ used (0.046 g) is determined by the weight difference between the SiCl₄ capillary tube source before and after vapor transfer. SiCl₄ and Si₈O₁₂(OSnMe₃)₈ react to form one equivalent of Me₃SnCl for every new siloxane bond formed. The volatile by-product Me₃SnCl is removed from the reaction vessel under dynamic vacuum at 100°C. The mass of the solid residue (0.840 g) is determined by the weight difference between the reaction vessel after the volatiles are removed under vacuum and the empty reaction vessel under vacuum. The weight difference between the reactants (1.000 g Si₈O₁₂(OSnMe₃)₈ and 0.046 g SiCl₄) and products (0.840 g solid residue) equals the amount of Me₃SnCl produced (0.206 g).

If all of the chlorides of SiCl₄ react then 0.215 g of Me₃SnCl would be produced. The connectivity (i.e. the number of chloride ligands that reacted or the number of new siloxane bonds formed) is determined from the equation below.

$$\frac{\text{Me}_3\text{SnCl produced}}{\text{Me}_3\text{SnCl possible}} \times \text{No. of Cl ligands} = \text{Connectivity} \quad \text{Equation 10}$$

$$\frac{0.206 \text{ g}}{0.215 \text{ g}} \times 4.0 = 3.8 \quad \text{Equation 11}$$

Gravimetric analysis is the first line of characterization, which provides information that can quickly be used to determine the immediate environment around the metal or silicon center.

Method of Sequential Additions

A synthetic strategy (the method of sequential additions) was developed to target specific catalyst ensembles.[95] The method of sequential additions relies on both the sequence and the size of doses of different linking agents in the above synthetic strategy. Two types of catalyst ensembles (“embedded” and “surface”) can be synthesized using this method. Figure 28 illustrates the dosing strategies used to synthesize the two types of catalyst ensembles.

Embedded catalyst ensembles within a silicate building block support are obtained when a limiting amount of a linking agent (generally ≤ 0.5 metal chloride to building block) is initially reacted with the building block (top portion of Figure 28). All of the chloride ligands on the metal chloride should react forming the maximum number of linkages to the building block support. The “system” following the first cross-linking reaction should consist of small, oligomeric species and possibly unreacted building blocks. The small oligomeric species will contain metal centers with the maximum number of linkages the support and the immediate environment around every metal center should be identical. These small oligomers and building blocks may subsequently be exposed to a second dose of an inert linking agent which will link the oligomers and building blocks together to produce a macroscopic rigid polymeric structure and generate porosity. The porosity generated during the second cross-linking reaction can easily be tailored by simply adjusting the ratio of inert linking agent to building block (vide infra). Following the second cross-linking reaction, the metal centers will be dispersed throughout the silicate support and the immediate environment around every metal center should be identical and should remain unchanged during the second cross-linking reaction.

Surface catalyst ensembles on a silicate building block support are obtained by reversing the sequence of linking reactions (bottom portion of Figure 28). First, a silicate building block support which has some unreact Me_3Sn groups still present is generated when a limiting amount of an inert linking agent is initially reacted with the building block. The number of Me_3Sn groups reacted and porosity generated during the first cross-linking reaction can easily be tailored by simply adjusting the ratio of the inert linking agent to building block. If a large

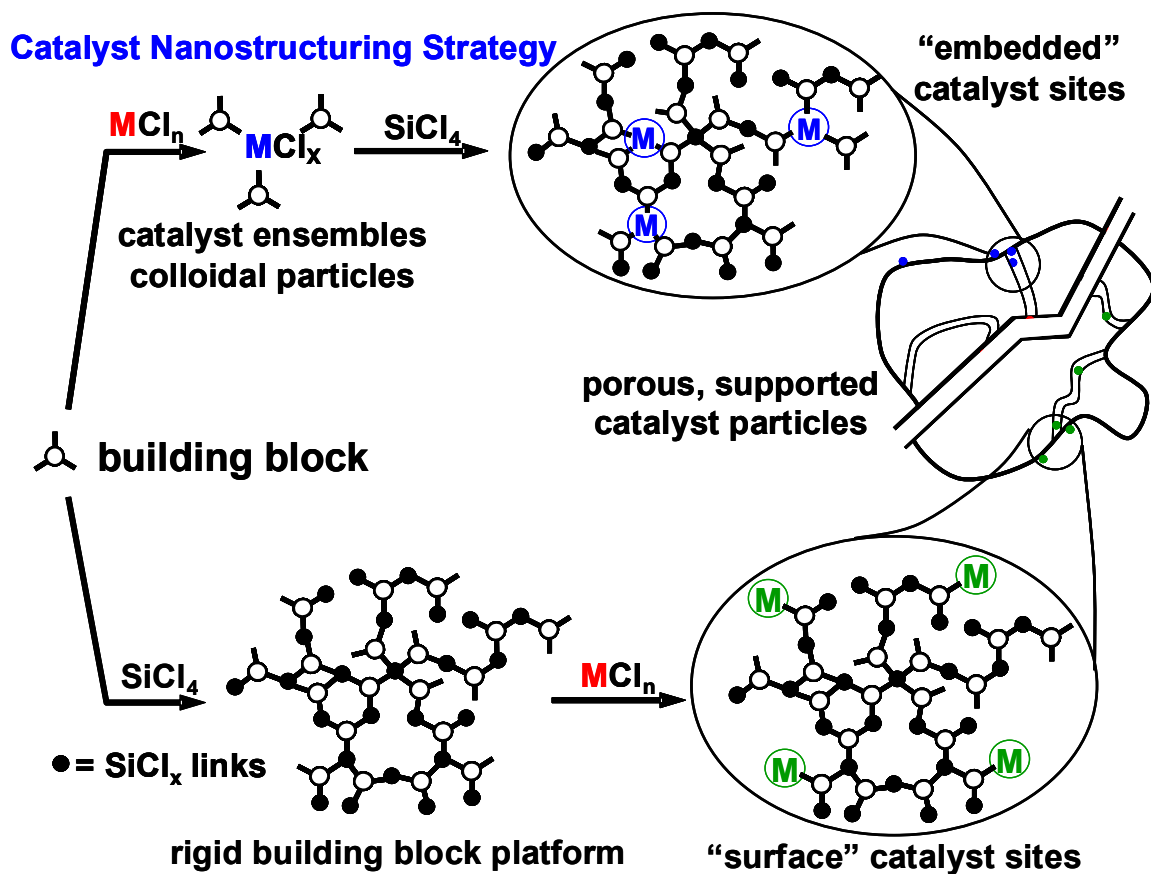


Figure 28: Illustration of the method of sequential additions synthetic strategy. (Figure was reproduced from Ref [95]).

enough dose (≥ 3 inert linking agent to building block) is used then few Me_3Sn will be close enough together on the support to form additional linkages when a second linking agent is delivered, regardless of the size of the dose. Thus, when a second linking agent (typically a metal chloride) is introduced the subsequent reaction with Me_3Sn groups then leads to isolated, “one-connected” surface catalyst ensembles.

Two distinct types of catalyst ensembles can easily be synthesized using the same precursors ($\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and metal/main group chlorides) via the method of sequential additions. While the strategy is fairly intuitive on paper, the resulting nanostructured materials need to be characterized to prove that two separate single site catalysts (“embedded” and “surface”) have indeed been prepared.

Targeted Sites

Several examples of single site heterogeneous catalysts can be found in the literature with TS-1 and Sn- β being two classic examples of such catalysts.[67-71] Even though both systems are often cited examples of single site catalysts, as has been described traditional synthetic methods generally do not produce truly single site catalysts because there is always a small fraction of other potential active sites present in the matrix. The proposed active sites for TS-1[73] and Sn- β [74] are presented in Figure 12. Using the building block approach and the method of sequential additions, the proposed active sites present in both materials could be individually targeted. The ensembles in these systems are ideal for targeting via the building block approach because both TS-1 and Sn- β have been well-characterized and the catalytic activity is known. Current efforts in the Barnes group focus on targeting a variety of active sites (e.g. Ti(IV), B(III), Al(III), Ga(III), W(VI), Zr(IV)) in silicate matrices. This building block approach has also been used to target vandyl active sites in silicate matrices.[96]

In general, there are two types of catalyst ensembles that can be targeted using the previously described building block approach. Embedded ensembles have the maximum number of linkages to the building block support and do not contain any unreacted chloride ligands on the metal center. Embedded ensembles are generally thought to be the most stable ensembles because multiple linkages to the support would need to be broken for leaching to occur. Surface ensembles on the other hand have only one linkage to the building block support and contain numerous unreacted chloride ligands on the metal center. Surface ensembles are generally

thought to be the least stable ensembles because only one linkages to the support would need to be broken. The synthesis and characterization of six catalyst ensembles (3 embedded and 3 surface) that contain either W(VI) or Zr(IV) will be the focus of this dissertation using the building block approach (Figure 29).

Traditional Characterization Methods

The characterization of supports and heterogeneous catalysts is quite challenging. Zeolites are crystalline materials which can be characterized using x-ray diffraction techniques whereas amorphous materials require the use of numerous physical and spectroscopic techniques the results from which must then be pieced together in order to develop a picture of the surface functionality and catalyst ensemble.

A primary focus of heterogeneous catalyst characterization is identifying the components that make up the catalyst ensemble and their properties. The characterization of heterogeneous catalysts generally begins with the identification of the three main components of the catalyst ensemble (metal cations, terminating ligands, and links to surface). First the identities of the metal atoms present in the catalyst ensemble must be determined. Frequently the metals in the system are fairly well determined by the synthetic reagents used. However the number of metal atoms involved in the ensemble must be carefully determined, even if the nuclearity is well defined in a precursor used in synthesis. The ligands are usually standard ligands found in inorganic and organometallic chemistry (e.g. hydroxyl groups (M-OH), oxo groups (M=O), alkoxy groups (M-OR), alkyl groups (M-R), halides (M-X), etc). Their identification can be routine for simple ligands and challenging for more complex ligands. The metal-to-support interactions are probably the easiest to intuit and the most challenging component to “see”. Based on the synthetic procedure, it should be easy to make an educated guess as to what types of metal-to-support interactions are present in the material. The challenge comes when trying to find a spectroscopic technique that can “see” these typically long-range interactions. After the components of the catalyst ensemble have been identified several other properties of the metal core need to be determined. The concentration, acidity, accessibility, coordination geometry, and oxidation state of the metal centers are all properties that aid in the development of a reasonably clear picture of the catalyst ensemble. At a larger length scale, the porosity of the

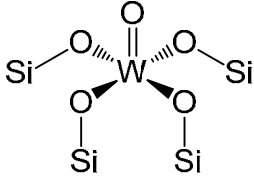
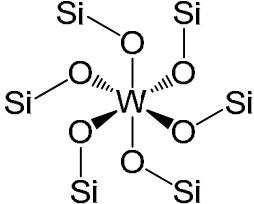
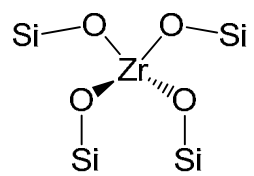
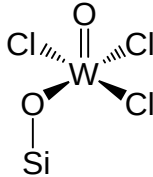
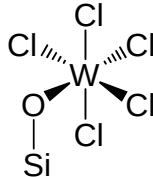
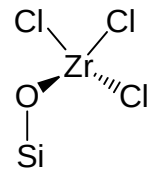
	Illustration	Nomenclature
Embedded Catalyst Ensembles		“Isolated Embedded Tungsten Oxo Centers”
		“Isolated Embedded Tungsten Centers”
		“Isolated Embedded Zirconium Centers”
Surface Catalyst Ensembles		“Isolated Surface Tungsten Oxo Centers”
		“Isolated Surface Tungsten Centers”
		“Isolated Surface Zirconium Centers”

Figure 29: Illustration of the six catalyst ensembles to be targeted in this dissertation.

support determines the accessibility of the catalyst ensembles and so measurements that probe the porosity are also required. Finally catalytic activity often is not thought of as a characterization technique even though it provides some of the most important information about a catalyst.

Understanding the capabilities of each characterization technique and which components and/or properties can be determined using each technique is of vital importance in proving that one has truly obtained single site catalysts.

As previously mentioned, numerous physical and spectroscopic techniques are required to characterize amorphous heterogeneous catalysts. Infrared (IR) and Raman spectroscopy are vibrational techniques that are used to identify, and sometimes quantify, the functional groups (e.g. ligands and in some cases metal-to-surface interactions) that are present in the material. The use of probe molecules can provide information about the acidity and accessibility of the catalyst ensembles. Elemental analyses, specifically inductive coupled plasma optical emission spectroscopy, may typically be used to determine the concentration of metal centers in a material. Solid state nuclear magnetic resonance spectroscopy (SSNMR) can directly probe the catalyst ensemble if the metal center is a NMR active nucleus otherwise this technique can be used to identify ligands that contain NMR active nuclei. X-ray adsorption spectroscopy (XAS) is a element specific technique that probes the immediate environment around the metal center providing information about the coordination geometry, oxidation state, and surrounding elements. The porosity of the material is probed by gas adsorption/desorption measurements. Catalytic activity tests determine if the material increases the rate of reaction without the material being consumed during the process. The following sections will provide a brief overview of some of the characterization techniques that have been used to study the materials prepared in this dissertation research.

Infrared (IR) Spectroscopy

IR spectroscopy is one of the most common spectroscopic techniques used to characterize supports and heterogeneous catalysts. IR is a spectroscopic technique used to study the vibrational and rotational modes of a sample and is a complementary technique to Raman. Practically every study that characterizes supports and heterogeneous catalysts includes the IR spectra so assigning IR features is fairly straightforward. Some of common vibrational modes of

metal oxides and mixed metal oxides that are identified using IR spectroscopy include $\nu_{\text{sym}}(\text{Si-O-Si})$, $\nu(\text{Si-OH})$, and $\nu(\text{M-O-Si})$ where $\text{M} = \text{Ti, V, Mo, Sn, Zr, W, etc.}$

A representative example of an IR spectrum, the IR spectrum of the trimethyltin functionalized building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, is shown in Figure 30 with the main IR features labeled.

Acidity Determination using Probe Molecules

The use of probe molecules to determine the concentration, strength, and accessibility of acid sites in heterogeneous catalysts has been extensively studied.[100-103] All three of these properties influence the catalytic activity of the heterogeneous catalysts.

The IR spectrum of pyridine absorbed on acidic heterogeneous catalysts can be used to identify the types of acid sites present in the material. Pyridine is an excellent probe molecule which allows one to distinguish between Bronsted and Lewis acidic sites. Metal cations in heterogeneous catalysts act as Lewis acidic sites while surface metal hydroxyl groups are able to protonate probe molecules, thus acting as Bronsted sites.[101] As seen in Figure 31, pyridine coordinately binds to Lewis acidic sites, forms hydrogen bonds to silanols, and is protonated by Bronsted sites forming the pyridinium ion. The ring vibrations of pyridine produce characteristic bands in the IR spectrum between 1400 and 1700 cm^{-1} depending on the type of pyridine interactions present. An IR feature at $\sim 1450\text{ cm}^{-1}$ is characteristic of Lewis acidic sites, one at $\sim 1540\text{ cm}^{-1}$ is characteristic of Bronsted acidic sites, and one at $\sim 1590\text{ cm}^{-1}$ is characteristic of silanols.[100,102]

Alkyl substituted pyridines such as 2, 6-di-tert-butyl-pyridine can also be used as a probe molecules which gives researchers that ability to vary the base strength and sterics of the probe molecule.[104] The use of probe molecules of different base strengths allows researchers to determine the strength of the acid sites via desorption studies. In general, stronger acid sites will bind weaker basic probe molecules than weaker acid sites. In addition, stronger acid sites desorb basic probe molecules at higher temperatures than weaker acid sites. The use of probe molecules with different steric signatures allows researchers to determine the accessibility of the acid sites.

Other IR probe molecules include ammonia, aliphatic amines, nitriles, benzene, substituted benzenes, and carbon monoxide.[102]

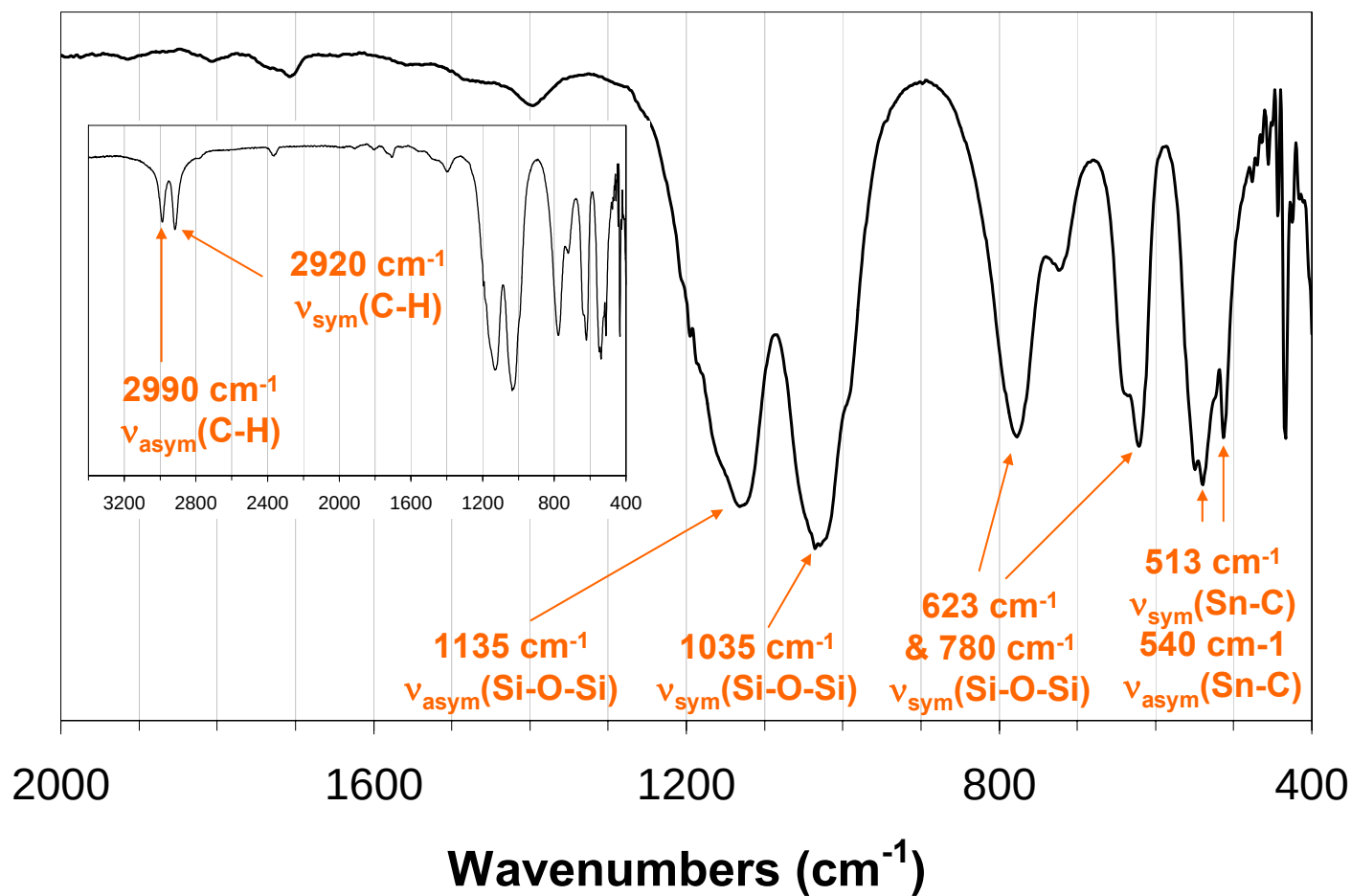


Figure 30: IR spectrum (400-2000 cm^{-1}) of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with the vibrational frequencies and modes labeled. The inset contains the entire IR spectrum (400-3400 cm^{-1}).

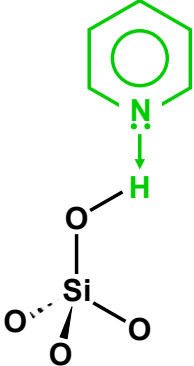
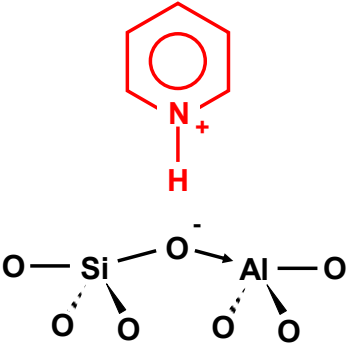
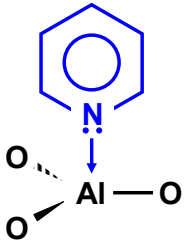
		
Silanol Hydrogen bonded py	Bronsted Acid Pyridinium ion	Lewis Acid Coordinately bonded py
~1445 cm⁻¹ ~1485 cm⁻¹ ~1590 cm⁻¹	~1490 cm⁻¹ ~1540 cm⁻¹ ~1620 cm⁻¹ ~1640 cm⁻¹	~1450 cm⁻¹ ~1490 cm⁻¹ ~1580 cm⁻¹ ~1615 cm⁻¹

Figure 31: Illustration of the types of pyridine interactions with acidic sites found in heterogeneous catalysts.[100]

Raman Spectroscopy

Raman spectroscopy is considered a powerful spectroscopic technique because of its high resolution ($\sim 1 \text{ cm}^{-1}$) and wide spectral range ($50\text{-}5000 \text{ cm}^{-1}$). Raman is a spectroscopic technique used to study the vibrational and rotational modes of a sample and is a complementary technique to IR. An important advantage of Raman spectra over infrared lies in the fact that water does not produce a significant Raman signal. Also glass or quartz windows can be used instead of sodium chloride windows like in IR.

Raman spectra are acquired by irradiating a sample with an intense source of monochromatic radiation, typically a visible laser. The monochromatic radiation can be scattered either elastically (i.e. Rayleigh scattering) or inelastically (i.e. Raman scattering). Rayleigh scattering is more intense than Raman scattering therefore when light is scattered from a sample, most photons are elastically scattered such that the scattered photons have the same energy as the incident photons (Figure 32). A small percentage of the light is inelastically scattered such that the scattered photons do not have the same energy as the incident photons. The amount of light that is inelastically scattered is inversely proportional to the wavelength of the incident light to the fourth power (Equation 12).

$$\text{Raman scattering} \propto \frac{1}{\lambda^4} \quad \text{Equation 12}$$

Raman scattering can be divided into two types: Stokes and anti-Stokes. In the case of Stokes scattering, the sample absorbs energy and the emitted photon has less energy than the incident photon (i.e. red-shifted relative to the incident photon). In the case of anti-Stokes scattering, the sample loses energy and the emitted photon has more energy than the incident photon (i.e. blue-shifted relative to the incident photon). Stokes scattering originates from the lowest vibrational level of the ground electronic state while anti-Stokes scattering originates from an excited vibrational level of the ground electronic state. Anti-Stokes scattering is weaker than Stokes scattering due to the population difference between the excited vibrational level and the lowest vibrational level. An illustration of Stokes, and anti-Stokes scattering is shown in Figure 32.

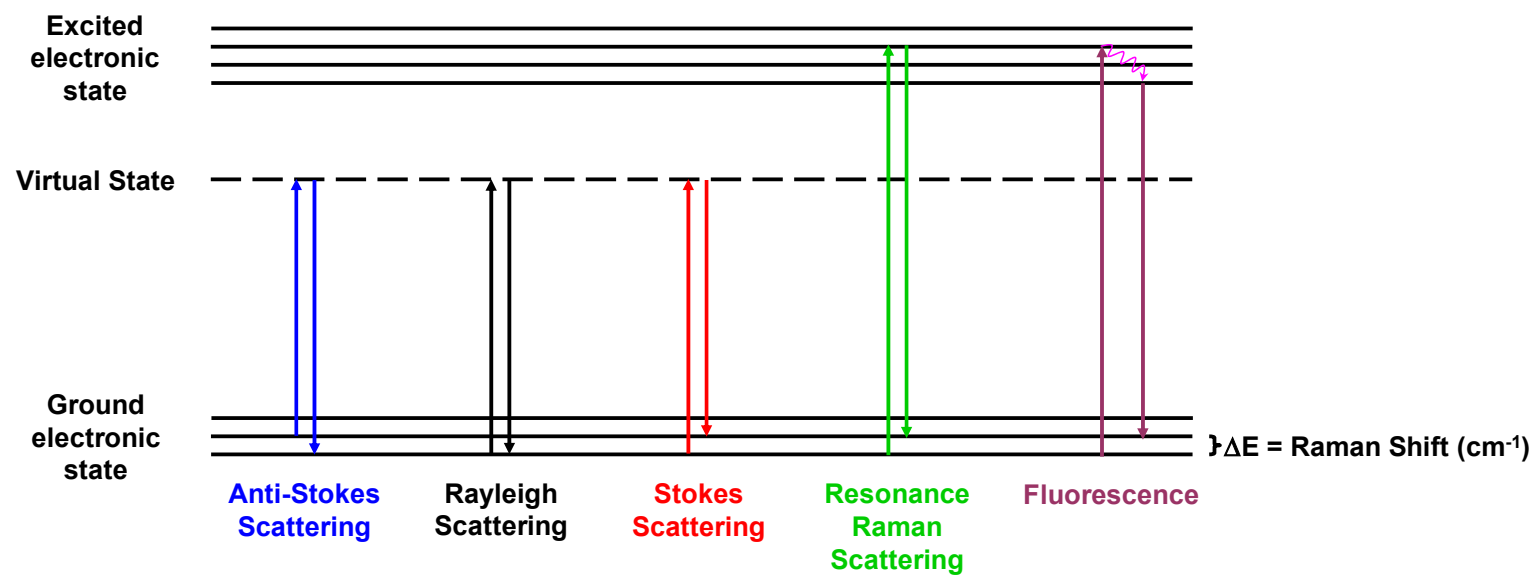


Figure 32: Illustration of anti-Stokes, Rayleigh, and Stokes scattering in addition to resonance Raman scattering and fluorescence.

The difference in energy between the incident photon and the emitted photon for both Stokes and anti-Stokes scattering is referred to as the Raman shift (Equation 13). Raman shifts have a positive value for Stokes scattering and a negative value for anti-Stokes scattering.

$$\text{Raman Shift}(\text{cm}^{-1}) = \Delta E = E_{\text{incident}} - E_{\text{emitted}} \quad \text{Equation 13}$$

A representative example of a Raman spectrum, the Raman spectrum of the trimethyltin functionalized building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, is shown in Figure 33 with the main Raman features labeled.

It is important to note that if the vibrational mode is both Raman and IR active then the Raman shift and the IR frequency are identical. The Raman shift is independent of the wavelength of excitation and thus the same spectrum should be obtained for a given sample when using different wavelengths. This however is not always the case and will be further discussed in the following sections.

Fluorescence

One of the main reasons why different spectra may be obtained at different excitation wavelengths is due to fluorescence interference. It is difficult to obtain Raman spectra once the sample fluoresces.[105] In fact interference from fluorescence is a common problem when visible excitation sources are used and has been a major hindrance to the application of Raman spectroscopy in catalyst characterization.[106] Fluorescence intensity can be several orders of magnitude greater than the Raman intensity ($I_{\text{fluorescence}} : I_{\text{Raman}} \sim 10^6$) so fluorescence from even a minor impurity (e.g. residual aromatic hydrocarbon solvents) can render the Raman spectrum undetectable.[106]

An example of an impurity that causes fluorescence problems is silicon grease which is known to have strong fluorescence.[105] As seen in Figure 34, the Raman spectrum of silicon grease is obscured by fluorescence.

Methods Developed to Avoid or Minimize Fluorescence

Two methods developed to avoid or minimize fluorescence are FT-Raman spectroscopy and UV-Raman spectroscopy. Both techniques will briefly be discussed here however there are excellent references that cover both FT-Raman[107-109] and UV-Raman[105,106] in more detail.

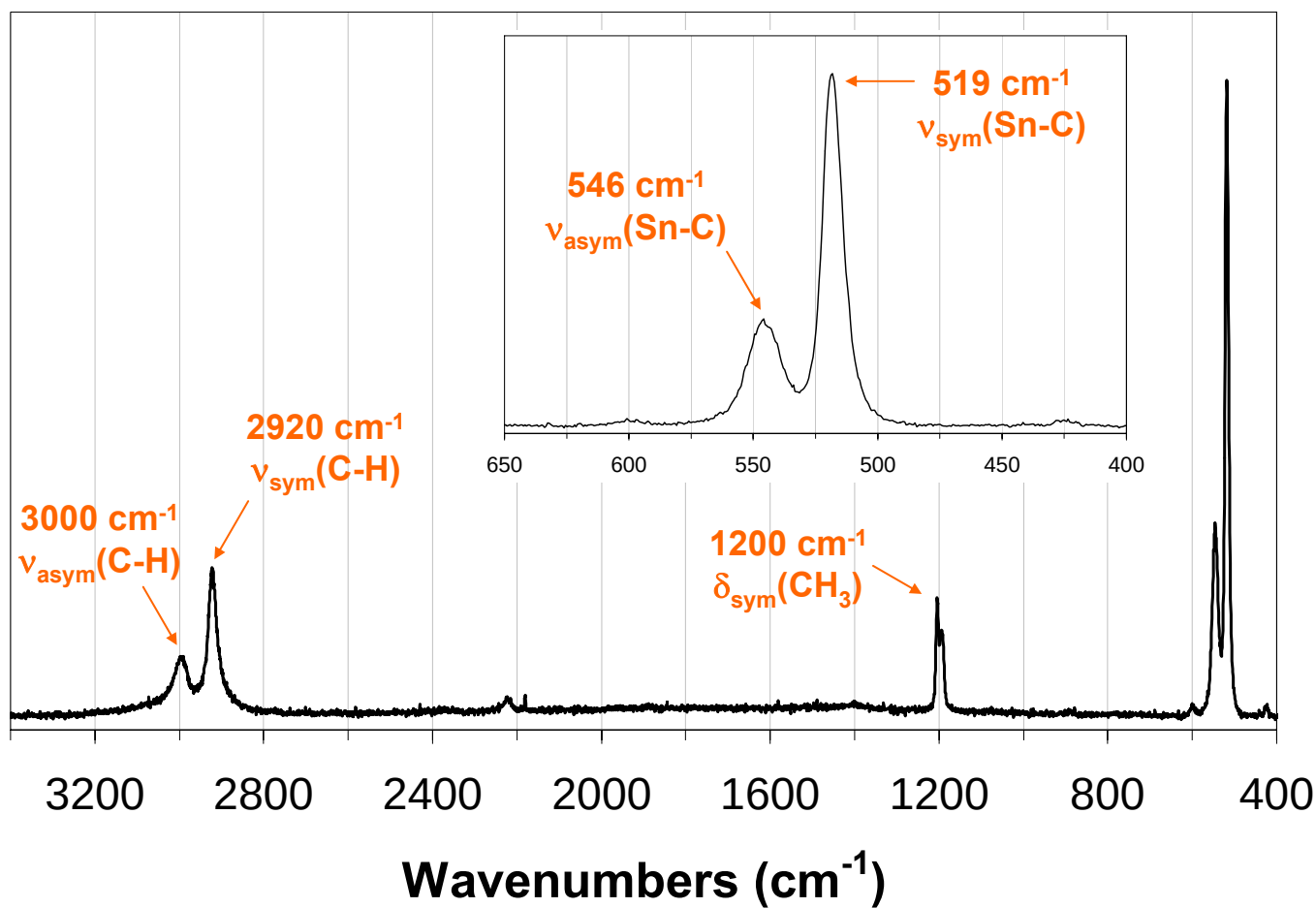


Figure 33: Raman spectrum ($400\text{--}3400 \text{ cm}^{-1}$) of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with the Raman shifts and vibrational modes labeled. The inset contains the expanded Raman spectrum ($400\text{--}650 \text{ cm}^{-1}$).

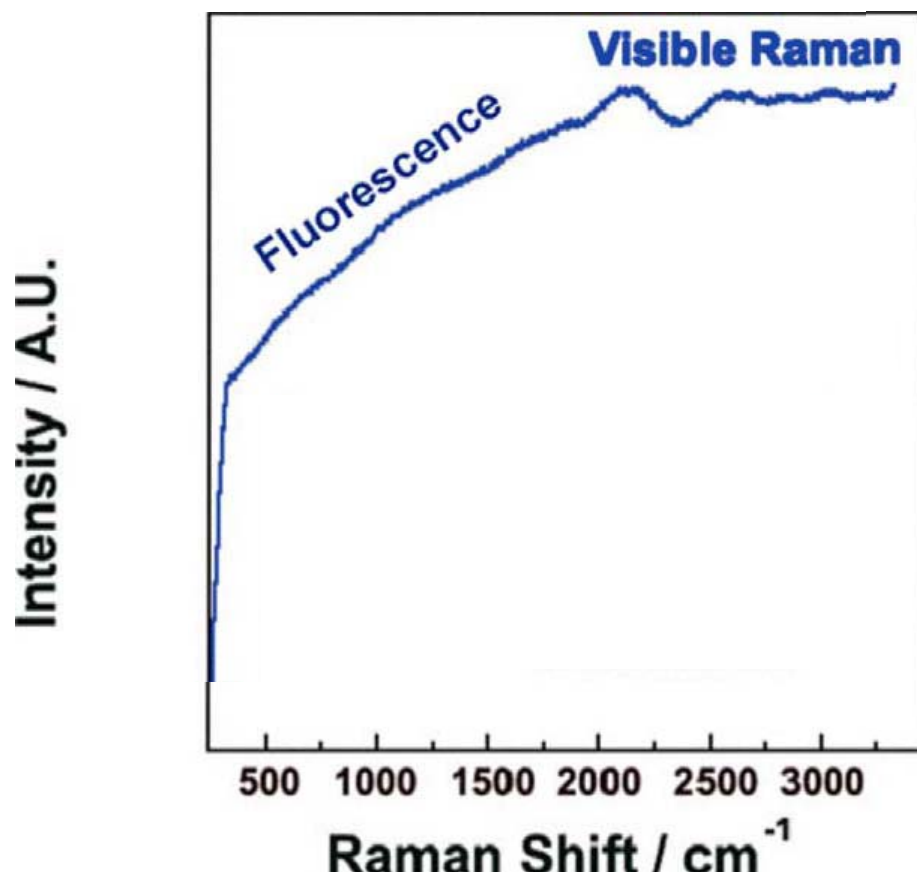


Figure 34: Raman spectrum (500-3500 cm⁻¹) of silicon grease using visible excitation (Figure was reproduced from Ref [105]).

FT-Raman Spectroscopy

FT-Raman spectra are acquired by irradiating a sample with near IR radiation (typically a Nd/YAG laser, 1064 nm) and the spectrometer typically uses a Michelson interferometer (just like FT-IR) to detect and analyze the scattered light. Fluorescence is less likely to occur when lower excitation energies are used so using near IR radiation may avoid fluorescence but at the expense of Raman scattering intensity which is significantly decreased.[106] There is a loss of approximately a factor of 18 going from 514 nm excitation to 1064 nm excitation. Fourier transform data collection allows one to regain sensitivity by fast signal averaging relative to more traditional dispersive Raman methods.

The Raman spectra of anthracene, poly(p-phenylene)terephthalamide, and a cyanine dye are all obscured by fluorescence interference when a visible excitation source is used in all cases however the fluorescence interference is removed or minimized when a near IR excitation source is used as shown in Figure 35.

UV Raman Spectroscopy

UV-Raman spectra are acquired by irradiating a sample with UV radiation, typically below 260 nm. Even though the UV laser still excites fluorescence, its interference is minimized because the Raman peaks typically appear at shorter wavelengths than fluorescence, which would otherwise obscure the spectrum (Figure 36).[105,106] The physical origin of this surprising result is the rapid rate of internal conversion from the high energy electronic states excited at wavelengths less than 260 nm to lower energy singlet or triplet states that fluoresce at wavelengths greater than 300 nm.[106]

One of the main drawbacks of UV-Raman is that the UV laser can cause sample degradation in the form of sample burning when a particular spot is irradiated for too long. Sample degradation can be avoided or minimized by spinning or rastering the sample such that a particular spot is not irradiated long enough to cause damage.

Referring back to the Raman spectrum of silicon grease that is obscured by fluorescence when a visible excitation source is used (Figure 34) one can see that fluorescence interference is completely removed when a UV excitation source is used as shown in Figure 37.

In addition to the reduction of fluorescence interference, UV-Raman can also benefit

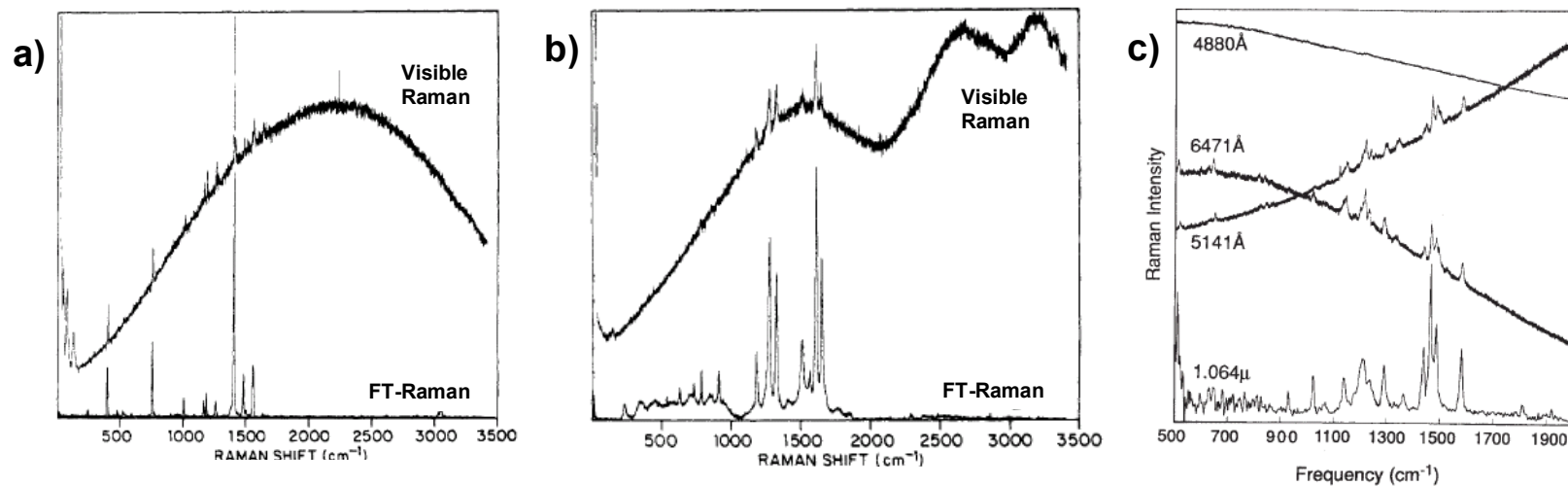


Figure 35: Examples of how FT-Raman removes or minimizes fluorescence interference. (a) Raman spectra of anthracene (Figure was reproduced from Ref [109]), (b) Raman spectra of poly(p-phenylene)terephthalimide (Figure was reproduced from Ref [109]), and (c) Raman spectra of a cyanine dye[110] (Figure was reproduced from Ref [108]).

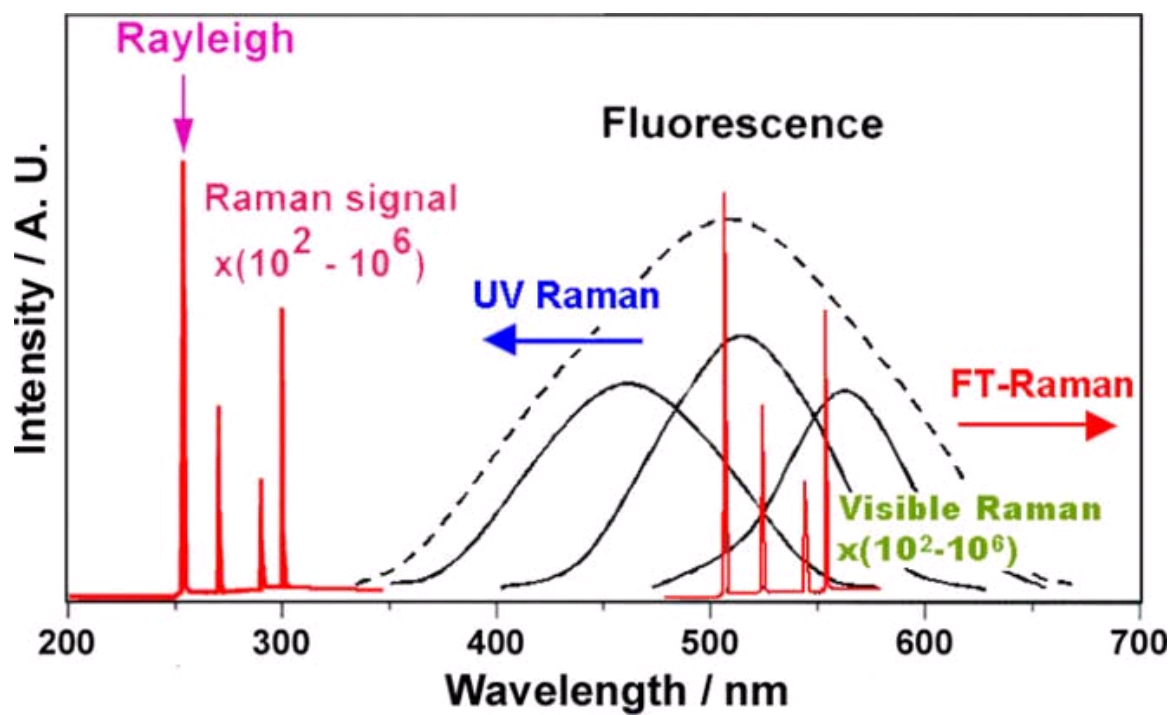


Figure 36: Illustration showing fluorescence at longer wavelengths than Raman scattering (Figure was reproduced from Ref [105]).

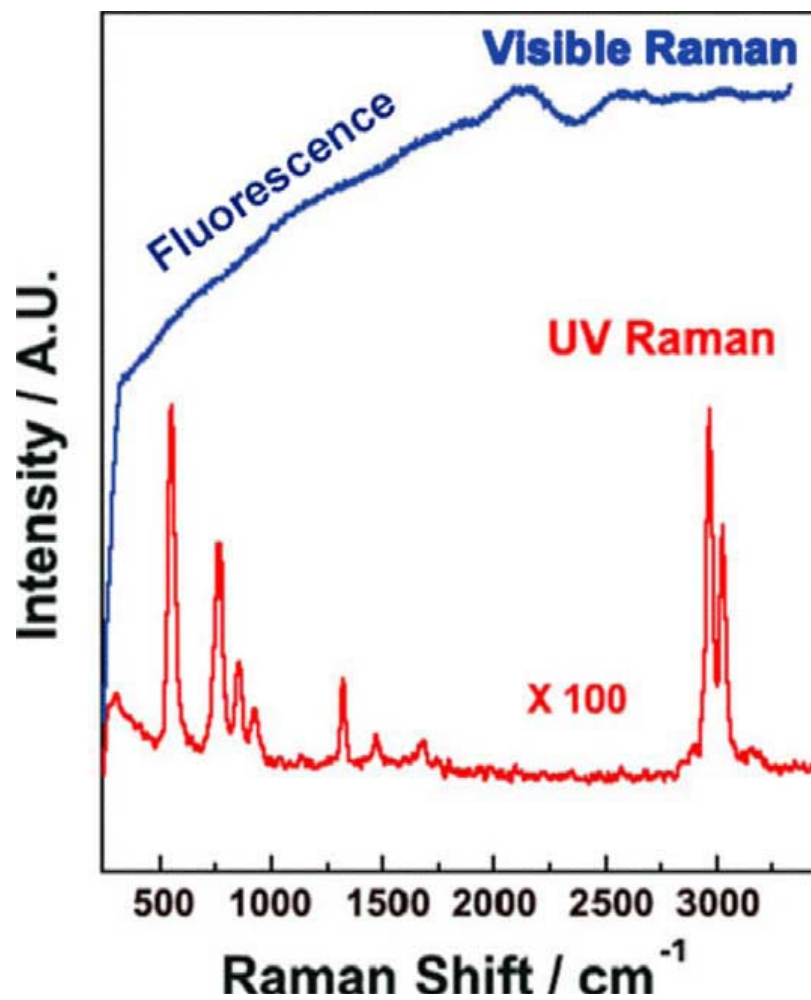


Figure 37: Raman spectra ($500\text{--}3500\text{ cm}^{-1}$) at silicon grease using both visible (blue spectrum) and UV (red spectrum) excitation (Figure was reproduced from Ref [105]).

from resonance enhancement. An illustration of resonance Raman scattering is shown in Figure 32. UV resonance Raman spectroscopy occurs when the incident photon has enough energy to excite an electronic transition that is coupled to the vibrations in the molecule. UV resonance Raman spectroscopy has been used to identify isolated transition metal ions that have been incorporated into framework positions of silica based materials. There typically is a charge transfer transition between the framework oxygen anion and the framework transition metal cation that is generally located in the UV region (e.g. 220 nm $\rightarrow$ TS-1; 250 nm $\rightarrow$ Fe-ZSM-5; 280 nm $\rightarrow$ V-MCM-41).[105] The intensity of Raman bands, which originate from electronic transitions between those states, may be enhanced three-to-five orders of magnitude.

UV resonance Raman enhancement is exhibited when TS-1 is irradiated with 244 nm radiation. As shown in Figure 38, the Raman feature at 1125 cm^{-1} , which is assigned to Ti-O-Si vibrations, is significantly enhanced when UV excitation is used.[111]

X-ray Adsorption Spectroscopy (XAS)

X-ray Absorption Spectroscopy (XAS) is an element specific averaging spectroscopic technique that probes the immediate environment (within about 6 Å) of the absorbing element and provides both structural and electronic information about the element. XAS can be used to characterize a variety of materials, both crystalline and amorphous. XAS has proven to be an especially powerful characterization tool in several areas of chemistry, biology, and material science where crystalline materials are impossible to obtain or samples are inherently amorphous (e.g. glasses). XAS has been used extensively to characterize heterogeneous catalysts.[67,71,112] The following will provide a brief introduction to XAS, the collection of XAS data, and the analysis of XAS data. Two excellent references for the theoretical and practical aspects of XAS are the website xas.org and Chapter 14 (Analysis of Soils and Minerals Using X-ray Absorption Spectroscopy) in *Methods of Soil Analysis Part 5 – Mineralogical Methods*. [113] Furthermore, a book written by Scott Calvin (*XAFS for Everyone*) is currently being revised and should be published in the near future.

The fundamentals of X-ray Absorption Spectroscopy

X-ray absorption occurs when an atom absorbs a photon of the appropriate energy which results in the excitation of core electrons into higher energy unoccupied electron orbitals or into

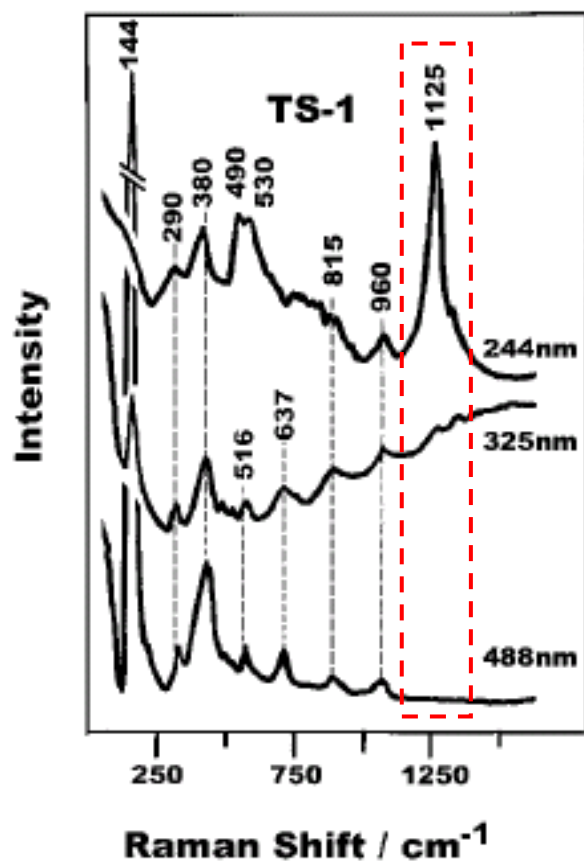


Figure 38: Raman spectra of TS-1 illustrating UV resonance Raman enhancement (Figure was reproduced from Ref [111]).

the continuum where the electron is no longer associated with the atom (Figure 39). The resulting core-hole pair is then filled by an electron from a higher energy orbital which produces fluorescence radiation. Table 2 summarizes the nomenclature for specific X-ray absorption transitions (frequently referred to as absorption edges) and Figure 40 shows energies of edges for the elements according to their atomic number (Z).

XAS may be divided into two distinct areas: X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) (Figure 41).

The XANES portion (approximately -50 to +100 eV relative to the absorption edge energy) of an X-ray absorption spectrum includes any pre-edge features, the absorption edge itself, and other features on or just above the absorption edge (Figure 42).

Pre-edge features generally refer to features below the absorption edge that are the result of dipole-allowed transitions between two bound states (typically $s \rightarrow d$ transitions) of the atom. Since the excited electron remains bound, the excitation process must adhere to the selection rules for electric dipole transitions. The presence and intensities of pre-edge features depends on the symmetry around a metal site. For example, the ground states of a d^0 Ti(IV) center in octahedral or tetrahedral environments are A_{1g} and A_1 respectively.[114] The pre-edge feature observed below the Ti K edge in Figure 42 is assigned to the $1s \rightarrow 3d$ transition, i.e. a bound electronic transition. When the Ti(IV) sites have octahedral (O_h) symmetry, the symmetry of the dipole operator is T_{1u} and the symmetry of the empty d orbitals are T_{2g} and E_g . Thus, the direct product for the electronic transitions ($A_{1g} \rightarrow T_{2g}$ and $A_{1g} \rightarrow E_g$) does not contain A_{1g} so the electronic transitions are Laporte forbidden. Consequently, the pre-edge feature is not expected to be observed when the Ti(IV) sites have octahedral symmetry. When the Ti(IV) sites have tetrahedral (T_d) symmetry, the symmetry of the dipole operator is T_2 and the symmetry of the empty d orbitals are T_2 and E . Thus, the direct product for the electronic transitions ($A_1 \rightarrow T_2$ and $A_1 \rightarrow E$) does contain A_1 so the electronic transitions are Laporte allowed. Consequently, the pre-edge feature is expected to be observed when the Ti(IV) sites have tetrahedral symmetry.

Pre-edge features (defined as $s \rightarrow d$ transitions) can only be observed at the K and L_I edges of an absorbing atom with the appropriate symmetry and unoccupied valence orbitals. For example, XAS spectra collected at the Sn K edge (29200 eV) does not exhibit pre-edge features

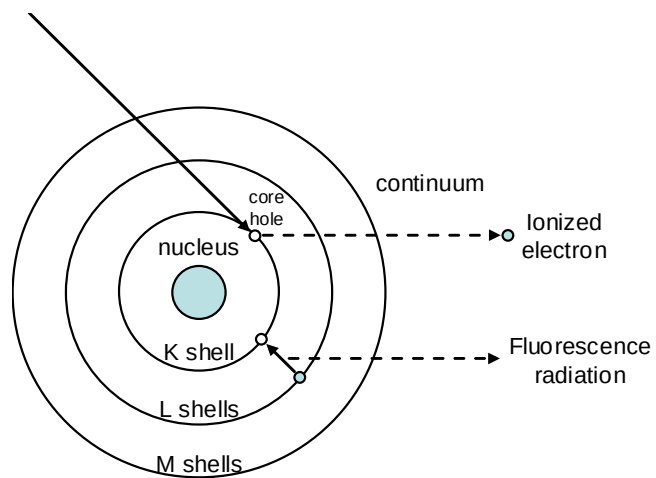


Figure 39: Illustration of X-ray absorption and fluorescence.

Table 2: Summary of the nomenclature for specific X-ray absorption transitions (X-ray absorption edges)

Edge	Excited Core Electron
K	1s
L _I	2s
L _{II}	2p _{1/2}
L _{III}	2p _{3/2}

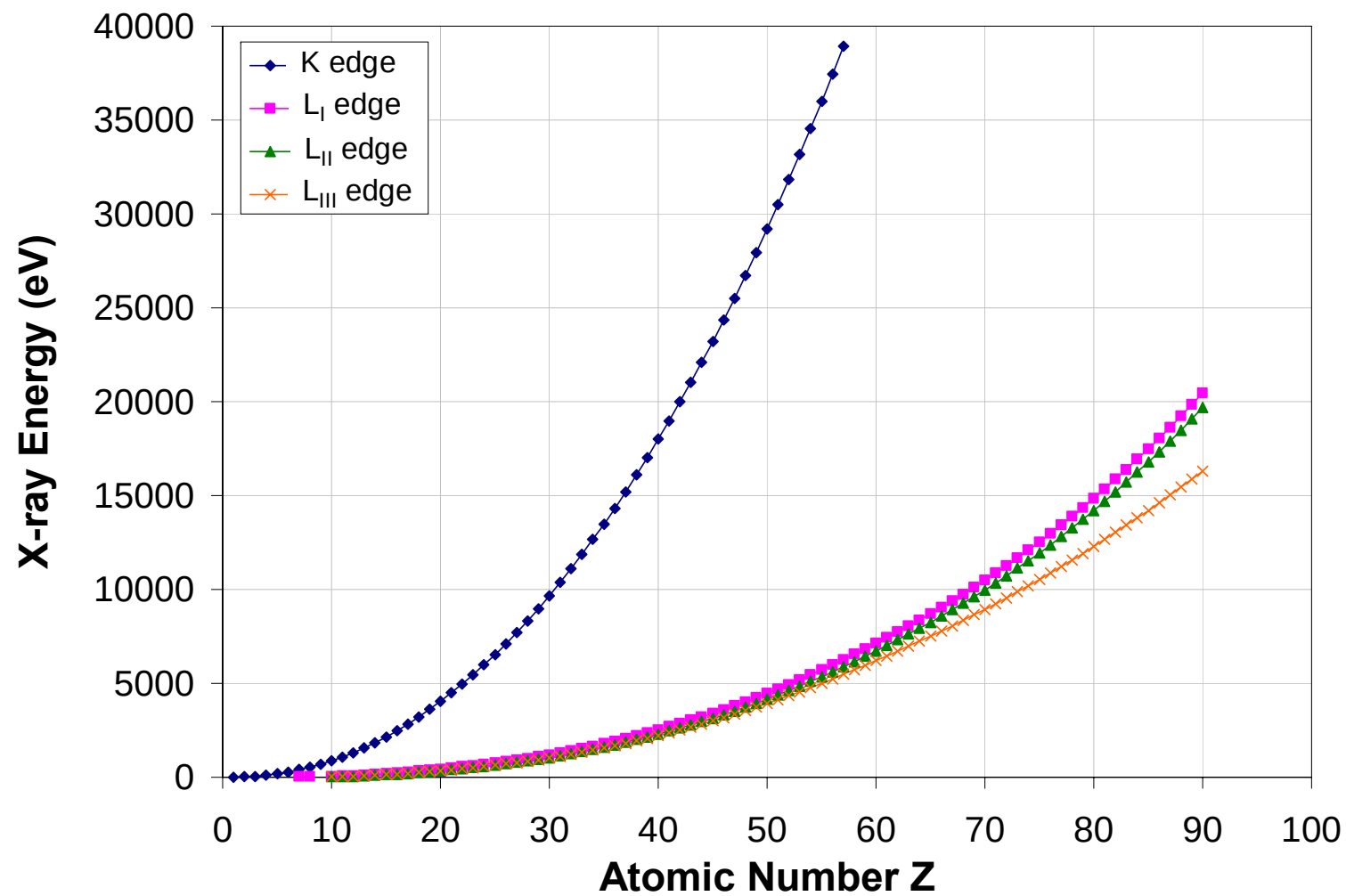


Figure 40: Plot of X-ray absorption energies as a function of atomic number.

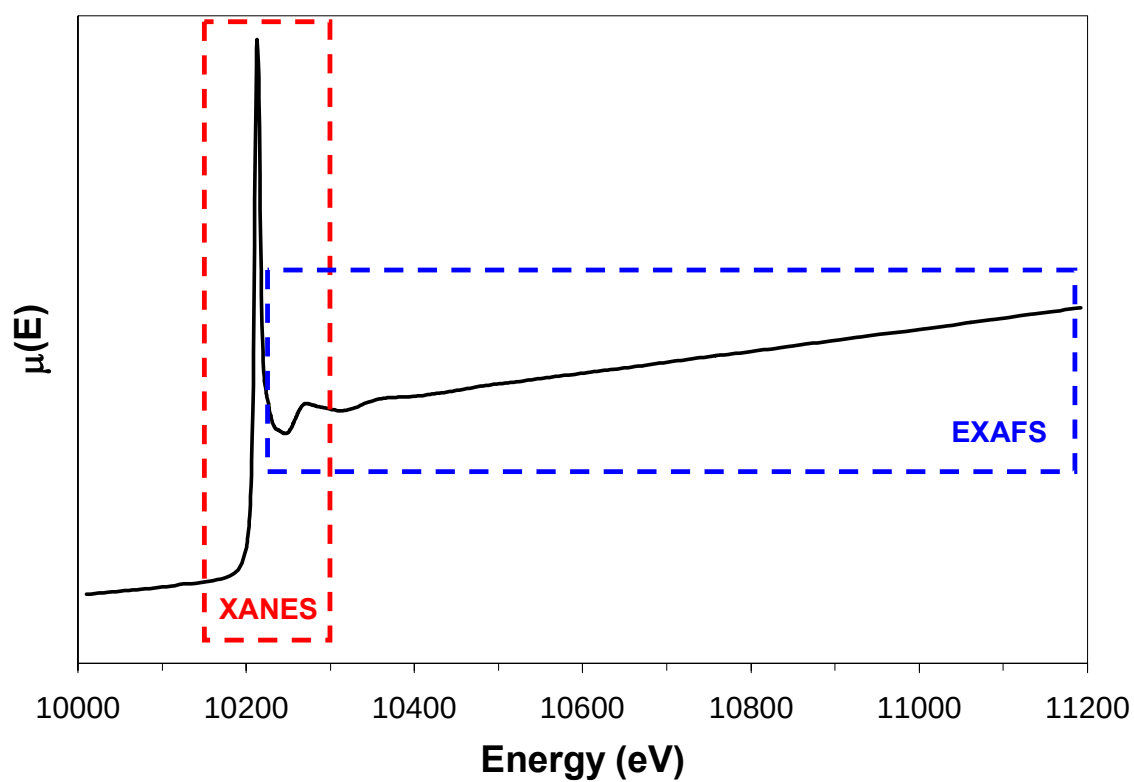


Figure 41: Representative XAS spectrum (W L_{III} edge) divided into two distinct areas: XANES and EXAFS.

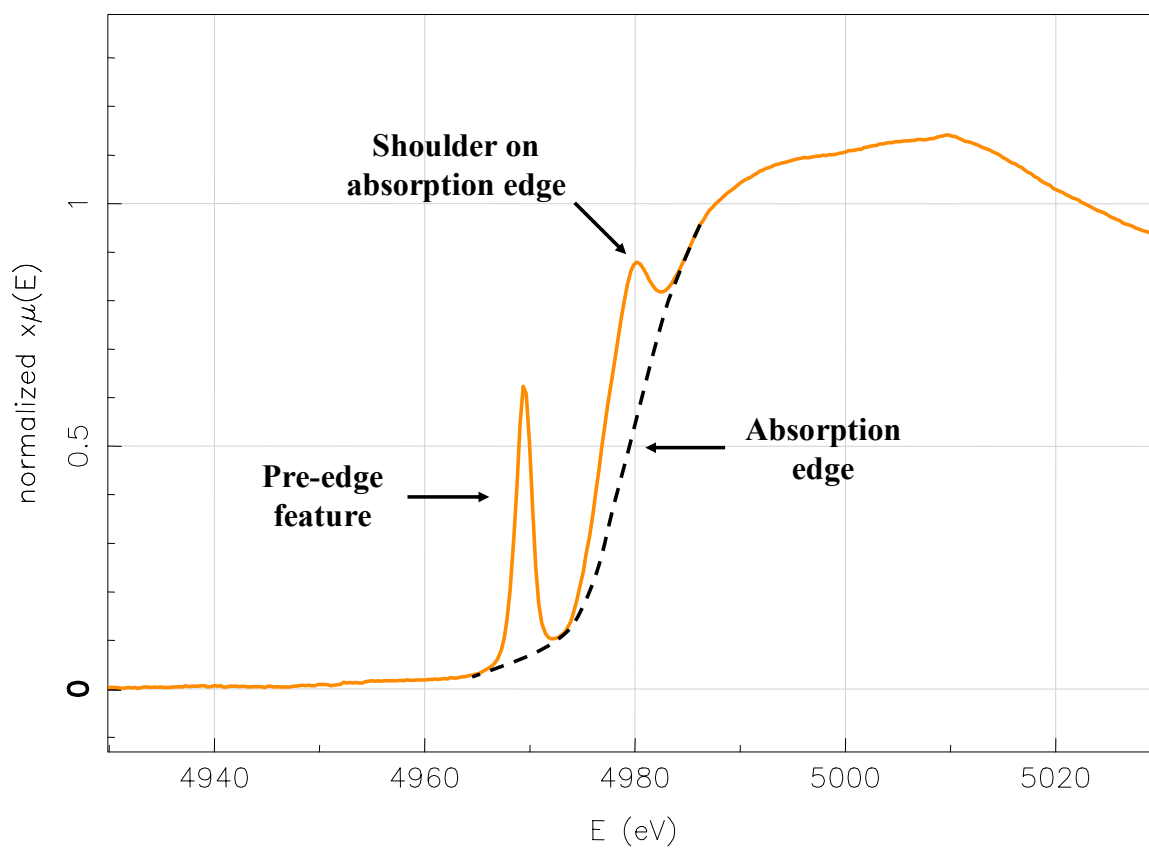


Figure 42: Representative XANES spectrum (Ti K edge) for a tetrahedral Ti(IV) center in a silicate matrix.

because the Sn d-orbitals are occupied. XAS spectra collected at the W L_{III} edge (10207 eV) do not exhibit pre-edge features because core s electrons are not being excited. While various theoretical and computational models for these processes exist[115] simple, qualitative predictions for the intensities of pre-edge features relative to the absorption edge are more commonly used in the interpretation of XANES features for transition metal sites.[116-118] The intensity, width, and position of the pre-edge feature can provide information about the coordination geometry and the oxidation state of the absorbing atom.[114] Figure 43 illustrates one such relationship between the intensity of the pre-edge versus the position of the pre-edge feature for fourfold, fivefold and sixfold coordinated Ti.[118] Several other examples illustrating the relationship between the pre-edge feature and the coordination geometry and/or oxidation state of the absorbing atom are present in the literature.[96,119,120]

The threshold energy, or position of the absorption edge, E_0 (generally defined as the point of inflection of the absorption edge) can provide information about the oxidation state of the absorbing atom. Figure 44 illustrates a typical XANES spectrum at the tungsten L_{III} edge with E_0 labeled.

In an atom, the positive charge of the nucleus is screened by the negative charge of the electrons. In an atom of higher formal oxidation state with fewer electrons than protons, the energy states of the remaining electrons are lowered slightly, which causes the ionization energy defined by absorption edge to increase. That is, an X-ray with slightly greater energy is required to ionize a core electron. The position of the absorption edge for an atom in a higher oxidation state is usually shifted to a higher energy relative to the neutral atom (Figure 45).

Several examples illustrating the relationship between the position of the absorption edge and the oxidation state of the absorbing atom are present in the literature.[96,120,121] Even though these relationships are well known, there are numerous published XAS data and analyses that never mention the E_0 value. This is because E_0 has little influence on EXAFS fitting so the exact value is not extremely important unless a XANES analysis is being conducted.

White lines or X-ray absorption threshold resonances[122], generally refer to features on the absorption edge that are the result of dipole-allowed transitions between two bound states (typically $p \rightarrow d$ transitions). Since the excited electron remains bound, the excitation process

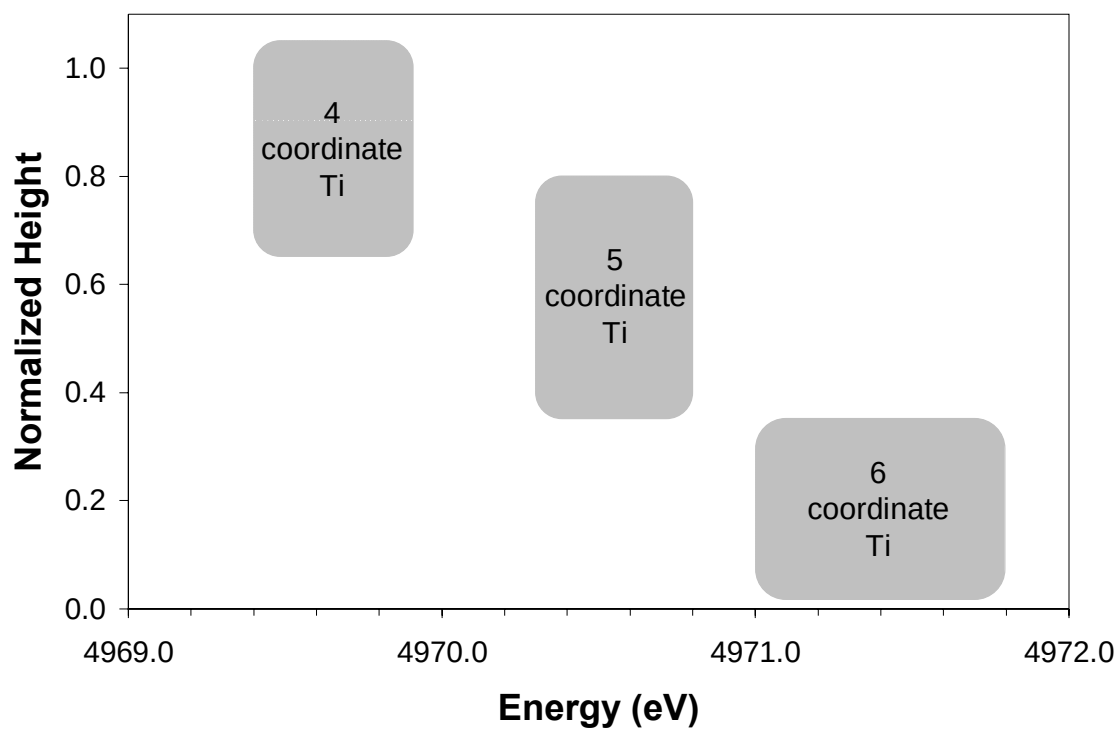


Figure 43: Plot illustrating how the coordination geometry of the titanium atom influences the Ti (K edge) pre-edge feature intensity and the position of the pre-edge feature. (Figure was reproduced from Ref [118]).

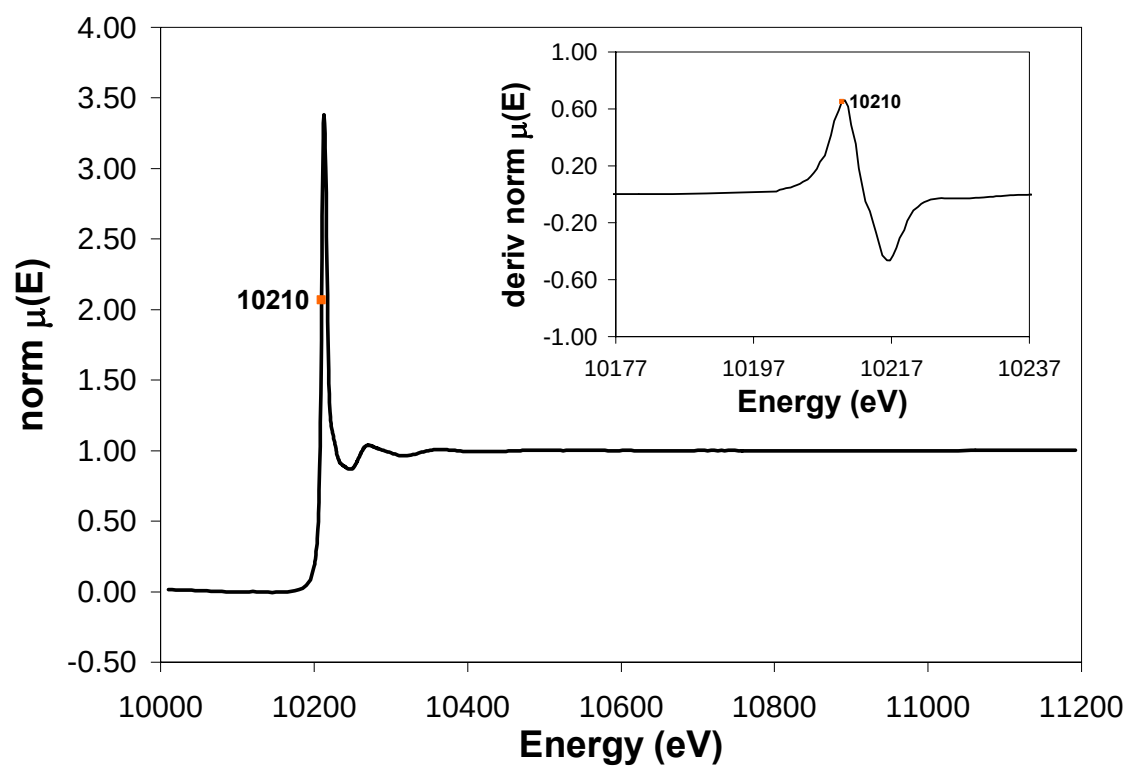


Figure 44: XAS spectrum (W L_{III} edge) with E_0 labeled at 10210 eV. The inset contains the derivative XANES spectrum with E_0 labeled.

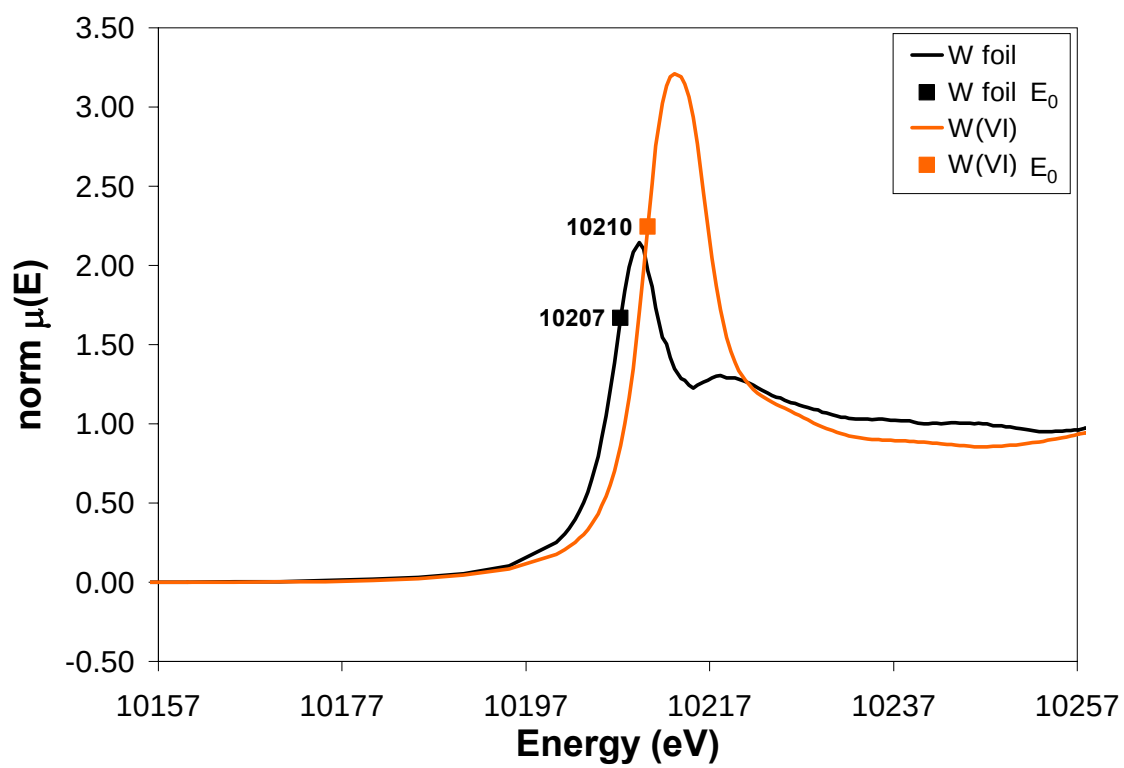


Figure 45: XANES spectra (W L_{III} edge) comparing the edge position of tungsten(VI) oxide (WO₃, W(VI)) and tungsten foil (W(0)).

must adhere to the selection rules for electric dipole transitions. The transitions ascribed to white lines ($p \rightarrow d$) associated with L_{II} and L_{III} edges are not affected by the symmetry around the absorbing atom. The intensity of the white line observed at the L_{III} edge reflects occupancy of the d orbitals of the absorbing atom.[117,122] Thus, filling the d-orbitals of the absorbing atom suppresses the observed white line. Figure 46 illustrates the effect of filling the d-orbitals has on the white line intensity for 5d transition metals Ta (5 valence electrons) through Au (11 valence electrons).

The presence of other features on or above the absorption edge can provide information about certain ligands bound to the absorbing atom as well as the coordination geometry around the absorbing atom. For example, the presence of a shoulder on the K absorption edge of titanium, as seen in Figure 42, has been shown to qualitatively indicate whether a chloride ligand is bound to the absorbing atom.[96] Figure 47 illustrates three examples of additional features just above the absorption edge. At the tungsten L_{III} -edge the white line is split into two peaks when the tungsten centers have octahedral symmetry (Cr_2WO_6 and Ba_2NiWO_6) and one peak when the tungsten centers do not have octahedral symmetry (Figure 47a).[117] At the tungsten L_I -edge a peak around 12130 eV is observed when the tungsten centers have octahedral symmetry (Cr_2WO_6 and Ba_2NiWO_6) (Figure 47b).[117] At the zirconium K-edge a prominent peak is observed ~ 20 eV above the absorption edge when the zirconium centers have tetrahedral symmetry (e.g. $ZrSiO_4$) and at ~ 40 eV above the edge when the zirconium centers have octahedral symmetry (e.g. $ZrBaO_3$) (Figure 47c).[116,123]

In summary, the XANES portion of an XAS spectrum is affected by the coordination geometry and/or oxidation state of the absorbing atom. In most cases, assignment of these features is based upon empirically based correlations observed for reference compounds.

The EXAFS portion (approximately +20 to +1000 eV above to the edge energy) of an X-ray absorption spectrum contains fine structure superimposed on the absorption edge background (Figure 48).

This fine structure is derived from backscattering of the outgoing photoelectron wave by shells of neighboring nuclei around the absorbing atom (Figure 49).

In contrast to XANES, an analytical theory has been developed that is frequently used to

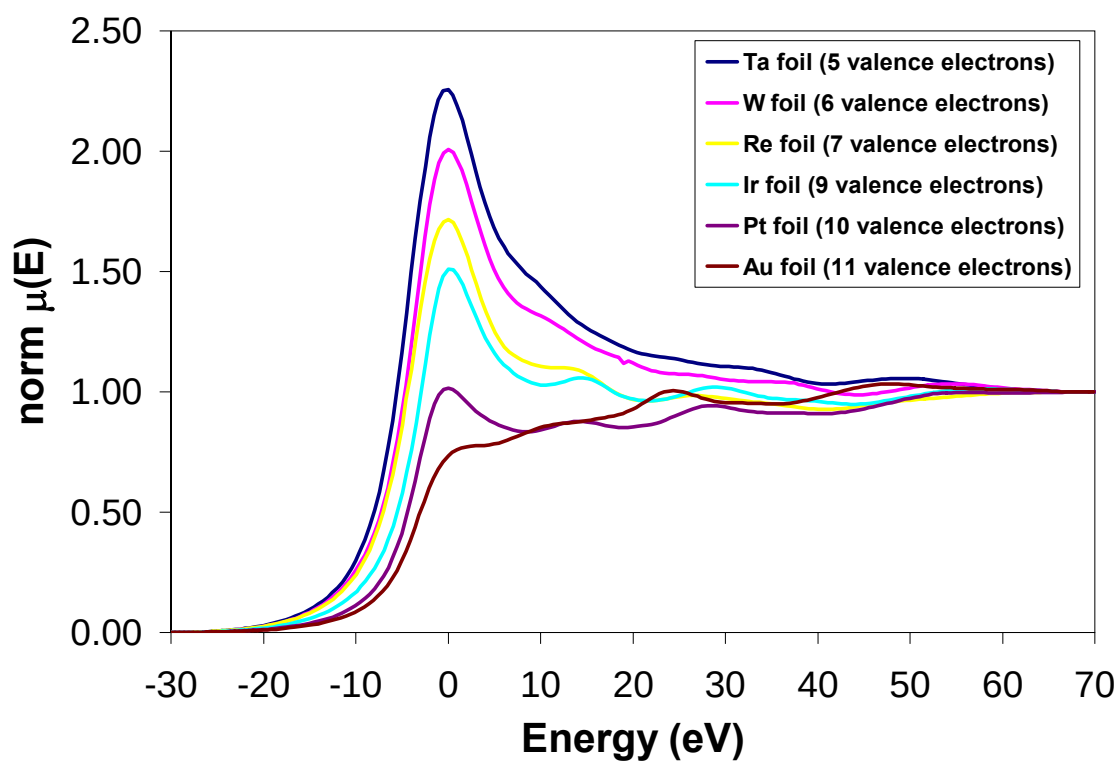


Figure 46: XANES spectra (L_{III} edge) of the 5d transition metals (tantalum (5 valence electrons) through gold (11 valence electrons)) illustrating how the intensity of the white line decreases as more valence electrons are added.[122]

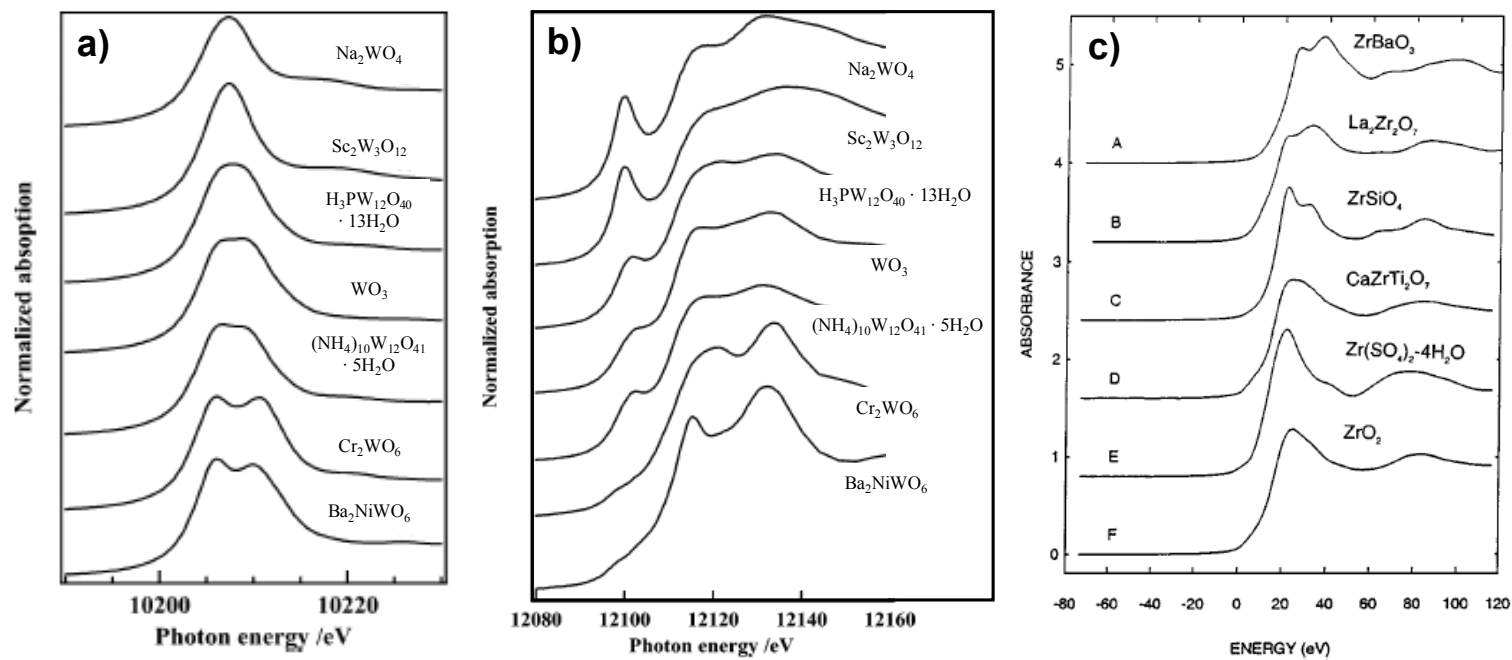


Figure 47: Examples of other features on or above the absorption edge (a) XANES spectra (W L_{III} edge) showing that the shape of the white line changes with the tungsten coordination geometry (Figure was reproduced from Ref [117]), (b) XANES spectra (W L_I edge) showing a feature above the absorption edge (Figure was reproduced from Ref [117]), and (c) XANES spectra (Zr K edge) showing a feature above the absorption edge (Figure was reproduced from Ref [123]).

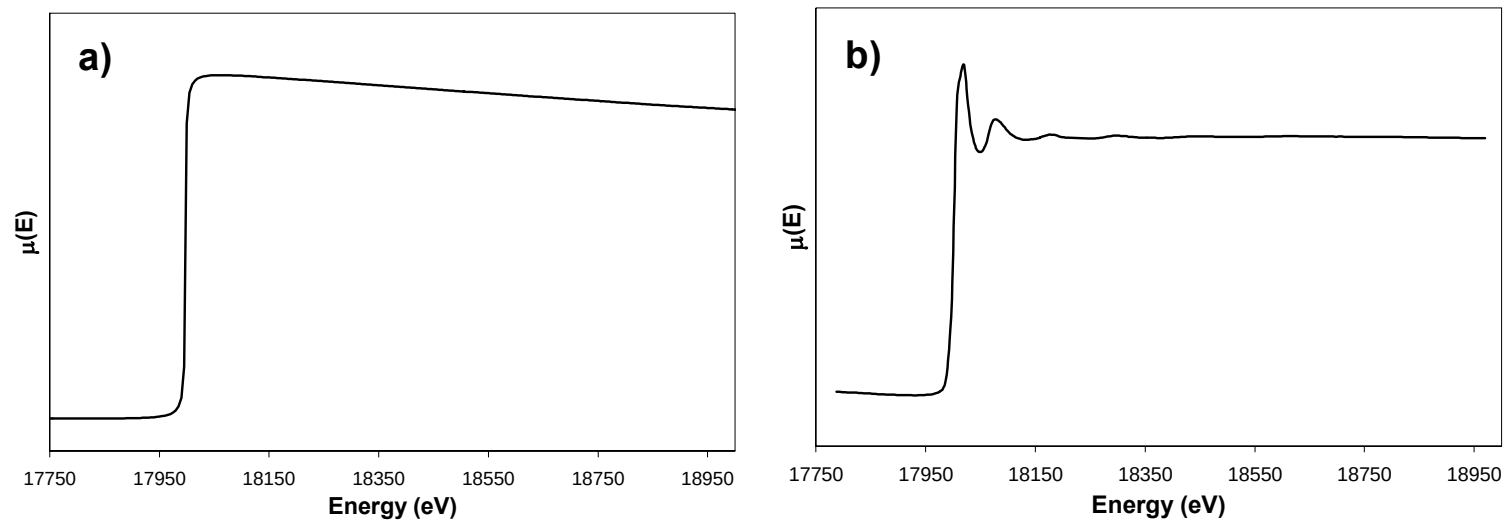


Figure 48: a) XAS spectrum (Zr K edge) showing the absorption edge background (smooth “bare atom” background) and b) XAS spectrum (Zr K edge) showing fine structure superimposed on the absorption edge.

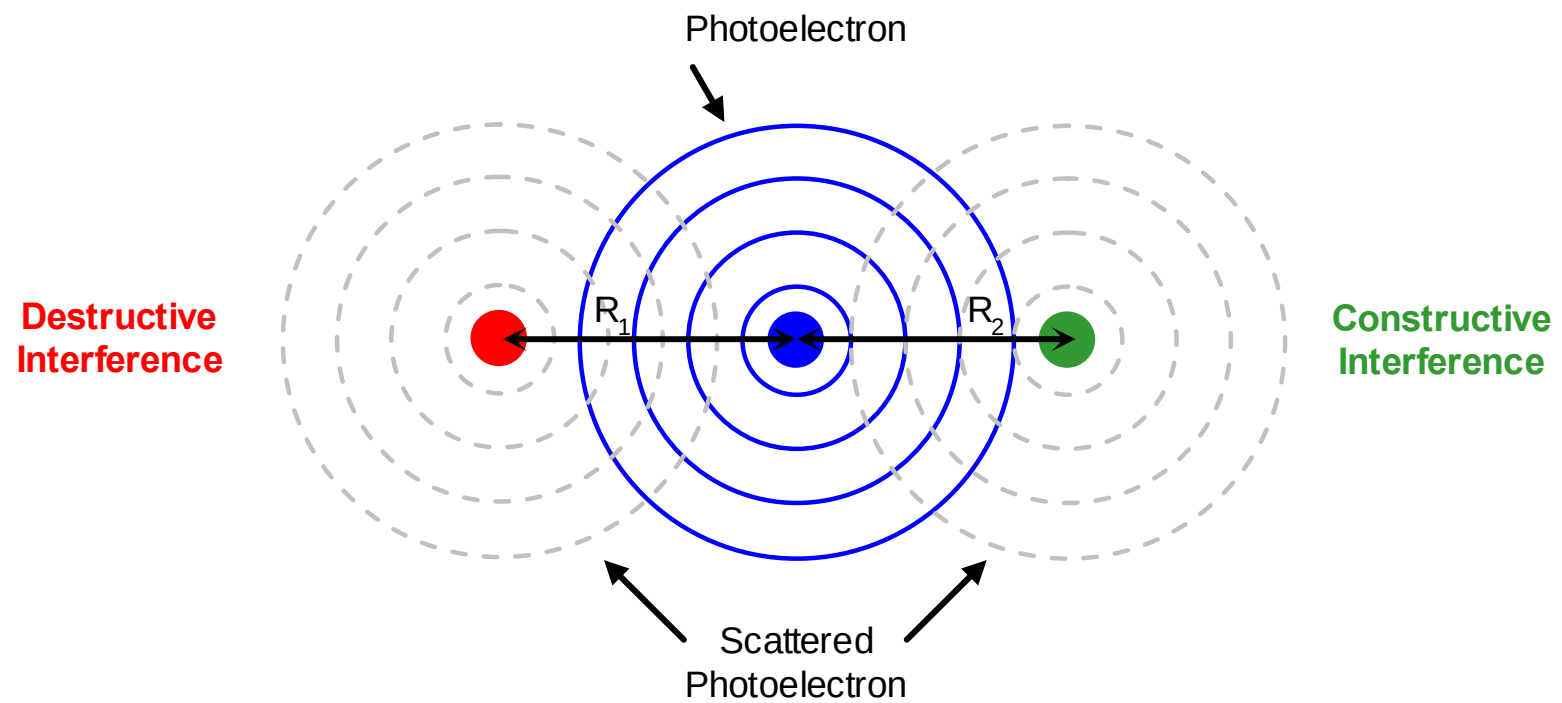


Figure 49: Illustration of constructive (right side) and destructive (left side) interference, absorbing atom is blue and the backscattering atoms are red and green.

model the EXAFS fine structure. This theory may be used to develop a quantitative model for the immediate environment around the absorbing atom (usually within 6 Å of the absorbing atom). The EXAFS spectrum contains both qualitative and quantitative information about the coordination spheres around the absorbing atom in a sample. Typically the first scattering (or coordination) sphere is defined as atoms directly bound to the absorbing atom while scattering spheres beyond the first are defined as atoms bound to the first scattering sphere but not directly bound to the absorbing atom (Figure 50).

The information derived from successful modeling of EXAFS data includes the identity of backscattering atoms around the absorbing atom, the bond/separation distance, the number of these bonds/interactions present in the shell (i.e. coordination number), and the amount of disorder in the backscatterer shell.

EXAFS is the modulation of the X-ray absorption coefficient, μ , at energies near and above an X-ray absorption edge. The intensity of an X-ray beam passing through a material of thickness t is given by the following equation

$$I_t = I_0 e^{-\mu t} \quad \text{Equation 14}$$

where I_t is the intensity transmitted through the material, I_0 is the X-ray intensity impinging on the material, and μ is the X-ray absorption coefficient (Figure 51).

The X-ray absorption coefficient μ depends strongly on the X-ray energy E , the atomic number Z of every atom in the sample, on the density ρ of the sample, and the atomic mass A .

$$\mu \approx \frac{r Z^4}{A E^3} \quad \text{Equation 15}$$

XAS measures the energy dependence of the X-ray absorption coefficient (denoted as $\mu(E)$) at and above the absorption edge of a selected element. $\mu(E)$ can be measured in transmission or fluorescence mode. In transmission mode, $\mu(E)$ is determined directly by measuring the photons transmitted through the sample.

$$I_t = I_0 e^{-\mu(E)t} \quad \text{Equation 16}$$

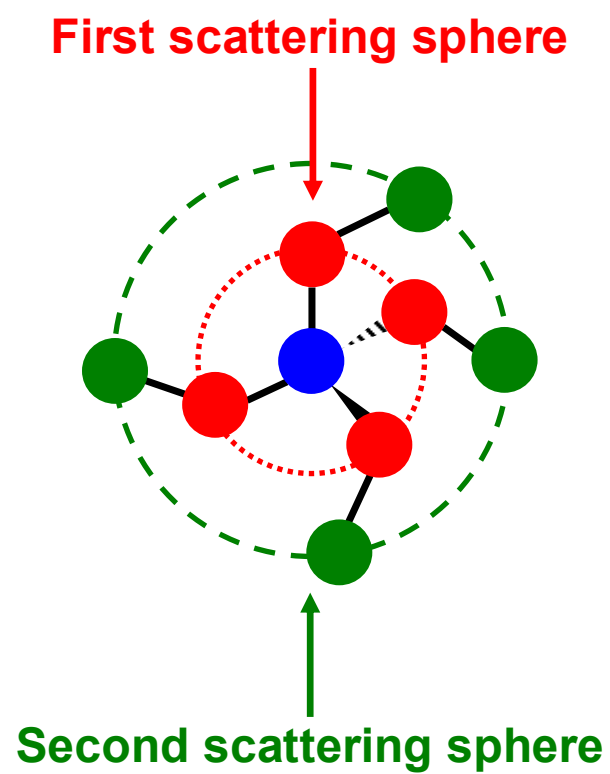


Figure 50: Illustration of the scattering spheres.

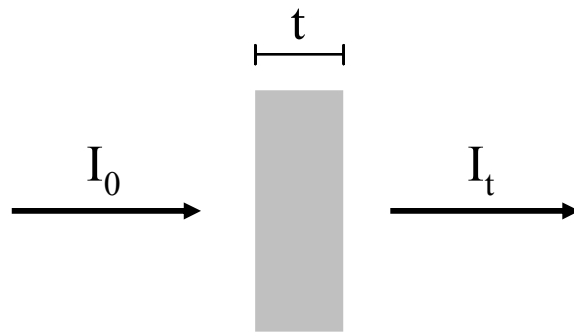


Figure 51: Illustration of X-rays with intensity I_0 impinging on a material of thickness t and the X-rays that are transmitted through the material with intensity I_t .

$$\mu(E)t = -\ln\left(\frac{I_t}{I_0}\right) = \ln\left(\frac{I_0}{I_t}\right) \quad \text{Equation 17}$$

In fluorescence mode, the absorption coefficient is proportional to the ratio of the measured fluorescence signal (I_{fluor}) and the initial signal (I_0).

$$\mu(E) \propto \frac{I_{\text{fluor}}}{I_0} \quad \text{Equation 18}$$

Once the data has been collected, the energy dependent EXAFS signal is defined as

$$\chi(E) = \frac{\mu(E) - \mu_0(E)}{\Delta\mu_0(E_0)} \quad \text{Equation 19}$$

where $\mu(E)$ is the energy dependent absorption coefficient, $\mu_0(E)$ is the absorption edge background (smooth “bare atom” background), and $\Delta\mu_0(E_0)$ is the edge jump. EXAFS is an interference effect (Figure 49) and depends on the wave-nature of the photoelectron as it scatters from atoms near the absorber. Thus it's convenient to think of EXAFS in terms of photoelectron wavenumber, k , rather than X-ray energy. k is defined as

$$|k| = \frac{2\pi}{\lambda} = \sqrt{\frac{8\pi^2 m(E_x - E_0)}{h^2}} = \sqrt{0.2624E} \quad \text{Equation 20}$$

Typically the EXAFS signal is defined as $\chi(k)$ and an EXAFS spectrum can be understood in terms of the EXAFS equation which can be written in terms of a sum of all the contributions from all scattering paths of the photoelectron

$$\chi(k) = \sum_i \chi_i(k) \quad \text{Equation 21}$$

Each path can be written in the form:

$$\chi_i(k) = \frac{(N_i S_0^2) F_{\text{eff}_i}(k)}{k R_i^2} \sin[2kR_i + \phi(k)] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}} \quad \text{Equation 22}$$

with

$$k^2 = \frac{2m_e(E - E_0)}{\hbar} \quad \text{Equation 23}$$

where N_i is the coordination number of the i^{th} shell of backscatterers, S_0^2 is the amplitude reduction factor (also referred to as passive electron reduction factor), $F_{\text{eff}}(k)$ is effective scattering amplitude, $\phi_i(k)$ is the effective scattering phase shift, σ_i^2 is the mean-square

displacement of the bond length between the absorber atom and the coordination atoms in a shell (also referred to as Debye-Waller factor), and $\lambda(k)$ is the mean free path of the photoelectron. $\phi_i(k)$ is defined as the phase-shift experienced by the photoelectron at the central atom and when it bounces off the scattering atom. $\lambda(k)$ is defined as the mean distance that a photoelectron travels after excitation (Figure 52). This term includes both the inelastic scattering of the photoelectron and the effect of the finite lifetime of the core-hole. Standard EXAFS processing and analysis software programs calculate $F_{\text{eff}}(k)$, $\phi_i(k)$, and $\lambda(k)$ for each scattering path of the photoelectron based on a given structural mode for the local environment of the absorbing atom (vide infra).

Collection of XAS data

XAS requires tunable monochromatic X-rays. Furthermore due to the attenuation of the EXAFS signal with respect to increasing R , a high flux of these X-rays is needed to accurately measure EXAFS fine structure at high k . For these reasons, XAS measurements are most commonly made at synchrotron radiation facilities. In the United States, there are three major synchrotron user facilities capable of making XAS measurements: the Advanced Photon Source (APS) at Argonne National Laboratory, the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory, and the Stanford Synchrotron Radiation Laboratory (SSRL) at Stanford Linear Accelerator Center. A fourth major synchrotron user facility, National Synchrotron Light Source II (NSLS-II), is currently being constructed at Brookhaven National Laboratory and is expected to be operational in 2015. NSLS-II will be a new state-of-the-art, medium-energy electron storage ring designed to deliver world-leading intensity and brightness, and will produce X-rays more than 10,000 times brighter than currently available at the NSLS.

Figure 53 presents a schematic illustration of the general experimental setup for making XAS measurements. In general, white light from a synchrotron X-ray source passes through a tunable monochromator producing a monochromatic X-ray beam. The beam then encounters vertical and horizontal slits which trim it to the appropriate size. The beam passes through an initial ion chamber detector I_0 before impinging on the sample which can be perpendicular or at a 45° angle to the incoming beam. The transmitted light passes through detector I_t while the fluorescence signal is detected as I_{fluor} .

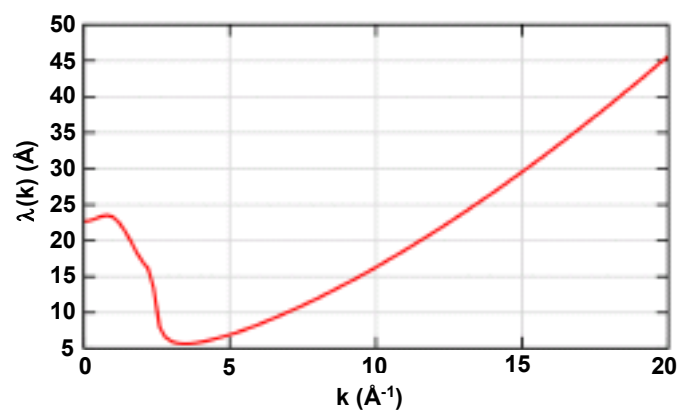


Figure 52: Plot of the mean free path of the photoelectron $\lambda(k)$ versus the photoelectron wavenumber k (Figure was reproduced from Ref [124]).

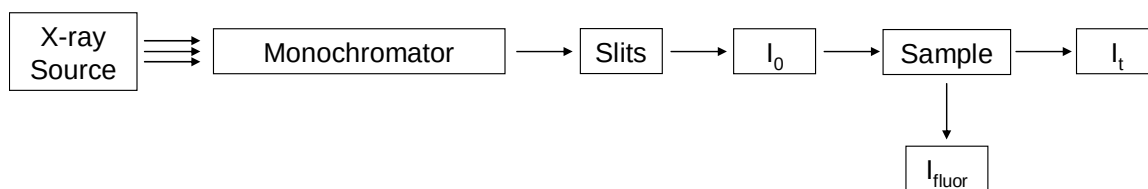


Figure 53: Illustration of a typical XAS setup.

XAS data collection is typically divided into four energy regions: pre-XANES (-150 to -15 eV relative to the absorption edge), XANES (-15 to +75 eV relative to the absorption edge), EXAFS near the absorption edge (+75 to +550 eV relative to the absorption edge), and EXAFS farther from the absorption edge (+550 to +1000 eV relative to the absorption edge). The monochromator step size and integration time are often adjusted depending on the intensity of the EXAFS signal for each energy region mentioned above, which decreases as the energy of the X-ray beam increases above the absorption edge. The monochromator step size defines the spectral resolution for each energy region. The smallest possible step size should be used through the XANES region in order to observe narrow preedge features and edge structure present in this region accurately. The step size is defined by the monochromator stepper motor which controls the angle of a matched pair of Si crystals. A step size of 0.3 eV at low energy (5000 eV) corresponds to moving the Si crystal 0.001480° while a step size of 0.3 eV at high energy (20000 eV) corresponds to moving the Si crystal 0.000085° , a significantly smaller change in the angle of the Si crystal. Generally the monochromator stepper motor moves in discrete steps and if these discrete steps do not correspond to small enough angle changes for the desired resolution then a coarser resolution must be used in order to get the monochromator stepper motor to function properly. Typical step sizes for the different regions are: pre-XANES region is 5 eV, 0.3-1.5 eV for the XANES region, ~ 1.5 -4.5 eV (0.05k) in the EXAFS near the absorption edge region, and ~ 4.5 -6.1 eV (0.05k) in the EXAFS farther from the absorption edge region. The EXAFS signal decreases significantly at energies above the edge so the integration time is increased in order to increase the signal to noise ratio of the data. A typical integration time for the pre-XANES region is 1 s, followed by 2 s for the XANES region, 3 s in the EXAFS near the absorption edge region, and 4 s in the EXAFS farther from the absorption edge region.

The specific data collection parameters used to collect the XAS data presented in this dissertation can be found in the experimental section of chapters 3 and 4.

Analysis of XAS data

In general, there are two different methods of X-ray absorption analysis. The first method is based on comparing unknown spectra with those of well-characterized, physical “standards.” For EXAFS analysis, spectra for physical standards can be used to make comparisons, optimize the theoretical models, and assess the performance of the beamline. The second method involves

modeling the experimental spectrum for an unknown sample with a theoretical spectrum generated using a structural model and theoretically calculated phase and amplitude factors. The theoretical spectrum is then fit to the experimental spectrum via a non-linear least squares analysis to determine if the structural model is accurate. Usually a combination of these two techniques is used for EXAFS analysis. On the other hand, XANES analysis relies heavily on comparisons with standards although recently developed theoretical and computational programs are becoming more accurate and useful for XANES analysis.

Data processing and analysis can be performed using one of several computational programs (e.g. IFEFFIT[125], WinXAS[126], GNXAS[127,128], etc). The data analysis procedure used to analyze the XAS data presented in this dissertation can be found in the experimental section of chapters 3 and 4.

As mentioned earlier an EXAFS spectrum is defined by the EXAFS equation, which is easiest to understand for a single scattering path. The EXAFS equation is slightly modified when attempting to fit a model to experiment data. Thus each path can be written in the following form:

$$\chi_i(k) = \frac{(N_i S_0^2) F_{eff_i}(k)}{k R_i^2} \sin[2kR_i + \phi(k)] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\lambda(k)}} \quad \text{Equation 24}$$

with

$$R_i = R_{0i} + \Delta R_i \quad \text{Equation 25}$$

and

$$k^2 = \frac{2m_e(E - E_0 + \Delta E_0)}{\hbar} \quad \text{Equation 26}$$

where R_i is the refined distance between the absorbing atom and the backscattering atom, R_{0i} is the distance between the absorbing atom and the backscattering atom in the theoretical model, ΔR_i is the resulting calculated difference between R_{0i} and R_i , and ΔE_0 is the resulting calculated adjustment of the initial E_0 assignment. The contribution of each term to the EXAFS signal is summarized briefly in the table below. The parameters that are often determined from a fit to the EXAFS spectrum affect either the amplitude of the EXAFS oscillations (N , S_0^2 , σ^2) or the phase of the oscillations (ΔE_0 and ΔR).

$(N_i S_0^2)$	These terms modify the amplitude of the EXAFS signal and do not have a k-dependence. S_0^2 usually has a value between 0.7 and 1.0.
$F_{eff_i}(k)$	This term is provided by the analysis software and does not affect any fit parameters.
$\frac{1}{R_i^2}$	The contribution from a shell of atoms at a distance R_i ; the inverse dependency on distance diminishes the EXAFS with increasing distance from the absorber. Attenuating Factor
$\sin[2kR_i + \phi(k)]$	This term accounts for the oscillations in the EXAFS signal with a phase give by $2kR_i + \phi_i(k)$.
$e^{-2\sigma_i^2 k^2}$	This exponential term is a classic Debye-Waller factor (σ^2). σ^2 attempts to model dynamic (thermal) disorder as well as static disorder (structural heterogeneity) within a single shell of backscatters. Attenuating Factor
$e^{\frac{-2R_i}{\lambda(k)}}$	This exponential term depends on $\lambda(k)$, which is provided/calculated by the analysis software and does not affect any fit parameters. Attenuating Factor
ΔR_i	This term represents a change in the interatomic distance relative to the initial path length R_i .
ΔE_0	This term relates to a change in the photoelectron energy. This value is used to align the energy scale of the theoretical spectrum to match the measured spectrum.

Typically the total XAS signal $\mu(E)$ ($\mu_0 + \mu_\chi$) is initially displayed as energy space (E-space) plots. Figure 54 shows a typical E-space plot for both transmission and fluorescence data. In general, the EXAFS signal for transmission data decreases as the energy increases while the EXAFS signal for fluorescence data increases as the energy increases.

Backscattering fine structure is extracted from the smooth absorption edge background and is displayed as $\chi(k)$ in reciprocal space (k-space) plots (Figure 55). Figure 56 is an example of a typical k-space plot that has been k^3 weighted to observe the EXAFS signal at high k.

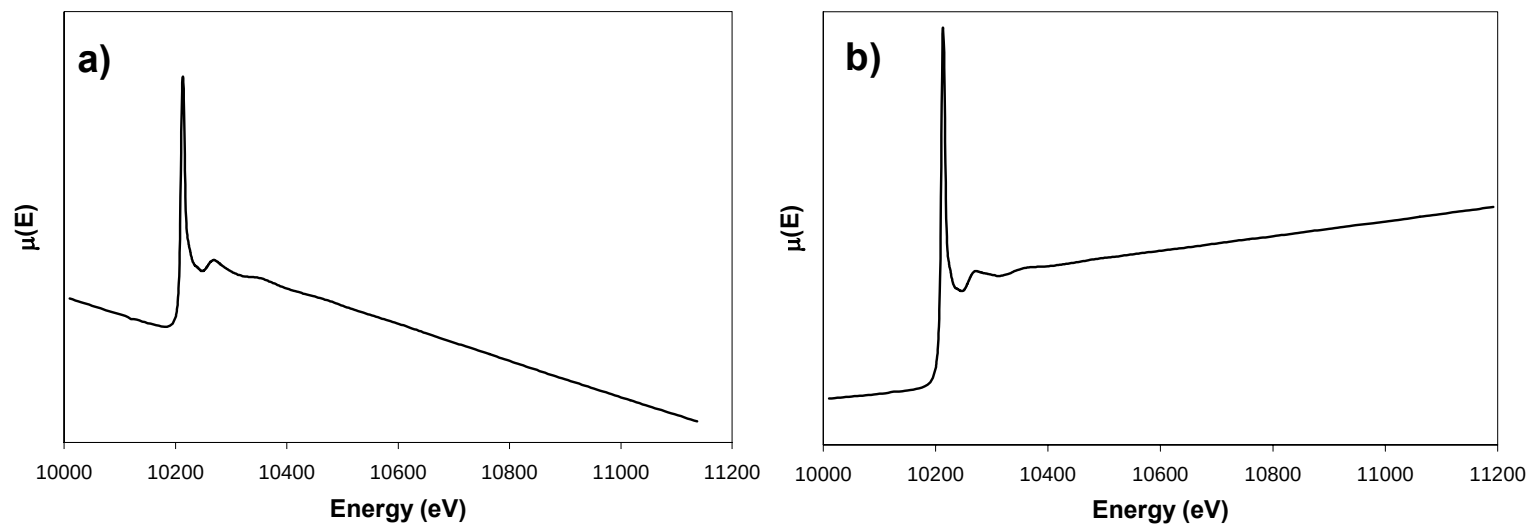


Figure 54: XAS spectra (W L_{III} edge) collected in a) transmission and b) fluorescence mode.

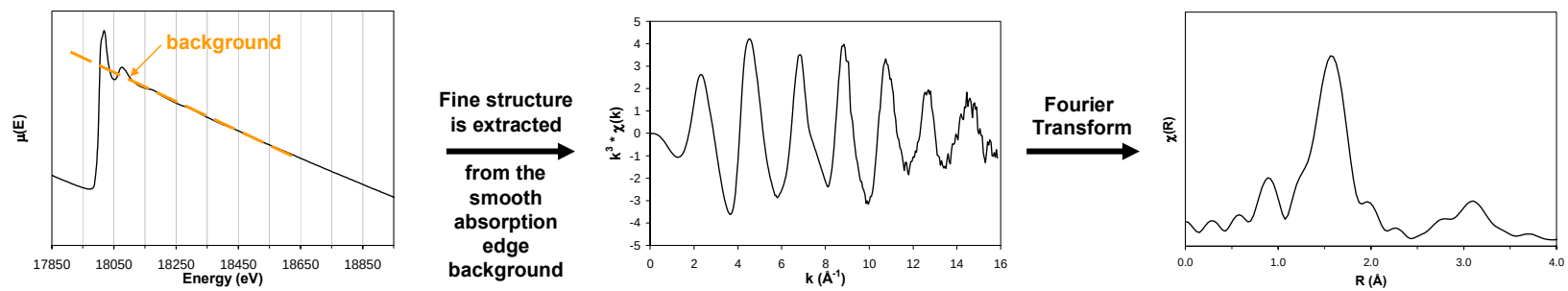


Figure 55: Illustration of the extraction of fine structure from the smooth absorption edge background to generate $\chi(k)$ which is then Fourier transformed to generate $\chi(R)$.

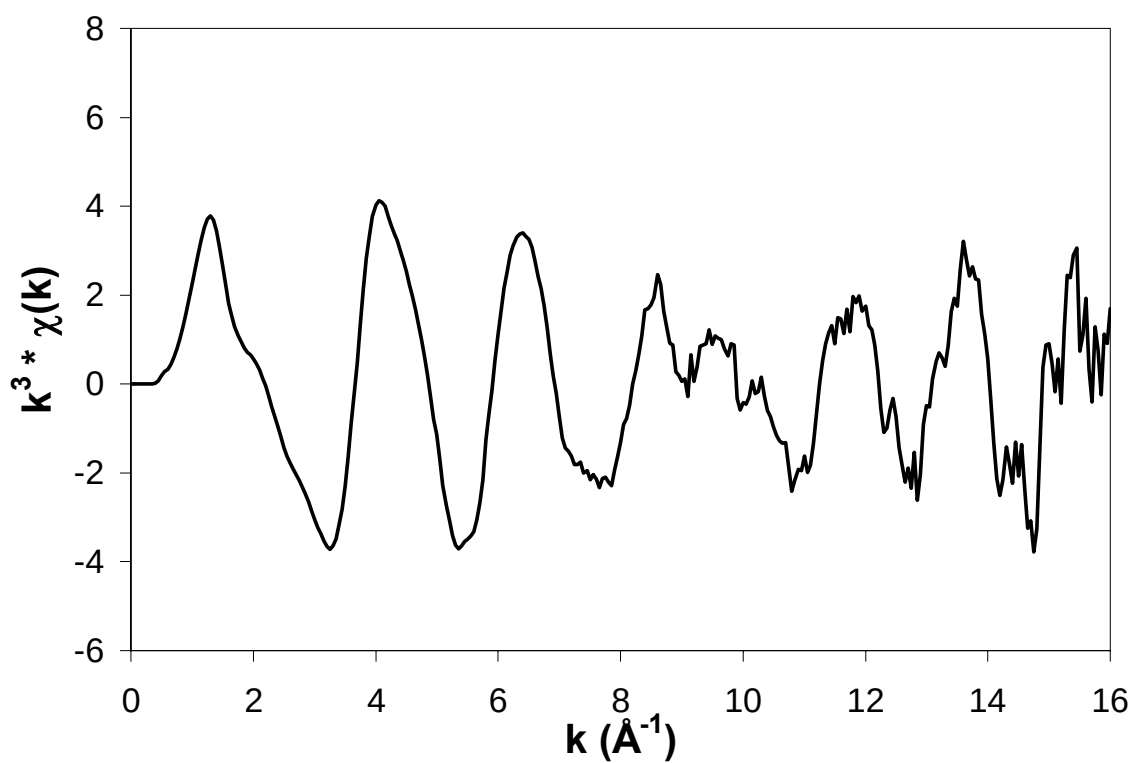


Figure 56: Example of a typical k-space plot that has been k^3 weighted to observe the EXAFS signal at high k.

The k-space data are then Fourier transformed and displayed as R-space plots (Figure 55). Figure 57 is an example of a typical R-space plot.

At this point, a structural model which will be used to calculate theoretical scattering amplitude and phase shift is constructed using estimates of bond lengths and angles found in the literature. Fit parameters (S_0^2 , N, ΔR , ΔE_0 , σ^2) are defined for each scattering path followed by an iterative refinement of these fit parameters. A fitting procedure is complete when the fit parameters converge to stable and acceptable values and the statistical measures of the fit (R-factor, χ^2 , and reduced χ^2) are also acceptable.

When the results of successful XAS analyses are published one should consult sources for the criteria for reporting XAS analyses.[113,129,130] Even though reporting criteria exists, there still seems to be a lack of a standard for reporting XAS data which can frustrate both EXAFS practitioners as well as scientists who, while needing such information, can find it difficult to access the accuracy of EXAFS analyses in the literature. There is no such thing as reporting “too much” information. It never hurts to report more information than you the writer thinks is necessary. If the reader is provided with all the information about data collection and analysis then the reader instead of the writer can decide what is important for the reader’s specific application.

Nitrogen Adsorption/Desorption Measurements

Gas, most often nitrogen, adsorption methods are techniques that assess the surface area, total pore volume, and pore size distribution of porous materials. The following will provide a brief introduction to adsorption/desorption isotherms and hysteresis loops, Brunauer-Emmett-Teller (BET) surface area, total pore volume determination, Barrett-Joyner-Halenda (BJH) pore size distributions, average pore radius determination, statistical thickness (t) plots and standard reduced adsorption (α_s) plots. The International Union of Pure and Applied Chemistry (IUPAC) has published a good reference that discusses many of the important topics associated with nitrogen adsorption/desorption measurements.[131] Nitrogen adsorption/desorption data for two types of silica gel (Davisil® Grade 635 and Aerosil 200) are presented to illustrate the concepts and calculations that are discussed in this section.

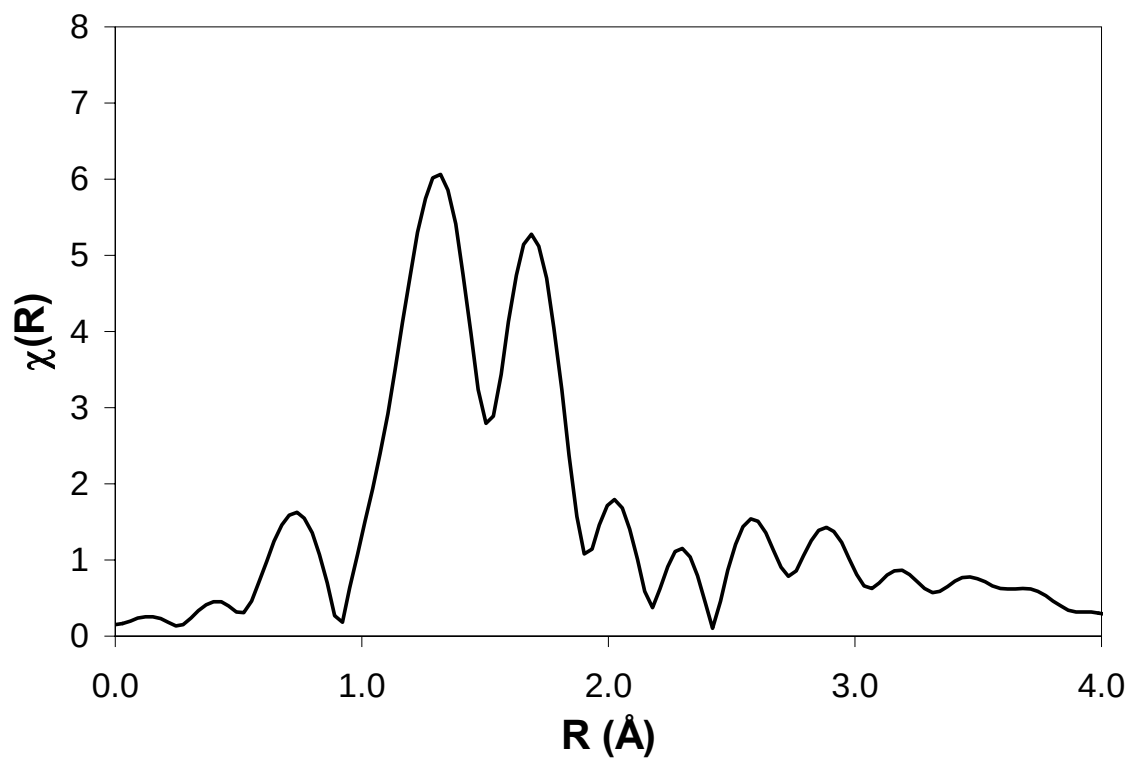


Figure 57: Example of a typical R-space plot.

Adsorption/Desorption Isotherms and Hysteresis Loops

The data collected by the instrument are the volume of nitrogen adsorbed (V_{ads}) at varying relative pressures (P/P_0) which, when graphically represented, are referred to as an adsorption/desorption isotherm. IUPAC has grouped all adsorption/desorption isotherms into one of six types which are presented in Figure 58.[131] These classifications are qualitative, so isotherms generally do not fit perfectly into one group but most will exhibit characteristics of a specific type. Type I isotherms are concave to the x-axis (P/P_0) exhibiting prominent adsorption at low relative pressures with the amount adsorbed (V_{ads}) leveling off as P/P_0 approaches 1. Type I isotherms are given by microporous materials. Type II isotherms are concave to the x-axis at low relative pressures then increase linearly and are convex to the x-axis at high relative pressures. Type II isotherms are given by non-porous or macroporous adsorbents. Type II isotherms represent unrestricted monolayer-multilayer adsorption. The point labeled B in Figure 58 is thought to be where monolayer coverage is complete and multilayer adsorption begins. Type III isotherms are convex to the x-axis (P/P_0) over the entire P/P_0 range. Type III isotherms are not common and are characteristic of weak gas-solid interactions.[132] Type IV isotherms are concave to the x-axis at low relative pressure (similar to Type II isotherms), exhibit prominent adsorption, followed by leveling off at high relative pressures. A characteristic of Type IV isotherms is the presence of a hysteresis loop, which is associated with capillary condensation taking place in mesopores. Type V isotherms visually appear to be similar to Type III isotherms at low P/P_0 and Type IV at high P/P_0 ; however, Type V are quite uncommon. Type VI isotherms are characterized by a series of adsorption “steps” over the relative pressure range. Type VI isotherms are given by samples that exhibit stepwise multilayer adsorption on a uniform nonporous surface. The height of each step represents the monolayer capacity for each adsorbed layer.

Table 3 summarizes the key characteristics of each type of adsorption/desorption isotherm.

Hysteresis loops appearing in the multilayer range ($P/P_0 = 0.4 - 0.8$) of isotherms are associated with capillary condensation in mesopores. IUPAC classifies hysteresis loops into one of four types (Figure 59).[131] H1 hysteresis loops exhibit parallel and nearly vertical

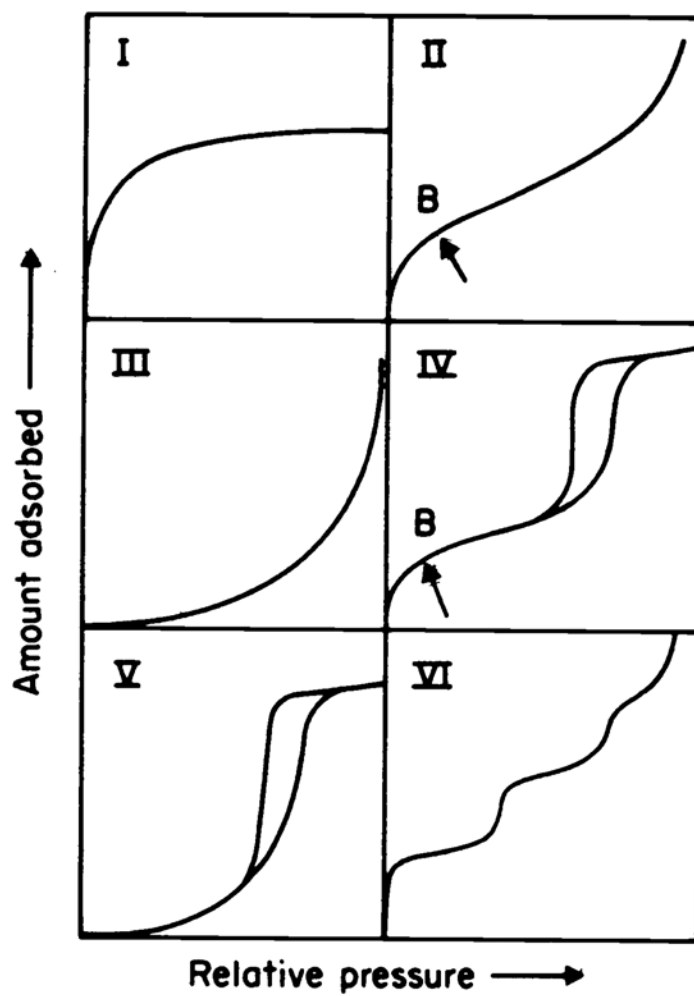


Figure 58: IUPAC adsorption/desorption isotherm classifications (Figure was reproduced from Ref [131]).

Table 3: Summary of the key characteristics for each type of adsorption/desorption isotherm

Isotherm Type	Key Characteristics	Comments
Type I	Prominent adsorption at low P/P_0 Levels off at high P/P_0	Microporous materials
Type II	Concave at low P/P_0 Linear in the middle of the P/P_0 range Convex at high P/P_0	Macroporous materials
Type III	Convex over the entire P/P_0 range	Uncommon
Type IV	Concave at low P/P_0 Hysteresis loop Levels off at high P/P_0	Mesoporous materials
Type V	Similar to Type III at low P/P_0 Similar to Type IV at high P/P_0	Uncommon
Type VI	Steps	

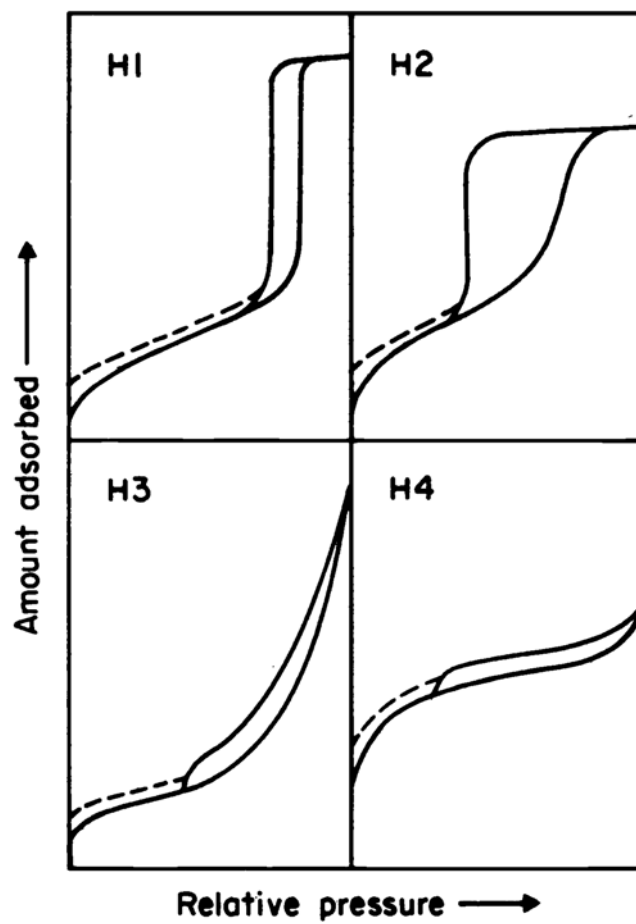


Figure 59: IUPAC hysteresis loop classifications (Figure was reproduced from Ref [131]).

adsorption and desorption branches. H1 hysteresis loops are often associated with porous materials known to relatively high pore size uniformity. H2 hysteresis loops are fairly common and have a triangular shape with a steep desorption branch. Many porous adsorbents such as inorganic oxide gels and porous glasses tend to give Type H2 hysteresis loops. In these systems the distribution of pore size and shape is not well-defined. H3 hysteresis loops do not exhibit any limiting adsorption at high P/P_0 ($P/P_0 \approx 1$) and are observed with aggregates of plate-like particles giving rise to slit-shaped pores. H4 hysteresis loops exhibit parallel and almost horizontal adsorption and desorption branches. H4 hysteresis loops have been associated with narrow slit-like pores and the presence of large mesopores embedded in a matrix with pores of much smaller size.[133]

Table 4 summarizes the key characteristics of each type of hysteresis loop.

The nitrogen adsorption/desorption isotherm for Davisil® silica gel is presented in Figure 60. The isotherm is concave to the x-axis at low P/P_0 , has a hysteresis loop, and limiting uptake over a range of high P/P_0 therefore the isotherm is classified as Type IV. The hysteresis loop is classified as Type H1 even though the branches are not absolutely parallel or vertical. Davisil® silica gel is known to be a mesoporous silica gel and the information obtained from the nitrogen adsorption/desorption isotherm is consistent with that classification.

Brunauer-Emmett-Teller (BET) Surface Area

The Brunauer-Emmett-Teller (BET) method is generally accepted as the standard procedure for the determination of the surface area of porous materials. The BET method is based around the five following assumptions: the surface is flat; all adsorption sites exhibit the same adsorption energy; there are no lateral interactions between adsorbed molecules; the heat of adsorption for all molecules except for the first layer is equal to the heat of condensation; and an infinite number of layers can form.[132,133] The BET equation is as follows

$$\frac{1}{w \left(\left(\frac{P_0}{P} \right) - 1 \right)} = \frac{1}{W_m C} + \frac{C-1}{W_m C} \left(\frac{P}{P_0} \right) \quad \text{Equation 27}$$

in which w is the weight of gas adsorbed at relative pressure (P/P_0), W_m is the weight of adsorbate constituting a monolayer of surface coverage, C (the BET C constant) is related to the

Table 4: Summary of the key characteristics for each type of hysteresis loop

Hysteresis Type	Key Characteristics	Comments
H1	Parallel and near vertical branches	Porous materials with uniform porosity
H2	Triangular shape with steep desorption	Broad nonuniform distribution of pores
H3	No limiting adsorption at high P/P_0	Slit-shaped pores
H4	Parallel and almost horizontal branches	Narrow slit-like pores with mesopores

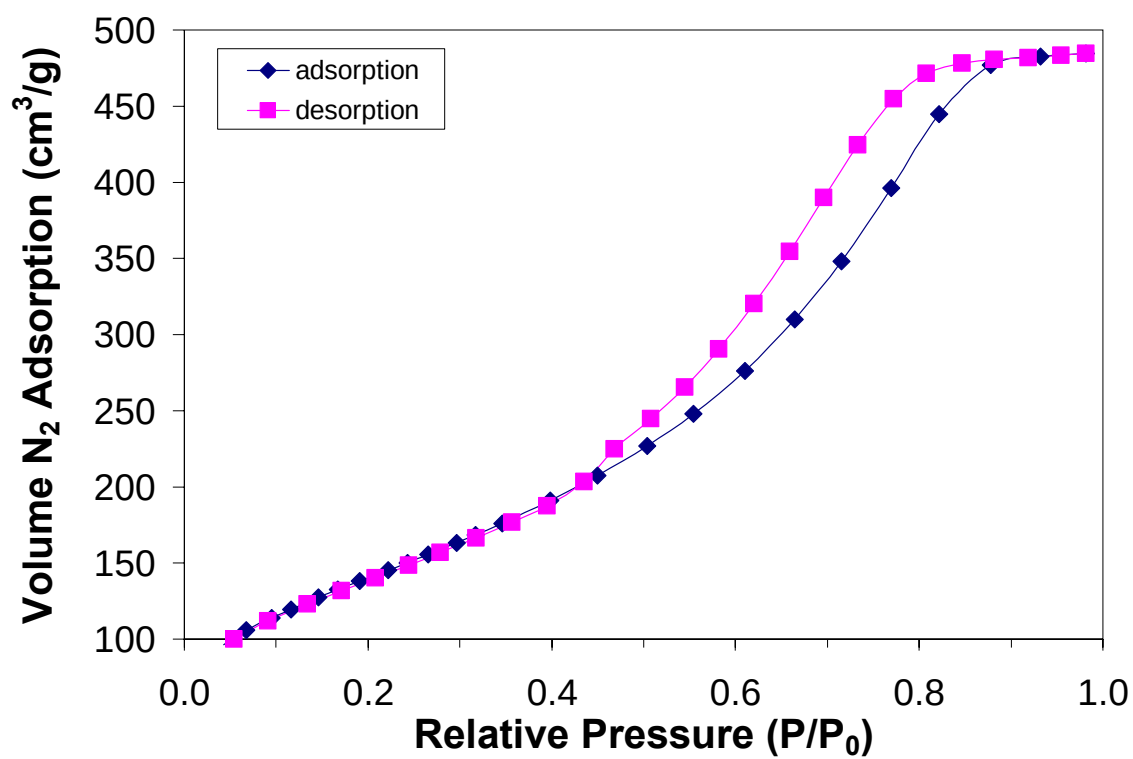


Figure 60: Nitrogen adsorption/desorption isotherm for Davisil® silica gel (the blue diamonds correspond to adsorption branch and the pink squares correspond to the desorption branch).

energy of adsorption in the first adsorbed layer and indicates the magnitude of the adsorbent/adsorbate interactions. As previously mentioned the raw data obtained is V_{ads} vs P/P_0 so some calculations are required to obtain the weight of gas adsorbed at a given relative pressure. The ideal gas equation is used to determine w .

A linear plot is obtained when the BET transform is plotted versus P/P_0 . Most instruments will automatically calculate the BET transform, but it is important to understand how it is determined.

$$\text{BET Transform} = \frac{1}{w \left(\left(\frac{P_0}{P} \right) - 1 \right)} \quad \text{Equation 28}$$

$$\text{slope} = \frac{C - 1}{W_m C} \quad \text{Equation 29}$$

$$\text{intercept} = \frac{1}{W_m C} \quad \text{Equation 30}$$

The plot deviates from linearity outside of the P/P_0 range of 0.05 to 0.35.[131,132,134] This linear region is shifted to lower relative pressures for microporous materials.

The weight of adsorbate constituting a monolayer of surface coverage (W_m) and the BET C constant can be determined from the slope and intercept of the BET plot (BET Transform vs P/P_0).

$$W_m = \frac{1}{\text{slope} + \text{intercept}} \quad \text{Equation 31}$$

$$C = 1 + \frac{\text{slope}}{\text{intercept}} \quad \text{Equation 32}$$

Once W_m has been determined, the BET surface area can be determined using the following equation

$$\text{BET surface area} = S_{\text{BET}} = \frac{W_m N A_{\text{cs}}}{M} \quad \text{Equation 33}$$

in which N is Avogadro's number (6.023×10^{23} molecules/mol), M is the molecular weight of adsorbate, A_{cs} is the cross-sectional area of an adsorbate ($16.2 \text{ \AA}^2$ for hexagonal close-packed nitrogen monolayer at 77K).

The BET plot for Davisil® silica gel is presented in Figure 61 and will be used to illustrate how the BET surface area is determined from a BET plot. The slope and intercept of the linear regression are 6.6461 g_{material}/g_{nitrogen} and 0.0988 g_{material}/g_{nitrogen} respectively. These values are used to determine W_m and the BET C constant for Davisil® silica gel. W_m is then used to determine the BET surface area for Davisil® silica gel (517 m²/g), which is consistent with the expected value given by the manufacturer (Sigma Aldrich, 480 m²/g).

$$W_m = \frac{1}{\text{slope} + \text{intercept}} = \frac{1}{6.6461 \frac{g_{\text{material}}}{g_{\text{nitrogen}}} + 0.0988 \frac{g_{\text{material}}}{g_{\text{nitrogen}}}} = 0.148 \frac{g_{\text{nitrogen}}}{g_{\text{material}}} \quad \text{Equation 34}$$

$$C = 1 + \frac{\text{slope}}{\text{intercept}} = 1 + \frac{6.6461 \frac{g_{\text{material}}}{g_{\text{nitrogen}}}}{0.0988 \frac{g_{\text{material}}}{g_{\text{nitrogen}}}} = 68 \quad \text{Equation 35}$$

$$S_{\text{BET}} = \frac{\left(0.148 \frac{g_{\text{nitrogen}}}{g_{\text{material}}}\right) \left(6.023 \times 10^{23} \frac{\text{molecules}}{\text{mol}}\right) \left(16.2 \times 10^{-20} \frac{\text{m}^2}{\text{molecules}}\right)}{28 \frac{g_{\text{nitrogen}}}{\text{mol}}} = 517 \frac{\text{m}^2}{\text{g}} \quad \text{Equation 36}$$

Total Pore Volume

The total pore volume reflects the volume of all pores in which the capillary condensation and micropore filling has taken place plus the volume of adsorbed film on the surface of the pores in which capillary condensation did not take place.

The total pore volume of a given adsorbent can be calculated from the amount adsorbed at a relative pressure close to the saturation vapor pressure simply by converting the amount adsorbed to the corresponding volume of liquid adsorbate at the temperature of the adsorption measurement. The volume of liquid adsorbate at the temperature of the adsorption measurement is determined using the following equation

$$\text{total pore volume} = V_{\text{liq}} = \frac{P_a V_{\text{ads}} V_m}{RT} \quad \text{Equation 37}$$

in which P_a is ambient pressure (1 atm), T is temperature (273 K), V_m is the molar volume of liquid adsorbate (34.7 cm³/mol for N₂), and V_{ads} is the amount adsorbed at a relative pressure

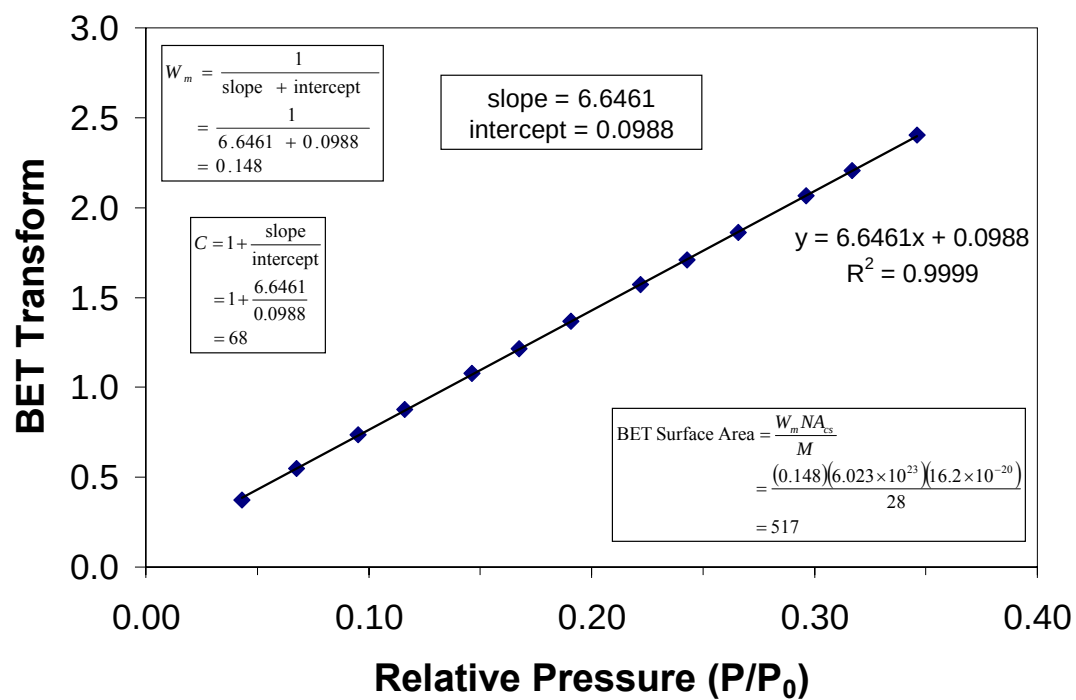


Figure 61: BET plot for Davisil® silica gel.

close to the saturation vapor pressure. Substituting the above values into Equation 37 gives the factor needed to convert V_{ads} to V_{liq} .

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT} = \frac{(1 \text{ atm}) V_{ads} (34.7 \text{ cm}^3 / \text{mol})}{\left(82.05746 \frac{\text{cm}^3 \text{ atm}}{\text{mol K}}\right) (273 \text{ K})} = 0.001548 V_{ads} \quad \text{Equation 38}$$

The amount adsorbed at a relative pressure close to the saturation vapor pressure ($P/P_0 = 0.99$) for Davisil® silica gel is $484 \text{ cm}^3/\text{g}$ (V_{ads}). The total pore volume for Davisil® silica gel is determined to be $0.749 \text{ cm}^3/\text{g}$ (V_{liq}), which is consistent with that given by the manufacturer (Sigma Aldrich, $0.750 \text{ cm}^3/\text{g}$).

$$V_{liq} = 0.001548 V_{ads} = (0.001548) \left(484 \frac{\text{cm}^3}{\text{g}}\right) = 0.749 \frac{\text{cm}^3}{\text{g}} \quad \text{Equation 39}$$

Barrett Joyner Halenda (BJH) Pore Size Distribution

The use of nitrogen adsorption data for pore size analysis is based on the application of the Kelvin equation, with a correction for the multilayer thickness on the pore walls. The method developed by Barrett, Joyner, and Halenda (BJH) is one of the most popular ways of deriving the pore size distribution from a nitrogen adsorption/desorption isotherm.[135] A BJH pore size distribution is a plot of the pore volume versus the average pore radius and is generally only useful for mesoporous samples.[131] The maximum in a BJH pore size distribution plot is interpreted as the BJH average pore radius of the sample.

Standard gas adsorption instrumentation automatically calculates the pore volume and average pore radius, but it is important to understand how the instrument determines these values. The pore radius is determined using the following equation

$$r_p = r_k + t \quad \text{Equation 40}$$

where r_p is the radius of the pore, r_k is the Kelvin radius of the pore, and t is the thickness of the adsorbed layer. The Kelvin radius of a pore (r_k) is determined using the following equation

$$r_k = \frac{-2\gamma V_m}{RT \ln\left(\frac{P}{P_0}\right)} \quad \text{Equation 41}$$

in which γ is the surface tension of nitrogen at its boiling point (8.85 ergs/mm^2 at 77K), V_m is the molar volume of liquid nitrogen ($34.7 \text{ cm}^3/\text{mol}$), R is the gas constant ($8.314 \times 10^7 \text{ ergs/deg mol}$),

T is the boiling point of nitrogen (77K), and P/P_0 is the relative pressure of nitrogen. The simplified equation below is obtained when the appropriate constants are substituted into the above equation.

$$r_k = \frac{4.15 \text{ \AA}}{\log\left(\frac{P_0}{P}\right)} \quad \text{Equation 42}$$

The thickness of the adsorbed layer is determined using the Halsey equation

$$t = 3.54 \text{ \AA} \left[\frac{5}{2.303 \log\left(\frac{P_0}{P}\right)} \right]^{1/3} \quad \text{Equation 43}$$

The average pore radius is obtained by averaging the pore radius at 2 sequential relative pressures. The corresponding pore volume is derived from the difference in volume adsorbed at the same two relative pressures.

A representative example of a BJH pore size distribution plot for Davisil® silica is presented in Figure 62. According to the plot, the BJH average pore radius (the maximum of the plot) for Davisil® silica gel is 46 Å (Sigma Aldrich, expected 30 Å).

Average Pore Radius

In addition to BJH plots for each of the samples, standard gas adsorption instruments determine another average pore radius. This value is not completely reliable because the instrument assumes all of the pores in the sample are cylindrical pores. This may be a poor assumption depending on the hysteresis type. Thus, the average pore radius reported by the instrument is not an accurate estimate of the average pore radius of a given material. The average pore radius is determined using the following equation

$$\text{average pore radius} = \frac{2V_{liq}}{S_{BET}} \quad \text{Equation 44}$$

where V_{liq} is the total pore volume and S_{BET} is the BET surface area.

Based on the nitrogen adsorption/desorption data, the average pore radius for Davisil® silica gel is 29.0 Å (expected 30 Å, Sigma Aldrich).

$$\text{average pore radius} = \frac{2V_{liq}}{S_{BET}} = \frac{2(0.750)}{517} = 29.0 \quad \text{Equation 45}$$

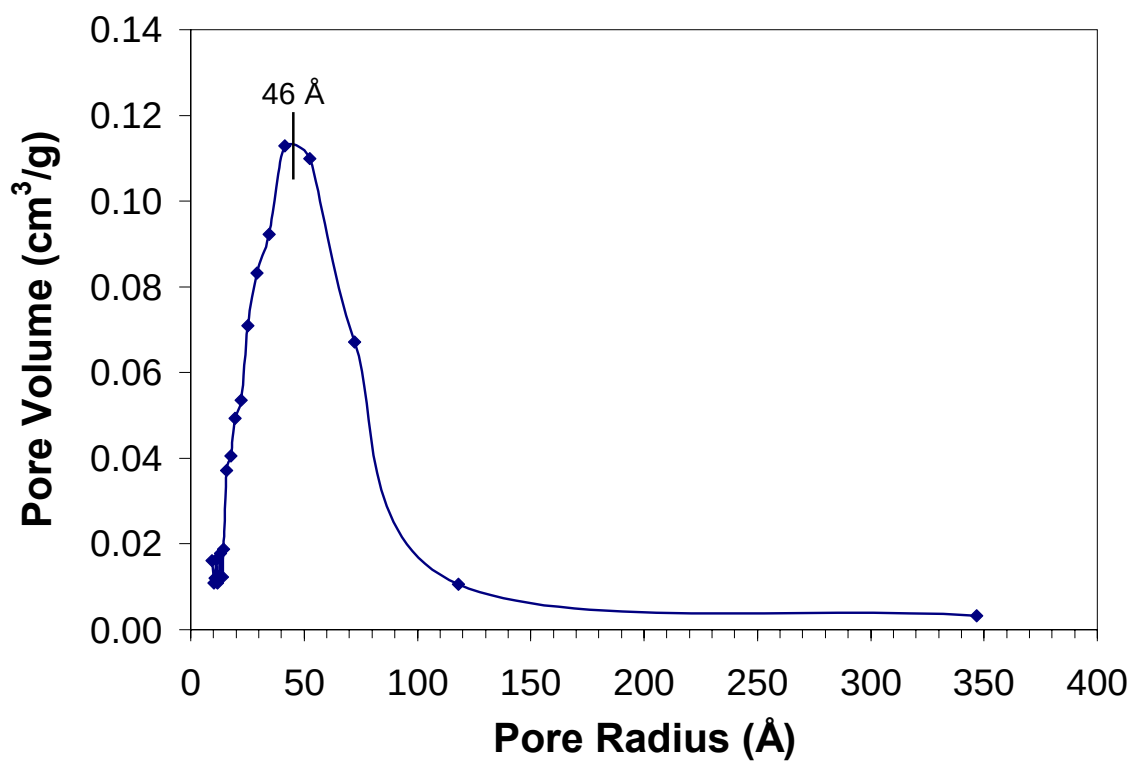


Figure 62: BJH pore size distribution plot for Davisil® silica gel. The BJH average pore radius is 46 Å.

Statistical thickness (t) plots

The statistical thickness (t) is the average thickness of the adsorbed nitrogen layer.[134,136] t-plots can be used to determine the presence (qualitative analysis) and the amount of micropores (semi-quantitative analysis) in a material. The t-plot compares the total volume of nitrogen adsorbed (V_{ads}) versus the statistical thickness (t). The following equation is used to calculate the Harkins-Jura statistical thickness t at a given relative pressure.[132]

$$t = \left(\frac{13.99}{\log\left(\frac{P_0}{P}\right) + 0.034} \right)^{1/2} \quad \text{Equation 46}$$

The above equation is in good agreement with experimental data at relative pressures between 0.1 and 0.8, which corresponds to t values between 3.7 Å and 10.3 Å.[132]

The porosity of a material can be qualitatively determined from the shape of the corresponding t-plot. Nonporous materials produce linear t-plots (Figure 63). Microporous materials produce t-plots that bend towards the x-axis (t) and mesoporous materials produce t-plots that bend towards the y-axis (V_{ads}) (Figure 63).[136] A good nonporous reference material is Aerosil 200,[137] which produces a linear t-plot (Figure 64). A good mesoporous reference material is Davisil® silica gel, which produces a t-plot that bends toward the y-axis (Figure 65).

The amount of micropores present in a material can be semi-quantitatively determined from a t-plot. As mentioned above, a t-plot for a material with some microporosity will bend toward the x-axis. The t-plot can then be divided into two linear portions, the lower portion, denoted by green triangles and a green regression line, and the upper portion, denoted by pink squares and a pink regression line (Figure 66).

Micropore volume and micropore surface area can be obtained from the upper portion of the t-plot.[132,134,137-139] The y-intercept of the linear regression of the upper (pink) portion is used to calculate the micropore volume of the sample, $V_{\text{micropore}}$, using the following equation,

$$V_{\text{micropore}} = \text{intercept} \times 0.001547 \quad \text{Equation 47}$$

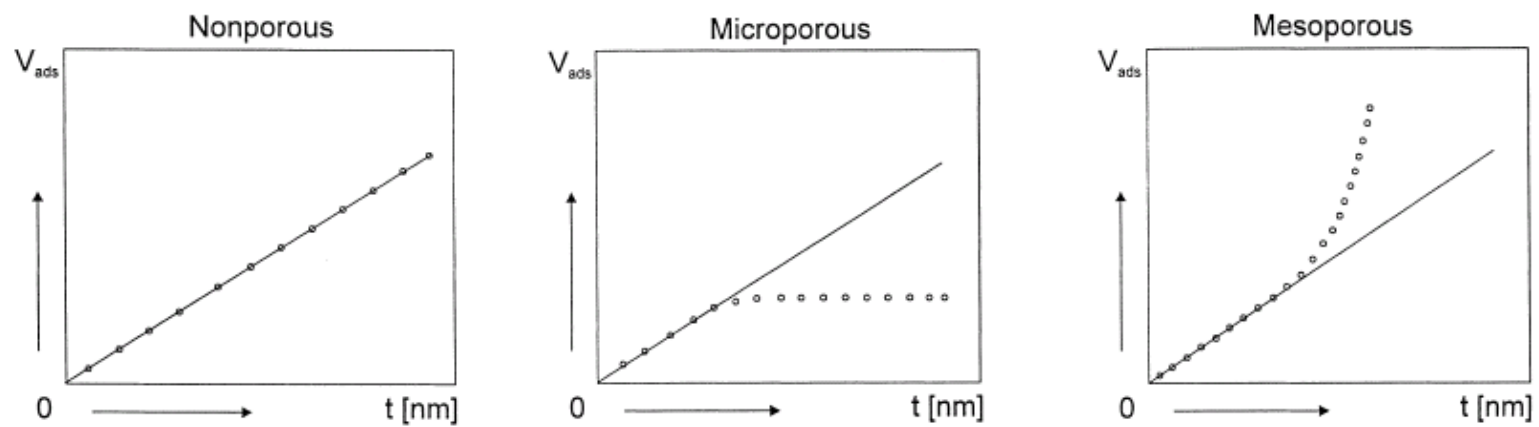


Figure 63: Representative t-plots for nonporous, microporous, and mesoporous materials (Figure was reproduced from Ref [136]).

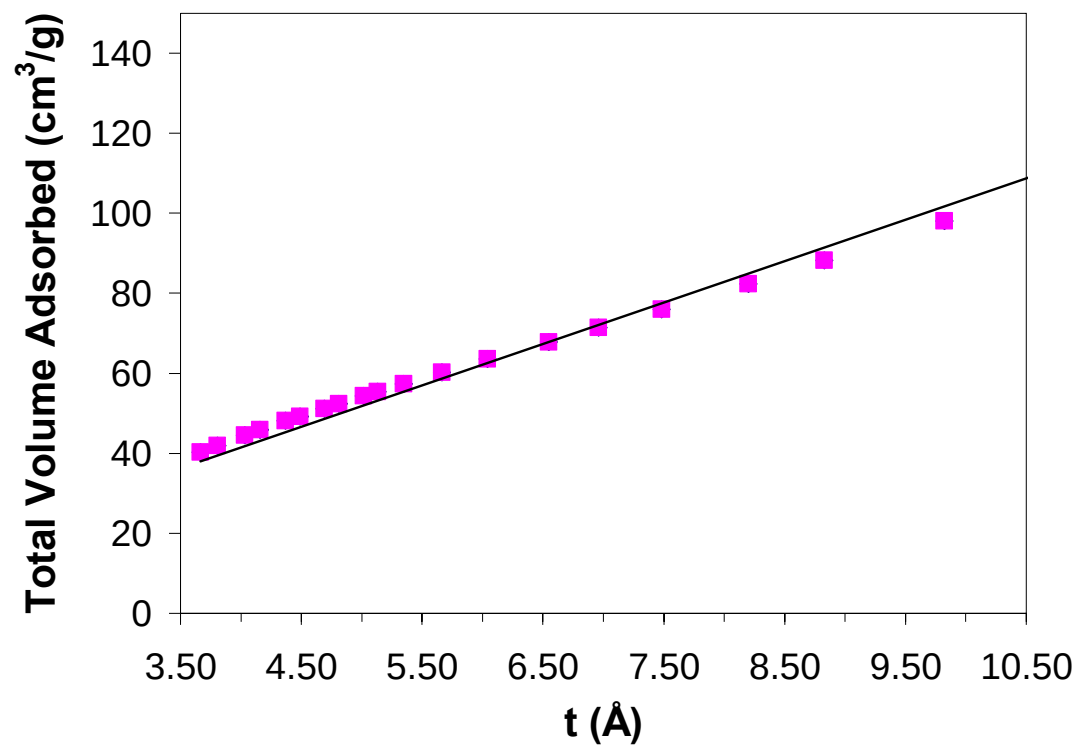


Figure 64: t-plot for Aerosil 200, a nonporous reference material.

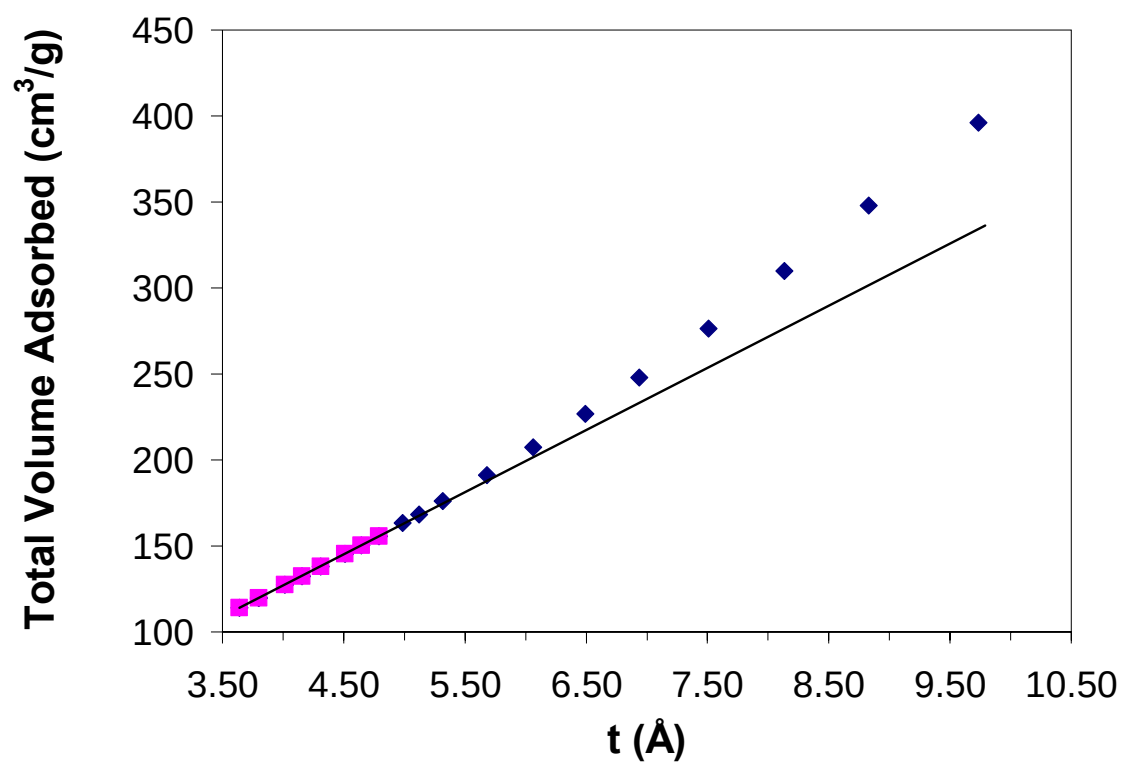


Figure 65: t-plot for Davisil® silica gel, a mesoporous reference material.

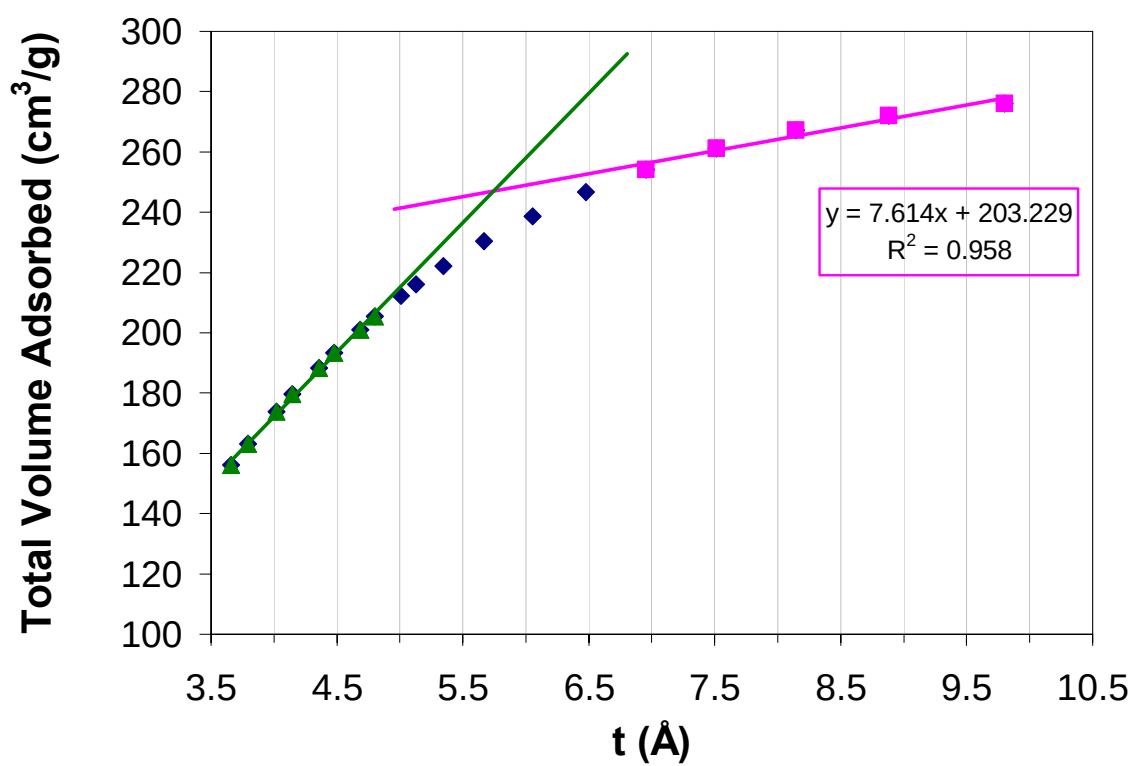


Figure 66: Representative t-plot for a microporous material.

The slope of the linear regression fit for the upper (pink) portion is used to calculate the external surface area, S_t , using the following equation,

$$S_t = \text{slope} \times 15.47 \quad \text{Equation 48}$$

The micropore surface area, $S_{\text{micropore}}$, is determined using the following equation,

$$S_{\text{micropore}} = S_{\text{BET}} - S_t \quad \text{Equation 49}$$

where S_{BET} is the BET surface area as determined by the instrument, S_t is the external surface area as determined by analysis of the t-plot.

Standard Reduced Adsorption (α_s) plots

Another way to obtain the above information is by using standard reduced adsorption (α_s) plots. α_s is the amount of nitrogen adsorbed on a porous solid relative to the amount of nitrogen adsorbed on a reference porous solid. The Jaroniec group at Kent State University are experts with respect to α_s -plots and have published several papers using α_s -plots.[140] The following equation is used to calculate the α_s values where V is the absorbed amount of nitrogen gas at an arbitrary relative pressure and $V_{0.4}$ is the absorbed amount of nitrogen gas at $P/P_0 = 0.4$. [141,142]

$$\alpha_s = \frac{V}{V_{0.4}} \quad \text{Equation 50}$$

The volume adsorbed (V_{ads}) is plotted versus the correspond α_s value to produce an α_s -plot. A t-plot and an α_s -plot are essentially equivalent methods for determining information about the microporosity of a material. t and α_s are proportional to one another so only a multiplicative factor is needed to convert from t to α_s and vice versa. Thus, a statistical thickness, t , (determined by Equation 46) can be converted to a standard reduced adsorption, α_s , value by dividing a given t value by 0.722 nm.[140]

$$\alpha_s = \frac{t}{0.722 \text{ nm}} \quad \text{Equation 51}$$

Summary

The materials discussed in this dissertation have been analyzed using several of the methods presented above. Analysis of the adsorption/desorption isotherm and hysteresis loop type have been conducted. The BET surface area and total pore volume for all materials have been determined. Both methods for determining the average pore radius of the materials will be

presented. The determination of micropore volume and micropore surface area was conducted using t-plots instead of α_s -plots.

Catalytic Test Reactions

Catalytic test reaction results often are not thought of as a characterization technique even though these results provide some of the most important information about a catalyst. Almost every research program focused on catalyst development conducts catalytic test reactions. Catalytic test reactions produce three pieces of important information that can be used to determine the effectiveness of a catalyst: selectivity, activity, and stability.

Selectivity

Selectivity is a measure of a specific product relative to all of the products of a reaction. Selectivity is generally represented as the percentage of the products that is a specific product. Selectivity is a property of great importance in industry because high selectivity means there will be less cost associated with the separation of products. Selectivity is fairly easy to determine as long as researchers can detect and quantify the products of a reaction.

Activity

Activity is a measure of the amount of substrate that is converted during the reaction to products. Conversion is sometimes considered an appropriate measure of activity however raw conversion data generally does not take into account the number of active sites present in the catalyst. Conversion can easily be increased by simply adding more catalyst (i.e. the addition of active sites) or decreasing the concentration of substrate. Therefore the observation of increased conversion does not necessarily mean a catalyst is more active. A more appropriate measure of activity is turnover number which measures the amount of substrate converted per active site. In addition to determining conversion, researchers must be able to quantify the number of active sites in a sample of the material in order to determine turnover numbers. Counting the number of active sites in a catalyst can present a number of challenges which is the reason that many catalysis studies still only report percent conversions.

Stability and Leaching

A component of catalytic test reactions involving heterogeneous catalysts that is infrequently reported is stability (leaching) studies. Leaching studies arguably provide information that is more critical in the determination of the effectiveness of a heterogeneous

catalyst than activity and selectivity. The ideal case is that the active sites do not leach and the observed catalysis is truly heterogeneous in nature. However if the components of the active sites of a heterogeneous catalyst leach during reaction one can envisage two different scenarios: either the leached species is not an active homogeneous catalyst or the leached species is an active homogeneous catalyst.[64] It is surprising that some catalysis groups still do not pay enough attention to the possibility of leaching.

Dissertation Overview

This dissertation describes work performed over the past five years aimed at demonstrating how the building block approach to constructing single site heterogeneous catalysts can be applied to tungsten and zirconium silicate catalysts. The materials that are described here can also be described as nanostructured materials in which their atomic scale (active site) and bulk (porosity, surface area) structures are simultaneously controlled during synthesis.

Four different projects which focused on the synthesis and characterization of nanostructured supports and heterogeneous catalysts were accomplished and are described in chapters two through five.

Chapter 2 describes how the pore structure of nanostructured silicate building block supports may be tailored without the use of templating agents. These supports are generated by reacting the silicate building block ($\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) with a variety of linking reagents, foremost among them silicon bispyridine (SiCl_4py_2). The ratio of SiCl_4py_2 to silicate building block was varied to produce nanostructured silicate building block supports that were classified according to their porosity. These investigations show that the surface area and porosity are correlated to the stoichiometric ratio of linking agent to silicate building block. This correlation can be used as a strategy to obtain materials with targeted surface area and porosity.

Chapter 3 describes the synthesis and characterization of nanostructured heterogeneous catalysts that contain a single type of isolated tungsten(VI) catalyst ensemble. The isolated tungsten(VI) catalyst ensembles are synthesized via the reaction of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with different tungsten reagents (WOCl_4 and WCl_6). Embedded tungsten(VI) catalyst ensembles are synthetically targeted by reacting the silicate building block with a limiting amount of a tungsten(VI) reagent (either WOCl_4 or WCl_6). The material is further cross

linked with a silyl chloride resulting in a high surface area silicate support that is generated around the embedded tungsten(VI) catalyst ensembles. Surprisingly the cross-linking reaction between WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ produces a different catalyst ensemble than was initially expected. The new catalyst ensemble was thoroughly characterized which resulted in the development of a reasonably clear picture of the immediate environment around the tungsten(VI) catalyst ensemble. Surface tungsten(VI) catalyst ensembles are synthetically targeted by reacting a silicate building block support with a limiting amount of a tungsten(VI) reagent (either WOCl_4 or WCl_6). Both tungsten(VI) reagents reacted with the silicate building block support to produce catalyst ensembles that were different than the ones initially targeted. The new catalyst ensembles were thoroughly characterized which resulted in the development of a reasonably clear picture of the immediate environment around each tungsten(VI) catalyst ensemble.

Chapter 4 describes the synthesis and characterization of nanostructured heterogeneous catalysts that contain a single type of isolated zirconium(IV) catalyst ensemble. The isolated zirconium(IV) catalyst ensembles are synthesized via the reaction of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with zirconium tetrachloride (ZrCl_4). Embedded and surface zirconium(IV) catalyst ensembles were synthetically targeted in a similar manner to the tungsten(VI) catalyst ensembles. The immediate environment around the zirconium(IV) catalyst ensembles was thoroughly characterized following each reaction.

Chapter 5 returns to the idea of tailoring the porosity of silicate building block supports and expands it to nanostructured heterogeneous catalysts. Embedded catalyst ensembles that contain tungsten(VI) or zirconium(IV) centers were synthesized using the procedures presented in chapters 3 and 4. The material was then further cross linked with SiCl_4py_2 resulting in the generation of a high surface area silicate support with tailored porosity. The silicate support with targeted porosity was generated around the embedded catalyst ensembles and did not change the immediate environment around the catalyst ensemble.

The final summary and conclusions, as well as potential future work, are described in Chapter 6. The synthetic methodology presented in this dissertation can be used to synthesize different heterogeneous catalysts that contain a variety of high valence transition metals. Future works may focus on the incorporation of metal clusters into the silicate building block matrices, the investigation of a variety of catalytic reactions using nanostructured heterogeneous catalysts

that contain different metal centers in silicate building block matrices, and the development of a new building block approach.

CHAPTER 2. SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED SILICATE BUILDING BLOCK SUPPORTS WITH TARGETED POROSITY

Introduction

Mesoporous silica is one of the most common support materials used in heterogeneous catalysis. The directed synthesis of mesoporous silica traditionally requires the use of a templating agent which provides researchers the ability to control the porosity of these materials. Templated mesoporous silica, such as SBA-15[19] and MCM-41[17], are amorphous materials with ordered pore structures. They have proven to be excellent supports due to their high surface area and large pore structure.

Traditionally mesoporous silica is synthesized via a sol-gel or hydrothermal approach which provides little synthetic control with respect to the surface functionality of the resulting material. Often calcination is required to remove the templating agent and the harsh conditions required for calcination also limits the type of surface functionality in the resulting material.

As part of our ongoing research program to develop new synthetic methodologies for heterogeneous catalysts, we considered the problem of preparing high surface area supports while maintaining control of surface functionality that is crucial in obtaining single site catalysts. In this chapter, a series of nanostructured silicate building block supports were synthesized wherein both the surface functionality and porosity of the support were controlled. Each nanostructured silicate building block support was synthetically targeted by reacting the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with a defined amount of SiCl_4py_2 . Rigid, robust, porous matrices were generated as the building blocks are linked together. The porosity and the concentration of the surface functionality in each material were synthetically controlled by the stoichiometric ratio of the reactants at the beginning of the reaction. The synthesis and characterization of the series of nanostructured silicate building block matrices with targeted porosity are described.

Experimental

Materials

The general procedures used for handling the chemicals used in the reactions reported here have previously been described.[95] Several steps were taken to exclude all sources of water from reactants, solvents, and glassware as well as any hydroxyl groups present on

glassware used in reactions. All Schlenk reaction vessels were treated with a chlorotrimethylsilane/triethylamine solution followed by flame drying under vacuum prior to use. Toluene (Fisher Scientific) was dried using sodium-potassium alloy and distilled. Pyridine (Fisher Scientific) was distilled and dried using calcium hydride. Toluene and pyridine were kept in solvent bulbs equipped with high vacuum Teflon® stopcocks with the appropriate drying agent. The solvent bulbs were degassed using freeze-pump-thaw cycles and stored under vacuum prior to use. $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ was synthesized using previously reported procedures.[97,99] $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ was heated overnight to 100°C under vacuum to remove waters of hydration in the crystal prior to use.[99] Silicon tetrachloride (SiCl_4 , Acros, 99.8+%) was distilled, degassed, and stored under vacuum in Schlenk vessels equipped with Teflon® stopcocks. The bispyridine complex of silicon tetrachloride (SiCl_4py_2) was produced according to the literature and added to reaction vessels in a nitrogen atmosphere glove box.[143] All volatile solvents and reagents were delivered into reaction vessels using vapor transfer methods.

General Synthetic Procedures

Synthesis of Nanostructured Silicate Building Block Supports

Nanostructured silicate building block supports may be synthesized following the procedure previously reported.[95] In general, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and SiCl_4py_2 are transferred to a Schlenk reaction vessel and followed by the addition of approximately 30 mL of toluene. The solution is stirred at 80°C under static vacuum for up to 24 hours whereupon all volatiles are removed. The resulting solid is used without further purification.

Instrumentation

Gravimetric analysis, nitrogen adsorption/desorption, and IR spectroscopy are used to characterize the synthesized materials.

Gravimetric Analysis

The reaction vessel is weighed before and after each reaction and the weight change is used to determine the amount of trimethyltin chloride (Me_3SnCl) and pyridine that is produced during the cross-linking reaction.

Infrared Spectroscopy

Infrared spectra are collected using a Thermo Nicolet IR100 in a MBraun LabMaster 130 N_2 dry box. 32 scans are collected using 4 cm^{-1} resolution from 400-4000 cm^{-1} for the

background and samples. A KBr pellet is prepared and collected as the background spectrum. A KBr pellet containing sample material (~1-5 wt%) is prepared and collected as the sample spectrum. The desorption of pyridine from the nanostructured silicate building block matrices was studied by IR spectroscopy and is discussed later in this chapter.

Nitrogen Adsorption/Desorption

Nitrogen adsorption-desorption analysis was performed using a Quanta Chrome Nova 1000 instrument. BET surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35.[131] t-plots or α_s -plot were used to determine micro- and mesoporosity of the materials.[132,136] The adsorption portion of the nitrogen gas adsorption/desorption isotherms was used to calculate the pore size distribution (BJH method) of the samples.

Results and Discussion

A series of nanostructured silicate building block supports has been synthesized without the use of templating agents via the reaction of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and SiCl_4py_2 which is known to proceed via a metathesis reaction where a bond between the terminal oxygen on the silicate building block and the silicon atom of SiCl_4py_2 is formed in addition to trimethyltin chloride (Figure 67). This process will continue until either all the chloride ligands on SiCl_4py_2 are consumed or the Me_3Sn groups are inaccessible to the chloride ligands on the silicon centers. The pyridine molecules desorb from the silicon centers during the cross-linking reaction however it is unclear exactly when it occurs. A reasonable assumption is that the pyridine molecules desorb simultaneously as the first bond between the terminal oxygen on the silicate building block and the silicon atom of SiCl_4py_2 is formed as shown in Figure 67.

The average connectivity of the silicon centers, also thought of as the number of reacted chloride ligands or the number of new siloxane bonds formed, for each material was determined via gravimetric analysis. The average connectivity of the silicon centers was determined assuming that all of the pyridine molecules had desorbed from the silicon centers and been removed from the matrix. As seen in Figure 68, there is a linear relationship between the average connectivity of the silicon centers and the stoichiometric ratio of the reactants (SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$). Accurate average connectivities could not be determined at stoichiometric ratios above 5:1 due to the presence of unreacted SiCl_4py_2 at the end of the cross-linking

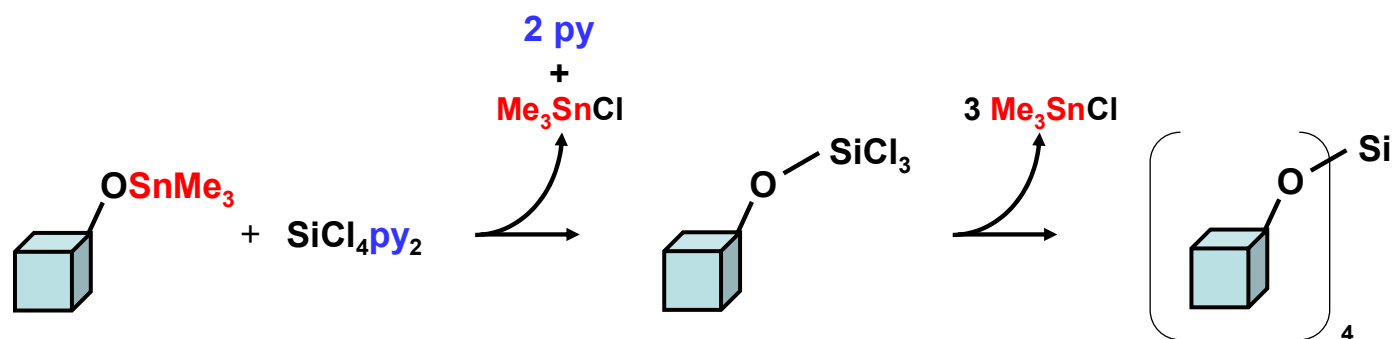


Figure 67: Illustration of the cross-linking reaction between the silicate building block and SiCl_4py_2 .

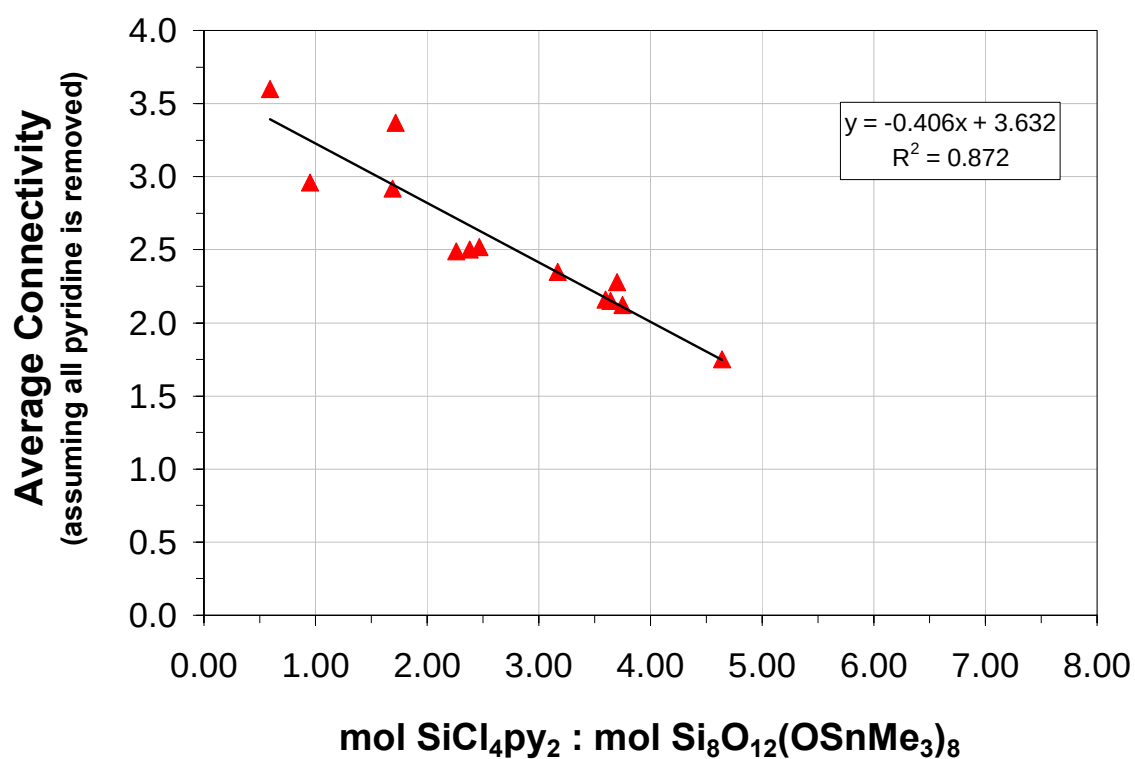


Figure 68: A plot of the connectivity of the silicon centers in the nanostructured silicate building block supports versus the stoichiometric ratio of the reactants (SiCl₄py₂ : Si₈O₁₂(OSnMe₃)₈).

reaction. As seen in Figure 69, there is no evidence of pyridine in the IR spectra ($1400\text{-}1700\text{ cm}^{-1}$) of the materials synthesized using stoichiometric ratios less than 5:1. However the presence of pyridine is evident in the IR spectrum ($1400\text{-}1700\text{ cm}^{-1}$) of the silicate matrices synthesized using stoichiometric ratios greater than 5:1. The pyridine is associated with unreacted SiCl_4py_2 not the silicon centers that have reacted with building blocks since it is known that the pyridine molecules desorb from the silicon centers once one linkage to a building block is formed. The relationship between the average connectivity and the stoichiometric ratio is reproducible which provides one with the ability to control the number of chloride ligands that react and/or the number of silicon-to-support linkages that are formed. Thus by simply knowing the initial stoichiometric ratio one can easily target the average connectivity of the silicon centers in the silicate building block matrix that is formed.

Since the amount of silicate building block initially used is known and the number of chloride ligands that react (i.e. the number of Me_3Sn groups that react) can be determined, then the amount of Me_3Sn left in the material can also be determined. Therefore, the concentration of surface functionality (i.e. Me_3Sn groups) can be targeted prior to the synthesis of the nanostructured supports. It is important to remember that the Me_3Sn groups on the building block are fixed in space and separated from one another and remain spatially isolated following the cross-linking reaction. Therefore the synthetic methodology provides researchers with complete control of the surface functionality in these nanostructured silicate building block supports. Obtaining this synthetic control was one of the primary focuses of this dissertation and will aid in the development of spatially isolated surface metal cation species discussed in more detail in chapters 3 and 4.

In addition to the average connectivity of the silicon centers, the BET surface area of the nanostructured silicate building block supports was investigated. Figure 70 illustrates how the BET surface area changed as the stoichiometric ratio was varied. One should immediately notice that significant surface area can be generated in these nanostructured supports without the use of a templating agent. In fact the amount of surface area generated is similar to the amount found in templated mesoporous silica. As seen in Figure 70, no measureable surface area is observed at stoichiometric ratios below 1:1. The surface area of the materials rapidly increases ($0\text{-}800\text{ m}^2/\text{g}$)

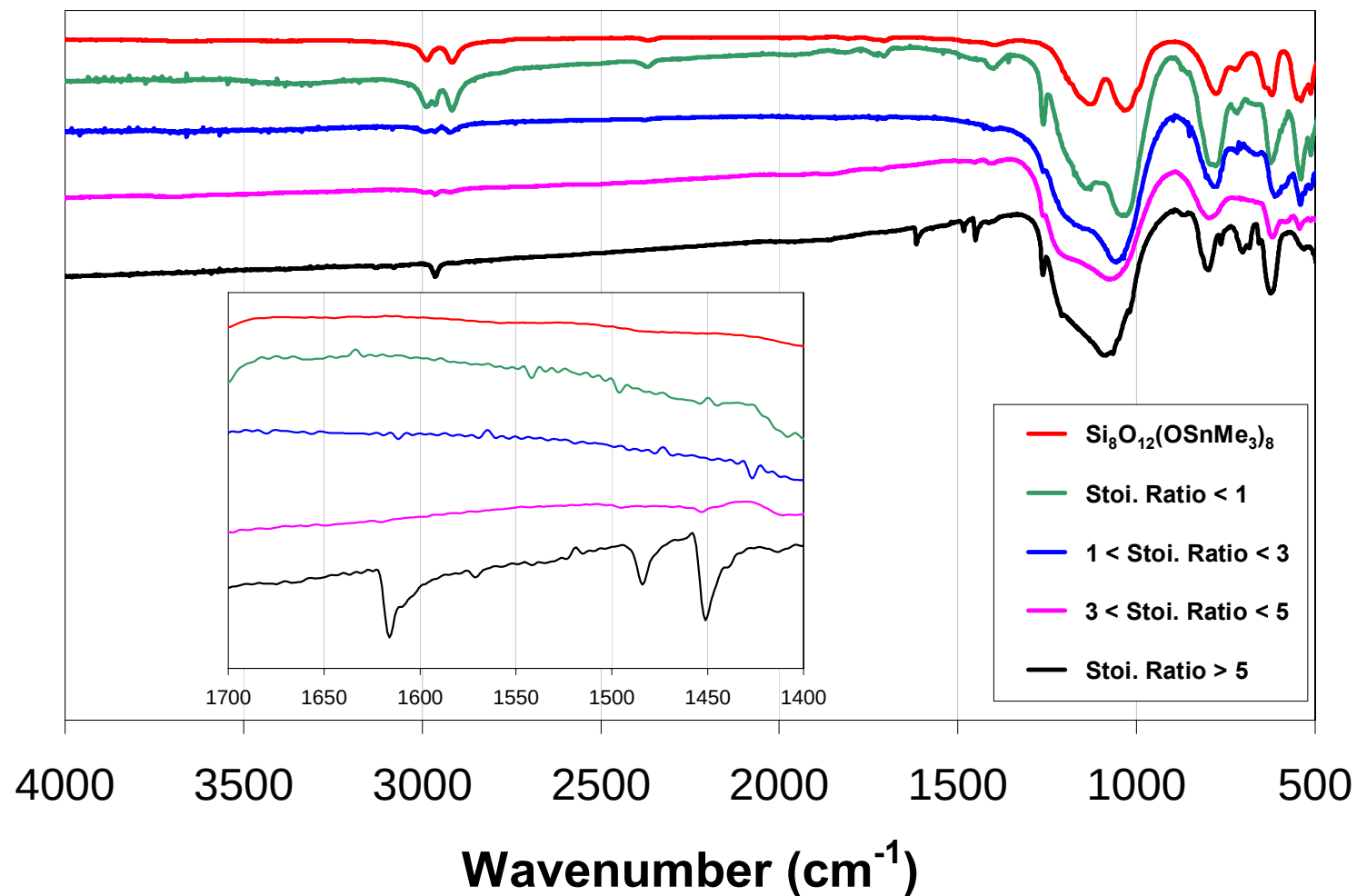


Figure 69: IR spectra (500-4000 cm^{-1}) of the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and a series of nanostructured silicate building block supports synthesized using a variety of stoichiometric ratios. The inset contains the expanded IR spectra (1400-1700 cm^{-1}) which illustrates the presence of pyridine in supports synthesized using stoichiometric ratios greater than 5.

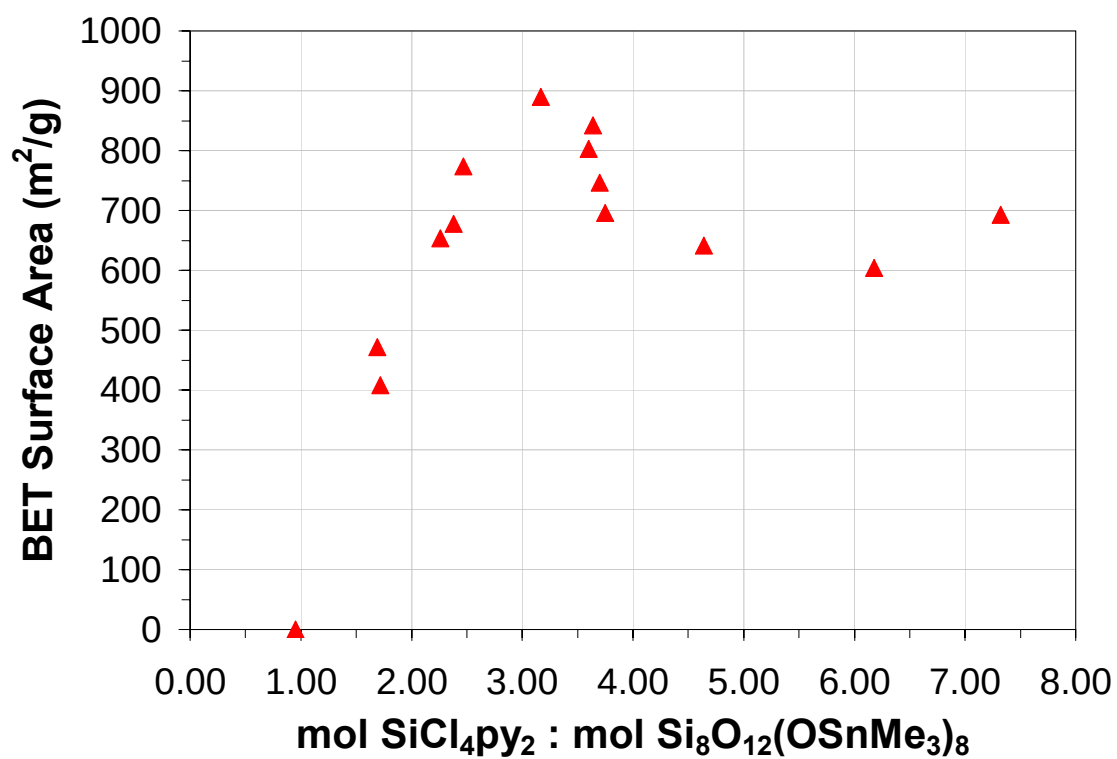


Figure 70: A plot of the BET surface area of the nanostructured silicate building block supports versus the stoichiometric ratio of the reactants (SiCl₄py₂ : Si₈O₁₂(OSnMe₃)₈).

as the stoichiometric ratio is increased from 1:1 to 3:1. The surface area of the resulting materials appears to plateau ($\sim 800 \text{ m}^2/\text{g}$) at stoichiometric ratios above 3:1. Surface area measurements conducted on materials synthesized using stoichiometric ratios greater than 5:1 were included in Figure 70 because it was assumed unreacted SiCl_4py_2 did not occupy the pores of the material and would have little effect on the observed surface area.

It is clear that the surface area of the resulting materials is strongly correlated with the stoichiometric ratio and that stoichiometric ratio controls the average connectivity of the silicon centers; however the correlation between surface area and the average connectivity of the silicon centers is not clear. Instead of concentrating on the average connectivity of the silicon centers, focus was shifted to the number of Me_3Sn group groups per silicate building block that react during the cross-linking reaction, which is defined by the following equation.

$$\frac{\text{Reacted Me}_3\text{Sn groups}}{\text{Silicate Building Block}} = \text{Connectivity} \times \text{Stoichiometric Ratio} \quad \text{Equation 52}$$

Figure 71 illustrates how the number of Me_3Sn groups that react per building block changed as the stoichiometric ratio was varied. In general, less than 3 Me_3Sn groups per silicate building block react at stoichiometric ratios below 1:1. Approximately 5.5 Me_3Sn groups per silicate building block react at stoichiometric ratios between 1:1 and 3:1. Virtually all eight of the Me_3Sn groups per silicate building block react at stoichiometric ratios between 3:1 and 5:1.

When comparing Figure 70 and Figure 71, there appears to be a correlation between the number of Me_3Sn groups that reacted per building block and the surface area of the resulting material. In general when less than 3 Me_3Sn groups per silicate building block are reacted then no measureable surface area is generated. When approximately 5.5 Me_3Sn groups per silicate building block are reacted significant surface area ($0\text{-}800 \text{ m}^2/\text{g}$) is generated. However, in this region of stoichiometric ratios, the exact surface area is extremely dependent on the stoichiometric ratio of the reactants. When essentially all of the Me_3Sn groups on the silicate building block are reacted, a high surface area material ($\sim 800 \text{ m}^2/\text{g}$) is generated regardless of the stoichiometric ratio.

All of the information compiled to this point was used to divide the plot of surface area

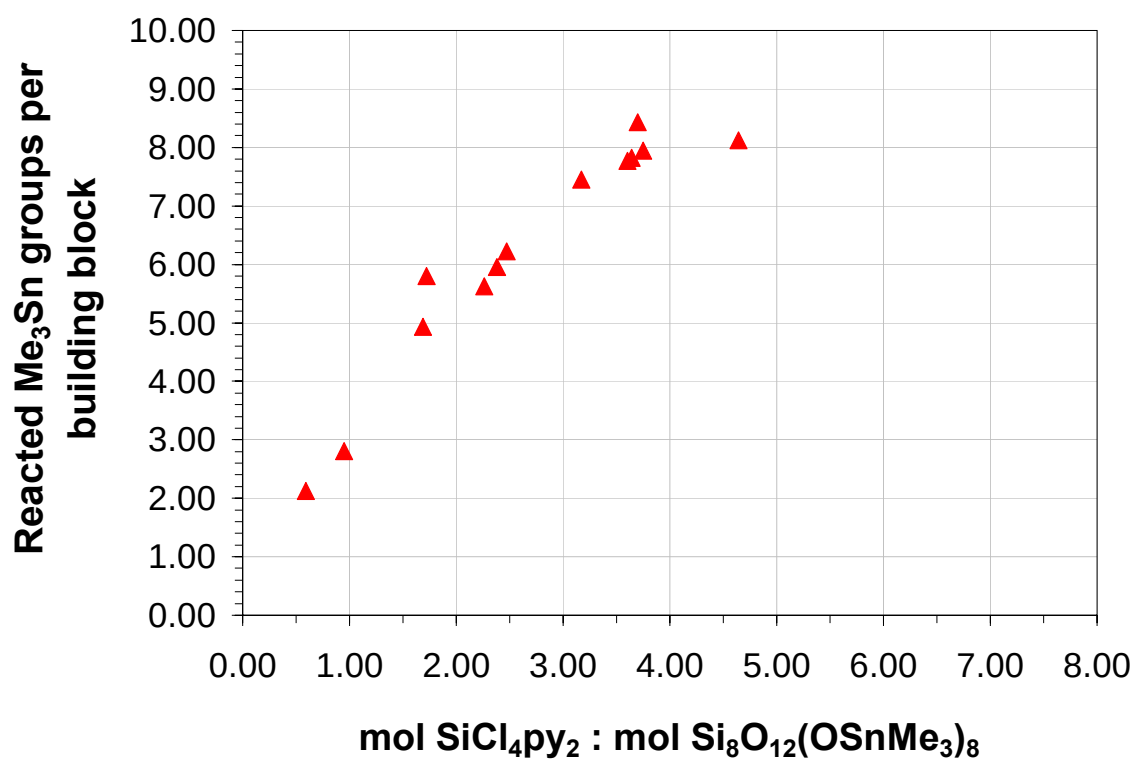


Figure 71: A plot of the number of Me₃Sn groups that reacted per building block during the cross-linking reaction versus the stoichiometric ratio of the reactants (SiCl₄py₂ : Si₈O₁₂(OSnMe₃)₈).

versus stoichiometric ratio into four regions as shown in Figure 72. The remainder of this chapter will focus on further characterizing the porosity of the nanostructured silicate building block supports in each region.

Region 1: Nanostructured Silicate Building Block Supports with No Porosity

The nanostructured building block supports that makeup region 1 of Figure 72 are synthesized by reacting the silicate building block, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, with SiCl_4py_2 without the use of templating agents where the stoichiometric ratio is less than 1:1. The silicate building blocks are linked together via a metathesis reaction where a new siloxane bond (Si-O-Si) and the volatile byproduct Me_3SnCl are formed and the pyridine molecules desorbed from the silicon centers. The first chloride ligand on SiCl_4py_2 is thought to react immediately with a Me_3Sn group on a building block and each subsequent chloride ligand reacts slower than the preceding chloride ligand. Since a limiting amount of SiCl_4py_2 is used, the cross-linking process generally continues until all of the chloride ligands on SiCl_4py_2 are consumed. The resulting material is thought to consist of small oligomers which contain highly connected (~ 4 silicon-to-building block) silicon centers (Figure 73).

As already mentioned, no measurable surface area was observed, which suggests the silicate building block supports after one stage of cross-linking with a limiting amount of SiCl_4py_2 contains small oligomers and that a rigid porous macromolecule has not been formed.

Nanostructured silicate building block supports that are represented in region 1 are referred to as “supports with no porosity” based on the analysis of the results of the nitrogen adsorption/desorption measurements.

Region 2: Nanostructured Silicate Building Block Supports with “Microporosity”

The nanostructured building block supports that makeup region 2 of Figure 72 are synthesized by reacting the silicate building block with SiCl_4py_2 without the use of templating agents where the stoichiometric ratio is between 1:1 and 3:1. The formation of a gel generally ends the cross-linking process because the Me_3Sn groups become inaccessible to the chloride ligands on the silicon centers. Surface area is not generated once the cross-linking process ends so all of the surface area is generated prior to the formation of the gel. Based on the information presented in Figure 71, gel formation appears to occur once 3 or more Me_3Sn groups per

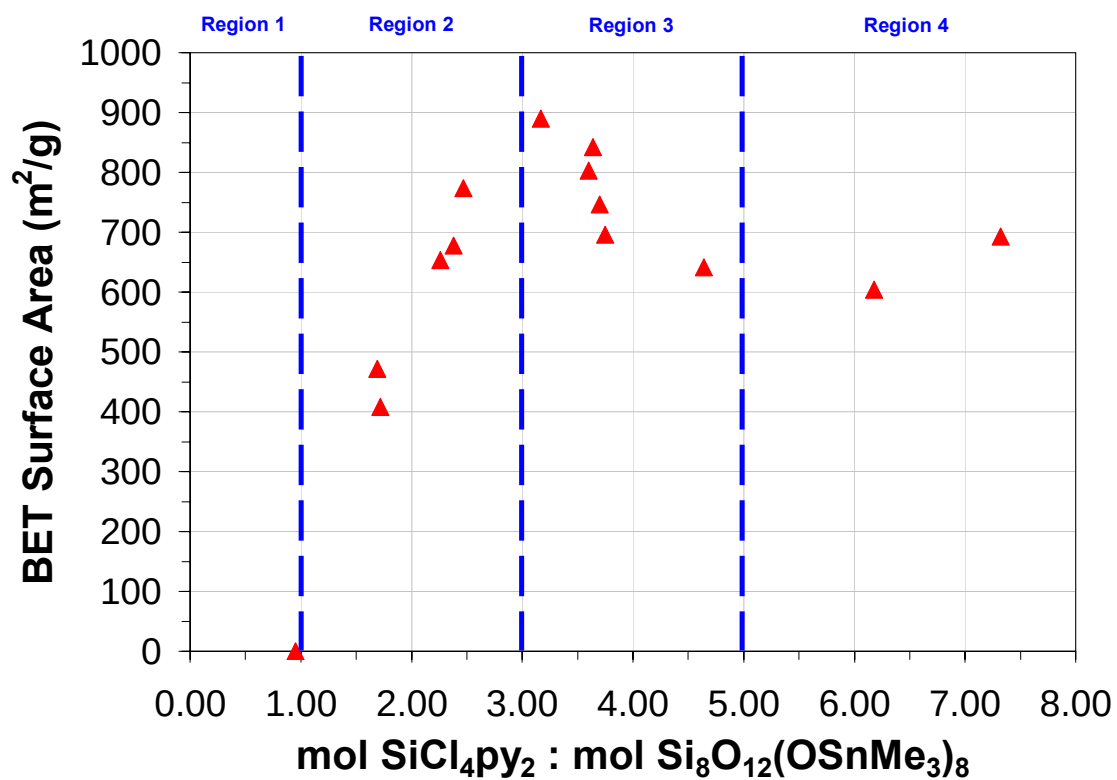


Figure 72: A plot of the BET surface area of the nanostructured silicate building block supports versus the stoichiometric ratio of the reactants (SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) after being divided into the four regions.

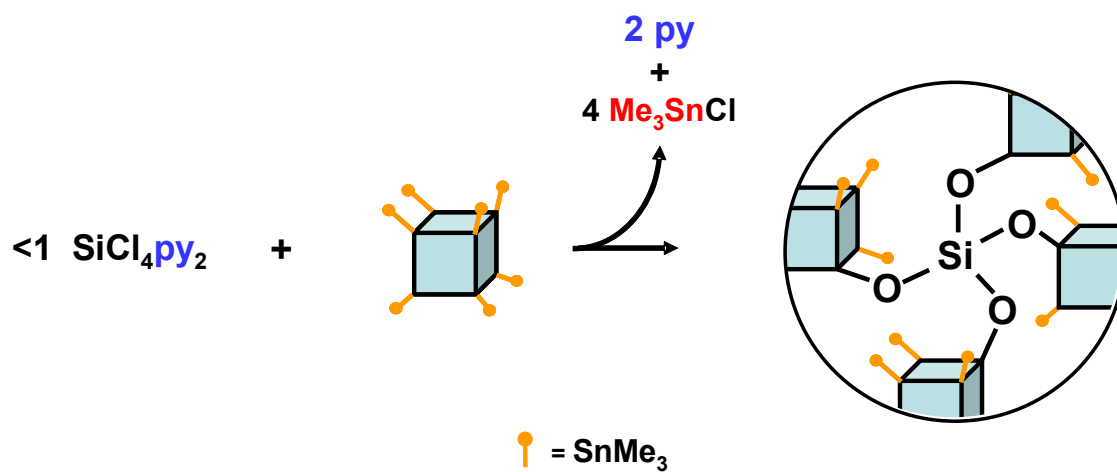


Figure 73: Illustration of the average connectivity of the silicon linking centers following the reaction of SiCl_4py_2 and the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ where the stoichiometric ratio is less than 1.

building block (the equivalent of 2-3 chloride ligands on SiCl_4py_2) have reacted. The resulting material which contains silicon centers that are on average connected to three building blocks (Figure 74) can be thought of as a small flexible macromolecule with some small oligomers still present. An explanation as to why more surface area is generated in region 2 than region 1 is that the silicon centers in region 2 materials are less connected which should result in the building blocks being separated more causing larger voids in the material. These voids are the pores of the material which account for a majority of the surface area.

The results of nitrogen adsorption/desorption measurements of a typical material represented in region 2 are presented below. As seen in Figure 75, the shape of the nitrogen adsorption/desorption isotherm for a typical material is similar to a Type I isotherm which is generally characteristic of a microporous material.[131] Qualitative analysis of the shape of the t-plot for a typical material suggests the nanostructured silicate building block support is primarily microporous because the t-plot bends towards the x-axis at high values of t which is indicative of microporosity (Figure 76).[136] The presence of a hysteresis loop (Type H4) in the nitrogen adsorption/desorption isotherm seen in Figure 75 suggests the material contains some mesopores. Quantitative analysis of the t-plot suggests the nanostructured silicate building block support is primarily microporous with respect to pore volume (74%) and surface area (87%). A typical BJH plot for materials in region 2 (Figure 77) does not display a significant maximum which also suggests the material is primarily microporous.

Nanostructured silicate building block supports that are represented in region 2 are referred to as “microporous supports” based on the analysis of the results of the nitrogen adsorption/desorption measurements.

Region 3: Nanostructured Silicate Building Block Supports with “Mesoporosity”

The nanostructured building block supports that makeup region 3 of Figure 72 are synthesized by reacting the silicate building block with SiCl_4py_2 without the use of templating agents where the stoichiometric ratio is between 3:1 and 5:1. In this region, the cross-linking process generally continues until all the Me_3Sn groups have reacted or the Me_3Sn groups are inaccessible to the chloride ligands on the silicon centers. This results in the formation of a gel. All of the surface area is generated prior to the formation of the gel. The first chloride ligand on

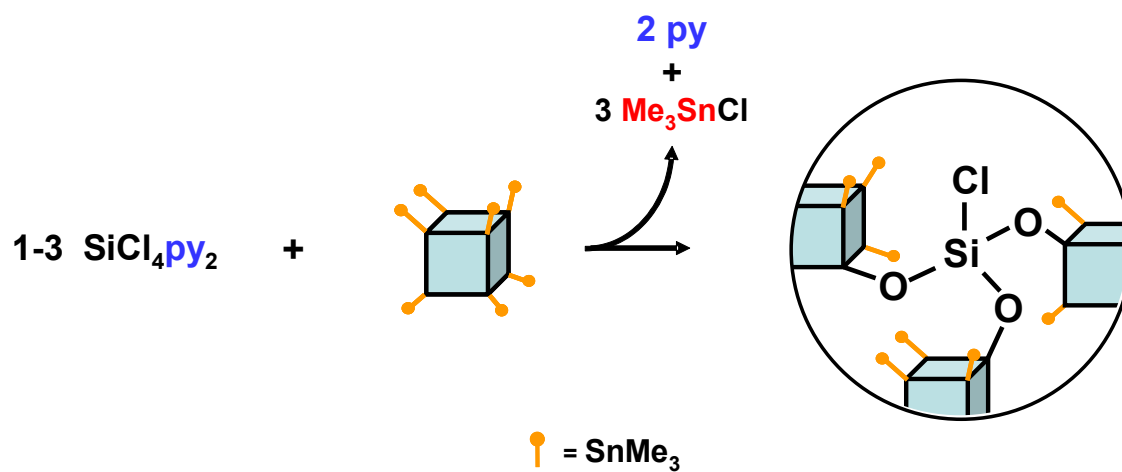
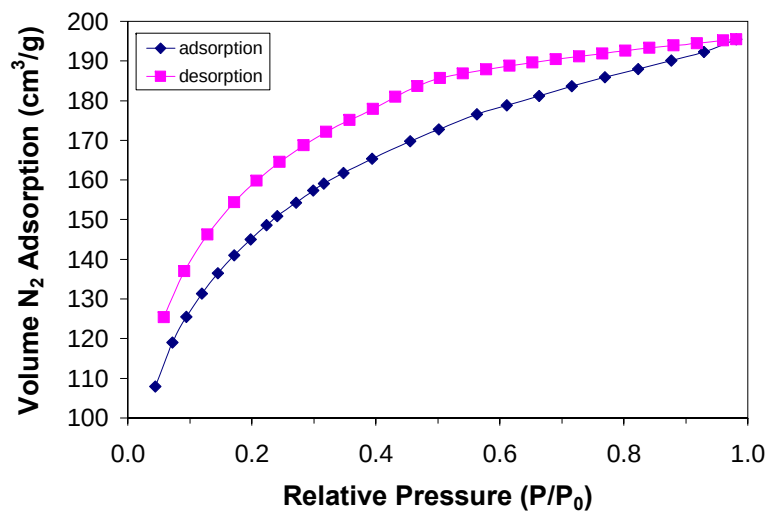
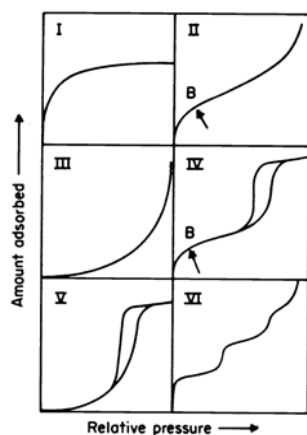


Figure 74: Illustration of the average connectivity of the silicon linking centers following the reaction of SiCl_4py_2 and the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ where the stoichiometric ratio is between 1 and 3.

Standard Isotherms



Standard Hysteresis Loops

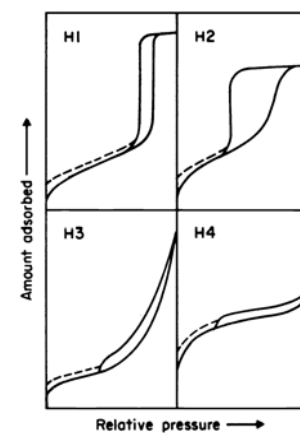


Figure 75: Nitrogen isotherm for a nanostructured silicate building block support with "microporosity." Standard isotherm and hysteresis loops were obtained from the literature.[131]

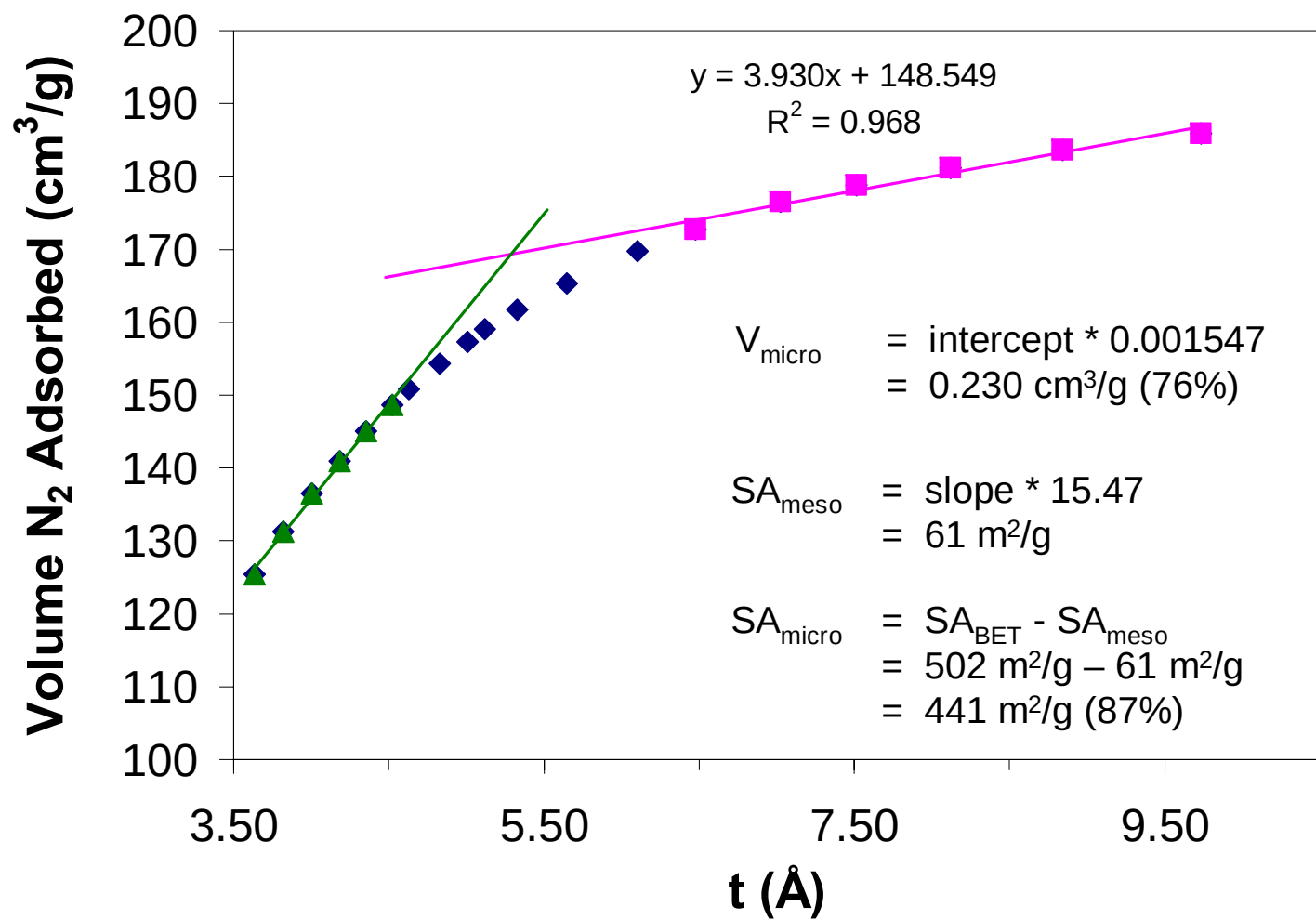


Figure 76: t-plot for a nanostructured silicate building block support with "microporosity."

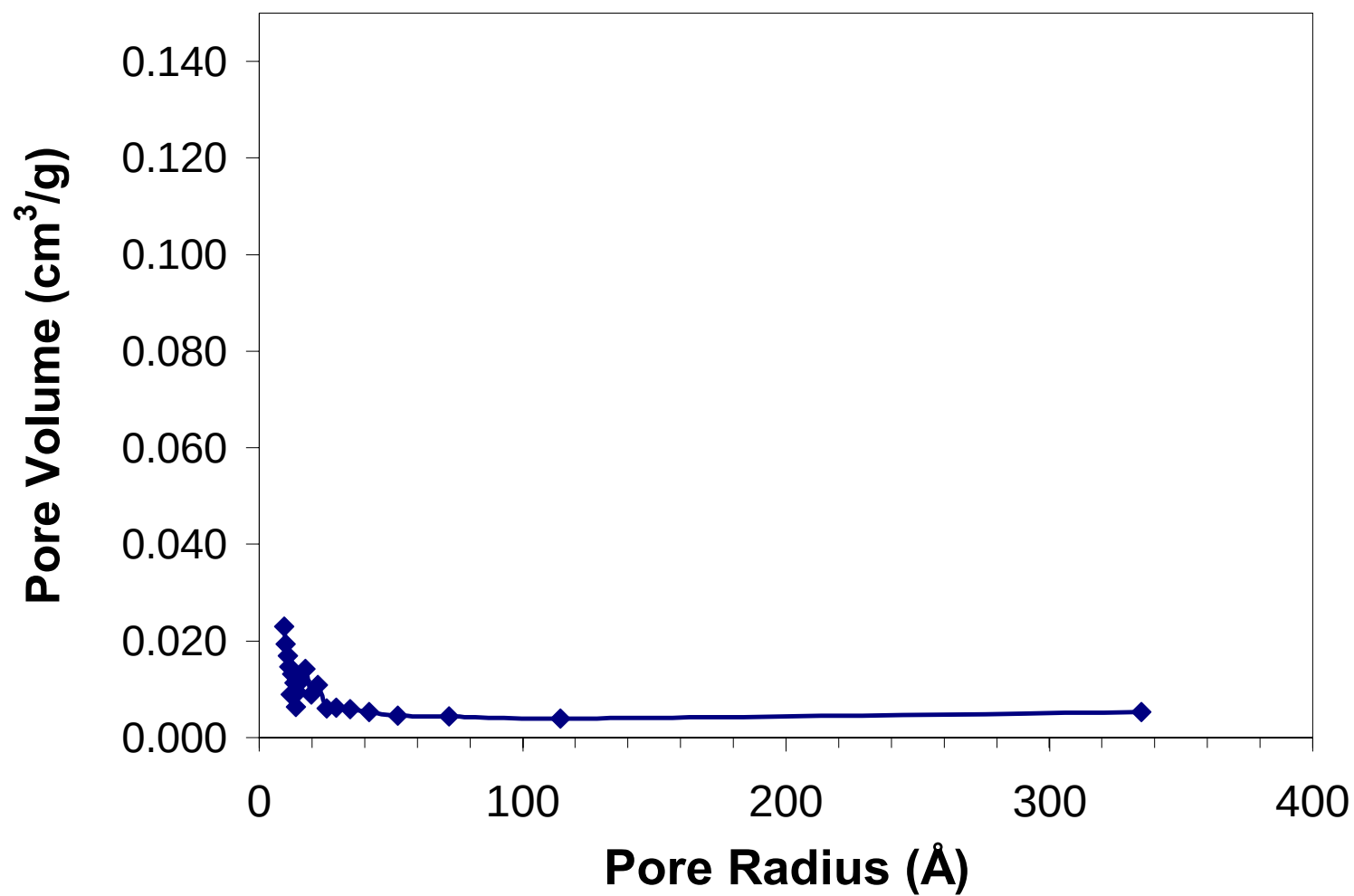


Figure 77: BJH pore size distribution plot for a nanostructured silicate building block support with "microporosity."

SiCl_4py_2 reacts immediately which results in the production of molecular species, specifically silicate building blocks with 3 to 5 Me_3Sn groups replaced by $-\text{SiCl}_3$ groups. Based on the information presented in Figure 71, gel formation appears to occur once approximately 2 chloride ligands on the silicon centers (the equivalent of 8 Me_3Sn groups per building block) have reacted. The resulting nanostructured silicate building block support which contains silicon centers that are on average connected to two building blocks (Figure 78) can be thought of as a rigid macromolecule.

As seen in Figure 79, the shape of the nitrogen adsorption/desorption isotherm for a typical material from region 3 of Figure 72 is similar to a Type IV isotherm which is generally characteristic of a mesoporous material.[131] The presence of a hysteresis loop (Type H4) in the nitrogen adsorption/desorption seen in Figure 79 suggests the nanostructured silicate building block support contains mesopores. Qualitative analysis of the shape of the t-plot for a typical material suggests the nanostructured silicate building block support contains mesopores and micropores because the t-plot appears to slightly bend towards the x-axis which is interpreted as a mesoporous materials with some micropores (Figure 80).[136] Quantitative analysis of the t-plot suggests the nanostructured silicate building block support is primarily mesoporous with respect to pore volume (~100%) and surface area (~99%). A typical BJH plot for materials in region 3 (Figure 81) displays a maximum which generally corresponds to a BJH average pore radius of 52.7 Å.

Nanostructured silicate building block supports that are represented in region 3 are referred to as “mesoporous supports” based on the analysis of the results of the nitrogen adsorption/desorption measurements. The generation of mesoporosity using a sol-gel based reaction scheme without the use of templating agents is quite remarkable.

Region 4: Nanostructured Silicate Building Block Supports with “Macroporosity”

The nanostructured building block supports that makeup region 4 of Figure 72 are synthesized by reacting the silicate building block, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, with SiCl_4py_2 where the stoichiometric ratio greater than 5:1. The development of a cross-linking model is ongoing and is complicated by the fact that not all of the SiCl_4py_2 reacts with the building blocks.

As seen in Figure 82, the shape of the nitrogen adsorption/desorption isotherm for a

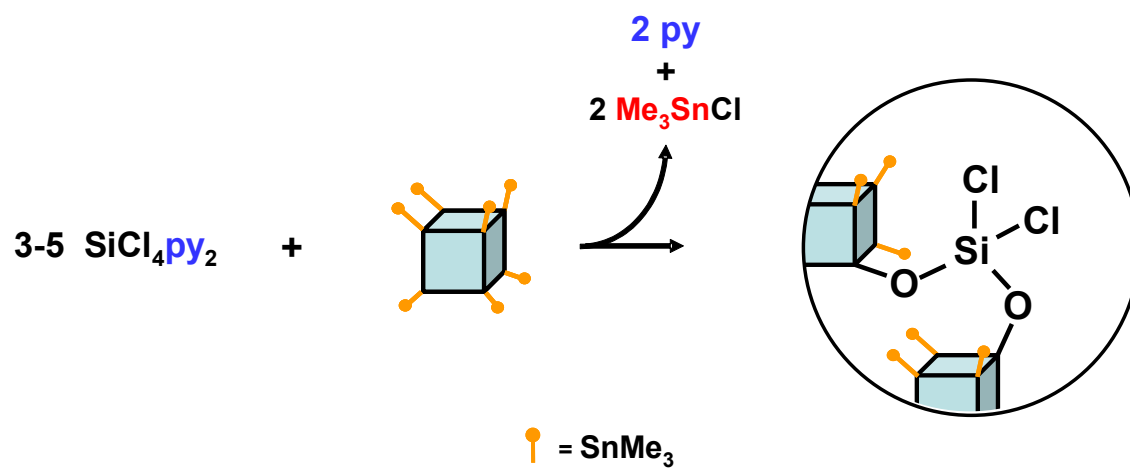
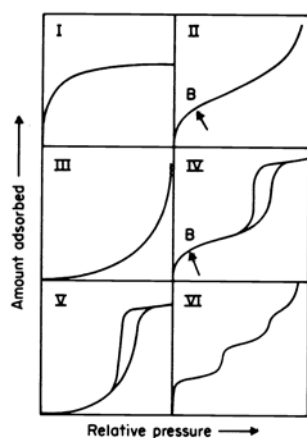


Figure 78: Illustration of the average connectivity of the silicon linking centers following the reaction of SiCl_4py_2 and the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ where the stoichiometric ratio is between 3 and 5.

Standard Isotherms



Standard Hysteresis Loops

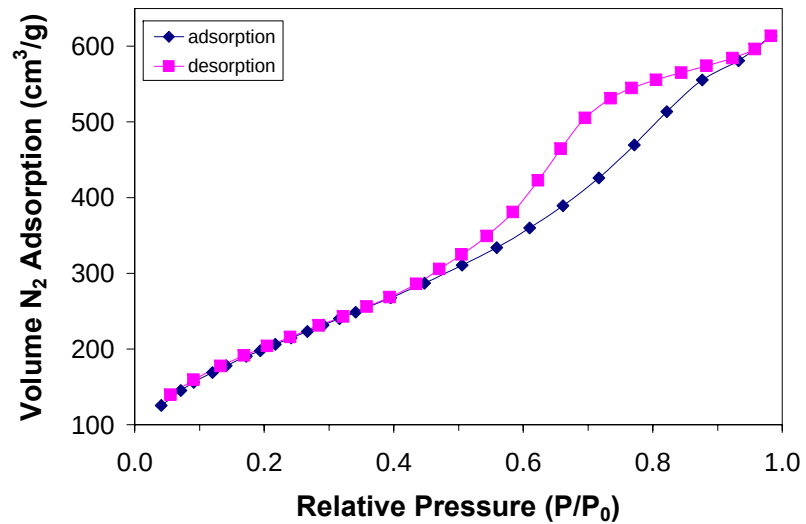
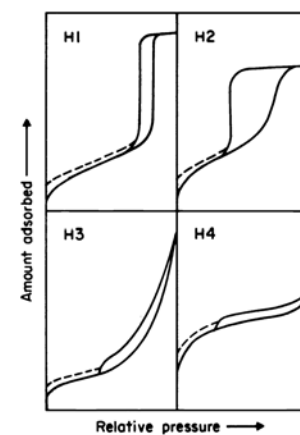


Figure 79: Nitrogen isotherm for a nanostructured silicate building block support with "mesoporosity." Standard isotherm and hysteresis loops were obtained from the literature.[131]

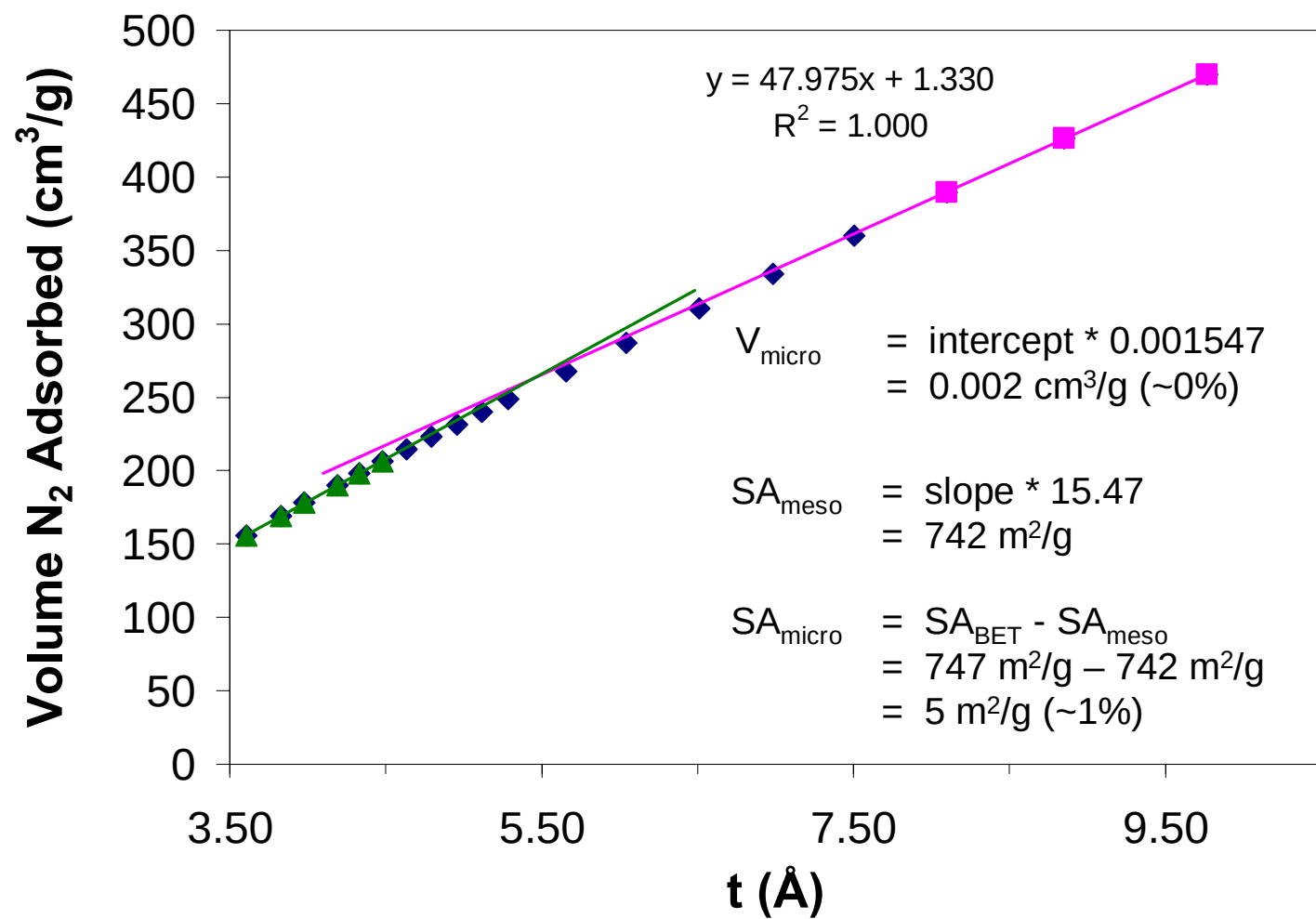


Figure 80: t-plot for a nanostructured silicate building block support with "mesoporosity."

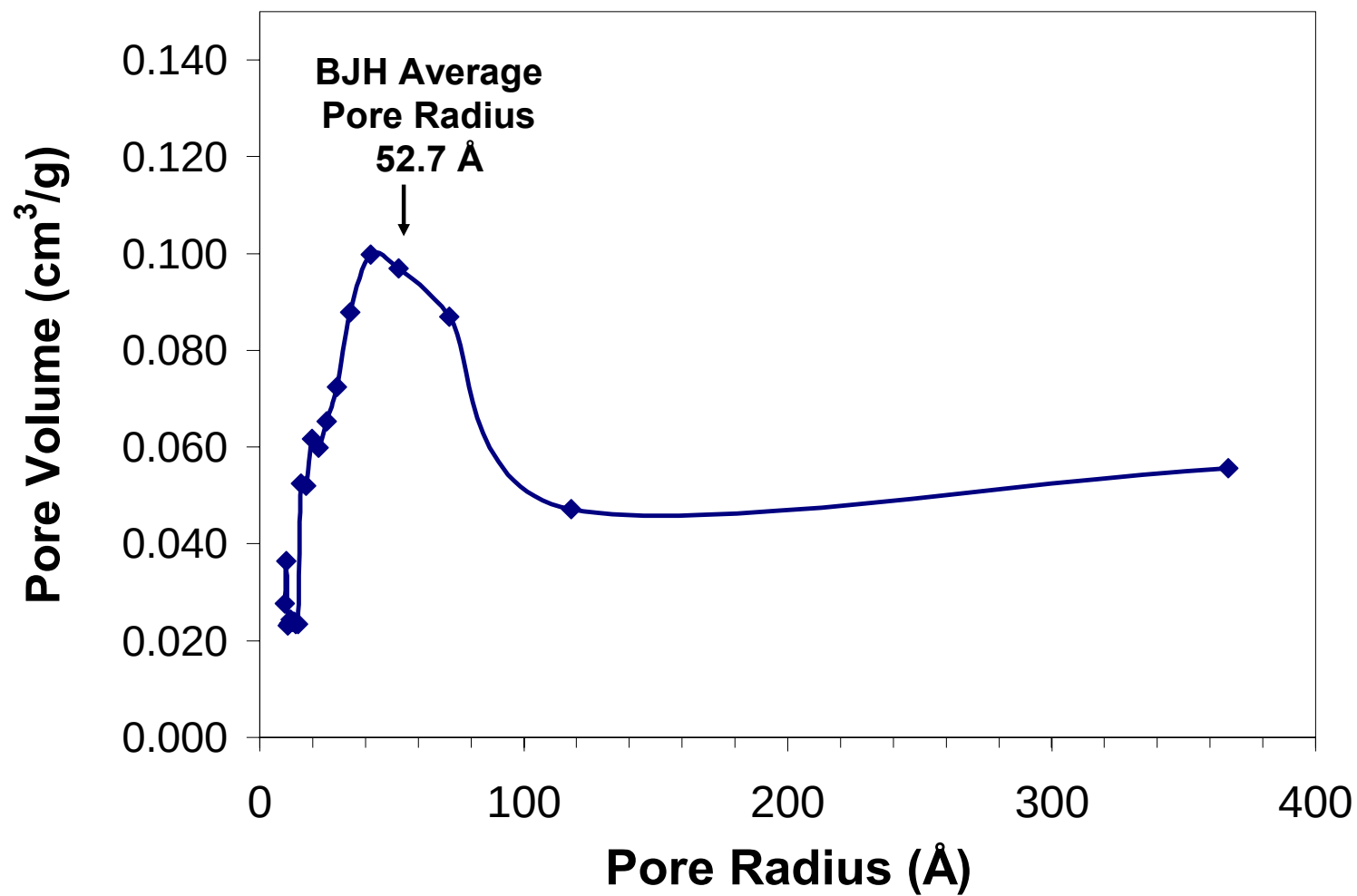
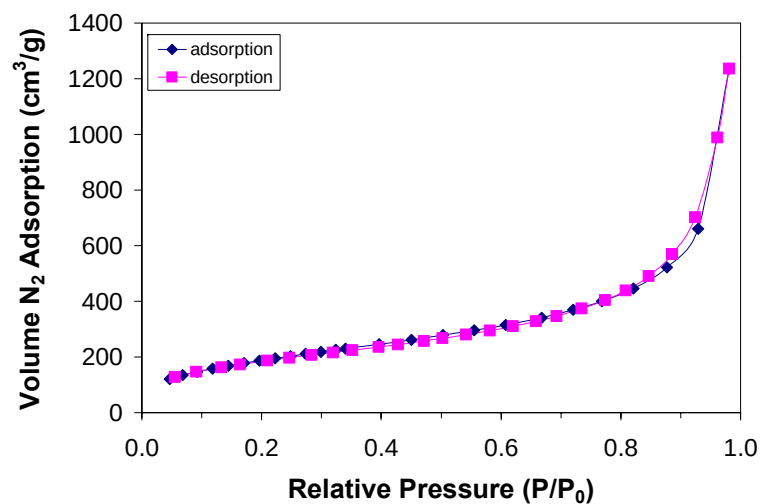
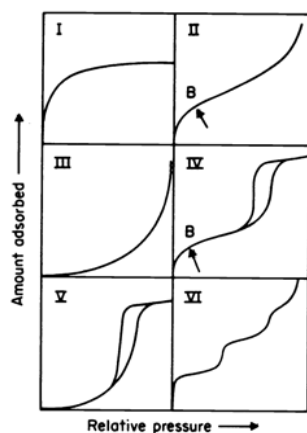


Figure 81: BJH pore size distribution plot for a nanostructured silicate building block support with "mesoporosity."

Standard Isotherms



Standard Hysteresis Loops

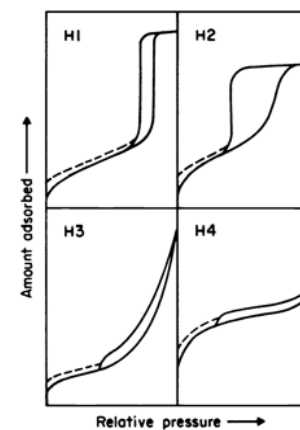


Figure 82: Nitrogen isotherm for a nanostructured silicate building block support with "macroporosity." Standard isotherm and hysteresis loops were obtained from the literature.[131]

typical material from region 4 of Figure 72 is similar to a Type II isotherm which is generally characteristic of a macroporous material.[131] The absence of a hysteresis loop in the nitrogen adsorption/desorption seen in Figure 82 suggests the nanostructured silicate building block support does not contain mesopores. Qualitative analysis of the shape of the t-plot for a typical material suggests the nanostructured silicate building block support contains macropores because the t-plot appears to be nearly linear (Figure 83).[136] Quantitative analysis of the t-plot suggests the nanostructured silicate building block support is primarily macroporous with respect to pore volume (97%) and surface area (84%). The BJH plot of materials in region 4 generally does not provide much information about the average pore size. This is due to the sharp increase in amount of nitrogen adsorbed near saturation ($P/P_0 \sim 1$). A typical BJH plot for a material in region 4 is shown in Figure 84.

Nanostructured silicate building block supports that are represented in region 4 are referred to as “macroporous supports” based on the analysis of the results of the nitrogen adsorption/desorption measurements.

Summary and Conclusions

A methodology by which nanostructured silicate building block supports with targeted surface area and porosity has been developed. The generation of surface area and porosity in the nanostructured supports was accomplished under nonaqueous conditions and without the use of templating agents. The surface area and porosity were synthetically controlled by the stoichiometric ratio of the reactants at the beginning of the reaction.

The use of a building block approach resulted in the synthesis of nanostructured supports that contain spatially isolated surface functionality (i.e. Me_3Sn groups) without requiring a thermal treatment. The concentration of the isolated surface functionality was synthetically controlled by the stoichiometric ratio of the reactants at the beginning of the reaction.

The synthesis of nanostructured supports will be revisited in chapters 3 and 4 when isolated metal cation species, specifically tungsten(VI) or zirconium(IV), will be attached to the surface of the nanostructured supports. The idea of tailoring the porosity of silicate building block supports will be revisited in chapter 5 and expanded to nanostructured heterogeneous catalysts that contain embedded metal cation species, specifically tungsten(VI) or zirconium(IV).

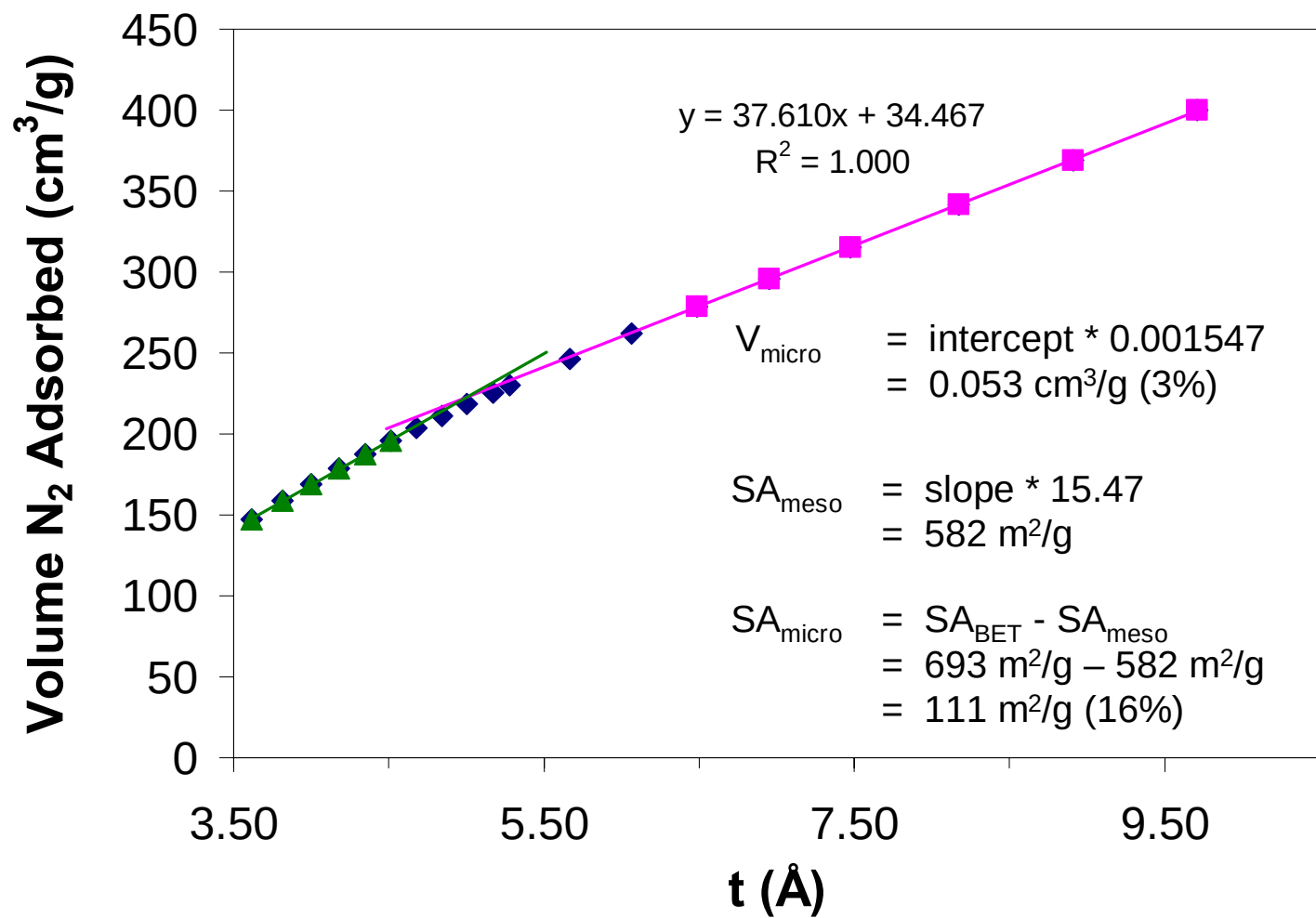


Figure 83: t-plot for a nanostructured silicate building block support with "macroporosity."

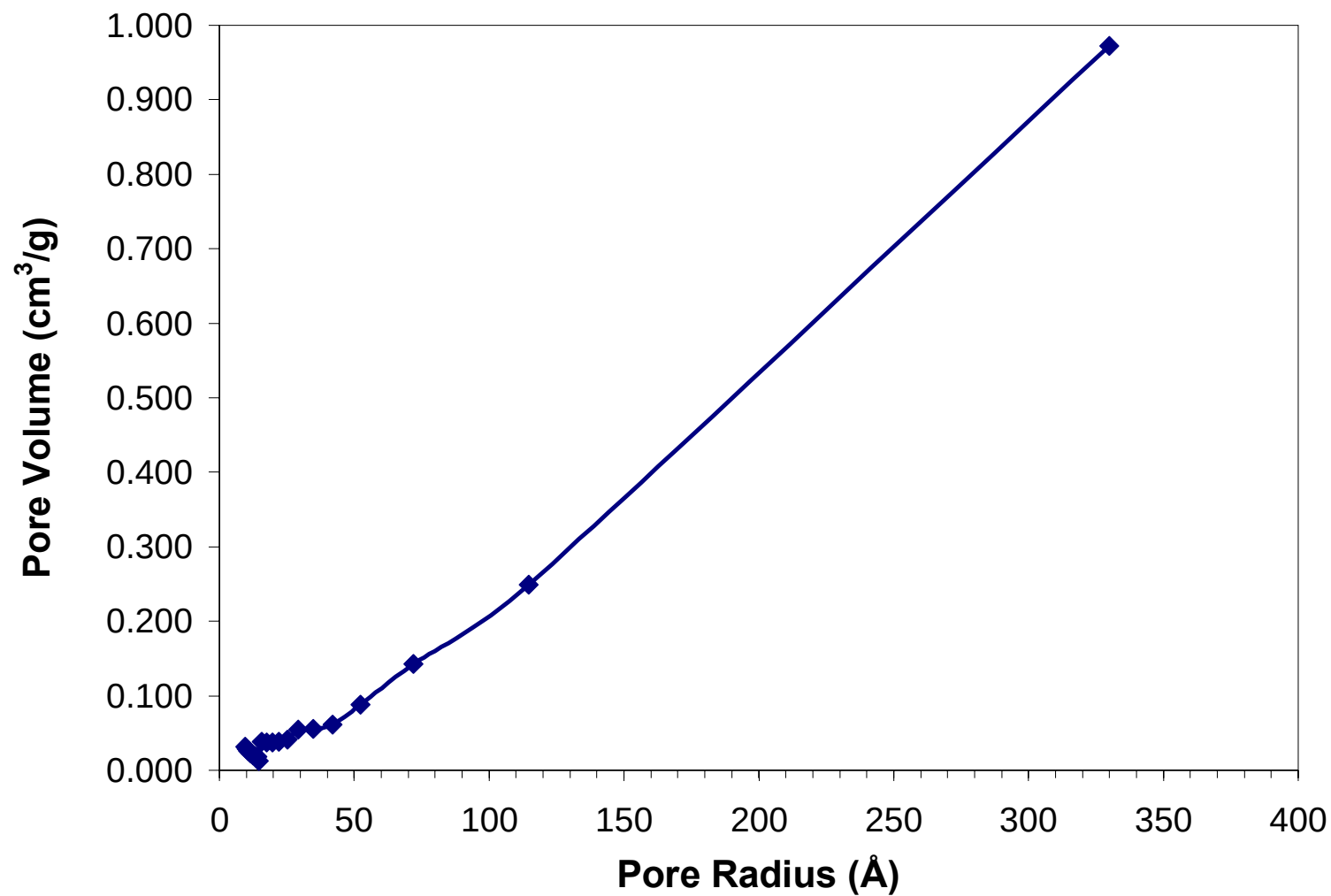


Figure 84: BJH pore size distribution plot for a nanostructured silicate building block support with "macroporosity."

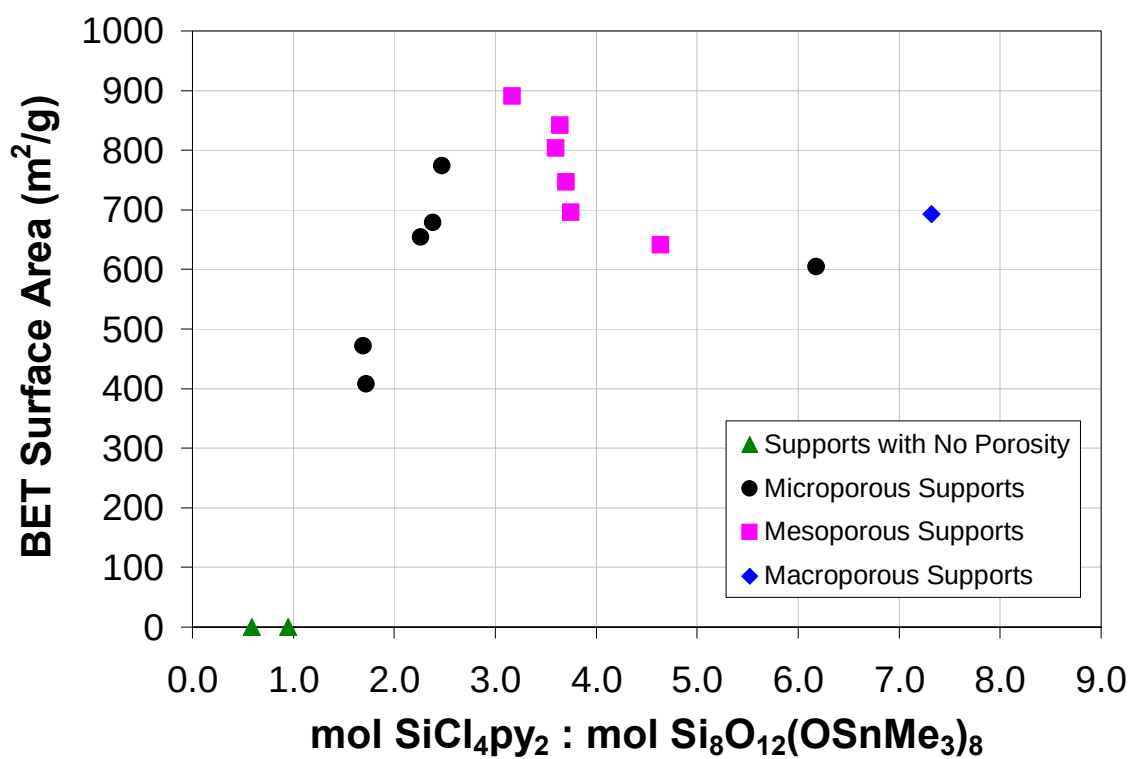


Figure 85: A plot of the BET surface area of the nanostructured silicate building block supports versus the stoichiometric ratio of the reactants (SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) with the porosity of each support identified.

Acknowledgments

I gratefully acknowledge the significant contributions made by Katherine P. Sharp and James R. Humble in this chapter and the support of the U.S. Department of Energy-Office of Basic Energy Sciences, grant DE-FG02-01ER15259.

CHAPTER 3. SYNTHESIS AND CHARACTERIZATION OF ISOLATED TUNGSTEN(VI) CATALYST ENSEMBLES IN AND ON SILICATE BUILDING BLOCK MATRICES

Introduction

Silica based heterogeneous catalysts that contain tungsten(VI) active sites have recently been investigated because of the interesting catalytic behavior exhibited in a number of selective oxidation,[36,44,84,144-152] solid acid,[153-158] and olefin metathesis[37,159-161] reactions.

Several different conditions and procedures have been described in the literature to obtain a wide variety of tungsten containing silica based catalysts. The traditional synthetic approaches do not provide the necessary synthetic control to tailor the local environment of the tungsten centers present in these materials. Typical heterogeneous catalysts containing tungsten can be divided into three groups. Those that contain multiple tungsten sites,[46,146,161] those that contain WO₃ or WO_x domains,[44,84,147,151,154,157,162,163] and those that contain isolated tungsten sites that are described as incorporated into the framework of the support.[37,45,148,152,158,160,164,165] Incipient wetness procedures are known to produce multiple tungsten sites and tungsten oxide domains while providing little synthetic control to allow one to target any one specifically.[45,146,162] Templating procedures generally require the catalyst to be calcined at the end of the synthetic process and the harsh conditions of calcination provide little control.[45,148] Grafting procedures have been reported to produce heterogeneous catalysts that contain isolated tungsten centers.[144,159] An example of a grafted heterogeneous catalyst that contains isolated tungsten centers was prepared by grafting W(=N(Ar))(=CHtBu)(CH₂tBu)₂ (Ar = 2,6-iPrC₆H₃) onto a silica surface that has been thermally pretreated to reduce the number of hydroxyl groups.[159] Another example of a grafted heterogeneous catalyst that contains isolated tungsten centers was prepared by grafting W(OSi(O^tBu)₃)₄ onto the surface of SBA-15.[144] Both of these examples illustrate how the successful synthesis of the grafted species is dependent on the surface functionality of the support. The amount of surface functionality must be reduced prior to grafting in order to obtain isolated grafted species which limits the loading of such species. Therefore these grafting processes do not provide enough synthetic control to synthetically target specific tungsten

species. A third example of a grafted heterogeneous catalyst that contains isolated tungsten centers was prepared by grafting $\text{W}(\text{OEt})_5$ onto the surface of MCM-48 followed by calcination.[46] In this case, the nature of the active site present in the heterogeneous catalyst that is responsible for the observed catalytic activity has not been established. In several reported cases, heterogeneous catalysts containing tungsten are poorly-defined because characterization procedures lack a direct probe of the tungsten center and mainly rely on indirect probes to gain information about them (e.g. IR, Raman, DRUV, etc). For these reasons, a detailed study of the targeted synthesis of silicate building block matrices that contain a single type of well-defined, isolated tungsten(VI) catalyst ensemble was initiated.

The synthesis of isolated W(VI) catalyst ensembles in the framework and on the surfaces of silicate building block matrices is described. Heterogeneous catalysts are notoriously difficult to characterize due to the fact that a wide variety of (direct and indirect) spectroscopic probes are needed to piece together a reasonably clear picture of the immediate environment around the catalyst ensembles. X-ray absorption spectroscopy (XAS) directly probes the immediate environment around the catalyst ensemble and provides information about the oxidation state of the absorbing metal, the coordination geometry of the absorbing metal, and structural information about the elements around the absorbing metal. Elemental analysis (ICP-OES) provides information about the catalyst ensemble concentration. Infrared spectroscopy (IR) is used to verify linkage to the support. Raman spectroscopy is used to determine the presence of certain functionalities and metal oxide domains. Solid state nuclear magnetic resonance spectroscopy (SSNMR) provides information about the silicate support and possibly the linkage of the catalyst ensemble to the support. Nitrogen adsorption/desorption measurements provide information about the porosity of the material.

In this chapter, four unique catalyst ensembles are targeted with only one being successfully synthesized (Figure 86). The three catalyst ensembles that were targeted but not successfully synthesized were thoroughly characterized resulting in a reasonably clear picture of the tungsten ensembles present in each material. Embedded catalyst ensembles were synthetically targeted by reacting the silicate building block with a limiting amount of a tungsten chloride reagent, either WOCl_4 or WCl_6 . The material is further cross linked with a silyl chloride

	Illustration	Nomenclature	
Embedded Catalyst Ensembles		“Isolated Embedded Tungsten Oxo Centers”	Successfully Targeted
		“Isolated Embedded Tungsten Centers”	Thoroughly Characterized
Surface Catalyst Ensembles		“Isolated Surface Tungsten Oxo Centers”	Thoroughly Characterized
		“Isolated Surface Tungsten Centers”	Thoroughly Characterized

Figure 86: Illustration of the catalyst ensembles targeted in this chapter.

resulting in a high surface area silicate support that is generated around the tungsten ensembles. Surface catalyst ensembles were synthetically targeted by reacting a silicate building block support with a defined amount of a tungsten chloride reagent, either WOCl_4 or WCl_6 . In all cases, the immediate environment around the tungsten centers was thoroughly characterized following each reaction resulting in well-defined materials at the end of the synthetic procedure. The synthesis and characterization of the silicate building block matrices containing embedded tungsten catalyst ensembles and those containing surface tungsten catalyst ensembles is described.

Experimental

Materials

Tungsten(VI) hexachloride (WCl_6 , Strem 99.9%) was sublimed under vacuum at 70°C and stored in a nitrogen filled glovebox before use. Purple needle-like crystals collected on the cold finger and sides of the Schlenk vessel while a reddish purple powder remained at the bottom of the Schlenk vessel. Tungsten(VI) oxychloride (WOCl_4 , Aldrich, 98%) was sublimed under vacuum at 70°C and stored in a nitrogen filled glovebox. Tungsten(VI) oxychloride (WOCl_4) was also synthesized from freshly sublimed WCl_6 using a previously reported procedure[166]. Tin (1000 mg/L, Fluka TraceCert®) and tungsten (1000 ppm, Ricca Chemical) ICP standard solutions were used to prepare calibration standards. Hydrofluoric acid (Sigma Aldrich, semiconductor grade MOS PURANAL™) and nitric acid (Certified ACS Plus, Fisher Chemical) were used as received. Information about the other materials used in this chapter has already been presented in chapter two.

General Synthetic Procedures

Isolated Embedded Tungsten Oxo Centers

The isolated tungsten oxo centers in a silicate building block matrix are synthesized following general procedures reported previously.[96] In a Schlenk reaction vessel, 3.054 g (1.646 mmol) of dry $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and 0.156 g (0.457 mmol) of WOCl_4 [0.28:1 $\text{WOCl}_4/\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$; 0.14:1 Cl/ Me_3Sn] are dissolved in 30 mL of diethyl ether. The solution is stirred at room temperature under static vacuum for 27 hours whereupon all volatiles are removed. The residue solid is cross linked further with SiCl_4 [0.669 g, 3.938 mmol, 2.39:1

SiCl_4 / $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$] in toluene at 80°C under static vacuum for 49 hours whereupon all volatiles are removed.

Isolated Embedded Tungsten Centers

Isolated tungsten centers in a silicate building block matrix were synthesized as follows. In a Schlenk reaction vessel, 2.992 g (1.613 mmol) of dry $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and 0.175 g (0.441 mmol) of WCl_6 [0.27:1 $\text{WCl}_6/\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$; 0.20:1 $\text{Cl}/\text{Me}_3\text{Sn}$] are dissolved in 30 mL of diethyl ether. The solution is stirred at room temperature under static vacuum for 27 hours whereupon all volatiles are removed. The residue solid is cross linked further with SiCl_4 [0.710 g, 4.179 mmol, 2.59:1 SiCl_4 / $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$] in toluene at 80°C under static vacuum for 47 hours whereupon all volatiles are removed.

Isolated Surface Tungsten Oxo Centers

Synthesis of Silicate Building Block Support

A nanostructured silicate building block support is synthesized following the general procedure previously reported.[95] In a Schlenk reaction vessel, 2.037 g (1.098 mmol) of dry $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and 1.028 g (3.133 mmol) of SiCl_4py_2 [2.85:1 $\text{SiCl}_4\text{py}_2/\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$; 1.43:1 $\text{Cl}/\text{Me}_3\text{Sn}$] are dissolved in 30 mL of toluene. A gel forms within 1 hour. The solution is stirred at 80°C under static vacuum for up to 24 hours whereupon all volatiles are removed. The resulting fine powder solid is used without further purification.

Synthesis of Isolated Surface Tungsten Oxo Centers

In a N_2 atmosphere glove box, 0.191 g (0.559 mmol) of WOCl_4 [0.51:1 $\text{WOCl}_4/\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$] is added to the reaction vessel containing the nanostructured silicate building block support described above followed by 30 mL of diethyl ether (vapor transferred). The solution is stirred at room temperature under static vacuum for 27 hours whereupon all volatiles are removed. The fine powder solid is used without further purification.

Isolated Surface Tungsten Centers

Synthesis of Isolated Surface Tungsten Centers

In a N_2 atmosphere glove box, 0.194 g (0.489 mmol) of WCl_6 [0.45:1 $\text{WCl}_6/\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$] is added to the reaction vessel containing the nanostructured silicate support described above followed by 30 mL of diethyl ether (vapor transferred). The solution is

stirred at room temperature under static vacuum for 28 hours whereupon all volatiles are removed. The fine powder solid is used without further purification.

Instrumentation

Gravimetric analysis, nitrogen adsorption/desorption, and a variety of spectroscopic techniques (IR, Raman, ^{29}Si SSNMR, ICP-OES, XAS (XANES and EXAFS)) are used to characterize the synthesized materials. Pyridine adsorption and the corresponding IR spectra are used to probe the acidity of the sites present in the synthesized materials.

Gravimetric Analysis

The reaction vessel is weighed before and after each step in the synthetic reactions described above and the weight change is used to determine the amount of trimethyltin chloride (Me_3SnCl) that is produced during the cross-linking reaction.

X-ray Absorption Spectroscopy

XAS data at the tungsten L_{III} (10207 eV) and L_{I} (12100 eV) were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on beamlines X18B and X19A, operated at 2.8 GeV with a current of 300 mA. The beam dimensions (i.e. spot size) on sample was 10 x 1 mm (w x h) for X18B and 3 x 1 mm (w x h) for X19A. Spectra were collected at room temperature. X-rays were monochromatized via reflection from Si(111) crystals through a 1 mm entrance slit. The incident beam was detuned 40% to suppress harmonics. Samples were mounted 45° to the beam, to collect transmission and fluorescence spectra simultaneously. The intensity of the incident beam was measured with a 10 cm N_2 -filled ion chamber detector (I_0). Transmitted x-rays were detected in a 30 cm 50:50 Ar: N_2 -filled ion chamber (I_t). The fluorescence signal from the sample was recorded with a Canberra PIPS detector (I_{fluor}). Spectra were recorded at room temperature in four energy regions about the tungsten L_3 edge at 10207 eV: -150 to -15 eV (below the edge) in 5 eV steps (1 s integration), -15 to 75 eV (through the edge) in 0.5 eV steps (2 s integration), 75 to 12 k in 0.05-k steps (3 s integration), and 12k to 16k in 0.05-k steps (4 s integration).

Sample powders were held in copper plates between windows of 7.5 μm polyimide (Kapton®) film (Chemplex 442) affixed with double sided tape to each side of the plate. Samples were loaded in a N_2 dry box to prevent hydrolysis. Two to three scans were collected for each sample. Data processing and analysis were performed using the IFEFFIT data analysis

software suite (Athena & Artemis).[125,167] The Athena program was used for XANES analysis and extraction of EXAFS from the smooth absorption edge background using standard procedures. The pre-edge background was modeled with a linear function. The post edge, smooth background was approximated with a stiff spline function and adjusted to minimize Fourier components that produce low R ($< 1 \text{ \AA}$) features in R -space plots. Low frequency Fourier components were also filtered from the EXAFS via the R_{bkgd} parameter that was kept smaller than 0.5 times the distance of the closest backscattering shell. Merged files were generated after auto aligning scans in Athena program. The Artemis program was used for modeling EXAFS $\chi(k)$ data. Theoretical phase and amplitude functions based on structural models were developed using FEFF6L in Artemis.[168] Single scattering paths for the first coordination sphere around tungsten (W=O, W-O, W-Cl, W $\cdots$ Si) were included in all models where appropriate. Preliminary fits to structural models were initiated with coordination numbers set to expected values (based on gravimetric analysis) while backscatterer identity (atomic number) was verified and other structural parameters were iteratively refined. Once these model parameters converged and were stable, coordination numbers were allowed to vary and generally converged to within 20% of expected values based on the connectivity for the sample determined from gravimetric data.

Elemental Analysis

Elemental analysis data were collected using a Perkin Elmer Optima 2100 DV ICP - Optical Emission Spectrometer equipped with a Scott spray chamber. Typically 25 mg of material was digested/dissolved into approximately 50 mL of solution ($\sim 1.5 \text{ mL HNO}_3$, $\sim 1.5 \text{ mL HF}$, and $\sim 47 \text{ mL}$ ultrapure ($18\text{M}\Omega$) deionized water). The procedure for sample preparation is as follows. Three sample solutions are analysis for each material. For each solution an empty 60 mL plastic bottle is weighed. In a glovebox the appropriate amount of material ($\sim 25 \text{ mg}$) is added to the plastic bottle. The exact mass of material added to the plastic bottle needs to be known. The three aliquots of each material are digested in a HNO_3 ($\sim 1.5 \text{ mL}$) and HF ($\sim 1.5 \text{ mL}$) solution for 2 hours followed by dilution to the appropriate volume using ultrapure deionized water ($\sim 47 \text{ mL}$).[169]

The data collection procedure is as follows. Emission data for three to five replicates were collected and averaged for each solution at four tungsten (207.912 nm, 224.876 nm,

239.708 nm, 248.923 nm) and four tin (189.927 nm, 235.485 nm, 283.998 nm, 242.170 nm) emission lines. A HNO₃/HF solution is used as the blank solution. A series of at least 5 standard solutions are used to construct a calibration curve for each metal being analyzed. Each sample solution is then collected and the concentration of the metal in solution determined using the corresponding calibration curve.

Infrared Spectroscopy

Infrared spectra were collected using a Thermo Nicolet IR100 in a MBraun LabMaster 130 N₂ dry box. 32 scans are collected using 4 cm⁻¹ resolution from 400-4000 cm⁻¹ for the background and samples. A KBr pellet is prepared and collected as the background spectrum. A KBr pellet containing sample material (~1-5 wt%) is prepared and collected as the sample spectrum.

Pyridine adsorption was monitored using IR spectroscopy to identify the acidity (either Lewis or Bronsted) of the metal centers in the silicate building block matrix. Pyridine adsorption measurements are conducted as follows. A KBr pellet containing a sample of the tungsten-silicate building block material was prepared in the N₂ dry box and collected as the background spectrum. The pellet was placed in a Schlenk vessel and degassed under dynamic vacuum at 100°C for one hour. The Schlenk vessel was cooled and pyridine was vapor transferred into the Schlenk vessel. The vessel sat at room temperature for approximately 5 minutes followed by degassing under vacuum at room temperature for two hours. A final spectrum was collected in the N₂ dry box. The features observed between 1400 cm⁻¹ and 1700 cm⁻¹ and values previously reported in the literature were used to classify the acidity of the metal centers in the silicate building block matrix.[100,151,170]

Raman Spectroscopy

Raman spectra were collected using a Horiba Jobin Yvon T64000 spectrometer (600 or 1800 grooves / mm) equipped with a Synapse CCD detector. Spectra were obtained using the single or triple subtractive spectrograph mode of operation. The single spectrograph mode of operation yielded a spectral window of ~2200 cm⁻¹ and spectral resolution of ~2.4 cm⁻¹ while the triple subtractive spectrograph mode of operation yielded a spectral window of ~700 cm⁻¹ and spectral resolution of <1 cm⁻¹. 487.9 nm or 514.5 nm excitation from a Coherent Innova 200 argon ion laser is used. In a N₂ dry box, the samples were pressed into pellets and sealed

between two cover slides, pretreated with a chlorotrimethylsilane/triethylamine solution, using double sided tape. Approximately 1-10 mW of the laser is focused onto the sample through a microscope objective (10x, 50x, or 80x). Multiple spectra at different parts of the sample are collected and compared to determine if sample degradation had occurred.

Solid State Nuclear Magnetic Resonance Spectroscopy

Procedures used for ^{29}Si SSNMR experiments have been previously reported.[95] ^{29}Si SSNMR experiments were acquired at 79.43 MHz at spin rates of 5.00 kHz on a Varian Inova spectrometer. Samples were placed in 5 mm pencil rotors in a N_2 dry box and sealed using paraffin wax. Normal one pulse magic angle spinning (MAS) spectra were collected using a 30° pulse and relaxation delays of 30 s.

Nitrogen Adsorption/Desorption

Nitrogen adsorption-desorption analysis was performed using a Quanta Chrome Nova 1000 instrument. BET surface area was calculated using adsorption data in the relative pressure range from 0.05 to 0.35.[131] t-plots or α_s -plot were used to determine micro- and mesoporosity of the materials.[132,136] The adsorption portion of the nitrogen gas adsorption/desorption isotherms was used to calculate the pore size distribution (BJH method) of the samples.

Results and Discussion

Isolated Embedded W(VI) Catalyst Ensemble using WOCl_4

The combination of a building block approach and a sequential addition strategy is used in the targeted synthesis of an embedded catalyst ensemble which contains a W(VI) center with one terminal oxo group and four links to the silicate support (Figure 87). This embedded catalyst ensemble will be referred to as “*isolated embedded tungsten oxo centers.*”

First Cross-Linking Reaction: Reaction of WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

The synthesis of isolated tungsten oxo centers that are connected to four silicate building blocks is achieved by reacting a trimethyltin functionalized silicate building block, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, with a limiting amount of WOCl_4 (~1 WOCl_4 : 4 $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ at room temperature in ether for 24 hours) (Figure 88). The cross-linking process proceeds via a metathesis reaction where a chloride ligand of WOCl_4 cleanly reacts with a Me_3Sn group to form a new siloxane bond (W-O-Si) and Me_3SnCl , a volatile byproduct. This process will continue

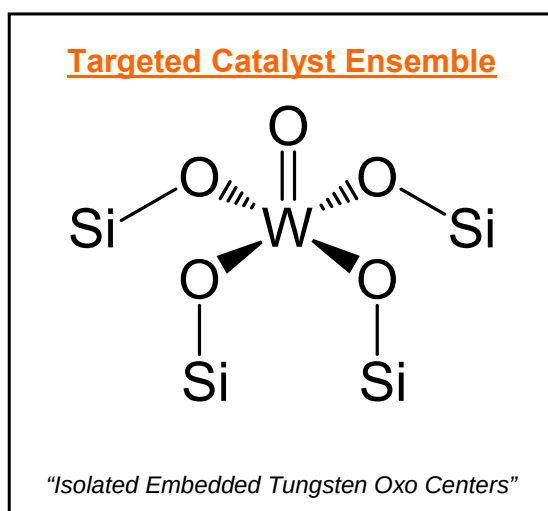


Figure 87: Illustration of the targeted catalyst ensemble referred to as "isolated embedded tungsten oxo centers."

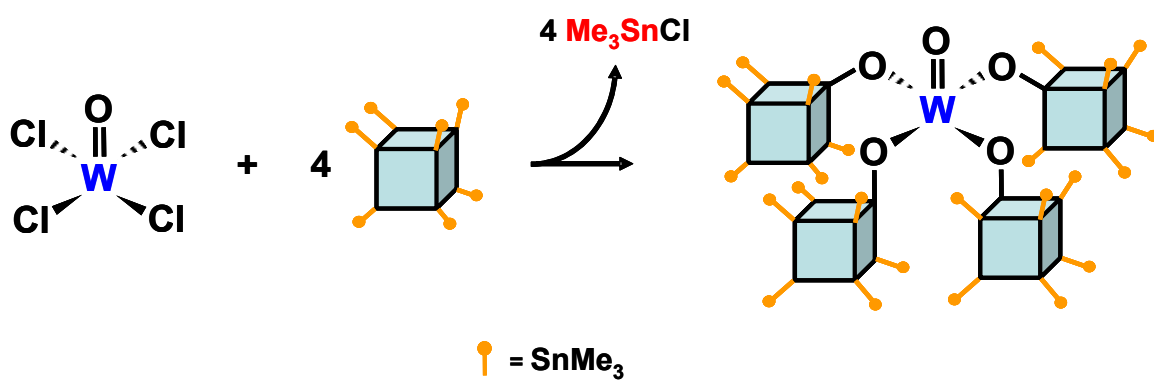


Figure 88: First Cross-Linking Reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

until either all the chloride ligands on WOCl_4 are consumed or a chloride ligand becomes unreactive as more W-O-Si bonds are formed to the tungsten center. A limiting amount of WOCl_4 was used to insure that all the chloride ligands could react with the Me_3Sn groups on the silicate building block. The volatiles of the reaction were analyzed using ^1H NMR and Me_3SnCl was the only byproduct observed. Gravimetric analysis (4.4 ± 0.3 equivalents of Me_3SnCl) is consistent with all the chloride ligands on the tungsten center reacting. Based gravimetric data, the tungsten centers contain one terminal oxo group and four newly formed siloxane bonds (W-O-Si) (Figure 88).

The ratio of tungsten atoms to tin atoms in the silicate building block material following this first cross-linking reaction can be determined from the initial reaction stoichiometry and was confirmed using ICP-OES. The initial ratio was 1 tungsten atom for every 28.6 tin atoms ($0.28 \text{ WOCl}_4 : 1 \text{ Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$). According to gravimetric data, every tungsten atom reacted with 4 Me_3Sn groups resulting in the loss of 4 tin atoms (as Me_3SnCl) from the silicate building block matrix. Thus, the expected W : Sn ratio would be 1 : 24.6 following the first cross-linking reaction. The actual concentration of tungsten ($3.5 \pm 0.03 \text{ wt\%}$) and tin ($56.1 \pm 1.4 \text{ wt\%}$) in the sample at this stage of the synthesis was determined using ICP-OES. The ICP-OES results are consistent with 1.0 W : 24.8 Sn in the silicate building block matrix or the loss of 3.8 tin atoms per tungsten atom. Therefore both the connectivity of the tungsten centers determined by gravimetric analysis (4.4 ± 0.3) and the connectivity determined by ICP-OES (3.8 ± 0.7) suggest all of the chloride ligands initially on the tungsten centers have reacted.

Infrared spectroscopy was used to verify the formation of the W-O-Si linkages. The band at 1040 cm^{-1} , which is commonly assigned to the Si-O-Si stretching mode,[46,171] was observed in the IR spectra of a tungsten-free silicate building block support and the material following the reaction of WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ (Figure 89). A shoulder on the Si-O-Si feature was observed at approximately 950 cm^{-1} in the IR spectrum of the material following the reaction of WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, which is characteristic of the presence of M-O-Si groups, in this case W, in the matrix.[36,44,84,144,164,165] The observation of this weak shoulder provides additional evidence on the formation of W-O-Si groups and suggesting the metathesis reaction proceeded as expected.

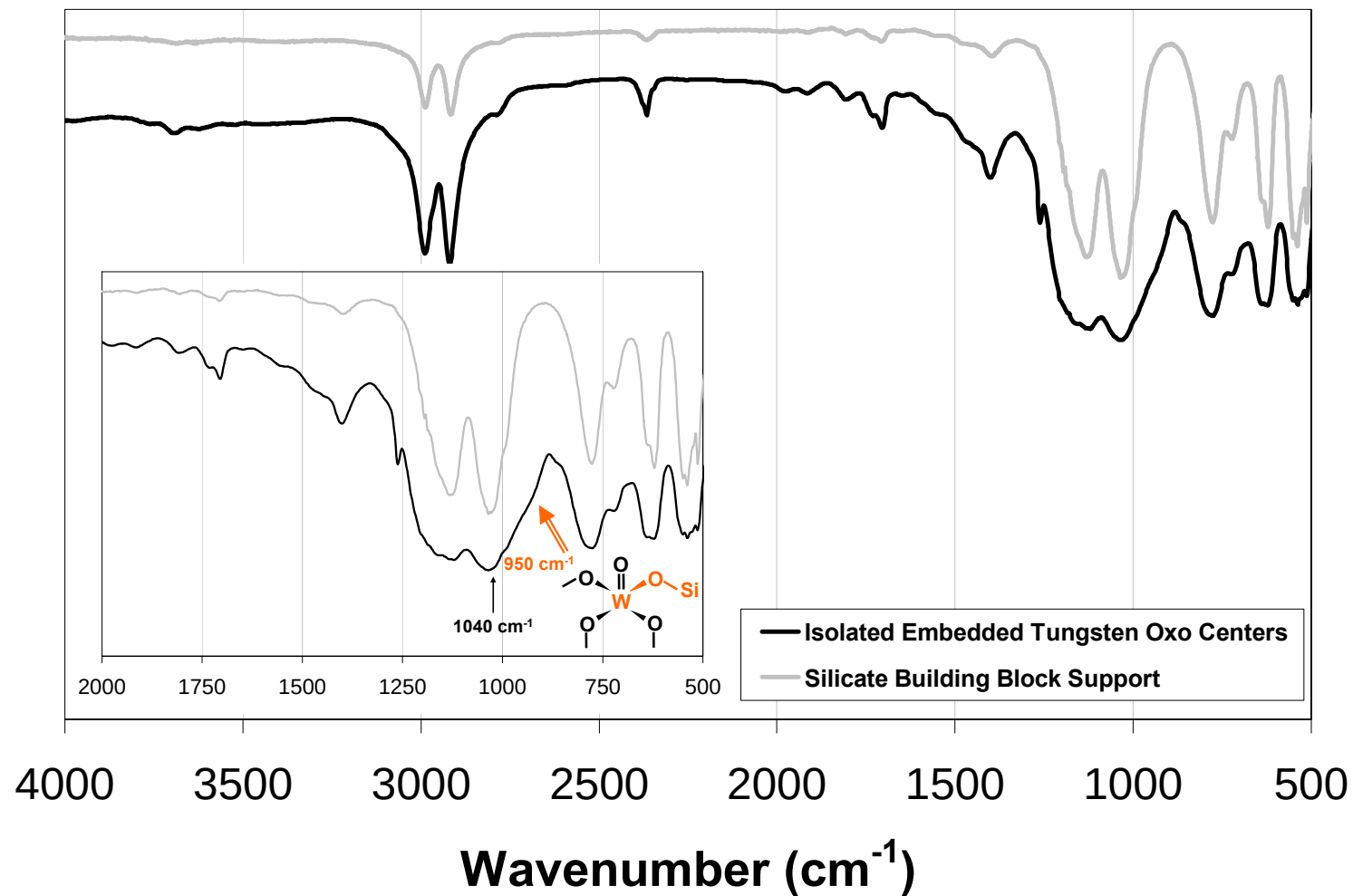


Figure 89: IR spectra (500-4000 cm⁻¹) of a tungsten-free silicate building block support and the material following the first cross-linking reaction, WOCl₄ and Si₈O₁₂(OSnMe₃)₈. The inset contains the expanded IR spectrum (500-2000 cm⁻¹) which illustrates the W-O-Si shoulder (950 cm⁻¹).

Raman spectroscopy is a powerful tool used by material scientists to confirm the presence of metal oxide domains and functional groups such as metal oxo groups.[162] The characteristic features of tungsten trioxide (270 cm^{-1} , 715 cm^{-1} , and 805 cm^{-1}) and of W-O-W linkages (215 cm^{-1}) were not observed in the Raman spectrum of this material, which supports the claim that the tungsten oxo centers in the matrix are spatially isolated.[36,160,172-174] Furthermore, the characteristic feature for W-Cl ($400\text{-}410\text{ cm}^{-1}$) was not observed,[175,176] which is consistent with the loss of all of the chloride ligands from around tungsten. A feature at 982 cm^{-1} was observed, which is characteristic of the presence of a tungsten oxo group (Figure 90).[144,149,172,177] This feature is also reported in the Raman spectrum[144] of the model complex $\text{WO}[\text{OSi}(\text{O}^t\text{Bu})_3]_4$ (literature Raman shift = 982 cm^{-1}).

Figure 91 shows the ^{29}Si SSNMR spectrum for the isolated embedded tungsten oxo centers. When a limiting amount of WOCl_4 is reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ two signals are expected. The absence of signals between -22 to -100 ppm in Figure 91 indicates that no silyl chlorides are present in the matrix (i.e. $(\equiv\text{SiO})_{4-x}\text{SiCl}_x$).[95] The asymmetric signal (Figure 92) observed between -100 ppm and -110 ppm is assigned to silicon corners on the building block which are connected to unreacted Me_3Sn groups and three other corner silicon atoms ($(\equiv\text{SiO})_3\text{Si}(\text{OSnMe}_3)$) and the silicon corners on the building block which are connected to the tungsten oxo centers ($(\equiv\text{SiO})_3\text{Si}(\text{OW}\equiv)$). Deconvolution of the asymmetric peak between -100 ppm and -110 ppm gives rise to two signals, one at -102 ppm which is assigned to the silicon corners on the building block connected to unreacted Me_3Sn groups (i.e. $(\equiv\text{SiO})_3\text{Si}(\text{OSnMe}_3)$)[95] and a second signal at -104 ppm which is assigned to the silicon corners bound to a tungsten atom (through an oxygen atom), specifically a silicon atom associated with an embedded tungsten oxo group (i.e. $(\equiv\text{SiO})_3\text{Si}(\text{OW}\equiv)$).[37,45,160]

One potential side reaction that should be considered in this context is the possible transfer of a chloride ligand from tungsten to silicon as illustrated in Figure 93. The chemical shift regions for various $\text{SiCl}_x(\text{OSi}\equiv)_{4-x}$ groups have been described in the literature.[95] The silicon chemical shift moves to lower field (less negative) chemical shift values as the number of chloride substituents increases on silicon. As already mentioned the absence of signals between -22 and -100 ppm in Figure 91 indicates that no silyl chlorides are present in the matrix

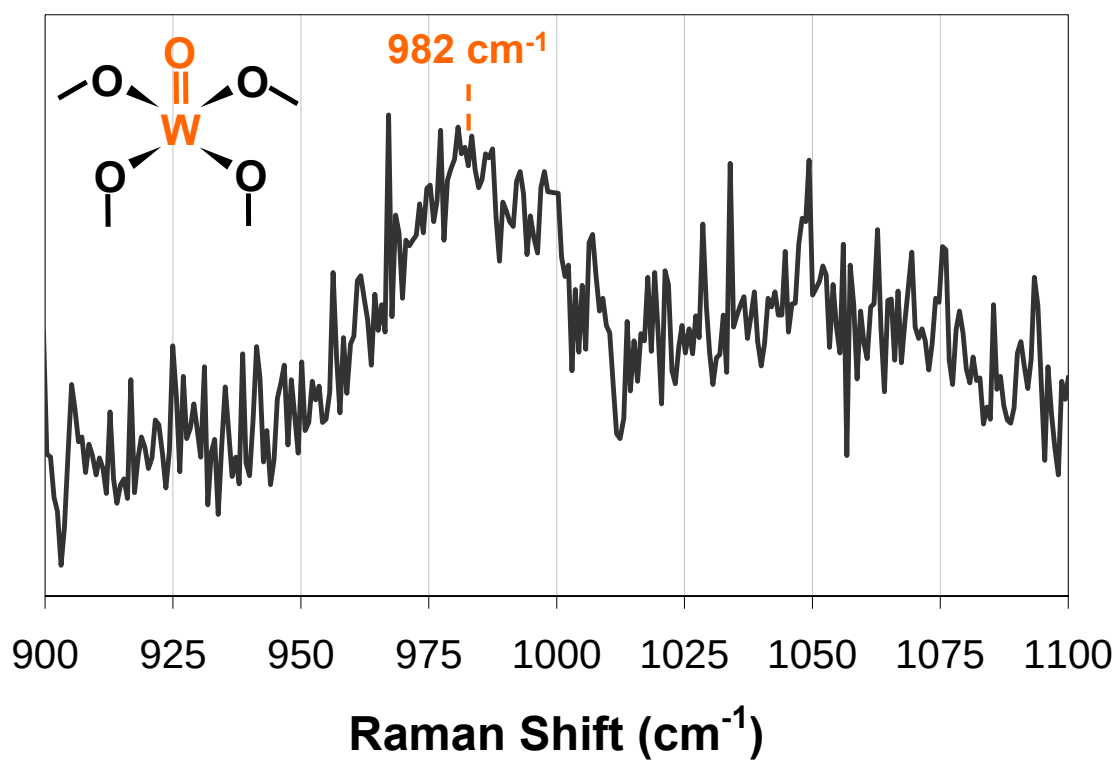


Figure 90: Raman spectrum following the first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

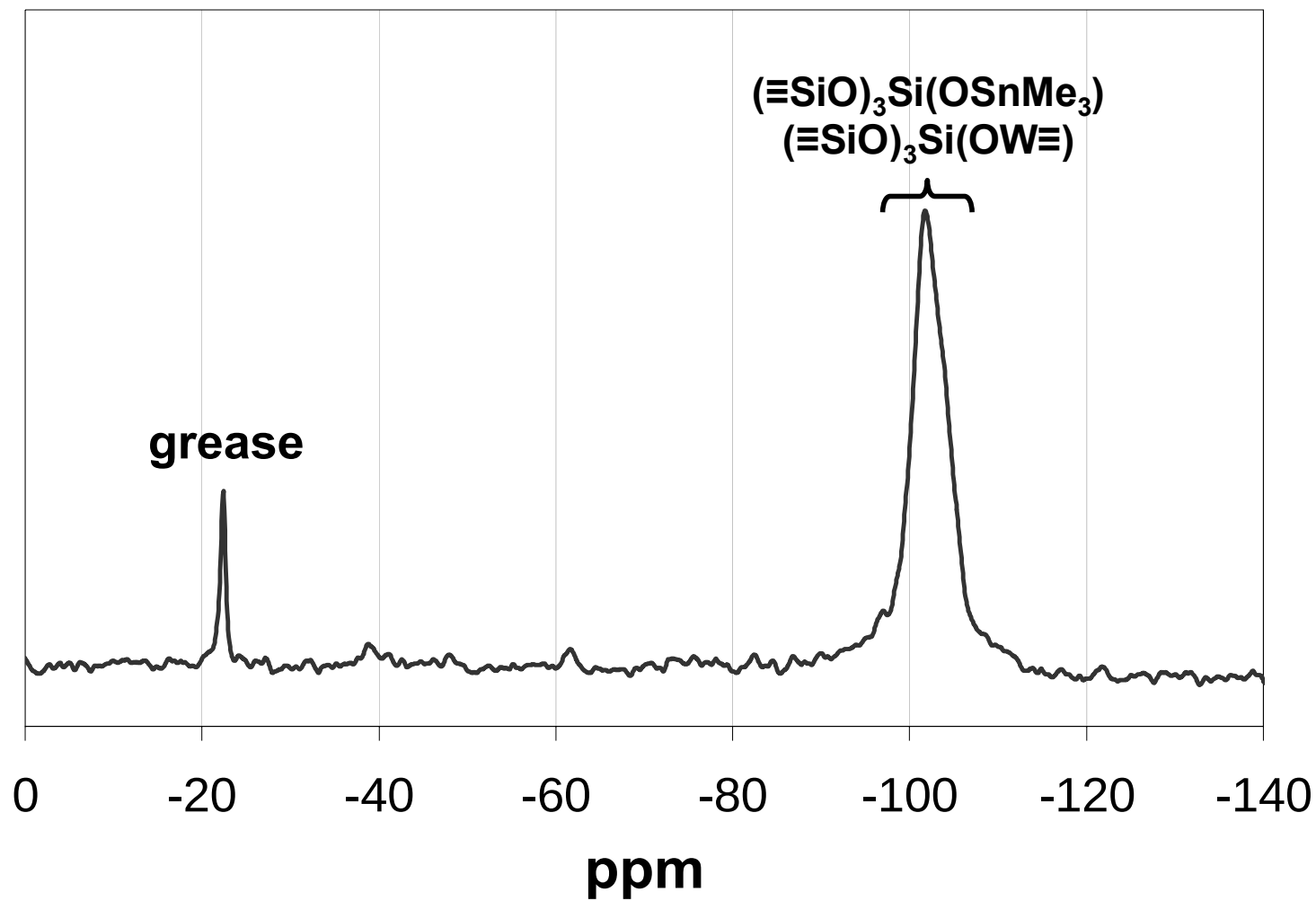


Figure 91: ^{29}Si SSNMR spectrum (-140 to 0 ppm) following the first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The peak at -22 ppm is assigned to silicon grease used to seal the sample from air.

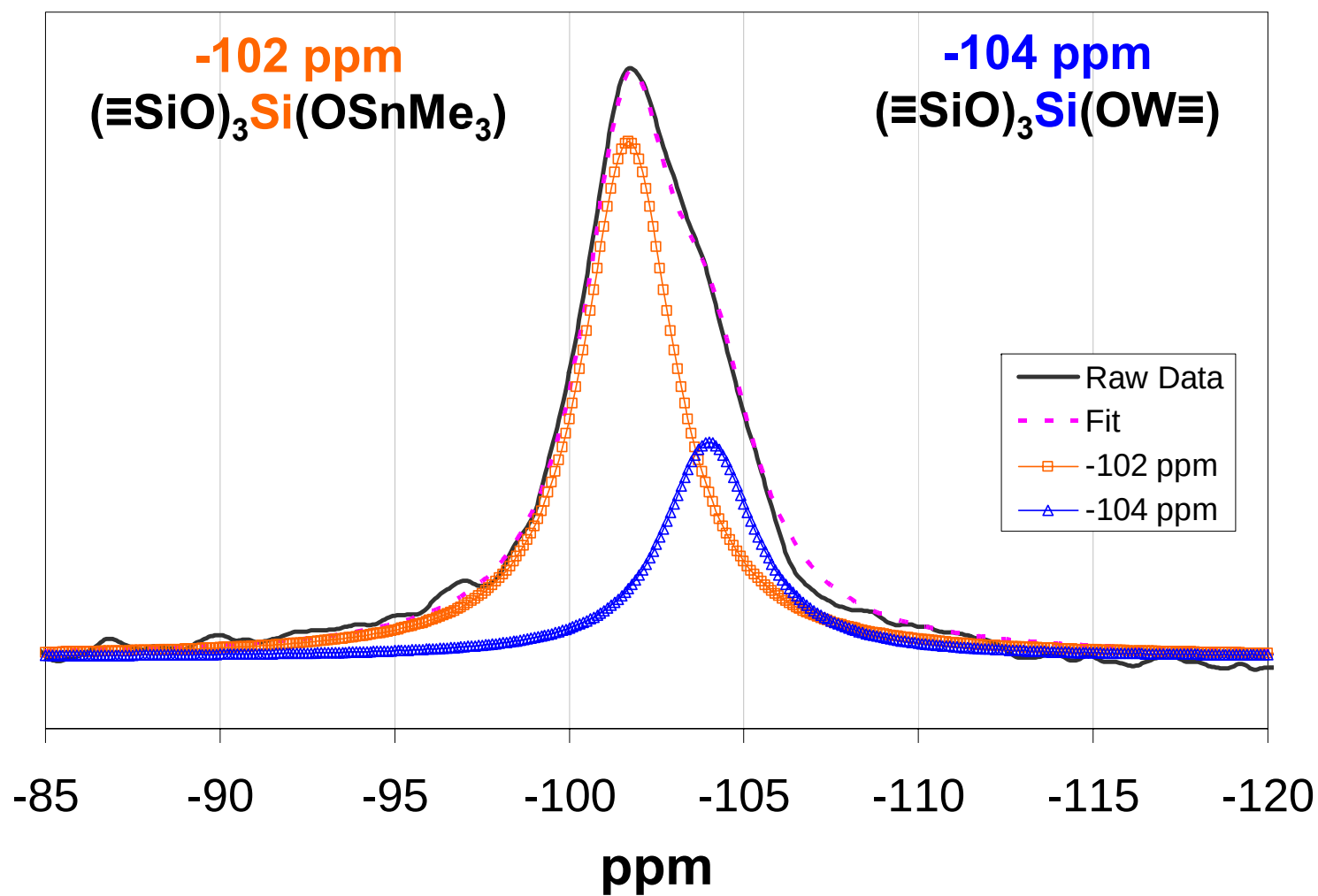


Figure 92: Deconvolution of the ^{29}Si SSNMR spectrum (-120 to -85 ppm) following the first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

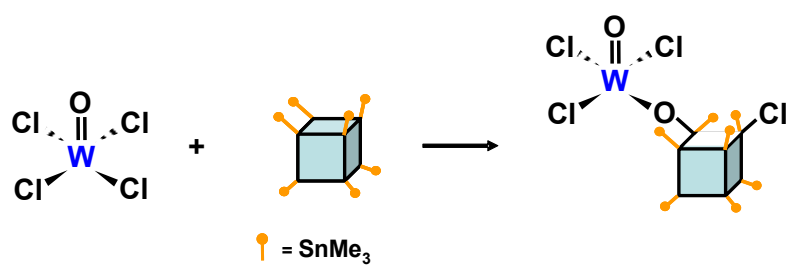


Figure 93: Illustration of possible disruption of Si_8O_{20} core structure.

(i.e. $(\equiv\text{SiO})_{4-x}\text{SiCl}_x$).[95] Generally the Sn-O-Si bond is more labile than the Si-O-Si bond.[97] Therefore the cross-linking metathesis is expected to be favored so the disruption of the Si_8O_{20} core structure, while possible, is unlikely.

Another mechanism by which silyl chlorides could be formed is if the tungsten oxo center was converted into a tungsten dioxo center as shown in Figure 94. This reaction has been reported to occur under forcing conditions (i.e. refluxing at 100°C in petroleum ether) and therefore is possible but unlikely to occur given the reaction conditions.[166] Also, the absence of signals between -105 and -110 ppm, which is the region generally assigned to $\text{Si}(\text{OSi}\equiv)_4$ groups,[95] indicates none of the silicate building blocks have become linked with each other without a tungsten atom serving as a linking point. Due to complementary functionalities on the linking reactants and the silicate building blocks, the only way two silicate building blocks should link together without tungsten serving as a linking point is if a silyl chloride, generated in-situ, reacted with a corner Me_3Sn group as illustrated in Figure 95 and Figure 96.

Nitrogen adsorption/desorption experiments were conducted to determine the BET surface area and total pore volume. No measurable BET surface area or pore volume was observed, which supports the conclusion that the silicate building block material after one stage of cross-linking with a limiting amount of WOCl_4 contains small oligomers and that a rigid porous macromolecule has not been formed.

XAS is one of the techniques that can probe the immediate environment around the tungsten oxo centers and provide the important information needed to verify the metathesis reaction proceeded as expected. Thus XAS data were used to obtain more information about the coordination geometry and oxidation state of the tungsten oxo centers (XANES) in addition to the connectivity of the tungsten oxo centers (EXAFS) in this material.

XANES data for both the L_{III} (10207 eV) and the L_{I} (12100 eV) edges provide information about the coordination geometry and oxidation state of the tungsten oxo centers.[117] The position of the L_{III} edge and the intensity of the white line provide information about the oxidation state while the width of the white line provides information about the coordination geometry.

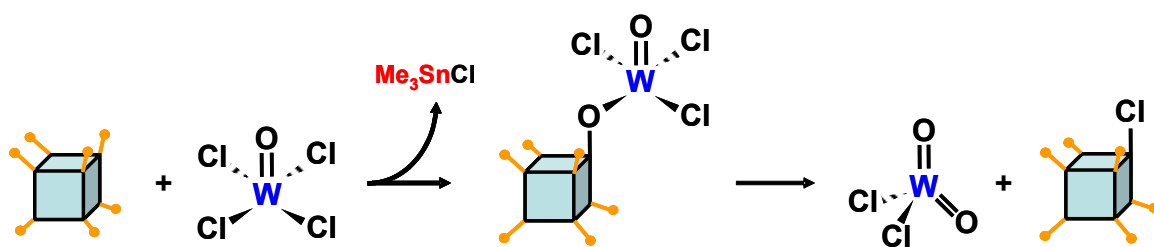


Figure 94: Illustration of the possible conversion of a tungsten oxo center to a tungsten dioxo center.

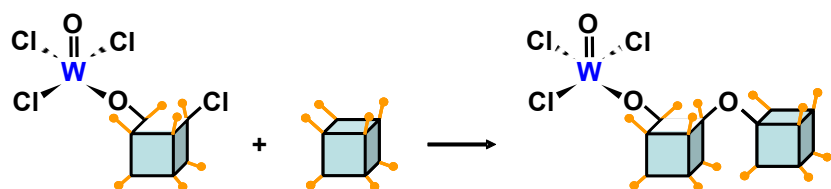


Figure 95: Illustration of chloride generated in-situ during Si₈O₂₀ core disruption reacting with a corner Me₃Sn group.

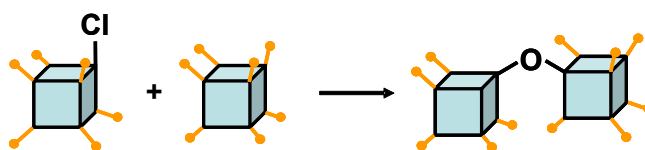


Figure 96: Illustration of chloride generated in-situ during tungsten dioxo formation reacting with a corner Me_3Sn group.

Figure 97 shows the edge position of standard tungsten materials with different oxidation states (W(0), W(III), W(IV), W(VI)). The edge position for tungsten foil (W(0)) is 10207 eV, tungsten boride (WB, W(III)) is 10207 eV, tungsten(IV) oxide (WO₂, W(IV)) is 10208 eV, and tungsten(VI) oxide (WO₃, W(VI)) is 10209 eV (Table 5). The edge position does not appear to vary in a systematic manner with the oxidation state of tungsten, but still can be used to determine oxidation state.

Yamazoe et al. provide the XANES spectra for several tungsten complexes at the L_{III} edge and stated that the width of the white line could be used to determine the coordination geometry of the tungsten centers present in the material. In general the width of the white line is approximately 4.9 eV when the coordination geometry around the tungsten center is tetrahedral, approximately 7.4 eV when the coordination geometry is distorted octahedral, and approximately 9.4 eV when the coordination geometry around the tungsten center is octahedral (Figure 98). Therefore the width of the white line can be used to provide information about the coordination geometry of the tungsten centers in a material.

As was already mentioned in Chapter 1, the intensity of the white line reflects the occupancy of the d-orbitals of the absorbing atom thus filling the d-orbitals of the absorbing atom suppresses the observed white line (Figure 46).[117] The ratio of the intensity of the white line relative to the edge jump for 5d transition metals ($I_{WL}/I_{\Delta\mu(E)}$) shows a linear relationship with the number of valence electrons (Figure 99). This relationship was used to estimate the oxidation state of the tungsten oxo centers present in the oligomers. The value for the ratio for the tungsten oxo oligomers (3.38) supports the claim that the oxidation state of the tungsten centers is +6 (Figure 99).

Figure 100 shows the XANES and the derivative XANES spectra at the L_{III} edge of the material at this stage in the synthesis. The edge position of the tungsten oxo oligomers supports the claim that the oxidation state of the tungsten centers is +6. The width of the white line for the tungsten oxo oligomers was compared to the width of the white line for the tungsten complexes. The width of the white line for the tungsten oxo oligomers provides evidence that the coordination geometry around the tungsten centers is not octahedral and suggests the

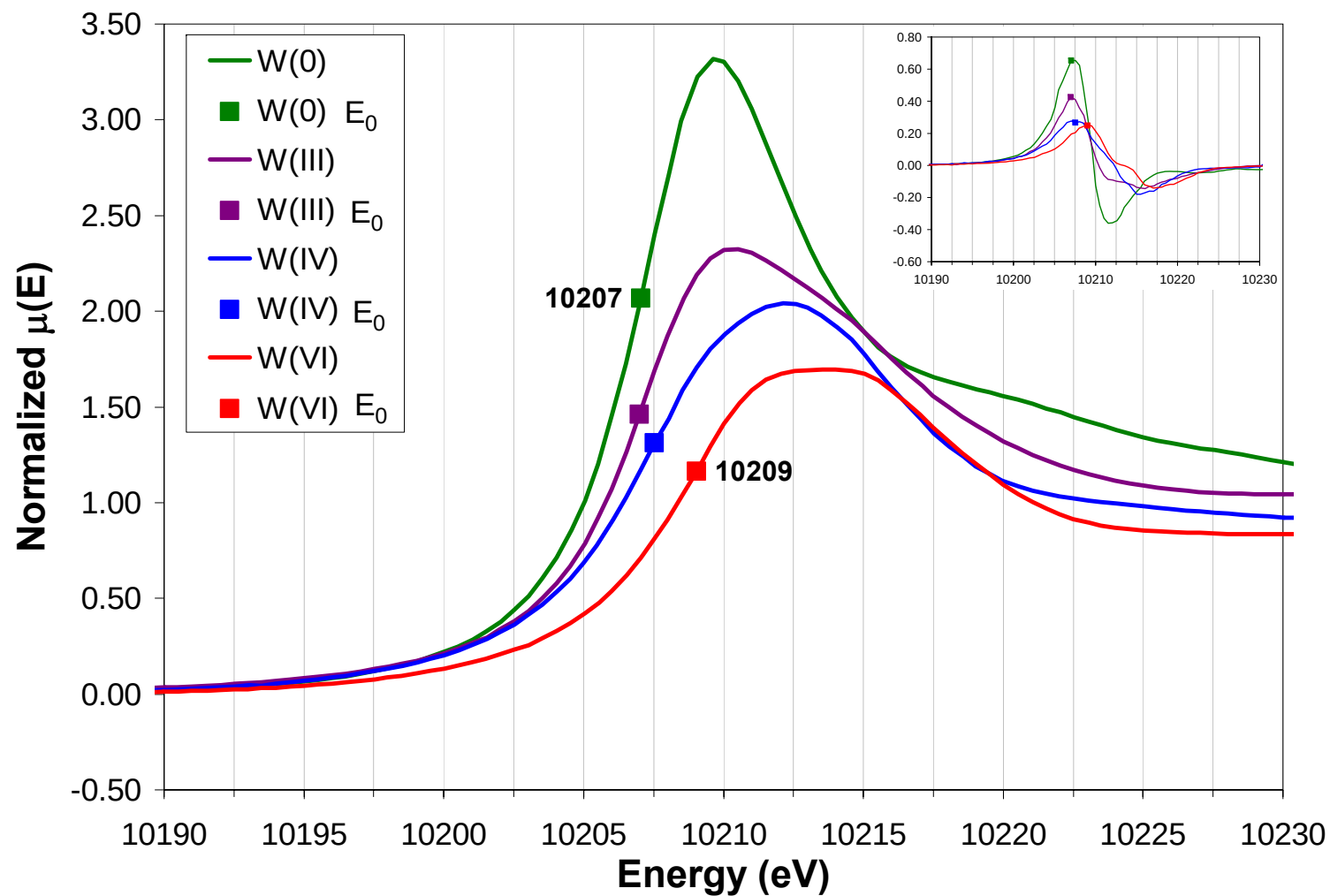


Figure 97: XANES spectra (W L_{III} edge) of standard tungsten materials with varying oxidation state. The inset contains the derivative XANES spectrum which shows the absorption edge position of each material.

Table 5: XANES analysis for embedded and surface catalyst ensembles and standard tungsten materials

Compound	Geometry	L _I edge		L _{III} edge
		Pre-edge (eV)	E ₀ (eV)	E ₀ (eV)
Embedded tungsten oxo centers, 1 st Cross-linking		12096	12105	10210
Embedded tungsten oxo centers, 2 nd Cross-linking		12096	12105	10210
Embedded tungsten centers, 1 st Cross-linking		12096	12106	10210
Embedded tungsten centers, 2 nd Cross-linking		12097	12105	10210
Surface tungsten oxo centers		12097	12106	10210
Surface tungsten centers		12097	12105	10210
W foil, W(0)			12100	10207
WB, W(III)			12100	10207
WO ₂ , W(IV)			12101	10208
WO ₃ , W(VI)			12106	10209

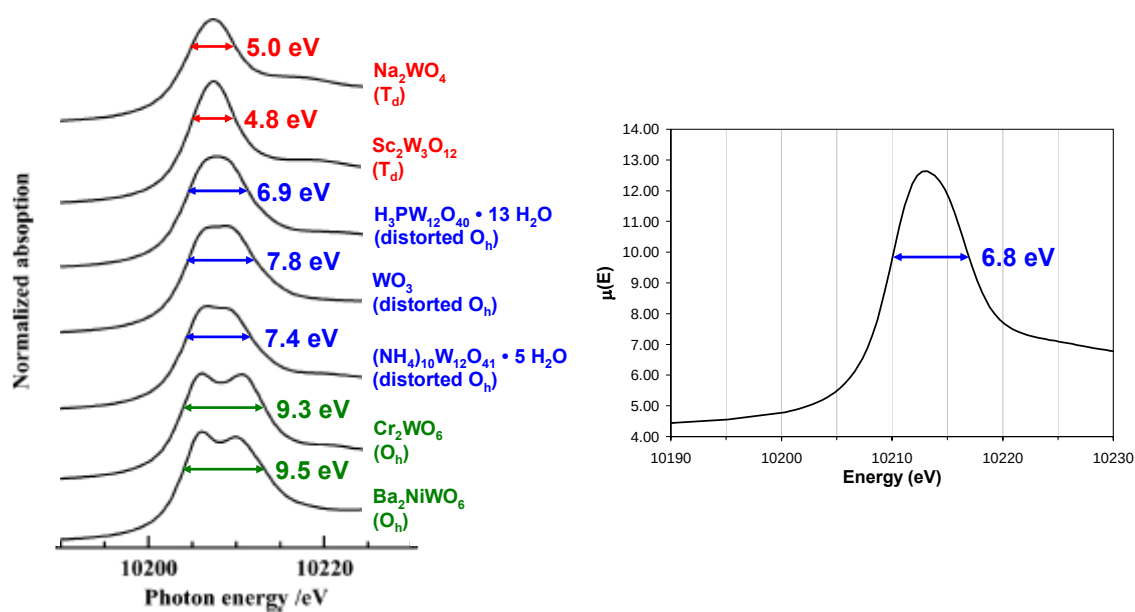


Figure 98: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ (right).

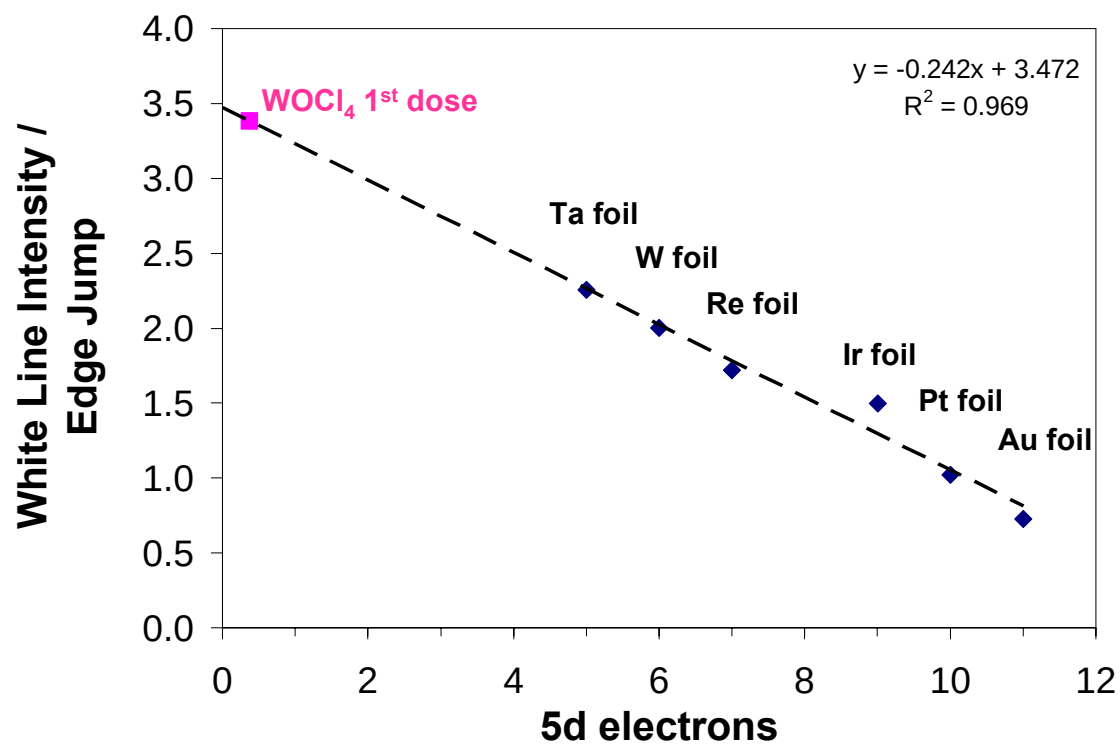


Figure 99: Relationship between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the first cross-linking reaction, WOCl₄ and Si₈O₁₂(OSnMe₃)₈.

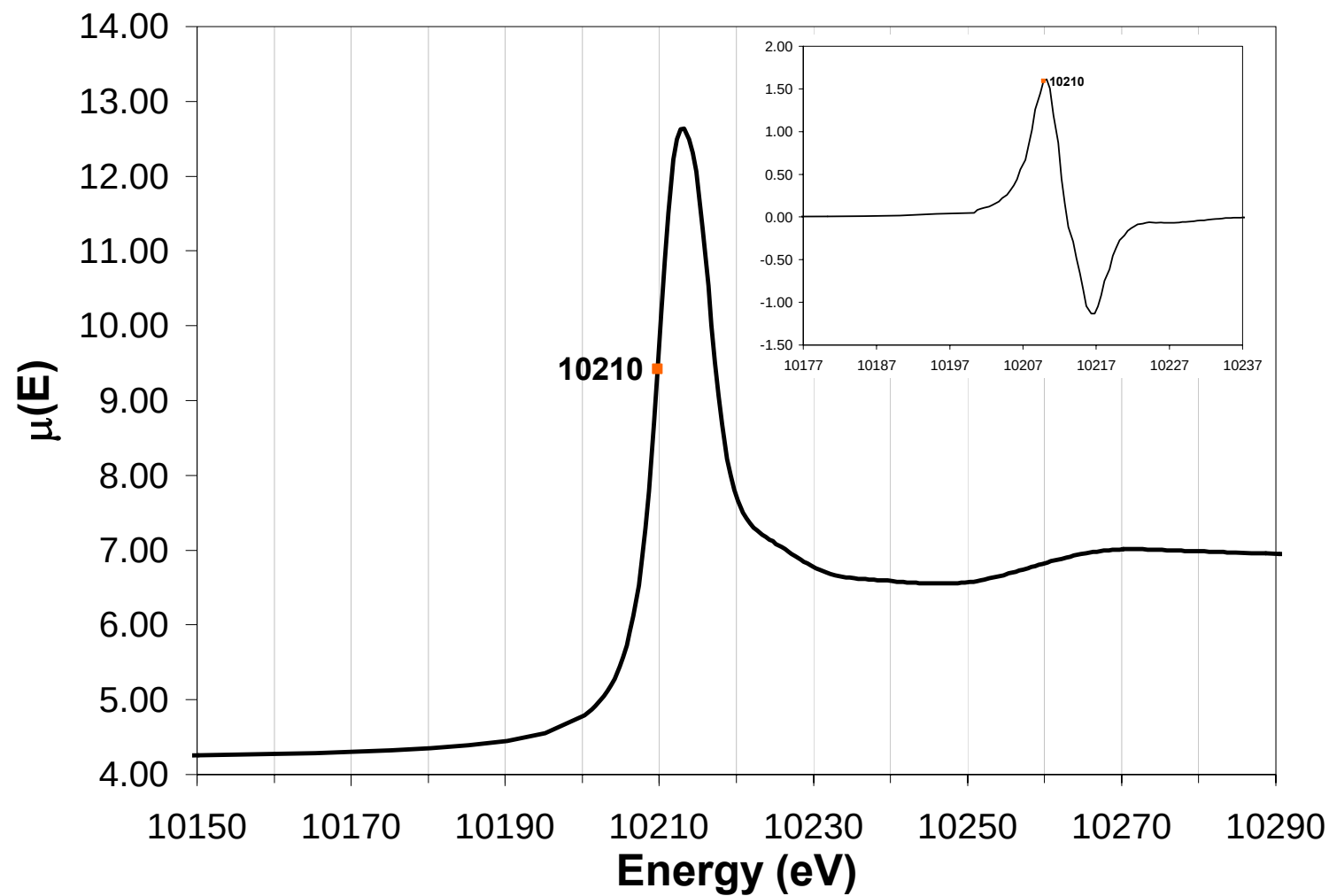


Figure 100: XANES spectrum (W L_{III} edge) following the first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The inset contains the derivative XANES spectrum with the position of the absorption edge labeled (orange square).

coordination geometry is either tetrahedral or distorted octahedral. The white line appears to be broad (width = 6.8 eV) which would suggest the coordination geometry is distorted octahedral (width = 7.4 eV) instead of tetrahedral (width = 4.9 eV) (Figure 98).

The position of the L_I edge provides information about the oxidation state while the presence and intensity of the pre-edge feature provides information about the coordination geometry.

Figure 101 shows the edge position of standard tungsten materials with different oxidation states (W(0), W(III), W(IV), W(VI)). The edge position for tungsten foil (W(0)) is 12100 eV, the edge position of tungsten boride (WB, W(III)) is 12100 eV, the edge position of tungsten(IV) oxide (WO_2 , W(IV)) is 12101 eV, and the edge position for tungsten(VI) oxide (WO_3 , W(VI)) is 12106 eV (Table 5). The edge position does not appear to be too sensitive to the oxidation of tungsten, but still can be used to determine oxidation state.

The presence of a pre-edge feature ($2s \rightarrow 5d$ transition) provides evidence that the coordination geometry around the tungsten oxo center is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. Yamazoe et al. provide the XANES spectra for several tungsten complexes at the L_I edge (Figure 102). In general the intensity of the pre-edge feature is approximately 65% of the edge jump when the coordination geometry around the tungsten center is tetrahedral and is approximately 40% when the coordination geometry around the tungsten center is distorted octahedral.

Figure 103 shows the XANES spectrum at the L_I edge of the material at this stage in the synthesis. The edge position of the tungsten oxo oligomers (12105 eV) supports the assertion that the oxidation state of the tungsten centers is +6. The intensity of the pre-edge for the tungsten oxo oligomers is approximately 35% which suggests the coordination geometry is distorted octahedral.

EXAFS data were used to obtain additional information about the connectivity of the tungsten oxo centers in the silicate building block matrix. EXAFS data can provide both qualitative and quantitative information about the tungsten oxo centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around tungsten) can be qualitatively determined by looking at the magnitude R-space plot (Figure 104). Assuming some

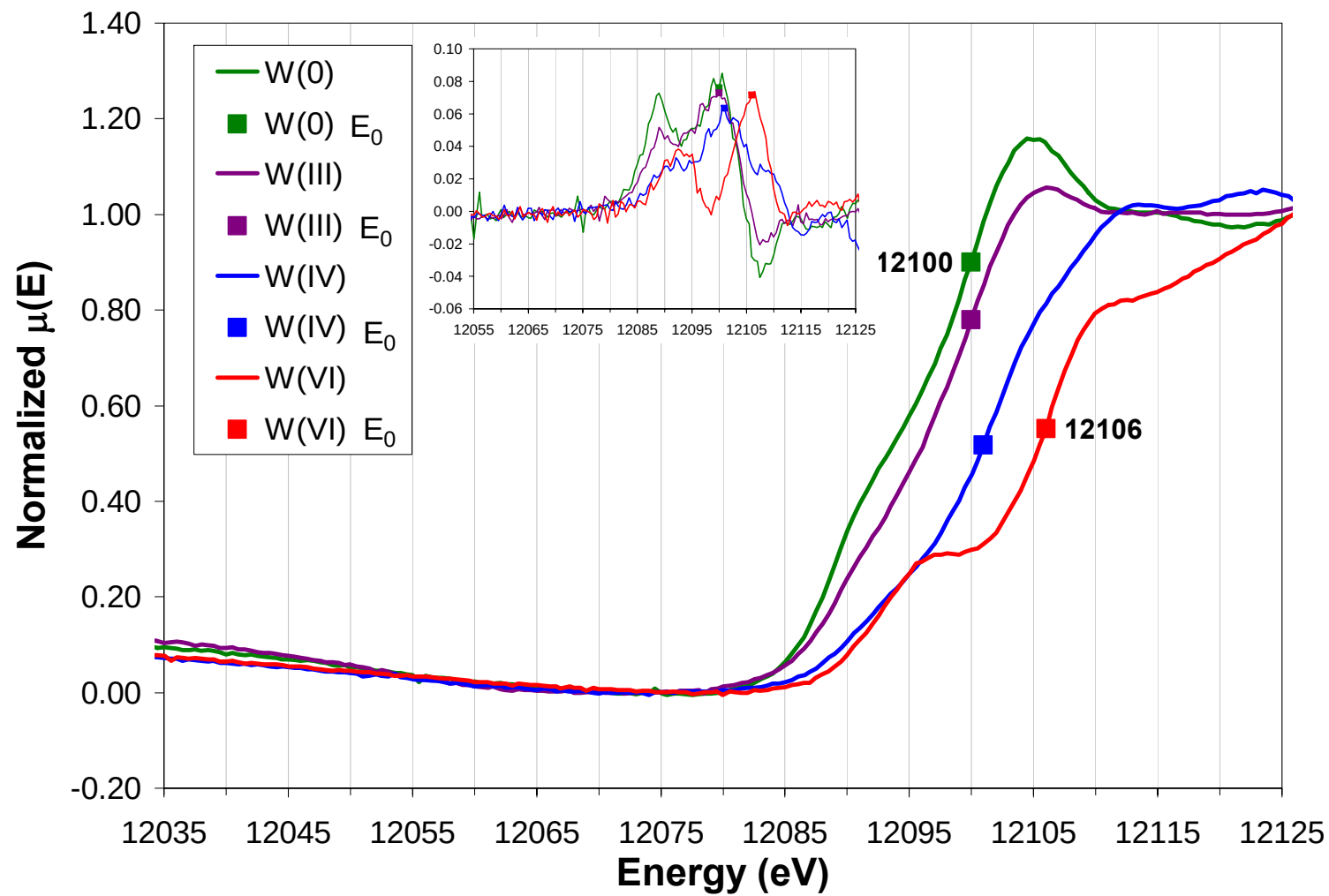


Figure 101: XANES spectra (W L_1 edge) of standard tungsten materials with varying oxidation state. The inset contains the derivative XANES spectra with the position of the absorption edge position of each material labeled.

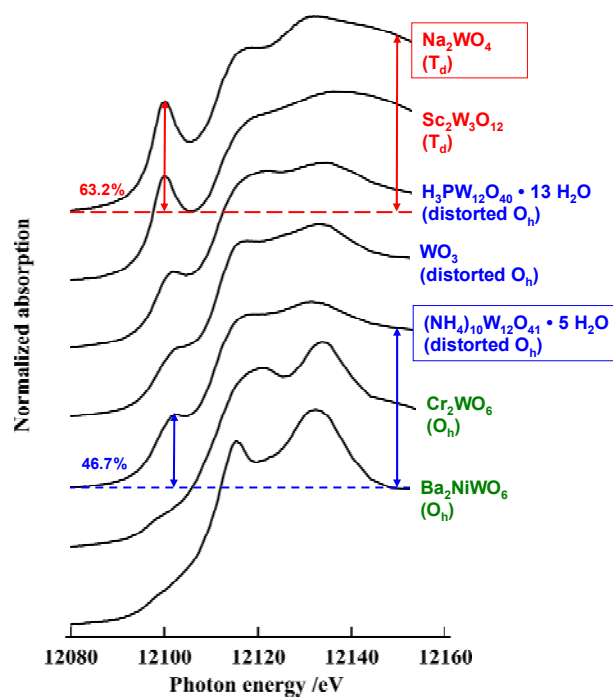


Figure 102: Analysis of the intensity of the pre-edge at the L_I edge for published standards.[117]

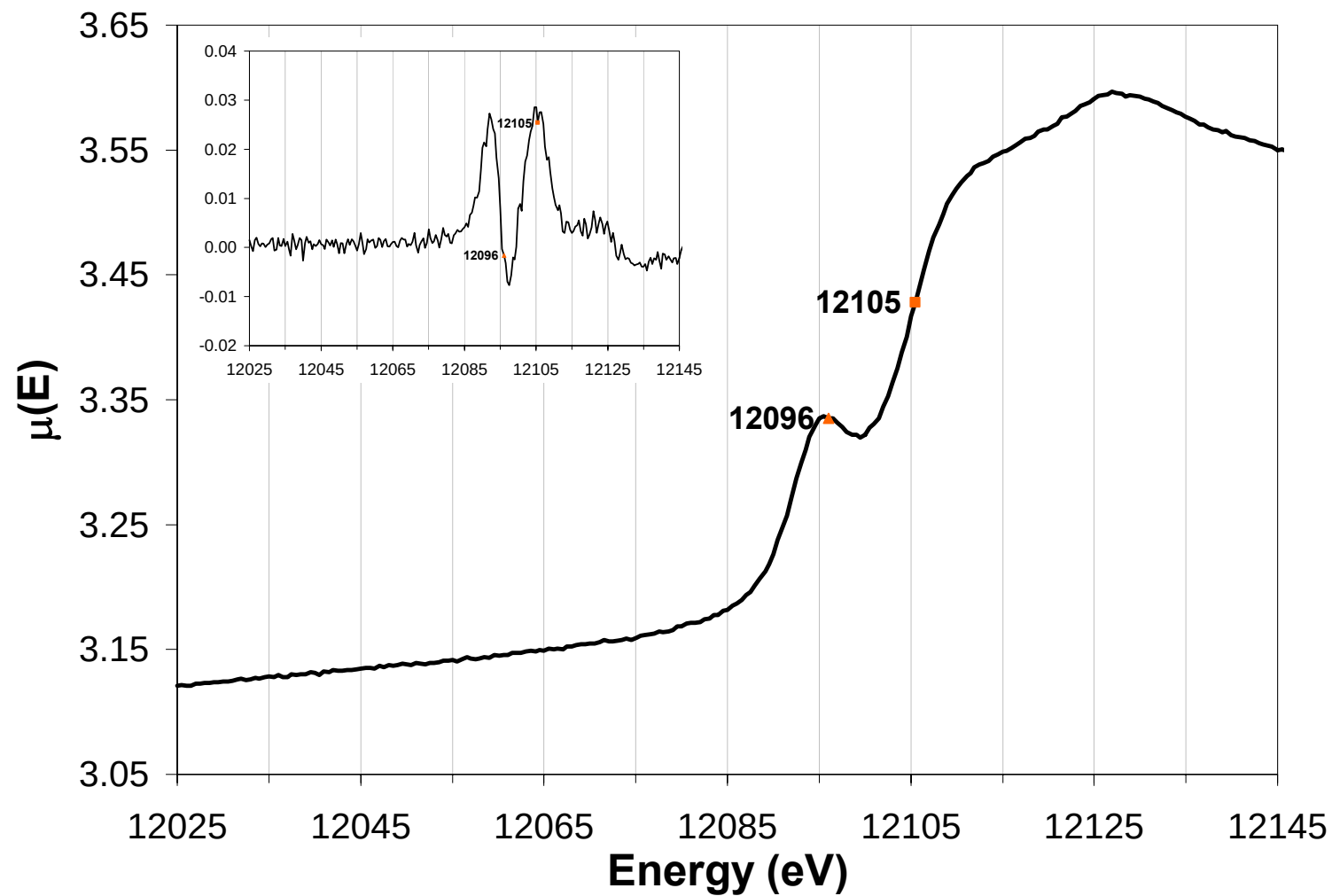


Figure 103: XANES spectrum (W L₁ edge) following the first cross-linking reaction, WOCl₄ and Si₈O₁₂(OSnMe₃)₈. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

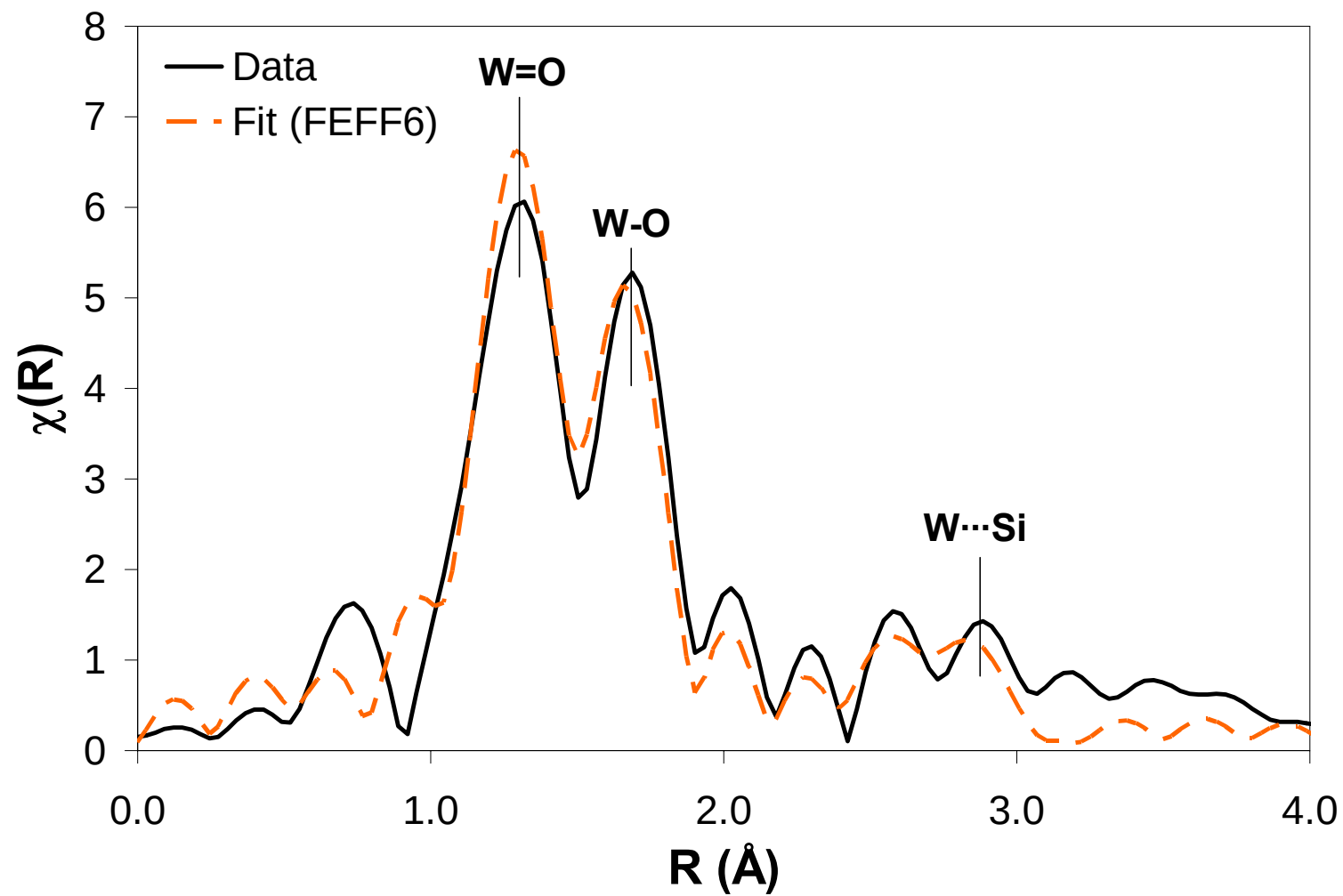


Figure 104: EXAFS R-space plot following first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

or all of the chloride ligands are replaced by new siloxanes linkages (W-O-Si), as many as four shells may be present around the tungsten centers after the first cross-linking reaction: a shell of terminal doubly bound oxygen atoms (W=O), a shell of singly bound oxygen atoms (W-O), one for any unreacted chloride ligands (W-Cl), and a shell of nonbonded silicon atoms (W $\cdots$ Si). The feature corresponding to W-Cl should not be observed based on both gravimetric and Raman that data indicate all of the chloride ligands initially associated with WOCl₄ were lost from the system as Me₃SnCl. Figure 104 shows the three features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot.

Quantitative information is obtained from the EXAFS data via an iterative computational modeling refinement. The information derived from successful modeling of EXAFS data includes the identity of the backscattering atom around the tungsten atom, the bond/separation distance, and the number of these bonds/interactions present (i.e. coordination number). Based on the qualitative analysis of the EXAFS data the first coordination sphere (defined as atoms directly bound to the tungsten) of the embedded tungsten oxo centers should have at least one terminal doubly bound oxygen atoms (W=O), at least one singly bound oxygen atoms (W-O) and no unreacted chloride ligands (W-Cl). The second coordination sphere should have as many nonbonded silicon atoms (W $\cdots$ Si) as the first shell of singly bound oxygen atoms. A structural model, based on bond lengths[20,177-181] and geometries[144,155,161,173] found in the literature, was constructed using ChemDraw (Figure 105). Theoretical phase and amplitude factors were generated using FEFF6[168], which is incorporated in the IFEFFIT software suite. A model containing only the single scattering paths (W=O, W-O, W $\cdots$ Si) generated by FEFF6 was used to fit the EXAFS data and thereby obtain quantitative structural parameters.

In the modeling scheme for EXAFS, the coordination number, CN, is directly correlated to the amplitude reduction factor, S_0^2 . Therefore, CNs and S_0^2 should not be determined independent of one another. A more recent version of the FEFF code, FEFF8[115], may be used to independently estimate the value of S_0^2 , which was then fixed for the rest of the refinement.[113] The value of S_0^2 obtained from FEFF8 was 0.92. The CN values based on the results of gravimetric analysis and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the isolated

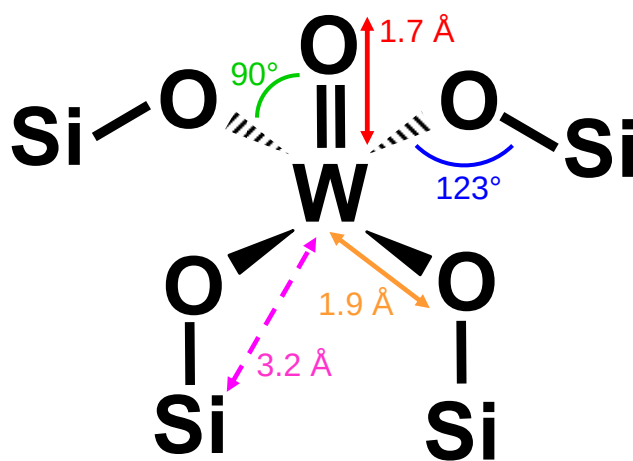


Figure 105: Structural model used for EXAFS data analysis of the isolated embedded tungsten oxo centers.
The model contains a tungsten center with one terminal doubly bound oxygen (W=O), four singly bound oxygen atoms (W-O), and four nonbonded silicon atoms (W...Si).

embedded tungsten oxo centers in a silicate building block matrix is presented in Figure 106 with the EXAFS data range used to fit the model is boxed (3.4 to 14.0 Å⁻¹). In R-space, the fit range is from 1.0 to 4.0 Å and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 104 and Figure 107 respectively. Table 6 summarizes the refined values of the structural parameters. The value of $\sigma^2(\text{W=O})$ is slightly negative, which generally suggests the value of $\sigma^2(\text{W=O})$ is small or the model is incorrect. To test which scenario is correct the value of $\sigma^2(\text{W=O})$ was fixed to 0.0015 Å² and all of the other structural parameters were allowed to refine. The other structural parameters did not fluctuate significantly, so it may be concluded the overall model is correct but that the value of $\sigma^2(\text{W=O})$ is small but cannot be determined quantitatively from the data. Table 7 contains the refined values of the structural parameters. As shown in Table 8 the refined bond lengths are in agreement with values found in the literature.[20,177-181] At this point, the structural parameters were fixed to the refined values and the value of the CNs were allowed to vary. Table 7 contains the refined values of the CNs, which are within 10% of the values determined by gravimetric analysis.

The tungsten oxo centers in these oligomers are expected to be strong Lewis acidic sites and there should be no other acidic sites present in the material. Therefore, they should readily bind Lewis bases such as pyridine. Infrared spectroscopy may be used to determine the acidity of the tungsten oxo centers when the silicate building block material is exposed to pyridine.[151,170] Three features were observed in the IR spectrum (Figure 108) after exposure to pyridine (1448 cm⁻¹, 1489 cm⁻¹, and 1603 cm⁻¹). These features are characteristic of Lewis acidic tungsten centers in silica.[170] As expected features characteristic of Bronsted acidic tungsten centers were not observed (1488 cm⁻¹, 1545 cm⁻¹, 1635 cm⁻¹).[151] The conclusion that a single type of Lewis acidic tungsten oxo center is present in the material is supported by the pyridine binding data.

The combination of the techniques described above provides a reasonably clear picture of the products in the reaction of a limiting amount of WOCl₄ and the silicate building block Si₈O₁₂(OSnMe₃)₈. Small oligomers are formed that contain isolated embedded tungsten oxo centers bound through oxygen atoms to four separate silicate building blocks (Figure 109). Gravimetric analysis provided evidence that all of the chloride ligands on the tungsten oxo

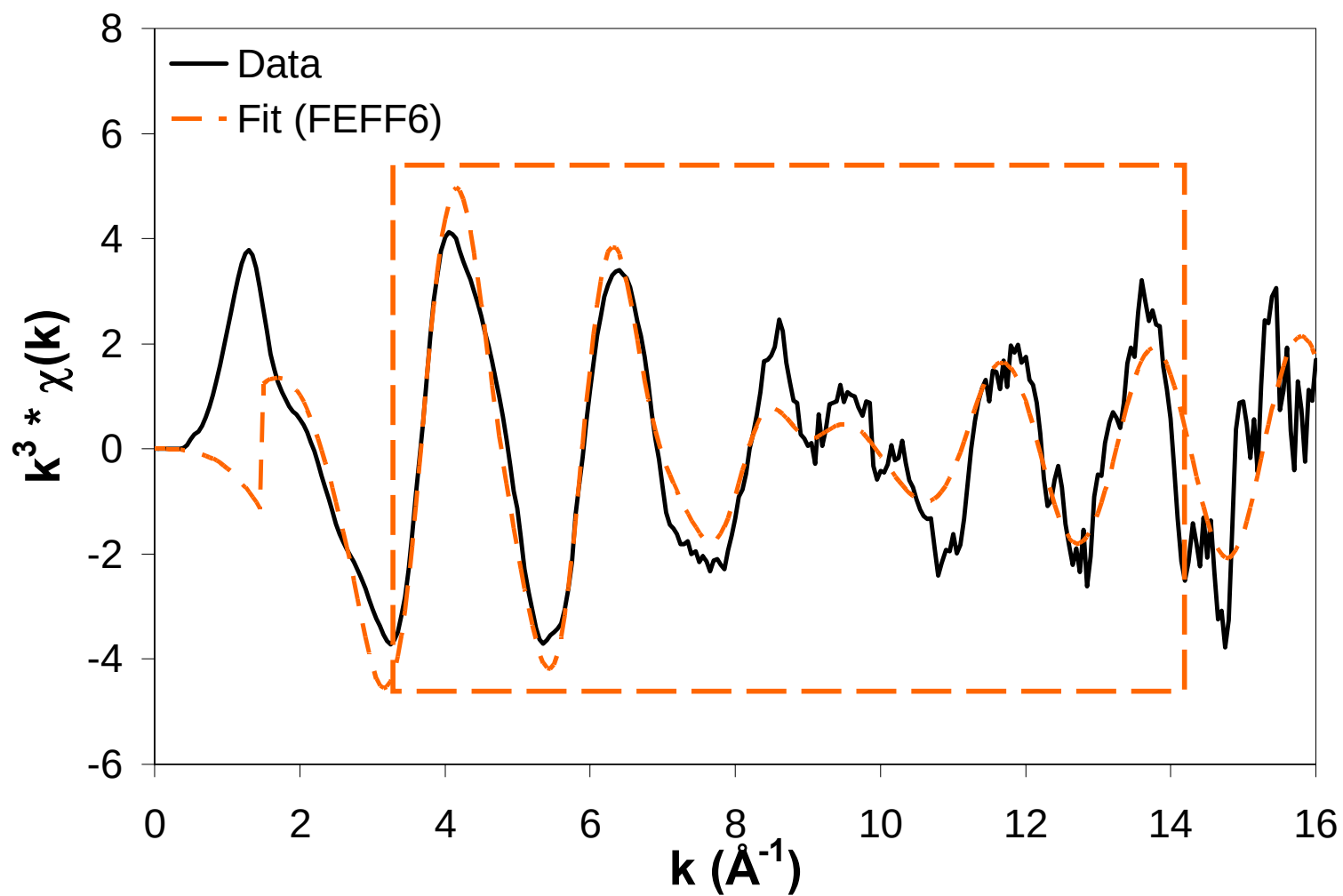


Figure 106: EXAFS k-space plot following first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

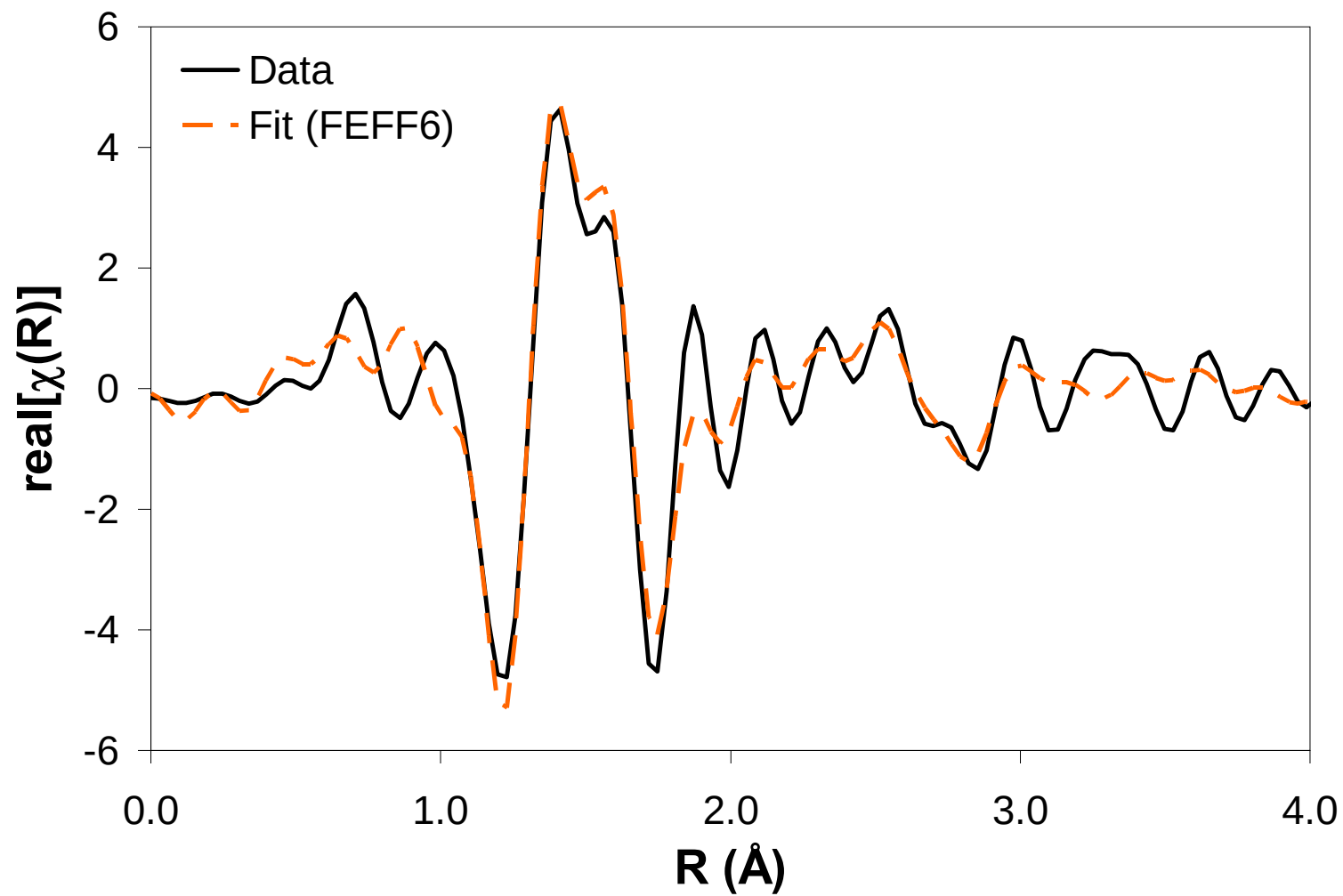


Figure 107: EXAFS real R-space plot following first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

Table 6: EXAFS fit values following 1st dose (WOCl₄ and Si₈O₁₂(OSnMe₃)₈)

Path	CN	R (Å)	σ^2 (x 10 ⁻³ Å ²)
W=O	1 (set)	1.715	-0.26
W-O	4 (set)	1.890	7.56
W...Si	4 (set)	3.222	19.05

$S_0^2 = 0.92$ (set), $E_0(\text{W=O, W-O, W}\cdots\text{Si}) = 8.338 \pm 1.995$ eV

number of independent points = 20.0, number of variables = 7

$\chi^2 = 1425$, reduced $\chi^2 = 110$, R factor = 0.083

FT k region = 3.377 – 13.973 Å⁻¹, Fit range = 1.0 – 4.0 Å

Table 7: EXAFS fit values for embedded and surface tungsten oxo centers

Embedded WOCl₄ 1st dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.715	1.890	---	3.222
σ^2 (Å ²)	1.50 x 10 ⁻³ (set)	9.09 x 10 ⁻³	---	19.00 x 10 ⁻³
E ₀ (eV)	8.1 ± 2.7	8.1 ± 2.7	---	8.1 ± 2.7
CN	0.95 ± 0.09	3.66 ± 0.27	---	3.66 ± 0.27
S ₀ ² = 0.92 (set), N _{idp} = 20.0, N _{var} = 6, χ^2 = 1999, reduced χ^2 = 143, R-factor = 0.117, FT k region = 3.377 – 13.973 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Embedded WOCl₄ 2nd dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.690	1.898	---	3.203
σ^2 (Å ²)	2.02 x 10 ⁻³	3.29 x 10 ⁻³	---	12.78 x 10 ⁻³
E ₀ (eV)	9.3 ± 1.9	9.3 ± 1.9	---	6.6 ± 5.4
CN	0.93 ± 0.14	3.85 ± 0.21	---	3.85 ± 0.21
S ₀ ² = 0.92 (set), N _{idp} = 19.4, N _{var} = 8, χ^2 = 559, reduced χ^2 = 49, R-factor = 0.049, FT k region = 3.348 – 13.623 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Surface WOCl₄				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.665	1.851	2.327	3.189
σ^2 (Å ²)	0.66 x 10 ⁻³	5.56 x 10 ⁻³	2.16 x 10 ⁻³	17.95 x 10 ⁻³
E ₀ (eV)	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8
CN	1 (set)	3 (set)	1 (set)	3 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.7, N _{var} = 9, χ^2 = 383, reduced χ^2 = 40, R-factor = 0.055, FT k region = 3.570 – 13.491 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

Table 8: Comparison of EXAFS refined bond lengths to literature values

	W=O (Å)	W-O (Å)	W-Cl (Å)	W...Si (Å)
WOCl ₄ 1 st dose (this work)	1.715	1.890	---	3.222
WOCl ₄ 2 nd dose (this work)	1.690	1.898	---	3.203
WCl ₆ 1 st dose (this work)	1.713	1.876	---	3.205
WCl ₆ 2 nd dose (this work)	1.691	1.890	---	3.207
Surface WOCl ₄ (this work)	1.665	1.851	2.327	3.189
Surface WCl ₆ (this work)	1.661	1.823	2.317	3.156
Ref [177]	1.69	1.83		
Ref [178]		1.91		2.92 (W-O-Ti)
Ref [179]	1.70		2.32	
Ref [180]	1.73	1.93		
Ref [159]		1.94		2.96
Ref [182]	1.68	1.90		3.32
Ref [20]				3.13-3.34 (V-O-Si)
Ref [181]			2.39	
Ref [183]			2.26	

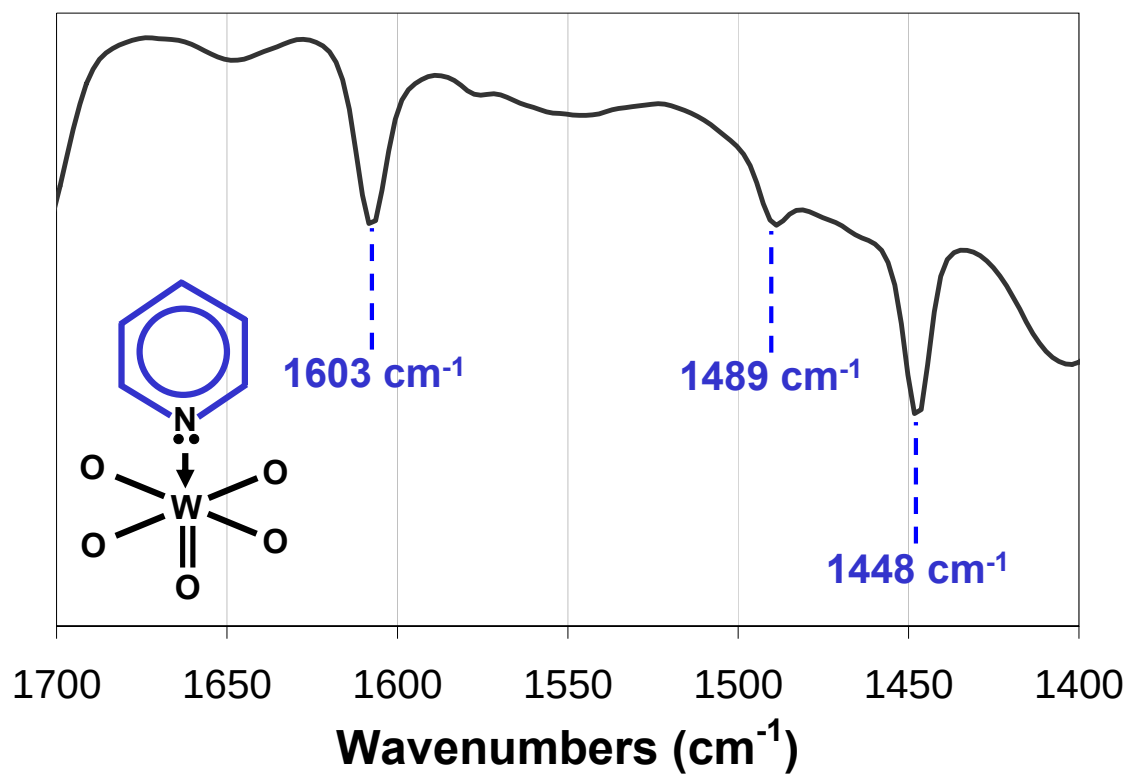


Figure 108: IR spectrum of pyridine bond to Lewis acidic tungsten centers synthesized after first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

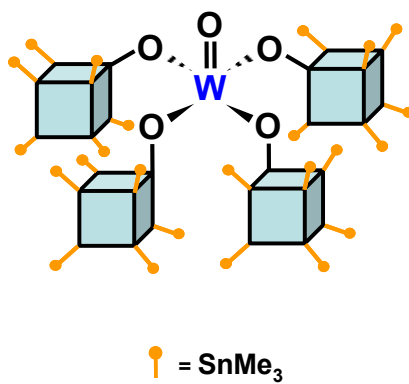


Figure 109: Proposed representation of the catalyst ensemble following first cross-linking reaction, WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

centers reacted with the trimethyltin functional groups on the silicate building block (formation of W-O, control of the ligands). IR and SSNMR spectra provided evidence of the formation of linkages between the tungsten oxo centers and the silicate building blocks (formation of W-O-Si, control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the tungsten oxo centers remained unchanged during the cross-linking reaction (preservation of tungsten(VI) centers, control of the metal cation). Refinement of a structural model consisting of one tungsten oxo group and four W-O-Si linkages strongly supports the claim that the local environment around each tungsten oxo center is identical. The building block approach and sequential dosing strategy provides control of all the necessary components of the embedded tungsten oxo catalyst ensemble. In the next step of the synthesis these oligomers will be linked together to form a robust, high surface area silicate support around the embedded tungsten oxo catalyst ensembles. The local environment of the ensembles should remain unchanged during the growth of the robust, high surface area silicate support.

Second Cross-Linking Reaction: Linking Tungsten Oxo Oligomers Together

The oligomers synthesized from WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ are further cross linked with SiCl_4 via the same metathesis reaction where the silyl chloride groups (from SiCl_4) replace unreacted Me_3Sn groups to form new siloxane bonds (Si-O-Si) and Me_3SnCl (Figure 110). The volatiles of the reaction were analyzed and Me_3SnCl was the only byproduct observed using ^1H NMR. Gravimetric data are consistent with two chloride ligands of SiCl_4 reacting with the Me_3Sn groups (1.9 ± 0.2 equivalents of Me_3SnCl). Therefore the oligomers are linked together by silicon centers that on average contain two unreacted chloride ligands and two linkages to tungsten oxo oligomers ($\text{Cl}_2\text{Si}(\text{OSi}_{\text{W-oligomer}})_2$).

The ratio of W atoms to Sn atoms in the silicate building block matrix was determined before this second cross-linking to be 1 W atom for every 24.8 Sn atoms. 2.39 molar equivalents of SiCl_4 to silicate building block were used for the second cross-linking reaction. According to gravimetric analysis, every Si atom reacted with approximately 1.9 Me_3Sn groups resulting in the loss of 4.54 Sn atoms per silicate building block. From these data the W : Sn ratio is calculated to be 1 : 8.6 following the second cross-linking reaction. The actual concentration of tungsten (4.7 ± 0.03 wt%) and tin (25.6 ± 0.5 wt%) in the sample at this stage of the synthesis

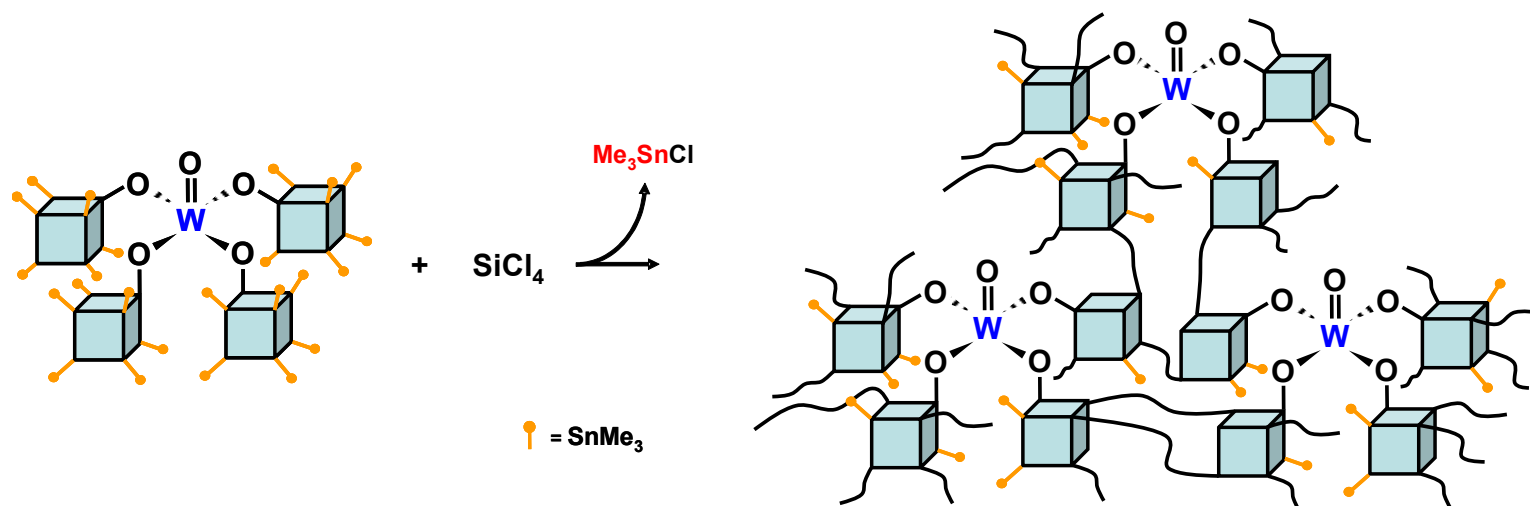


Figure 110: Second Cross-Linking Reaction, Tungsten oxo oligomers and SiCl_4 .

was determined using ICP-OES. ICP-OES data independently gave a value for the ratio of 1.0 W : 8.4 Sn in the matrix. Therefore both the connectivity of the silicon centers determined by gravimetric analysis (1.9 ± 0.2) and the connectivity determined by ICP-OES (1.8 ± 0.2) are consistent with one another.

Infrared spectroscopy was used to verify the W-O-Si linkage remained intact, throughout the second cross-linking reaction. Both the band at 1080 cm^{-1} and a shoulder at approximately 950 cm^{-1} were observed in the IR spectrum of the material at this stage in the synthesis (Figure 111). IR spectral data are consistent with the continued presence of W-O-Si groups in the matrix thus the W-O-Si linkage was not disrupted during the cross-linking reaction with SiCl_4 .

The material was again exposed to pyridine to evaluate what types of isolated acidic centers were present. Three features were observed in the IR spectrum (Figure 112) after exposure to pyridine (1450 cm^{-1} , 1491 cm^{-1} , and 1614 cm^{-1}) which are characteristic of Lewis acidic tungsten centers in silica.[170] No evidence for Bronsted sties ($\sim 1545\text{ cm}^{-1}$) or silanol groups ($\sim 1590\text{ cm}^{-1}$) is observed.

Raman spectroscopy confirmed the absence of tungsten oxide domains and W-O-W linkages in the material, which supports the conclusion that the tungsten oxo centers in the matrix are spatially isolated.[36,160,172-174] A weak feature at 1005 cm^{-1} was observed (Figure 113), which suggests the tungsten oxo group remains in the matrix.[155,161,173,184-186] The movement of the Raman feature from 982 cm^{-1} to 1004 cm^{-1} is not unexpected. As previously mentioned, the feature at 982 cm^{-1} is characteristic of molecular species containing tungsten oxo groups.[144,172] As these molecular species are linked together, the tungsten centers remain unchanged and a rigid silicate building block matrix is formed resulting in the feature at 1004 cm^{-1} , which is characteristic of isolated tungsten oxo groups in similar silicate building block matrices.[155,161,173,184-186]

Figure 114 shows the ^{29}Si SSNMR spectrum for the isolated embedded tungsten oxo centers. Following the second cross-linking reaction six main features are observed. The signals between -22 and -100 ppm in the spectrum are characteristic of the different silyl chlorides generated during the second cross-linking reaction (i.e. $(\equiv\text{SiO})_{4-x}\text{SiCl}_x$).[95] The signals between -100 and -110 ppm are assigned to the silicon corners on the building block which are connected

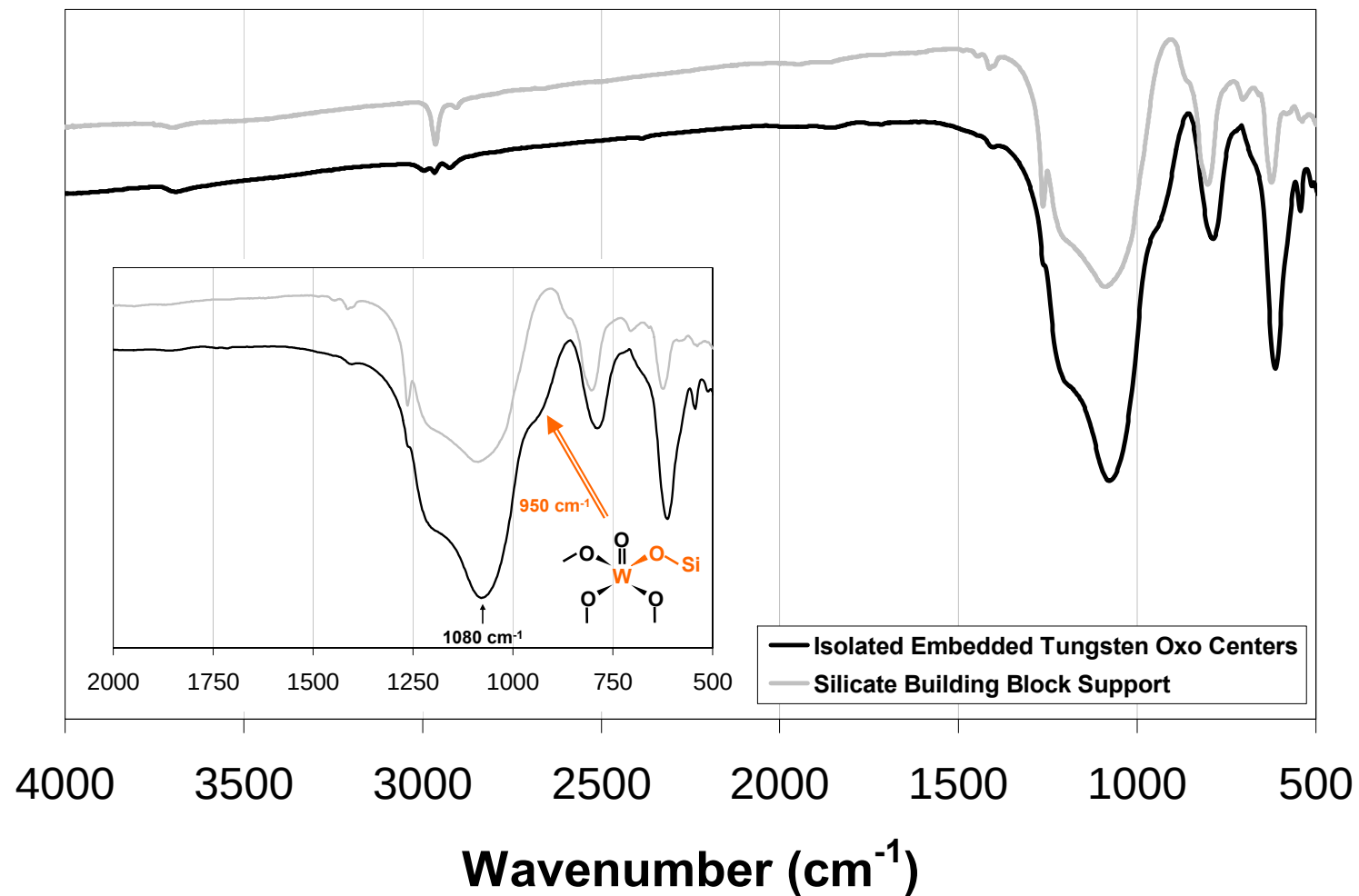


Figure 111: IR spectra (500-4000 cm⁻¹) of a tungsten-free silicate building block support and the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl₄. The inset contains the expand IR spectra (500-2000 cm⁻¹) which illustrates the W-O-Si shoulder (950 cm⁻¹).

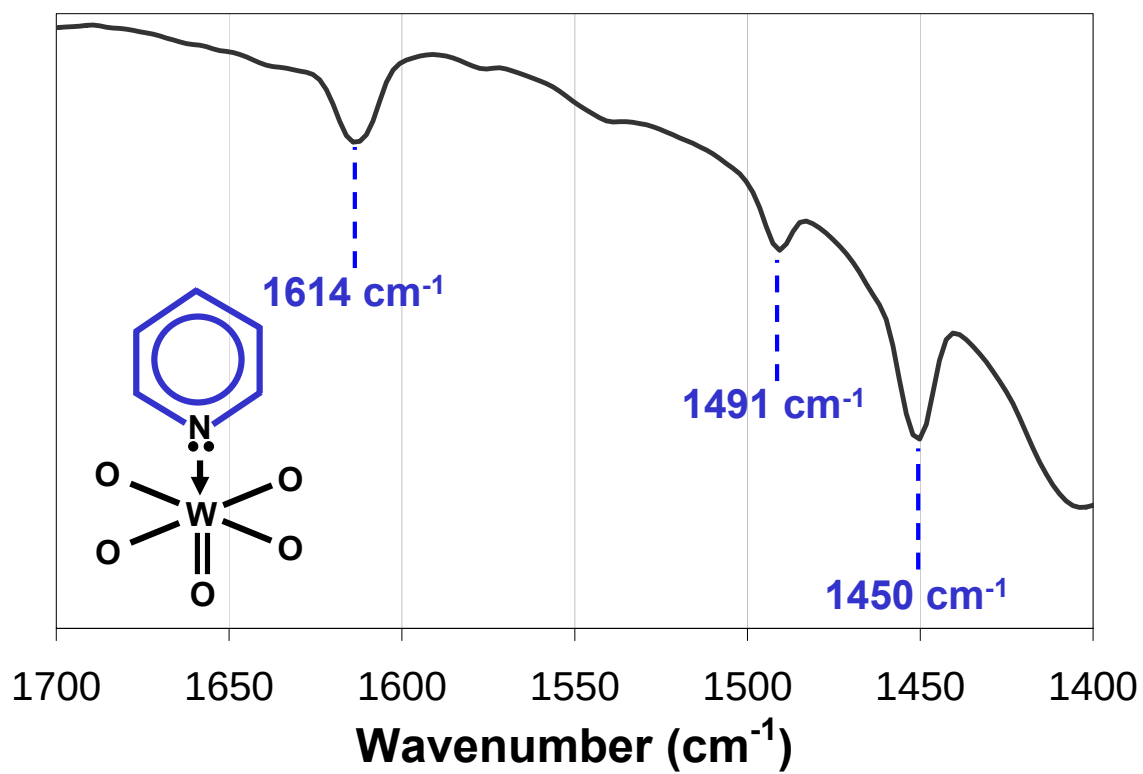


Figure 112: IR spectrum of pyridine bond to Lewis acidic tungsten centers present in the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

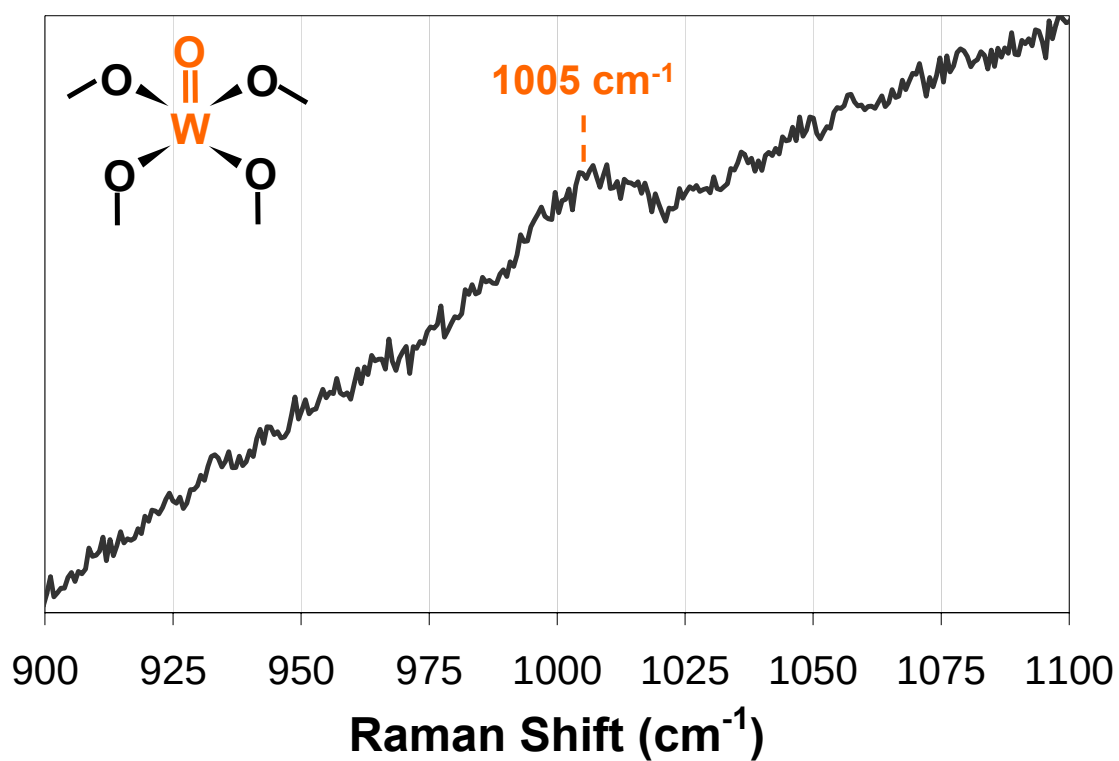


Figure 113: Raman spectrum following the second cross-linking reaction, tungsten oxo oligomers and SiCl₄.

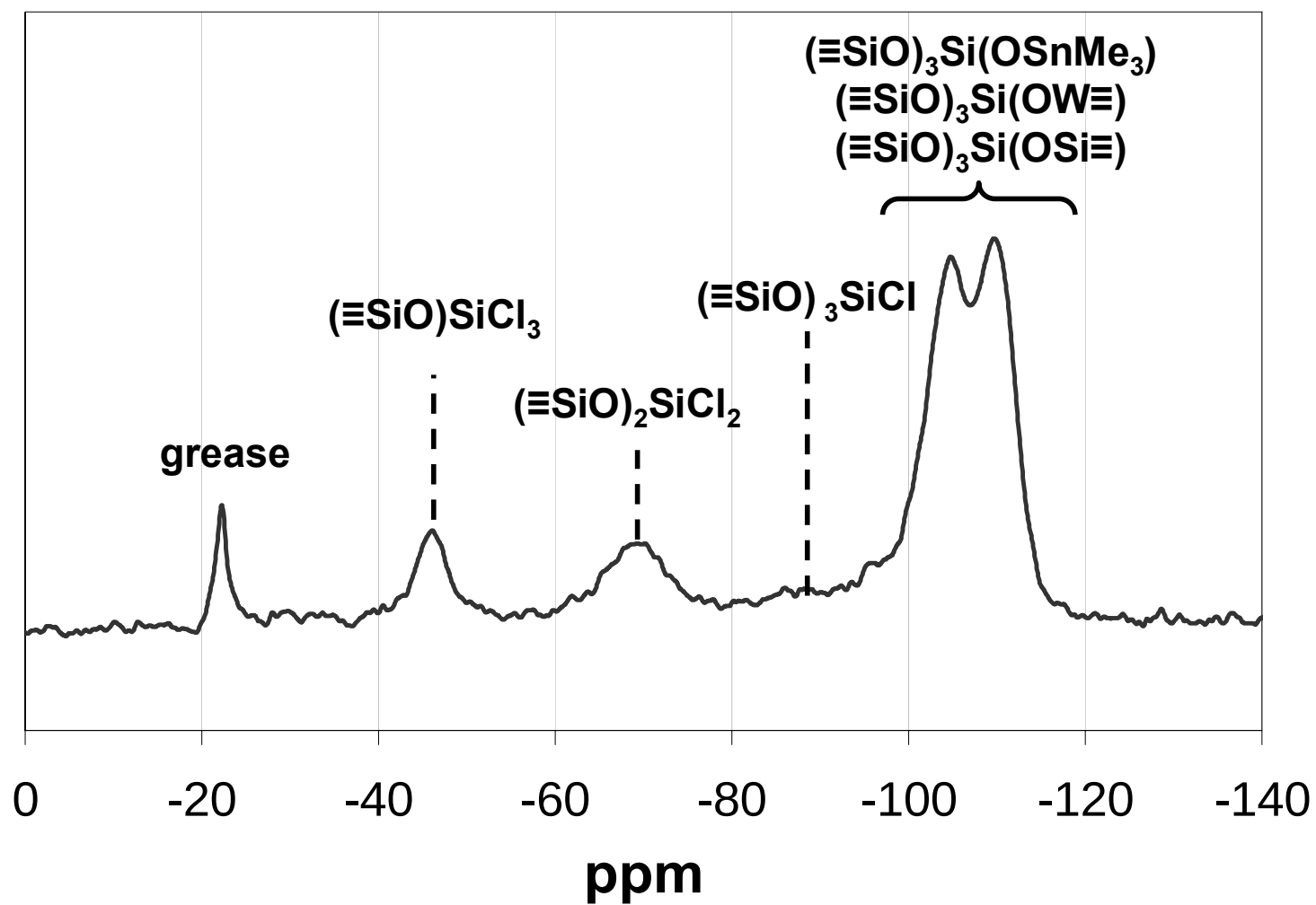


Figure 114: ^{29}Si SSNMR spectrum (-140 to 0 ppm) following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

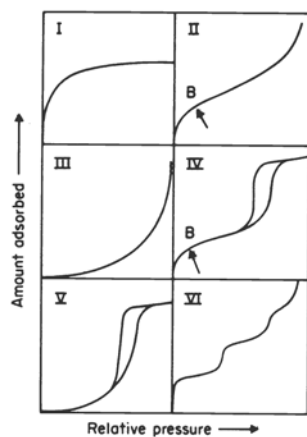
to unreacted Me_3Sn groups ($(\equiv\text{SiO})_3\text{Si}(\text{OSnMe}_3)$), connected to the tungsten oxo centers ($(\equiv\text{SiO})_3\text{Si}(\text{OW}\equiv)$), and connected to the silicon centers ($(\equiv\text{SiO})_3\text{Si}(\text{OSi}\equiv)$). The presence of a signal at -110 ppm is assigned to $\text{Si}(\text{OSi}\equiv)_4$ indicates the silicate building blocks have been linked together via the silicon atoms inserted during the second cross-linking reaction.

Nitrogen adsorption/desorption experiments were conducted to determine the BET surface area and total pore volume. Qualitative analysis of the nitrogen adsorption/desorption isotherm (Type I) and t-plot suggests this material is a primarily microporous material;[136] however, a hysteresis (Type H4) is observed in the adsorption/desorption isotherm indicating the presence of some mesopores (Figure 115 & Figure 116). The t-plot method was used to confirm the material is primarily microporous with respect to pore volume (88%) and surface area (96%). The BET surface area of this material is $400 \text{ m}^2/\text{g}$ (Figure 117) and the total pore volume is $0.250 \text{ cm}^3/\text{g}$. The BJH plot (Figure 118) does not display a significant maximum, which suggests the material has micropores and/or some small mesopores. Thus a high surface area, primarily microporous, silicate building block matrix was grown around the isolated embedded tungsten oxo centers.

Figure 119 shows the XANES spectrum at the L_{III} edge of the material at this stage in the synthesis. The edge position of the isolated embedded tungsten oxo centers is consistent with a +6 oxidation state of the tungsten centers. The ratio ($I_{\text{WL}}/I_{\Delta\mu(\text{E})}$) for the isolated tungsten oxo centers (3.21) estimates the oxidation state of the tungsten oxo centers is +5, which is reasonably close to the expected value of +6 considering the empirical approach that was used (Figure 120). The width of the white line for the isolated embedded tungsten oxo centers (width = 6.9 eV) provides evidence that the coordination geometry around the tungsten oxo centers is not octahedral and suggests the coordination geometry is distorted octahedral (width = 7.4 eV) instead of tetrahedral (width = 4.9 eV) (Figure 121).

Figure 122 shows the XANES spectrum at the L_1 edge of the material at this stage in the synthesis. The edge position of the isolated embedded tungsten oxo centers supports the claim the oxidation state of the tungsten centers is +6. The presence of a pre-edge feature is strong evidence that the coordination geometry around the tungsten oxo center is not octahedral and

Standard Isotherms



Standard Hysteresis Loops

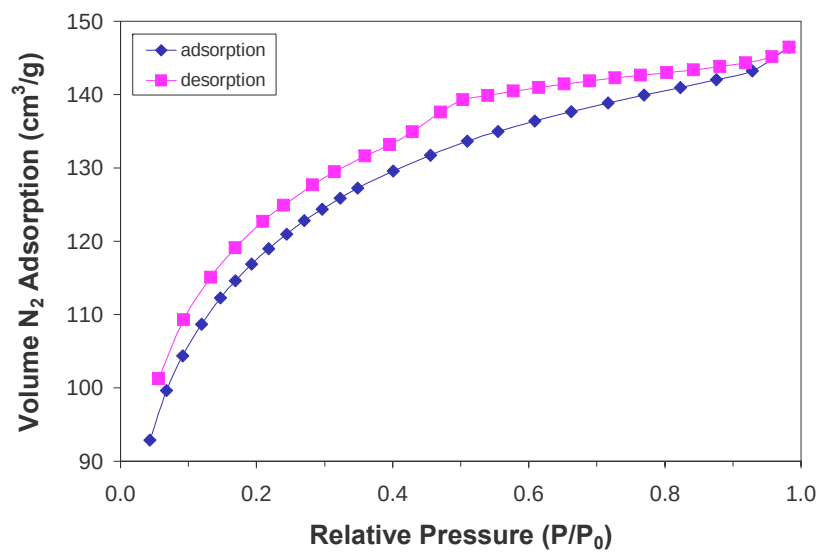
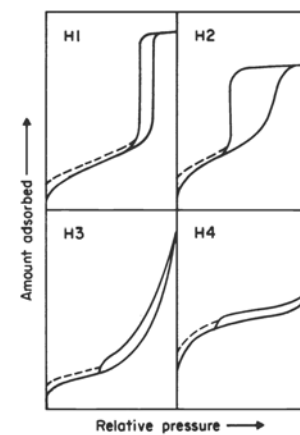


Figure 115: Nitrogen isotherm for the material following the second cross-linking reaction, tungsten oxo oligomers and $SiCl_4$. Standard isotherms and hysteresis loops were obtained from the literature.[131]

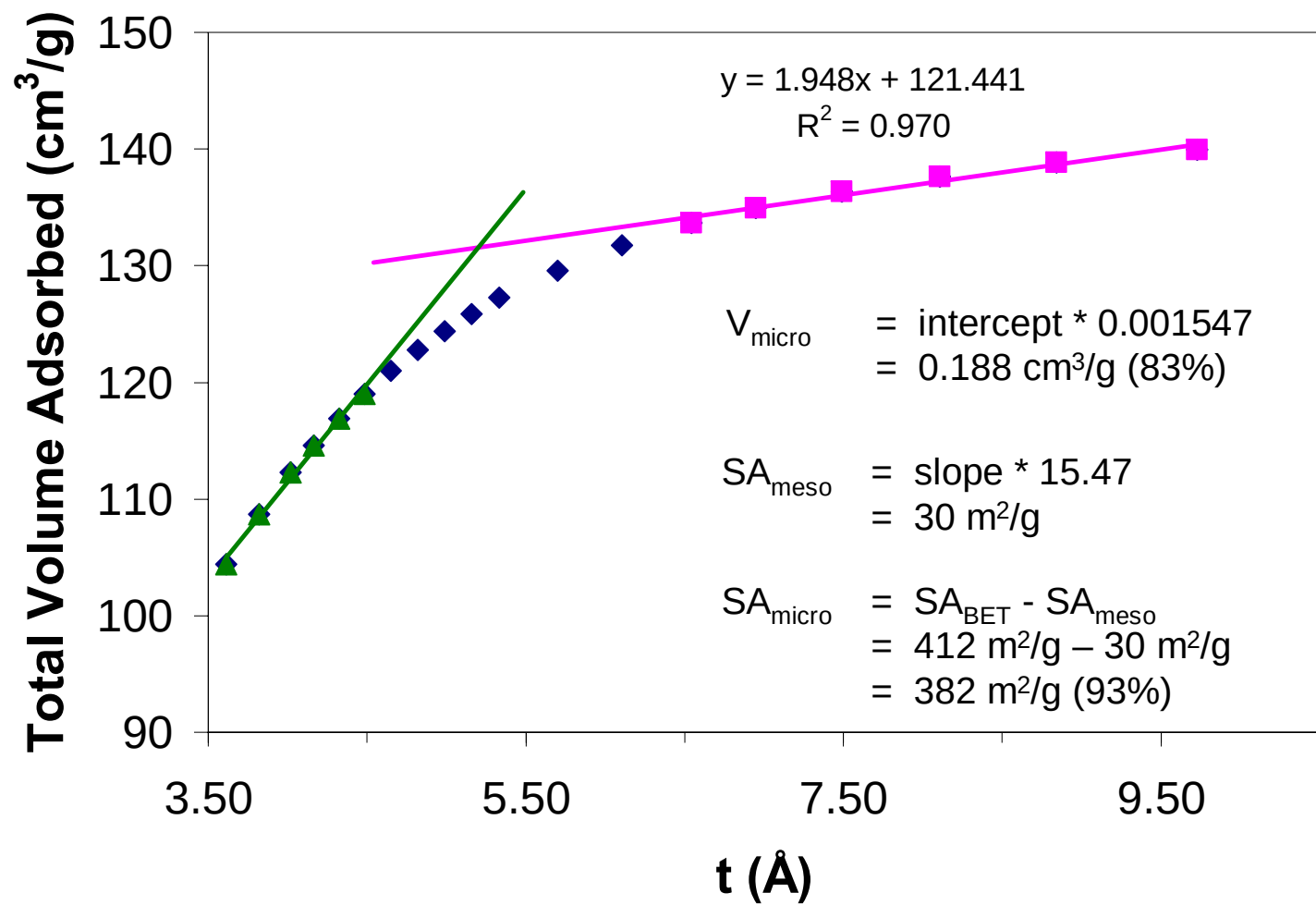


Figure 116: t-plot for the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

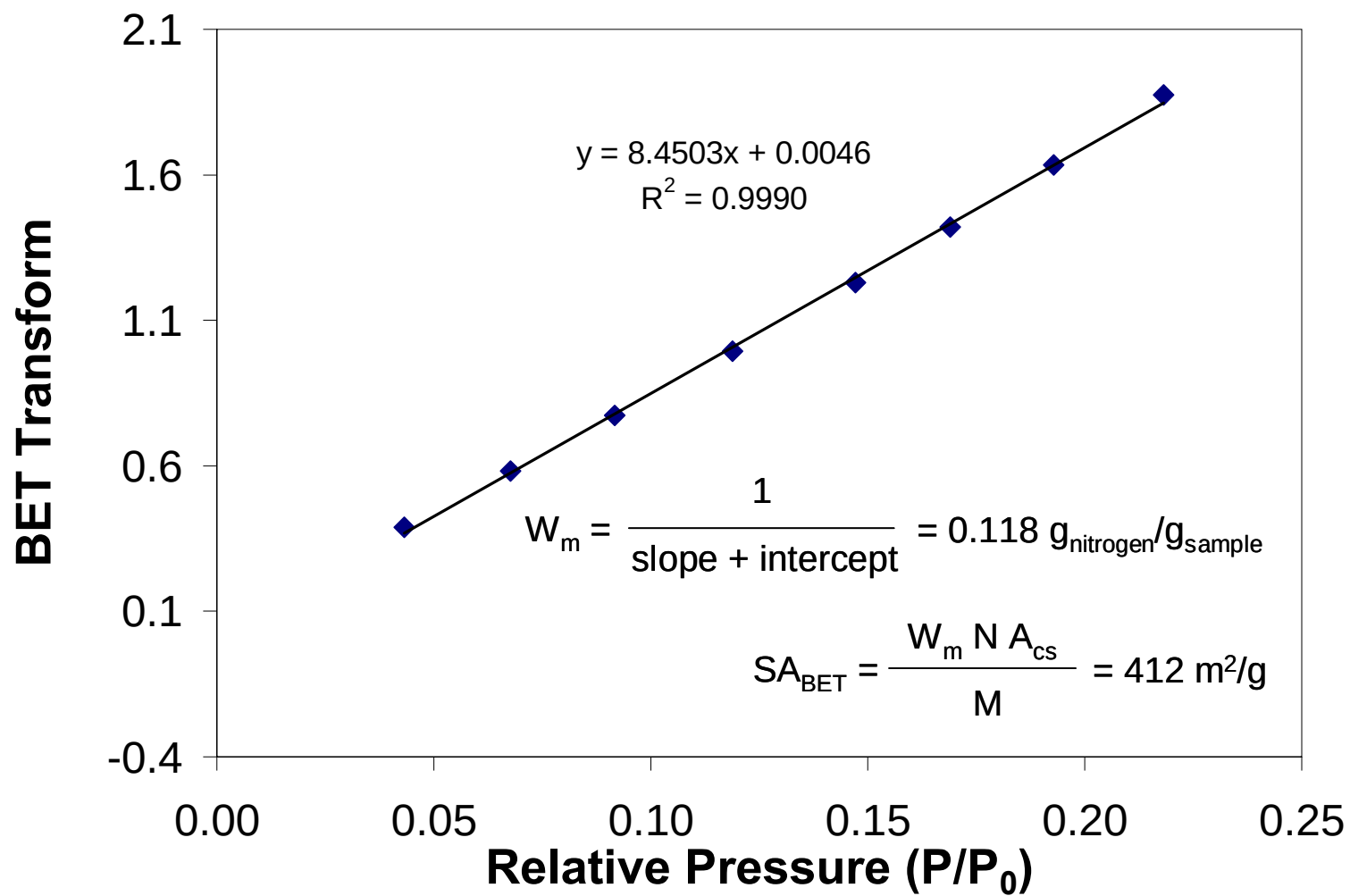


Figure 117: BET plot for the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

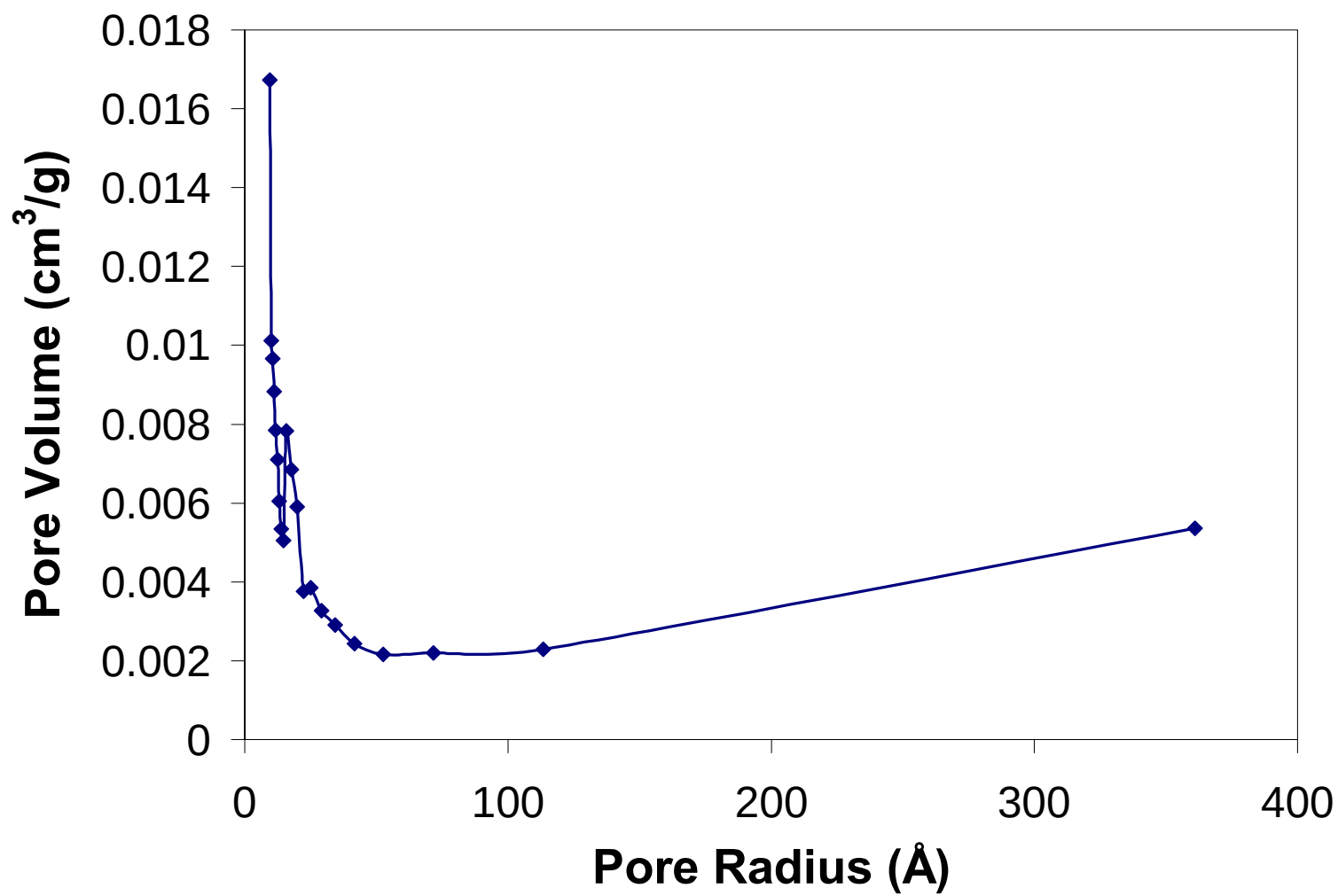


Figure 118: BJH pore size distribution plot for the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl₄.

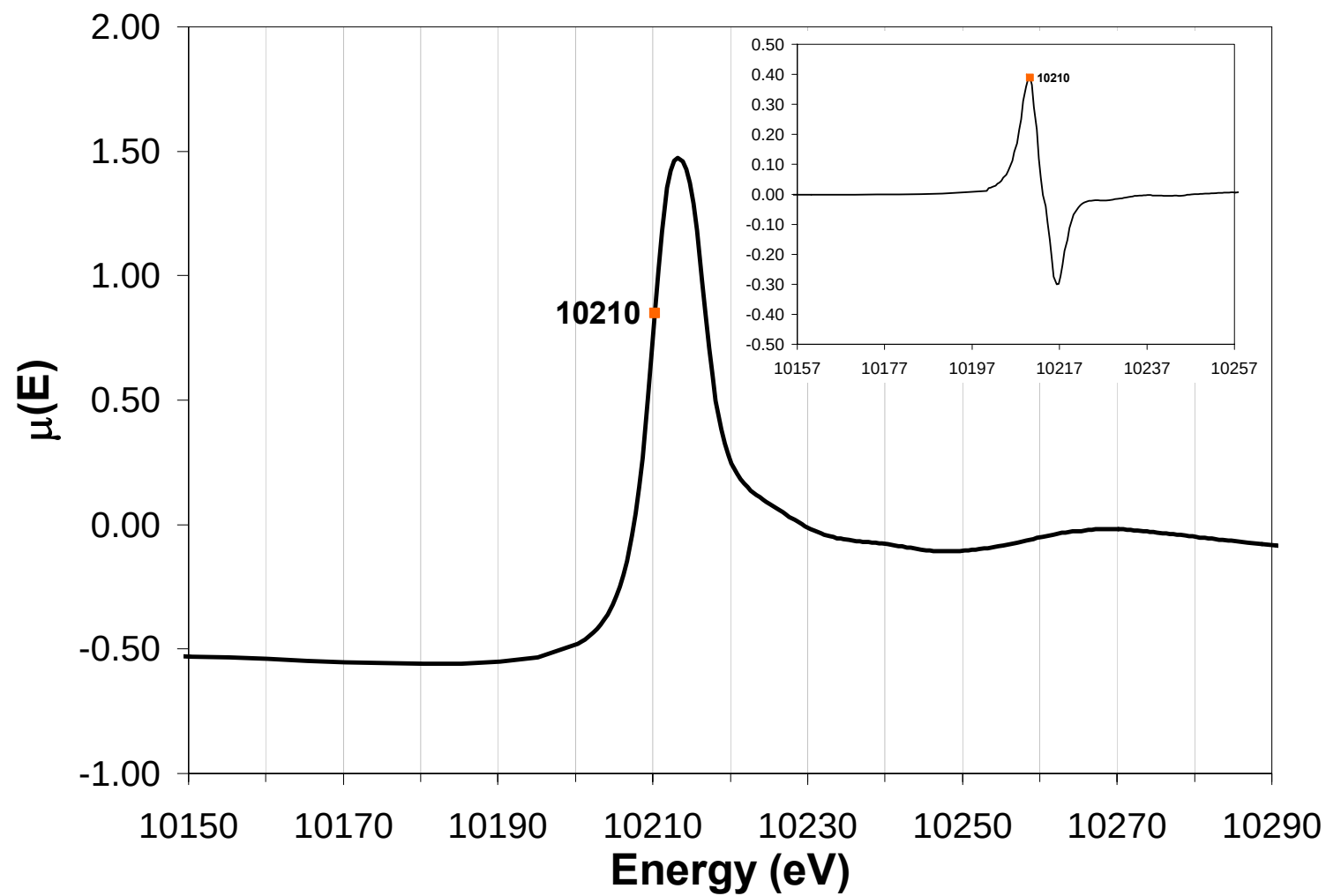


Figure 119: XANES spectrum (W L_{III} edge) following the second cross-linking reaction, tungsten oxo oligomers and SiCl₄. The inset contains the derivative XANES spectrum with the position of the absorption edge (orange square) labeled.

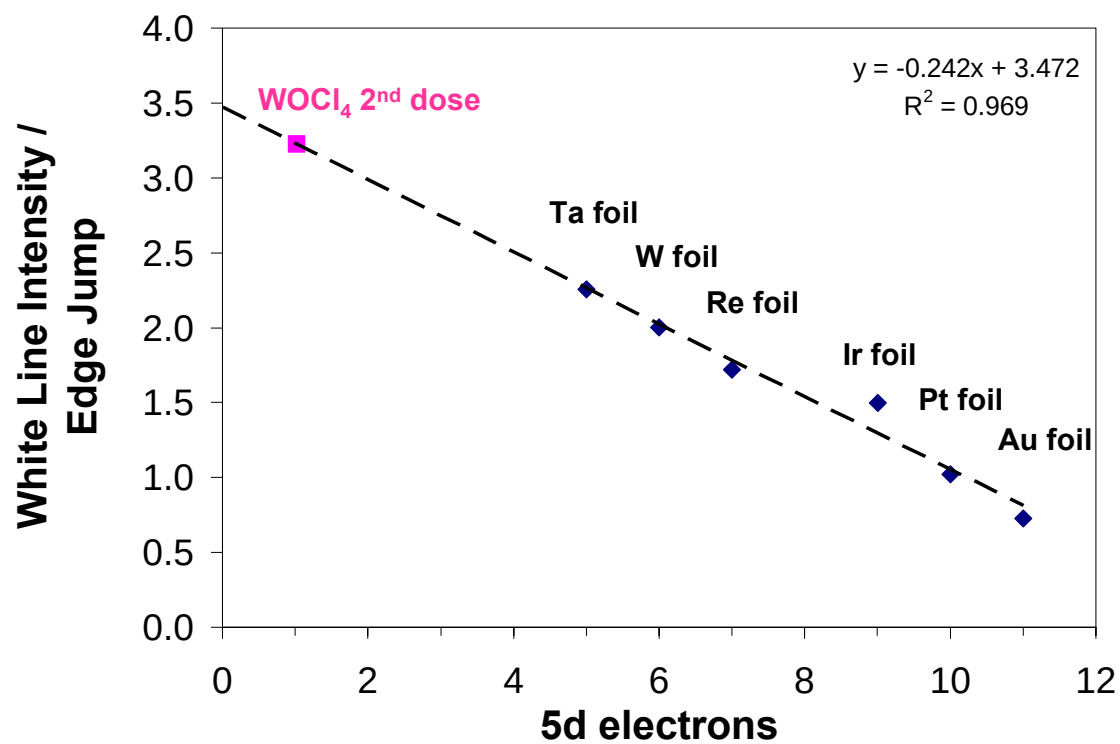


Figure 120: Relation between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the second cross-linking reaction, tungsten oxo oligomers and SiCl₄.

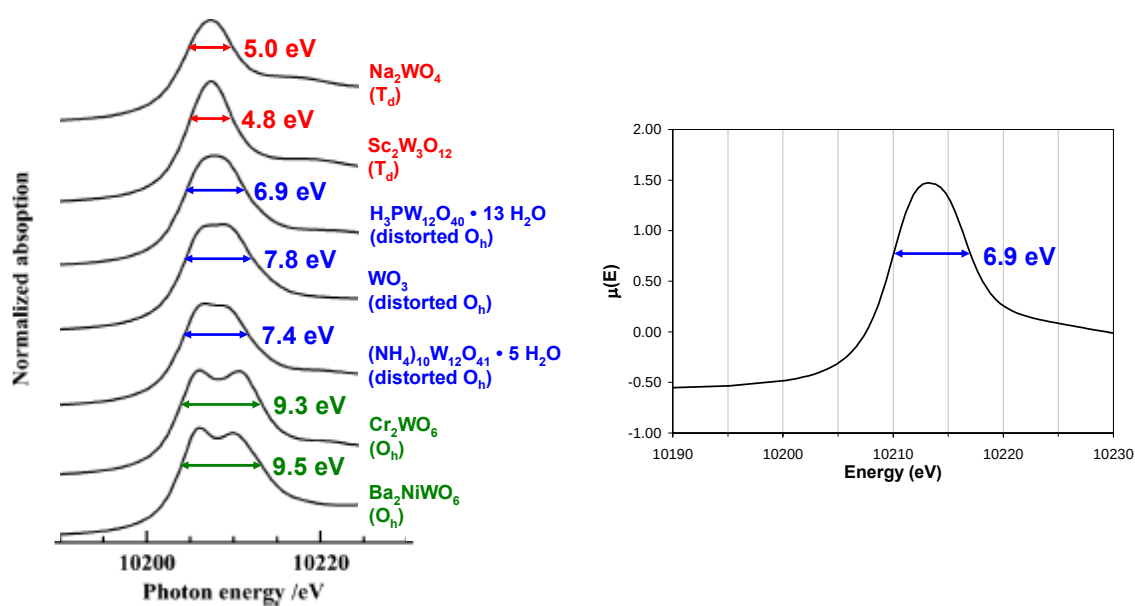


Figure 121: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 (right).

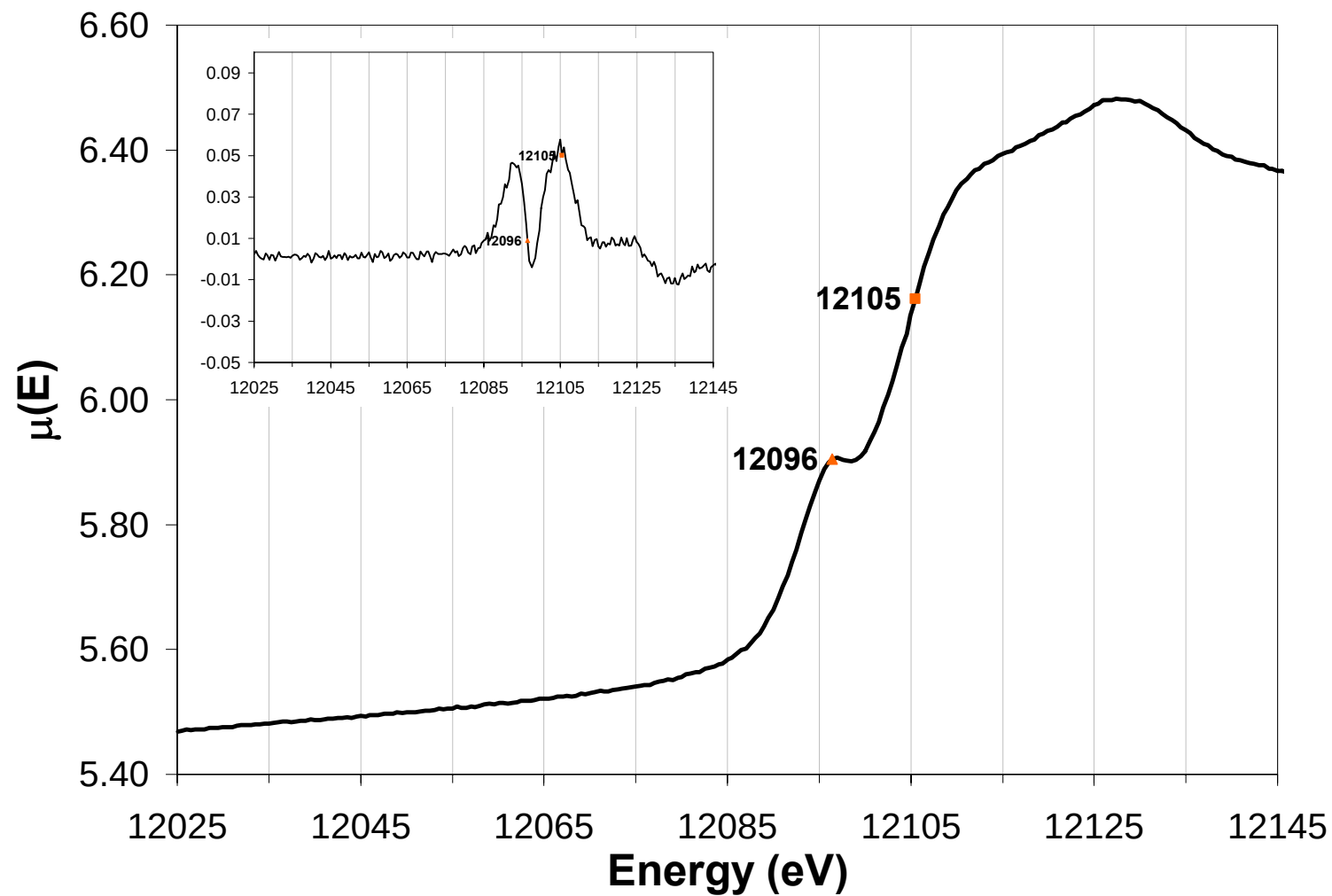


Figure 122: XANES spectrum (W L₁ edge) following the second dosing reaction, tungsten oxo oligomers and SiCl₄. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

suggests the coordination geometry is either tetrahedral or distorted octahedral. The intensity of the pre-edge for the isolated embedded tungsten oxo centers is approximately 35% and consistent with a distorted octahedral coordination geometry.

Finally, EXAFS data were used to obtain structural information on the connectivity and geometry of the tungsten oxo centers in the silicate building block matrix. The number of shells can be qualitatively determined by looking at the magnitude R-space plot. Figure 123 shows three features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot. It is important to note that there is no evidence of W-Cl bonds in Figure 123. The same structural model (Figure 105), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.92), and refinement procedure were used to model the data. The EXAFS signal ($\chi(k) * k^3$) for isolated tungsten oxo centers in a silicate building block matrix is presented in Figure 124 with the FT data range boxed (3.3 to 13.6 Å⁻¹). The fit range is from 1.0 to 4.0 Å and the magnitude and real part of the FT of the data and FEFF model are presented in Figure 123 and Figure 125 respectively. Table 7 summarizes the refined values of the structural parameters. As shown in Table 8 the refined bond lengths are in agreement with values determined for the tungsten oxo centers following the first cross-linking reaction and found in the literature.[20,177-181] Fixing bond distances and atom separations and allowing coordination numbers to refine yielded the results summarized in Table 7. The refined values of the CNs are in agreement with the refined values following the first cross-linking reaction and within 10% of the values determined by gravimetric analysis.

The combination of the techniques described above provides a reasonably clear picture of the isolated embedded tungsten oxo ensembles that are present in the robust, high surface area silicate building block support. The silicate building block support was generated around the tungsten oxo ensembles which were unchanged during the final formation of the support. IR and SSNMR spectra provided evidence that the linkages between the tungsten oxo centers and the silicate building blocks remained unchanged (preservation of W-O-Si, control of the ligands and the metal-to-support linkages). XAS data confirmed that the oxidation state of the tungsten oxo centers remained unchanged during the generation of the high surface area silicate support around the tungsten oxo centers (preservation of tungsten(VI) centers, control of the metal

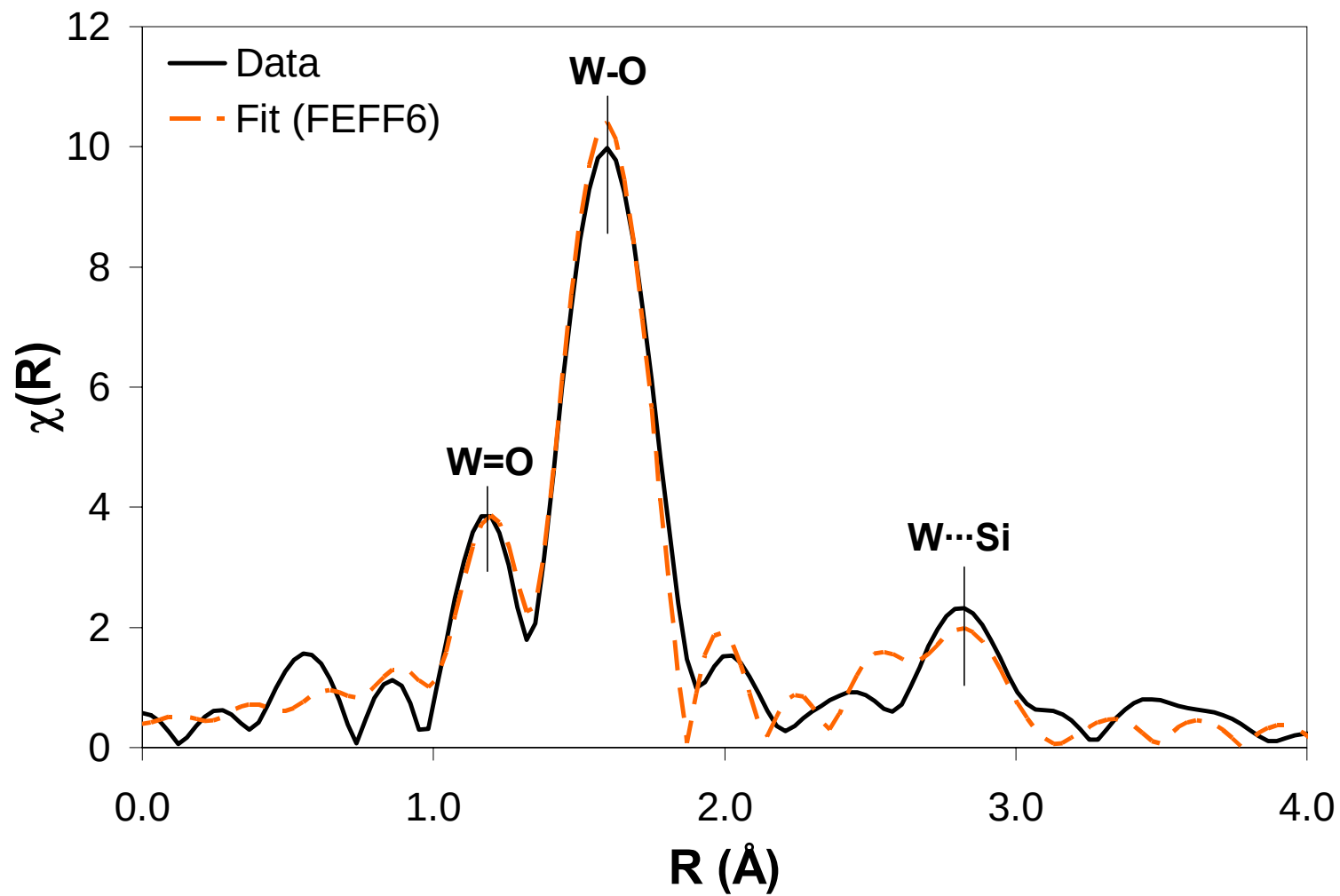


Figure 123: EXAFS R-space plot following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

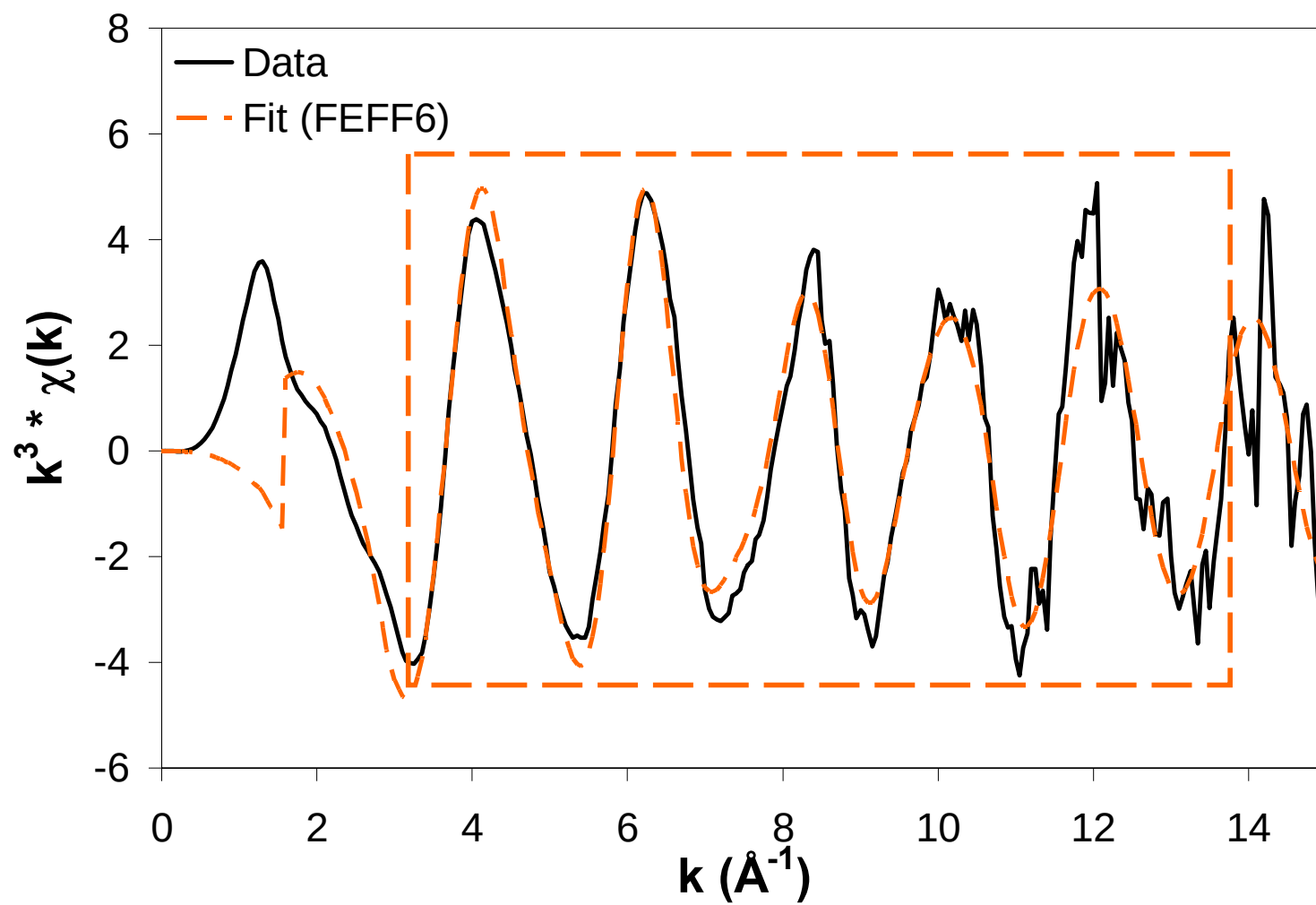


Figure 124: EXAFS k-space plot following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

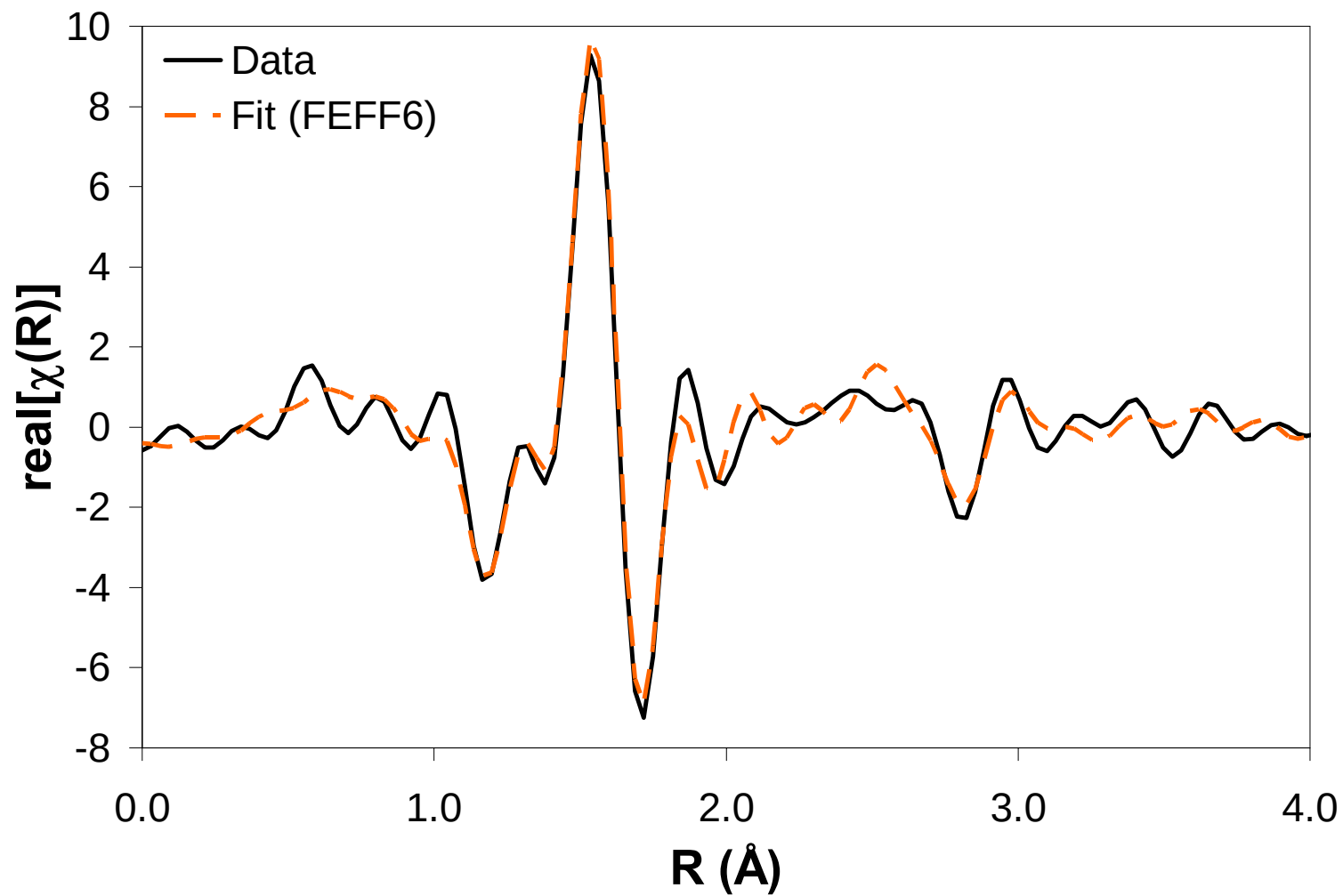


Figure 125: EXAFS real R-space plot following the second cross-linking reaction, tungsten oxo oligomers and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

cation). A structural model based on EXAFS data strongly supports a picture in which the local environment around each tungsten oxo center is identical and unchanged during each stage of the synthesis. The building block approach and sequential dosing strategy provides control of all the necessary components of the embedded tungsten oxo catalyst ensemble which results in the targeted synthesis of a single type of embedded tungsten oxo ensemble (Figure 126).

Removal of Residual Trimethyltin Groups

Following the second cross-linking reaction a significant amount of unreacted Me_3Sn groups remain in the silicate building block matrix. In fact the silicate building block matrix contains more Me_3Sn groups than embedded tungsten oxo centers (1 W : 8.4 Sn). Ideally all of the Me_3Sn groups would be removed from the matrix. Realizing that the complete removal of Me_3Sn groups might be unrealistic a more attainable goal was set (10 W : 1 Sn). A variety of reagents were tested in an attempt to reduce and hopefully eliminate tin from these materials.

Hydrochloric acid, either generated *ex situ* via the reaction of an alcohol and a nonvolatile metal chloride or *in situ* via the reaction of methanol or water with Si-Cl bonds in the matrix, was found to be an effective Me_3Sn removal agent. However, HCl also attacked W-O-Si linkages causing the catalyst ensemble to change in ways that are not easily predicted or controlled. Therefore HCl cannot be used as a third cross-linking reagent.

Silanes such as PhSiH_3 and EtSiH_3 did not appear to react with Me_3Sn groups in these matrices.

Chlorosilanes ($\text{R}_x\text{SiCl}_{4-x}$ where $x = 0-3$ and $\text{R} = \text{CH}_3$ or H) are known to react with Me_3Sn groups and were also explored as potential Me_3Sn removing agents. Fully chlorinated silanes such as SiCl_4 and SiCl_4py_2 were found to cleave W-O-Si bonds forming W-Cl and Si-O- SiCl_3 when used in excess and Me_3SiCl and Me_3SiBr were found to react with only a limited number of the remaining Me_3Sn groups. The best W : Sn ratio that was obtained using Me_3SiCl as a third cross-linking reagent was 1 W : 3.6 Sn while the best W : Sn ratio that was obtained using Me_3SiBr as a third cross-linking reagent was 1 W : 3.1 Sn. XAS data for the embedded tungsten oxo centers following a third cross-linking reaction were not collected due to limited beamtime.

The sequential dosing strategy that used SiCl_4 as a second cross-linking reagent seemed to be limited with respect to removal of unreacted Me_3Sn groups therefore a sequential dosing

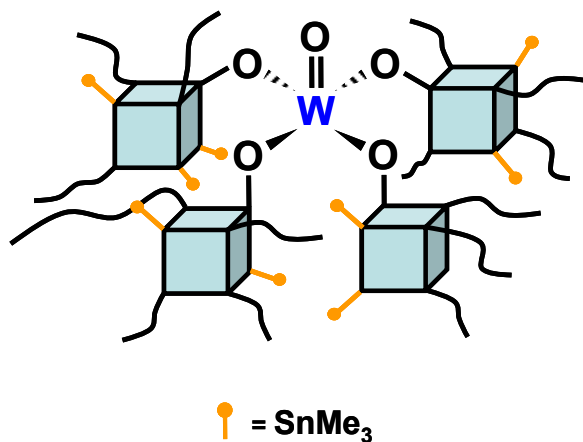


Figure 126: Proposed representation of the catalyst ensemble following second cross-linking reaction, tungsten oxo oligomers and SiCl_4 .

strategy using SiCl_4py_2 as second cross-linking reagent was explored ($\sim 2.5 \text{ SiCl}_4\text{py}_2 : 1.0 \text{ Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ in toluene at 80°C for approximately 24 hours). A significant amount of unreacted Me_3Sn groups still remained in the silicate building block matrix (1 W : 3.4 Sn) following a second cross-linking reaction where SiCl_4py_2 was used however the amount of Me_3Sn left is less than when SiCl_4 was used as the second cross-linking reagent (1 W : 8.4 Sn). Therefore it appears SiCl_4py_2 is a more effective Me_3Sn removal agent than SiCl_4 . The use of Me_3SiCl as a Me_3Sn removal reagent resulted in even more Me_3Sn groups being removed from the matrix (2.0 W : 1 Sn). XAS data for the embedded tungsten oxo centers where SiCl_4py_2 was used as the second cross-linking reagent will be discussed in Chapter 5 however XAS data following a third cross-linking reaction was not collected due to limited beamtime.

Catalytic Test Reactions

The isolated embedded tungsten oxo centers were tested in the selective oxidation of olefins. Tungsten containing silica based heterogeneous catalysts had been reported to be active in the epoxidation and the oxidative cleavage of olefins.[44,47,148,151] The reported procedure for both reactions used hydrogen peroxide as the oxidant and t-butanol as the solvent. Preliminary results showed that the embedded tungsten oxo centers appeared to be catalytically active in the epoxidation of cyclooctene. Before conducting more detailed analysis of the catalytic activity, studies to determine if the tungsten oxo centers were leached during the catalytic test reactions were initiated. The material was washed with several aliquots of ultrapure deionized water and then filtered. The filtrate was analyzed using ICP-OES for the presence of tungsten. Each aliquot contained tungsten which led to the conclusion that tungsten leached during the catalytic test reaction. The following procedure was used in order to test if the leached species were active. The tungsten(VI) catalyst, cyclooctene, hydrogen peroxide, and t-butanol were added to a reaction vessel and allowed to react for approximately 5 hours followed by the removal of all solids from the reaction mixture (cyclooctene, hydrogen peroxide, and t-butanol). At this point the progress of the catalytic test reaction was analyzed using GC-FID. The clear solution without tungsten(VI) catalyst was further reacted overnight to see if the reaction proceeded even after the isolated tungsten oxo centers were removed. The reaction did continue overnight without the catalyst present. Therefore the leached species are catalytically active and appeared to account for a significant amount of the observed catalytic activity.

Leaching most likely occurs due to the presence of HCl in the reaction vessel. Hydrolysis of unreacted Si-Cl groups occurs when water or alcohol is present in the reaction vessel produces HCl, which will react with the linkages between the isolated embedded tungsten oxo centers and the silicate building block support (W-O-Si) resulting in the cleavage of these linkages. In general there are more than enough unreacted Si-Cl groups in the material to generate the amount of HCl needed to completely leach the tungsten centers out of the silicate building block support. An efficient way to passivate the unreacted Si-Cl groups in the material following synthesis has not yet been developed and is needed before the isolated embedded tungsten oxo centers can be tested in catalytic test reactions that use alcohols and/or aqueous hydrogen peroxide.

Isolated Embedded W(VI) Catalyst Ensemble using WCl_6

Following the successful preparation of the isolated embedded tungsten oxo centers, we sought to determine if our synthetic methodology would allow us to target a second type of embedded tungsten center. The combination of a building block approach and a sequential addition strategy was used to target the synthesis of an embedded catalyst ensemble which contains a W(VI) center with six links to the silicate support (Figure 127). This embedded catalyst ensemble was not successfully synthesized because of a side reaction that occurred during the synthesis. The focus of this section is to understand what ensemble is produced and to thoroughly characterize the resulting ensemble. The resulting catalyst ensemble will be referred to as “*isolated embedded tungsten centers*.”

First Cross-Linking Reaction: Reaction of WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

The reaction of a trimethyltin functionalized silicate building block, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, with a limiting amount of WCl_6 was initially thought to produce tungsten centers connected to six silicate building blocks (Figure 128). The cross-linking process proceeds via a metathesis reaction where a chloride ligand of WCl_6 cleanly reacts with a Me_3Sn group to form a new siloxane bond (W-O-Si) and Me_3SnCl , a volatile byproduct. A limiting amount of WCl_6 was used to insure all the chloride ligands could react with the Me_3Sn groups on silicate building blocks. The volatiles of the reaction were analyzed using ^1H NMR and Me_3SnCl was the only

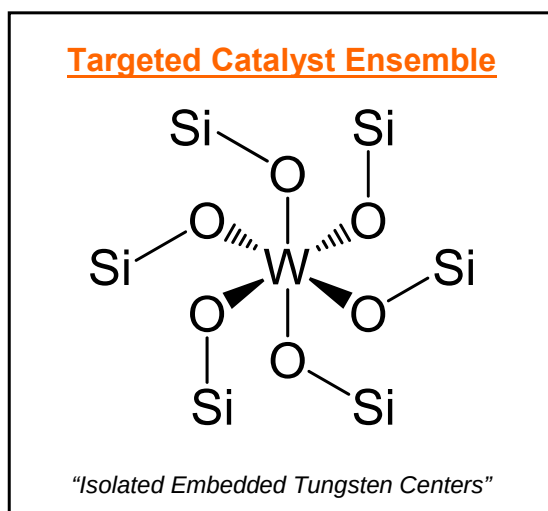


Figure 127: Illustration of the targeted catalyst ensemble referred to as "isolated embedded tungsten centers."

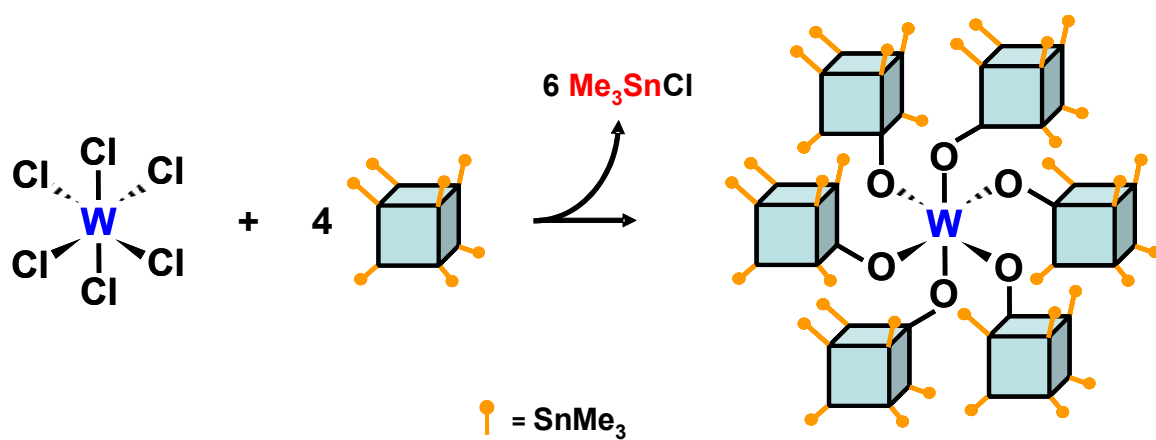


Figure 128: First Cross-Linking Reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

byproduct observed. Gravimetric analysis (6.2 ± 0.3 equivalents of Me_3SnCl) is consistent with all the chloride ligands on the tungsten center reacting. Based on gravimetric analysis, the tungsten centers contain six newly formed siloxane bonds (W-O-Si) as shown in Figure 128.

IR spectroscopy was used to verify the formation of the W-O-Si linkages. The band at 1040 cm^{-1} , which is commonly assigned to the Si-O-Si stretching mode, was observed in the IR spectrum of the material at this stage in the synthesis (Figure 129). A shoulder on the Si-O-Si feature was observed at approximately 950 cm^{-1} in the IR spectrum of the material at this stage of the synthesis, which is characteristic of the presence of M-O-Si, in this case W, in the matrix.[36,44,84,144,164,165] The observation of this weak shoulder provides direct evidence on the formation of W-O-Si suggesting the metathesis reaction proceed as expected.

The material was exposed to pyridine to evaluate what types of isolated acidic centers were present. Three features were observed in the IR spectrum (Figure 130) after exposure to pyridine (1444 cm^{-1} , 1489 cm^{-1} , and 1595 cm^{-1}) which are characteristic of Lewis acidic tungsten centers in silica.[170] No evidence for Bronsted sites ($\sim 1545\text{ cm}^{-1}$) or silanol groups ($\sim 1590\text{ cm}^{-1}$) is observed.

Nitrogen adsorption/desorption experiments were conducted to determine the BET surface area and total pore volume. No measurable BET surface area or pore volume was observed, which supports the conclusion that the silicate building block material contains small oligomers and that a rigid macromolecule has not been formed.

At this point, the gravimetric and IR data suggest that the material contains oligomers with a single type of tungsten center. However, the immediate environment around the tungsten centers has not been directly probed. XAS is one of the techniques that can probe the immediate environment around the tungsten centers and will provide the crucial information needed to verify the metathesis reaction proceeded as expected. Thus XAS data were used to obtain more information about the coordination geometry and oxidation state of the tungsten centers (XANES) in addition to the connectivity of the tungsten centers in this material (EXAFS).

XANES data for both the L_{III} (10207 eV) and the L_I (12100 eV) edges provide information about the coordination geometry and oxidation state of the tungsten centers.[117]

Figure 131 shows the XANES spectrum at the L_{III} edge of the material at this stage in the

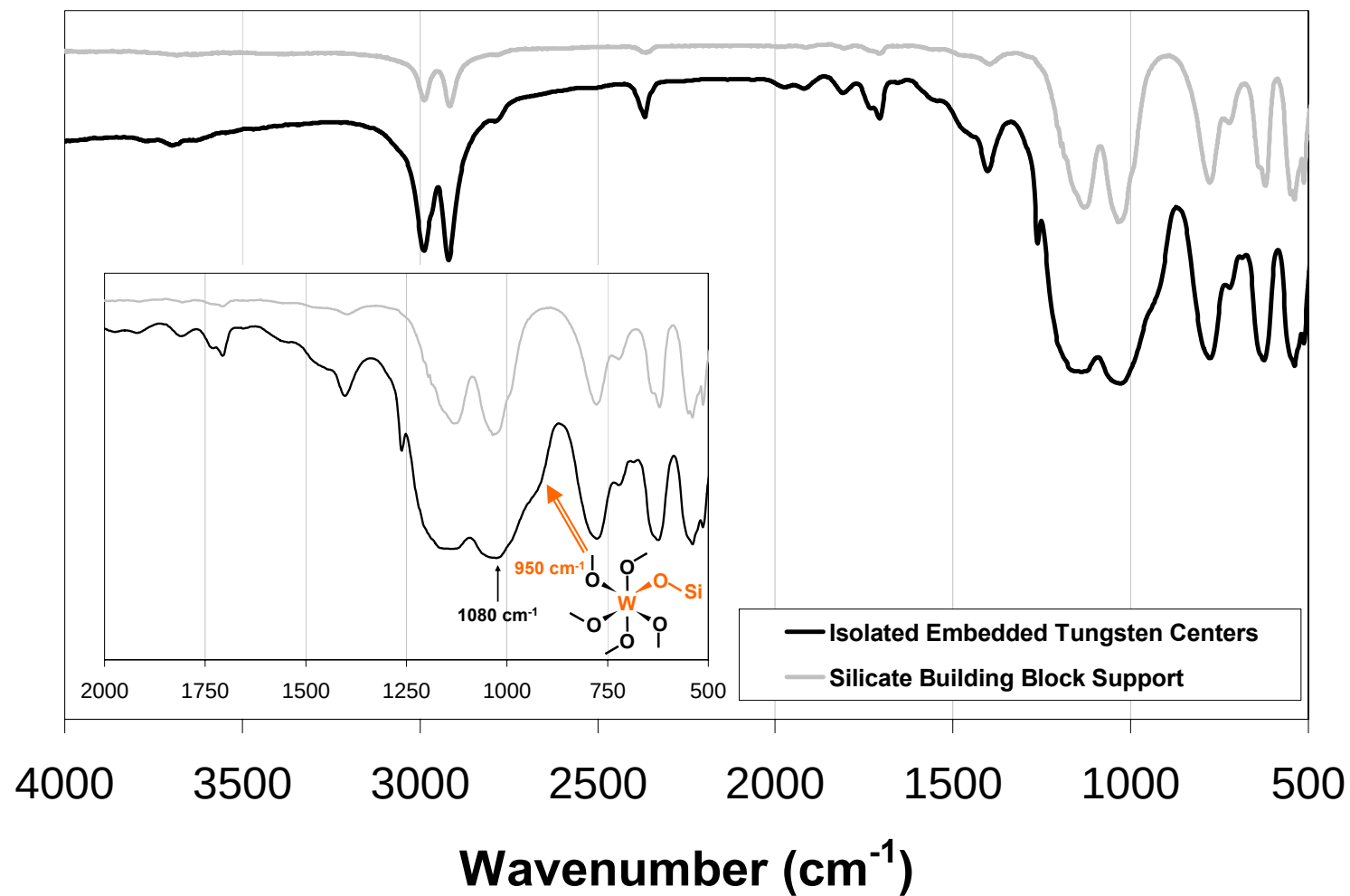


Figure 129: IR spectra (500-4000 cm⁻¹) of a tungsten-free silicate building block support and the material following the first cross-linking reaction, WCl₆ and Si₈O₁₂(OSnMe₃)₈. The inset contains the expanded IR spectrum (500-2000 cm⁻¹) which illustrates the W-O-Si shoulder (950 cm⁻¹).

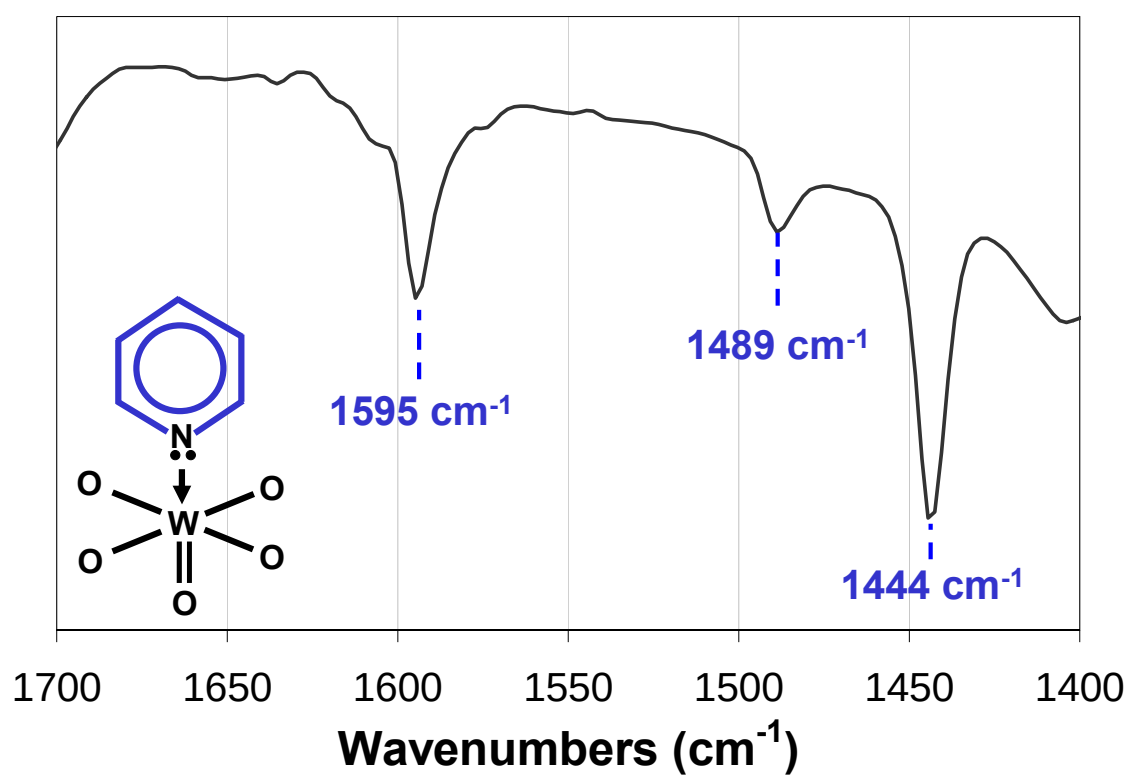


Figure 130: IR spectrum of pyridine bond to Lewis acidic tungsten centers synthesized during first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

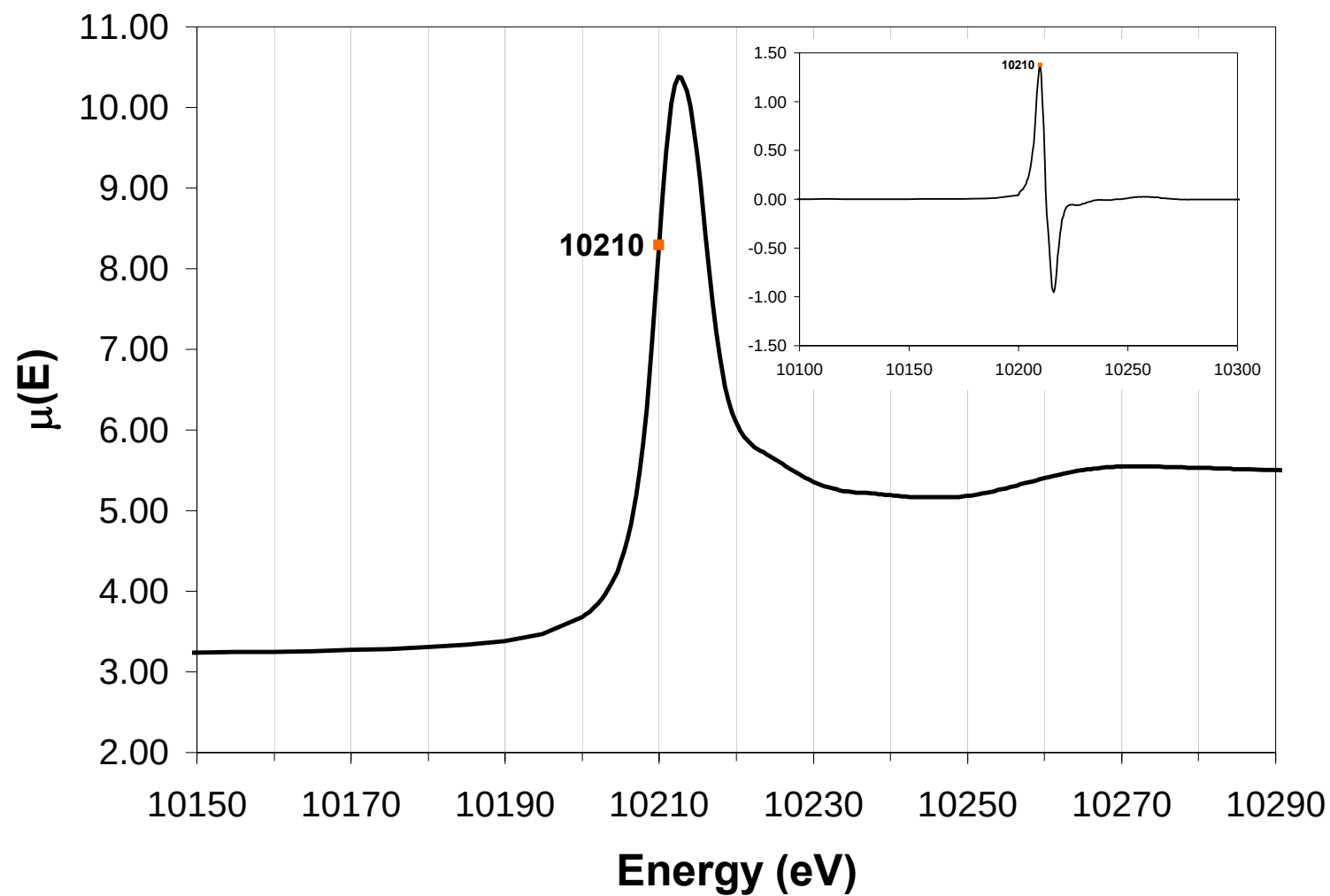


Figure 131: XANES spectrum (W L_{III} edge) following the first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The inset contains the derivative XANES spectrum with the position of the absorption edge (orange square) labeled.

synthesis. The edge position of the material is consistent with a +6 oxidation state for the tungsten centers. The $I_{WL}/I_{\Delta\mu(E)}$ ratio for the tungsten oligomers (3.39) supports the claim the oxidation state of the tungsten centers is +6 (Figure 132). The width of the white line is 6.5 eV which would suggest the coordination geometry is distorted octahedral (width = 7.4 eV) (Figure 133). This is the first piece of data to suggest the immediate environment around the tungsten sites is not as expected. It is important to note that the results of the XANES analysis at the L_{III} edge for the tungsten oligomers are similar to the results for the tungsten oxo oligomers.

Figure 134 shows the XANES spectrum at the L_I edge of the material at this stage in the synthesis. The edge position of the tungsten oligomers supports the claim that the oxidation state of the tungsten centers is +6. The presence of a pre-edge feature ($2s \rightarrow 5d$ transition) provides evidence that the coordination geometry around the tungsten center is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. This is another piece of data to suggest the immediate environment around the tungsten sites is not as expected. The intensity of the pre-edge for the tungsten oligomers is approximately 35% which suggests the coordination geometry is distorted octahedral. Again it is important to note that the results of the XANES analysis at the L_I edge for the tungsten oligomers are similar to the results for the tungsten oxo oligomers.

In summary, the analysis of the XANES spectra at the L_{III} and the L_I edges suggests the tungsten centers have distorted octahedral coordination geometry and that the oxidation state of the tungsten centers is +6. Interestingly the results of the XANES analysis at both edges are very similar to those observed when $WOCl_4$ was used as the initial cross-linking agent.

EXAFS data were used to obtain more information about the connectivity of the tungsten centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around tungsten) can be qualitatively determined by looking at the magnitude R-space plot (Figure 135). Initially only three shells were thought to possibly be present around the tungsten centers after the first cross-linking reaction: a shell of singly bound oxygen atoms (W-O), one for any unreacted chloride ligands (W-Cl), and a shell of nonbonded silicon atoms (W $\cdots$ Si). The feature corresponding to W-Cl should not be observed based on gravimetric analysis. Figure 135 shows what was observed in the magnitude R-space plot and the tentative assignment of each feature.

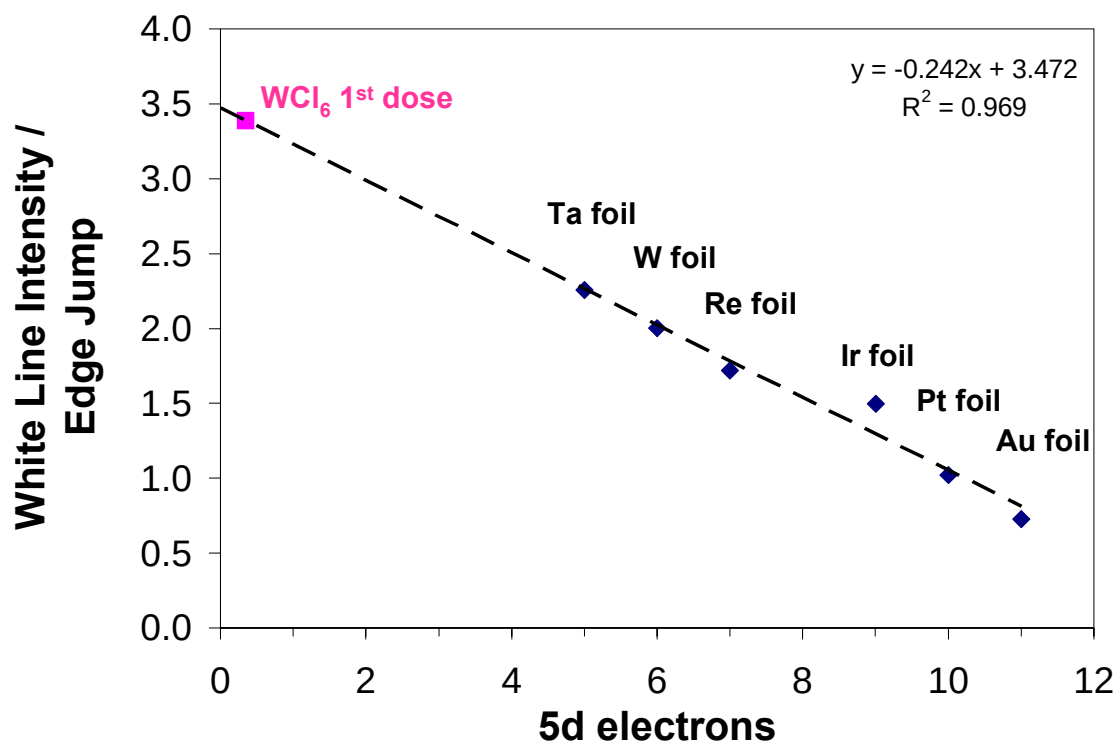


Figure 132: Relationship between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the first cross-linking reaction, WCl₆ and Si₈O₁₂(OSnMe₃)₈.

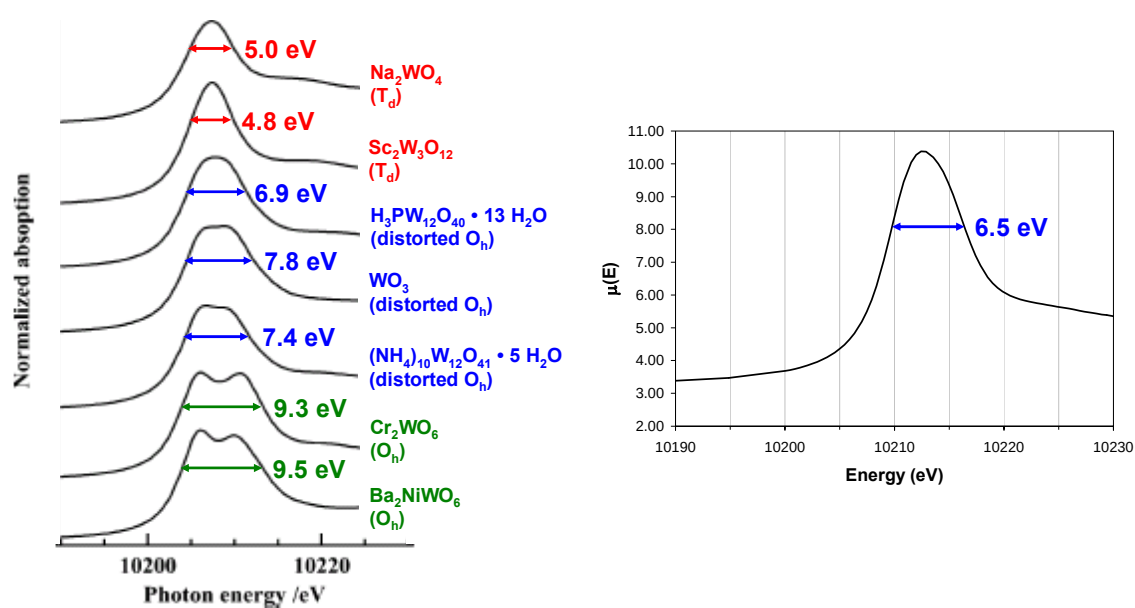


Figure 133: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ (right).

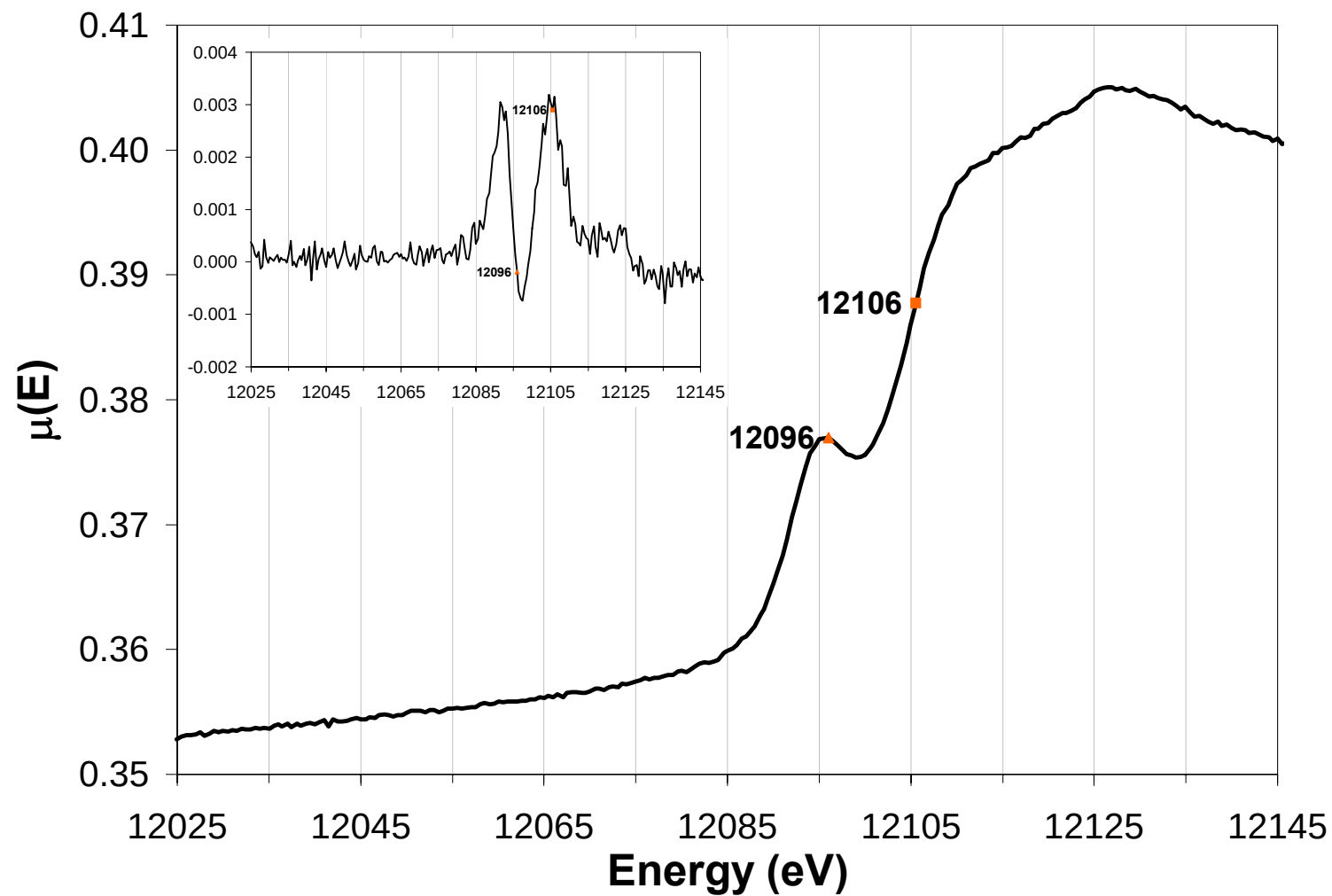


Figure 134: XANES spectrum (W L₁ edge) following the first cross-linking reaction, WCl₆ and Si₈O₁₂(OSnMe₃)₈. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

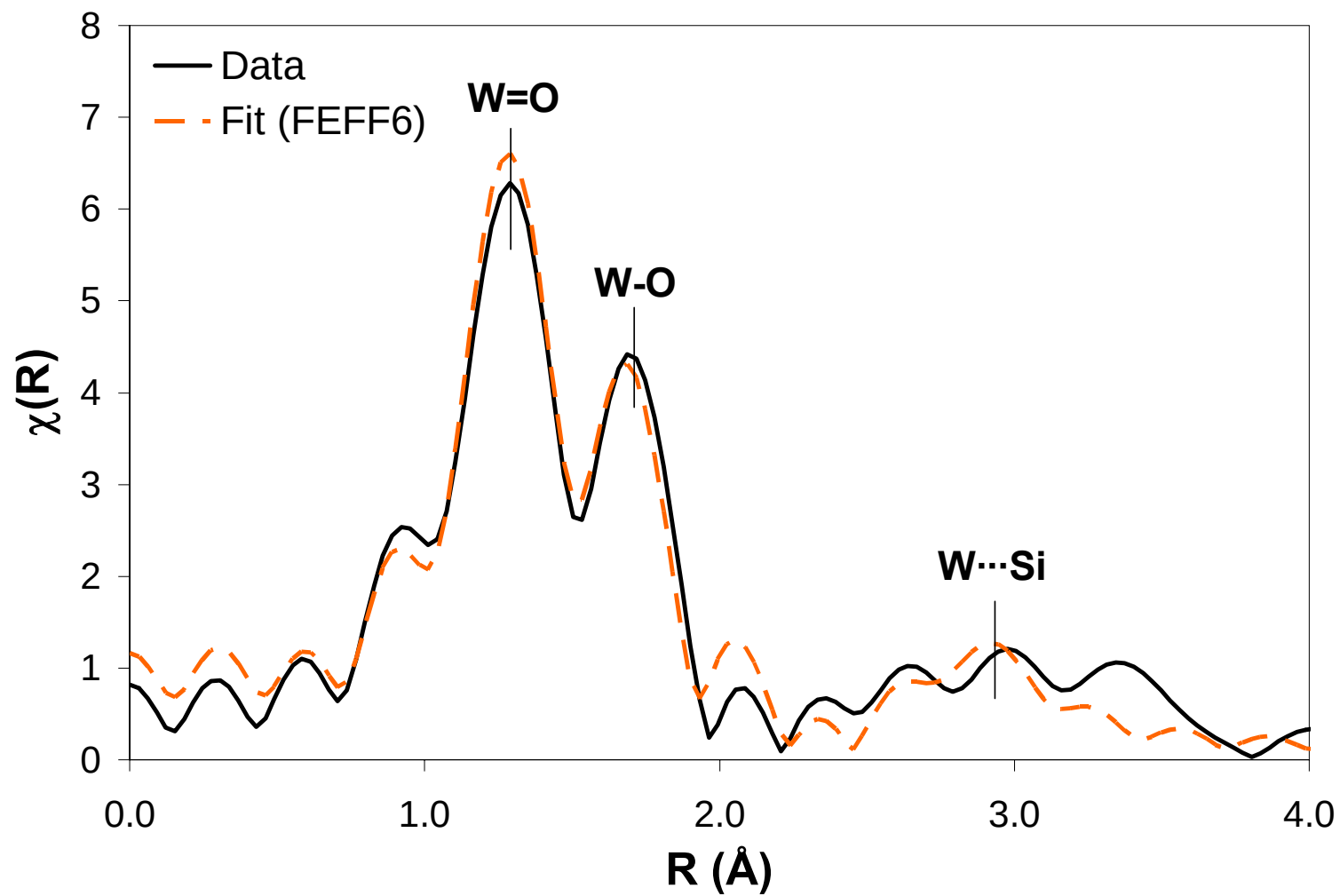


Figure 135: EXAFS R-space plot following first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phase corrected and will appear to be shorter than “real” bond/separation distances.

Based on the qualitative analysis of the EXAFS data, the first coordination sphere (defined as atoms directly bound to the tungsten) of the embedded tungsten centers unexpectedly have at least one terminal doubly bound oxygen atom (W=O) in addition to at least one singly bound oxygen atoms (W-O) and no chloride ligands (W-Cl). The second coordination sphere should have as many nonbonded silicon atoms as first shell singly bound oxygen atoms (W...Si). At this point it was determined that the tungsten centers might actually be tungsten oxo centers so the same structural model (Figure 105), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.92), and refinement procedure were used.

The EXAFS signal ($\chi(k) * k^3$) for the isolated tungsten centers in a silicate building block matrix is presented in Figure 136 with the EXAFS data range used to fit the model is boxed (3.6 to 14.1 Å⁻¹). In R-space, the fit range is from 1.0 to 4.0 Å and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 135 and Figure 137 respectively. Table 9 summarizes the refined values of the structural parameters. As referenced in Table 8, the refined bond lengths are in agreement with values found in the literature.[20,177-181] At this point, the structural parameters were fixed to the refined values and the value of the CNs were allowed to vary. Table 9 contains the refined values of the CNs, which are within 10% of the values determined by gravimetric analysis.

In summary, the EXAFS data analysis provides strong evidence that the immediate environment around the tungsten centers is not as expected (6 W-O and 6 W...Si) but is the same as the tungsten oxo centers (1 W=O, 4 W-O, and 4 W...Si). The data analysis is consistent with the conclusions drawn from the other gravimetric and spectroscopic techniques, which all support the claim that the material contains a single type of tungsten oxo center that is atomically dispersed throughout the silicate material.

The combination of the techniques described above provides a reasonably clear picture of the products in the reaction of a limiting amount of WCl₆ and the silicate building block Si₈O₁₂(OSnMe₃)₈. Small oligomers are formed that contain isolated embedded tungsten oxo centers with one terminal oxo group and four W-O-Si linkages to the building block support (Figure 138).

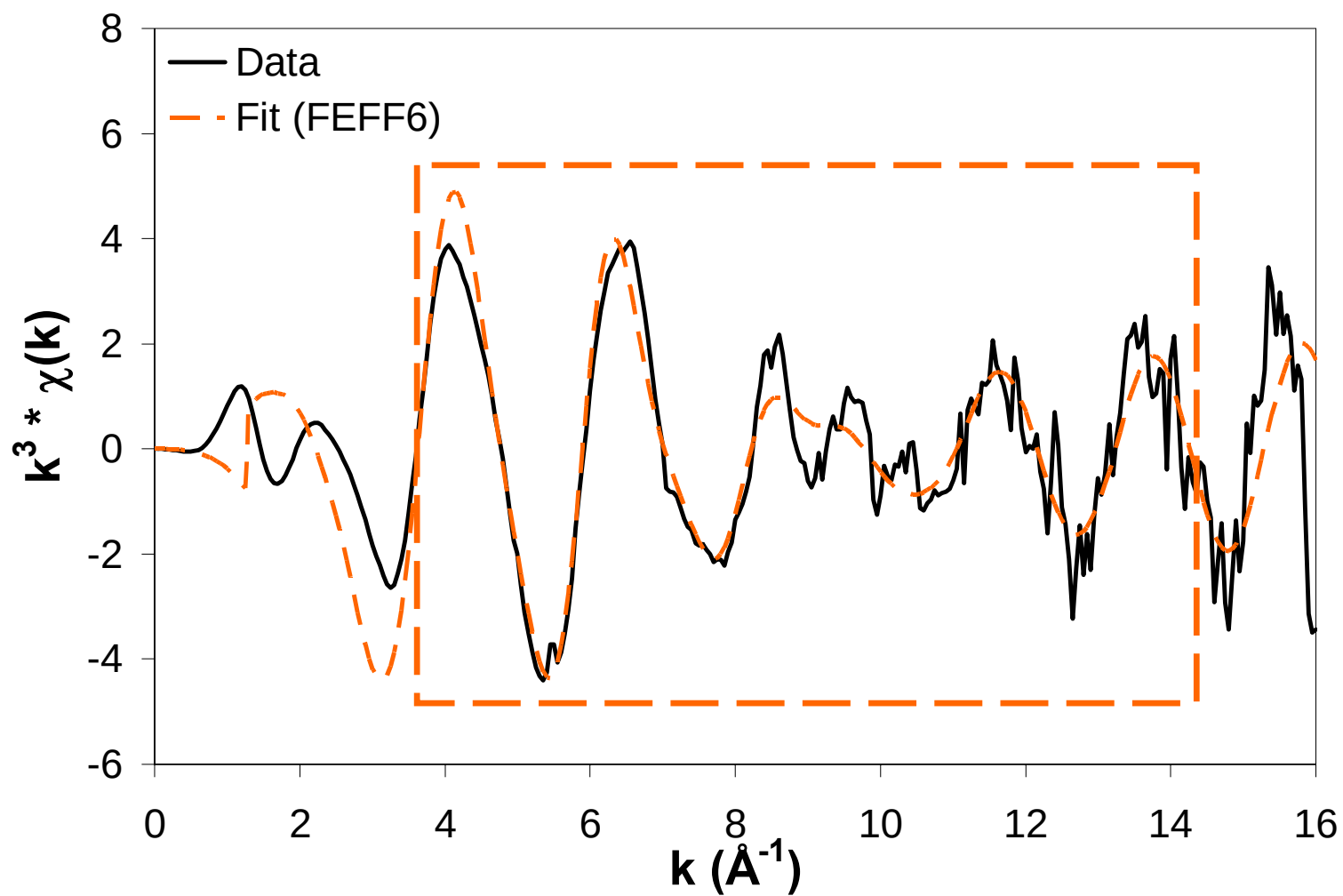


Figure 136: EXAFS k-space plot following first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

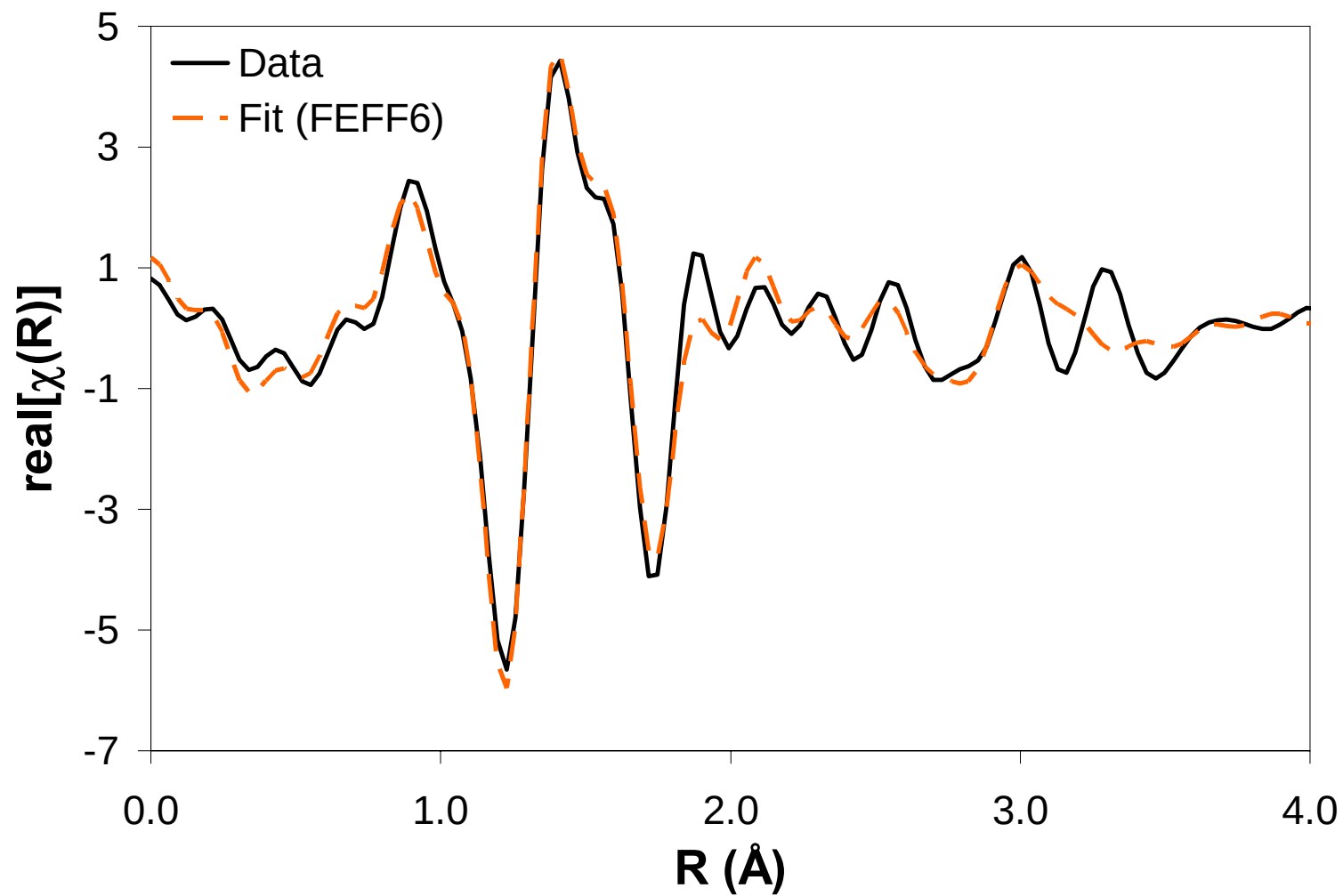


Figure 137: EXAFS real R-space plot following first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phase corrected and will appear to be shorter than “real” bond/separation distances.

Table 9: EXAFS fit values for embedded and surface tungsten centers

Embedded WCl₆ 1st dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.713	1.876	---	3.205
σ^2 (Å ²)	0.18 x 10 ⁻³	8.16 x 10 ⁻³	---	18.36 x 10 ⁻³
E ₀ (eV)	6.4 ± 2.1	6.4 ± 2.1	---	6.4 ± 2.1
CN	0.96 ± 0.08	3.79 ± 0.25	---	3.79 ± 0.25
S ₀ ² = 0.92 (set), N _{idp} = 19.9, N _{var} = 7, χ^2 = 427, reduced χ^2 = 33, R-factor = 0.064, FT k region = 3.587 – 14.149 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Embedded WCl₆ 2nd dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.691	1.890	---	3.207
σ^2 (Å ²)	0.23 x 10 ⁻³	3.25 x 10 ⁻³	---	13.77 x 10 ⁻³
E ₀ (eV)	6.9 ± 1.6	6.9 ± 1.6	---	6.9 ± 1.6
CN	0.96 ± 0.08	3.79 ± 0.25	---	3.79 ± 0.25
S ₀ ² = 0.92 (set), N _{idp} = 18.6, N _{var} = 7, χ^2 = 1261, reduced χ^2 = 109, R-factor = 0.045, FT k region = 3.614 – 13.485 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Surface WCl₆				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.661	1.823	2.317	3.156
σ^2 (Å ²)	2.28 x 10 ⁻³	9.85 x 10 ⁻³	0.85 x 10 ⁻³	22.97 x 10 ⁻³
E ₀ (eV)	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0
CN	1 (set)	3 (set)	1 (set)	3 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.4, N _{var} = 9, χ^2 = 377, reduced χ^2 = 40, R-factor = 0.078, FT k region = 3.544 – 13.274 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

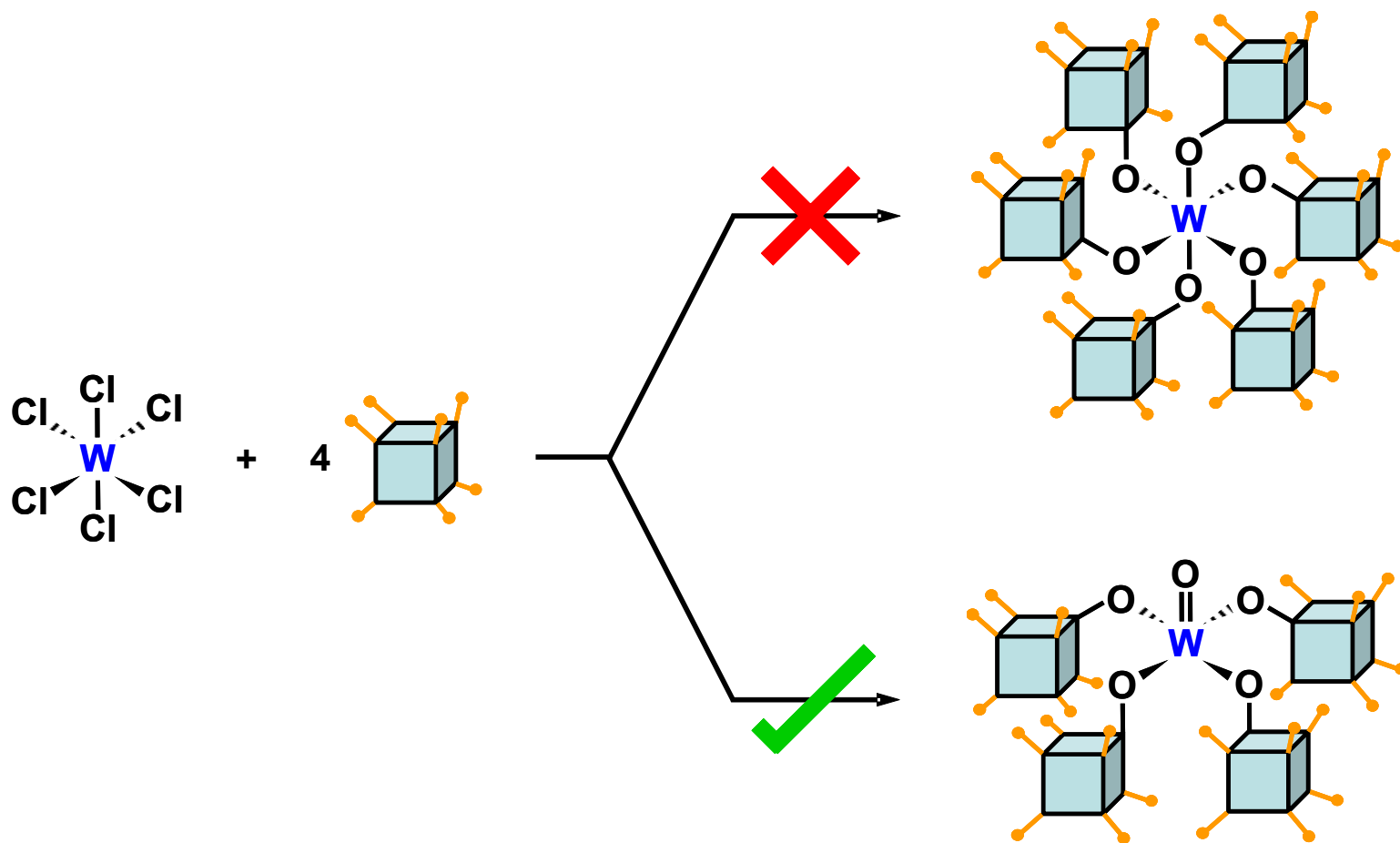


Figure 138: Proposed representation of the catalyst ensemble following first cross-linking reaction, WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

Chemical Transformation of WCl_6 to WOCl_4

An obvious question at this stage is how did a tungsten oxo group ($\text{W}=\text{O}$) form during the reaction of WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$? A previous report in the literature provides some insight into how the tungsten oxo group forms. WCl_6 can be converted to WOCl_4 when reacted with hexamethyldisiloxane.[166] The tungsten atom in WCl_6 extracts an the oxygen atom from hexamethyldisiloxane which is quite remarkable since 2 Si-O bonds must be broken. Figure 139 illustrates the chemical transformation of WCl_6 to WOCl_4 . It is proposed here that initially one chloride ligand of WCl_6 reacts with a Me_3Si group to form a new siloxane bond ($\text{W}-\text{O}-\text{Si}$) and Me_3SiCl . This is followed by bond rearrangement where two bonds break ($\text{Si}-\text{O}$ and $\text{W}-\text{Cl}$) and two bonds form ($\text{Si}-\text{Cl}$ and an additional bond between tungsten and oxygen resulting in a tungsten oxo, $\text{W}=\text{O}$). Therefore 1 equivalent of WCl_6 will react with 1 equivalent of hexamethyldisiloxane to form 1 equivalent of WOCl_4 and 2 equivalents of Me_3SiCl . This reaction is carried out under mild conditions (at room temperature in CH_2Cl_2) and therefore $\text{W}=\text{O}$ formation is a favorable process.

Based on the characterization results indicating a tungsten oxo formed and the reaction just mentioned which can be used to explain how the tungsten oxo was formed, a proposed mechanism for the chemical transformation of WCl_6 to WOCl_4 has been developed. Figure 140 illustrates how WCl_6 is transformed into WOCl_4 when reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The transformation is initiated when a chloride ligand of WCl_6 reacts with a Me_3Sn group to form a new siloxane bond ($\text{W}-\text{O}-\text{Si}$) and Me_3SnCl . This is followed by bond rearrangement where $\text{Si}-\text{Cl}$ and $\text{W}=\text{O}$ form. Thus it is proposed that WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ react to form WOCl_4 , Me_3SnCl , and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_7\text{Cl}$.

Neither WOCl_4 nor $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_7\text{Cl}$ was observed because the chloride ligands on each will react further producing tungsten oxo centers linked to building blocks (Figure 141). While the reaction between WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ is carried out in ether it is not thought that the oxygen atom comes from the solvent because all of the chloride ligands leave the system as Me_3SnCl as determined by ^1H NMR and gravimetric analysis. If ether was chlorinated then $\text{CH}_3\text{CH}_2\text{Cl}$ should be present in the volatiles which was not observed via ^1H NMR. There is also a significant weight difference between $\text{CH}_3\text{CH}_2\text{Cl}$ (64.5 g/mol) and Me_3SnCl (199.2 g/mol) which would effect gravimetric analysis.

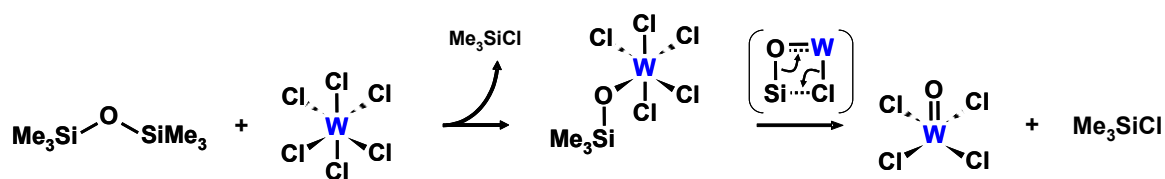


Figure 139: Chemical transformation of WCl_6 to WOCl_4 using $(\text{Me}_3\text{Si})_2\text{O}$.

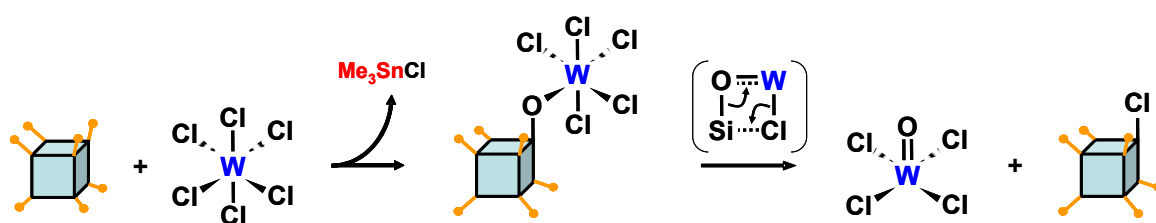


Figure 140: Proposed mechanism for how WCl_6 is transformed into WOCl_4 when reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

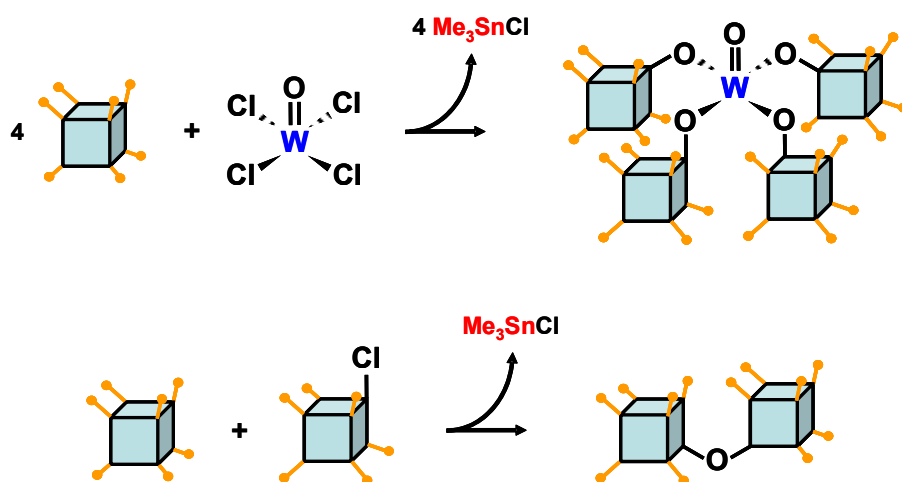


Figure 141: Illustration of the immediate reaction of WOCl₄ (top) and Si₈O₁₂(OSnMe₃)₇Cl (bottom) with additional silicate building blocks.

The oxygen atom that is added to the tungsten center to form the oxo group most likely comes from one of the oxygen atoms off the corner of the silicate building and not from one of the bridging oxygen atoms (Figure 140). The corner oxygen atoms are more labile because the Sn-O-Si linkage is generally weaker than Si-O-Si and Si-O-Sn bonds are more accessible than Si-O-Si.

In summary, spectroscopic evidence verified the presence of tungsten oxo groups in the material following the first cross-linking reaction and a possible explanation as to how the tungsten oxo groups formed has been presented. In the next stage of our synthetic strategy these oligomers will be subsequently linked together to form a robust, high surface area silicate support that contains a single type of isolated tungsten oxo centers.

Second Cross-Linking Reaction: Linking the Oligomers Together using SiCl₄

The oligomers synthesized from WCl₆ and Si₈O₁₂(OSnMe₃)₈ are further cross linked with SiCl₄ via the same metathesis reaction where the silyl chloride groups (from SiCl₄) replace Me₃Sn groups to form new siloxane bonds (Si-O-Si) and Me₃SnCl (Figure 142). The volatiles of the reaction were analyzed and Me₃SnCl was the only byproduct observed using ¹H NMR. Gravimetric data are consistent with two chloride ligands reacting with the Me₃Sn groups (1.7 ± 0.2 equivalents of Me₃SnCl).

IR spectroscopy was used to verify the W-O-Si linkages remained intact. As seen in Figure 143 both the Si-O-Si band (1080 cm⁻¹) and the W-O-Si shoulder (~950 cm⁻¹) were observed in the IR spectrum of the material at this stage in the synthesis. The IR data are consistent with the continued presence of W-O-Si groups in the matrix thus the W-O-Si linkage was not disrupted during the cross-linking reaction with SiCl₄.

The material was again exposed to pyridine to evaluate what types of isolated acidic centers were present. Three features were observed in the IR spectrum (Figure 144) after exposure to pyridine (1450 cm⁻¹, 1491 cm⁻¹, and 1612 cm⁻¹) which are characteristic of Lewis acidic tungsten centers in silica.[170] No evidence for Bronsted sites (~1545 cm⁻¹) or silanol groups (~1590 cm⁻¹) is observed.

Nitrogen adsorption/desorption experiments were conducted to determine the BET surface area and total pore volume. Qualitative analysis of the nitrogen adsorption isotherm

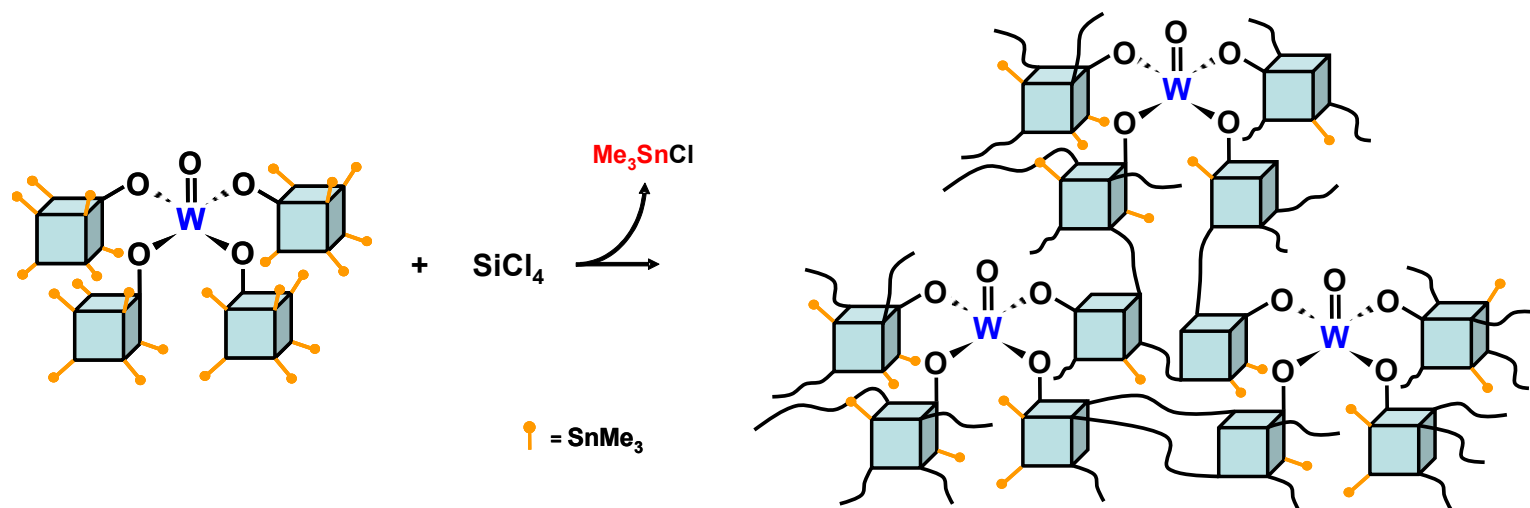


Figure 142: Second Cross-Linking Reaction, Tungsten oxo oligomers (via WCl_6) and SiCl_4 .

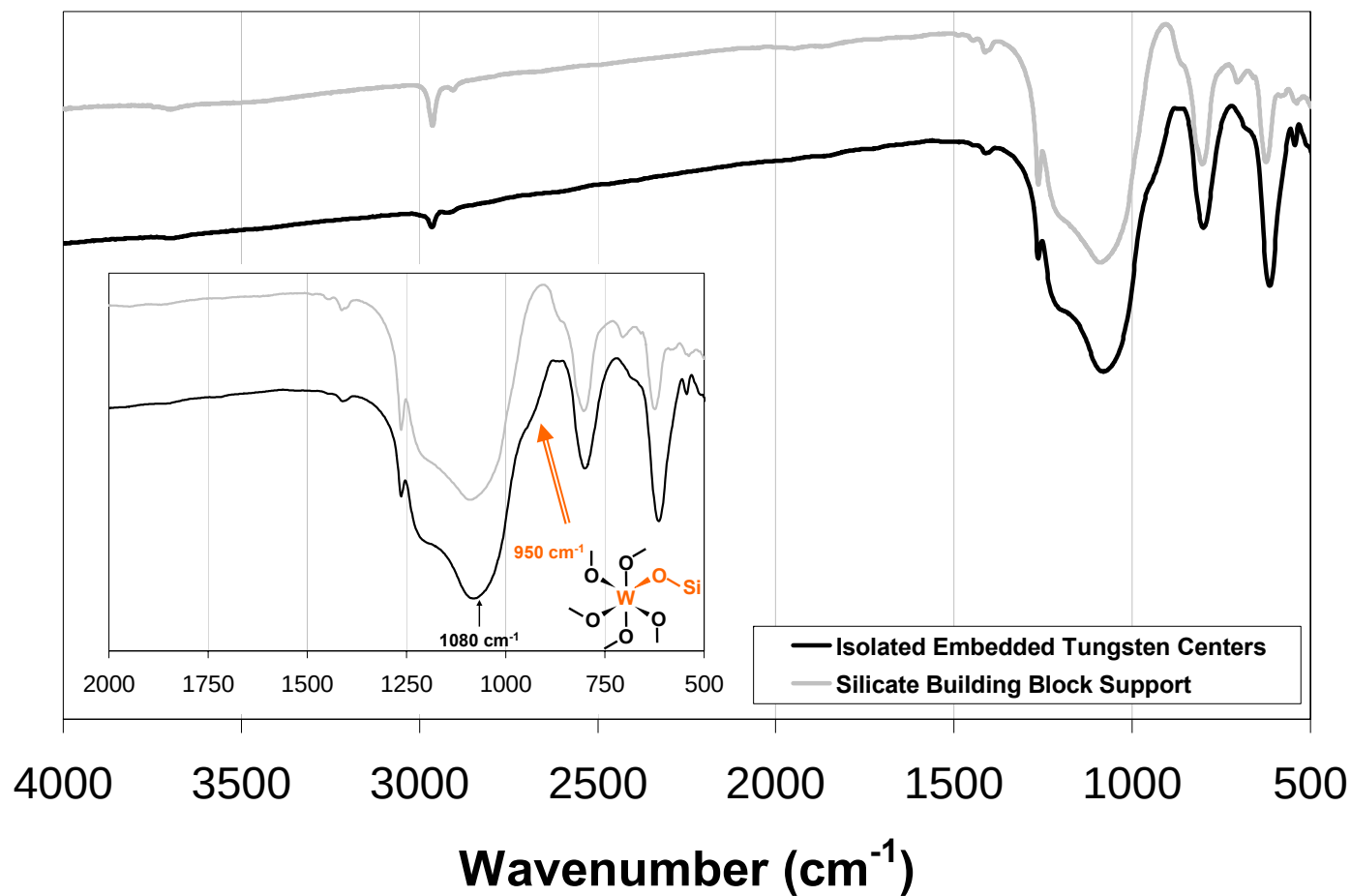


Figure 143: IR spectra (500-4000 cm^{-1}) of a tungsten-free silicate building block support and the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 . The inset contains the expanded IR spectra (500-2000 cm^{-1}) which illustrates the W-O-Si shoulder (950 cm^{-1}).

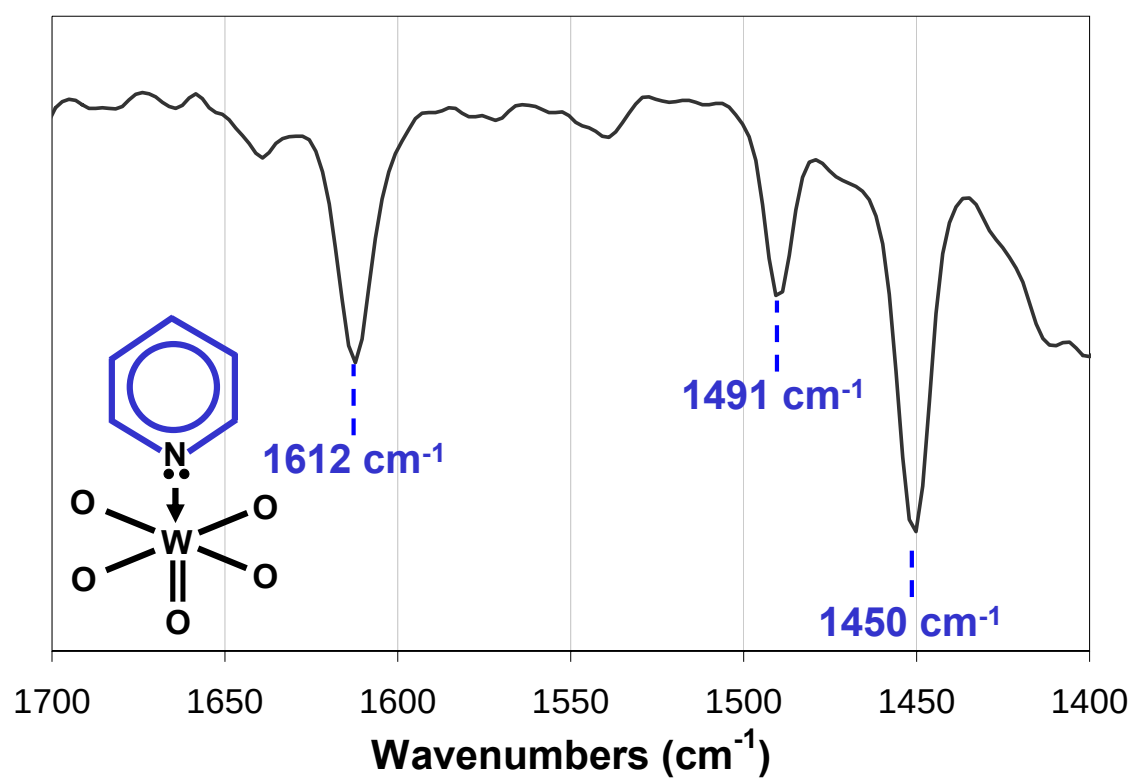


Figure 144: IR spectrum of pyridine bond to Lewis acidic tungsten centers present in the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

(Type I) and t-plot suggests this material is a primarily microporous material;[136] however, a hysteresis (Type H4) is observed in the adsorption/desorption isotherm indicating the presence of some mesopores (Figure 145 & Figure 146). The t-plot method was used to confirm the material is primarily microporous with respect to pore volume (80%) and surface area (91%). The BET surface area of this material is 450 m²/g (Figure 147) and the total pore volume is 0.290 cm³/g. The BJH plot (Figure 148) does not display a significant maximum, which suggests the material has micropores and/or some small mesopores. Thus a high surface area, primarily microporous, silicate building block matrix was grown around the isolated tungsten centers.

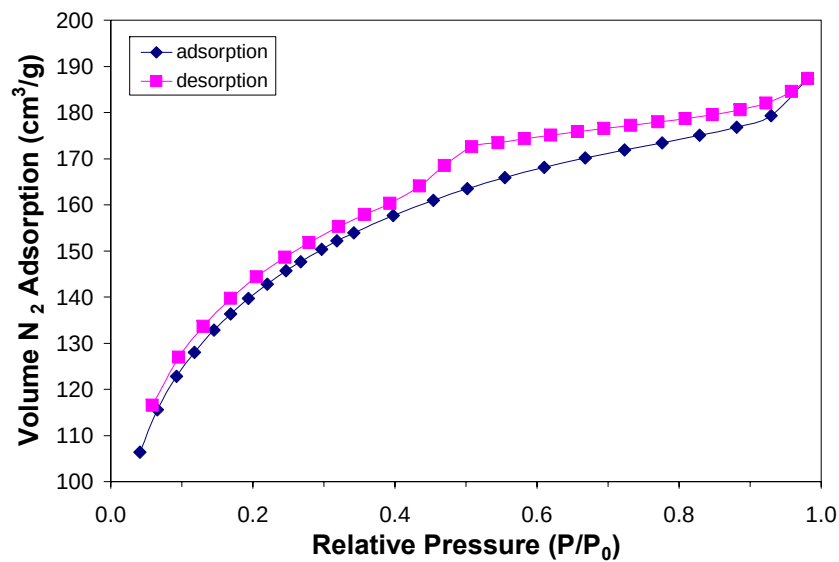
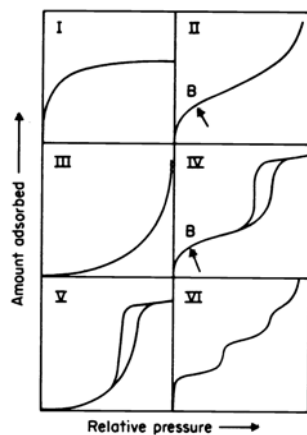
Figure 149 shows the XANES spectrum at the L_{III} edge of the material at this stage in the synthesis. The edge position of the isolated tungsten centers supports the claim the oxidation state of the tungsten centers is +6. The ratio for the isolated tungsten centers (3.41) suggests the oxidation state of the tungsten centers is +6 (Figure 150). The shape of the white line for the isolated tungsten oxo centers provides evidence that the coordination geometry around the tungsten centers is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. The white line appears to be broad (width = 6.7 eV) which would suggest the coordination geometry is distorted octahedral (width = 7.4 eV) instead of tetrahedral (width = 4.9 eV) (Figure 151).

Figure 152 shows the XANES spectrum at the L_I edge of the material at this stage in the synthesis. The edge position of the isolated tungsten centers supports the claim that the oxidation state of the tungsten centers is +6. The presence of a pre-edge feature provides evidence that the coordination geometry around the tungsten center is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. The intensity of the pre-edge for the isolated tungsten oxo centers is approximately 40% which suggests the coordination geometry is distorted octahedral.

In summary, the analysis of the XANES spectra at the L_{III} and the L_I edges suggests the tungsten centers have distorted octahedral coordination geometry and that the oxidation state of the tungsten centers is +6.

Finally, EXAFS data were used to obtain information on the connectivity and geometry of the tungsten centers in the silicate building block matrix. Again the number of shells can be

Standard Isotherms



Standard Hysteresis Loops

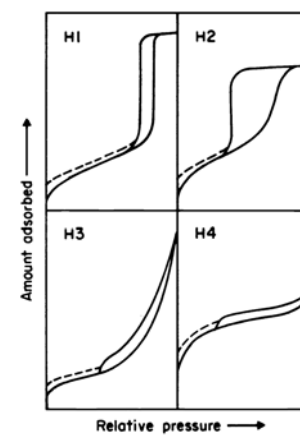


Figure 145: Nitrogen isotherm for the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 . Standard isotherms and hysteresis loops were obtained from the literature.[131]

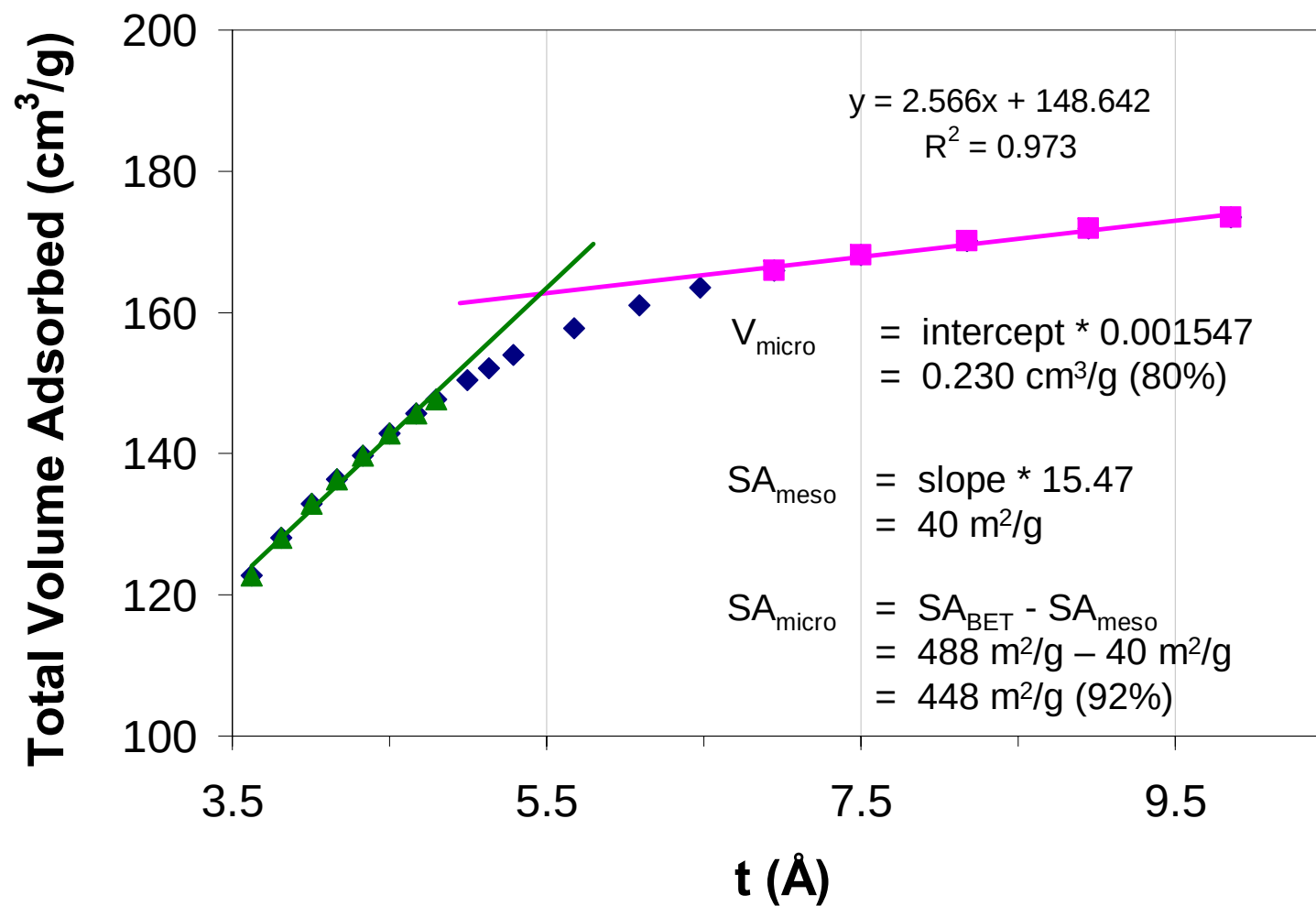


Figure 146: t-plot for the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

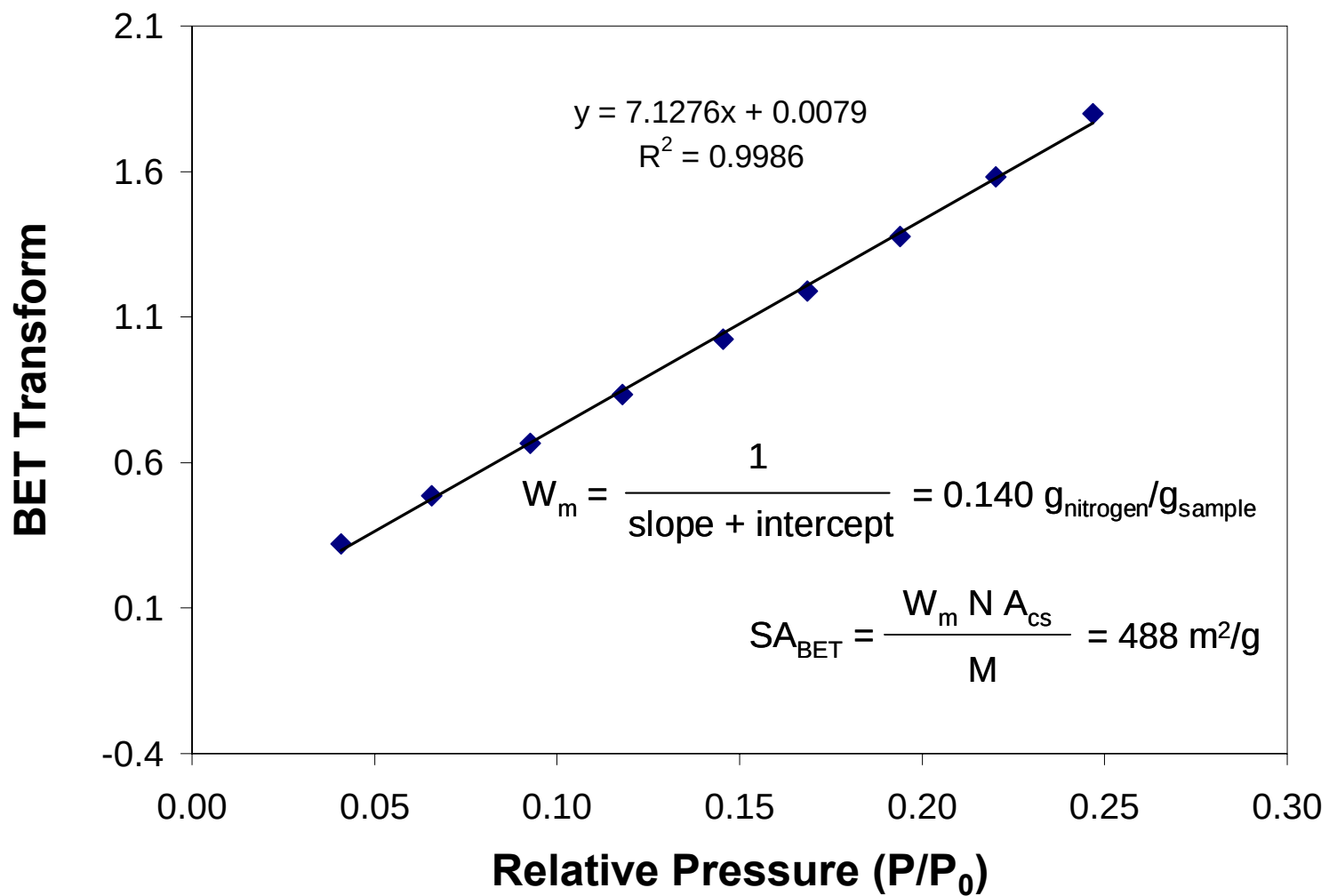


Figure 147: BET plot for the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

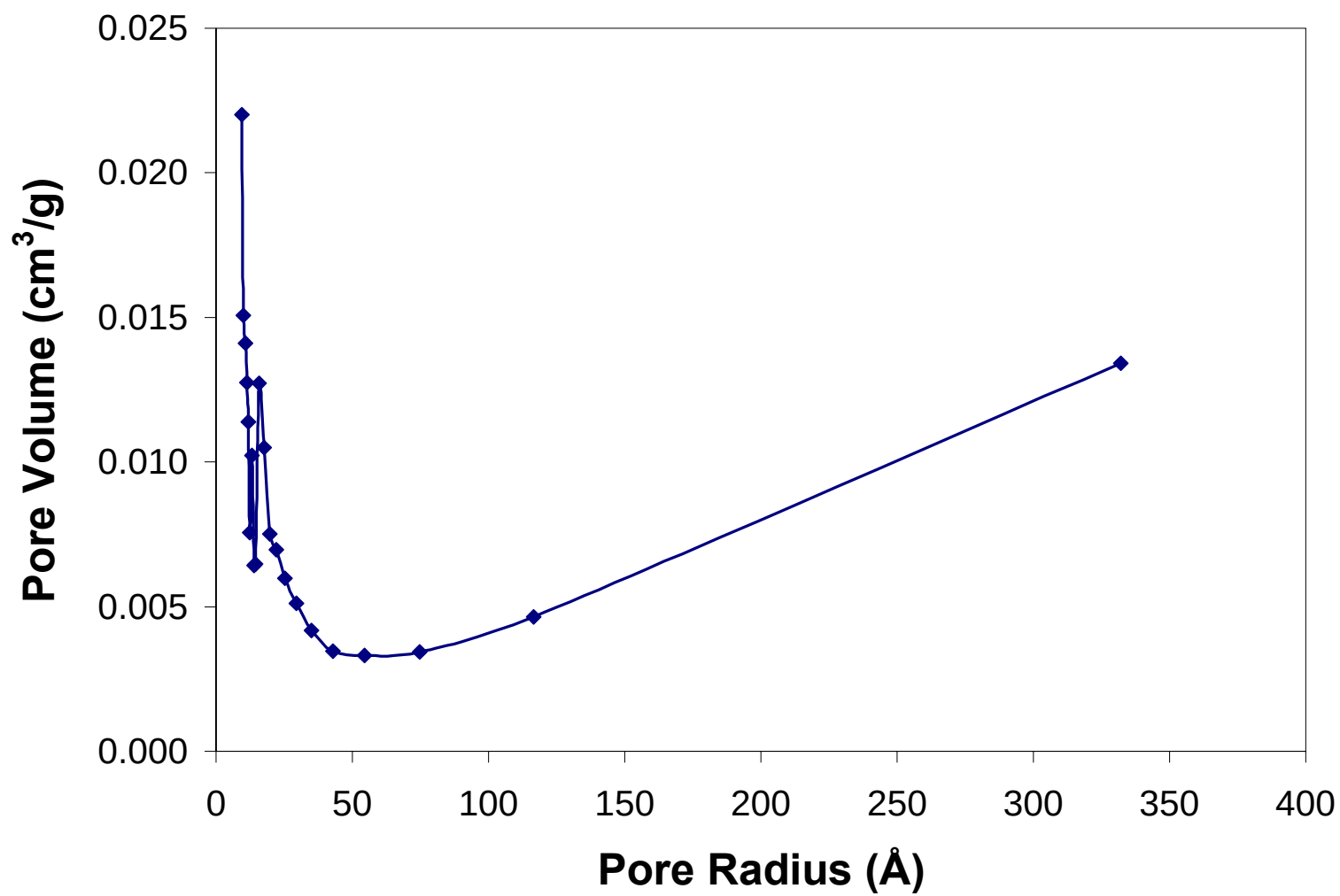


Figure 148: BJH pore size distribution plot for the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

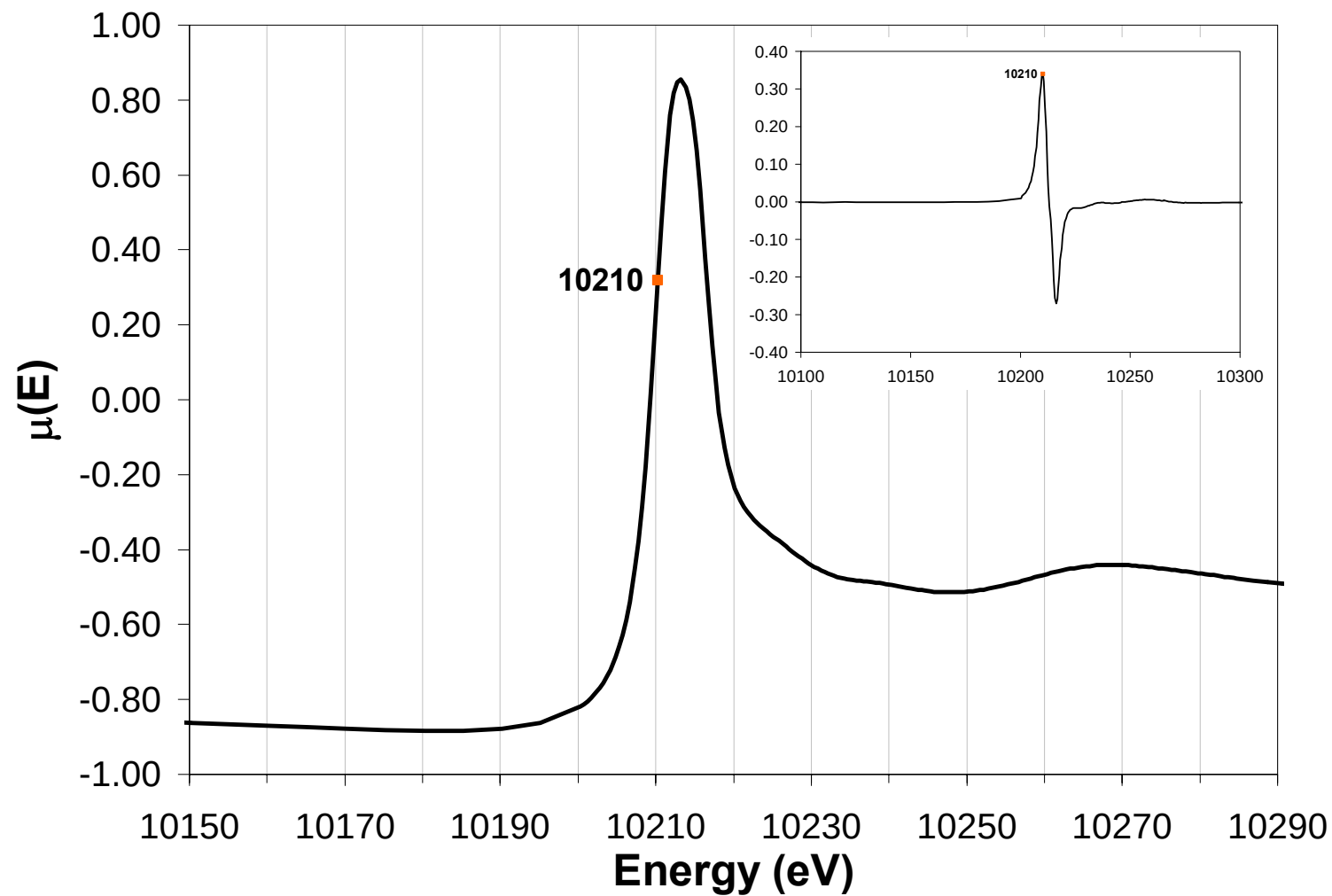


Figure 149: XANES spectrum (W L_{III} edge) following the second cross-linking reaction, tungsten oxo oligomers (via WCl₆) and SiCl₄. The inset contains the derivative XANES spectrum with the position of the absorption edge (orange square) labeled.

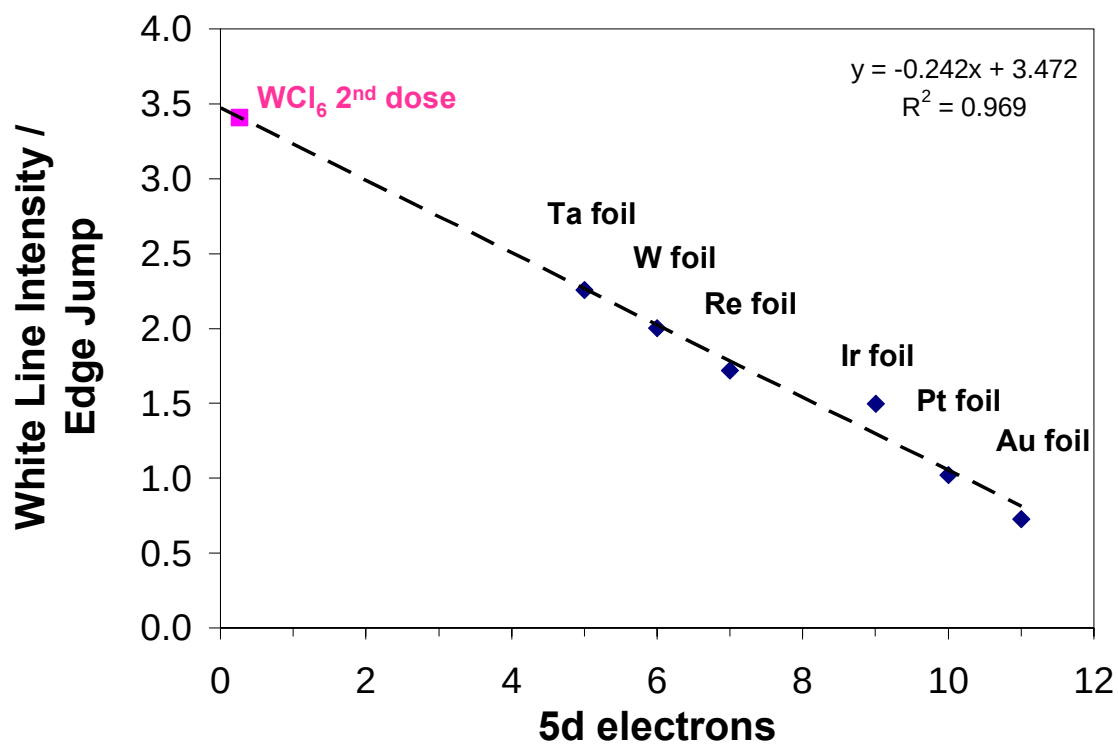


Figure 150: Relation between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the second cross-linking reaction, tungsten oxo oligomers (via WCl₆) and SiCl₄.

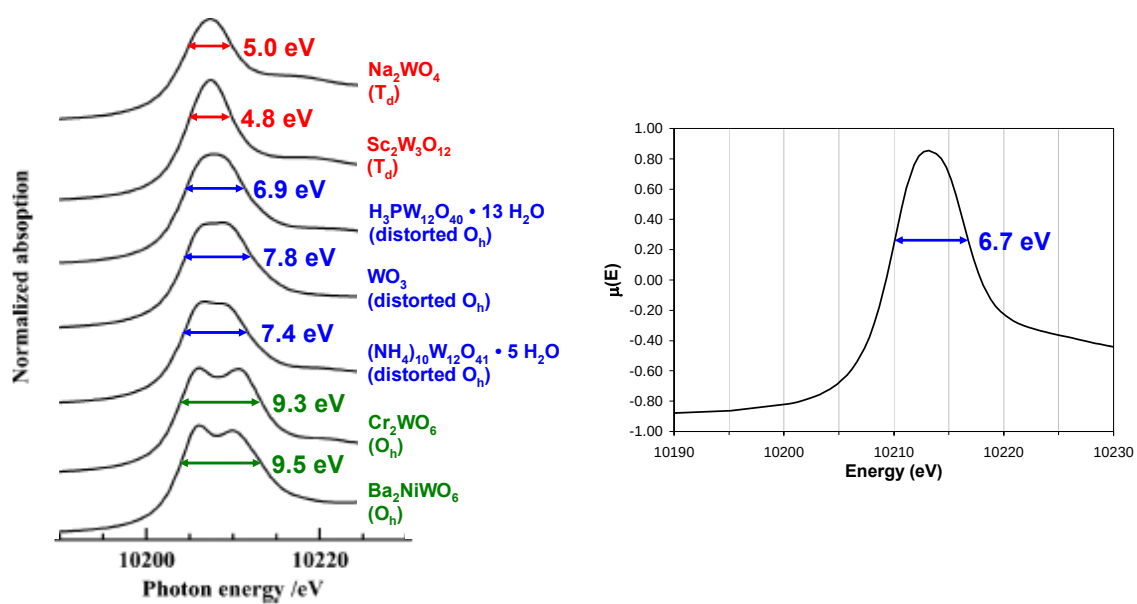


Figure 151: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 (right).

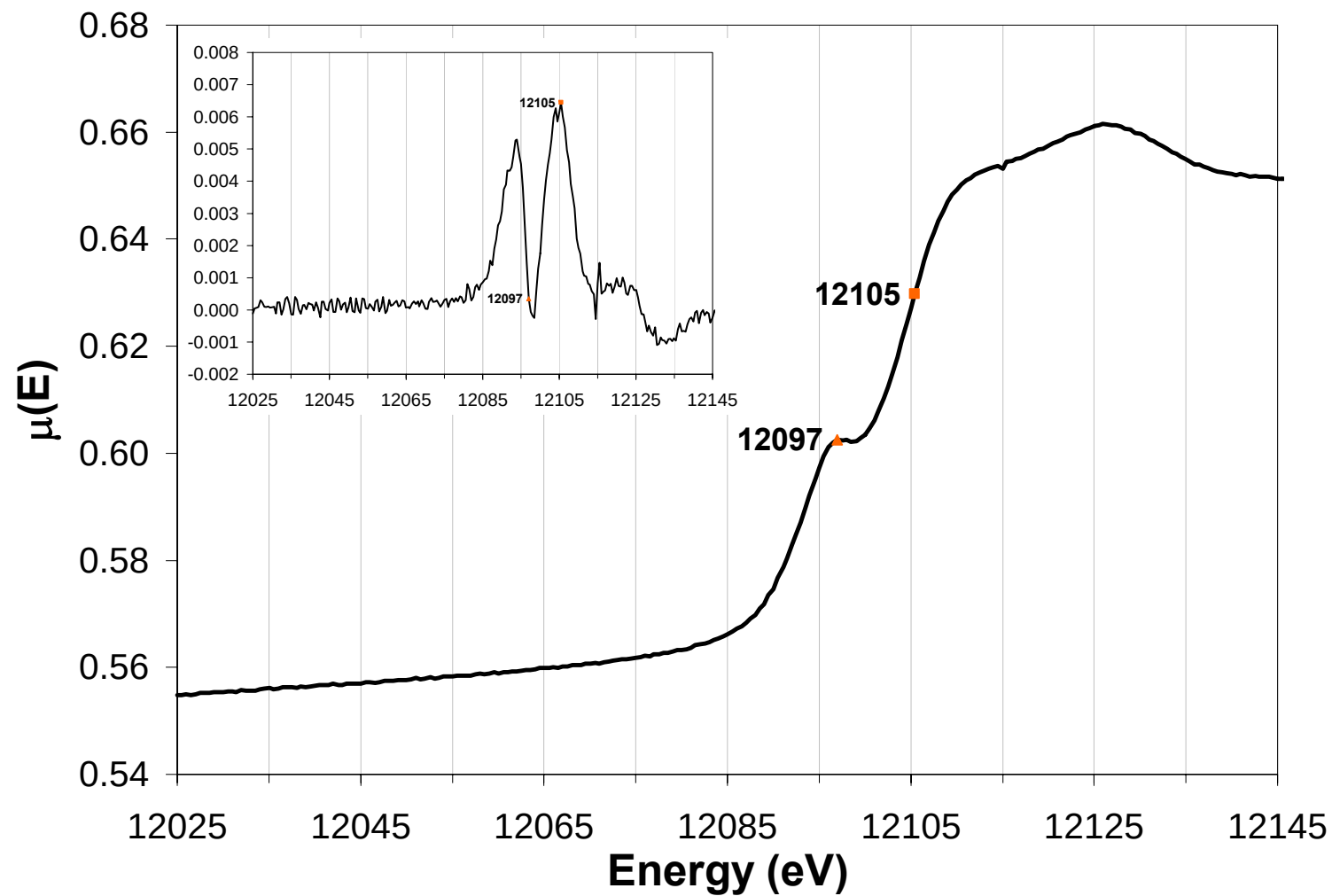


Figure 152: XANES spectrum (W L₁ edge) following the second dosing reaction, tungsten oxo oligomers (via WCl₆) and SiCl₄. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

qualitatively determined by looking at the magnitude R-space plot. Figure 153 shows three features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot. It is important to note that there is no evidence of W-Cl bonds which supports the claim that the tungsten centers remain unchanged following the second cross-linking reaction. The same structural model (Figure 105), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.92), and refinement procedure were used. The EXAFS signal ($\chi(k) * k^3$) for isolated tungsten centers in a silicate building block matrix is presented in Figure 154 with the FT data range boxed (3.6 to 13.5 Å⁻¹). The fit range is from 1.0 to 4.0 Å and the magnitude and real part of the FT of the data and FEFF model are presented in Figure 153 and Figure 155 respectively. Table 9 summarizes the refined values of the structural parameters. As seen in Table 8 the refined bond lengths are in agreement with values determined following the first cross-linking reaction and found in the literature.[20,177-181] Fixing bond distances and atom separations and allowing coordination numbers to refine yielded the results summarized in Table 9. The refined values of the CNs are in agreement with the refined values following the first cross-linking reaction and within 10% of the values determined by gravimetric analysis.

In summary, an unexpected second synthetic pathway to synthesize well-defined isolated embedded tungsten oxo centers in a high surface area silicate building block matrix has been discovered (Figure 156).

The combination of the techniques described above provides a reasonably clear picture of the isolated embedded tungsten ensembles that are present in the robust, high surface area silicate building block support. The silicate building block support was generated around the tungsten ensembles which were unchanged during the generation of the support. IR and SSNMR spectra provided evidence that the linkages between the tungsten centers and the silicate building blocks remained unchanged (preservation of W-O-Si, control of the ligands and the metal-to-support linkages). XAS data confirmed that the oxidation state of the tungsten centers remained unchanged during the generation of the high surface area silicate support around the tungsten centers (preservation of tungsten(VI) centers, control of the metal cation). A structural model based on EXAFS data strongly supports the claim that the local environment around each

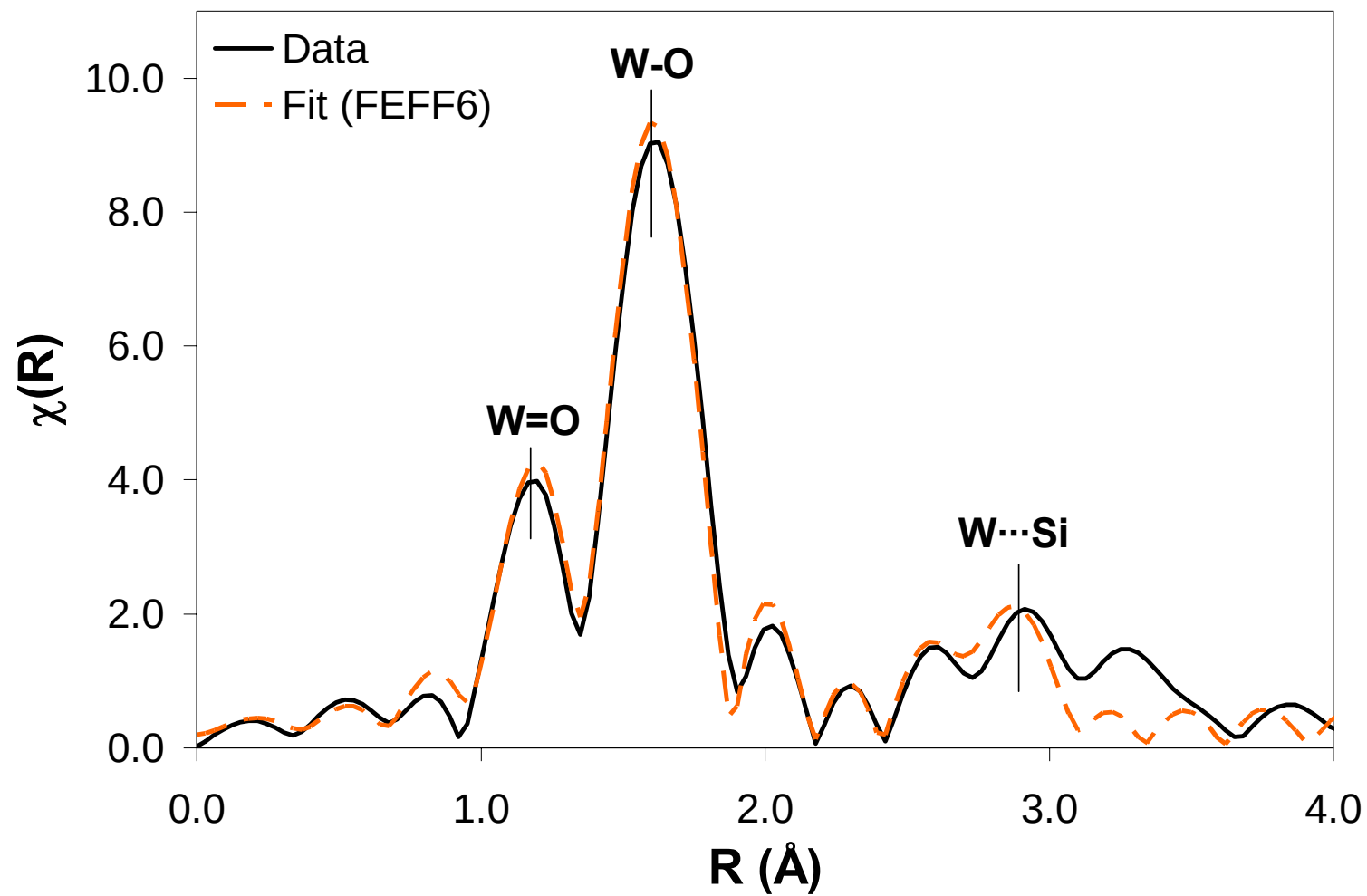


Figure 153: EXAFS R-space plot following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

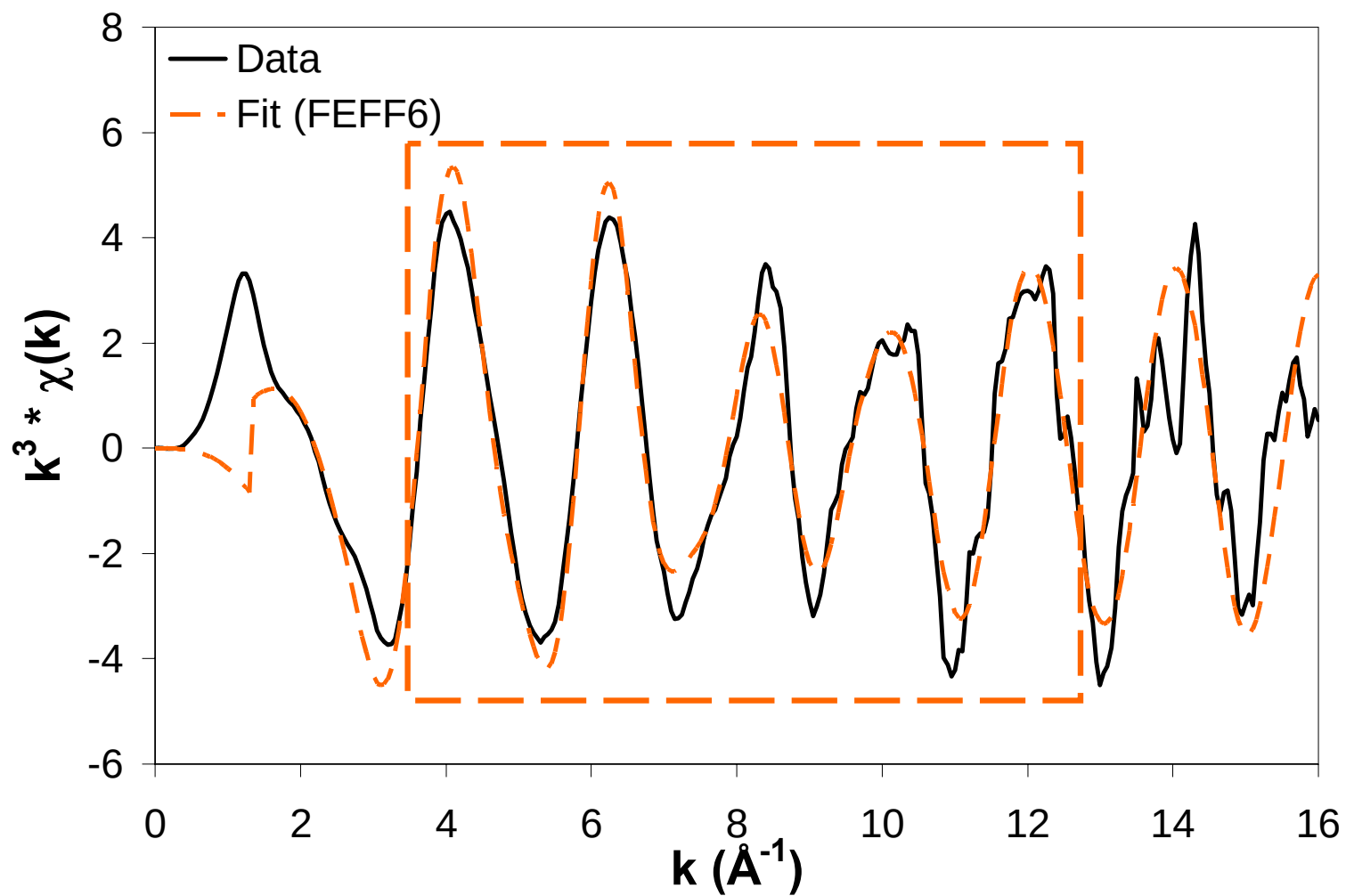


Figure 154: EXAFS k-space plot following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

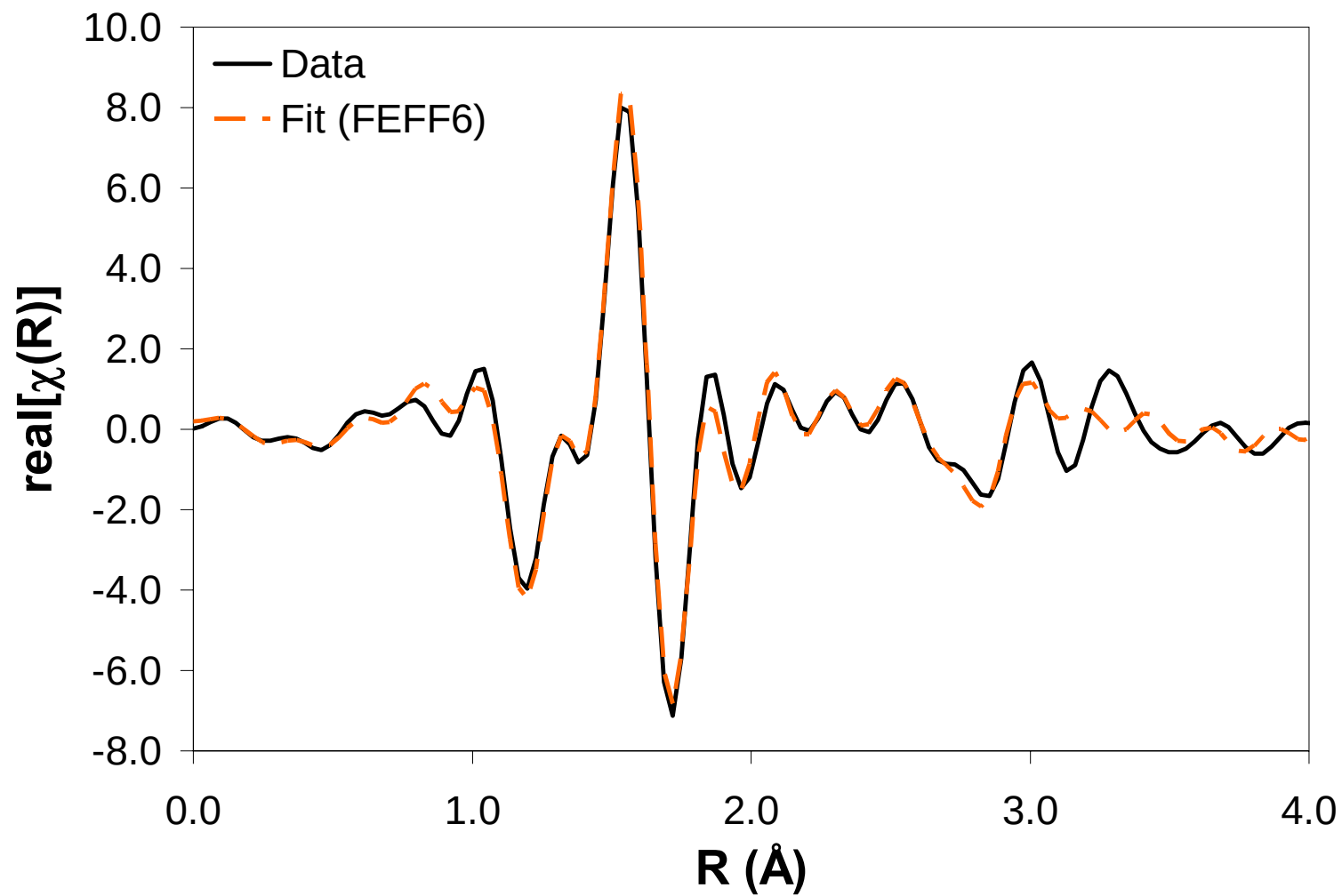


Figure 155: EXAFS real R-space plot following the second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

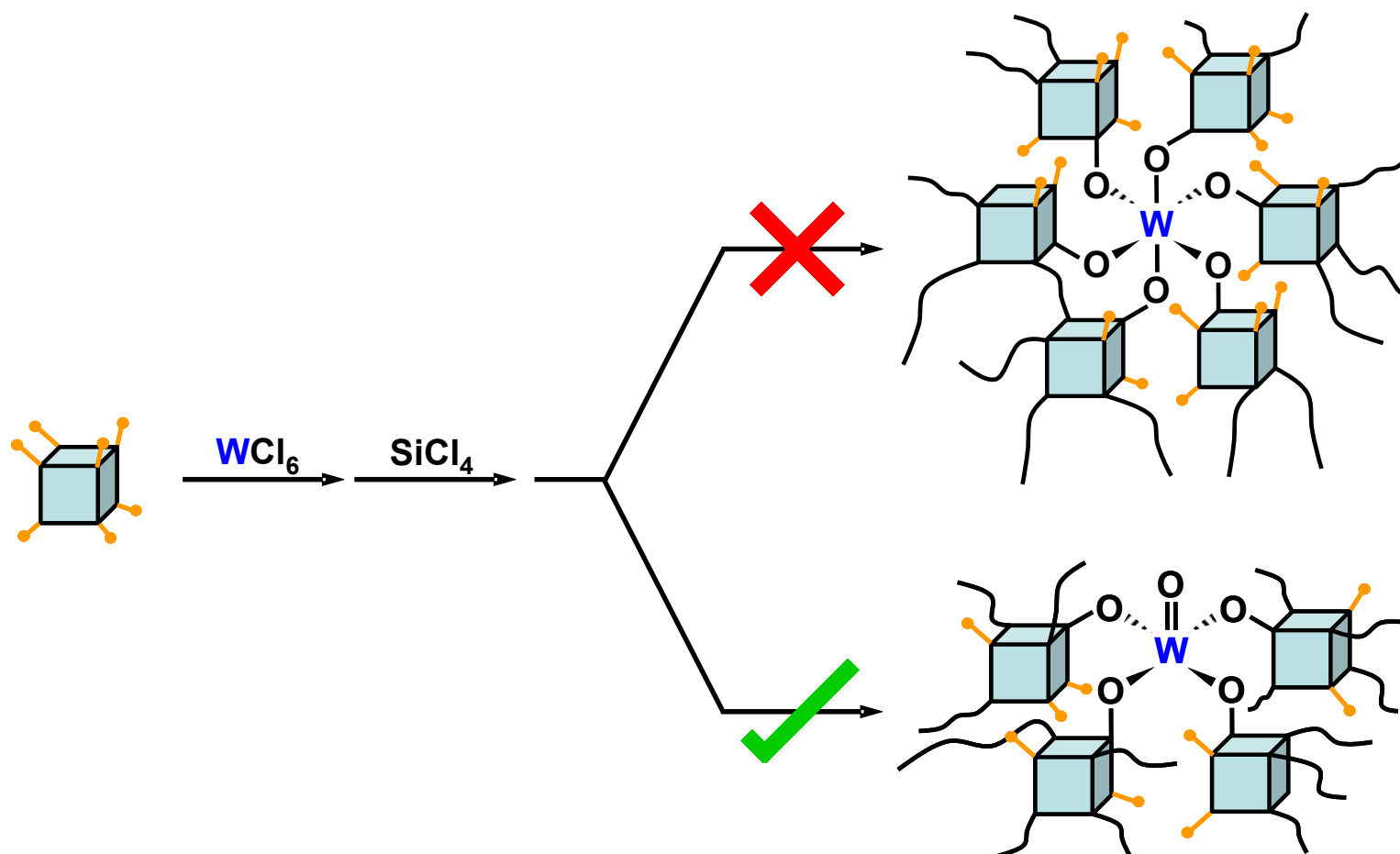


Figure 156: Proposed representation of the catalyst ensemble following second cross-linking reaction, tungsten oxo oligomers (via WCl_6) and SiCl_4 .

tungsten center is identical and unchanged during each stage of the synthesis. The building block approach and sequential dosing strategy provided control of all the necessary components of the embedded tungsten catalyst ensemble which resulted in the targeted synthesis of a single type of embedded tungsten ensemble (Figure 156).

Isolated Surface W(VI) Catalyst Ensemble using WOCl₄

On the other end of the spectrum, we sought to determine whether our synthetic methodology would allow us to target atomically dispersed surface tungsten species that are connected to the support by as little as one bond. A nanostructured silicate support with spatially isolated binding sites was used to target the synthesis of a surface catalyst ensemble which contains a W(VI) center with one terminal oxo group, three chloride ligands, and one link to the silicate support (Figure 157). The surface catalyst ensemble was not successfully synthesized for reason yet to be determined. The focus of this section is to understand what ensemble is produced and to thoroughly characterize the resulting ensemble using a variety of characterization techniques. The resulting catalyst ensemble will be referred to as “*isolated surface tungsten oxo centers*.”

Reaction of WOCl₄ and Silicate Building Block Support

The synthesis of isolated surface tungsten oxo centers that are connected to one silicate building blocks was targeted by reacting a silicate building block support (2.85 SiCl₄py₂ : 1.0 Si₈O₁₂(OSnMe₃)₈) with a limiting amount of WOCl₄ (0.5 WOCl₄ : 1 Si₈O₁₂(OSnMe₃)₈) (Figure 158). The cross-linking process proceeds via a metathesis reaction where a chloride ligand of WOCl₄ cleanly reacts with a Me₃Sn group to form a new siloxane bond (W-O-Si) and Me₃SnCl, a volatile byproduct. Only one chloride ligand on WOCl₄ should react because the binding sites on the silicate building block support are spatially isolated from one another, which prevents each tungsten center from accessing two binding sites. A limiting amount of WOCl₄ was used so that gravimetric analysis could be used to determine the connectivity of the W(VI) center to the support. The volatiles of the reaction were analyzed using ¹H NMR and Me₃SnCl was the only byproduct observed. Gravimetric analysis (1.7 ± 0.4 equivalents of Me₃SnCl) suggests that

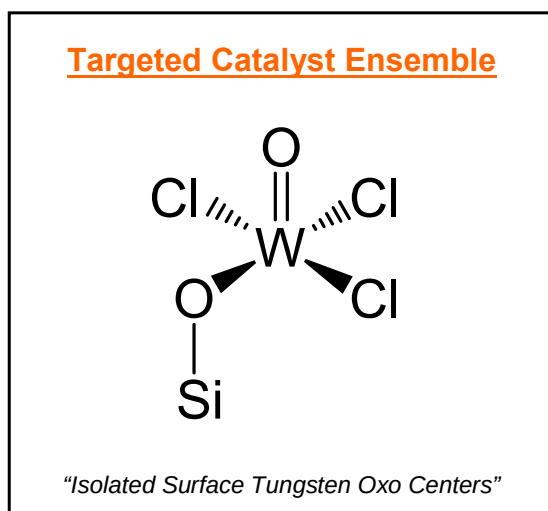


Figure 157: Illustration of the targeted catalyst ensemble referred to as "isolated surface tungsten oxo centers."

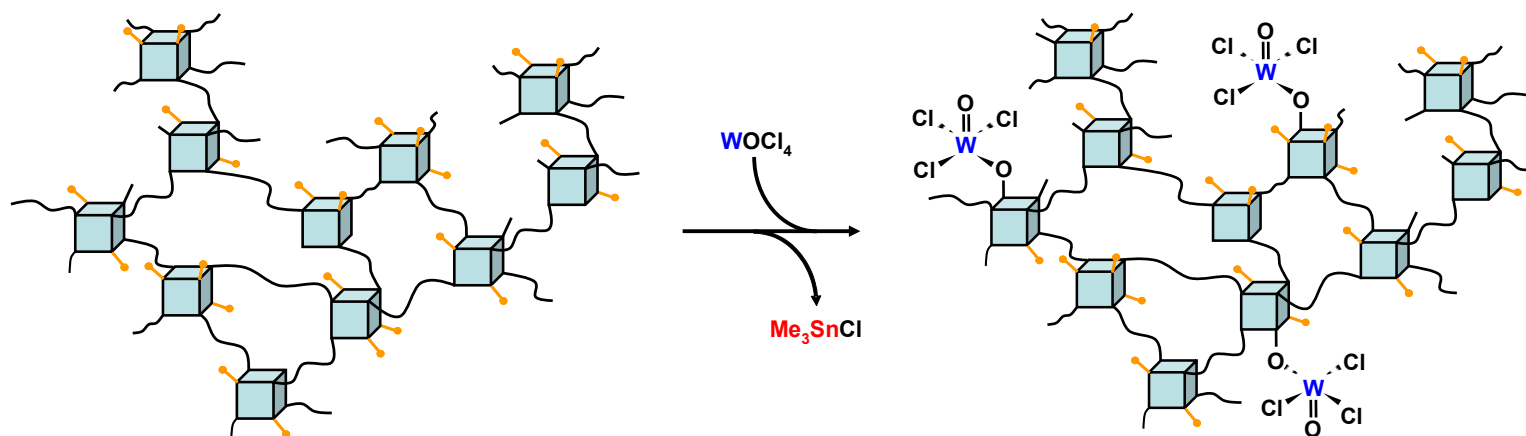


Figure 158: Reaction of WOCl_4 and the premade silicate building block support.

approximately 2 chloride ligands on the tungsten center reacted with Me_3Sn groups on the support.

Figure 159 shows the IR spectra of a tungsten-free silicate building block support and the isolated surface tungsten oxo centers. The materials are synthesized under nonaqueous aprotic conditions which results in the production of a hydroxyl-free surfaces. As expected, little to no evidence for the presence of silanol groups ($3600\text{--}4000\text{ cm}^{-1}$) is observed in the IR spectra. IR spectroscopy is also used to verify the formation of the W-O-Si linkages. The band at 1080 cm^{-1} , which is commonly assigned to the Si-O-Si stretching mode,[171] was observed in the IR spectra as seen in Figure 159. A shoulder on the Si-O-Si feature was observed at approximately 930 cm^{-1} in the IR spectrum, which is characteristic of the presence of M-O-Si groups, in this case W, in the matrix.[36,44,84,144,164,165] The observation of this weak shoulder provides direct evidence on the formation of W-O-Si groups and suggests the metathesis reaction proceeded as expected.

Nitrogen adsorption/desorption measurements were conducted on the silicate building block support before and after the addition of the tungsten oxo centers to determine the BET surface area and total pore volume. In the case of the silicate building block support, qualitative analysis of the nitrogen adsorption isotherm (Type IV) and t-plot suggests this material is a primarily mesoporous material (Figure 160 & Figure 161).[136] The presence of a hysteresis (Type H4) also indicates the presence of mesopores. The t-plot method was used to confirm the material is primarily mesoporous with respect to pore volume (66%) and surface area (51%). The BET surface area of this material is $743\text{ m}^2/\text{g}$ (Figure 162) and the total pore volume is $0.667\text{ cm}^3/\text{g}$. The BJH plot (Figure 163) does display a maximum, which suggests the BJH average pore radius is $34.0\text{ \AA}$. The porosity of the material did not significantly change with the addition of isolated surface tungsten oxo centers. The nitrogen adsorption isotherm (Type IV), hysteresis (Type H4), and t-plot still suggests this material is a primarily mesoporous material (Figure 164 & Figure 165).[136] The t-plot method was used to confirm the material is primarily mesoporous with respect to pore volume (70%) and surface area (55%). The BET surface area of this material is $759\text{ m}^2/\text{g}$ (Figure 166) and the total pore volume is $0.718\text{ cm}^3/\text{g}$. The BJH plot (Figure 167) has a maximum at approximately $29.0\text{ \AA}$.

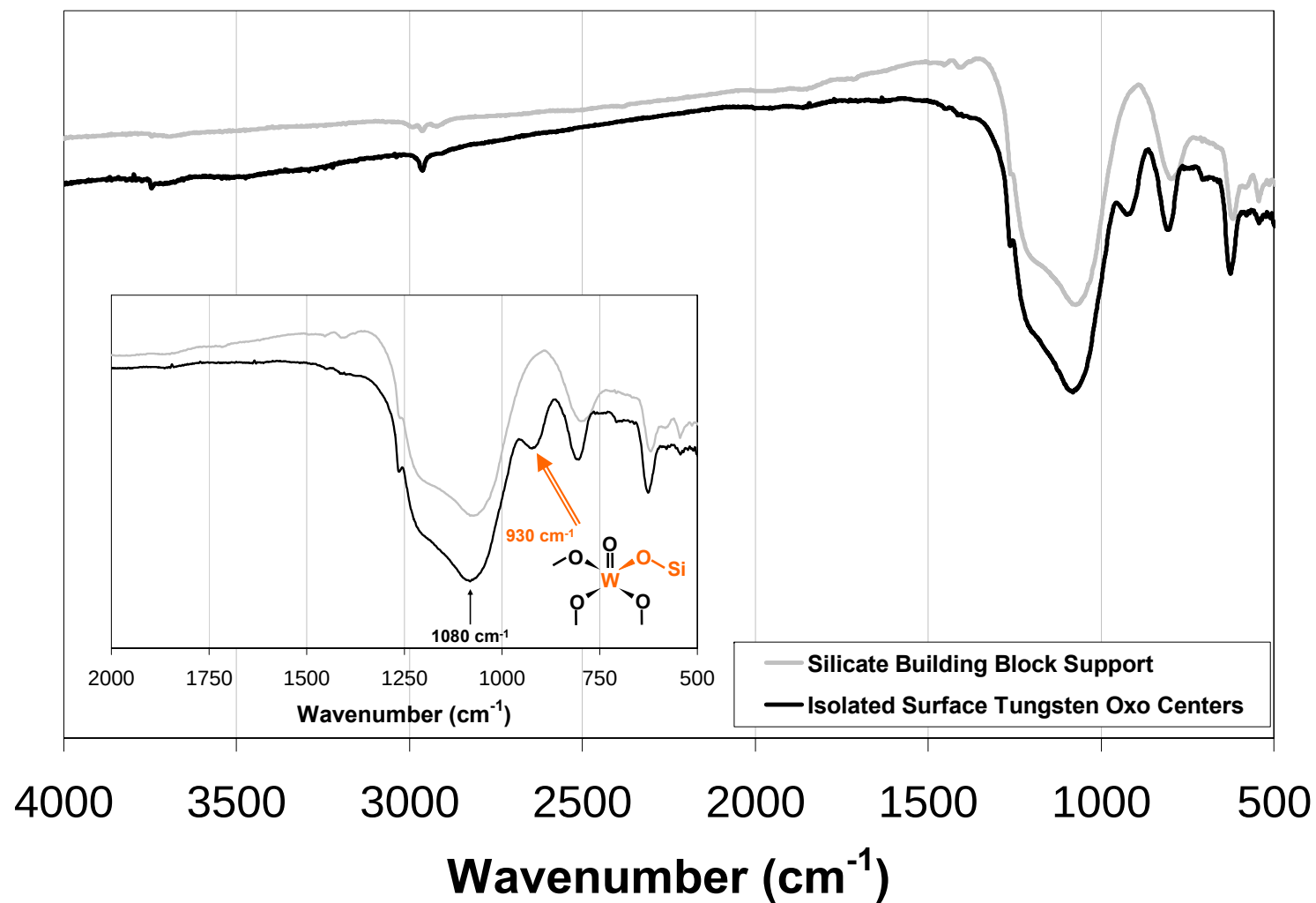
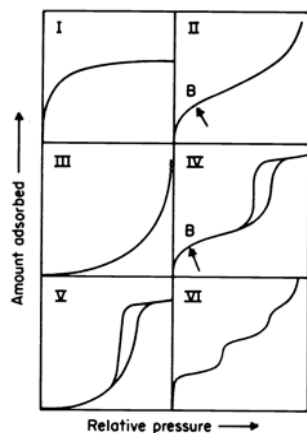


Figure 159: IR spectra (500-4000 cm⁻¹) of a premade tungsten-free silicate building block support and the material following the reaction of WOCl₄ and the premade silicate building block support. The inset contains the expanded IR spectrum (500-2000 cm⁻¹) which illustrates the W-O-Si shoulder (930 cm⁻¹).

Standard Isotherms



Standard Hysteresis Loops

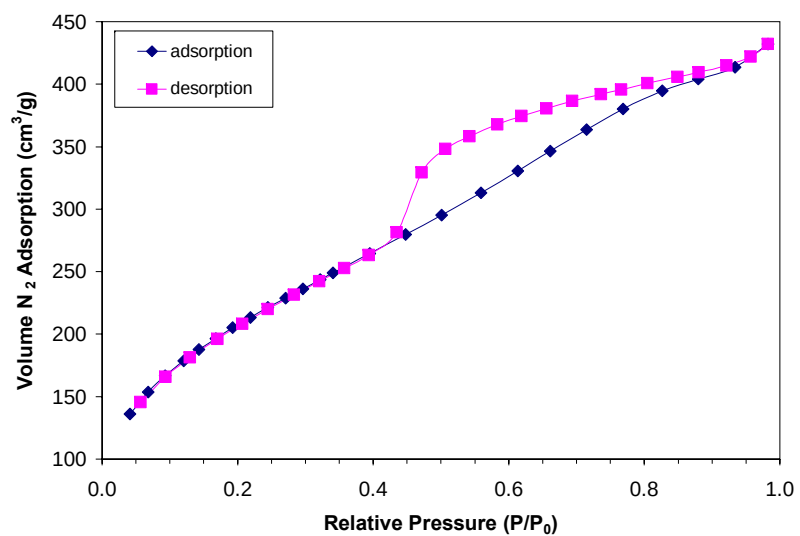
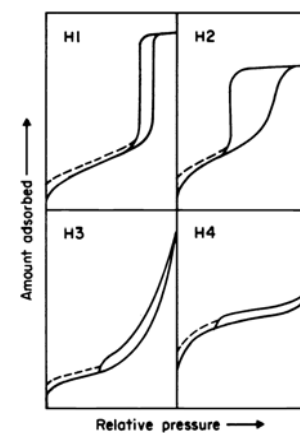


Figure 160: Nitrogen isotherm for the premade silicate building block support. Standard isotherms and hysteresis loops obtained from literature.[131]

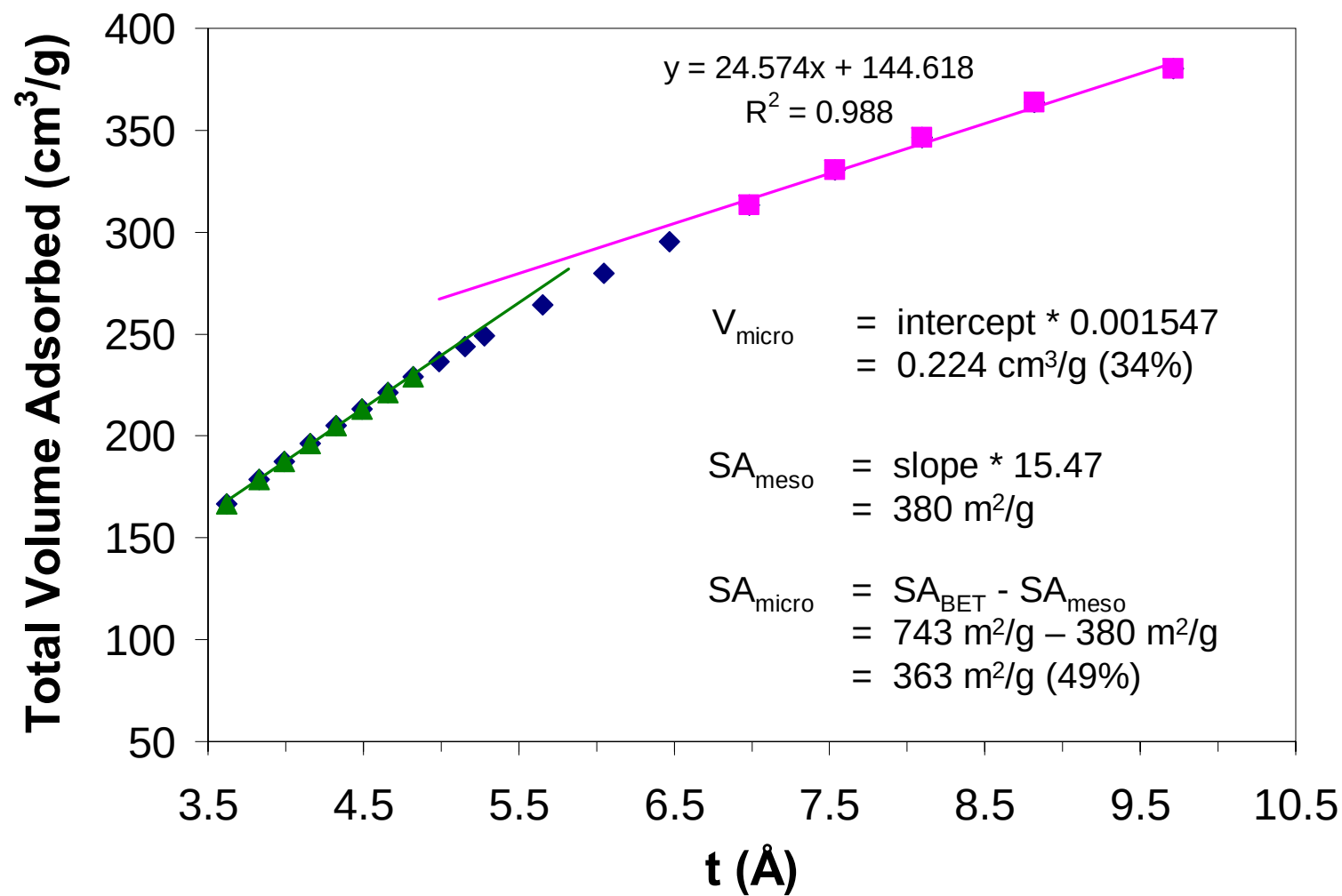


Figure 161: t-plot for the premade silicate building block support.

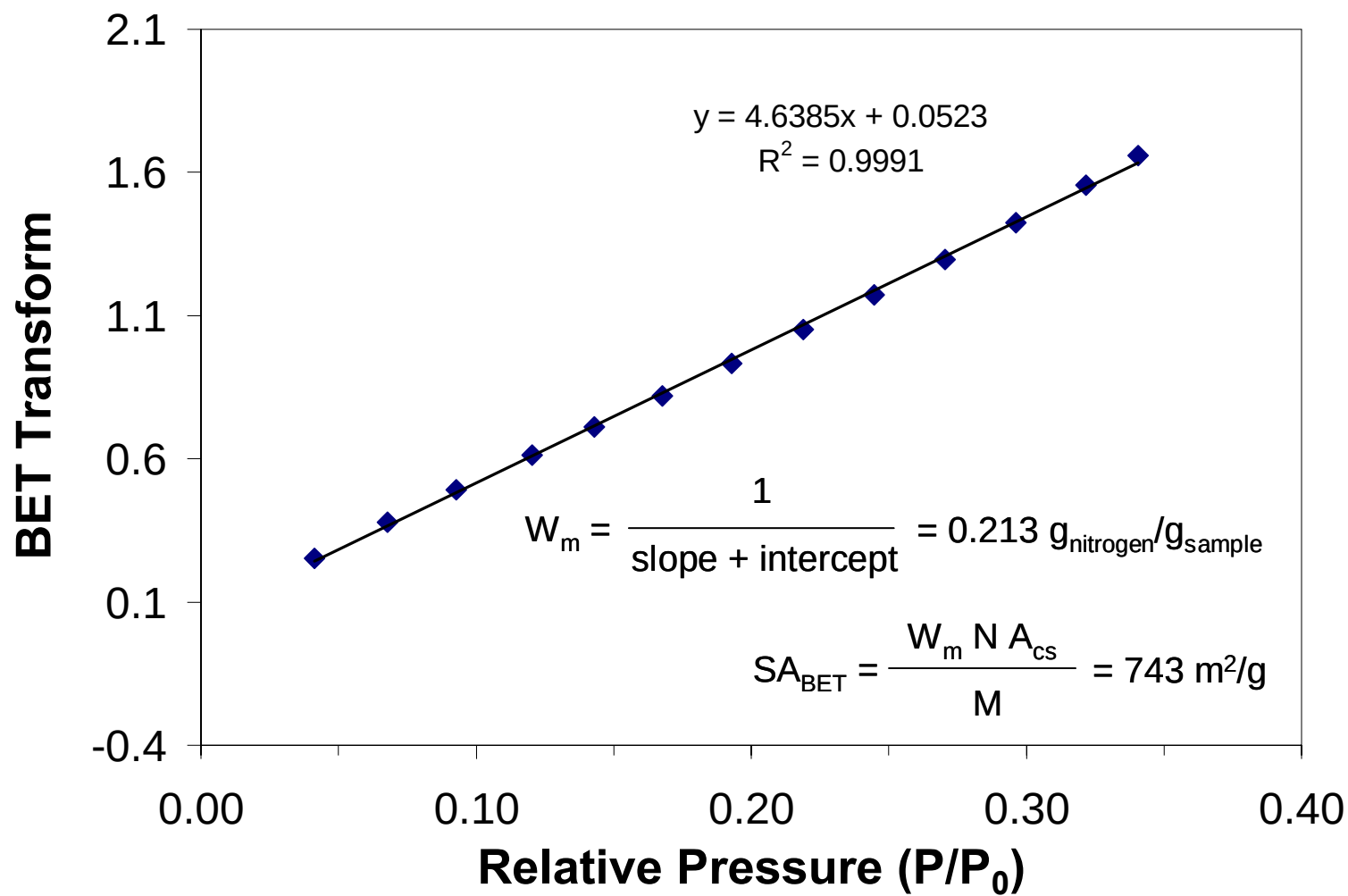


Figure 162: BET plot for the premade silicate building block support.

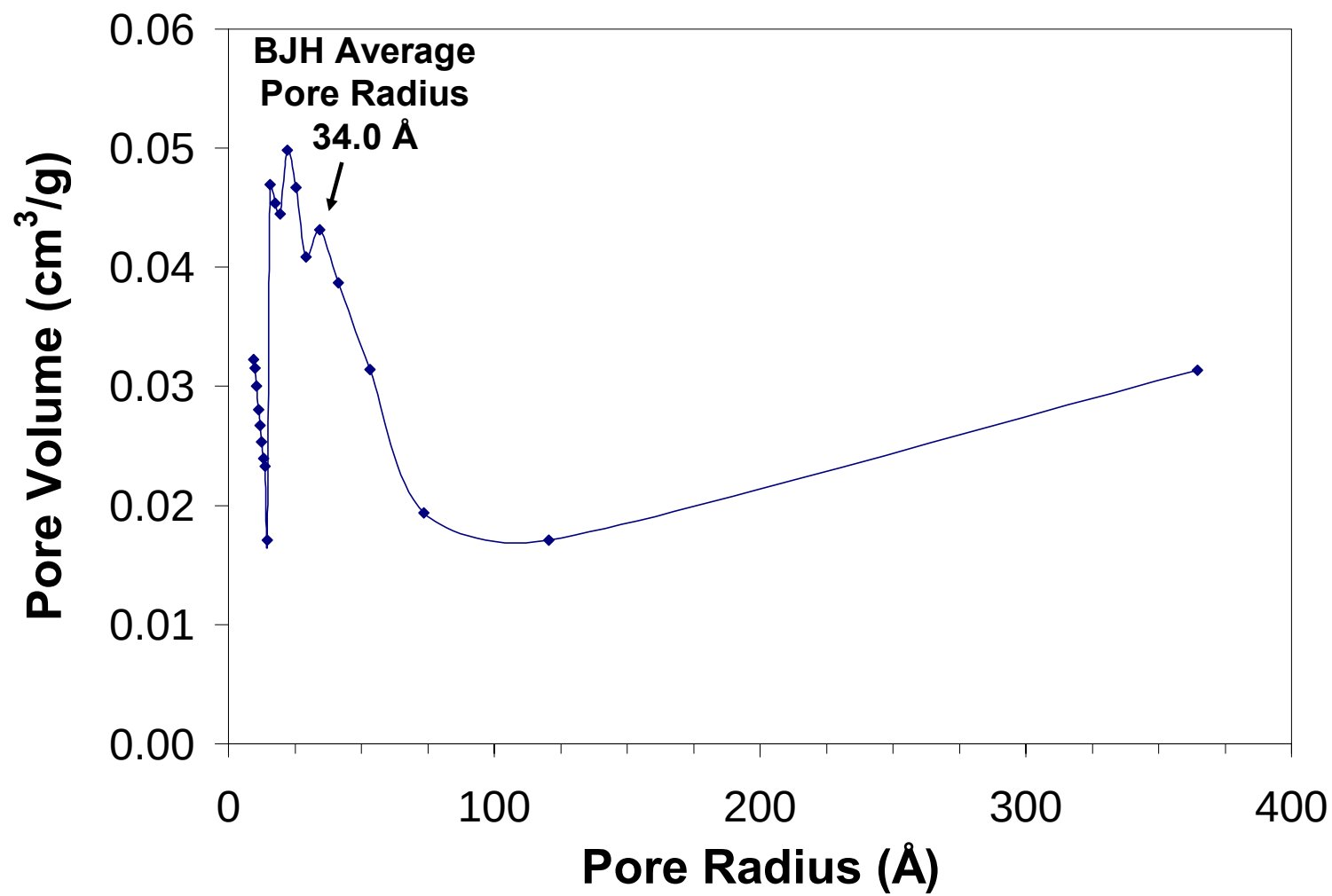
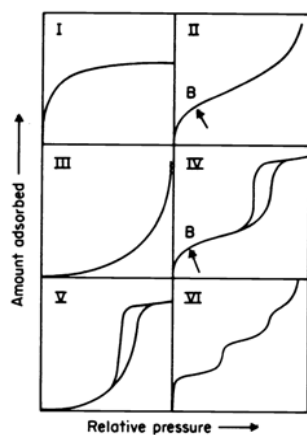


Figure 163: BJH pore size distribution plot for the premade silicate building block support.

Standard Isotherms



Standard Hysteresis Loops

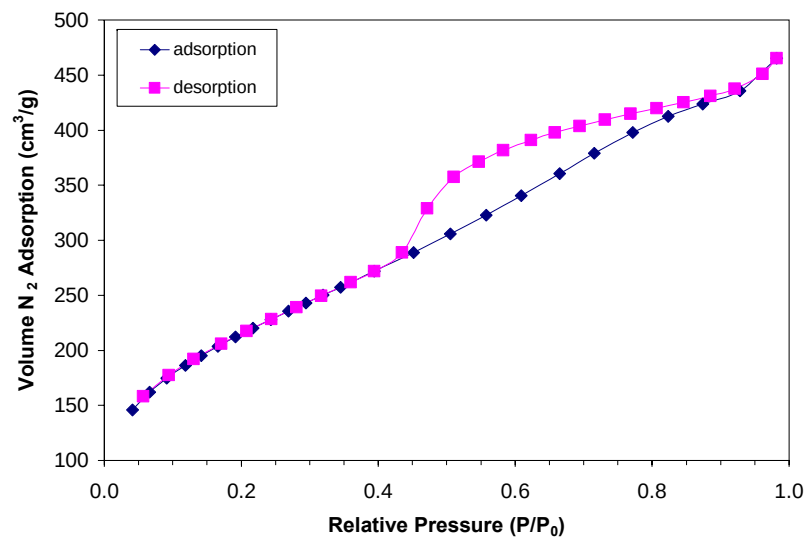
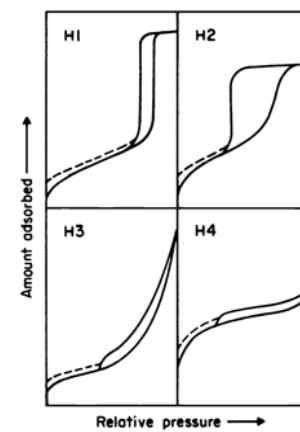


Figure 164: Nitrogen isotherm for the material following the reaction of WOCl_4 and the premade silicate building block support. Standard isotherms and hysteresis loops obtained from literature.[131]

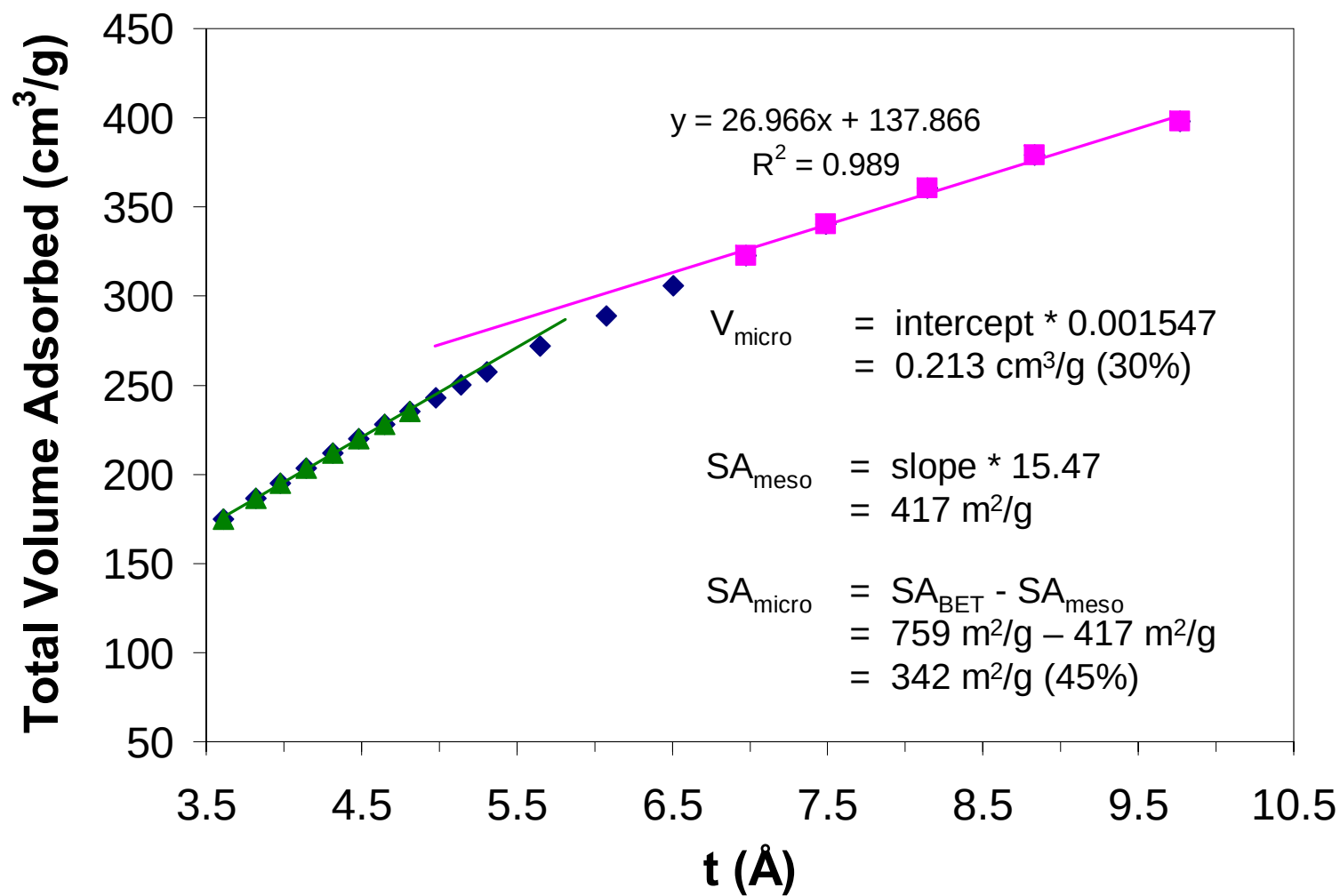


Figure 165: t-plot for the material following the reaction of WOCl_4 and the premade silicate building block support.

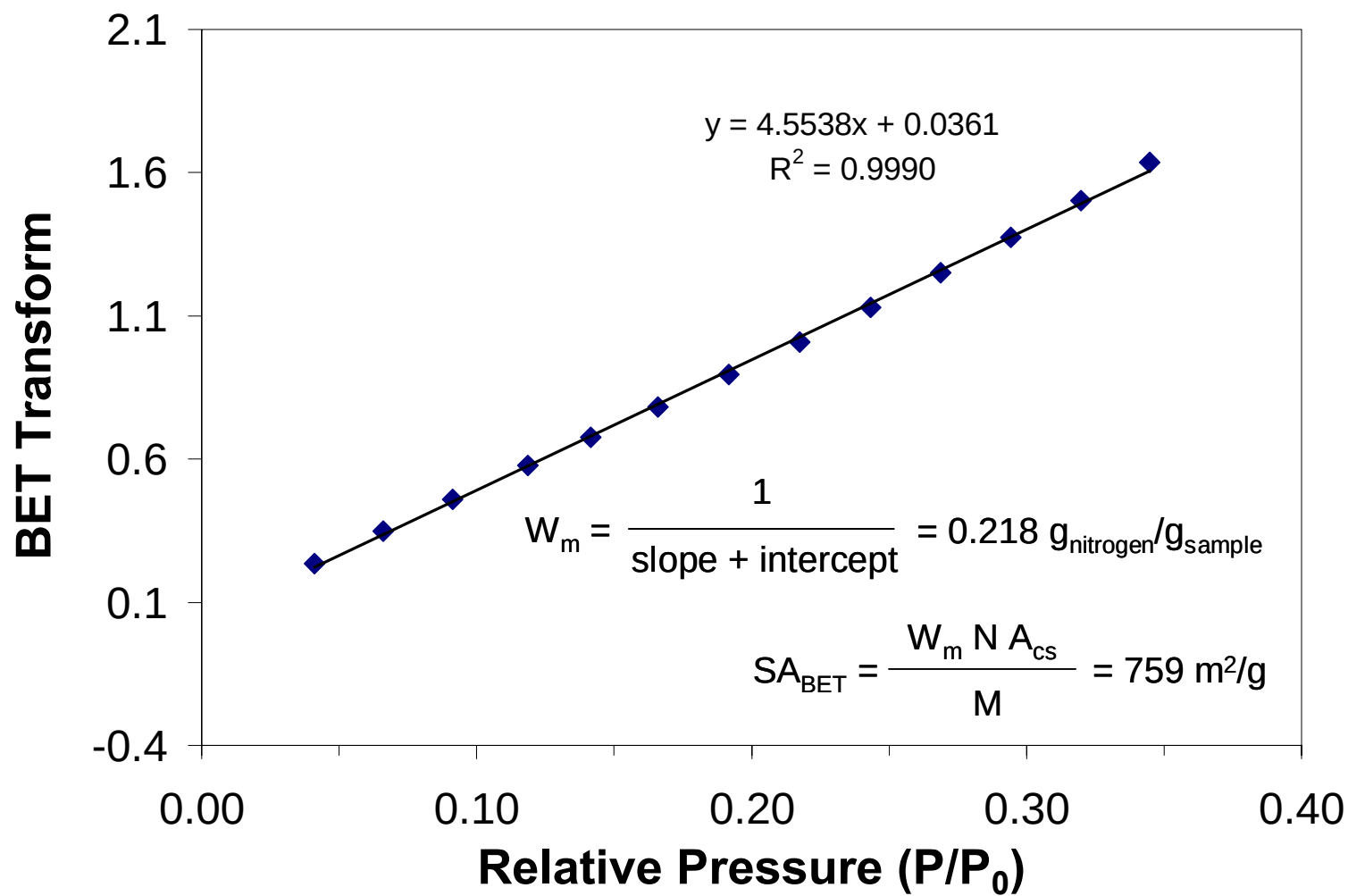


Figure 166: BET plot for the material following the reaction of WOCl_4 and the premade silicate building block support.

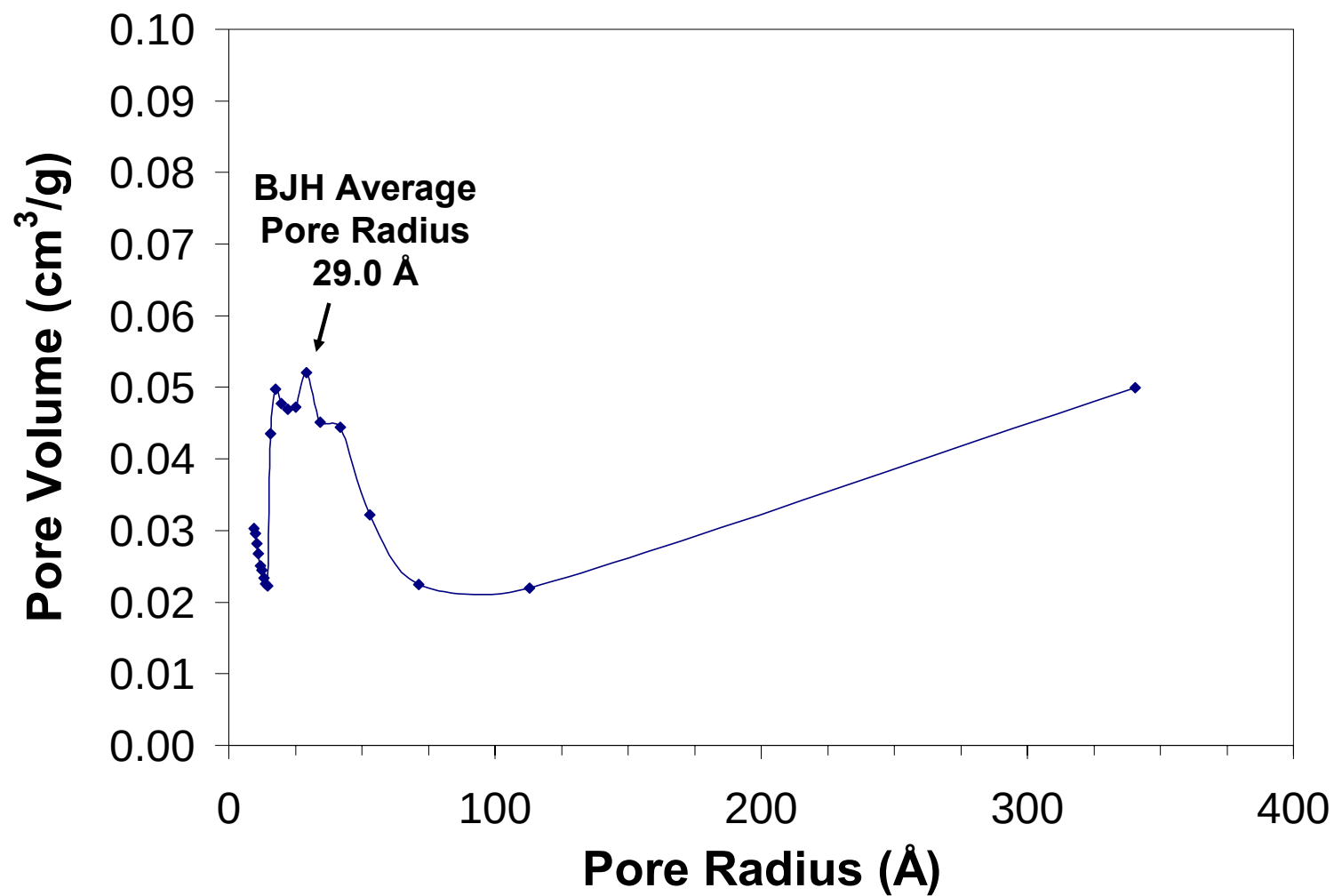


Figure 167: BJH pore size distribution plot for the material following the reaction of WOCl_4 and the premade silicate building block support.

XAS data were used to obtain more information about the coordination geometry and oxidation state of the tungsten oxo centers (XANES) in addition to the connectivity of the tungsten oxo centers (EXAFS).

XANES data for both the L_{III} (10207 eV) and the L_I (12100 eV) edges provide information about the coordination geometry and oxidation state of the tungsten oxo centers.[117]

Figure 168 shows the XANES and the derivative XANES spectra at the L_{III} edge of the material at this stage in the synthesis. The edge position of the surface tungsten oxo centers supports the claim that the oxidation state of the tungsten oxo centers is +6. As already mentioned, the intensity of the white line reflects the occupancy of the d-orbitals of the absorbing atom thus filling the d-orbitals of the absorbing atom suppresses the observed white line.[117] The ratio of the intensity of the white line relative to the edge jump for 5d transition metals shows a linear relationship with the number of valence electrons (Figure 169). This relationship was used to estimate the oxidation state of the tungsten centers present in the oligomers. The ratio for the surface tungsten oxo centers (3.45) supports the claim that the oxidation state of the tungsten centers is +6 (Figure 169). The width of the white line for the surface tungsten oxo centers provides evidence that the coordination geometry around the tungsten centers is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. The white line appears to be broad (width = 7.0 eV) which would suggest the coordination geometry is distorted octahedral (width = 7.4 eV) instead of tetrahedral (width = 4.9 eV) (Figure 170).

Figure 171 shows the XANES and the derivative XANES spectra at the L_I edge of the material at this stage in the synthesis. The edge position of the surface tungsten oxo centers supports the claim that the oxidation state of the tungsten oxo centers is +6. The presence of a pre-edge feature ($2s \rightarrow 5d$ transition) provides evidence that the coordination geometry around the tungsten oxo center is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. In general the intensity of the pre-edge feature is approximately 65% of the edge jump when the coordination geometry around the tungsten center is tetrahedral and is approximately 40% when the coordination geometry around the tungsten

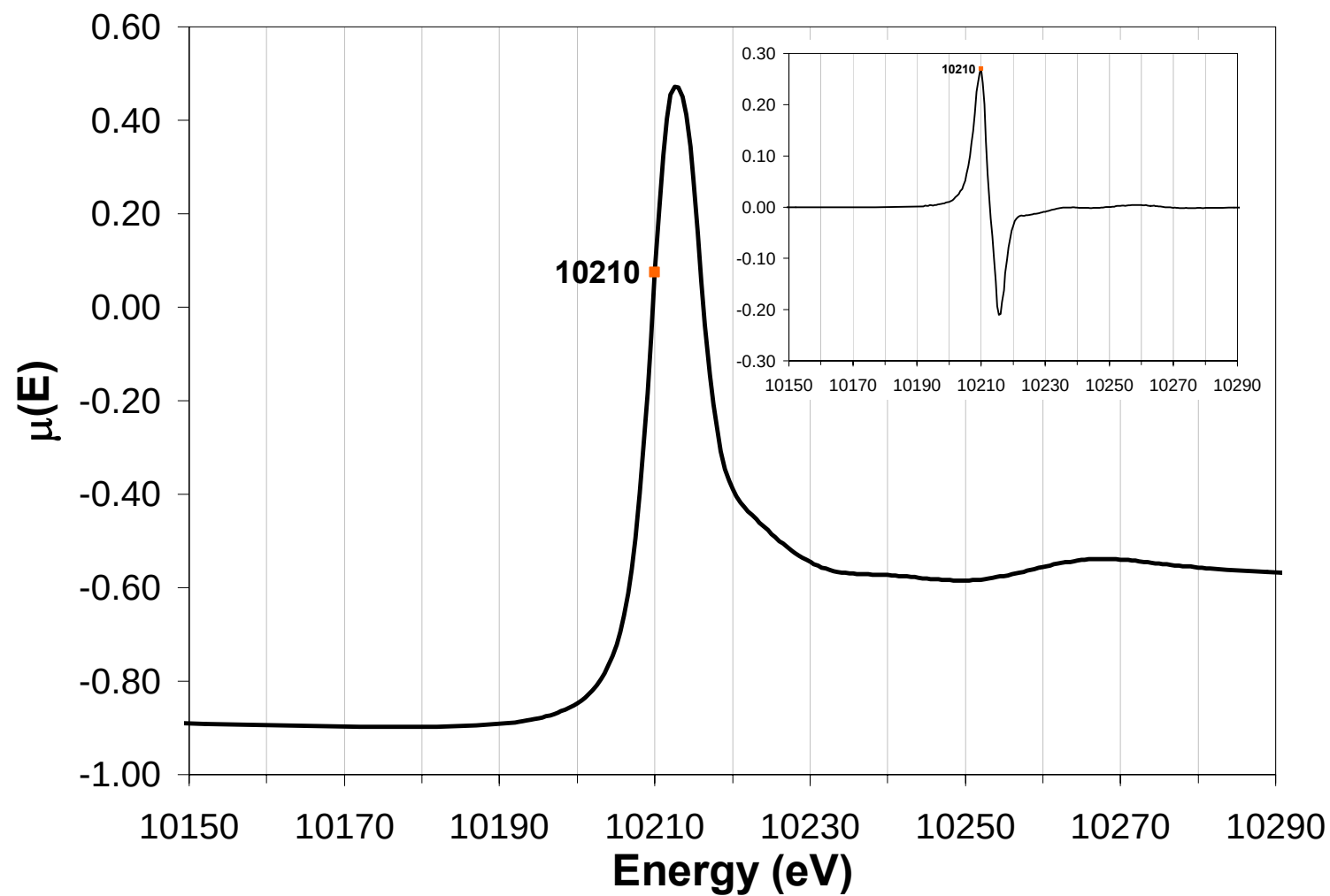


Figure 168: XANES spectrum (W L_{III} edge) following the reaction of WOCl₄ and the premade silicate building block support. The inset contains the derivative XANES spectrum with the position of the absorption edge (orange square) labeled.

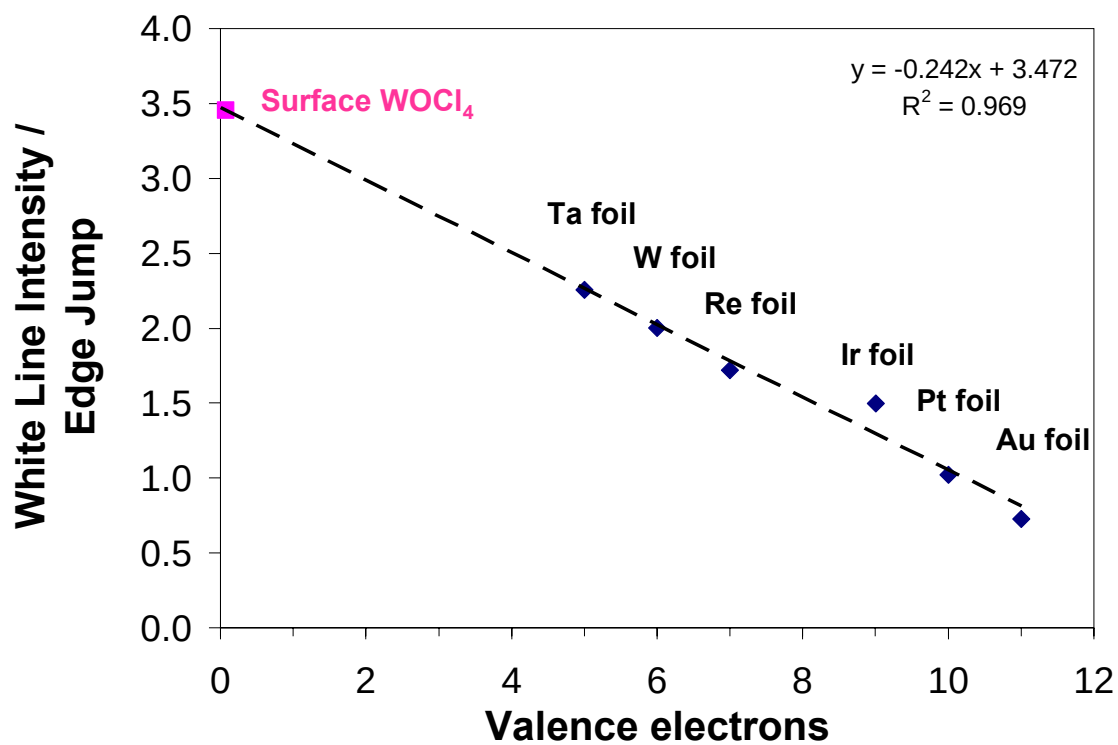


Figure 169: Relationship between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the reaction of WOCl₄ and the premade silicate building block support.

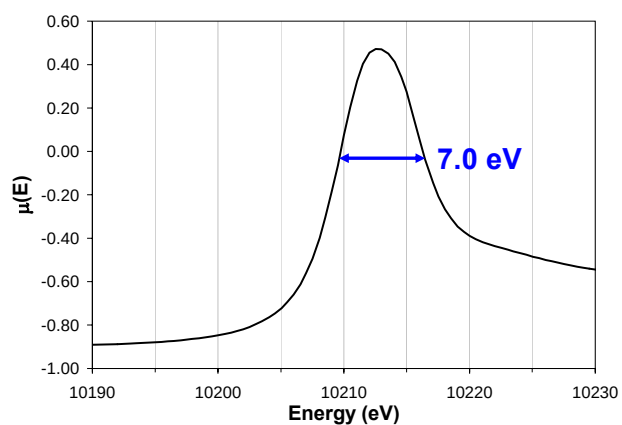
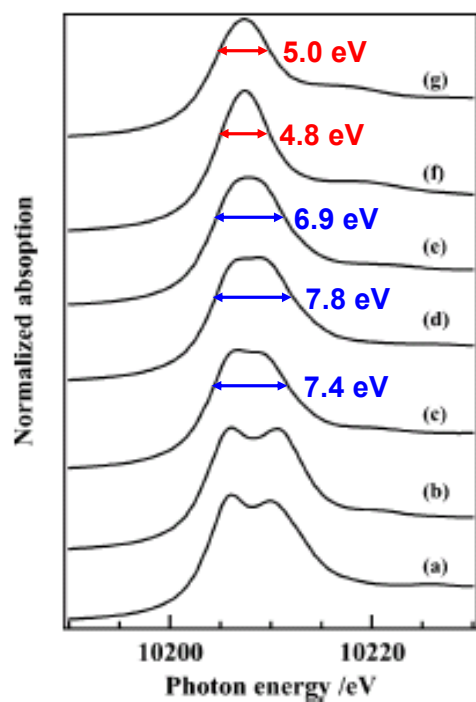


Figure 170: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the reaction of $WOCl_4$ and the premade silicate building block support (right).

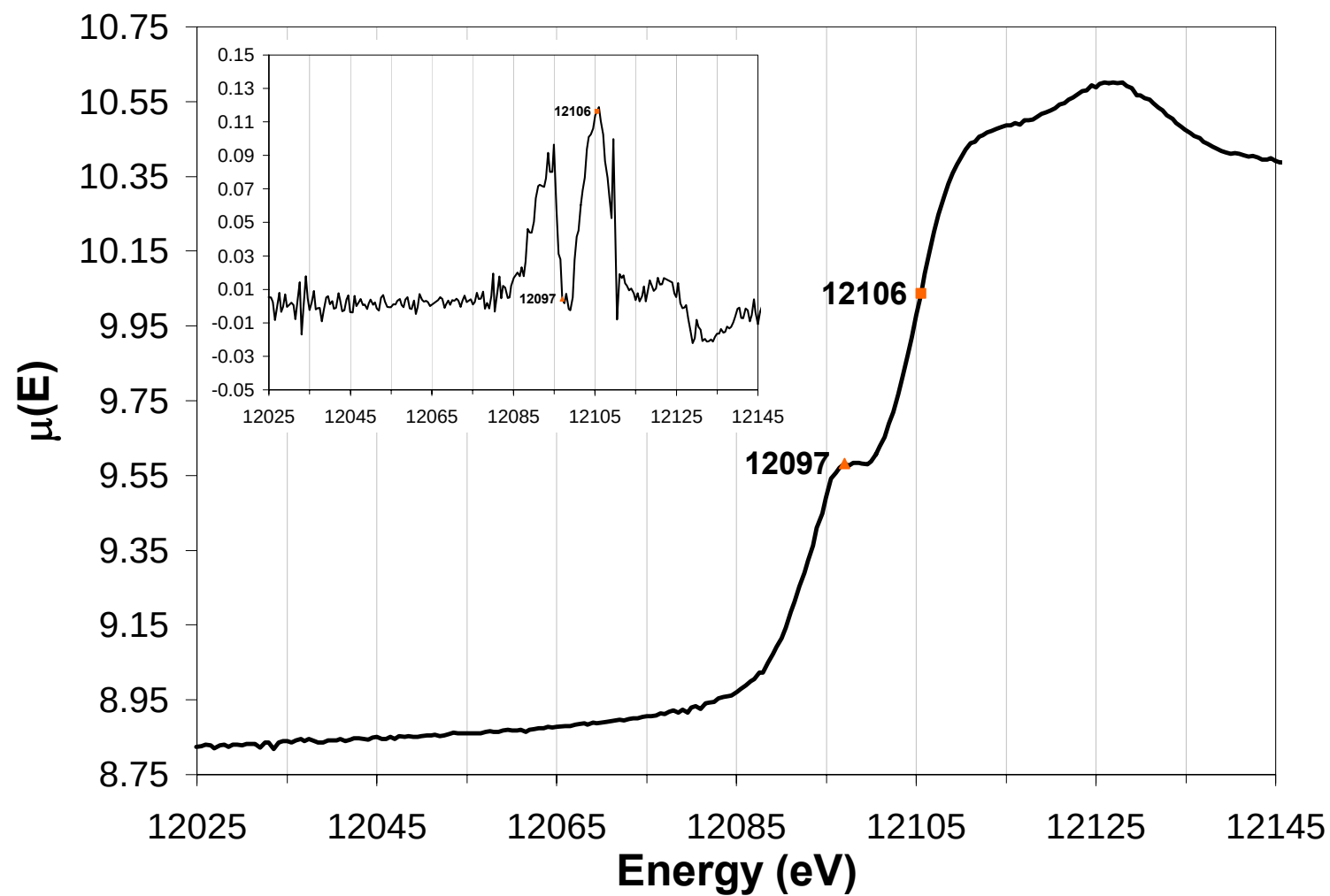


Figure 171: XANES spectrum (W L₁ edge) following the reaction of WOCl₄ and the premade silicate building block support. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

center is distorted octahedral.[117] The intensity of the pre-edge for the surface tungsten oxo centers is approximately 45% which suggests the coordination geometry is distorted octahedral.

In summary, the analysis of the XANES spectra at the L_{III} and the L_I edges suggests the surface tungsten oxo centers have distorted octahedral coordination geometry and that the oxidation state of the surface tungsten oxo centers is +6.

EXAFS data were used to obtain more information about the connectivity of the surface tungsten oxo centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around tungsten) can be qualitatively determined by looking at the magnitude R-space plot (Figure 172). Based on the data already presented, as many as four shells should be present around the tungsten centers after the first cross-linking reaction: a shell of terminal doubly bound oxygen atoms ($W=O$), a shell of singly bound oxygen atoms ($W-O$), a shell of any unreacted chloride ligands ($W-Cl$), and a shell of nonbonded silicon atoms ($W\cdots Si$). Figure 172 shows the four features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot.

Based on the qualitative analysis of the EXAFS data, the first coordination sphere (defined as atoms directly bound to the tungsten) of the surface tungsten oxo centers should have at least one terminal doubly bound oxygen atom ($W=O$), at least one singly bound oxygen atoms ($W-O$) and at least one singly bound chloride atoms ($W-Cl$). The second coordination sphere should have as many nonbonded silicon atoms as first shell singly bound oxygen atoms ($W\cdots Si$). In order to obtain quantitative information a structural model must first be proposed.

The first structural model that was used to fit the data was constructed based on the gravimetric data. A structural model containing $W=O$ (CN=1), $W-O$ (CN=2), $W-Cl$ (CN=2), and $W\cdots Si$ (CN=2) single scattering paths was constructed (Figure 173). The value of S_0^2 (0.92) was obtained from FEFF8. The CN values based on the results of gravimetric analysis and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 174 with the EXAFS data range used to fit the model is boxed (3.6 to 13.5 $\text{\AA}^{-1}$). In R-space, the fit range is from 1.0 to 4.0 $\text{\AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 175 and Figure 176

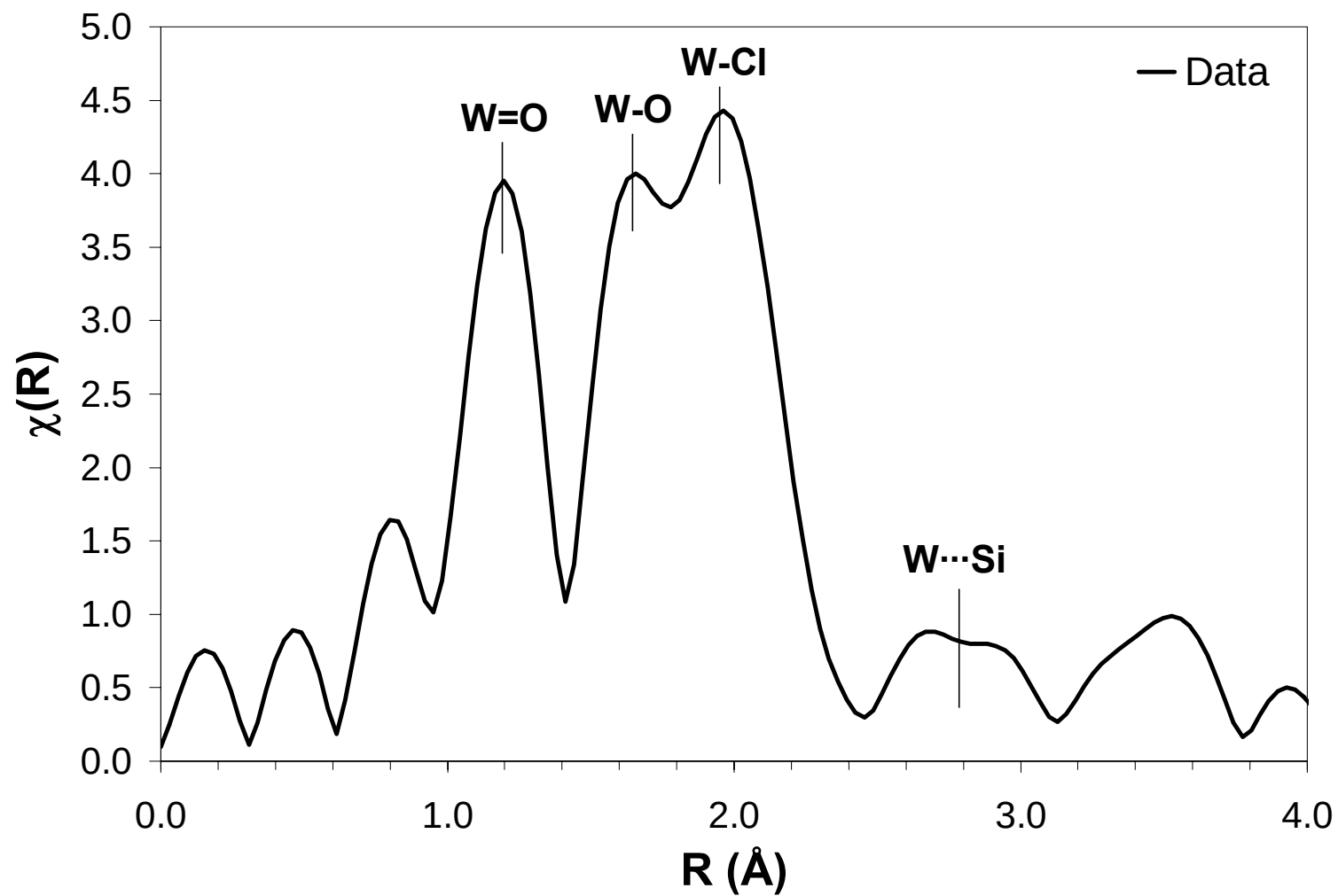


Figure 172: EXAFS R-space plot following the reaction of WOCl_4 and the premade silicate building block support. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

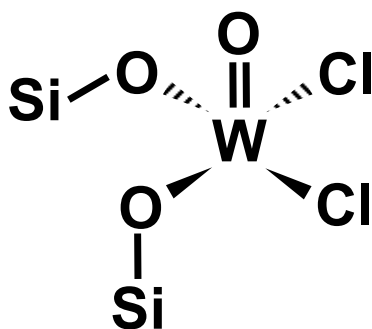


Figure 173: Structural model used for EXAFS data analysis of the isolated surface tungsten oxo centers. The model contains a tungsten center with one terminal doubly bound oxygen (W=O), two singly bound oxygen atoms (W-O), two singly bound chloride ligands (W-Cl), and two nonbonded silicon atoms (W $\cdots$ Si).

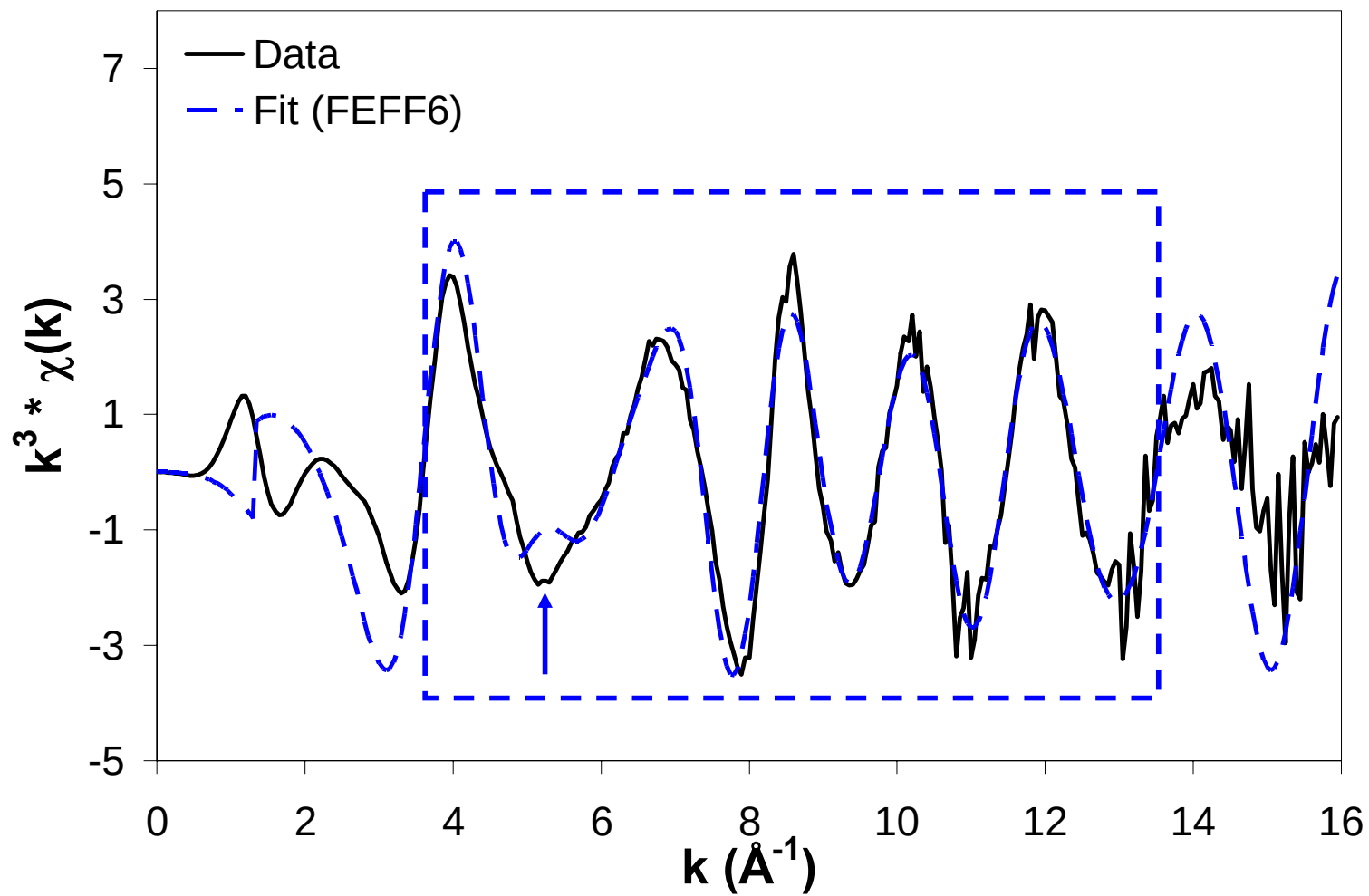


Figure 174: EXAFS k-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 173.

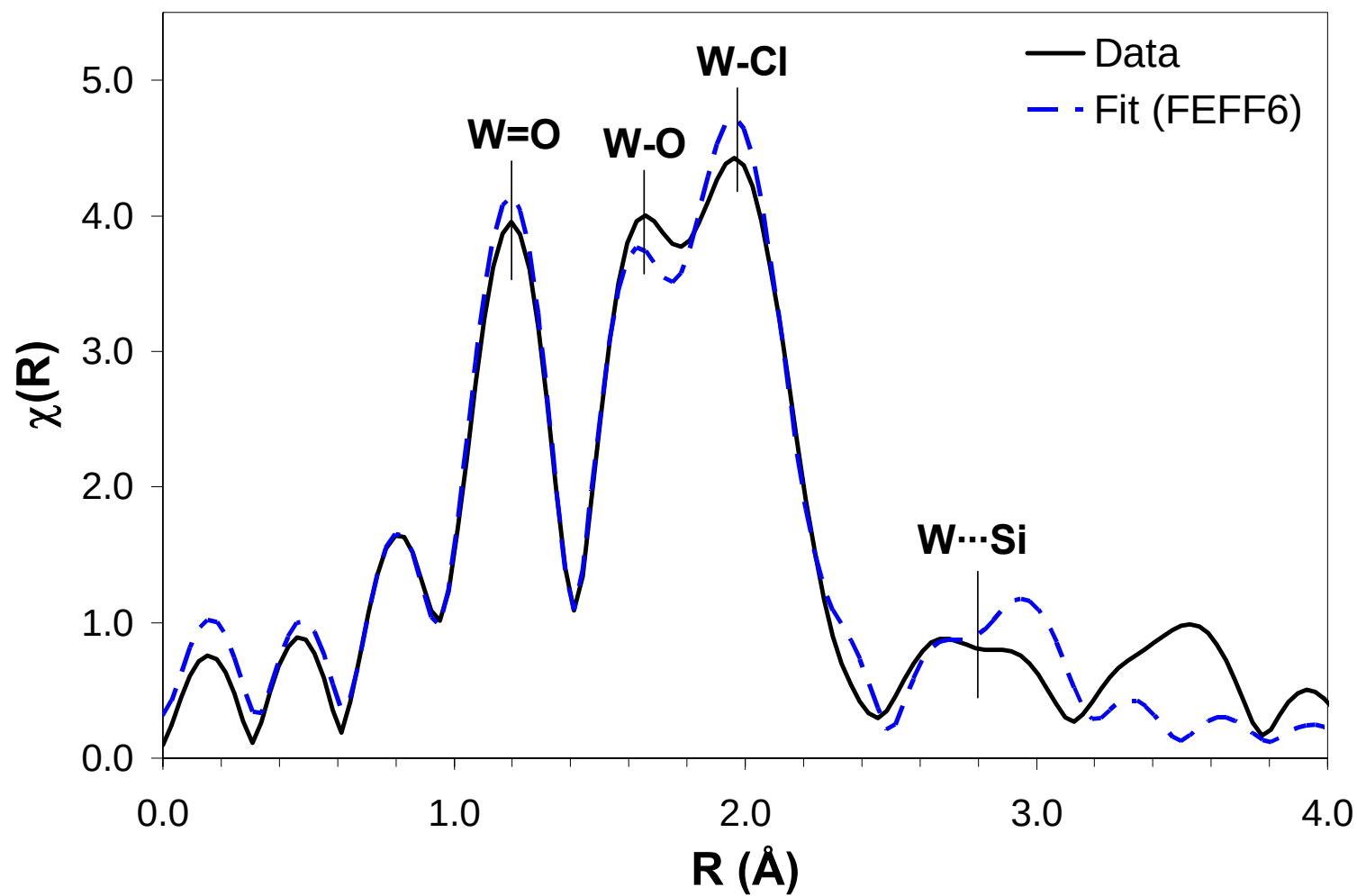


Figure 175: EXAFS R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 173. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

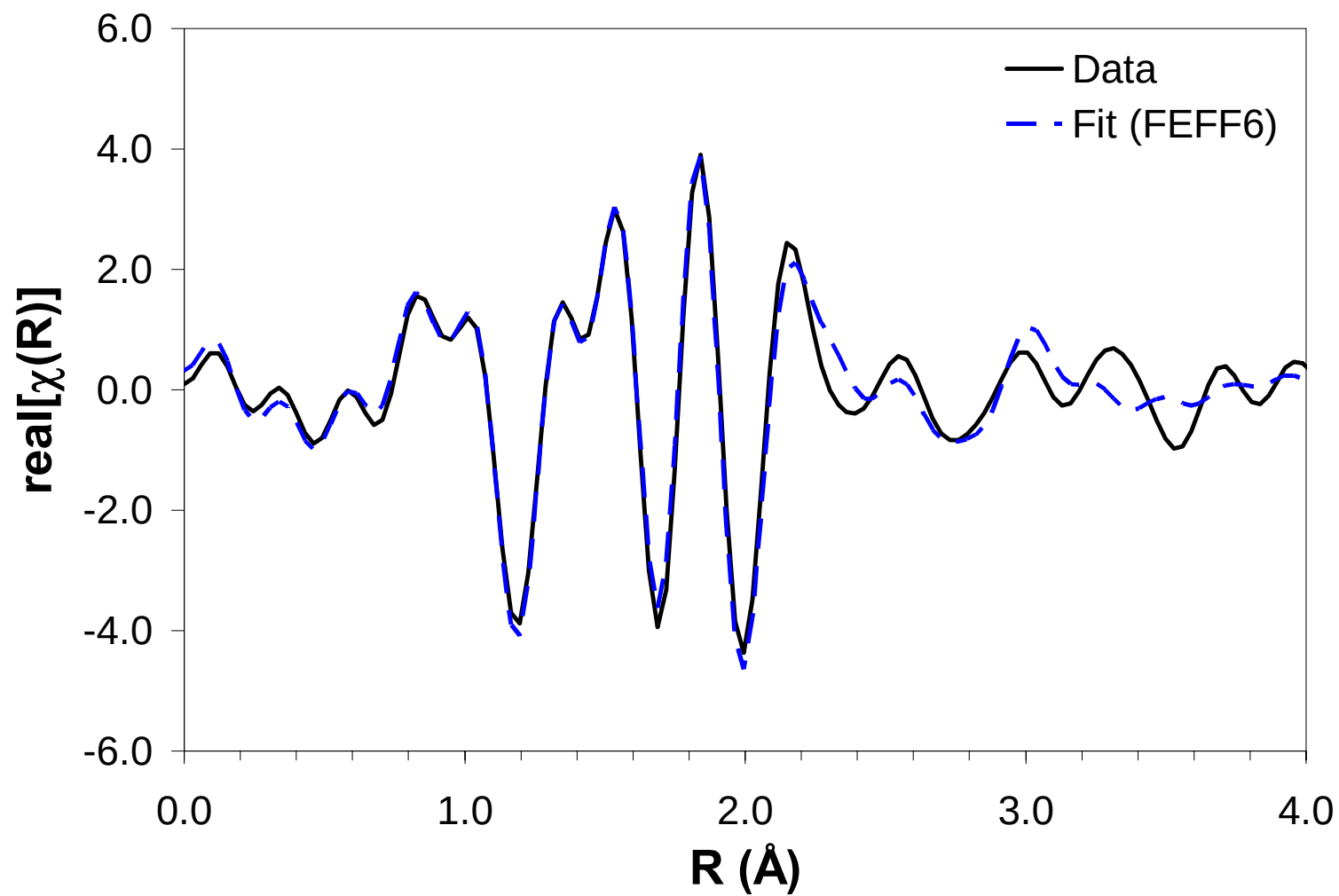


Figure 176: EXAFS real R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 173. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

respectively. Table 10 summarizes the refined values of the structural parameters. The value of $\sigma^2(\text{W}=\text{O})$ is slightly negative, which can be an indication that the model is incorrect. Also the model does not appear to fit the data well between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the blue arrow) as seen in Figure 174. For these reason a different model was tried to see if the fit improved.

The second structural model that was used to fit the data was constructed based on the original predicted catalyst ensemble. A structural model containing $\text{W}=\text{O}$ (CN=1), $\text{W}-\text{O}$ (CN=1), $\text{W}-\text{Cl}$ (CN=3), and $\text{W}\cdots\text{Si}$ (CN=1) single scattering paths was constructed (Figure 177). The same value of S_0^2 was used. The CN values based on the model and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 178 with the EXAFS data range used to fit the model is boxed (3.6 to $13.5 \text{ \AA}^{-1}$). In R-space, the fit range is from 1.0 to $4.0 \text{ \AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 179 and Figure 180 respectively. Table 10 summarizes the refined values of the structural parameters. The value of $\sigma^2(\text{W}=\text{O})$ and $\sigma^2(\text{W}-\text{O})$ are slightly negative, which can be an indication that the model is incorrect. Also the model does not appear to fit the data well between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the red arrow) as seen in Figure 178. For these reason a different model was tried to see if the fit improved.

The third structural model that was used to fit the data was constructed based on the gravimetric data. A structural model containing $\text{W}=\text{O}$ (CN=1), $\text{W}-\text{O}$ (CN=3), $\text{W}-\text{Cl}$ (CN=1), and $\text{W}\cdots\text{Si}$ (CN=3) single scattering paths was constructed (Figure 181). The same value of S_0^2 was used. The CN values based on the model and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 182 with the EXAFS data range used to fit the model is boxed (3.6 to $13.5 \text{ \AA}^{-1}$). In R-space, the fit range is from 1.0 to $4.0 \text{ \AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 183 and Figure 184 respectively. Table 10 summarizes the refined values of the structural parameters. This model fits the data much better than the other two, specifically all the refined values are within acceptable limits and there is little deviation between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the green arrow) as seen in Figure 182.

Table 10: EXAFS fit values for isolated surface tungsten oxo centers

Fit values using structural model in Figure 173				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.700	1.876	2.351	3.217
σ^2 (Å ²)	-0.078 x 10 ⁻³	1.42 x 10 ⁻³	6.95 x 10 ⁻³	12.50 x 10 ⁻³
E ₀ (eV)	6.7 ± 2.0	6.7 ± 2.0	6.7 ± 2.0	6.7 ± 2.0
CN	1 (set)	2 (set)	2 (set)	2 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.7, N _{var} = 9, χ ² = 370, reduced χ ² = 38, R-factor = 0.053, FT k region = 3.570 – 13.491 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Fit values using structural model in Figure 177				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.747	1.902	2.375	3.223
σ^2 (Å ²)	-0.061 x 10 ⁻³	-2.77 x 10 ⁻³	12.05 x 10 ⁻³	5.92 x 10 ⁻³
E ₀ (eV)	10.9 ± 2.9	10.9 ± 2.9	10.9 ± 2.9	10.9 ± 2.9
CN	1 (set)	1 (set)	3 (set)	1 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.7, N _{var} = 9, χ ² = 842, reduced χ ² = 87, R-factor = 0.120, FT k region = 3.570 – 13.491 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Fit values using structural model in Figure 181				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.665	1.851	2.327	3.189
σ^2 (Å ²)	0.66 x 10 ⁻³	5.56 x 10 ⁻³	2.16 x 10 ⁻³	17.95 x 10 ⁻³
E ₀ (eV)	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8
CN	1 (set)	3 (set)	1 (set)	3 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.7, N _{var} = 9, χ ² = 383, reduced χ ² = 40, R-factor = 0.055, FT k region = 3.570 – 13.491 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

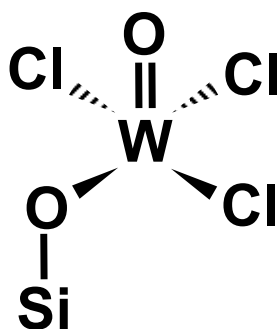


Figure 177: Structural model used for EXAFS data analysis of the isolated surface tungsten oxo centers. The model contains a tungsten center with one terminal doubly bound oxygen (W=O), one singly bound oxygen atoms (W-O), three singly bound chloride ligands (W-Cl), and one nonbonded silicon atoms (W $\cdots$ Si).

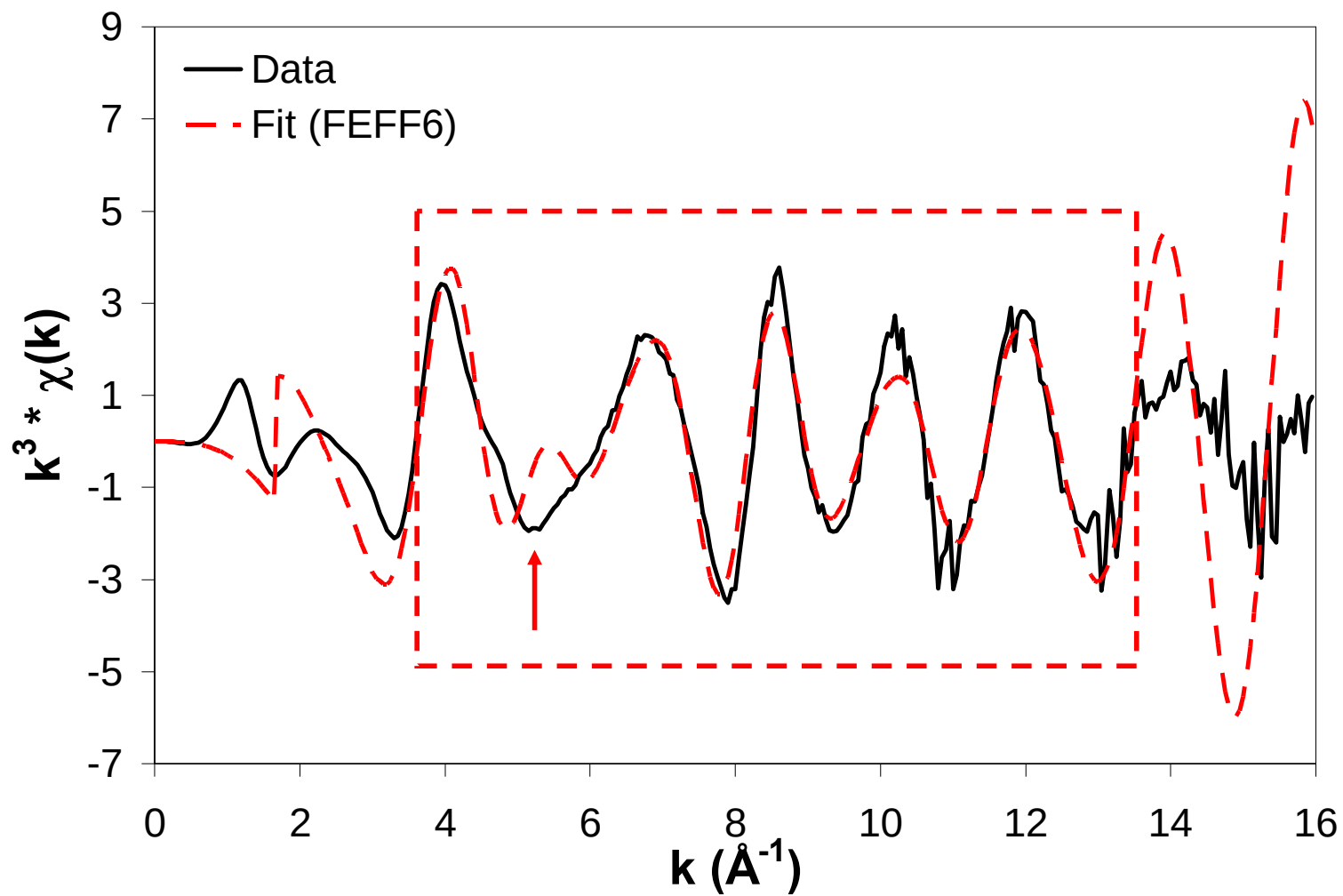


Figure 178: EXAFS k-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 177.

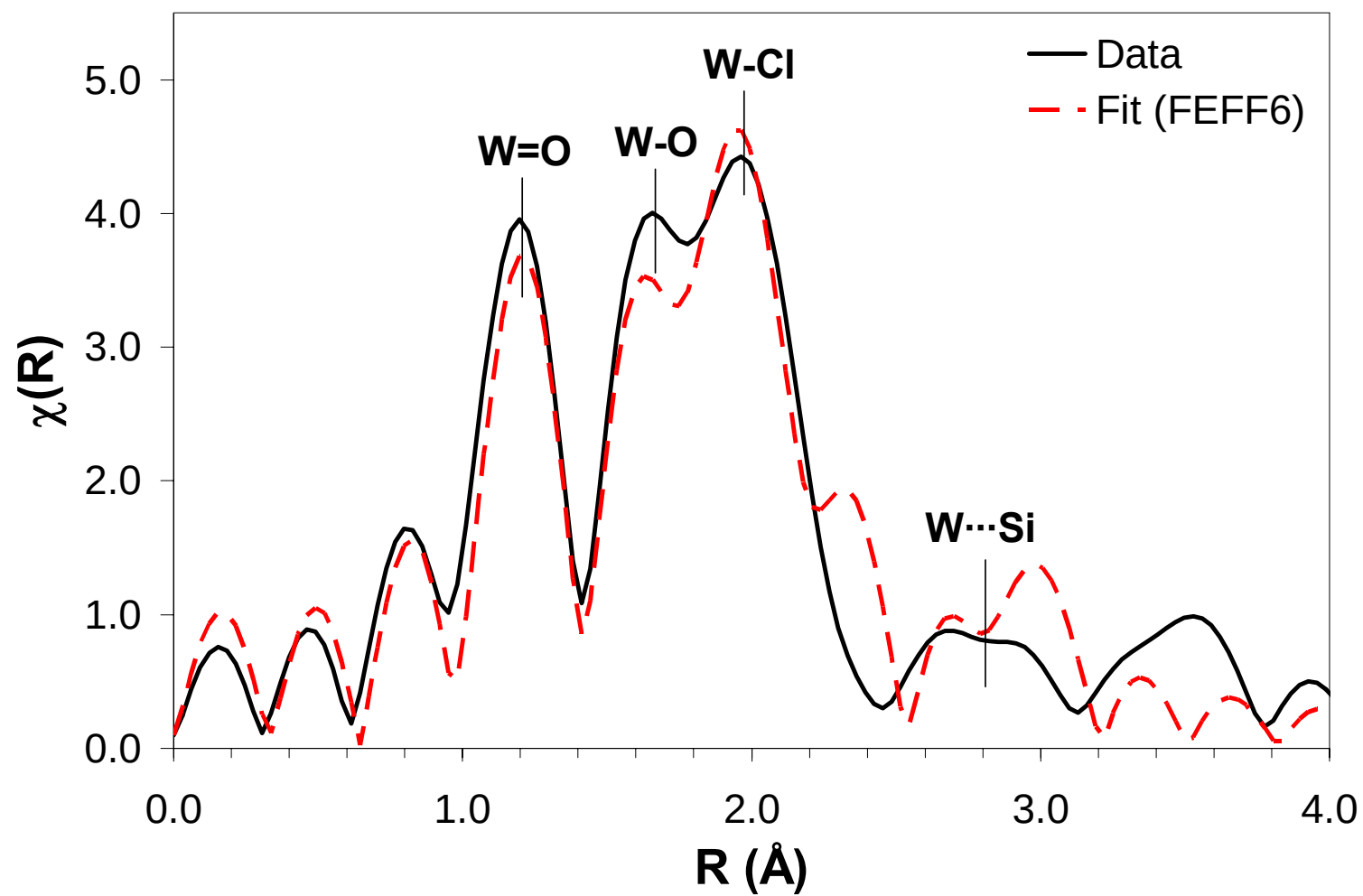


Figure 179: EXAFS R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 177. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

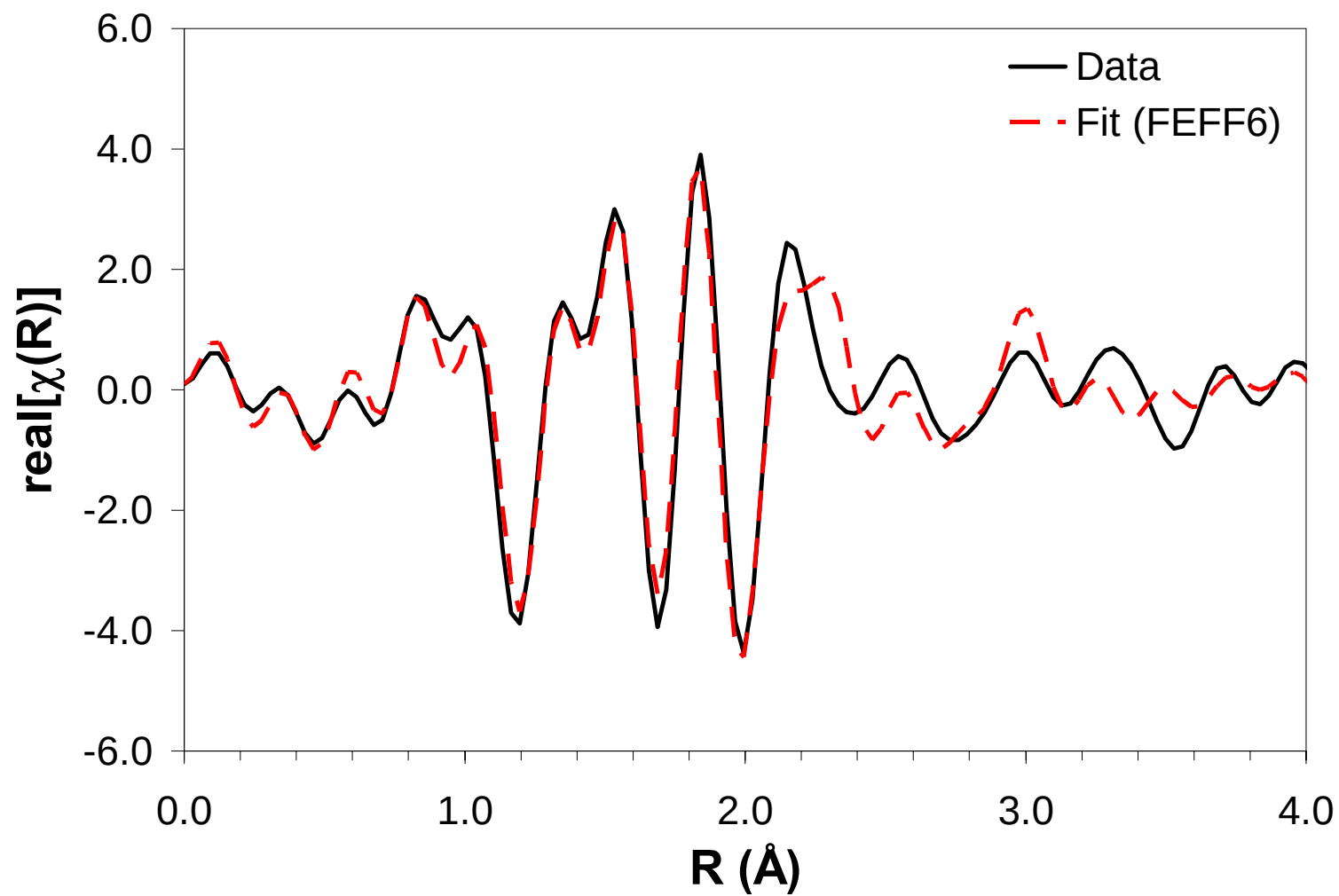


Figure 180: EXAFS real R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 177. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

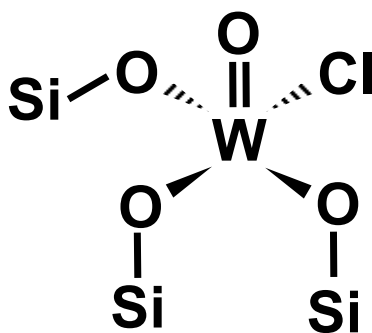


Figure 181: Structural model used for EXAFS data analysis of the isolated surface tungsten oxo centers. The model contains a tungsten center with one terminal doubly bound oxygen (W=O), three singly bound oxygen atoms (W-O), one singly bound chloride ligands (W-Cl), and three nonbonded silicon atoms (W...Si).

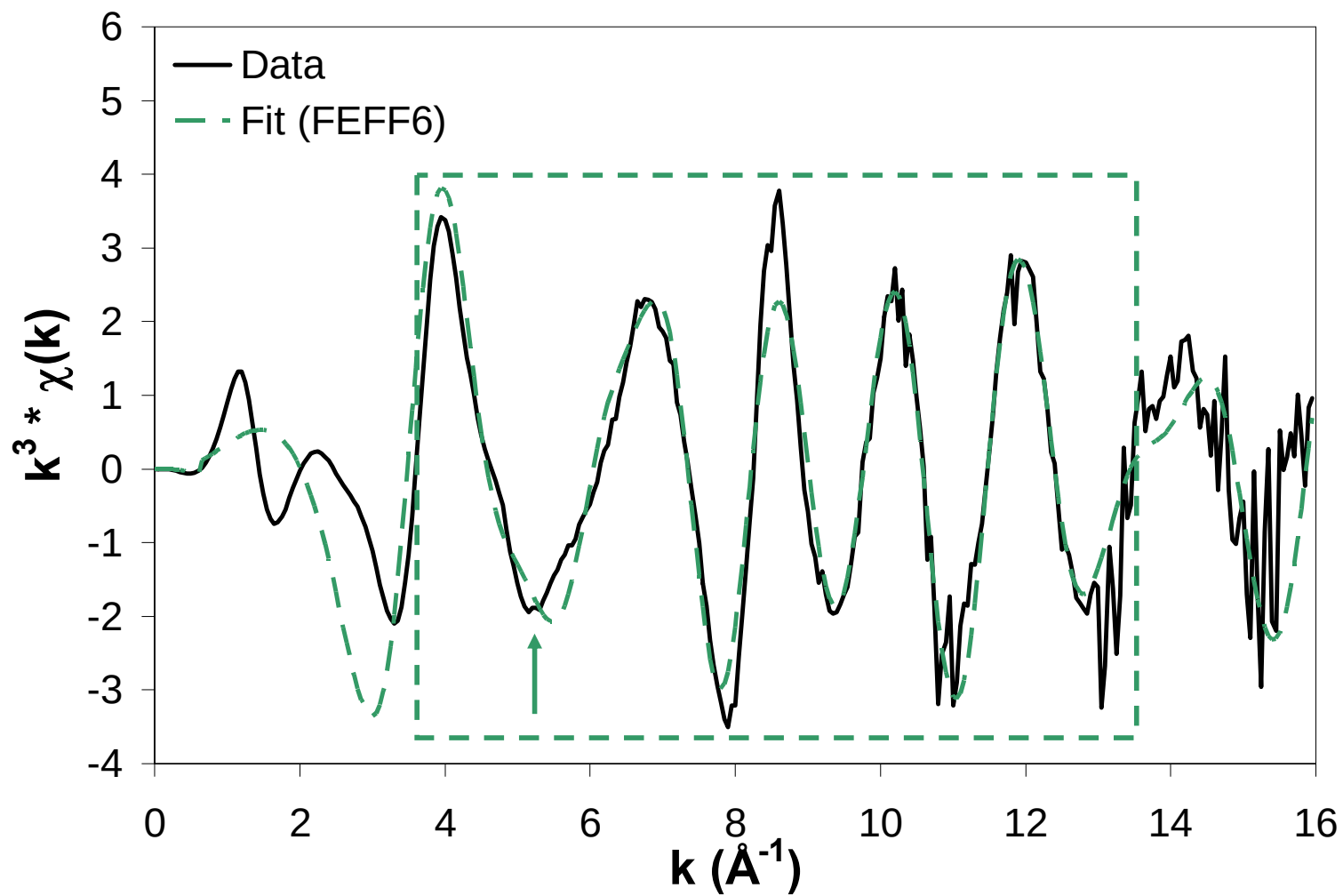


Figure 182: EXAFS k-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 181.

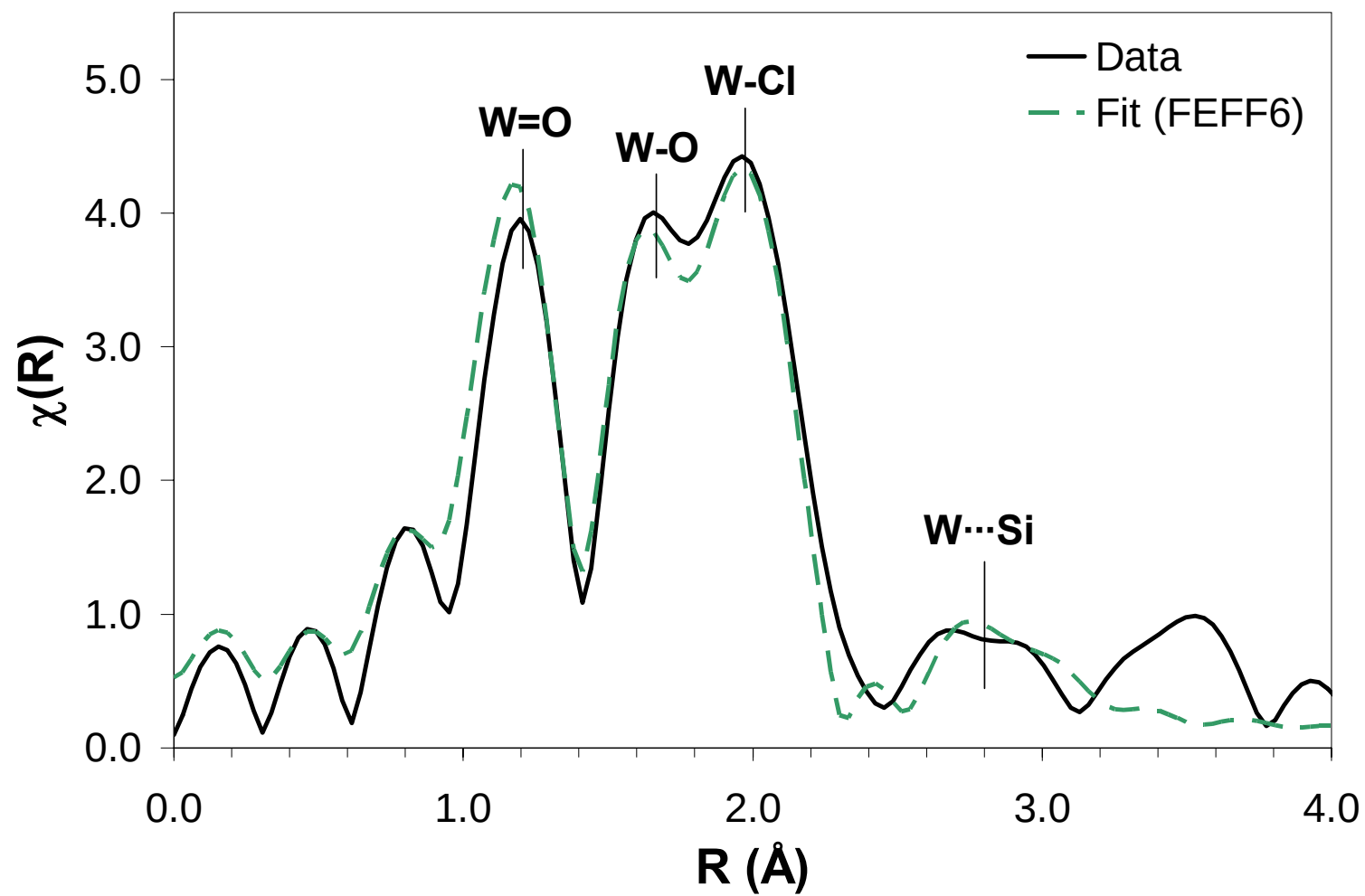


Figure 183: EXAFS R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 181. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

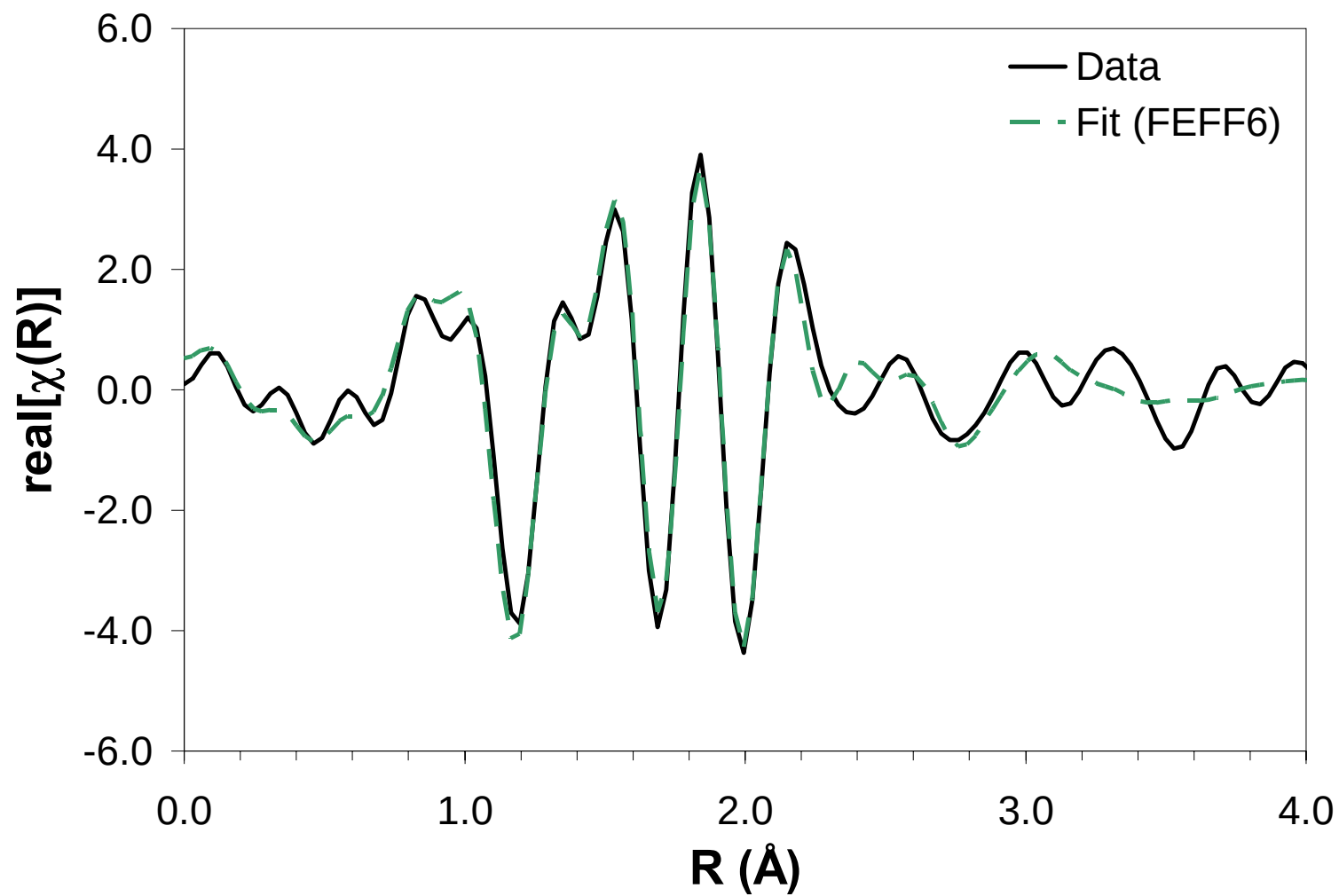


Figure 184: EXAFS real R-space plot following the reaction of WOCl_4 and the premade silicate building block support using the structural model in Figure 181. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

In summary, the EXAFS data analysis suggests that the immediate environment around the surface tungsten oxo centers (1 W=O, 3 W-O, 1 W-Cl and 3 W...Si) is different than initially predicted as seen in Figure 185.

Figure 186 shows the ^{29}Si SSNMR spectra of the premade tungsten-free silicate building block support and the isolated surface tungsten oxo centers. The signals between -22 and -100 ppm in the spectrum are characteristic of the different silyl chlorides generated during the second cross-linking reaction (i.e. $(=\text{SiO})_{4-x}\text{SiCl}_x$).^[95] The ^{29}Si SSNMR spectrum between -22 and -100 ppm does not change significantly following the linking of the surface tungsten oxo centers to the silicate building block support which suggests that the linking reaction does not disrupt the bulk of the silicate building block support. The major difference between the two spectra is observed between -100 and -110 ppm. The signals between -100 ppm and -110 ppm are assigned to the silicon corners on the building block which are connected to unreacted Me_3Sn groups ($(=\text{SiO})_3\text{Si}(\text{OSnMe}_3)$), connected to the tungsten centers ($(=\text{SiO})_3\text{Si}(\text{OW}=\equiv)$), and connected to the silicon centers ($(=\text{SiO})_3\text{Si}(\text{OSi}=\equiv)$). Signals assigned to $(=\text{SiO})_3\text{Si}(\text{OSnMe}_3)$ and $(=\text{SiO})_3\text{Si}(\text{OW}=\equiv)$ are typically observed around -104 ppm while signals assigned to $(=\text{SiO})_3\text{Si}(\text{OSi}=\equiv)$ are typically observed around -110 ppm. As seen in Figure 186 there appears to be a reduction in the intensity of the signal at -110 ppm which is consistent with the loss of $(=\text{SiO})_3\text{Si}(\text{OSi}=\equiv)$ from the matrix. $(=\text{SiO})_3\text{Si}(\text{OSi}=\equiv)$ corresponds to silicon atoms on the corner of a silicate building block which is connected to a silyl linking group. Figure 187 illustrates a proposed mechanism that could explain the connectivity of the tungsten oxo centers and the reduction of $(=\text{SiO})_3\text{Si}(\text{OSi}=\equiv)$ in the matrix. In this case, it appears that ^{29}Si SSNMR is not sensitive enough to detect the $(=\text{SiO})_3\text{SiCl}$ centers and the new siloxane linkages (Si-O-W) that presumably have formed.

The combination of the techniques described above provides a reasonable picture of the products in the reaction of WOCl_4 and a premade silicate building block support (Figure 185). IR provided evidence of the formation of linkages between the tungsten oxo centers and the premade silicate support (formation of W-O-Si, control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the tungsten oxo centers remained unchanged during the cross-linking reaction (preservation of tungsten oxo centers, control of the metal cation).

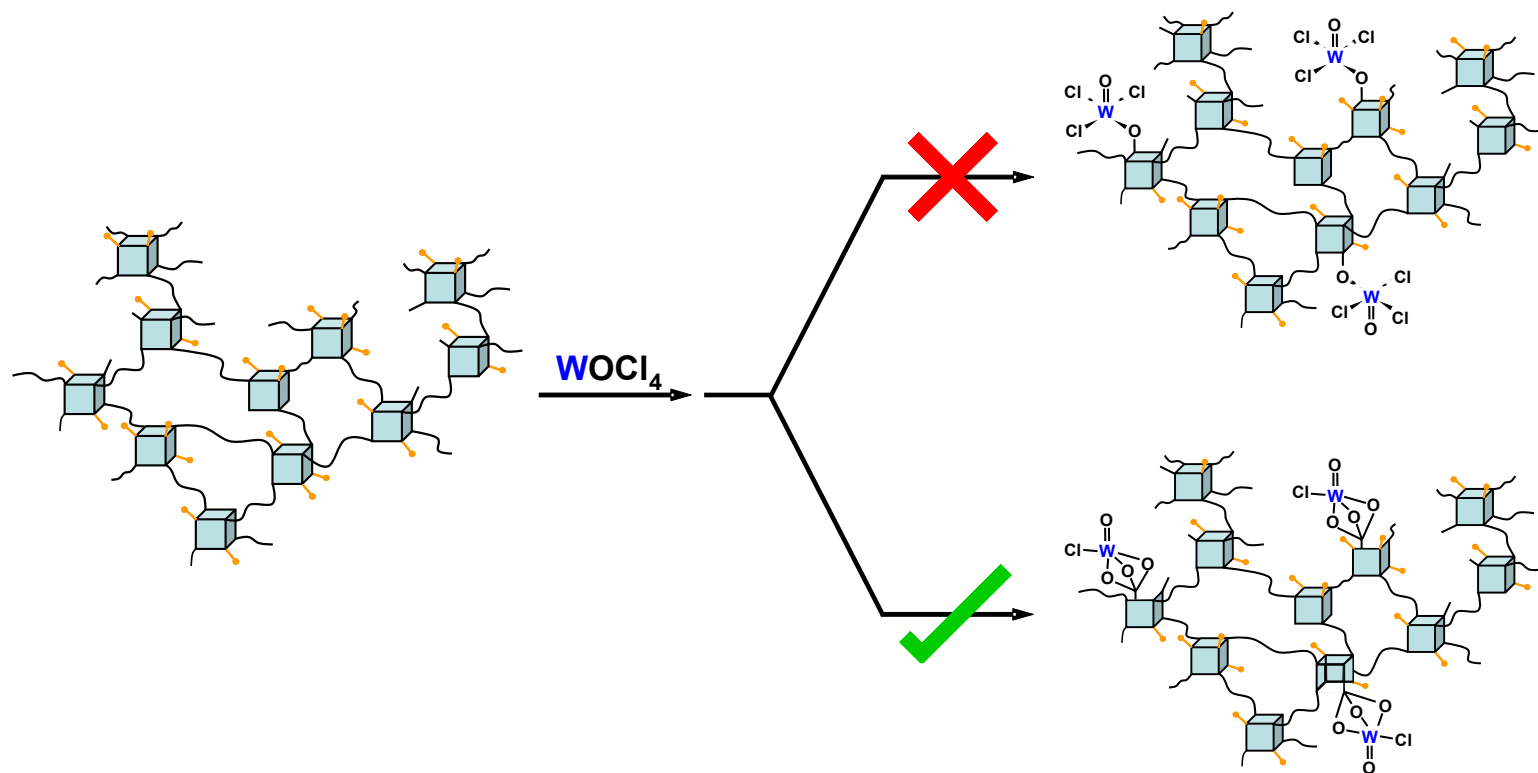


Figure 185: Proposed representation of the catalyst ensemble following the reaction of WOCl_4 and the premade silicate building block support.

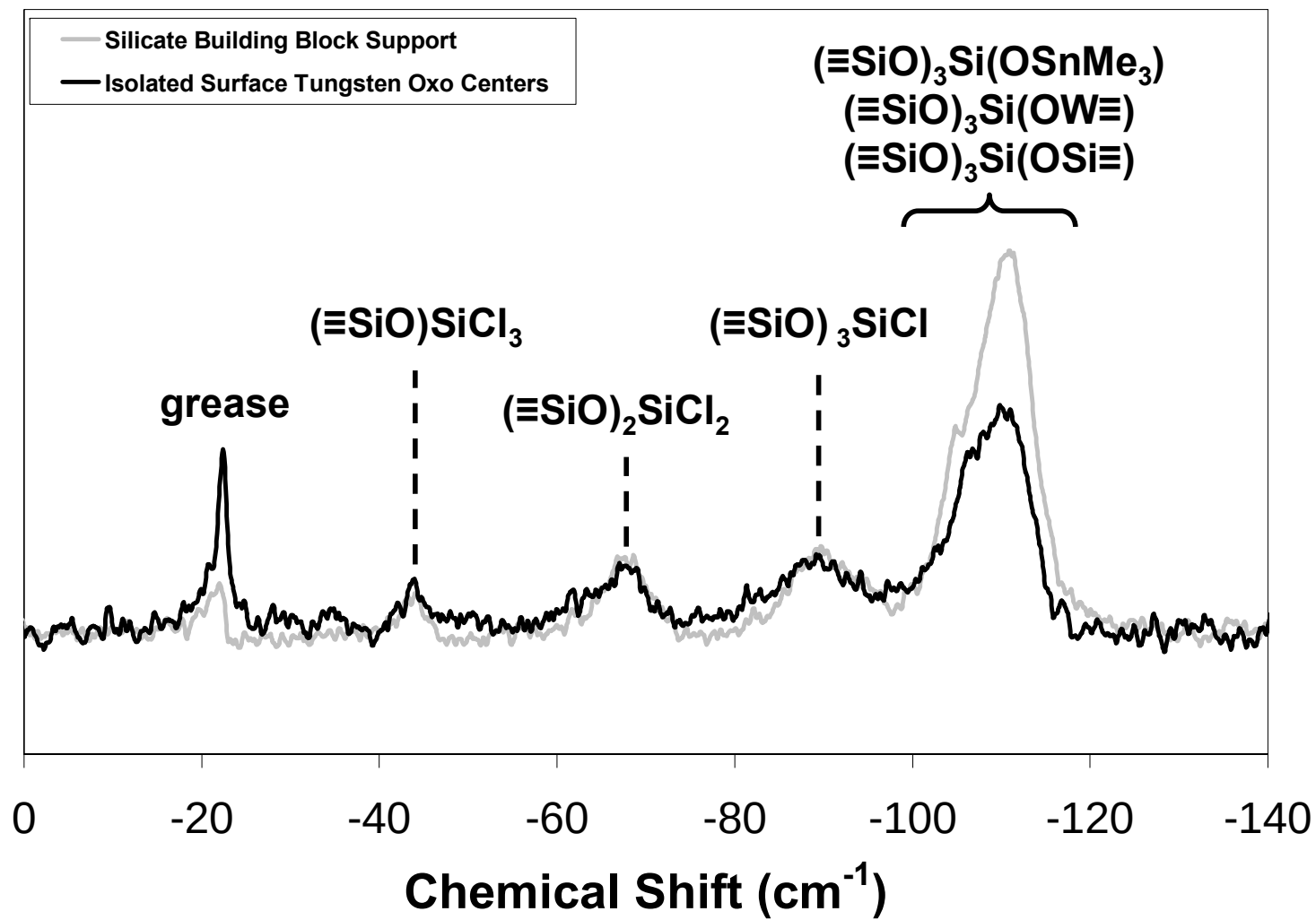


Figure 186: ^{29}Si SSNMR spectra (-140 to 0 ppm) of the premade tungsten-free silicate building block support and the material following the reaction of WOCl_4 and the premade silicate building block support.

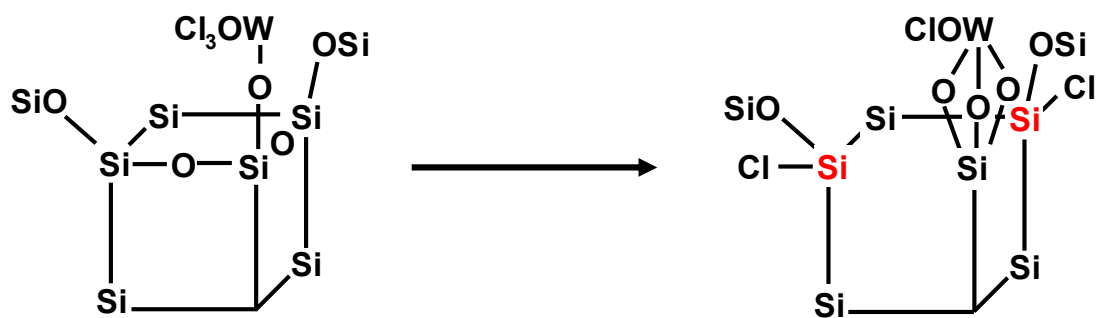


Figure 187: A proposed mechanism for the formation of surface tungsten oxo centers.

Isolated Surface W(VI) Catalyst Ensemble using WCl_6

A nanostructured silicate support with spatially isolated binding sites was used to target the synthesis of a surface catalyst ensemble which contains a W(VI) center with five chloride ligands and one linkage to the silicate support (Figure 188). The surface catalyst ensemble was not successfully synthesized for reason yet to be determined. The focus of this section is to understand what ensemble is produced and to thoroughly characterize the resulting ensemble using a variety of characterization techniques. The resulting catalyst ensemble will be referred to as “*isolated surface tungsten centers.*”

Reaction of WCl_6 and Silicate Building Block Support

The synthesis of surface tungsten centers that are connected to one silicate building blocks was attempted by reacting a trimethyltin functionalized silicate building block support with a limiting amount of WCl_6 ($0.5 \text{ WCl}_6 : 1 \text{ Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) (Figure 189). Only one chloride ligand on WCl_6 should react because the binding sites on the silicate building block support are spatially isolated, which prevents each tungsten center from accessing two binding sites. A limiting amount of WCl_6 was used so that gravimetric analysis could be used to determine the connectivity of the W(VI) center to the support. The volatiles of the reaction were analyzed using ^1H NMR and Me_3SnCl was the only byproduct observed. Gravimetric analysis (2.2 ± 0.4 equivalents of Me_3SnCl) suggests that approximately two chloride ligands on the tungsten center reacted with Me_3Sn groups on the support.

Figure 190 shows the IR spectra of a tungsten-free silicate building block support and the isolated surface tungsten centers. The materials are synthesized under nonaqueous aprotic conditions which results in the production of a hydroxyl-free surfaces. As expected, little to no evidence for the presence of silanol groups ($3600\text{-}4000 \text{ cm}^{-1}$) is observed in the IR spectra. IR spectroscopy is also used to verify the formation of the W-O-Si linkages. The band at 1090 cm^{-1} is commonly assigned to the Si-O-Si stretching mode (Figure 190).[171] A shoulder on the Si-O-Si feature was observed at approximately 930 cm^{-1} in the IR spectrum, which is characteristic of the presence of M-O-Si groups, in this case W, in the matrix.[36,44,84,144,164,165] The observation of this weak shoulder provides evidence on the formation of W-O-Si groups and suggests the metathesis reaction proceeded as expected.

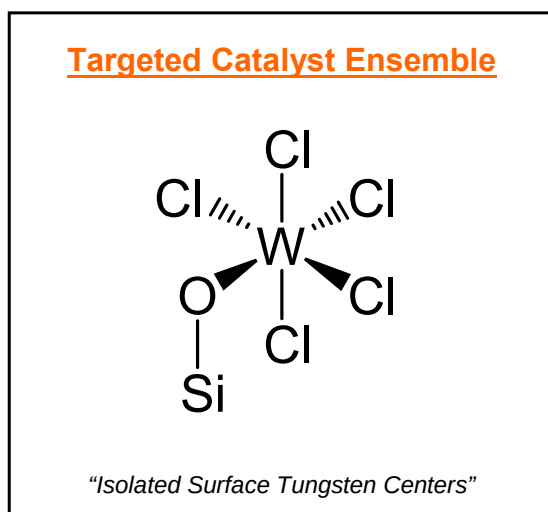


Figure 188: Illustration of the targeted catalyst ensemble referred to as "isolated surface tungsten centers."

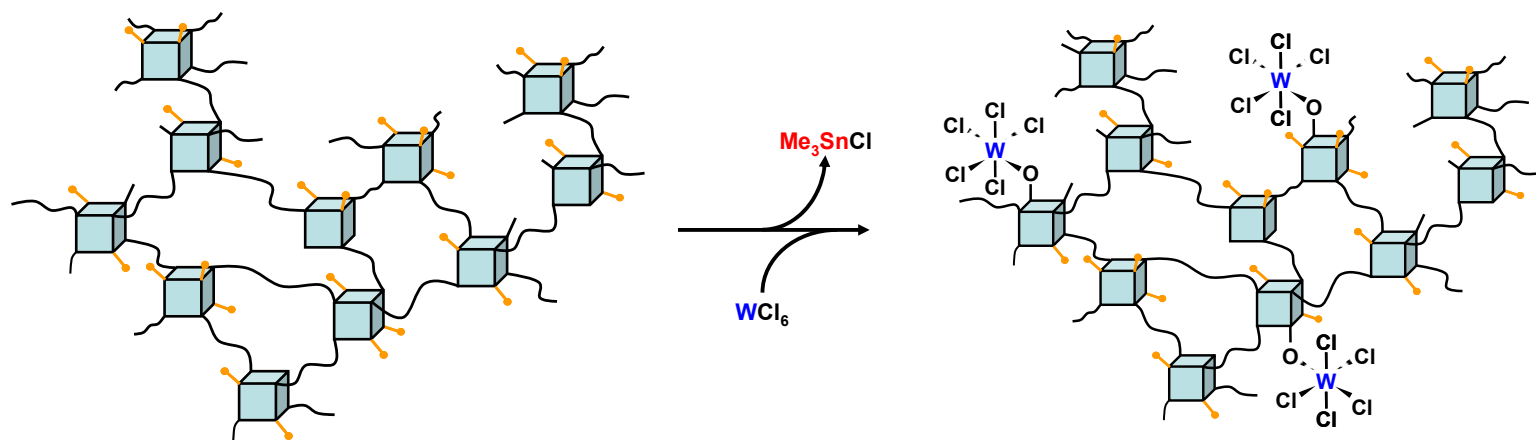


Figure 189: Reaction of WCl_6 and the premade silicate building block support.

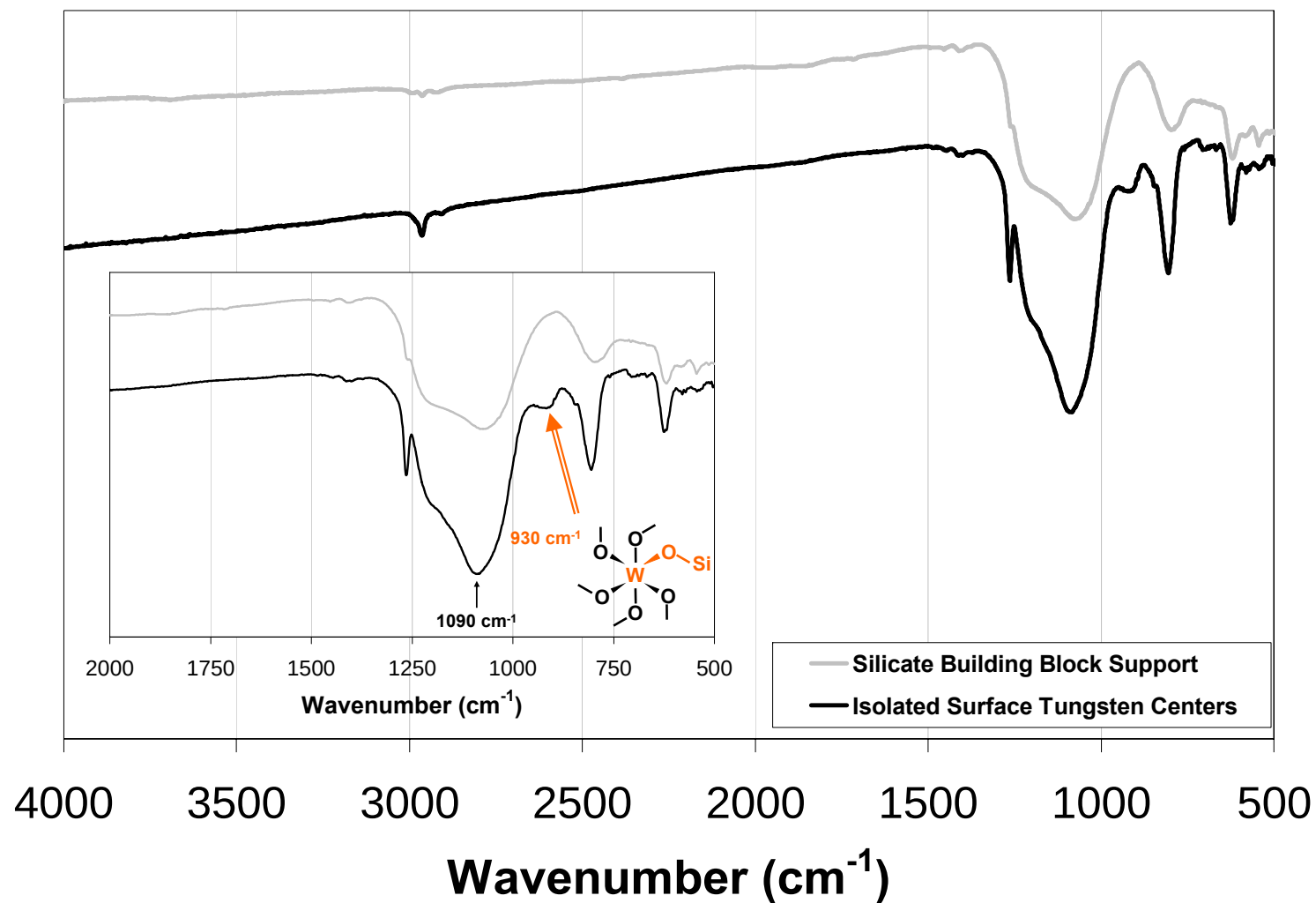


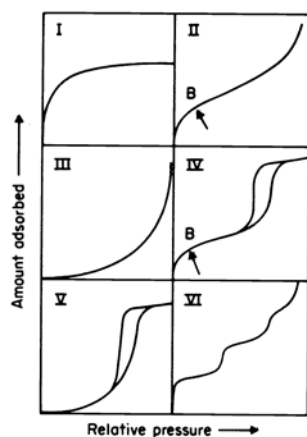
Figure 190: IR spectra (500-4000 cm^{-1}) of a premade tungsten-free support and the material following the reaction of WCl_6 and the premade silicate building block support. The inset contains the expanded IR spectrum (500-2000 cm^{-1}) which illustrates the W-O-Si shoulder (930 cm^{-1}).

Nitrogen adsorption/desorption measurements were conducted on the silicate building block support before and after the addition of the tungsten oxo centers to determine the BET surface area and total pore volume. In the case of the silicate building block support, qualitative analysis of the nitrogen adsorption isotherm (Type IV) and t-plot suggests this material is a primarily mesoporous material (Figure 160 & Figure 161).[136] The presence of a hysteresis (Type H4) also indicates the presence of mesopores. The t-plot method was used to confirm the material is primarily mesoporous with respect to pore volume (66%) and surface area (51%). The BET surface area of this material is 743 m²/g (Figure 162) and the total pore volume is 0.667 cm³/g. The BJH plot (Figure 163) does display a maximum, which suggests the BJH average pore radius is 34.0 Å. The porosity of the material did not significantly change with the addition of isolated surface tungsten oxo centers. The nitrogen adsorption isotherm (Type IV), hysteresis (Type H4), and t-plot still suggest this material is a primarily mesoporous material (Figure 191 & Figure 192).[136] The t-plot method was used to confirm the material is primarily mesoporous with respect to pore volume (75%) and surface area (60%). The BET surface area of this material is 546 m²/g (Figure 193) and the total pore volume is 0.559 cm³/g. The BJH plot (Figure 194) does display a maximum at 29.0 Å.

Figure 195 shows the XANES and the derivative XANES spectra at the L_{III} edge of the material at this stage in the synthesis. The position of the L_{III} edge and the intensity of the white line provide information about the oxidation state while the width of the white line provides information about the coordination geometry. The edge position of the surface tungsten centers supports the claim that the oxidation state of the surface tungsten centers is +6. The $I_{WL}/I_{\Delta\mu(E)}$ ratio for the surface tungsten centers (3.43) supports the claim that the oxidation state of the surface tungsten centers is +6 (Figure 196). The white line appears to be broad (width = 7.1 eV) which would suggest the coordination geometry is distorted octahedral (width = 7.4 eV) instead of tetrahedral (width = 4.9 eV) (Figure 197).

Figure 198 shows the XANES and the derivative XANES spectra at the L_I edge of the material at this stage in the synthesis. The edge position of the surface tungsten centers supports the claim that the oxidation state of the tungsten centers is +6. The presence of a pre-edge feature (2s → 5d transition) provides evidence that the coordination geometry around the surface

Standard Isotherms



Standard Hysteresis Loops

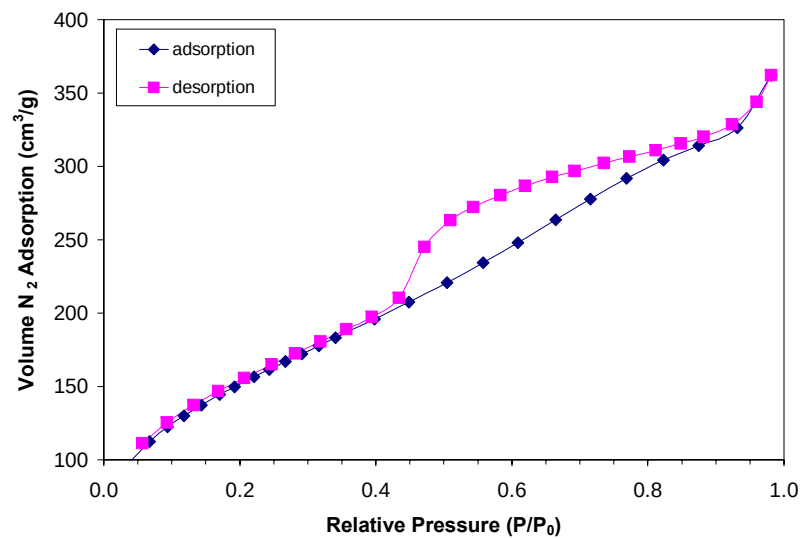
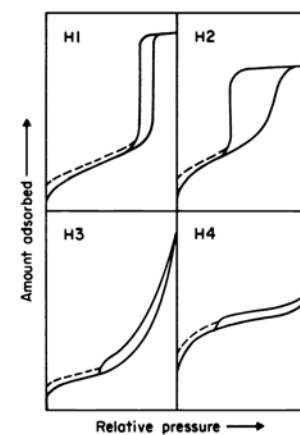


Figure 191: Nitrogen isotherm for the material following the reaction of WCl_6 and the premade silicate building block support. Standard isotherms and hysteresis loops obtained from literature.[131]

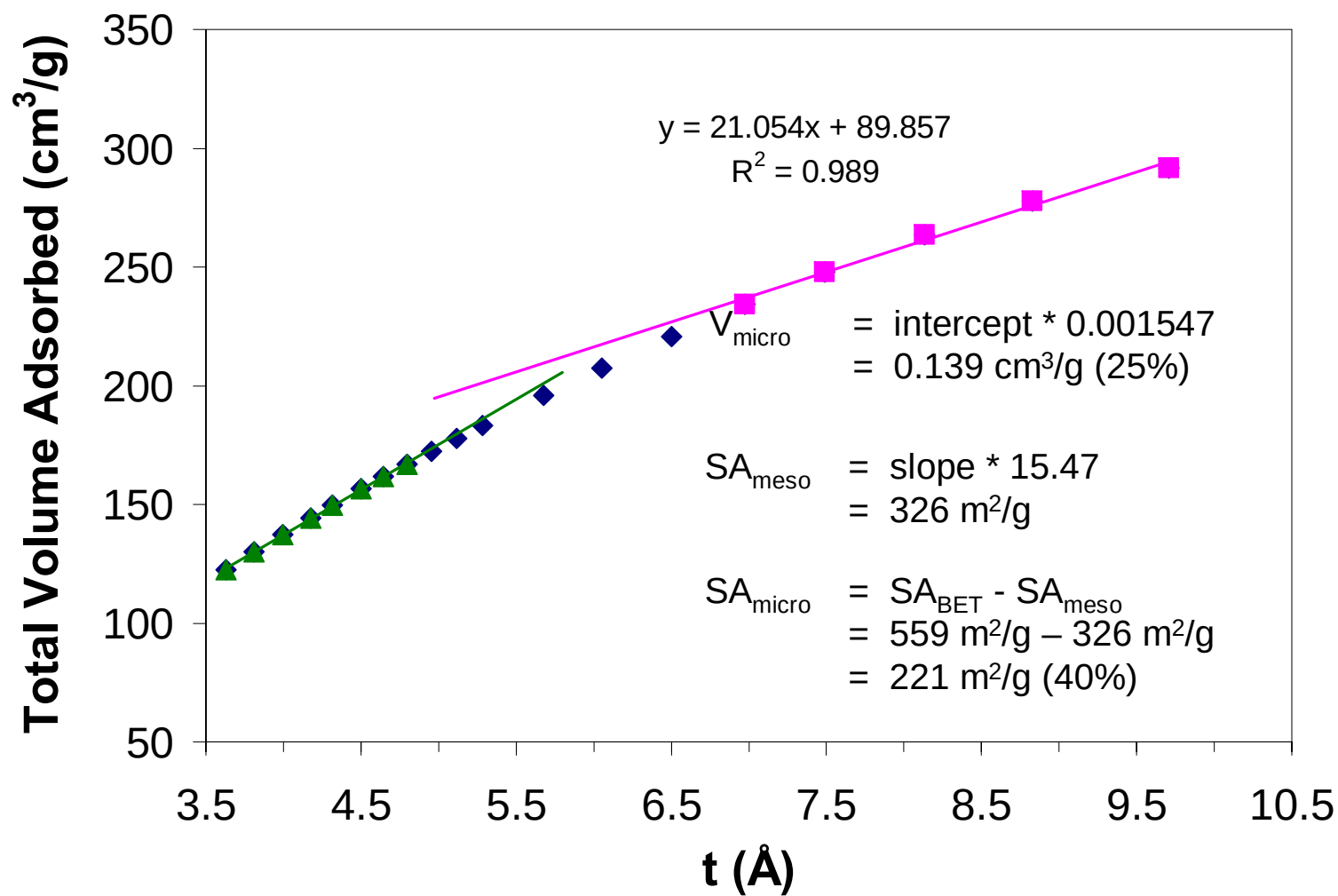


Figure 192: t-plot for the material following the reaction of WCl_6 and the premade silicate building block support.

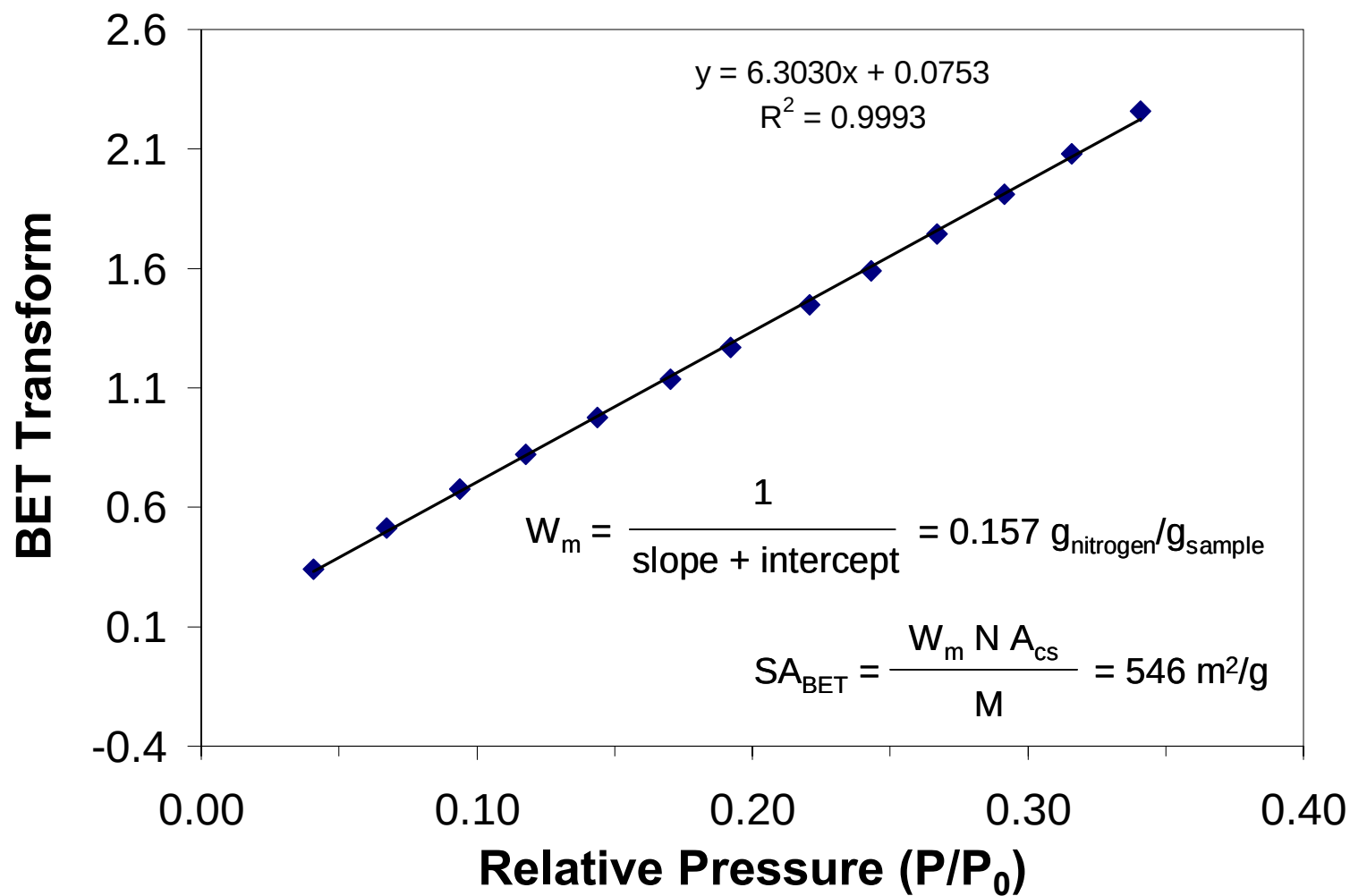


Figure 193: BET plot for the material following the reaction of WCl_6 and the premade silicate building block support.

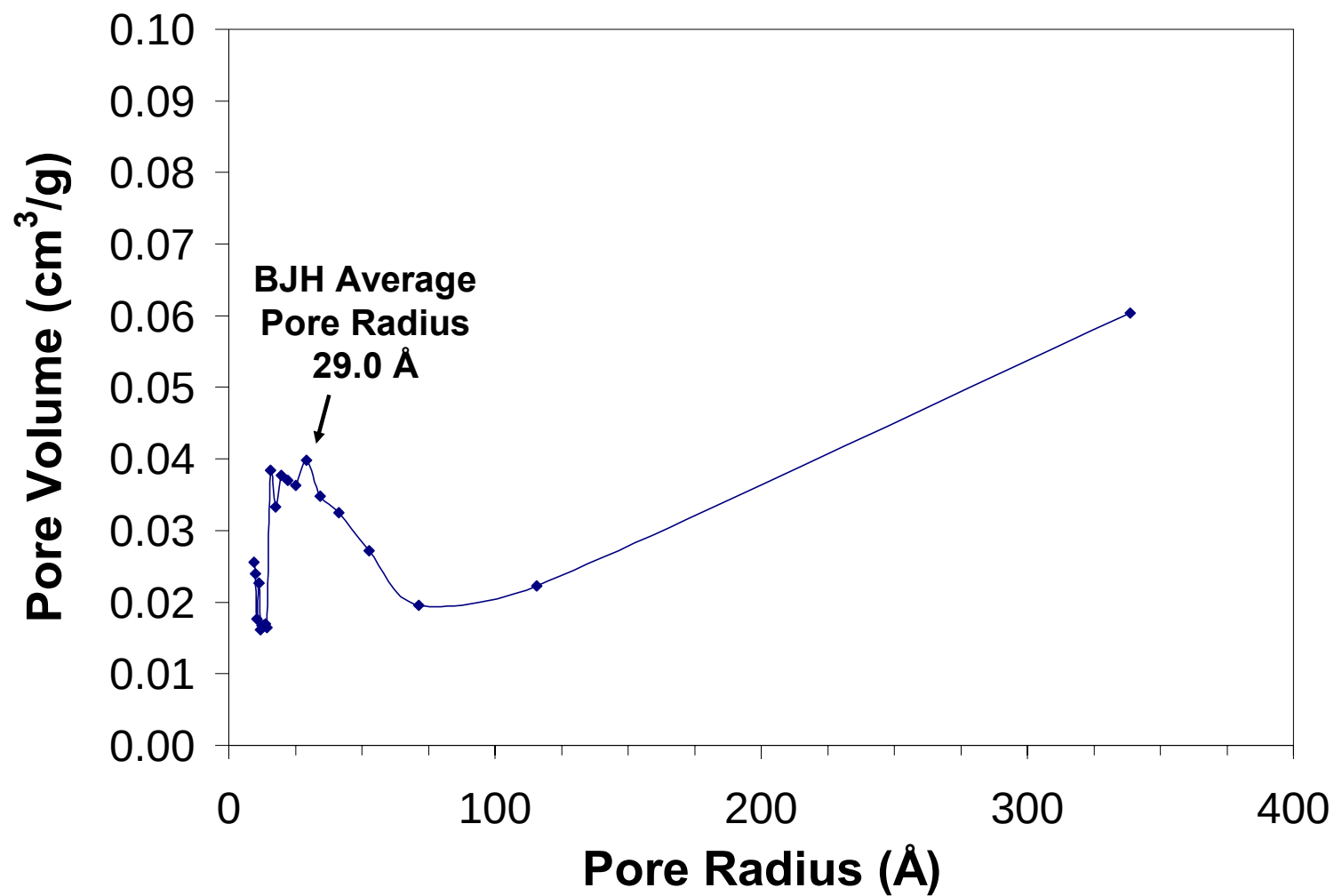


Figure 194: BJH pore size distribution plot for the material following the reaction of WCl_6 and the premade silicate building block support.

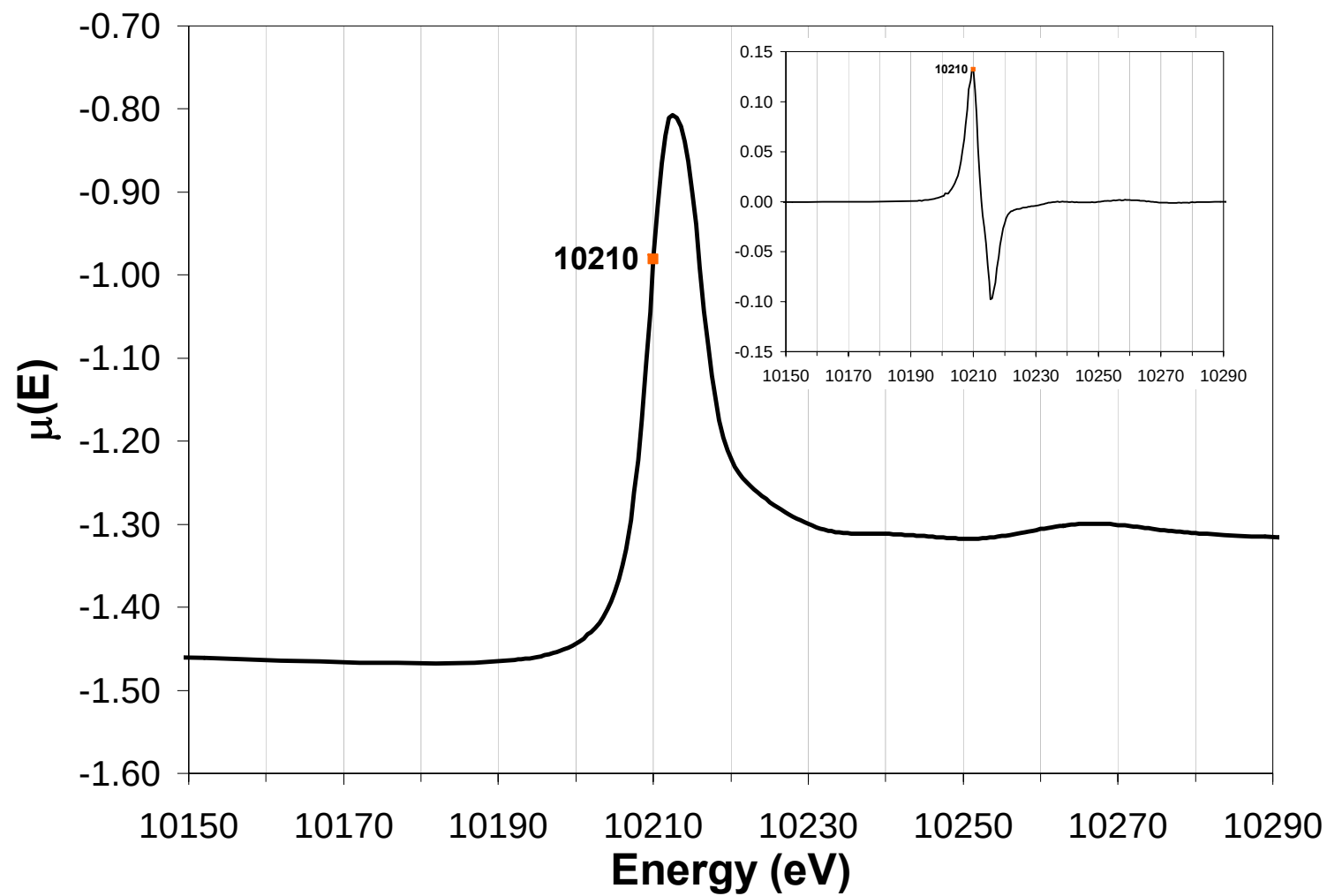


Figure 195: XANES spectrum (W L_{III} edge) following the reaction of WCl₆ and the premade silicate building block support. The inset contains the derivative XANES spectrum with the position of the absorption edge (orange square) labeled.

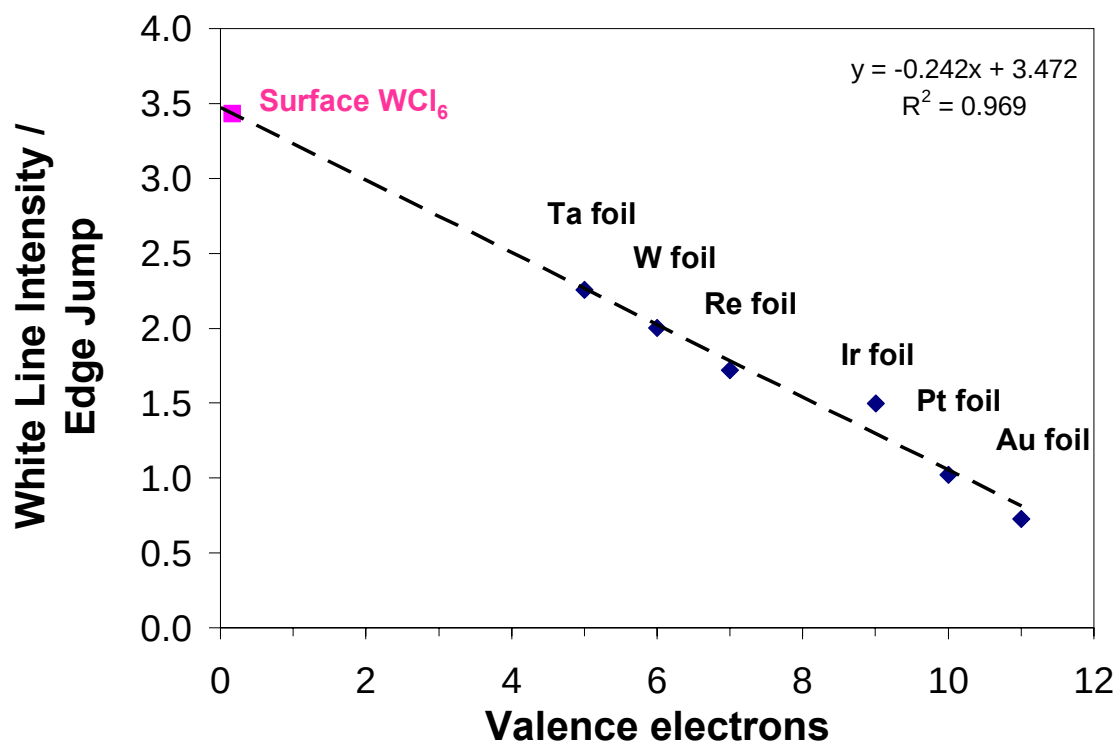


Figure 196: Relationship between white line intensity:edge jump ratio and number of valence electrons for several 5d transition metals and the material following the reaction of WCl₆ and the premade silicate building block support.

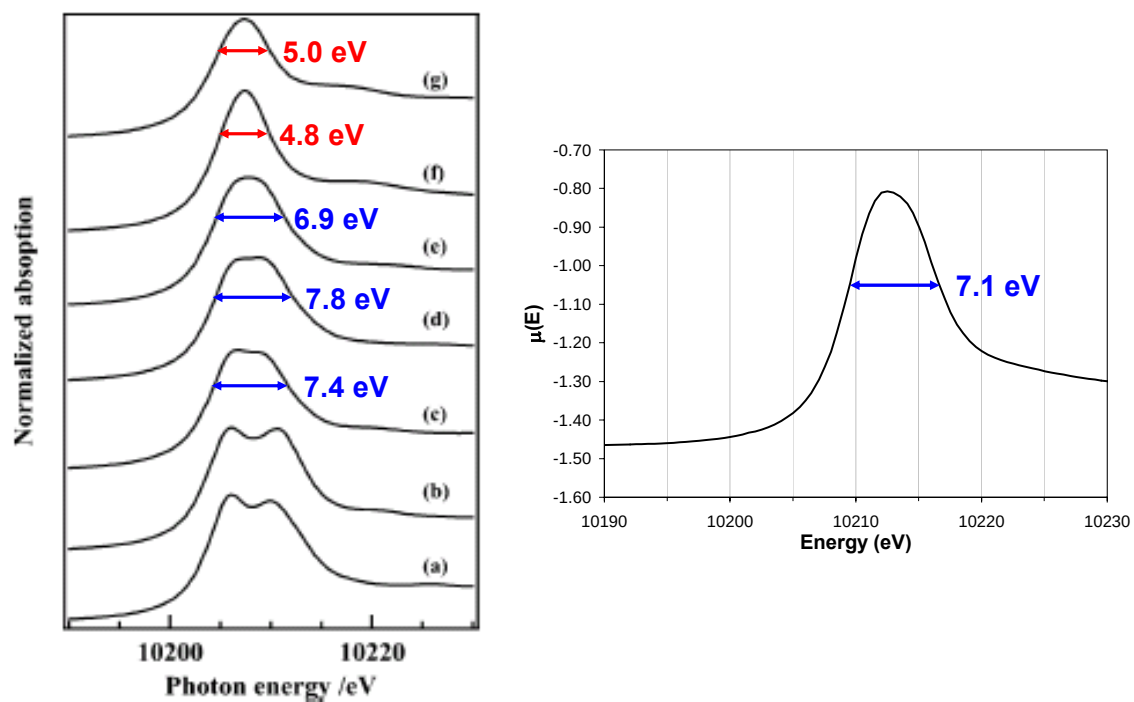


Figure 197: Analysis of the width of the white line at the L_{III} edge for published standards[117] (left) and sample following the reaction of WCl_6 and the premade silicate building block support (right).

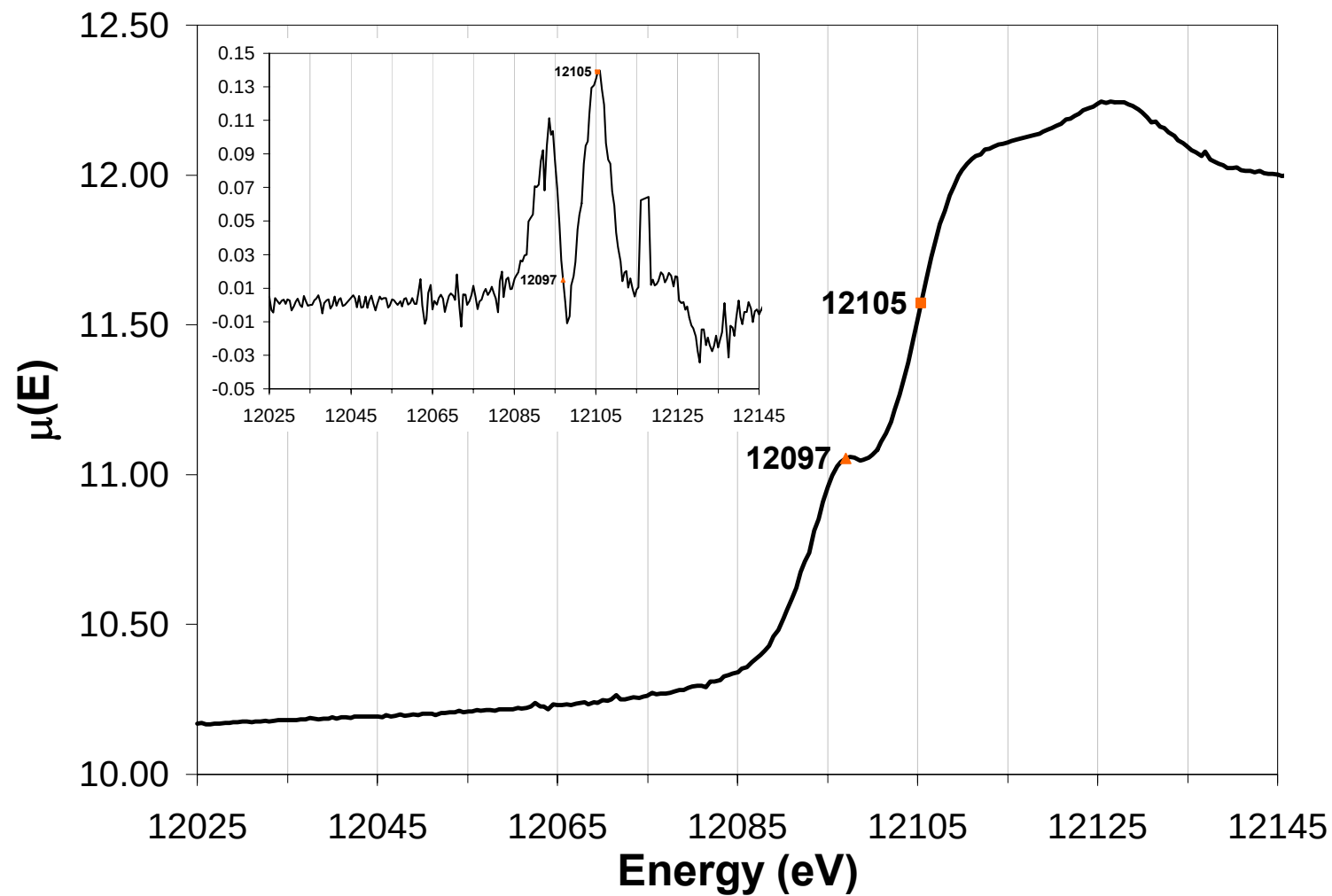


Figure 198: XANES spectrum (W L₁ edge) following the reaction of WCl₆ and the premade silicate building block support. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

tungsten center is not octahedral and suggests the coordination geometry is either tetrahedral or distorted octahedral. The intensity of the pre-edge for the tungsten oxo oligomers is approximately 45% which suggests the coordination geometry is distorted octahedral.

In summary, the analysis of the XANES spectra at the L_{III} and the L_I edges suggests the surface tungsten centers have distorted octahedral coordination geometry and that the oxidation state of the surface tungsten centers is +6.

EXAFS data were used to obtain more information about the connectivity of the surface tungsten centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around tungsten) can be qualitatively determined by looking at the magnitude R-space plot (Figure 199). Based on the data already presented, four shells should be present around the tungsten centers after the first cross-linking reaction: a terminal doubly bound oxygen ($W=O$), a shell of singly bound oxygens ($W-O$), a shell of unreacted chloride ligands ($W-Cl$), and a shell of nonbonded silicons ($W\cdots Si$). Figure 199 shows the four features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot.

Based on the qualitative analysis of the EXAFS data, the first coordination sphere (defined as atoms directly bound to the tungsten) of the surface tungsten centers should have at least one terminal doubly bound oxygen atom ($W=O$), at least one singly bound oxygen atoms ($W-O$) and at least one singly bound chloride atoms ($W-Cl$). The second coordination sphere should have as many nonbonded silicon atoms as first shell singly bound oxygen atoms ($W\cdots Si$). In order to obtain quantitative information a structural model must first be constructed.

The first structural model that was used to fit the data was constructed based on the gravimetric data. A structural model containing $W=O$ (CN=1), $W-O$ (CN=2), $W-Cl$ (CN=2), and $W\cdots Si$ (CN=2) single scattering paths was constructed (Figure 173). The value of S_0^2 obtained from FEFF8 was 0.92. The CN values based on the results of gravimetric analysis and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 200 with the EXAFS data range used to fit the model is boxed (3.5 to 13.3 $\text{\AA}^{-1}$). In R-space, the fit range is from 1.0 to 4.0 $\text{\AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 201 and Figure 202,

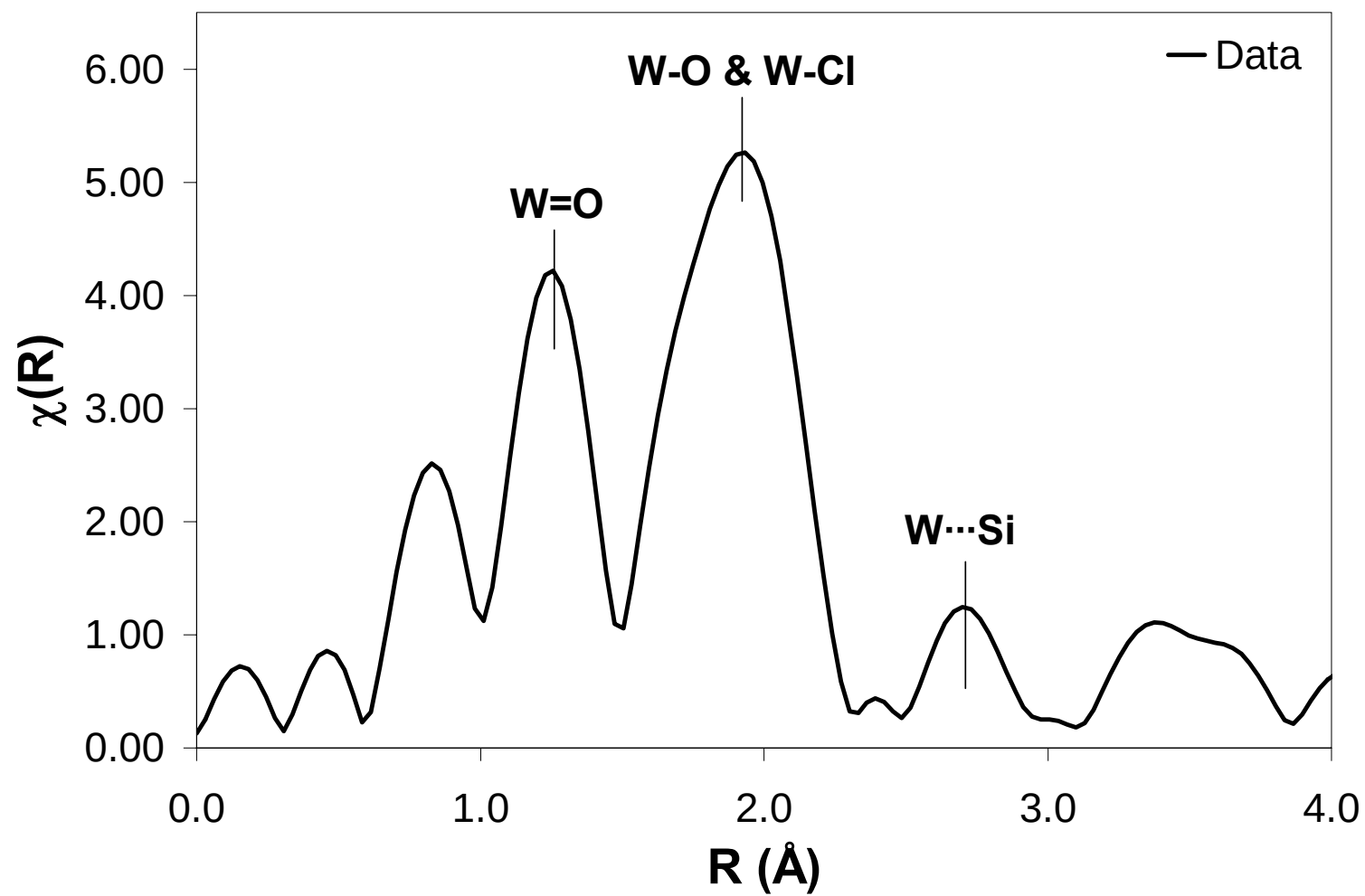


Figure 199: EXAFS R-space plot following the reaction of WCl_6 and the premade silicate building block support. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

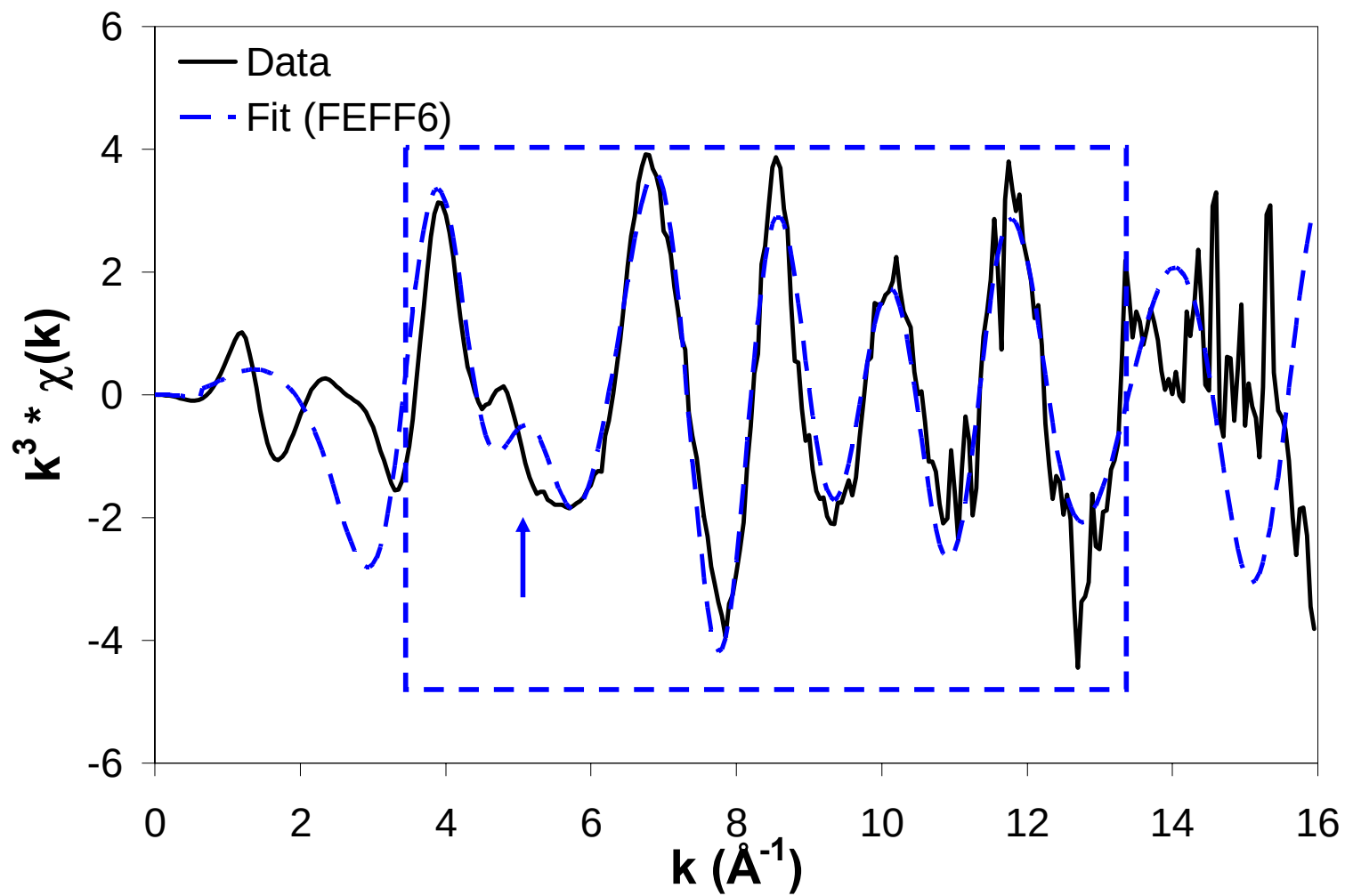


Figure 200: EXAFS k-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 173.

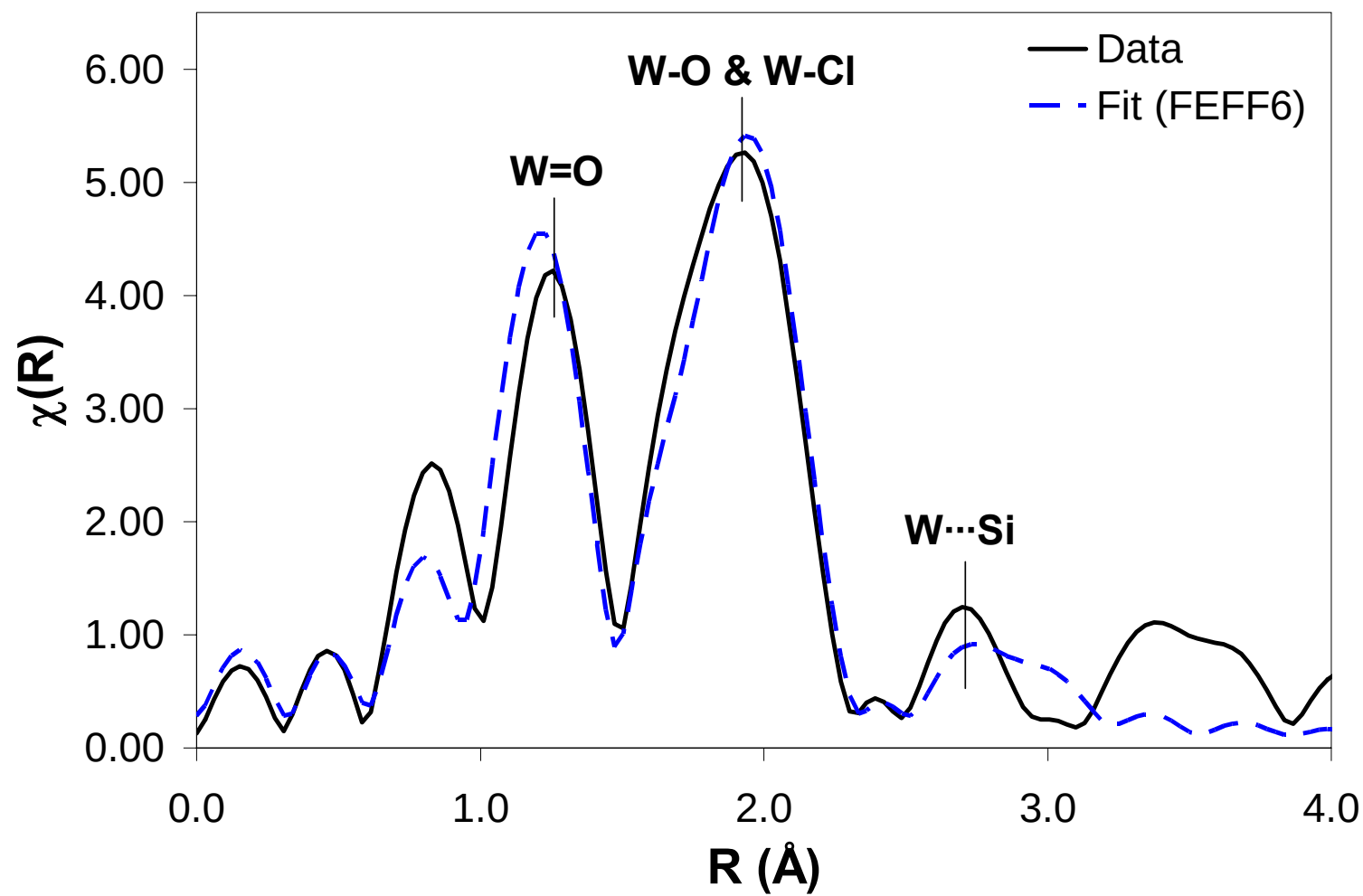


Figure 201: EXAFS R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 173. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

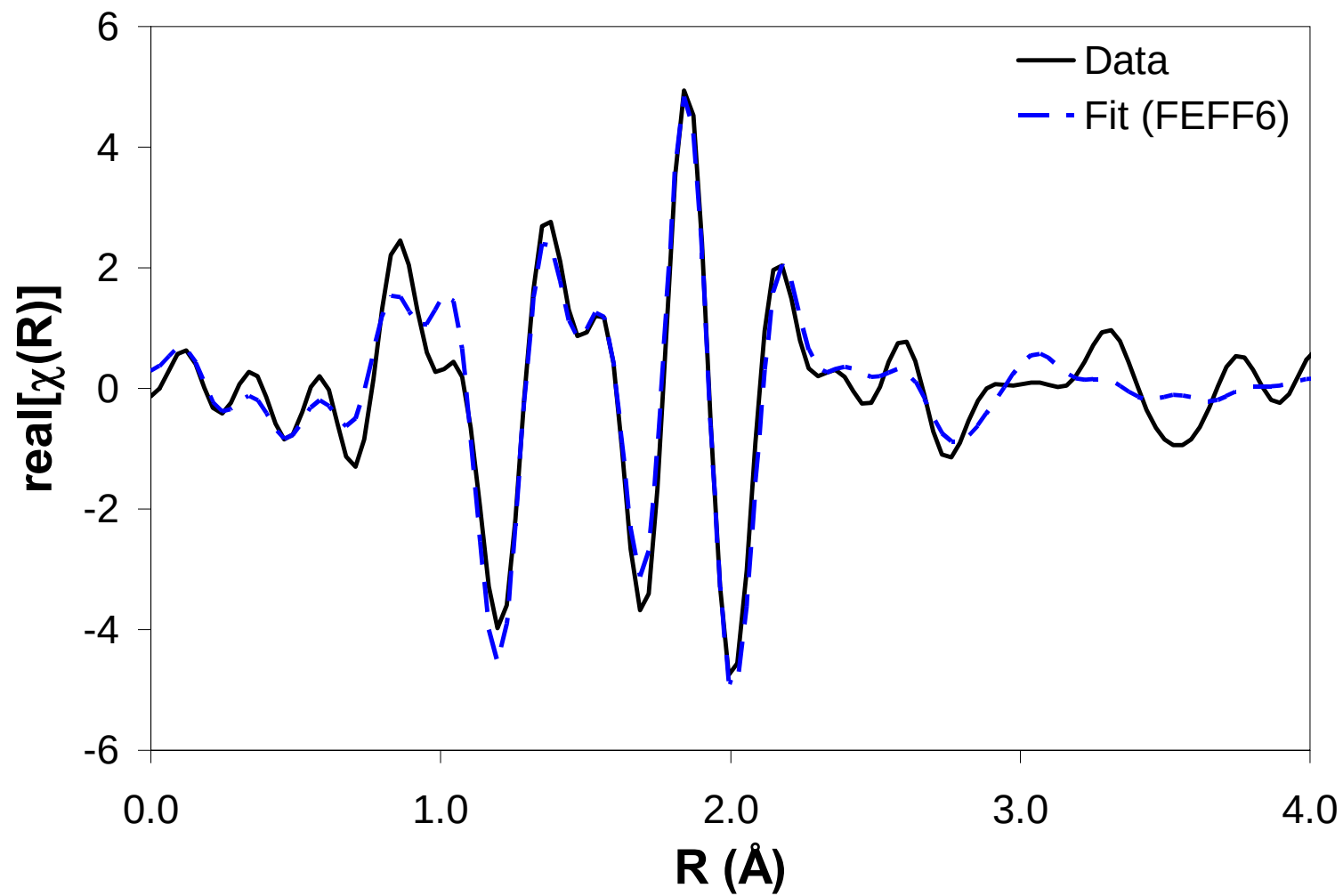


Figure 202: EXAFS real R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 173. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

respectively. Table 11 summarizes the refined values of the structural parameters. The value of $\sigma^2(\text{W}=\text{O})$ is slightly negative, which can be an indication that the model is incorrect. Also the model does not appear to fit the data well between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the blue arrow) as seen in Figure 200. For these reason a different model was tried to see if the fit improved.

The second structural model that was used to fit the data was constructed based on the original predicted catalyst ensemble. A structural model containing $\text{W}=\text{O}$ (CN=1), $\text{W}-\text{O}$ (CN=1), $\text{W}-\text{Cl}$ (CN=3), and $\text{W}\cdots\text{Si}$ (CN=1) single scattering paths was constructed (Figure 177). The CN values based on the model and S_0^2 were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 203 with the EXAFS data range used to fit the model is boxed (3.5 to $13.3 \text{ \AA}^{-1}$). In R-space, the fit range is from 1.0 to $4.0 \text{ \AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 204 and Figure 205 respectively. Table 11 summarizes the refined values of the structural parameters. The value of $\sigma^2(\text{W}=\text{O})$ and $\sigma^2(\text{W}-\text{O})$ are slightly negative, which can be an indication that the model is incorrect. Also the model does not appear to fit the data well between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the red arrow) as seen in Figure 203. For these reason a different model was tried to see if the fit improved.

The third structural model that was used to fit the data was constructed based on the gravimetric data. A structural model containing $\text{W}=\text{O}$ (CN=1), $\text{W}-\text{O}$ (CN=3), $\text{W}-\text{Cl}$ (CN=1), and $\text{W}\cdots\text{Si}$ (CN=3) single scattering paths was constructed (Figure 181). The CN values based on the model and S_0^2 were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface tungsten oxo centers in a silicate building block matrix is presented in Figure 206 with the EXAFS data range used to fit the model is boxed (3.5 to $13.3 \text{ \AA}^{-1}$). In R-space, the fit range is from 1.0 to $4.0 \text{ \AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 207 and Figure 208 respectively. Table 11 summarizes the refined values of the structural parameters. This model fits the data much better than the other two, specifically all the refined values are within acceptable limits and there is

Table 11: EXAFS fit values for isolated surface tungsten centers

Fit values using structural model in Figure 173				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.689	1.858	2.347	3.198
σ^2 (Å ²)	-0.55 x 10 ⁻³	2.92 x 10 ⁻³	5.33 x 10 ⁻³	14.16 x 10 ⁻³
E ₀ (eV)	1.5 ± 3.0	1.5 ± 3.0	1.5 ± 3.0	1.5 ± 3.0
CN	1 (set)	2 (set)	2 (set)	2 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.4, N _{var} = 9, χ^2 = 309, reduced χ^2 = 33, R-factor = 0.064, FT k region = 3.544 – 13.274 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Fit values using structural model in Figure 177				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.729	1.890	2.376	3.201
σ^2 (Å ²)	-1.70 x 10 ⁻³	-2.70 x 10 ⁻³	9.81 x 10 ⁻³	6.04 x 10 ⁻³
E ₀ (eV)	6.7 ± 3.4	6.7 ± 3.4	6.7 ± 3.4	6.7 ± 3.4
CN	1 (set)	1 (set)	3 (set)	1 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.4, N _{var} = 9, χ^2 = 519, reduced χ^2 = 55, R-factor = 0.108, FT k region = 3.544 – 13.274 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				
Fit values using structural model in Figure 181				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.661	1.823	2.317	3.156
σ^2 (Å ²)	2.28 x 10 ⁻³	9.85 x 10 ⁻³	0.85 x 10 ⁻³	22.97 x 10 ⁻³
E ₀ (eV)	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0
CN	1 (set)	3 (set)	1 (set)	3 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.4, N _{var} = 9, χ^2 = 377, reduced χ^2 = 40, R-factor = 0.078, FT k region = 3.544 – 13.274 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

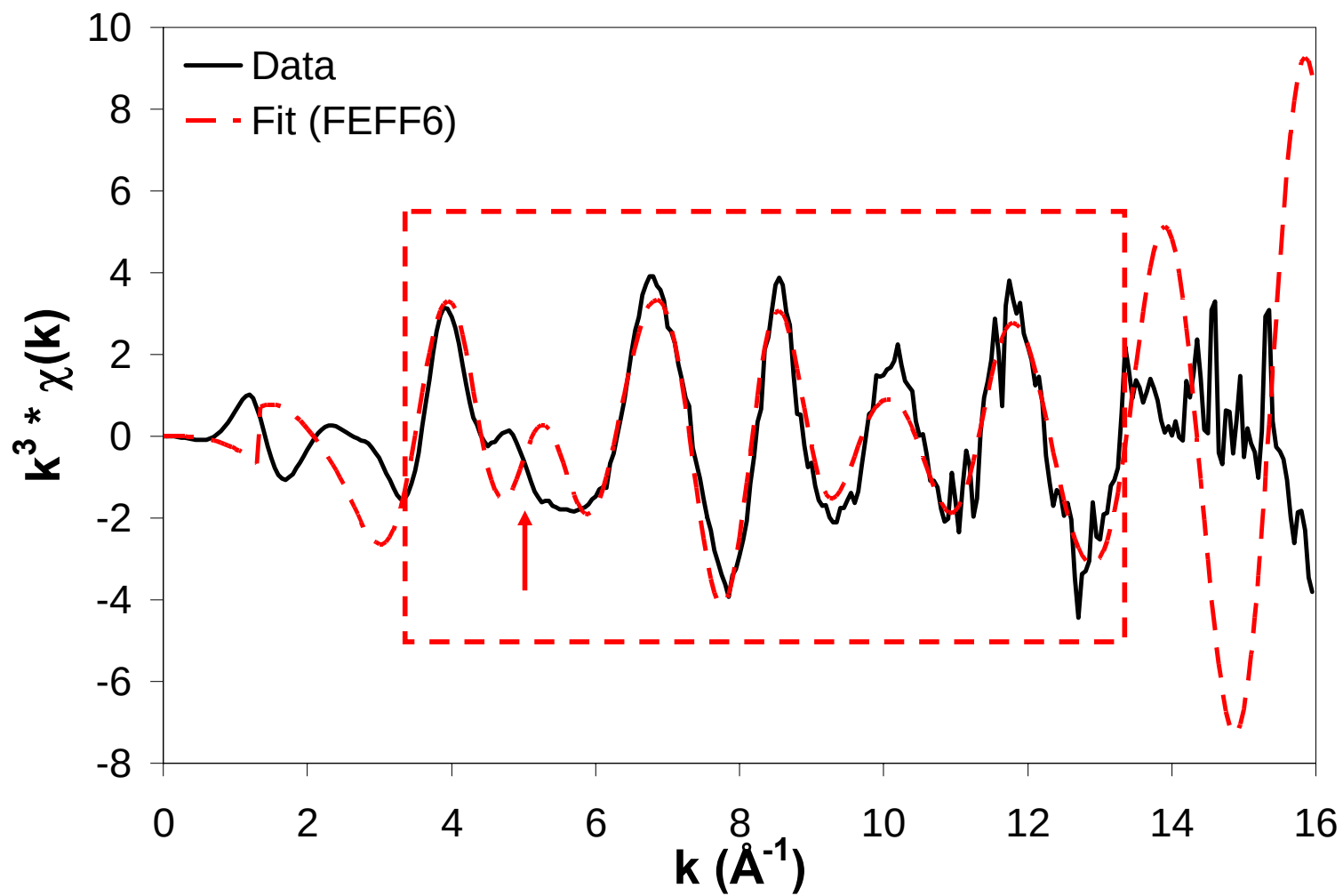


Figure 203: EXAFS k-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 177.

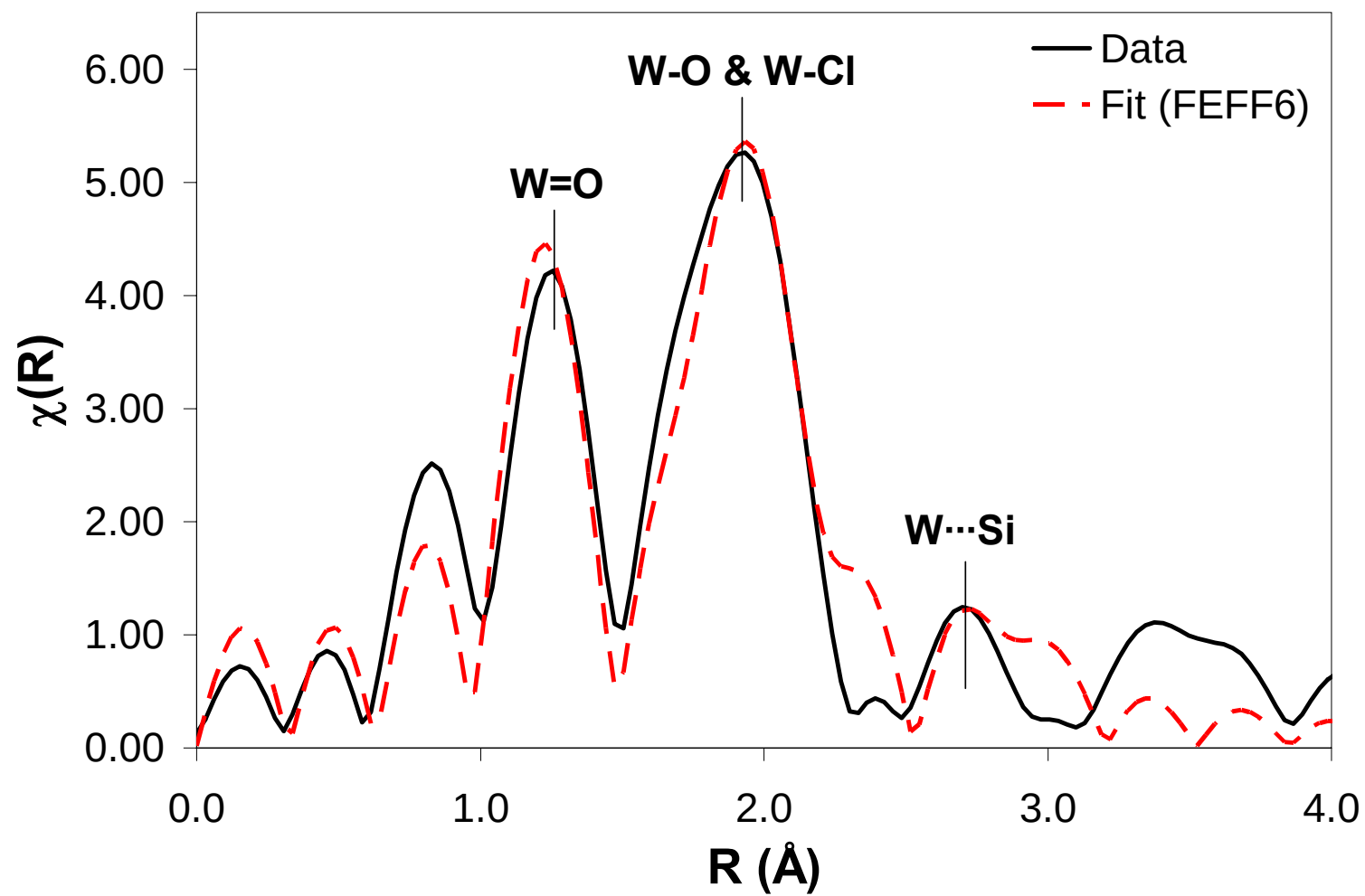


Figure 204: EXAFS R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 177. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

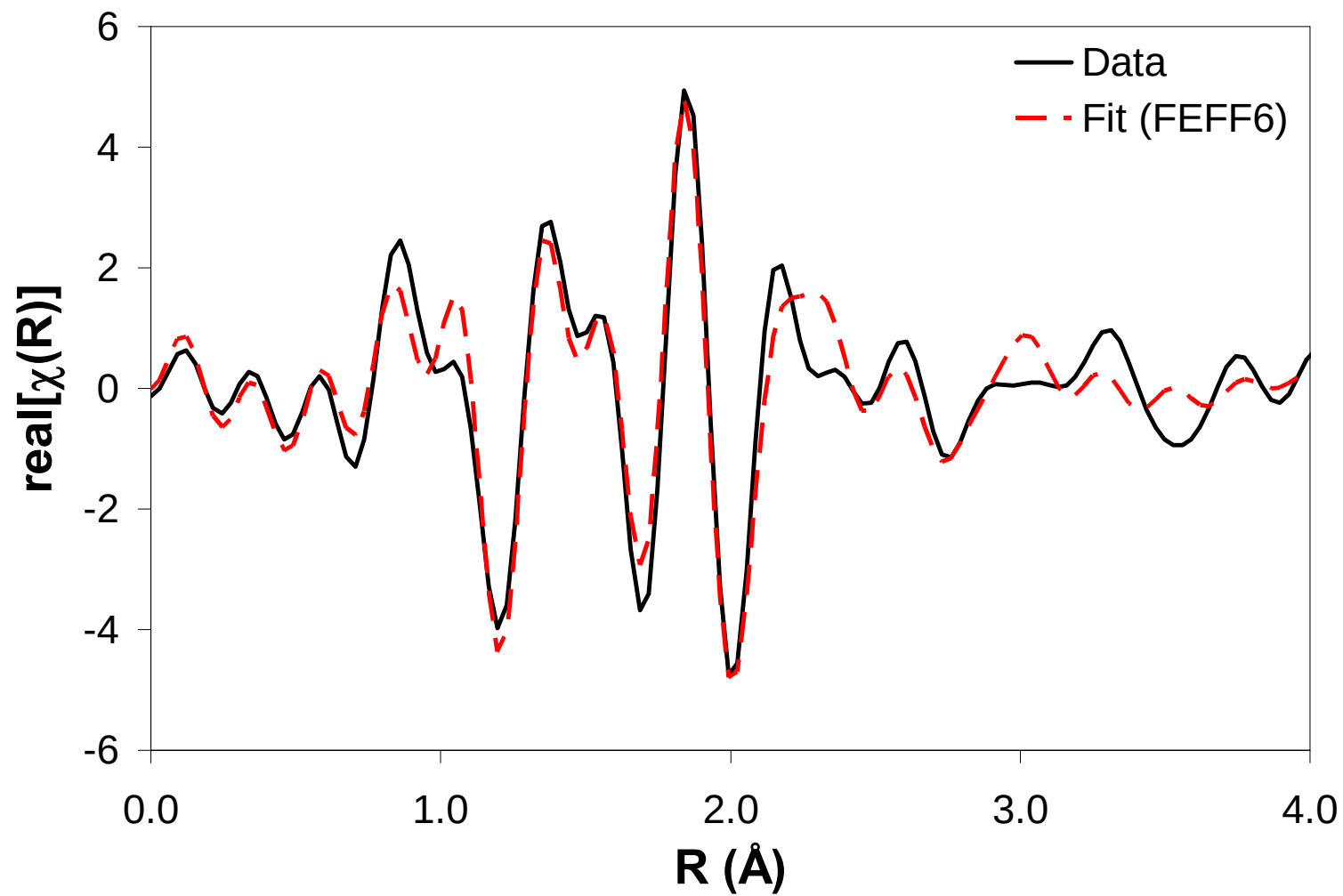


Figure 205: EXAFS real R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 177. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

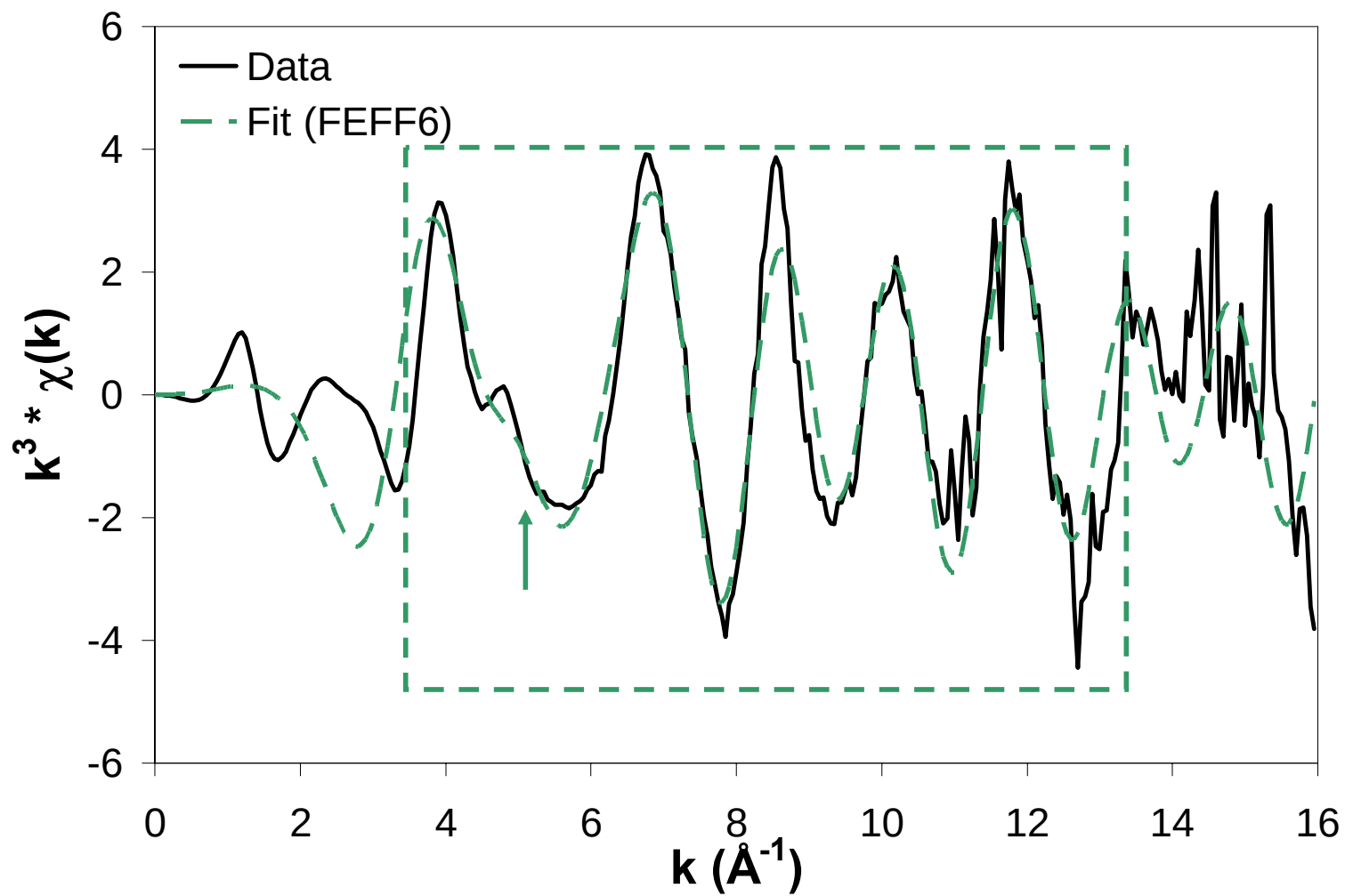


Figure 206: EXAFS k-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 181.

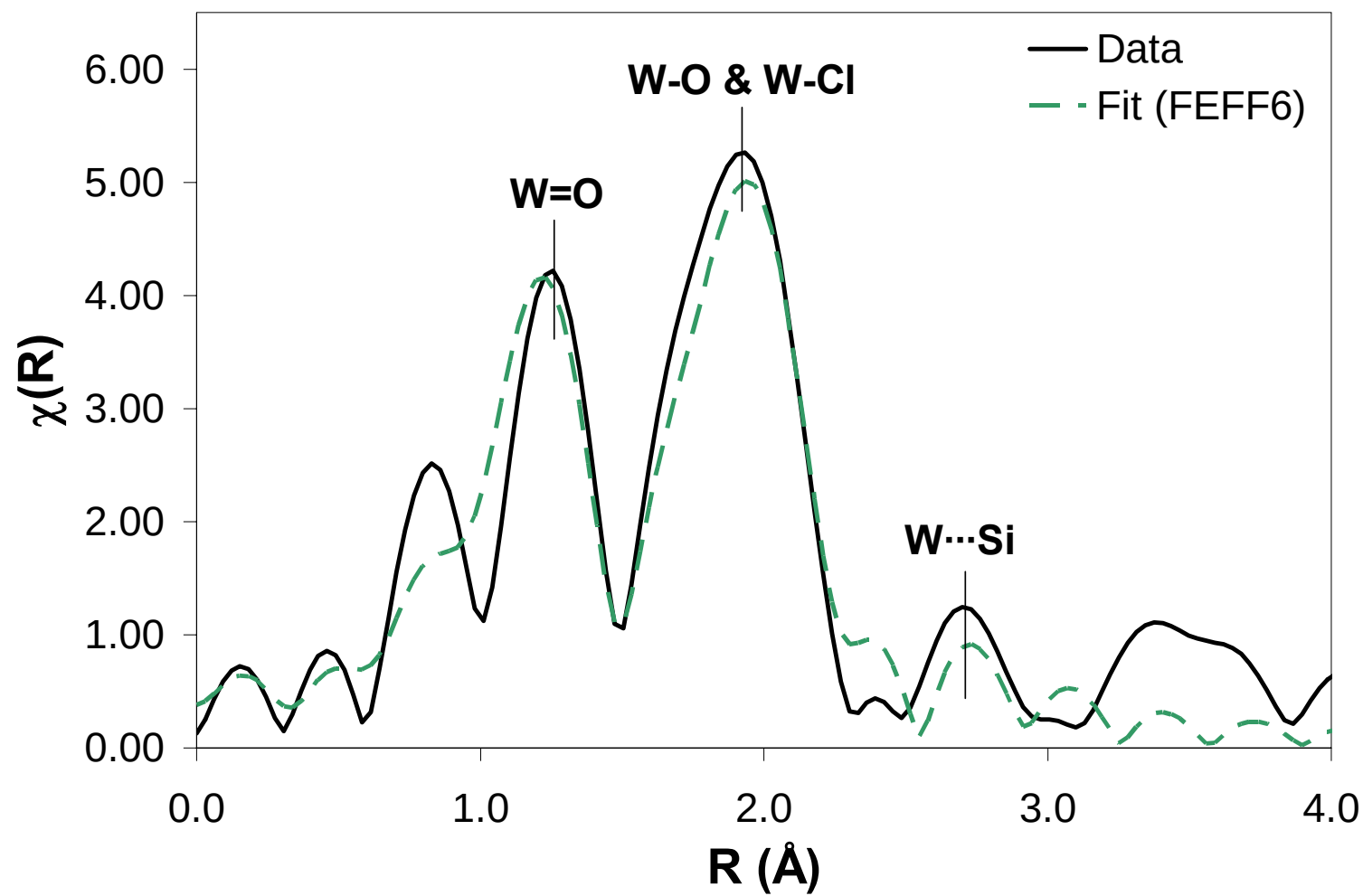


Figure 207: EXAFS R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 181. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

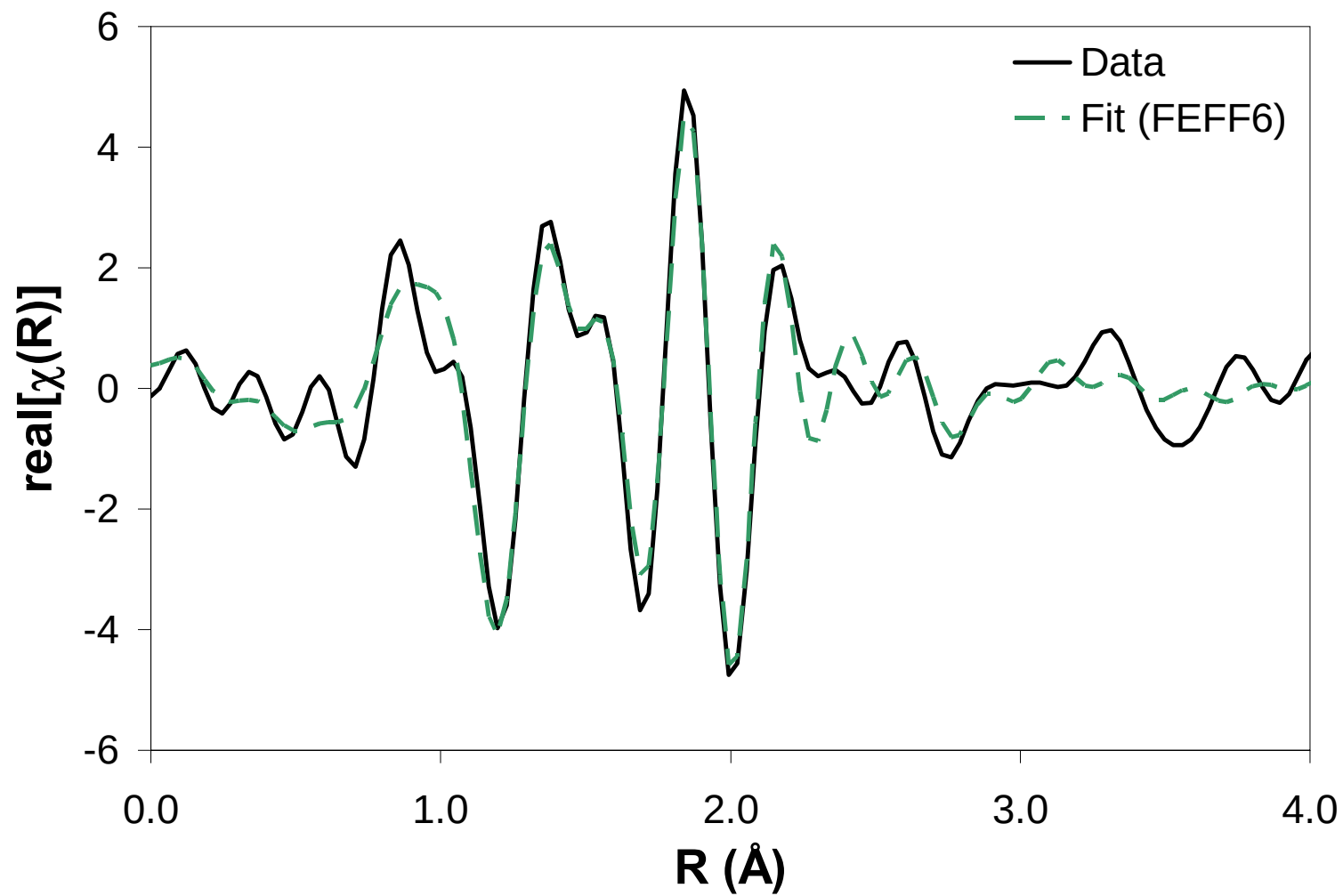


Figure 208: EXAFS real R-space plot following the reaction of WCl_6 and the premade silicate building block support using the structural model in Figure 181. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

little deviation between $k = 4 \text{ \AA}^{-1}$ and $6 \text{ \AA}^{-1}$ (marked with the green arrow) as seen in Figure 206.

In summary, the EXAFS data analysis provides evidence that the immediate environment around the surface tungsten centers (1 W=O, 3 W-O, 1 W-Cl and 3 W...Si) is different than initially predicted as seen in Figure 209.

Figure 210 shows the ^{29}Si SSNMR spectra of the premade tungsten-free silicate building block support and the isolated surface tungsten oxo centers. The signals between -22 and -100 ppm in the spectrum are characteristic of the different silyl chlorides generated during the second cross-linking reaction (i.e. $(=\text{SiO})_{4-x}\text{SiCl}_x$).^[95] The ^{29}Si SSNMR spectrum between -22 and -100 ppm does not change significantly following the linking of the surface tungsten oxo centers to the silicate building block support which suggests that the linking reaction does not disrupt the bulk of the silicate building block support. The major difference between the two spectra is observed between -100 and -110 ppm. The signals between -100 ppm and -110 ppm are assigned to the silicon corners on the building block which are connected to unreacted Me_3Sn groups $((=\text{SiO})_3\text{Si}(\text{OSnMe}_3))$, connected to the zirconium centers $((=\text{SiO})_3\text{Si}(\text{OW}\equiv))$, and connected to the silicon centers $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$. Signals assigned to $((=\text{SiO})_3\text{Si}(\text{OSnMe}_3))$ and $((=\text{SiO})_3\text{Si}(\text{OW}\equiv))$ are typically observed around -104 ppm while signals assigned to $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$ are typically observed around -110 ppm. As seen in Figure 210 there appears to be a slight reduction in the intensity of the signal at -110 ppm which probably corresponds to the loss of $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$ from the matrix. $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$ corresponds to silicon atoms on the corner of a silicate building block which is connected to a silyl linking group. A mechanism similar to the one illustrated in Figure 187 could explain the connectivity of the tungsten oxo centers and the reduction of $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$ in the matrix. In this case, it appears that ^{29}Si SSNMR is not sensitive enough to detect the $((=\text{SiO})_3\text{SiCl})$ centers and the new siloxane linkages (Si-O-W) that presumably have formed.

The combination of the techniques described above provides a reasonable picture of the products in the reaction of WCl_6 and the silicate building block support (Figure 209). IR provided evidence of the formation of linkages between the tungsten centers and the premade silicate support (formation of W-O-Si, control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the tungsten centers remained unchanged during the cross-linking reaction (preservation of tungsten(VI) centers, control of the metal cation).

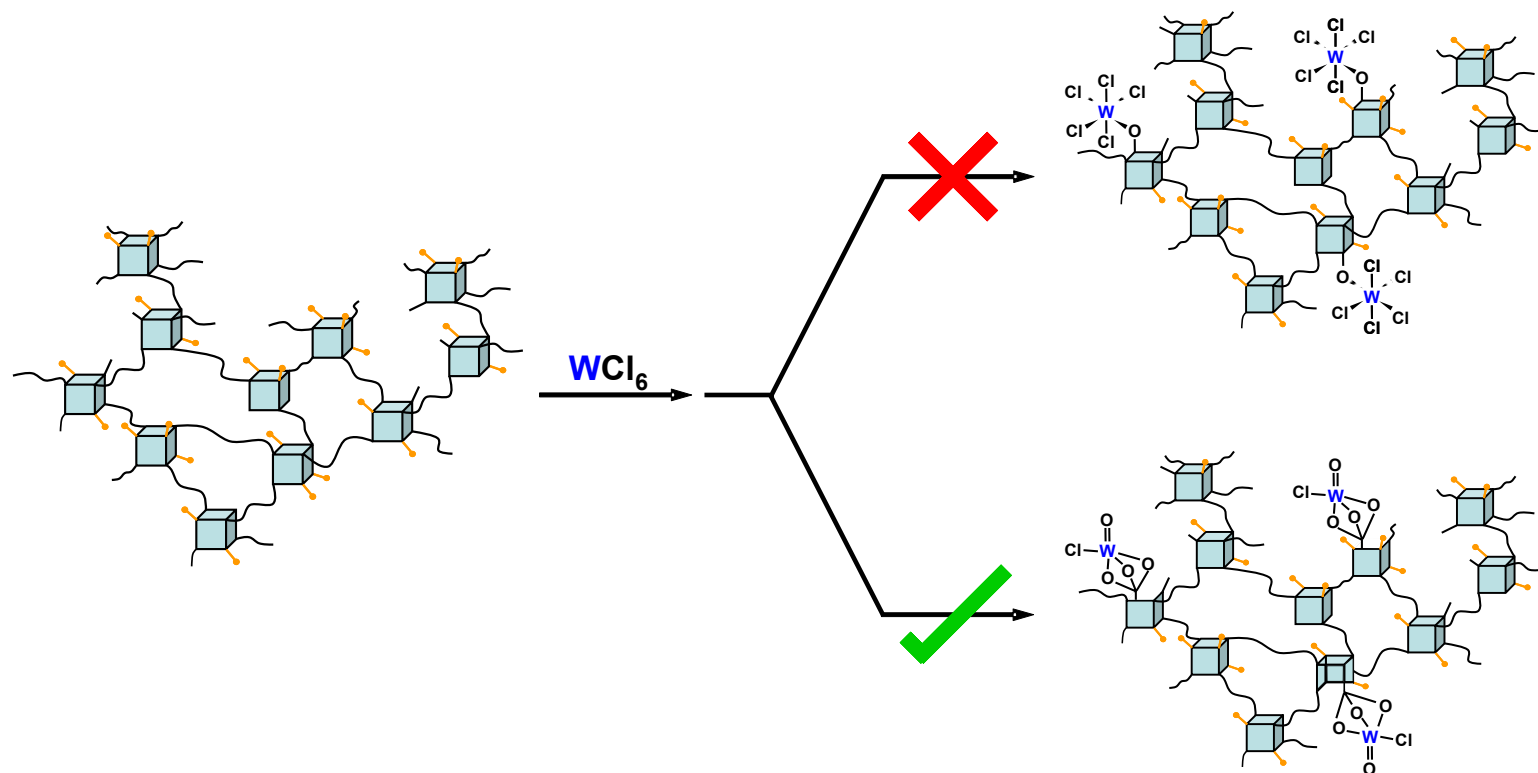


Figure 209: Proposed representation of the catalyst ensemble following the reaction of WCl_6 and the premade silicate building block support.

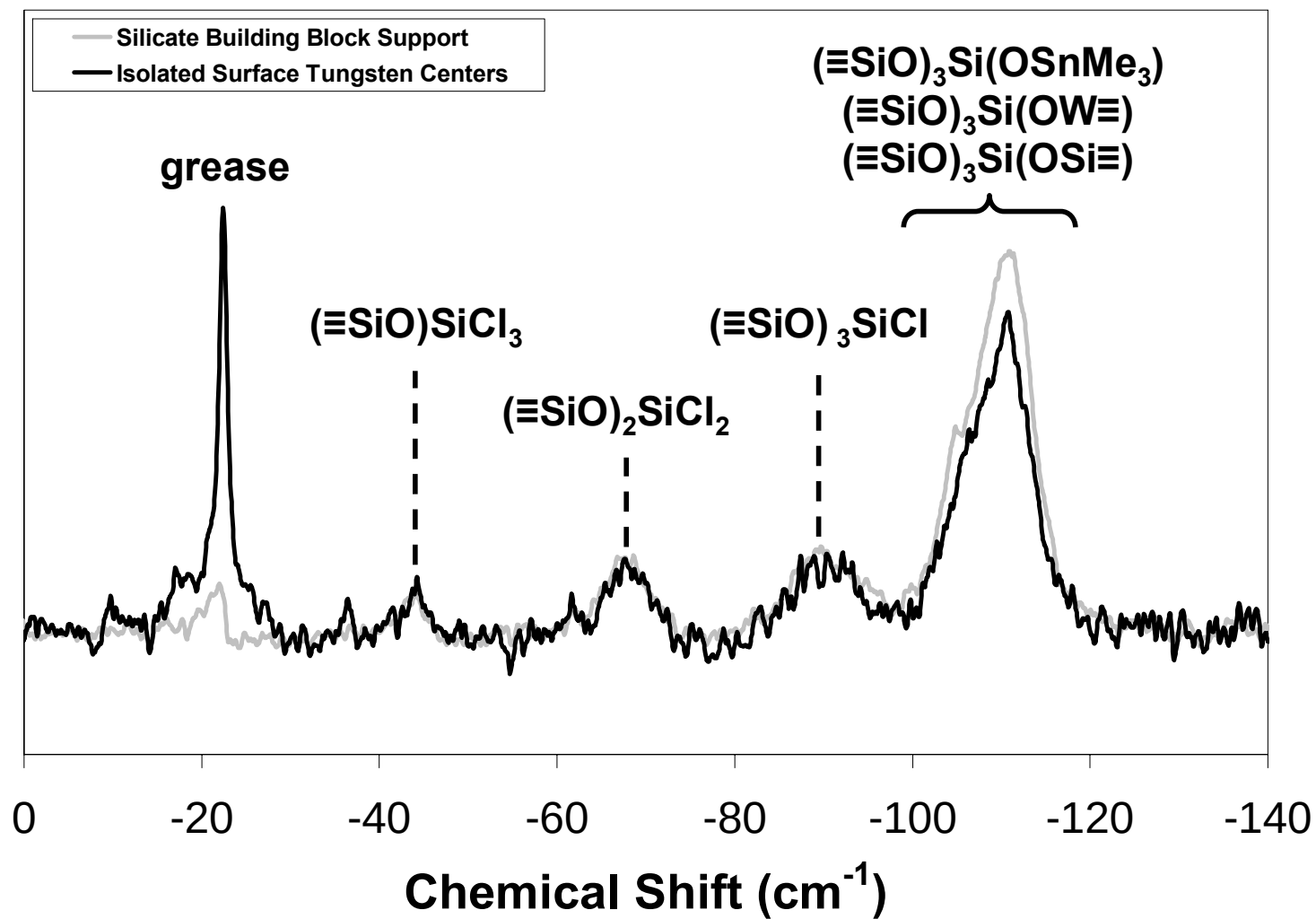


Figure 210: ^{29}Si SSNMR spectra (-140 to 0 ppm) of the premade tungsten-free silicate building block support and the material following the reaction of WCl_6 and the premade silicate building block support.

Summary and Conclusions

The synthesis of materials containing a single type of well-defined, isolated tungsten(VI) ensembles is demonstrated. The ensembles that are incorporated into the framework and on the surfaces of silicate building block matrices are readily synthesized using a targeted building block approach and sequential dosing synthetic strategy. Both embedded and surface catalyst ensembles were targeted using two different tungsten(VI) precursors (WOCl_4 and WCl_6).

Isolated embedded tungsten(VI) catalyst ensembles were synthesized by reacting the silicate building block with a limiting amount of tungsten(VI) precursor, either WOCl_4 or WCl_6 . The resulting material was further cross linked using SiCl_4 resulting in a high surface area silicate support containing isolated embedded tungsten(VI) catalyst ensembles. The reaction between WOCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ proceeded as expected resulting in the production of isolated embedded tungsten oxo centers (Figure 126). However the reaction between WCl_6 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ did not proceed as expected and actually also resulted in the production of isolated embedded tungsten oxo centers (Figure 156). In both cases the number of chloride ligands on the tungsten(VI) precursors and the number of tungsten-to-support linkages formed are reproducibly controlled. XAS data confirmed that the oxidation state of the tungsten centers remained unchanged during the cross-linking reaction (control of the metal cation). A structural model based on EXAFS data strongly supports this model for the local environment around each embedded tungsten center.

Isolated surface tungsten(VI) catalyst ensembles were synthesized by reacting a premade silicate building block support with a defined amount of a tungsten(VI) precursor, either WOCl_4 or WCl_6 . The reaction between both tungsten(VI) precursors (WOCl_4 and WCl_6) and the premade silicate building block support did not proceed as expected and actually resulted in the production of the same type of surface species (Figure 188 & Figure 209). In both cases the number of chloride ligands on the tungsten(VI) precursors and the number of tungsten-to-support linkages formed are reproducibly controlled. XAS data confirmed that the oxidation state of the tungsten centers remained unchanged during the cross-linking reaction (control of the metal cation). A structural model based on EXAFS data supports this model for the local environment around each surface tungsten center.

In conclusion, the building block approach and sequential dosing strategy provided control of all the necessary components of both embedded and surface tungsten(VI) catalyst ensembles.

Acknowledgments

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CHAPTER 4. SYNTHESIS AND CHARACTERIZATION OF ISOLATED ZIRCONIUM(IV) CATALYST ENSEMBLES IN AND ON SILICATE BUILDING BLOCK MATRICES

Introduction

Zirconium containing silica based heterogeneous catalysts have recently drawn interest because their titanium analogues such as TS-1, Ti- β , Ti-SBA-15, and Ti-MCM-41 have been extensively studied and are known to be active heterogeneous catalysts in a number of selective oxidation reactions. In some cases, the zirconium analogues have shown less reactivity than the titanium analogues[187,188] however silica based heterogeneous catalysts that contain zirconium(IV) active sites have exhibited interesting catalytic behavior in a number of selective oxidation,[187-190] solid acid,[191,192] and rearrangement[193] reactions.

The preparation of zirconium containing silica based heterogeneous catalysts using a variety of conditions and procedures (templating,[38,187,190,193] hydrothermal,[189] nonaqueous sol-gel,[188] grafting,[194] sol-gel,[116,171,195,196] incipient wetness[193]) has been described in the literature. Several reports claim that the zirconium centers are incorporated into the framework of the support[187-191,193] even though little, if any, evidence is provided to support this claim. In most cases the claim of incorporation is only supported by the lack of detection of crystalline ZrO_2 domains via XRD[189] or amorphous ZrO_2 domains via UV-vis[187] with the rationale being if there are no ZrO_2 domains then the zirconium centers must be highly dispersed. Few researchers actually probe the local environment around the zirconium centers[116,123,171,193-197] and those who do have difficulty concluding anything about the local environment because they cannot differentiate between the linkages to the support (Zr-O-Si) and the linkages to the oxide domains (Zr-O-Zr).

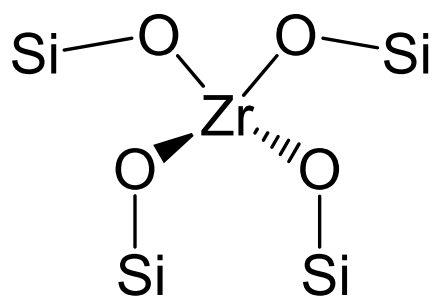
The traditional synthetic approaches used to prepare the zirconium-containing heterogeneous catalysts do not provide the necessary synthetic control to target specific types of sites in these materials. Sol-gel[116,171,195,196] and incipient wetness[193] procedures are known to produce ZrO_2 domains and provide little synthetic control to prevent the formation of these domains. Templating[187,190,193] and hydrothermal[189] procedures generally require the catalyst to be calcined at the end of the synthetic process and the harsh conditions of calcination provide little control. One of the few reports of well-defined, single site

heterogeneous catalysts that contain zirconium centers uses a grafting procedure to prepare the isolated zirconium centers. These heterogeneous catalysts were prepared by grafting either $\text{Zr}(\text{acac})_4$ or $\text{Zr}(\text{Np})_4$ onto a silica surface that has been thermally pretreated to reduce the number of hydroxyl groups.[194] In general the nature of the active site present in all of the heterogeneous catalysts mentioned above that is thought to be responsible for catalytic activity has not been established. For these reasons (the lack of synthetic control and the lack of knowledge of the local environment of the zirconium active species), a detailed study of the targeted synthesis of silicate building block matrices that contain a single type of well-defined, isolated zirconium(IV) catalyst ensemble was initiated.

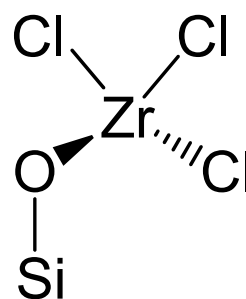
Heterogeneous catalysts are known to be difficult to characterize due to the fact that a wide variety of (direct and indirect) spectroscopic probes are needed to piece together a reasonably clear picture of the immediate environment around the catalyst ensembles present in the system. X-ray absorption spectroscopy (XAS) directly probes the immediate environment that defines the catalyst ensemble and provides information about the oxidation state of the absorbing metal, the coordination geometry, and structural information about the elements around the metal. Infrared spectroscopy (IR) can be used to verify linkages to the support as well as other ligands and grouping present via their vibrational signatures. Solid state nuclear magnetic resonance spectroscopy (SSNMR) provides information about the silicate support and possibly the linkages of the catalyst ensemble to the support. Nitrogen adsorption/desorption measurements provide information about the porosity of the material.

In this chapter, two unique catalyst ensembles are targeted and successfully synthesized (Figure 211). Embedded catalyst ensembles were synthetically targeted by reacting the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ with a limiting amount of zirconium(IV) chloride, ZrCl_4 , followed by further cross-linking with a silyl chloride. The resulting high surface area silicate support contained isolated, embedded zirconium ensembles. Surface catalyst ensembles were also synthetically targeted by reacting a premade silicate building block support with a defined amount of zirconium(IV) chloride, ZrCl_4 . In all cases, the immediate environment around the zirconium centers was thoroughly characterized following each reaction. The synthesis and characterization of the silicate building block matrices containing embedded zirconium catalyst ensembles and those containing surface zirconium catalyst ensembles is described.

Targeted Catalyst Ensembles



*"Isolated Embedded
Zirconium Centers"*



*"Isolated Surface
Zirconium Centers"*

Figure 211: Illustration of the targeted isolated zirconium(IV) catalyst ensembles.

Experimental

Materials

Zirconium(IV) chloride (ZrCl_4 , Aldrich 99.5%) was sublimed under vacuum at 175°C and stored in a nitrogen filled glovebox before use. The white powder product was collected on the cold finger and sides of the Schlenk vessel while a yellowish white powder remained at the bottom of the Schlenk vessel. Information about the other materials used in this chapter has already been presented in chapter two.

General Synthetic Procedures

Isolated Embedded Zirconium Centers

2.00 g (1.08 mmol) dehydrated $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and 0.126 g (0.54 mmol) ZrCl_4 were added to a Schlenk vessel. The solid metal chloride was added to the vessel in a N_2 atmosphere glove box, followed by 25 mL THF (vapor transferred) into the reaction vessel. The reaction was stirred vigorously under static vacuum for 24 h at 60°C . During the reaction process, no gel or precipitate was seen to form. After this time the solvent and byproduct, Me_3SnCl , were removed under vacuum at 100°C for an additional 24 h.

After the initial dosing reaction, which integrated zirconium into the silicon-based building block matrix, 25 mL of toluene was vapor transferred to the reaction vessel followed by 0.55 g SiCl_4 (3.24 mmol). The second linking agent was vapor transferred into the Schlenk vessel and after its addition the solution was allowed to stir under static vacuum for 24h at 80°C . Silicon tetrachloride bis-pyridine, SiCl_4py_2 , can also be used as a second linking agent at the same molar ratio to $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. During the reaction process a gelatinous product formed prior to solvent removal. After the removal of volatiles and drying under vacuum at 100°C , an off-white solid product was obtained. The product was characterized without any further steps for purification.

Isolated Surface Zirconium Centers

Synthesis of Silicate Building Block Support

A nanostructured silicate building block support is synthesized following the general procedure previously reported.[95] In a Schlenk reaction vessel, 2.481 g (1.337 mmol) of dry $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ and 1.261 g (3.843 mmol) of SiCl_4py_2 [2.87:1 SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$; 1.44:1 $\text{Cl}:\text{Me}_3\text{Sn}$] are dissolved in 30 mL of toluene. A gel forms within 1 hour. The solution is

stirred at 80°C under static vacuum for up to 24 hours whereupon all volatiles are removed. The resulting fine powder solid is used without further purification.

Addition of Surface Zirconium Centers

In a N₂ atmosphere glove box, 0.246 g (1.056 mmol) of ZrCl₄ [0.79:1 ZrCl₄:Si₈O₁₂(OSnMe₃)₈] is added to the reaction vessel containing the nanostructured silicate building block support followed by 30 mL of diethyl ether (vapor transferred) into the reaction vessel. The solution is stirred at room temperature under static vacuum for 27 hours whereupon all volatiles are removed. The resulting fine powder solid is used without further purification.

Instrumentation

Gravimetric analysis, nitrogen adsorption/desorption, and a variety of spectroscopic techniques (IR, ²⁹Si SSNMR, XAS (XANES and EXAFS)) are used to characterize the synthesized materials. Pyridine adsorption and the corresponding IR spectra are used to probe the acidity of the sites present in the synthesized materials. Information about gravimetric analysis, nitrogen adsorption/desorption, IR, and ²⁹Si SSNMR has already been presented in chapter two.

X-ray Absorption Spectroscopy

XAS data at the zirconium K edge (17998 eV) were obtained at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory on beamline X18B, operated at 2.8 GeV with a current of 300-200 mA. Spectra were collected at room temperature. The beam dimensions (i.e. spot size) on sample was 10 x 1 mm (w x h) for X18B. X-rays were monochromatized via reflection from Si(111) crystals through a 1 mm entrance slit. The incident beam was detuned 20% to suppress harmonics. Samples were mounted 45° to the beam, to collect transmission and fluorescence spectra simultaneously. The intensity of the incident beam was measured with a 18 cm 70:30 N₂:Ar-filled ion chamber detector (I₀). Transmitted x-rays were detected in a 30 cm 90:10 Ar:Kr-filled ion chamber (I_t). The fluorescence signal from the sample was recorded with a Canberra PIPS detector (I_{fluor}). Spectra were recorded at room temperature in four energy regions about the zirconium K edge at 17998 eV: -150 to -15 eV (below the edge) in 5 eV steps (1 s integration), -15 to 75 eV (through the edge) in 1.3 eV steps (2 s integration), 75 to 12 k in 0.05-k steps (3 s integration), and 12k to 18k in 0.05-k steps (4 s integration).

Sample powders were held in copper plates between windows of 7.5 μm polyimide (Kapton®) film (Chemplex 442) affixed with double sided tape to each side of the plate. Samples were loaded in a N_2 dry box to prevent hydrolysis. Two to three scans were collected for each sample. Data processing and analysis were performed using the IFEFFIT data analysis software suite (Athena & Artemis).[125,167] The Athena program was used for XANES analysis and extraction of EXAFS from the smooth absorption edge background using standard procedures. The pre-edge background was modeled with a linear function. The post edge, smooth background was approximated with a stiff spline function and adjusted to minimize Fourier components that produce low R ($< 1 \text{ \AA}$) features in R -space plots. Low frequency Fourier components were also filtered from the EXAFS via the R_{bkgd} parameter that was kept smaller than 0.5 times the distance of the closest backscattering shell. Merged files were generated after auto aligning scans in Athena program. The Artemis program was used for modeling EXAFS $\chi(k)$ data. Theoretical phase and amplitude functions based on structural models were developed using FEFF6L in Artemis.[168] Single scattering paths for the first coordination sphere around zirconium (Zr-O, Zr-Cl, Zr $\cdots$ Si) were included in all models where appropriate. Preliminary fits to structural models were initiated with coordination numbers set to expected values (based on gravimetric analysis) while backscatterer identity (atomic number) was verified and other structural parameters were iteratively refined. Once these model parameters converged and were stable, coordination numbers were allowed to vary and generally converged to within 20% of expected values based on the connectivity for the sample determined from gravimetric data.

Results and Discussion

Isolated Embedded Zr(IV) Catalyst Ensemble using ZrCl_4

The combination of a building block approach and a sequential addition strategy is used to target the synthesis of an embedded catalyst ensemble which contains a Zr(IV) center with four links to the silicate support (Figure 211). This embedded catalyst ensemble will be referred to as “*isolated embedded zirconium centers.*”

First Cross-Linking Reaction: Reaction of ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

The synthesis of isolated zirconium centers that are connected to four silicate building blocks is achieved by reacting a trimethyltin functionalized silicate building block,

$\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, with a limiting amount of ZrCl_4 (1 ZrCl_4 : 2 $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ at 60°C in tetrahydrofuran for 24 hours) (Figure 212). The cross-linking process proceeds via a metathesis reaction where a chloride ligand of ZrCl_4 cleanly reacts with a Me_3Sn group to form a new siloxane bond (Zr-O-Si) and Me_3SnCl , a volatile byproduct. This process will continue until either all the chloride ligands on ZrCl_4 are consumed or a chloride ligand becomes unreactive as more Zr-O-Si bonds are formed to the zirconium center. A limiting amount of ZrCl_4 was used to insure all the chloride ligands react with the Me_3Sn groups on the silicate building block. The volatiles of the reaction were analyzed using ^1H NMR and Me_3SnCl was the only byproduct observed. Gravimetric analysis (4.1 ± 0.2 equivalents of Me_3SnCl) is consistent with the replacement of all the chloride ligands on the zirconium center with oxygen ligands as illustrated in Figure 212 (Zr-O-Si).

Figure 213 shows the IR spectra for a silicate building block support and the isolated embedded zirconium centers. The material is synthesized under nonaqueous aprotic conditions which results in the production of a hydroxyl-free material. As expected, no evidence for the presence of silanol groups ($3600\text{-}4000\text{ cm}^{-1}$) is observed in the IR spectrum. IR spectroscopy is also used to verify the formation of the Zr-O-Si linkage. The band at 1030 cm^{-1} , is commonly assigned to the Si-O-Si stretching mode (Figure 213).[46,171] A shoulder on the Si-O-Si feature observed at approximately 965 cm^{-1} is characteristic of the presence of M-O-Si groups, in this case Zr, in the matrix.[171,188-190] The observation of this weak shoulder provides direct evidence on the formation of Zr-O-Si groups suggesting the metathesis reaction proceeded as expected.

The material described above was exposed to pyridine to evaluate what types of isolated acidic centers were present. Three features were observed in the IR spectrum (Figure 214) after exposure to pyridine (1445 cm^{-1} , 1489 cm^{-1} , and 1606 cm^{-1}) which are characteristic of Lewis acidic zirconium centers in silica.[198] No evidence for Bronsted sites (1540 cm^{-1}) or silanol groups (1590 cm^{-1}) is observed.

Figure 215 shows the ^{29}Si SSNMR spectrum for the isolated embedded zirconium centers. When a limiting amount of ZrCl_4 is reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, three signals are observed. The feature at -22 ppm is assigned to traces of silicon grease that contaminate the

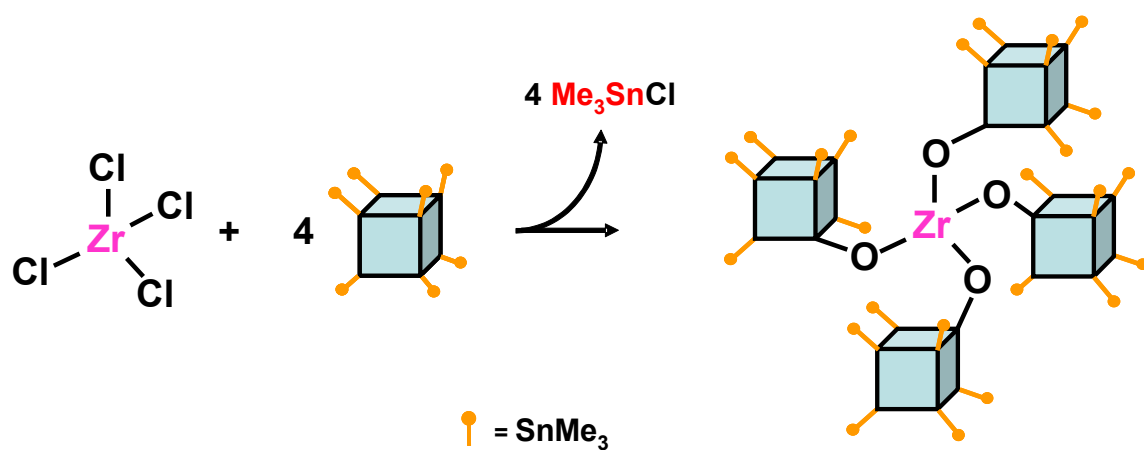


Figure 212: First Cross-Linking Reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

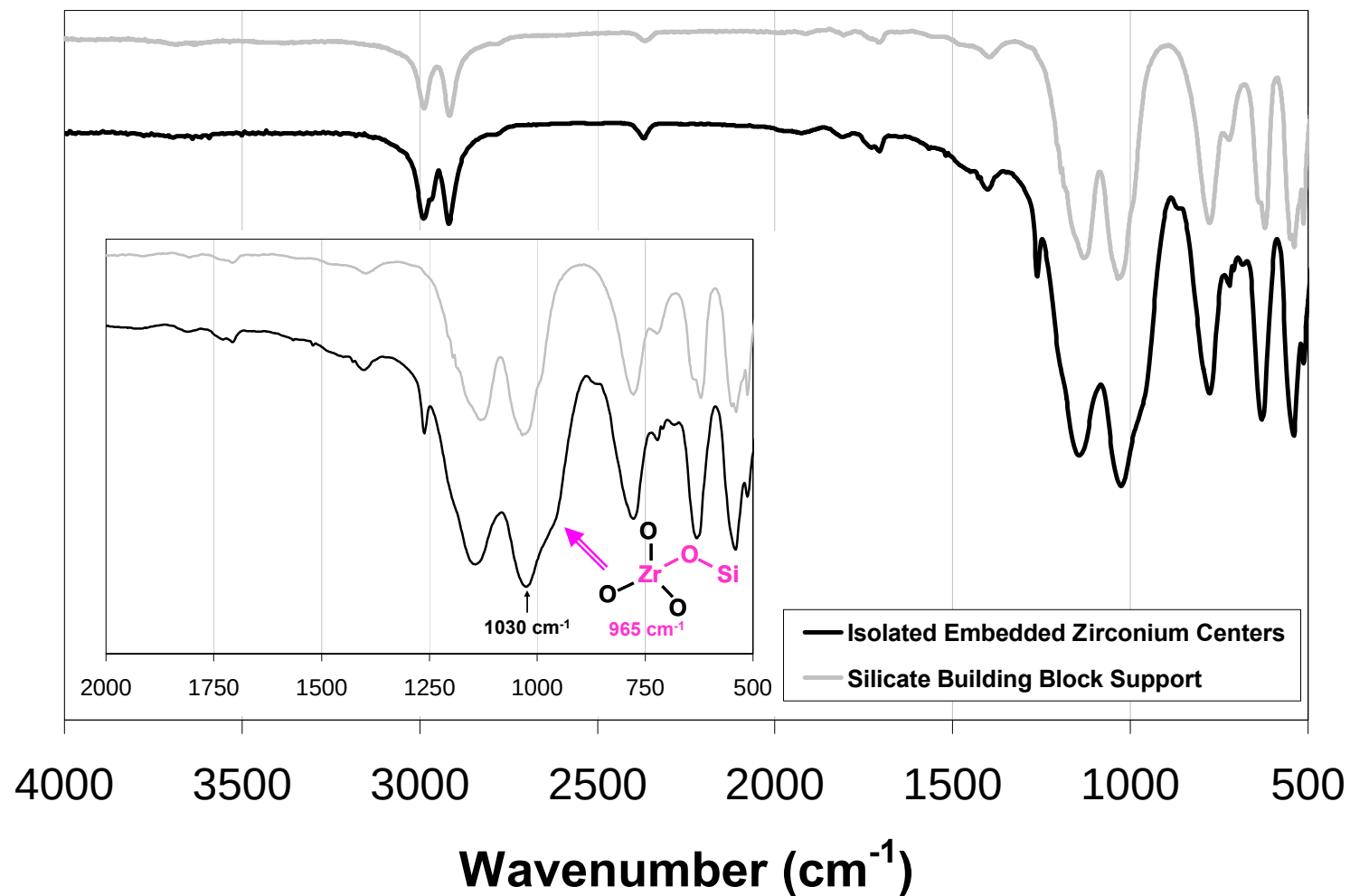


Figure 213: IR spectra (500–4000 cm⁻¹) of a zirconium-free silicate building block support (gray) and the material following the first cross-linking reaction, ZrCl₄ and Si₈O₁₂(OSnMe₃)₈ (black). The inset contains the expanded IR spectrum (500–2000 cm⁻¹) which illustrates the Zr-O-Si shoulder (965 cm⁻¹).

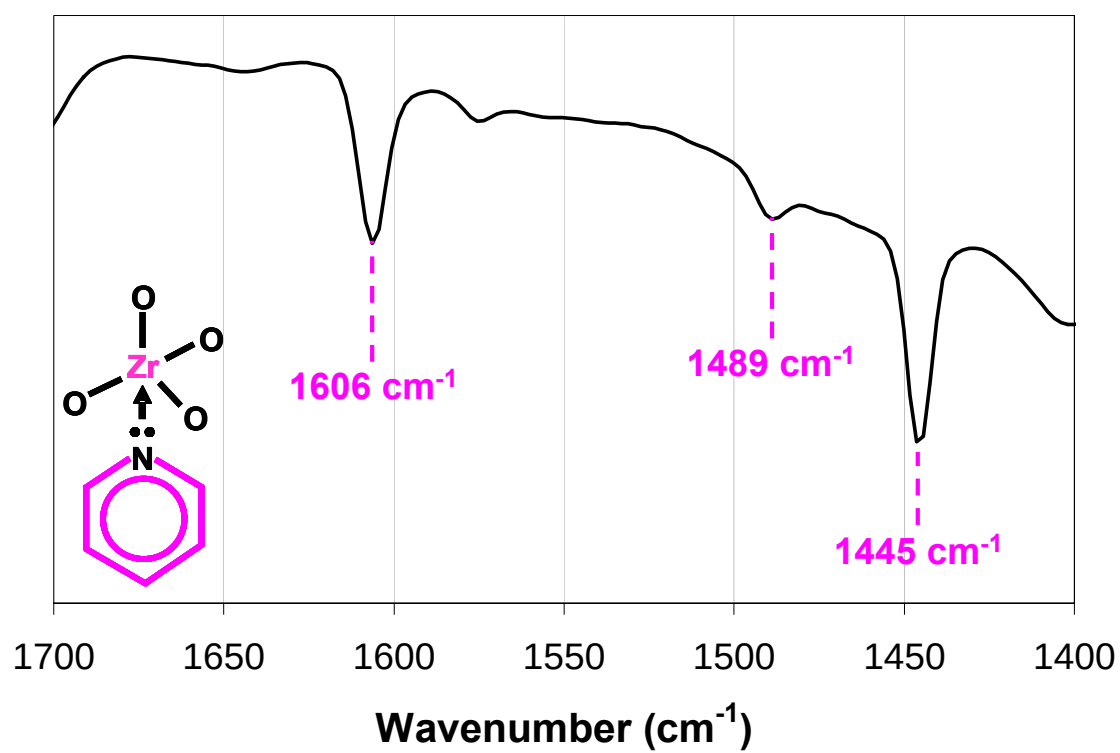


Figure 214: IR spectrum of pyridine bond to Lewis acidic zirconium centers synthesized after first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

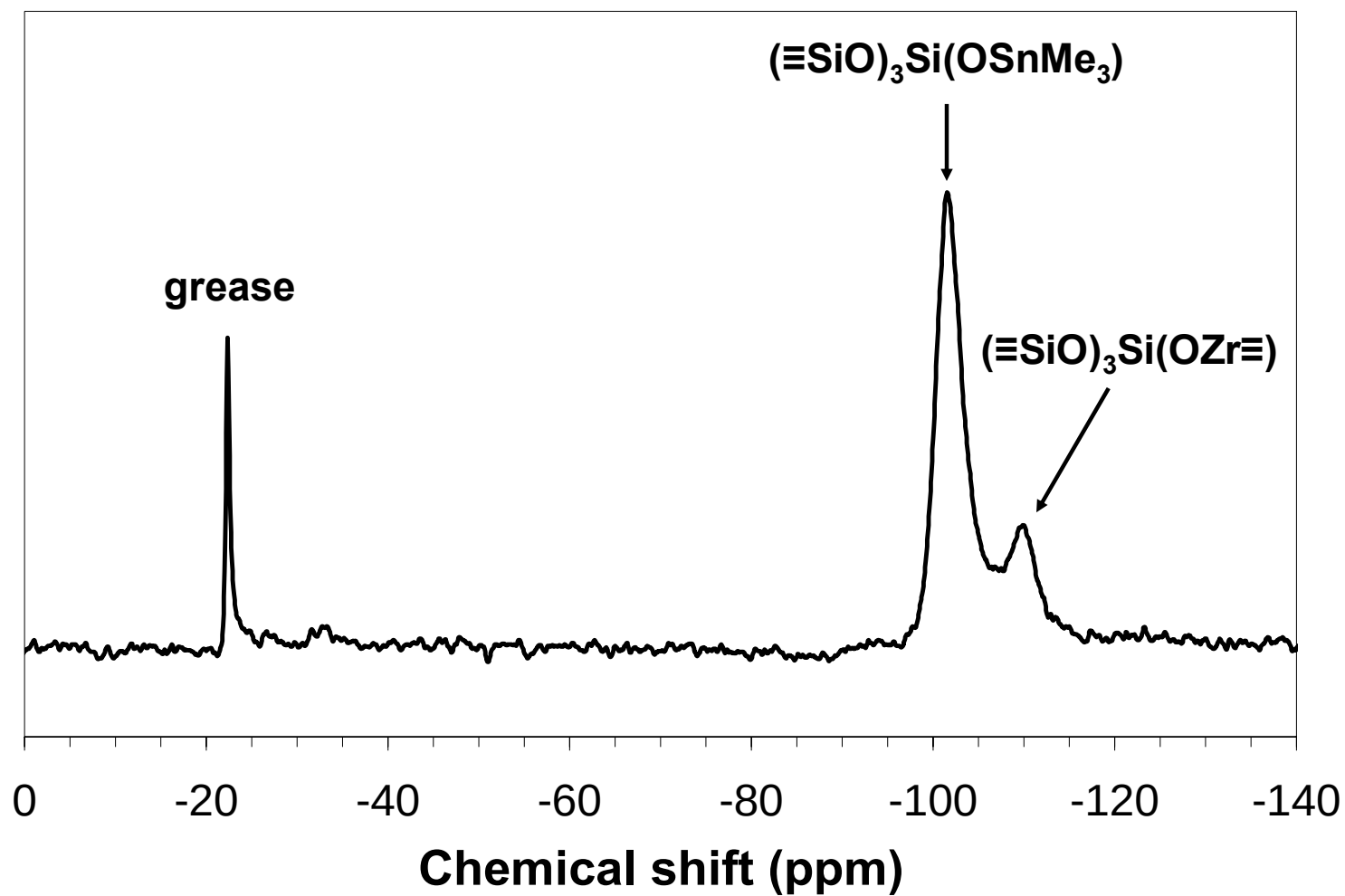


Figure 215: ^{29}Si SSNMR spectrum (-140 to 0 ppm) following the first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The peak at -22 ppm is assigned to silicon grease used to seal the sample from air.

sample. The absence of signals between -22 and -100 ppm in Figure 215 indicates that no silyl chlorides are present in the matrix (i.e. $(\equiv\text{SiO})_{4-x}\text{SiCl}_x$).[95] The feature at -101 ppm is assigned to the silicon corners on the building block which are connected to unreacted Me_3Sn groups and three other corner silicon atoms ($(\equiv\text{SiO})_3\text{Si}(\text{OSnMe}_3)$).[95] The feature at -110 is assigned to the silicon corners on the building block which are connected to the zirconium centers ($(\equiv\text{SiO})_3\text{Si}(\text{OZr}\equiv)$).

Nitrogen adsorption/desorption measurements were conducted to determine the BET surface area and total pore volume. No measurable BET surface area or pore volume was observed, which supports the conclusion that the silicate building block material after one stage of cross-linking with a limiting amount of ZrCl_4 contains small oligomers and that a rigid porous macromolecule has not been formed.

XAS is one of the techniques that can probe the immediate environment around the zirconium centers and provide the important information needed to verify the metathesis reaction proceeded as expected. Thus XAS data were used to obtain more information about the coordination geometry and oxidation state of the zirconium centers (XANES) in addition to the connectivity of the zirconium centers (EXAFS) in these matrices.

XANES data for the K edge (17998 eV) provide information about the coordination geometry (via the presence of a pre-edge feature) and oxidation state (via the position of the K edge) of the zirconium centers.[116,195,199]

Figure 216 shows the XANES and the derivative XANES spectra of several zirconium oxide reference compounds. It is difficult to determine the position of the K edge and the presence of a pre-edge feature using only the XANES spectra. The position of the K edge is defined by the maximum of the derivative XANES spectrum (i.e. the point of inflection) so the derivative XANES spectra should be used to determine the edge position. Edge positions and derivative XANES spectra are rarely reported in the literature for zirconium systems which can make analysis of XANES spectra challenging at times. Even though the derivative XANES spectra shown in Figure 216 are found in the literature it is important to note that the edge positions shown in Figure 216 are incorrect because the spectra were calibrated using m-ZrO_2 (Zr^{4+}) at 17998 eV (the known position of $\text{Zr}(0)$). Therefore the edge position of the zirconium

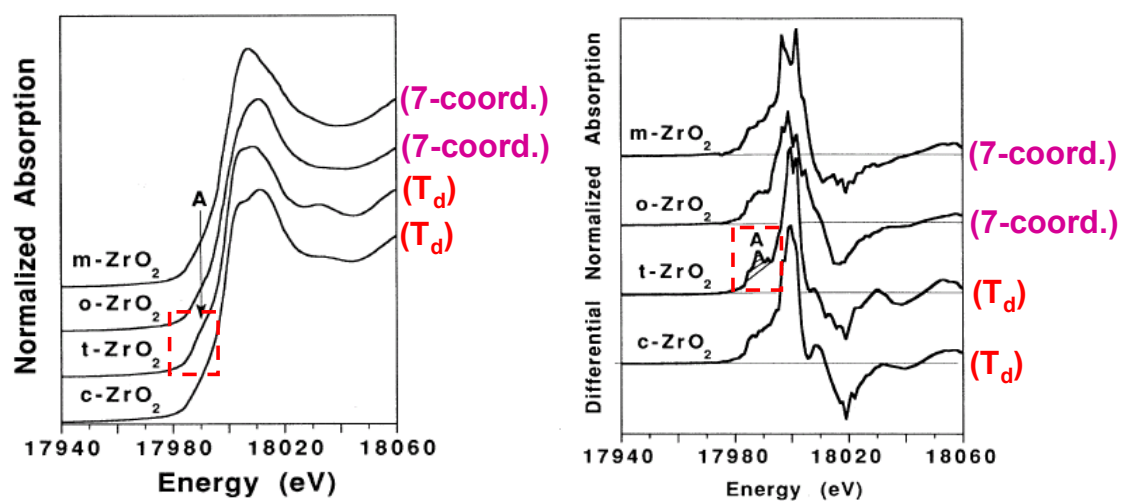


Figure 216: XANES spectra (Zr K edge) (left) and derivative XANES spectra (right) of several zirconium oxide reference compounds. NOTE: The energy axis for these plots was calibrated to 17998 eV using m-ZrO₂. (Figure was reproduced from Ref [199])

oxide reference compounds shown in Figure 216 cannot accurately be determined. Instead of trying to use literature edge positions to determine the oxidation state of zirconium, the XANES spectra for a series of standard zirconium materials with different oxidation states were collected and the edge positions were determined. Figure 217 shows the edge positions (defined as the maximum of the derivative XANES spectrum) of standard zirconium materials with different oxidation states (Zr(0), Zr(III), Zr(IV)). The edge position for zirconium foil (Zr(0)) is 17998 eV, the edge position for zirconium nitride (ZrN, Zr(III)) is 18001 eV, and the edge position for zirconium(IV) oxide (ZrO₂, Zr(IV)) is 18004 eV. The edge position appears to be sensitive to the oxidation state of zirconium, which means the edge position for the zirconium oligomers can be used to determine the zirconium oxidation state.

Using the derivative XANES spectrum also aids the determination of the presence of a pre-edge feature. As shown by the red box in Figure 216, the presence of a pre-edge is more evident in a derivative XANES spectrum than a XANES spectrum. Therefore, the derivative XANES spectrum of the zirconium oligomers should be used to determine the presence of a pre-edge feature.

Figure 218 shows the XANES spectra of several zirconium reference compounds which can be used to illustrate differences in the shape of XANES spectra. The differences in the XANES spectra can in some cases provide information that could help empirically correlate the shape of XANES spectrum to the zirconium coordination geometry. Zirconium compounds with tetrahedral coordination geometry (ZrSiO₄, tetragonal-ZrO₂, cubic-ZrO₂) tend to have a pre-edge feature while zirconium compounds with octahedral coordination geometry (BaZrO₃, Zr(OⁿPr)₄) tend to not have a pre-edge feature. The shape of the XANES spectrum for the zirconium oligomers will be compared to the spectra for the reference compounds in order to see if the shape of the XANES spectrum can be used to determine the zirconium coordination geometry. It is important to note the shape of the XANES spectra for c-ZrO₂ (T_d) and Zr(OⁿPr)₄ (O_h) are very similar even though the two compounds have different zirconium coordination geometries. Therefore one should exercise caution when assigning coordination geometry based solely on the shape of the XANES spectrum.

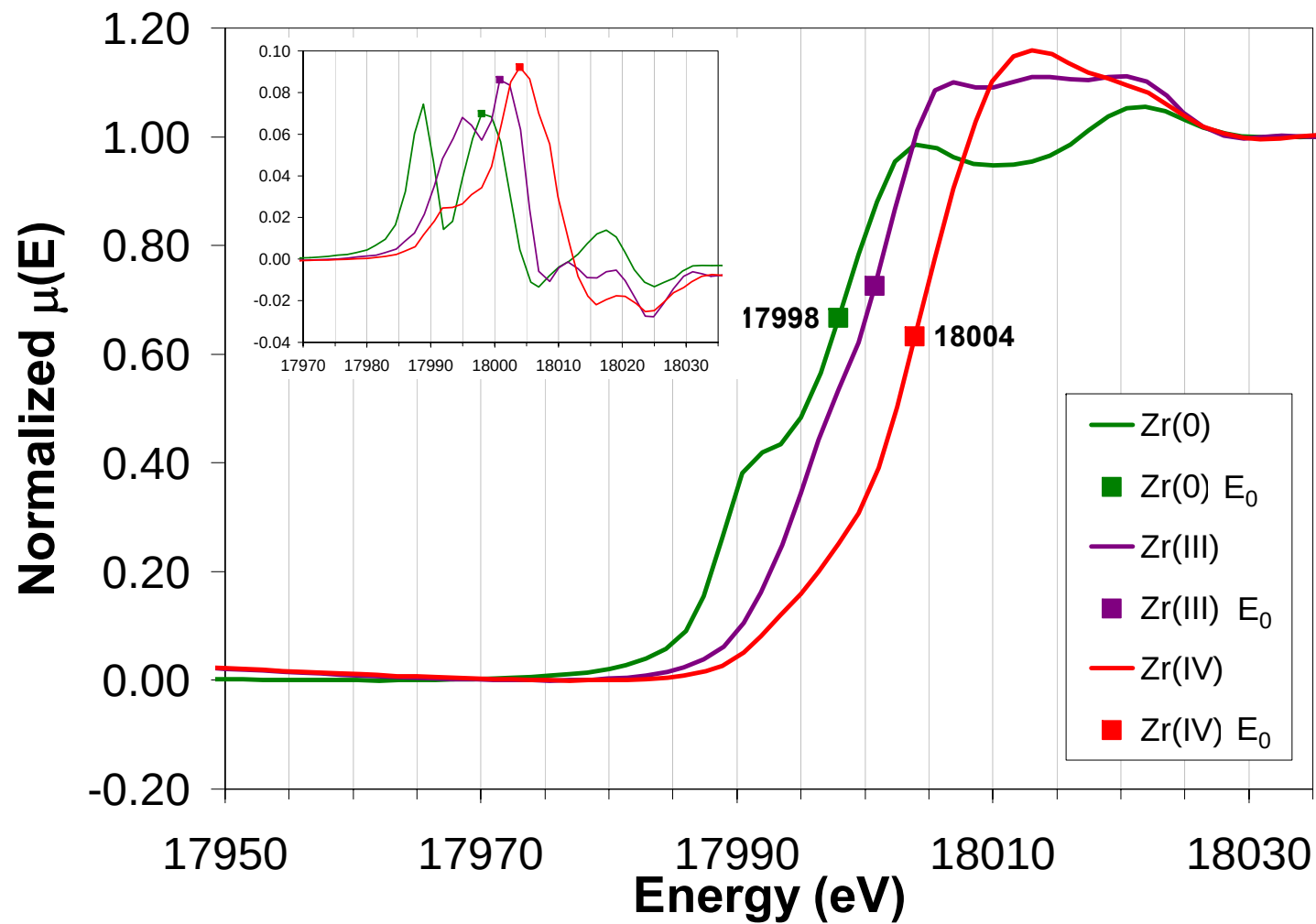


Figure 217: XANES spectra (Zr K edge) of standard zirconium materials with varying oxidation state. The inset contains the derivative XANES spectra which show the adsorption edge position of each material.

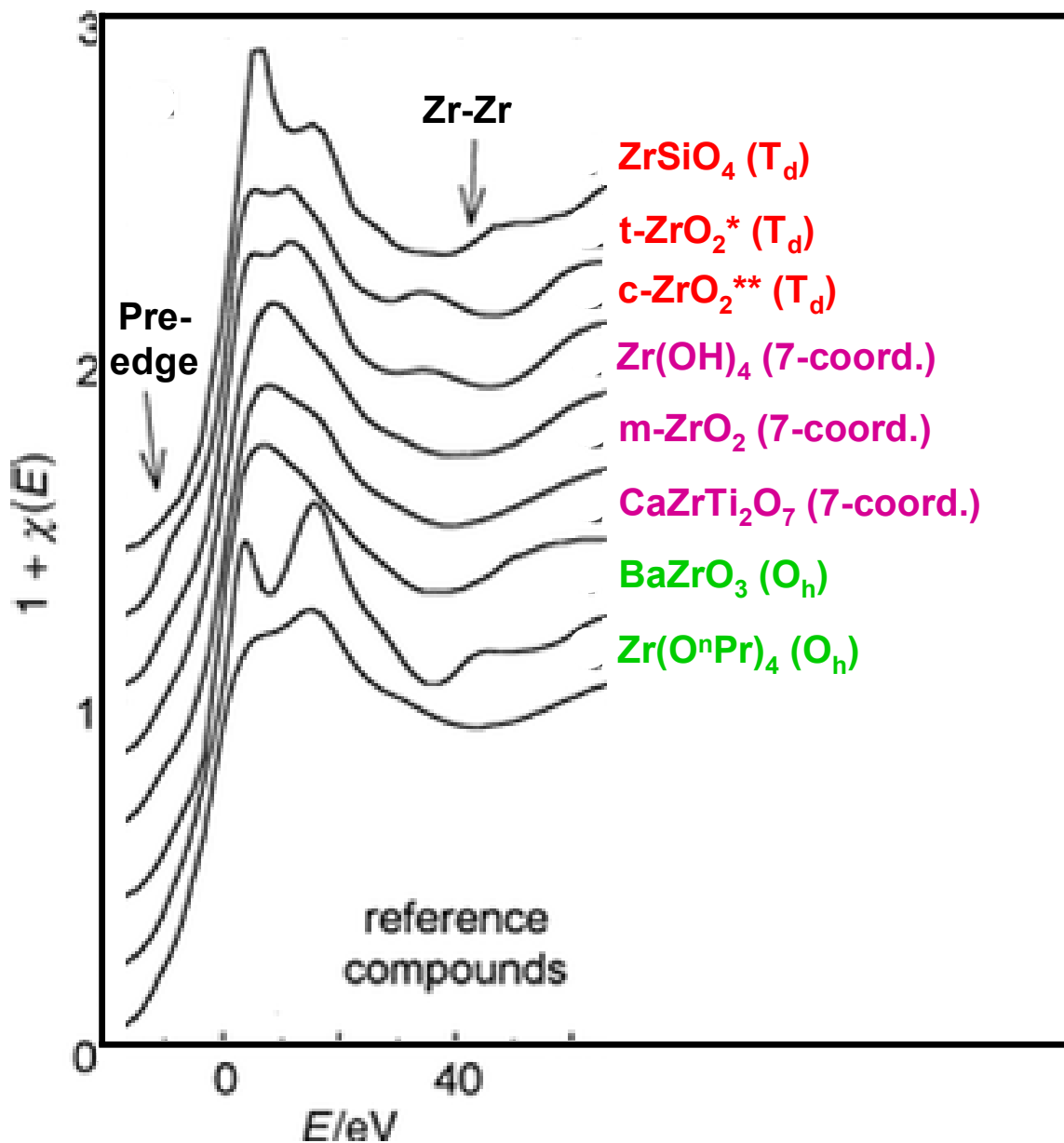


Figure 218: XANES spectra (Zr K edge) of Zr reference compounds with tetrahedral (ZrSiO_4 , tetragonal- ZrO_2 stabilized with Y_2O_3 , cubic- ZrO_2 stabilized with Y_2O_3), sevenfold (Zr(OH)_4 , monoclinic- ZrO_2 , $\text{CaZrTi}_2\text{O}_7$), and octahedral (BaZrO_3 , $\text{Zr(O}^n\text{Pr)}_4$) geometry. Tetragonal- ZrO_2 has the most evident pre-edge feature (see left arrow labeled Pre-edge). ZrSiO_4 has a feature ~ 45 eV above the absorption edge that corresponds to multiple scattering due to strong Zr-Zr correlations (see right arrow labeled Zr-Zr). (Figure was reproduced from Ref [116])

Figure 219 shows the XANES spectrum at the K edge of the embedded zirconium material at this stage in the synthesis. Two features are observed in Figure 219. The position of both features was determined using the derivative XANES spectrum (the inset of Figure 219). The first feature (17993 eV) is assigned to a pre-edge feature and the second feature (18003 eV) is assigned to the K absorption edge. The presence of a pre-edge feature ($1s \rightarrow 4d$ transition) provides evidence that the coordination geometry around the zirconium center is not octahedral and suggests the coordination geometry is tetrahedral.[116] Table 12 summarizes the pre-edge position and K edge ionization energy for each of the isolated zirconium(IV) catalyst ensembles discussed in this chapter as well as the edge position of zirconium foil, zirconium nitride, and zirconium(IV) oxide. The edge position of the isolated embedded zirconium centers (18003 eV) nearly matches the edge position of zirconium(IV) oxide and supports the claim that the oxidation state of the zirconium centers is +4. However the shape of the adsorption edge of the isolated zirconium centers is similar to the shape of the absorption edge of $c\text{-ZrO}_2$ (T_d) and $\text{Zr}(\text{O}^n\text{Pr})_4$ (O_h) (Figure 218).[116] Therefore the shape of the adsorption edge of the material cannot be used to conclusively determine the coordination geometry around the embedded zirconium centers.

In summary, the analysis of the XANES spectrum of the isolated embedded zirconium centers prepared here is consistent with an oxidation state of +4 while no conclusive determination of the coordination geometry can be made.

An analysis of EXAFS data was used to obtain more information about the connectivity of the zirconium centers in the silicate building block matrix. EXAFS data can provide both qualitative and quantitative information about the zirconium centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around zirconium) can be qualitatively determined by looking at the magnitude R-space plot (Figure 220). As many as three shells may be present around the zirconium centers after the first cross-linking reaction: a shell of singly bound oxygen atoms (Zr-O), one for any unreacted chloride ligands (Zr-Cl), and a shell of nonbonded silicon atoms ($\text{Zr}\cdots\text{Si}$). The feature corresponding to Zr-Cl should not be observed based on gravimetric analysis which indicated that all the chloride ligands initially associated with ZrCl_4 were lost from the system as Me_3SnCl . Figure 220 shows the features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot.

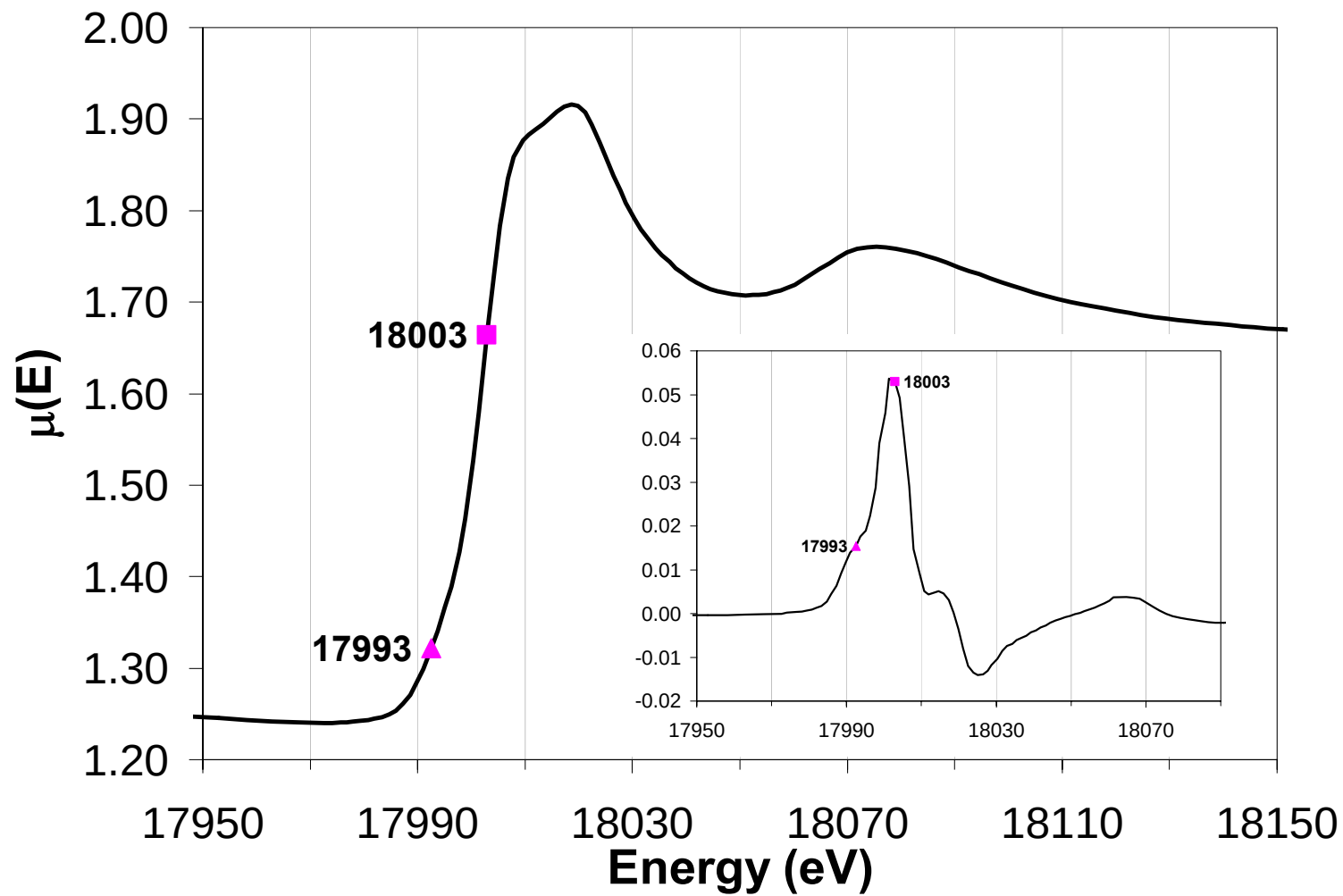


Figure 219: XANES spectrum (Zr K edge) following the first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The inset contains the derivative XANES spectrum which clearly shows the pre-edge feature (pink triangle) and the adsorption edge (pink square).

Table 12: XANES analysis for embedded and surface zirconium centers and standard zirconium materials

Compound	Geometry	K edge	
		Pre-edge (eV)	E ₀ (eV)
Embedded zirconium centers, 1 st Cross-linking	T _d	17993	18003
Embedded zirconium centers, 2 nd Cross-linking	T _d	17992	18002
Surface zirconium centers	T _d	17993	18000
Zr foil, Zr(0)			17998
ZrN, Zr(III)			18001
ZrO ₂ , Zr(IV)			18004

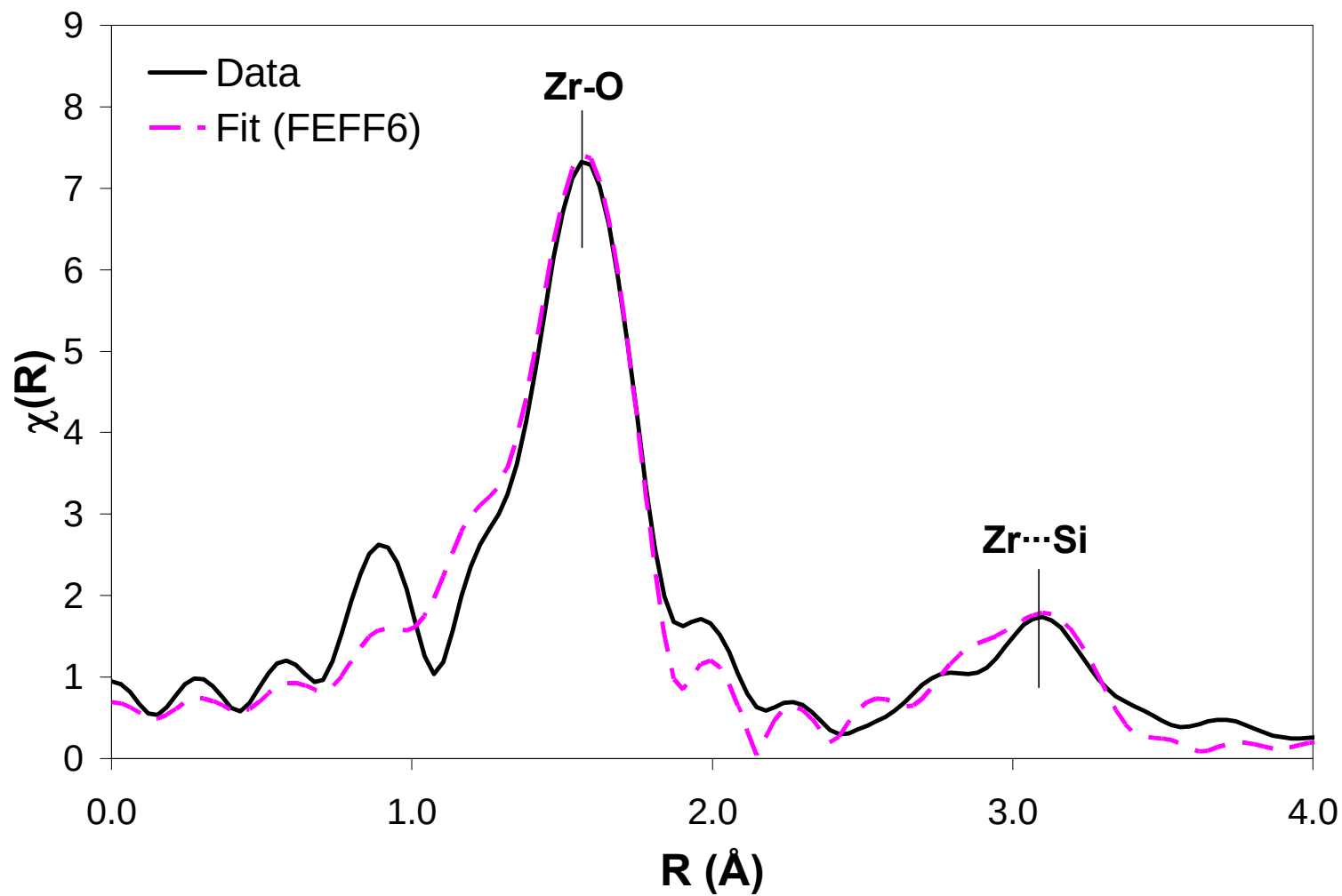


Figure 220: EXAFS R-space plot following first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

Based on the qualitative analysis of the EXAFS data, the first coordination sphere (defined as atoms directly bound to the zirconium) of the embedded zirconium centers should have at least one singly bound oxygen atom (Zr-O). The second coordination sphere should have as many nonbonded silicon atoms (Zr...Si) as the first shell of singly bound oxygen atoms. A structural model, based on bond lengths and geometries found in the literature,[116,193,195,200] was constructed using ChemDraw (Figure 221). Theoretical phase and amplitude factors were generated using FEFF6[168], which is incorporated in the IFEFFIT software suite. A model containing only the single scattering paths (Zr-O, Zr...Si) generated by FEFF6 was used to fit the EXAFS data and thereby obtain quantitative structural parameters. FEFF8[115] was used to estimate the value of the amplitude reduction factor ($S_0^2 = 0.928$).

The CN values based on the results of gravimetric analysis and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. Prior to finalizing the k-range used for modeling the experimental data, a non-EXAFS feature had to be removed at $\sim 7.7 \text{ \AA}^{-1}$, which has been attributed to a double electron transition.[195,197] For the sample following the first cross-linking reaction the data in the range of $k = 7.45$ to $8.00 \text{ \AA}^{-1}$ in the k-space plot were excluded from the fitting process, which is smaller than the range of $k = 7.0$ to $8.3 \text{ \AA}^{-1}$ excluded by Mountjoy et al.[195] The EXAFS signal ($\chi(k) * k^3$) for the isolated zirconium centers in a silicate building block matrix is presented in Figure 222 with the EXAFS data range used to fit the model boxed (4.0 to $15.1 \text{ \AA}^{-1}$). In R-space, the fit range is from 1.0 to $4.5 \text{ \AA}$ and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 220 and Figure 223 respectively. Table 13 summarizes the refined values of the structural parameters. As shown in Table 14 the refined bond lengths are in agreement with values found in the literature.[116,171,196,201-207] At this point, the structural parameters were fixed to the refined values and the value of the CNs were allowed to vary. Table 13 also contains the refined values of the CNs, which are within 10% of the values determined by gravimetric analysis.

In summary, the EXAFS data analysis provides strong evidence that the immediate environment around the zirconium centers is 4 Zr-O and 4 Zr...Si. The structural model derived from the EXAFS data are consistent with the conclusions drawn from both gravimetric and spectroscopic techniques, which all support the claim that the material contains a single type of zirconium center that is atomically dispersed throughout the silicate material.

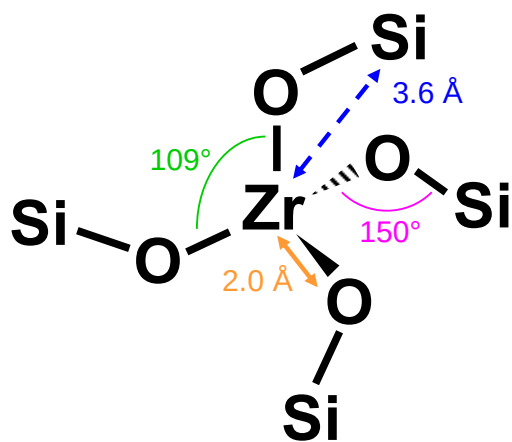


Figure 221: Structural model used for EXAFS data analysis of the isolated embedded zirconium centers. The model contains a zirconium center with four singly bound oxygen atoms (Zr-O) and four nonbonded silicon atoms (Zr...Si).

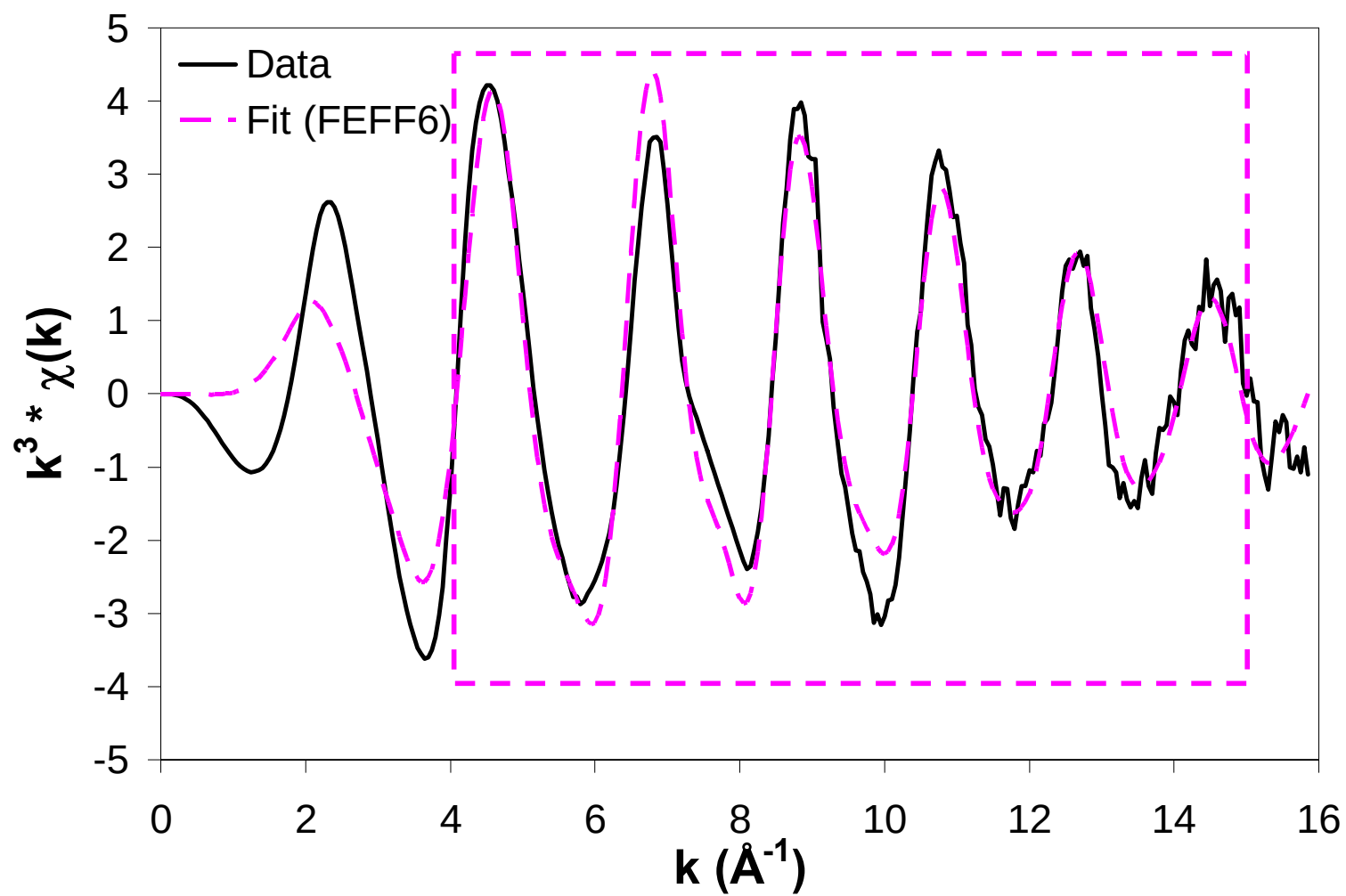


Figure 222: EXAFS k-space plot following first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

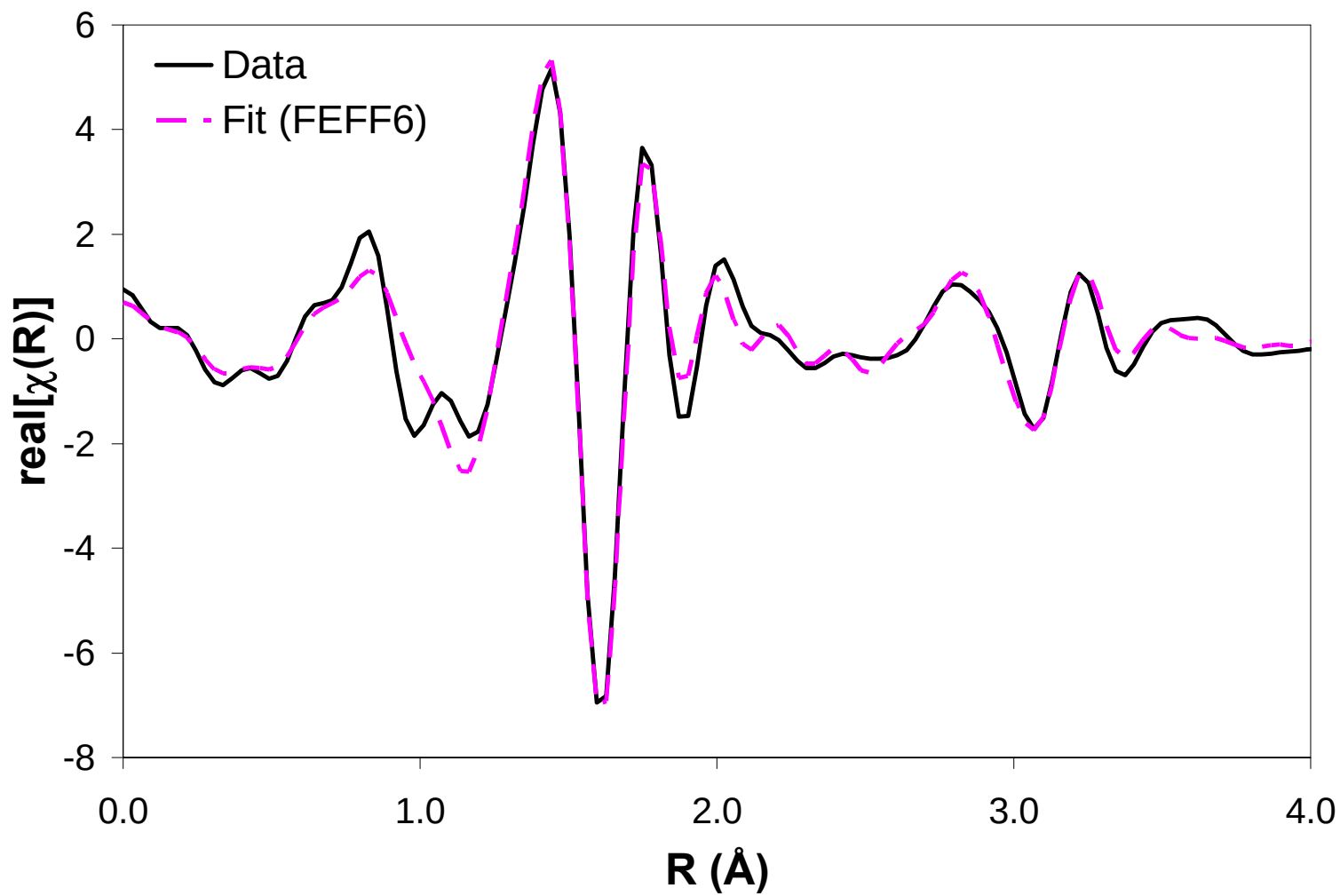


Figure 223: EXAFS real R-space plot following first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

Table 13: EXAFS fit values for embedded and surface zirconium centers

Isolated Embedded Zirconium Centers, 1st dose			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	2.002	---	3.615
σ^2 (Å ²)	3.66 x 10 ⁻³	---	7.37 x 10 ⁻³
E ₀ (eV)	-9.1 ± 1.4	---	-9.1 ± 1.4
CN	3.82 ± 0.15	---	3.82 ± 0.15
S ₀ ² = 0.928 (set), N _{idp} = 24.3, N _{var} = 5, χ^2 = 1366, reduced χ^2 = 71, R-factor = 0.038, FT k region = 4.057 – 15.141 Å ⁻¹ , Fit range = 1.0 – 4.5 Å			
Isolated Embedded Zirconium Centers, 2nd dose			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	1.977	---	3.609
σ^2 (Å ²)	3.55 x 10 ⁻³	---	6.32 x 10 ⁻³
E ₀ (eV)	-6.6 ± 1.9	---	-6.6 ± 1.9
CN	3.62 ± 0.19	---	3.62 ± 0.19
S ₀ ² = 0.928 (set), N _{idp} = 25.0, N _{var} = 5, χ^2 = 7737, reduced χ^2 = 386, R-factor = 0.076, FT k region = 4.159 – 15.590 Å ⁻¹ , Fit range = 1.0 – 4.5 Å			
Isolated Surface Zirconium Centers			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	1.929	2.376	3.606
σ^2 (Å ²)	2.45 x 10 ⁻³	7.55 x 10 ⁻³	3.80 x 10 ⁻³
E ₀ (eV)	-9.1 ± 2.0	-9.1 ± 2.0	-9.1 ± 2.0
CN	1.07 ± 0.10	2.93 ± 0.10	1.07 ± 0.10
S ₀ ² = 0.928 (set), N _{idp} = 21.3, N _{var} = 7, χ^2 = 1009, reduced χ^2 = 71, R-factor = 0.080, FT k region = 3.180 – 13.127 Å ⁻¹ , Fit range = 1.1 – 4.5 Å			

Table 14: Comparison of EXAFS refined bond lengths to literature values

	Zr-O (Å)	Zr-Cl (Å)	Zr...Si (Å)
Isolated Embedded Zirconium Centers, 1 st dose	2.002	---	3.615
Isolated Embedded Zirconium Centers, 2 nd dose	1.977	---	3.609
Isolated Surface Zirconium Centers	1.929	2.376	3.606
Ref [116]	1.96-2.18		
Ref [171]	1.98-2.00		
Ref [196]			3.42-3.67
Ref [204]		2.39-2.41	
Ref [205]		2.36-2.37	
Ref [201]	1.92-1.93	2.39	3.50-3.56
Ref [202]		2.30, 2.42	
Ref [207]		2.43	
Ref [203]	1.96	2.47	3.56
Ref [206]	1.96	2.46	3.54

The combination of the techniques described above provides a reasonably clear picture of the products in the reaction of a limiting amount of ZrCl_4 and the silicate building block $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. Small oligomers are formed that contain isolated embedded zirconium centers bound through oxygen atoms to four separate silicate building blocks (Figure 224). Gravimetric analysis provided evidence that all of the chloride ligands on the zirconium centers reacted with the trimethyltin groups on the silicate building blocks resulting in the formation of Zr-O bonds. IR and SSNMR spectra provided evidence of the formation of linkages between the zirconium centers and the silicate building blocks (formation of Zr-O-Si). XAS data confirmed that the oxidation state of the zirconium centers remained unchanged during the cross-linking reaction. A structural model based on EXAFS data strongly supports the claim that the local environment around all zirconium centers in the matrix is identical and composed of a zirconium center surrounded by four oxygen atoms. In the context of the first linking reaction, all of the chloride ligands have been removed from around zirconium and been replaced by four linkages to four separate silicate building blocks, and the zirconium centers are spatially isolated. The building block approach and sequential dosing strategy provides control of all the necessary components to produce identical, embedded zirconium catalyst ensemble. In the next state of the synthesis these oligomers will be linked together to form a robust, high surface area silicate support around the embedded zirconium catalyst ensembles. As will be shown, the local environment of the ensembles will remain unchanged during the growth of the robust, high surface area silicate support.

Second Cross-Linking Reaction: Linking the Oligomers Together using SiCl_4

The oligomers synthesized from ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ are further cross linked with SiCl_4 (3.0 SiCl_4 : 1.0 $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) via the same metathesis reaction where the silyl chloride groups (from SiCl_4) replace unreacted Me_3Sn groups to form new siloxane bonds (Si-O-Si) and Me_3SnCl (Figure 225). The volatiles of the reaction were analyzed and Me_3SnCl was the only byproduct observed using ^1H NMR. Gravimetric data are consistent with two chloride ligands reacting with the Me_3Sn groups (1.6 ± 0.1 equivalence of Me_3SnCl). Therefore the oligomers are linked together by silicon centers that on average contain two unreacted chloride ligands and two linkages to zirconium oligomers ($\text{Cl}_2\text{Si}(\text{OSi}_{\text{Zr-oligomer}})_2$).

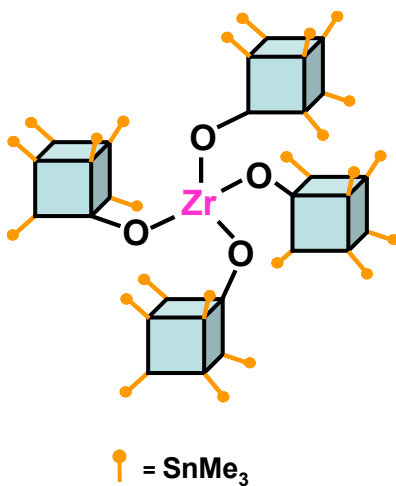


Figure 224: Proposed representation of the catalyst ensemble following first cross-linking reaction, ZrCl_4 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

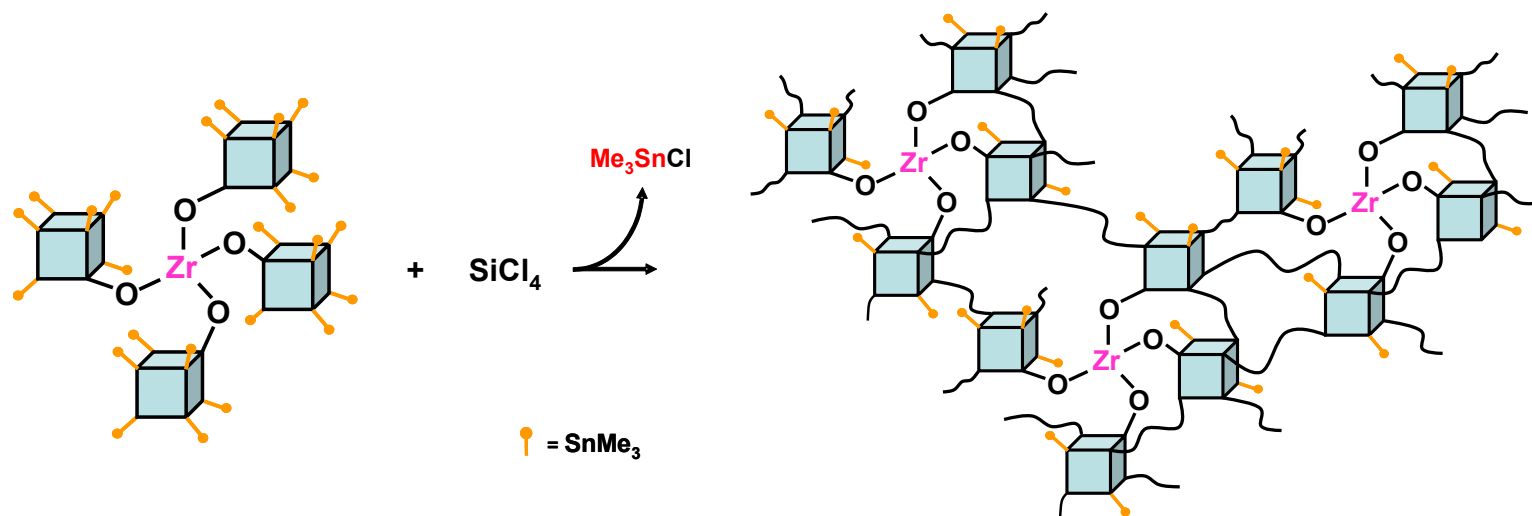


Figure 225: Second Cross-Linking Reaction, Zirconium oligomers and SiCl_4 .

Figure 226 shows the IR spectrum for the isolated zirconium centers. The material is synthesized under nonaqueous aprotic conditions which results in the production of a hydroxyl-free surface. As expected no evidence for the presence of silanol groups ($3600\text{--}4000\text{ cm}^{-1}$) is observed in the IR spectrum. IR spectroscopy is again used to verify the Zr-O-Si linkage remained intact throughout the second cross-linking reaction (Figure 226). Both the Si-O-Si band (1080 cm^{-1}) and the Zr-O-Si shoulder ($\sim 965\text{ cm}^{-1}$) were observed in the IR spectrum.[171] The IR is consistent with the continued presence of Zr-O-Si groups in the matrix thus the Zr-O-Si linkage was not disrupted during the cross-linking reaction with SiCl_4 .

The material was again exposed to pyridine to evaluate what types of isolated acidic centers were present. Three features were observed in the IR spectrum (Figure 227) after exposure to pyridine (1448 cm^{-1} , 1491 cm^{-1} , and 1609 cm^{-1}) which are characteristic of Lewis acidic zirconium centers in silica.[198] No evidence for Bronsted sites (1540 cm^{-1}) or silanol groups (1590 cm^{-1}) is observed.

Figure 228 shows the ^{29}Si SSNMR spectrum for the isolated zirconium centers. Following the second cross-linking reaction four signals are observed. The feature at -22 ppm is assigned to grease. The signals between -22 and -100 ppm in the spectrum are characteristic of the different silyl chlorides generated during the second cross-linking reaction (i.e. $(=\text{SiO})_{4-x}\text{SiCl}_x$).[95] The signals between -100 ppm and -110 ppm are assigned to the silicon corners on the building block which are connected to unreacted Me_3Sn groups ($(=\text{SiO})_3\text{Si}(\text{OSnMe}_3)$) (-101 to -104 ppm), the silicon corners connected to the zirconium centers ($(=\text{SiO})_3\text{Si}(\text{OZr}\equiv)$) ($\sim -110\text{ ppm}$), and the silicon corners connected to the silicon centers ($(=\text{SiO})_3\text{Si}(\text{OSi}\equiv)$) (-105 to -110 ppm).

Nitrogen adsorption/desorption measurements were conducted to determine the BET surface area and total pore volume. Qualitative analysis of the nitrogen adsorption/desorption isotherm (Type I) and t-plot suggests this material is a primarily microporous material;[136] however, a hysteresis (Type H4) is observed in the adsorption/desorption isotherm indicating the presence of some mesopores (Figure 229 & Figure 230). The t-plot method was used to confirm the material is primarily microporous with respect to pore volume (89%) and surface area (95%). The BET surface area of this material is $445\text{ m}^2/\text{g}$ (Figure 231) and the total pore volume is

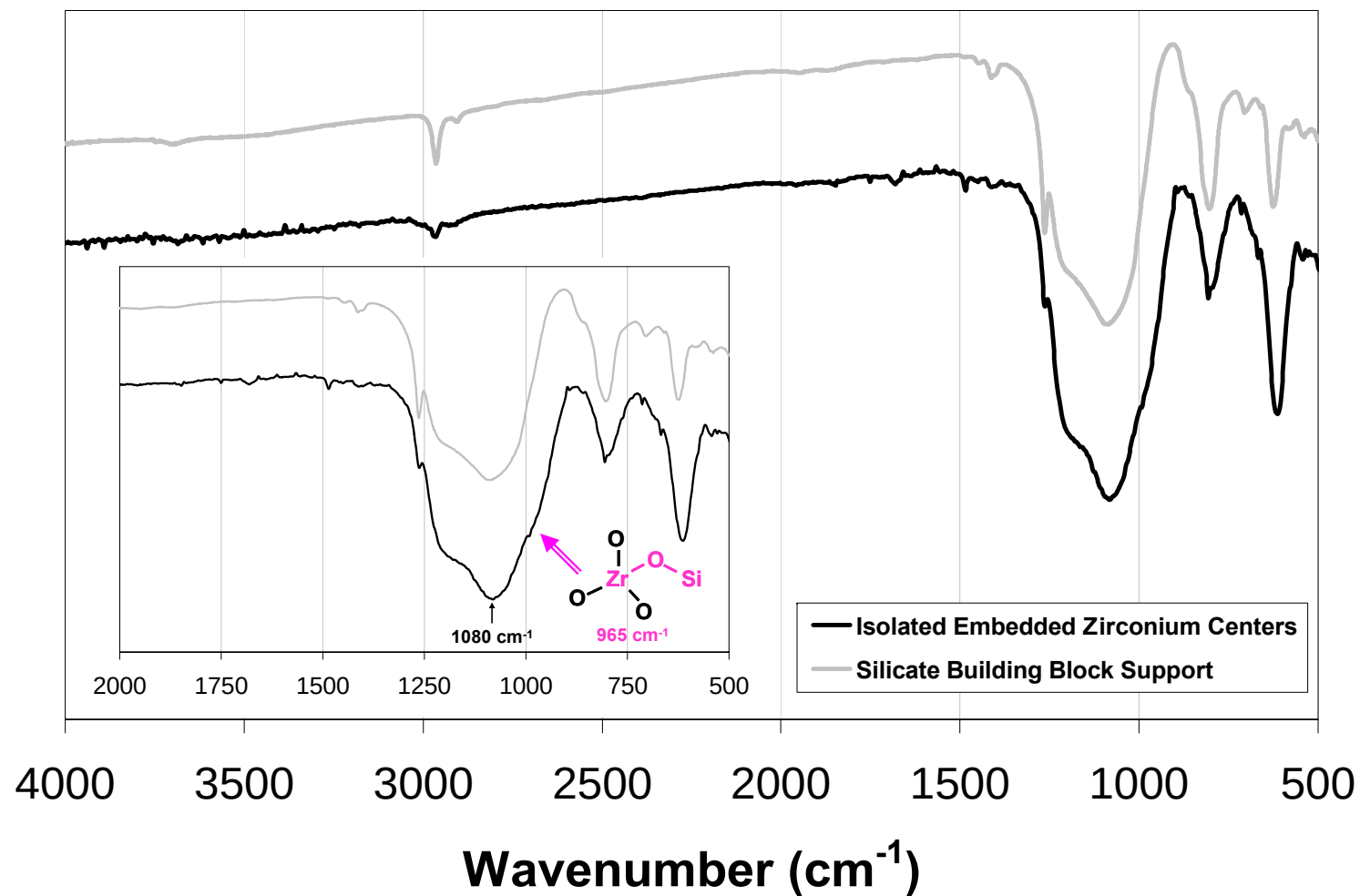


Figure 226: IR spectra (500–4000 cm⁻¹) of a zirconium-free silicate building block support and the material following the second cross-linking reaction, zirconium oligomers and SiCl₄. The inset contains the expanded IR spectra (500–2000 cm⁻¹) which illustrates the Zr-O-Si shoulder (965 cm⁻¹).

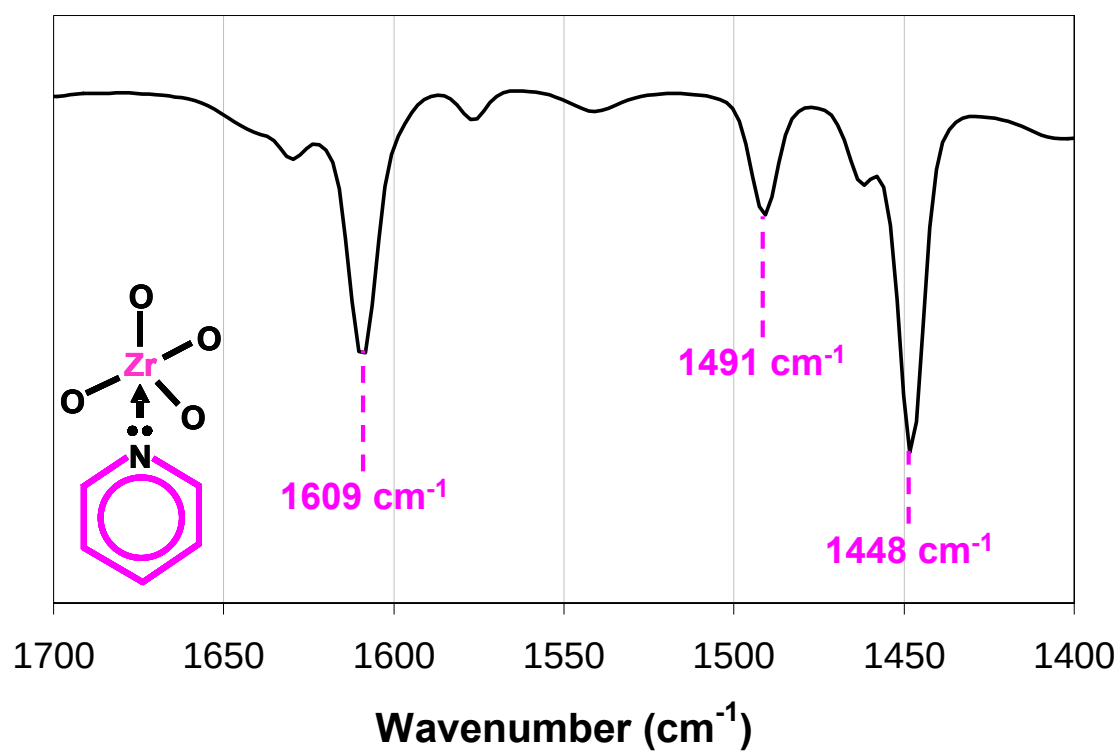


Figure 227: IR spectrum of pyridine bond to Lewis acidic zirconium centers present in the material following the second cross-linking reaction, zirconium oligomers and SiCl_4 .

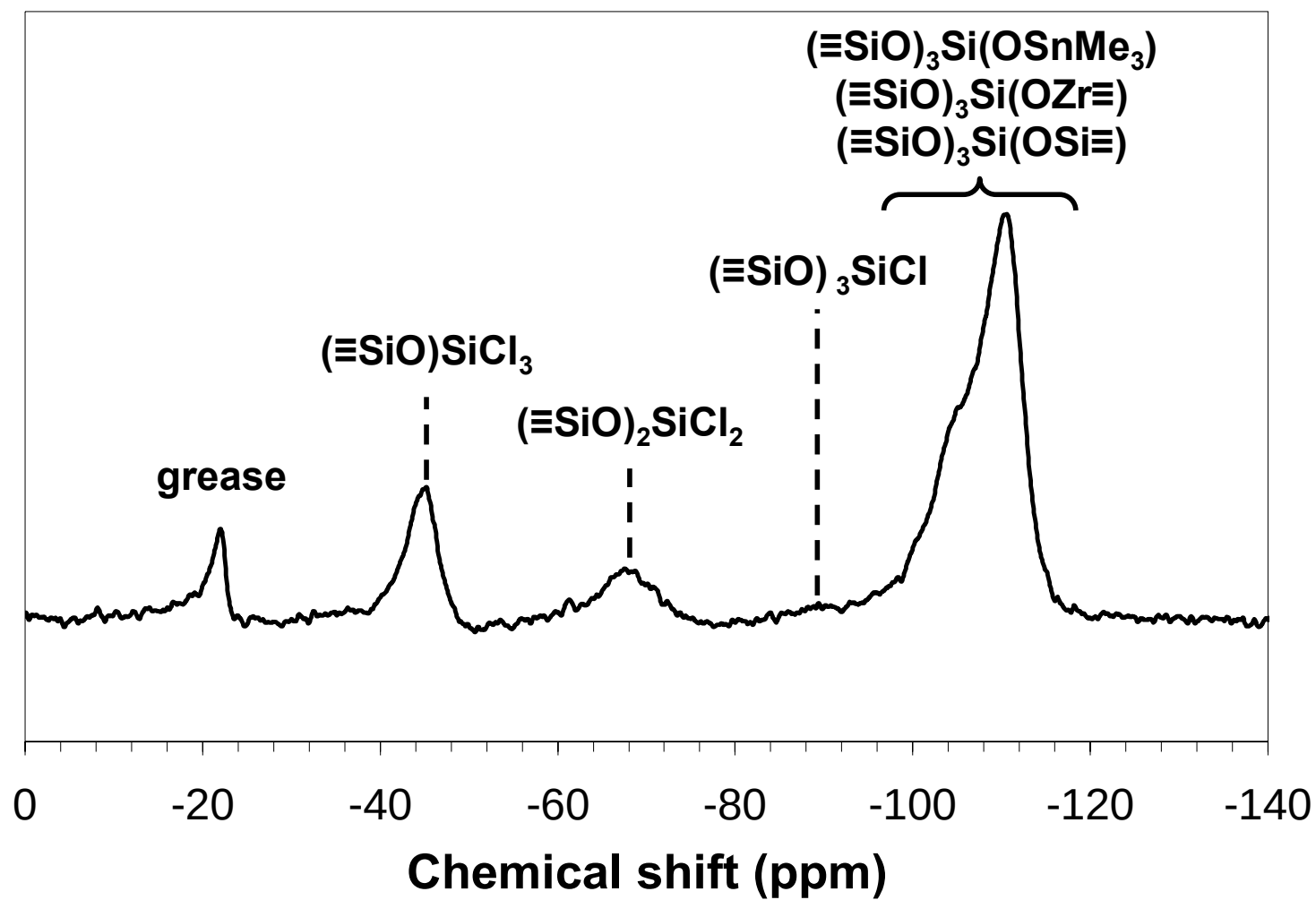
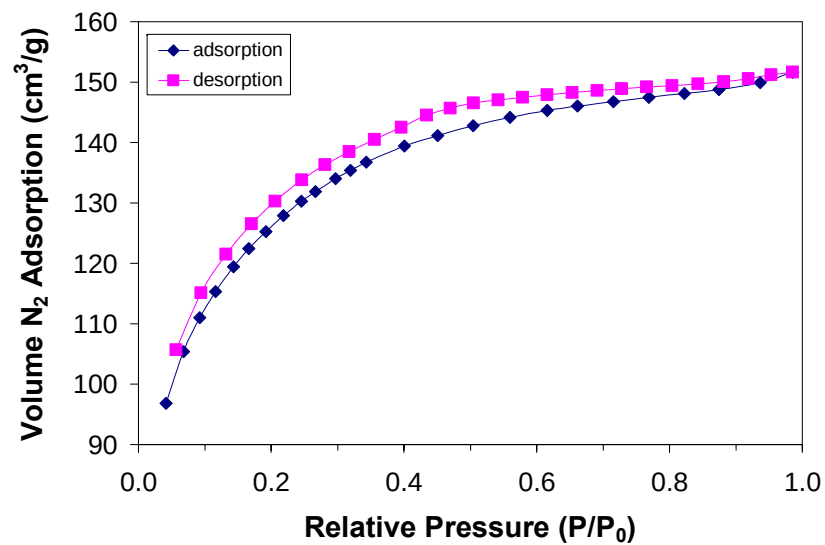
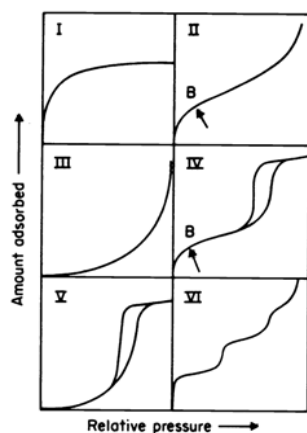


Figure 228: ^{29}Si SSNMR spectrum (-140 to 0 ppm) following the second cross-linking reaction, zirconium oligomers and SiCl_4 .

Standard Isotherms



Standard Hysteresis Loops

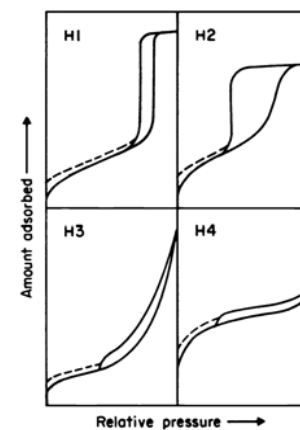


Figure 229: Nitrogen isotherm for the material following the second cross-linking reaction, zirconium oligomers and SiCl_4 . Standard isotherms and hysteresis loops were obtained from literature.[131]

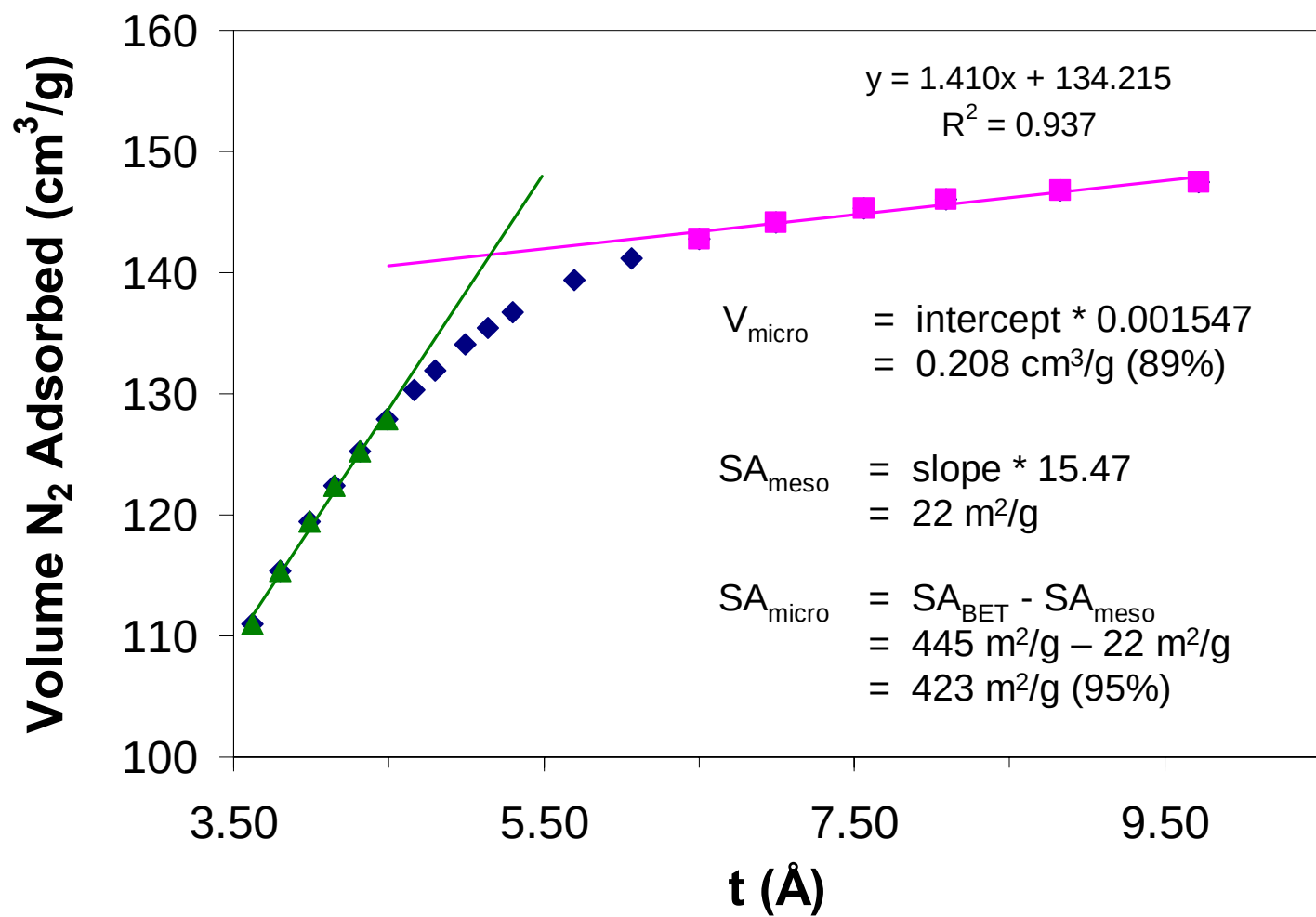


Figure 230: t-plot for the material following the second cross-linking reaction, zirconium oligomers and SiCl₄.

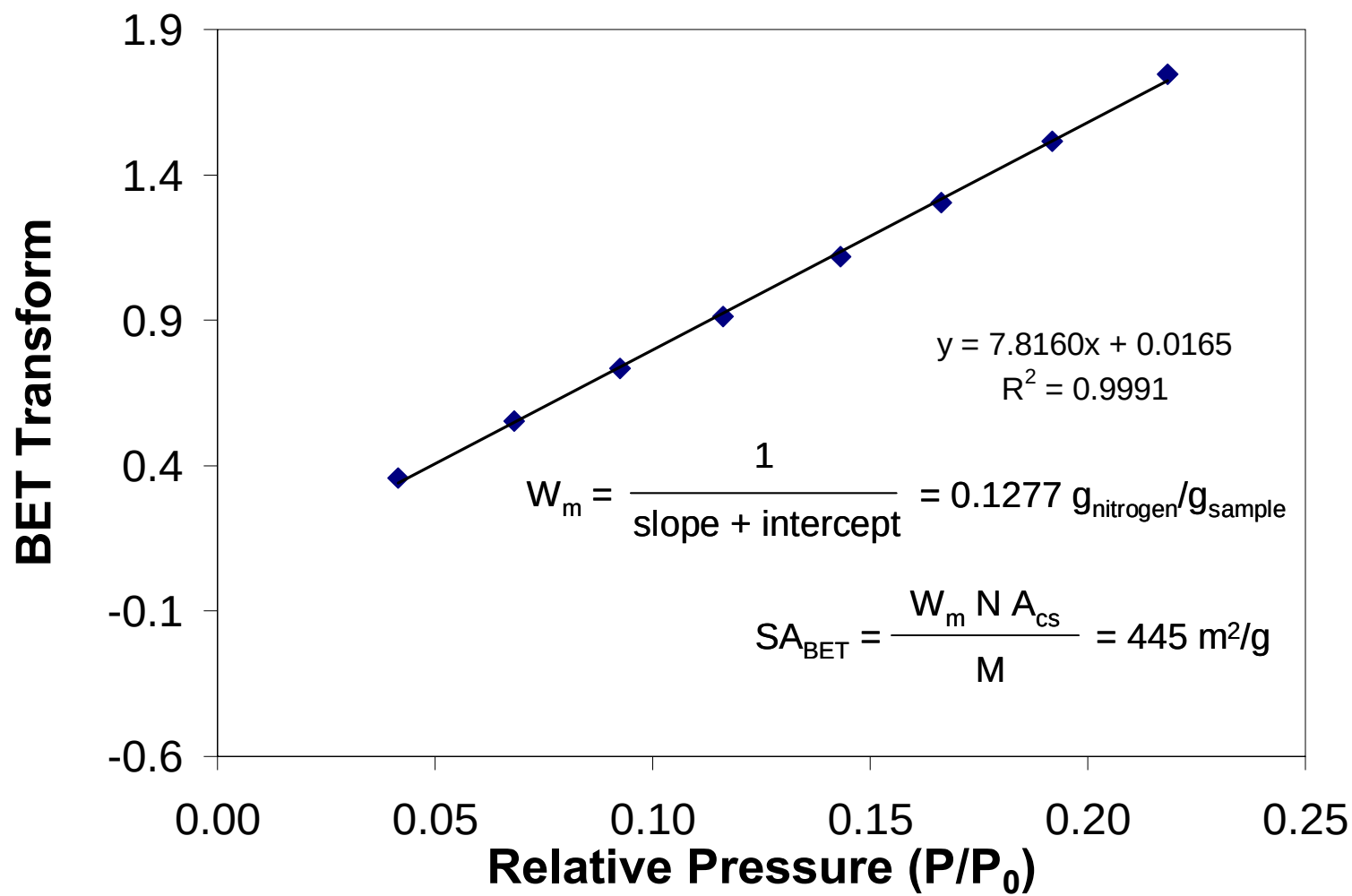


Figure 231: BET plot for the material following the second cross-linking reaction, zirconium oligomers and SiCl_4 .

0.234 cm³/g. The BJH plot (Figure 232) does not display a significant maximum which suggests the material has micropores and some small mesopores. Thus a high surface area, primarily microporous, silicate building block matrix was grown around the isolated Zr centers.

As seen in Figure 233, the shape and the position of the ionization edge (18002 eV) do not change significantly after the second cross-linking reaction. These observations support the claim the oxidation state of the zirconium centers is +4. Table 12 summarizes the pre-edge and edge positions for each of the isolated zirconium(IV) catalyst ensembles discussed in this chapter as well as the edge position of the standard zirconium materials. The presence of a pre-edge feature (17992 eV) provides evidence that the coordination geometry around the zirconium center is not octahedral and suggests the coordination geometry is tetrahedral. The shape of the adsorption edge of the isolated zirconium centers appears to be similar to the shape of the absorption edge of c-ZrO₂ (T_d) and Zr(OⁿPr)₄ (O_h) (Figure 218).[116] Therefore analysis of the shape of the adsorption edge of the material at this stage of the synthesis is inconclusive.

Finally, EXAFS data were used to obtain information on the connectivity of the zirconium centers in the silicate building block matrix. Again the number of shells can be qualitatively determined by looking at the magnitude R-space plot. Figure 234 shows two features, and the tentative assignment of each feature, that were observed in the magnitude R-space plot. It is important to note that there is no evidence of Zr-Cl bonds which supports the claim that the zirconium centers remain unchanged following the second cross-linking reaction. The same structural model (Figure 221), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.928), and refinement procedure were used. Prior to finalizing the k-range used for modeling the experimental data a non-EXAFS feature had to be removed at $\sim 7.7 \text{ \AA}^{-1}$, which has been attributed to a double electron transition.[195,197] The EXAFS signal ($\chi(k) * k^3$) for isolated zirconium centers in a silicate building block matrix is presented in Figure 235 with the FT data range boxed ($4.1 - 15.6 \text{ \AA}^{-1}$). The fit range is from 1.0 to 4.5 $\text{\AA}$ and the magnitude and real part of the FT of the data and FEFF model are presented in Figure 234 and Figure 236 respectively. Table 13 summarizes the refined values of the structural parameters. As shown in Table 14 the refined bond lengths are in agreement with values found in the literature.[116,171,196,201-207] Fixing bond distances and atom separations and

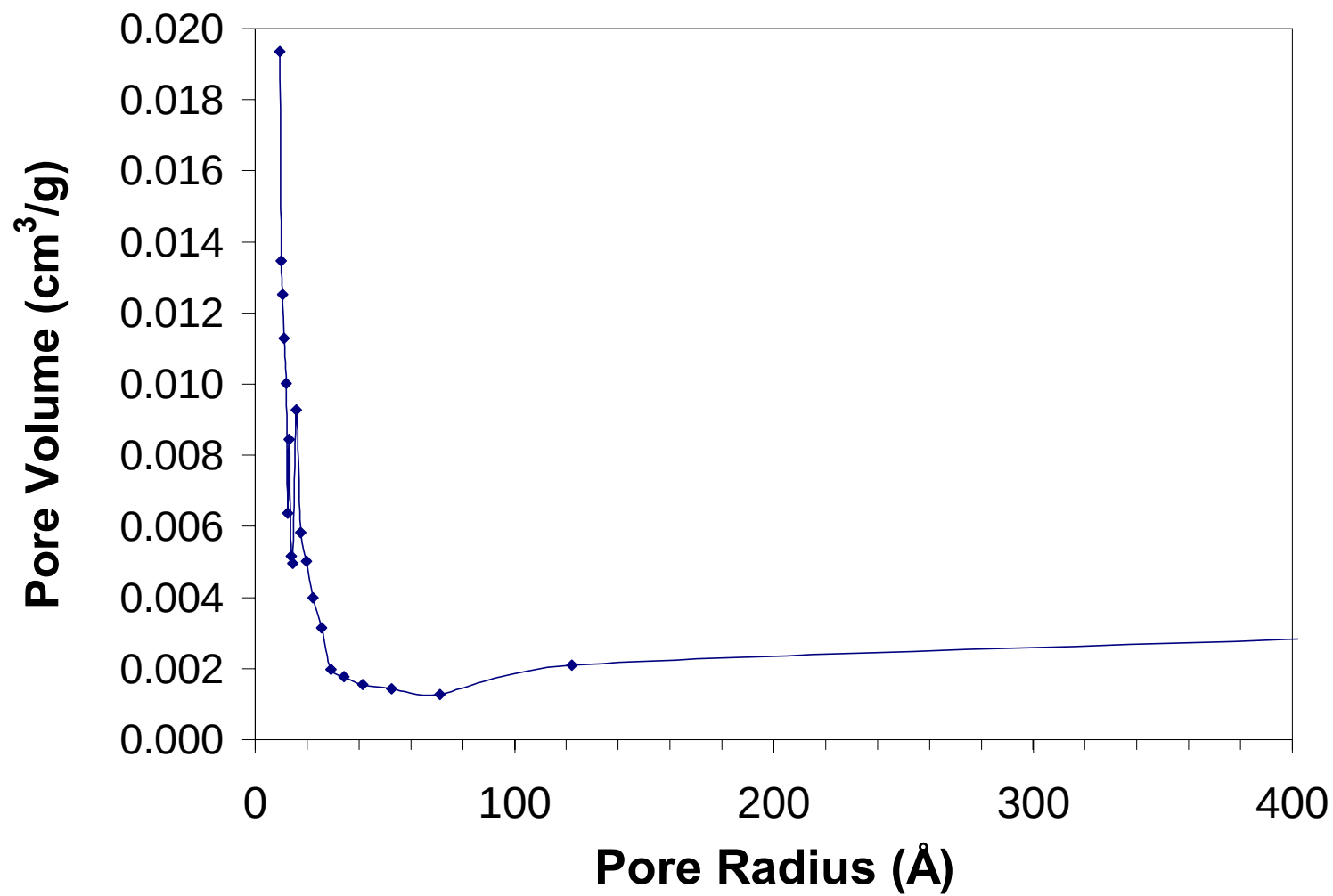


Figure 232: BJH pore size distribution plot for the material following the second cross-linking reaction, zirconium oligomers and SiCl_4 .

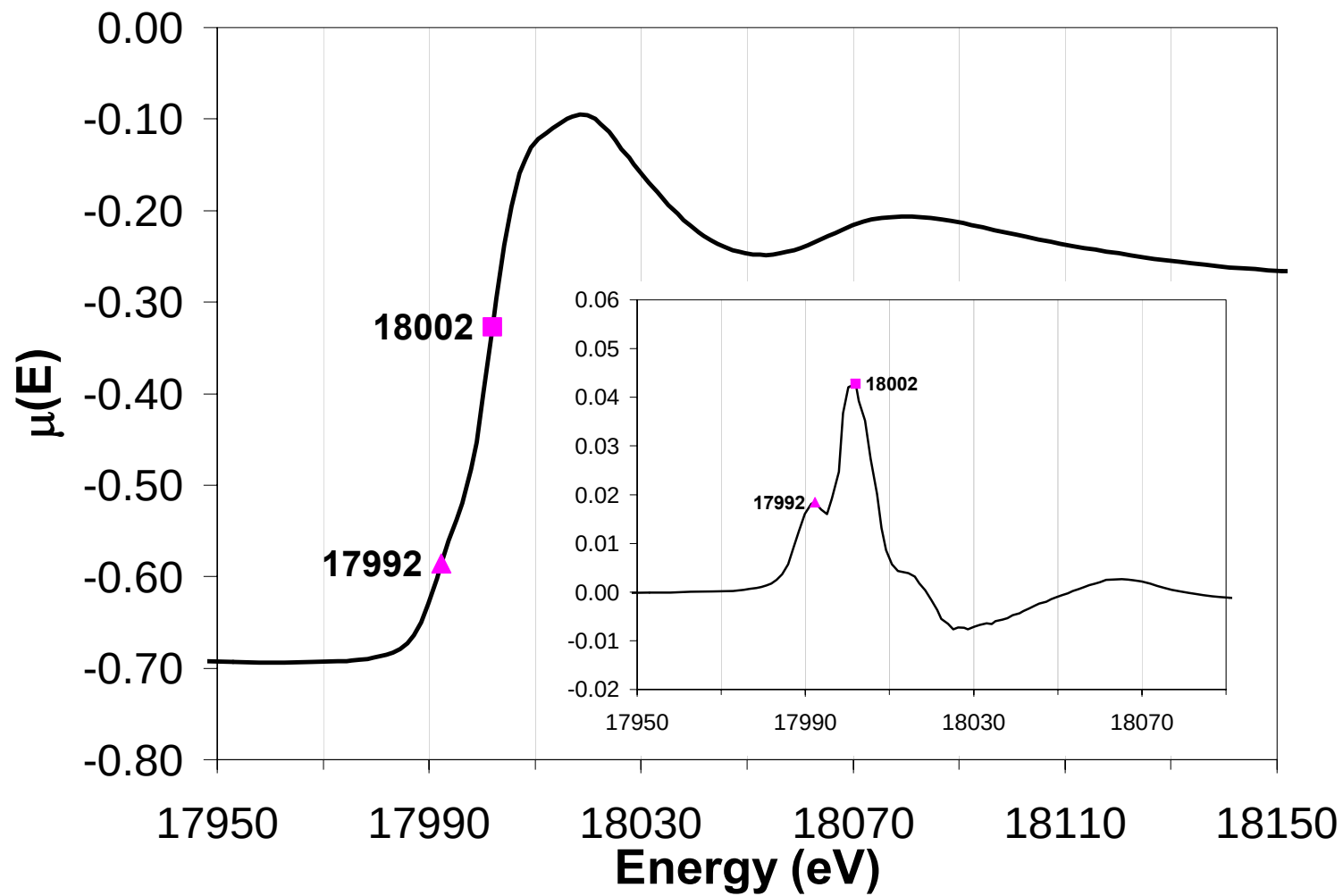


Figure 233: XANES spectrum (Zr K edge) following the second cross-linking reaction, zirconium oligomers and SiCl_4 . The inset contains the derivative XANES spectrum which clearly shows the pre-edge feature (pink triangle) and the adsorption edge (pink square).

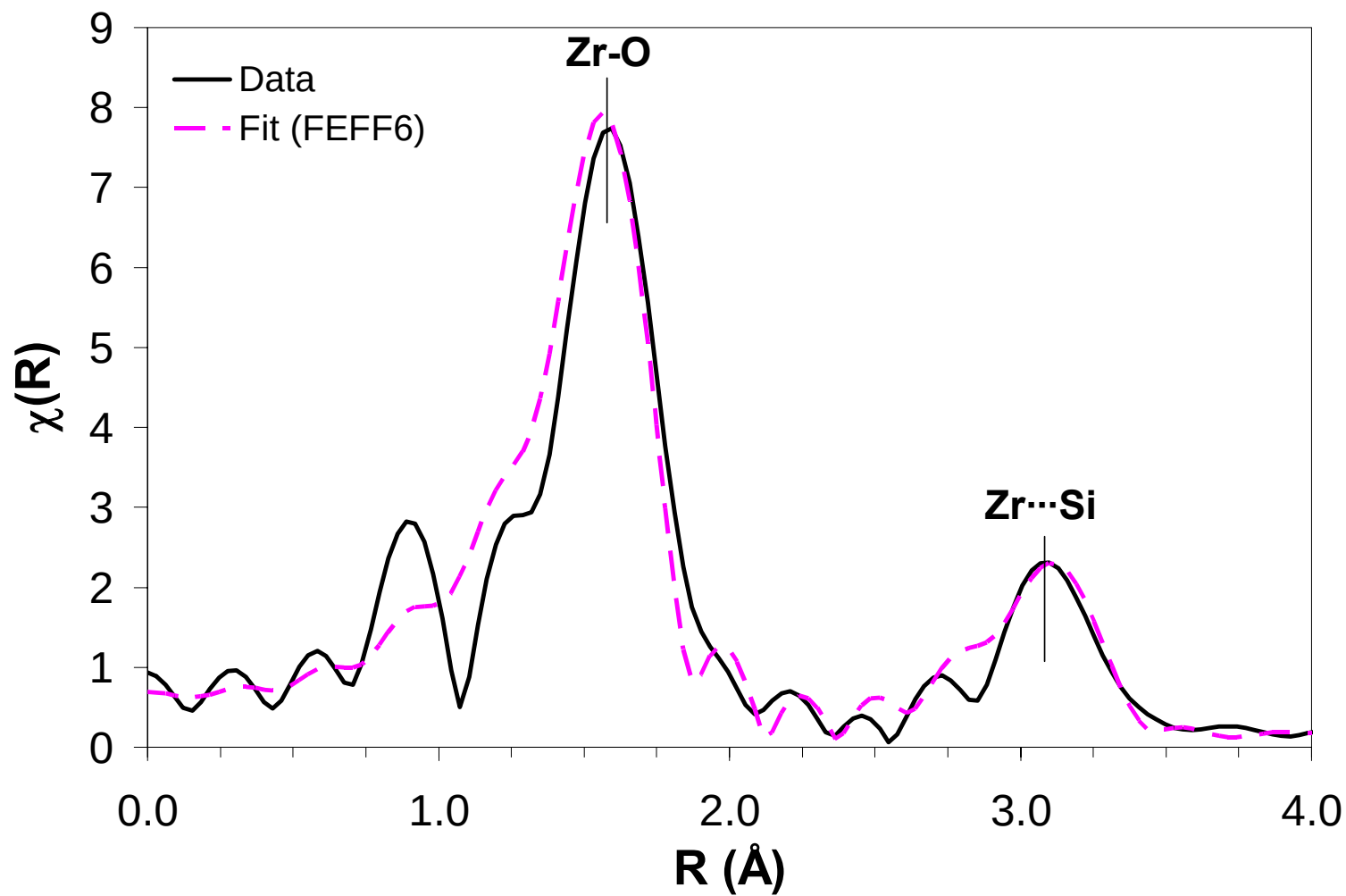


Figure 234: EXAFS R-space plot following the second cross-linking reaction, zirconium oligomers and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

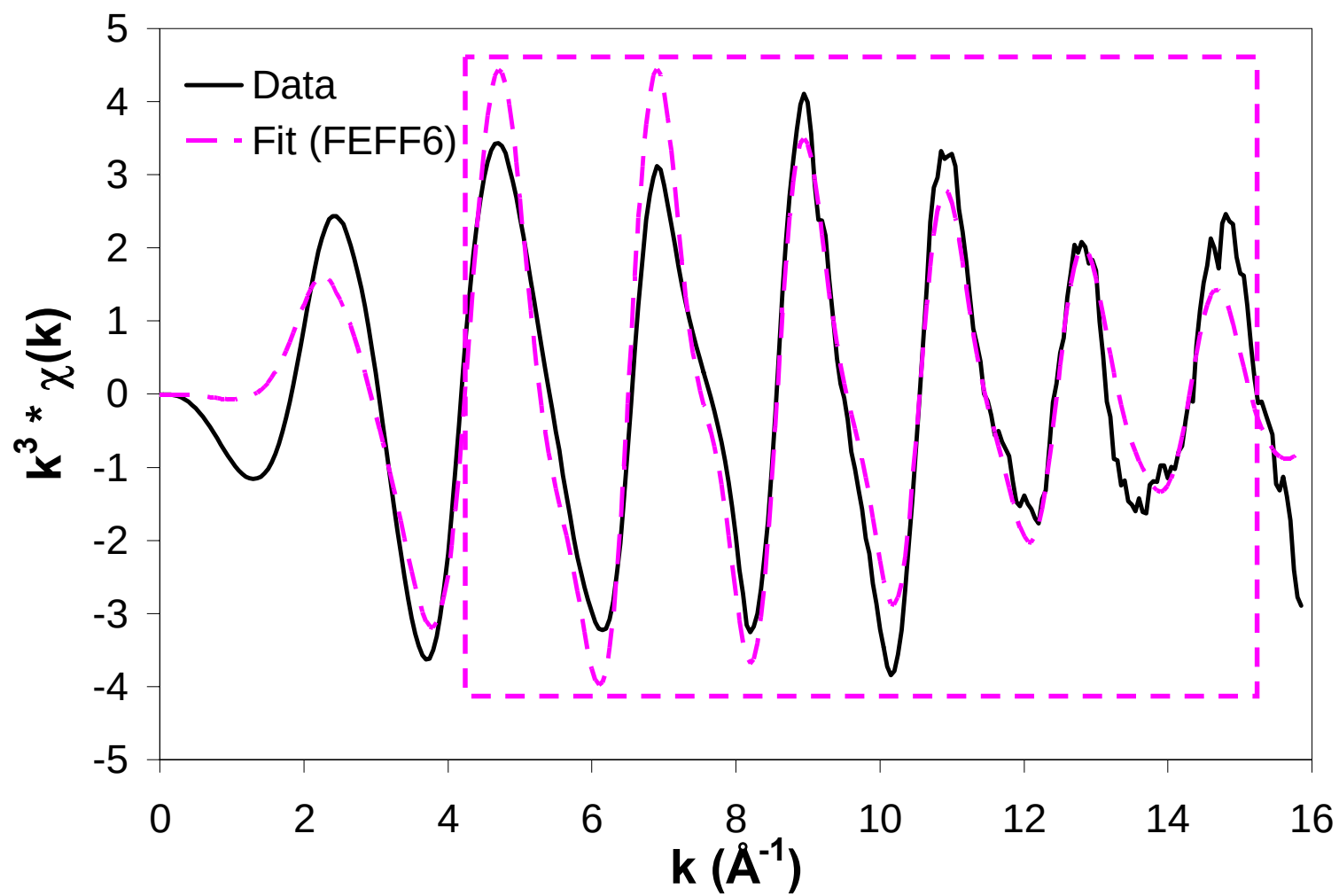


Figure 235: EXAFS k-space plot following the second cross-linking reaction, zirconium oligomers and SiCl_4 .

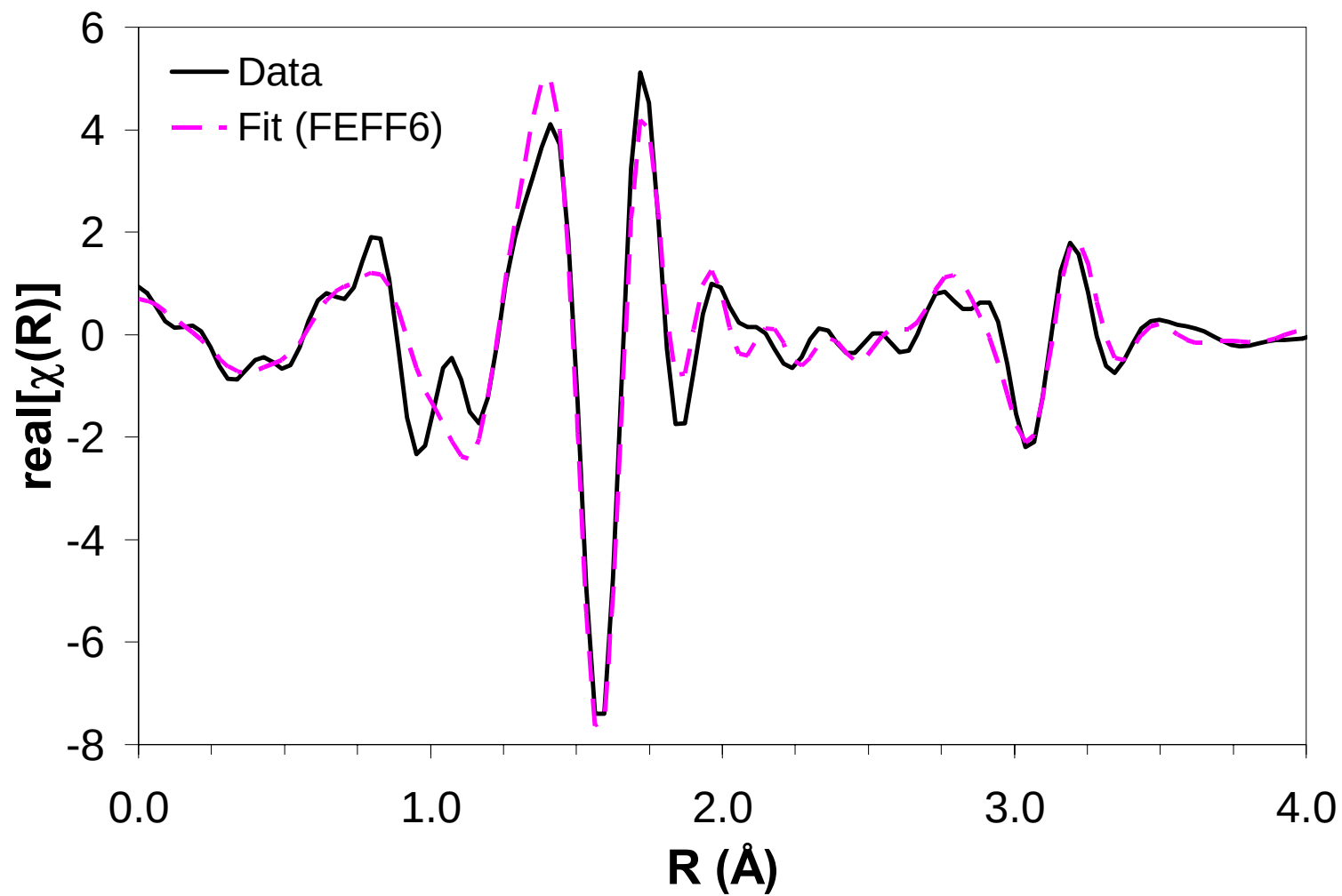


Figure 236: EXAFS real R-space plot following the second cross-linking reaction, zirconium oligomers and SiCl_4 . The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

allowing coordination numbers to refine yielded the results summarized in Table 13. The refined values of the CNs are in agreement with the refined values following the first cross-linking reaction and within 15% of the values determined by gravimetric analysis.

The combination of the techniques described above provides a reasonably clear picture of the isolated embedded zirconium ensembles that are present in the robust, high surface area silicate building block support. The silicate building block support was generated around the zirconium ensembles which were unchanged during the generation of the support. IR and SSNMR spectra provided evidence that the linkages between the zirconium centers and the silicate building blocks remained unchanged (preservation of Zr-O-Si, control of the ligands and the metal-to-support linkages). XAS data confirmed that the oxidation state of the zirconium centers remained unchanged during the generation of the high surface area silicate support around the zirconium centers (preservation of zirconium(IV) centers, control of the metal cation). A structural model based on EXAFS data strongly supports the claim that the local environment around each zirconium center is identical and unchanged during each stage of the synthesis. The building block approach and sequential dosing strategy provided control of all the necessary components of the embedded zirconium catalyst ensemble which resulted in the targeted synthesis of a single type of embedded zirconium ensemble (Figure 237).

Catalytic Test Reactions

The isolated embedded zirconium centers were tested in two different selective oxidation reactions: the oxidation of alkylphenols to benzoquinones[187,208] and the epoxidation of olefins.[187,190]

Zirconium containing silica based heterogeneous catalysts had been reported to be active in the oxidation of 2,6-di-tert-butylphenol.[187] The reported procedure for the oxidation of 2,6-di-tert-butylphenol used hydrogen peroxide as the oxidant and acetone as the solvent. Different reaction conditions were sought because of the associated dangers of mixing hydrogen peroxide and acetone.[209] Safer reaction conditions were found in the literature.[208] The safer procedure for the oxidation of 2,3,6-trimethylphenol used hydrogen peroxide as the oxidant and acetonitrile as the solvent. Initially both a zirconium-free silicate building block support and the isolated embedded zirconium centers showed minor catalytic activity in the oxidation of 2,3,6-trimethylphenol. These studies were abandoned due to the lack of significant catalytic activity.

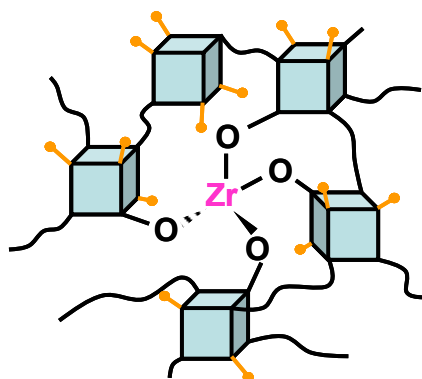


Figure 237: Proposed representation of the catalyst ensemble following second cross-linking reaction, zirconium oligomers and SiCl_4 .

Zirconium containing silica based heterogeneous catalysts had also been reported to be active in the epoxidation of cyclohexene.[187,190] The reported procedures for the epoxidation of cyclohexene again used hydrogen peroxide as the oxidant and acetone as the solvent. Different reaction conditions were sought because of the associated dangers of mixing hydrogen peroxide and acetone.[209] Studies were conducted to determine a more suitable solvent to use instead of acetone. Initially acetonitrile was selected due to the observed catalytic activity of the isolated embedded zirconium centers. The selection of acetonitrile turned out not to be the best choice. Acetonitrile and hydrogen peroxide are known to react with each other resulting in the formation of a peroxyimide acid which is known to epoxidize olefins.[210,211] It was determined that the observed catalytic activity was not due to the presence of the isolated embedded zirconium centers but instead due to the presence of the peroxyimide acid. Following this conclusion, t-butanol was selected as a more suitable solvent because it had been used in literature as a solvent in the epoxidation of olefins over different heterogeneous catalysts.[47] Preliminary results showed that the isolated embedded zirconium centers appeared to be catalytically active in the epoxidation of cyclooctene. Before conducting more detailed analysis of the catalytic activity, studies to determine if the isolated embedded zirconium centers were leaching during the catalytic test reactions were initiated. Ideally the isolated embedded zirconium centers should not leach during the catalytic test reactions. The material was washed with several aliquots of ultrapure deionized water and then filtered. The filtrate was analyzed using ICP-OES for the presence of zirconium. Each aliquot contained zirconium which led to the conclusion that the isolated embedded zirconium centers leached during the catalytic test reaction.

Leaching most likely occurs due to the presence of HCl in the reaction vessel. Hydrolysis of unreacted Si-Cl groups occurs when water or alcohol is present in the reaction vessel producing HCl, which will react with the linkages between the isolated embedded zirconium centers and the silicate building block support (Zr-O-Si) resulting in the cleavage of these linkages. In general there are more than enough unreacted Si-Cl groups in the material to generate the amount of HCl needed to completely leach the zirconium centers out of the silicate building block support. An efficient way to passivate the unreacted Si-Cl groups in the material following synthesis has not yet been developed and is needed before the isolated embedded

zirconium centers can be tested in catalytic test reactions that use alcohols and/or aqueous hydrogen peroxide.

Isolated Surface Zr(IV) Catalyst Ensemble using ZrCl₄

On the other end of the spectrum, we sought to demonstrate that our synthetic methodology would allow us to target atomically dispersed surface zirconium species that are connected to the surface by as little as one bond. A nanostructured silicate support with spatially isolated binding sites is used to target the synthesis of a surface catalyst ensemble which contains a Zr(IV) center with three hydroxide ligands and one link to the silicate support (Figure 211). This surface catalyst ensemble will be referred to as “*isolated surface zirconium centers.*”

Reaction of ZrCl₄ and Silicate Building Block Support

The synthesis of such isolated surface zirconium centers is achieved by reacting a premade silicate building block support (2.87 SiCl₄py₂ : 1.0 Si₈O₁₂(OSnMe₃)₈) with a limiting amount of ZrCl₄ (0.75 ZrCl₄ : 1 Si₈O₁₂(OSnMe₃)₈) (Figure 238). The reaction proceeds via a metathesis reaction where a chloride ligand of ZrCl₄ cleanly reacts with a Me₃Sn group to form a new siloxane bond (Zr-O-Si) and Me₃SnCl, a volatile byproduct. Only one chloride ligand on ZrCl₄ should react because the binding sites on the rigid silicate building block support (i.e. Me₃Sn group) are spatially isolated which prevents each zirconium center from linking two binding sites. A limiting amount of ZrCl₄ was used so that gravimetric analysis could be used to determine the connectivity of the Zr(IV) center to the support. The volatiles of the reaction were analyzed using ¹H NMR and Me₃SnCl was the only byproduct observed. Gravimetric analysis (1.1 ± 0.1 equivalents of Me₃SnCl) is consistent with approximately 1 chloride ligand on the zirconium center reacted with Me₃Sn groups on the support.

Figure 239 shows the IR spectra of a zirconium-free silicate building block support and the isolated surface zirconium centers. The materials are synthesized under nonaqueous aprotic conditions which results in the production of a hydroxyl-free materials. As expected, little evidence for the presence of silanol groups (3600-4000 cm⁻¹) is observed in the IR spectra. IR spectroscopy is also used to verify the formation of the Zr-O-Si linkage. The band at 1080 cm⁻¹, which is commonly assigned to the Si-O-Si stretching mode,[171] was observed in the IR spectrum (Figure 239). A shoulder on the Si-O-Si feature (inside the pink dashed box) was

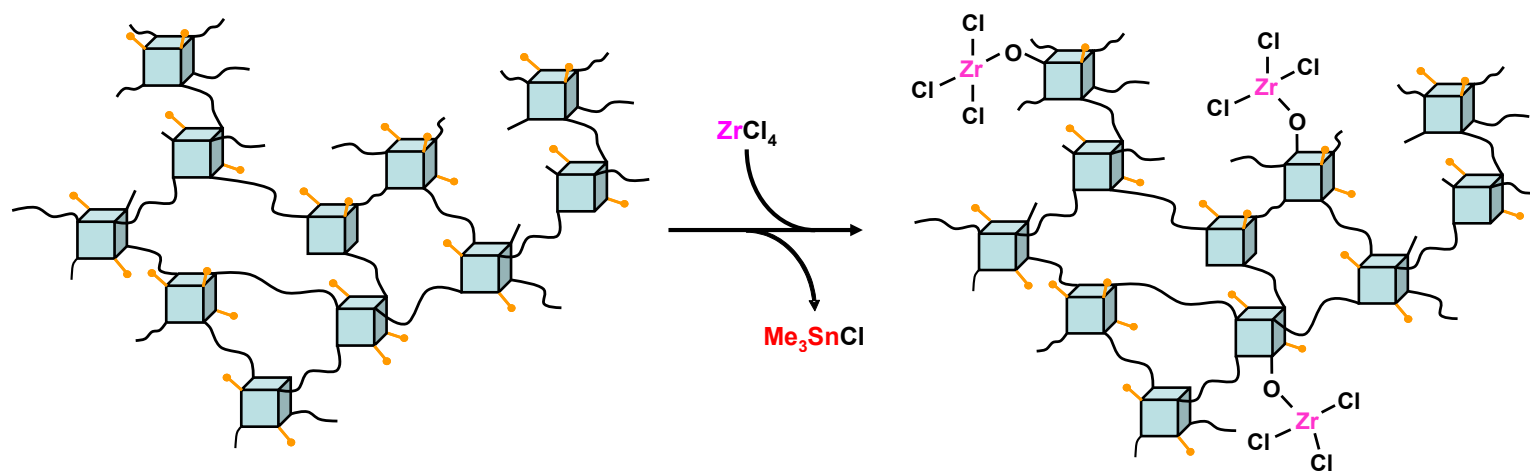


Figure 238: Reaction of ZrCl_4 and a premade silicate building block support.

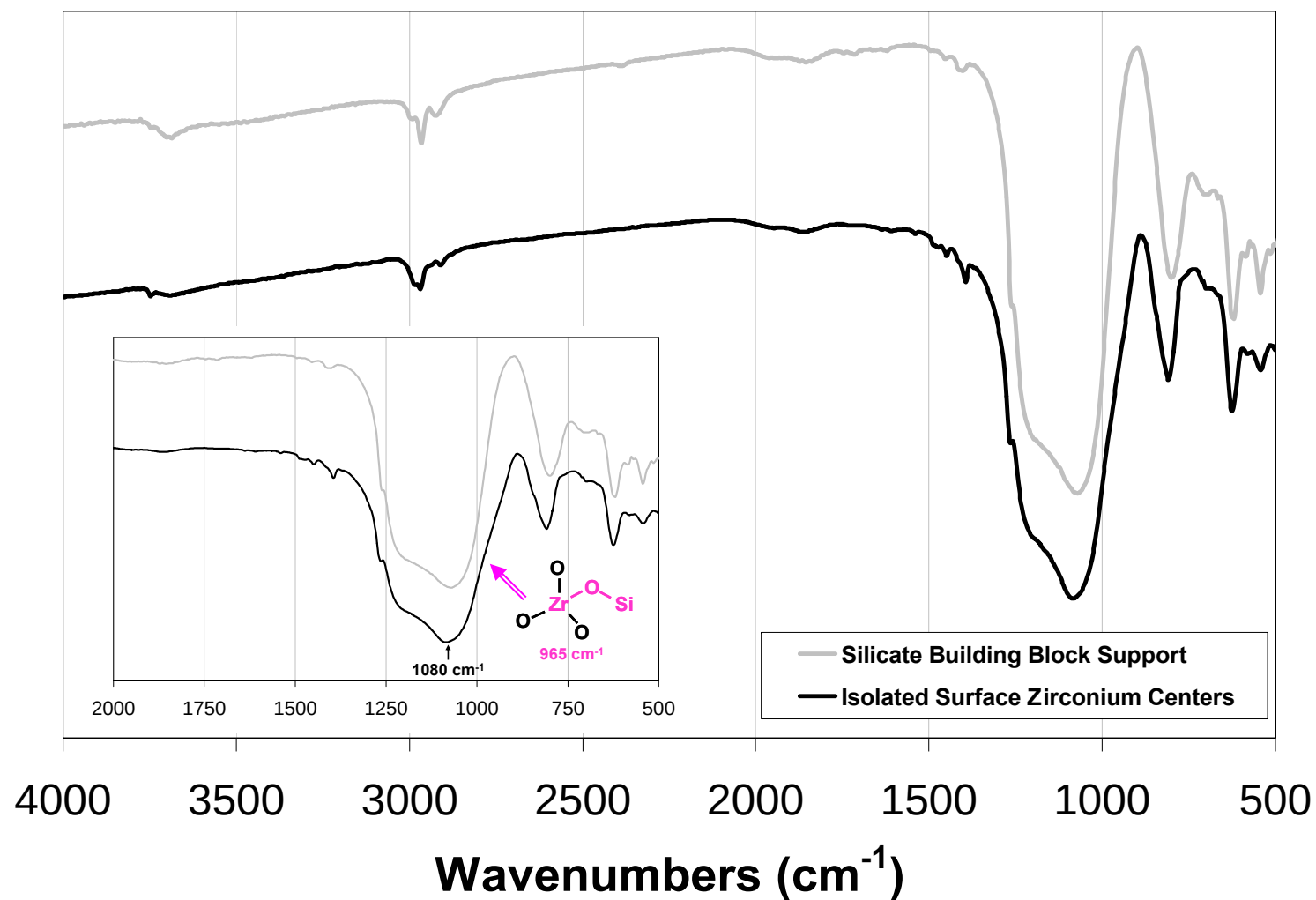


Figure 239: IR spectra ($500\text{--}4000\text{ cm}^{-1}$) of a zirconium-free silicate building block support (gray) and the material following the reaction of ZrCl_4 and a premade silicate building block support (black). The inset contains the expanded IR spectrum ($500\text{--}2000\text{ cm}^{-1}$) which illustrates the Zr-O-Si shoulder (965 cm^{-1}).

observed at approximately 965 cm^{-1} in the IR spectrum, which is characteristic of the presence of a transition metal atom, in this case Zr, bound to silicon through oxygen.[171,188-190] The weak shoulder provides direct evidence on the formation of Zr-O-Si groups and supports the validity of the metathesis reaction.

Figure 240 shows the ^{29}Si SSNMR spectrum for the silicate building block support and the surface zirconium centers. The ^{29}Si SSNMR spectrum does not change significantly following the linking of the surface zirconium centers to the silicate building block support which suggests that the linking reaction does not disrupt the silicate building block support. It also appears that ^{29}Si SSNMR is not sensitive enough to detect the new siloxane linkages (Si-O-Zr) that presumably have formed. The feature at -22 ppm is assigned to traces of silicon grease. The signals between -22 and -100 ppm in the spectrum are characteristic of the different silyl chlorides generated during the second cross-linking reaction (i.e. $(=\text{SiO})_{4-x}\text{SiCl}_x$).[95] The signals between -100 ppm and -110 ppm are assigned to the silicon corners on the building block which are connected to unreacted Me_3Sn groups $((=\text{SiO})_3\text{Si}(\text{OSnMe}_3))$, connected to the zirconium centers $((=\text{SiO})_3\text{Si}(\text{OZr}\equiv))$, and connected to the silicon centers $((=\text{SiO})_3\text{Si}(\text{OSi}\equiv))$.

Nitrogen adsorption/desorption measurements were conducted on the silicate building block support before and after the addition of the zirconium centers to determine the BET surface area and total pore volume. In the case of the silicate building block support, qualitative analysis of the nitrogen adsorption isotherm (Type IV) and t-plot suggests this material is a primarily mesoporous material (Figure 241 & Figure 242).[136] The presence of a hysteresis (Type H4) also indicates the presence of mesopores. The t-plot method was used to confirm the material is primarily microporous with respect to pore volume (11%) and surface area (22%). The BET surface area of this material is $794\text{ m}^2/\text{g}$ (Figure 243) and the total pore volume is $0.897\text{ cm}^3/\text{g}$. The BJH plot (Figure 244) does display a maximum at a pore radius of $41.5\text{ \AA}$. The porosity of the material does not significantly change with the addition of isolated surface zirconium centers. The nitrogen adsorption isotherm (Type IV), hysteresis (Type H4), and t-plot are again consistent with a material that is primarily mesoporous material (Figure 245 & Figure 246).[136] The t-plot method was used to confirm the material is primarily microporous with

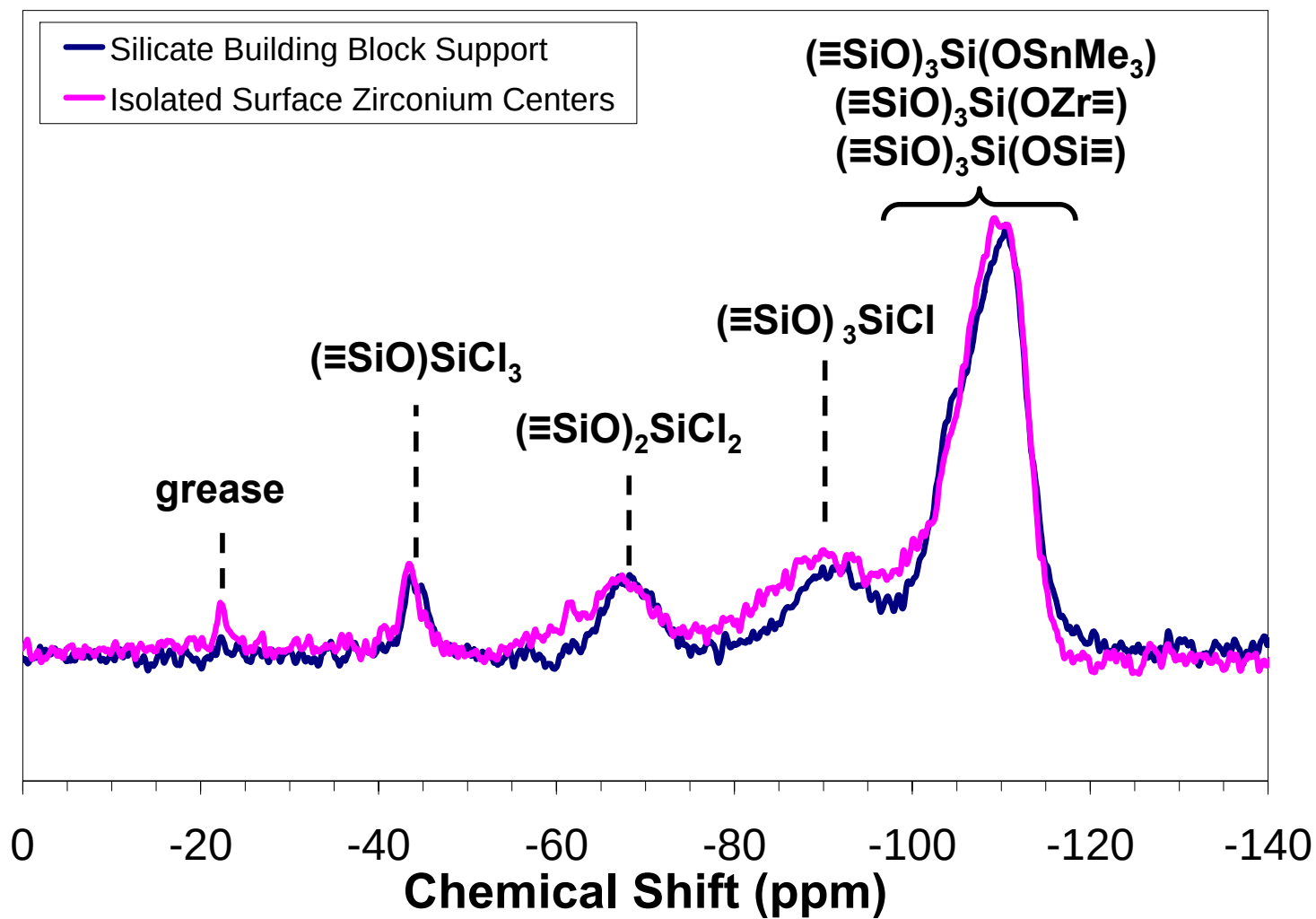
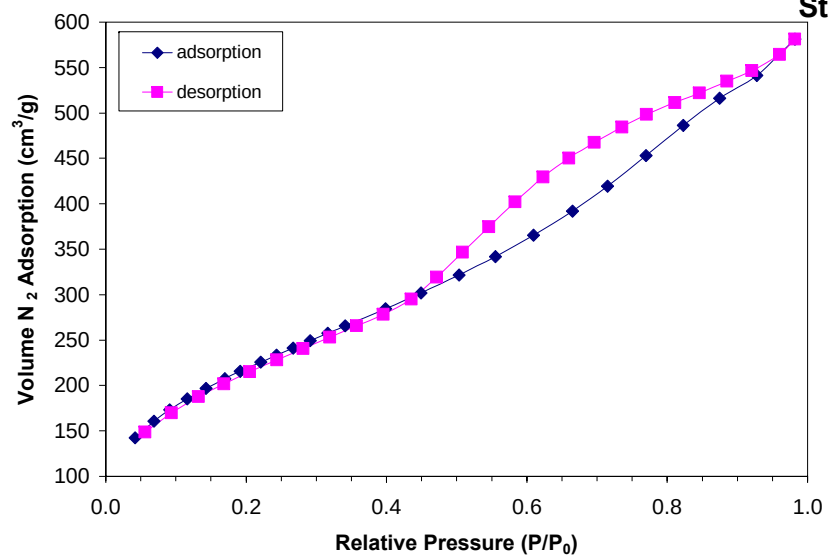
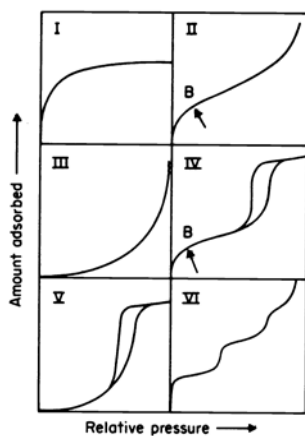


Figure 240: ^{29}Si SSNMR spectrum (-140 to 0 ppm) for the premade silicate building block support (navy blue) and following the reaction of ZrCl_4 and silicate building block support (pink).

Standard Isotherms



Standard Hysteresis Loops

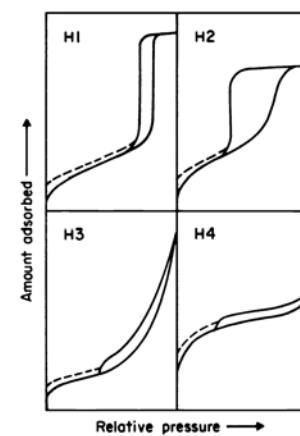


Figure 241: Nitrogen isotherm for the premade silicate building block support. Standard isotherms and hysteresis loops were obtained from literature.[131]

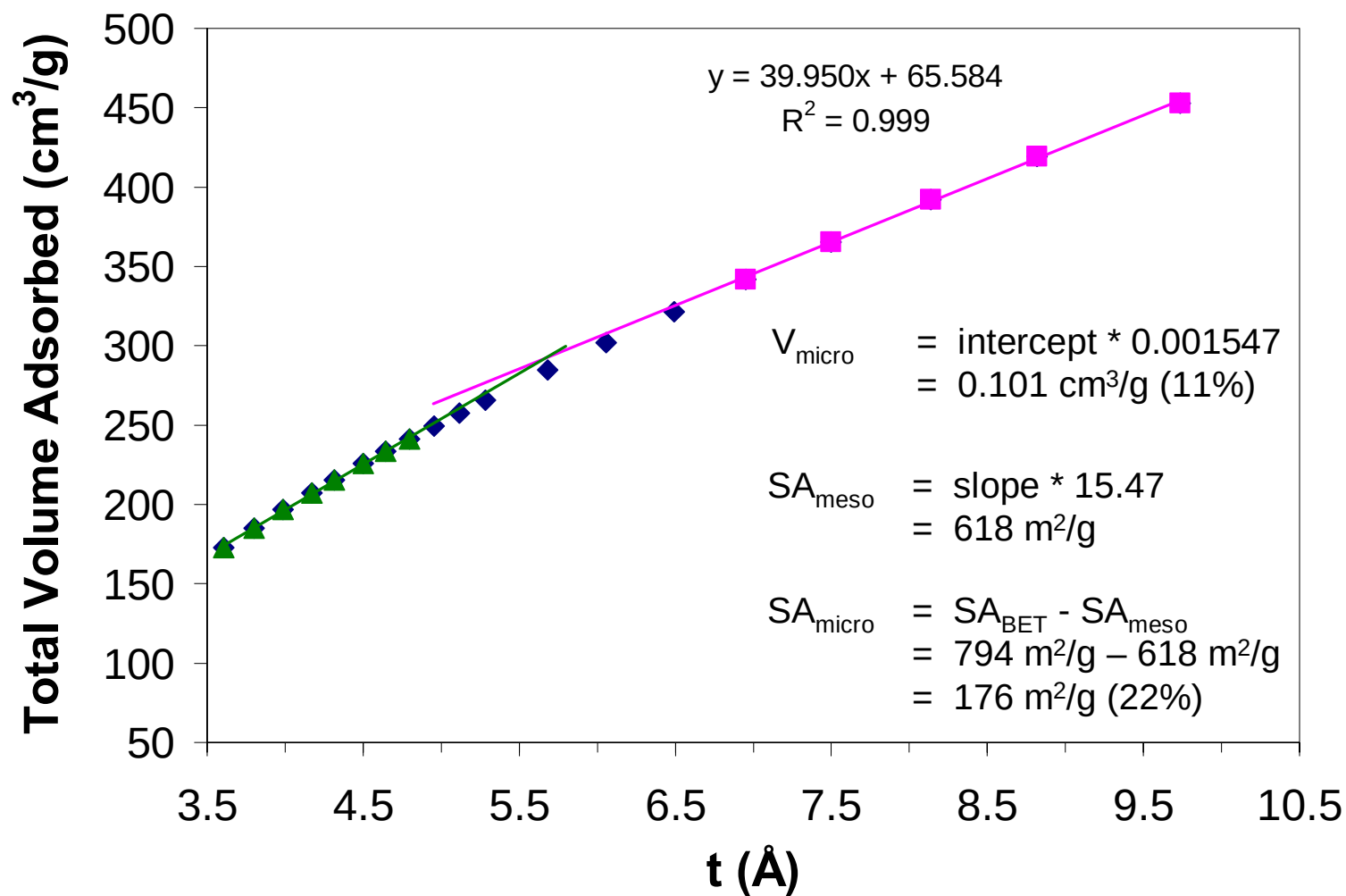


Figure 242: t-plot for the premade silicate building block support.

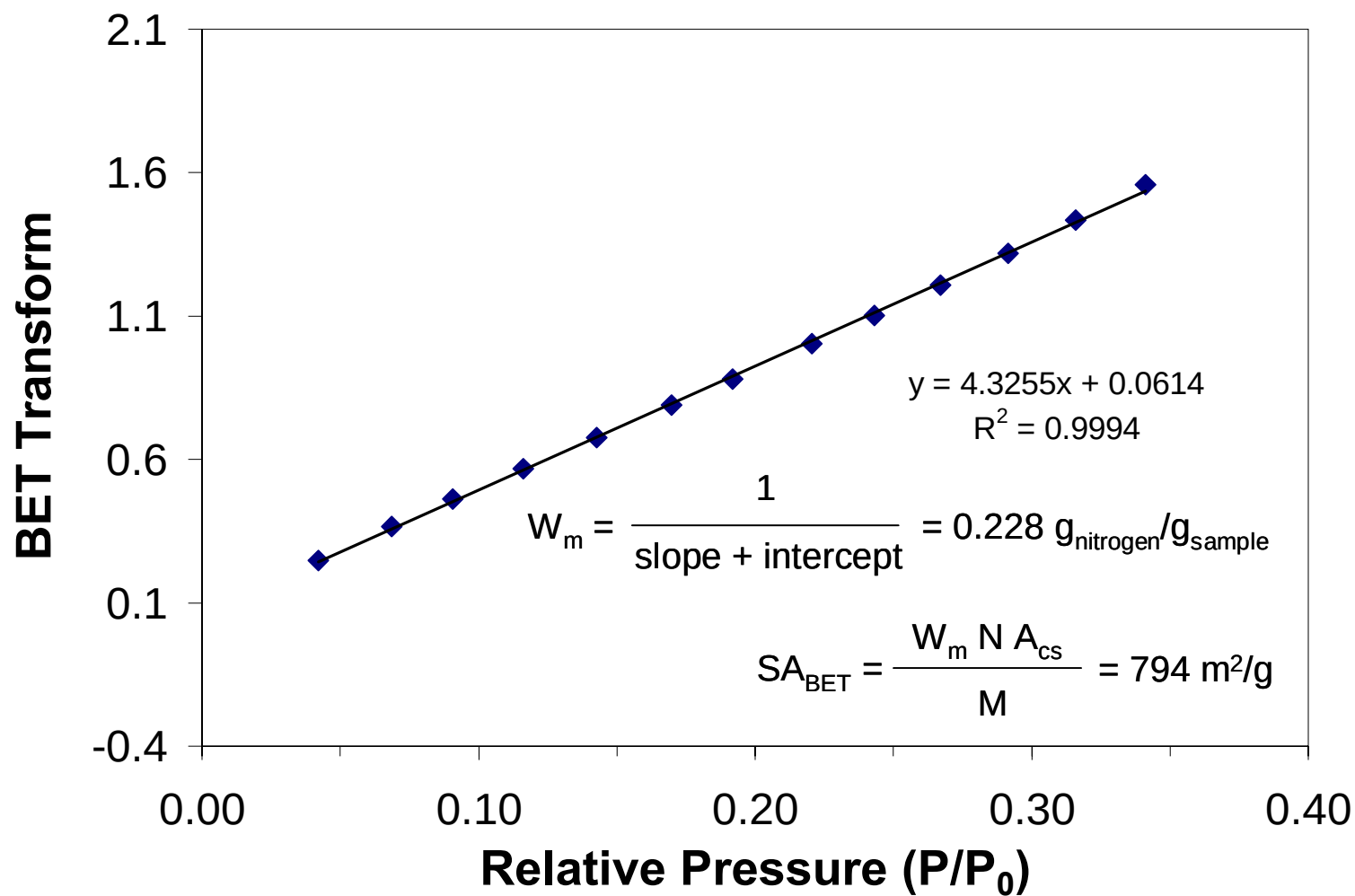


Figure 243: BET plot for the premade silicate building block support.

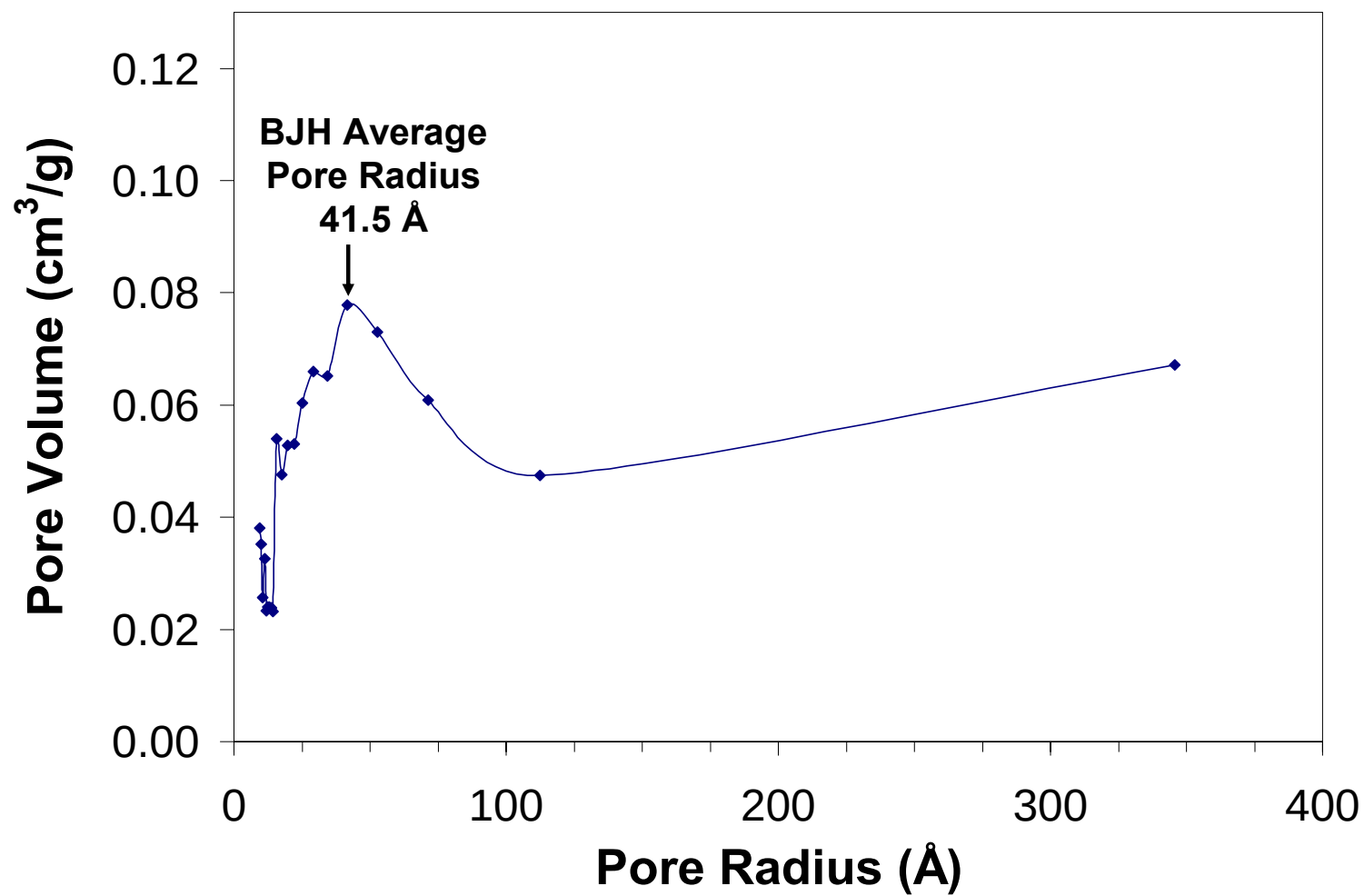
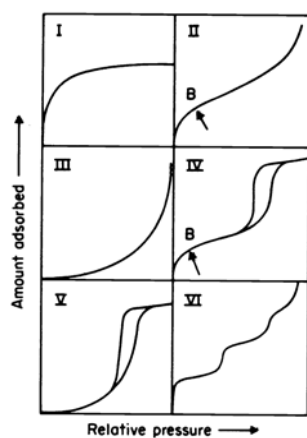


Figure 244: BJH pore size distribution plot for the premade silicate building block support.

Standard Isotherms



Standard Hysteresis Loops

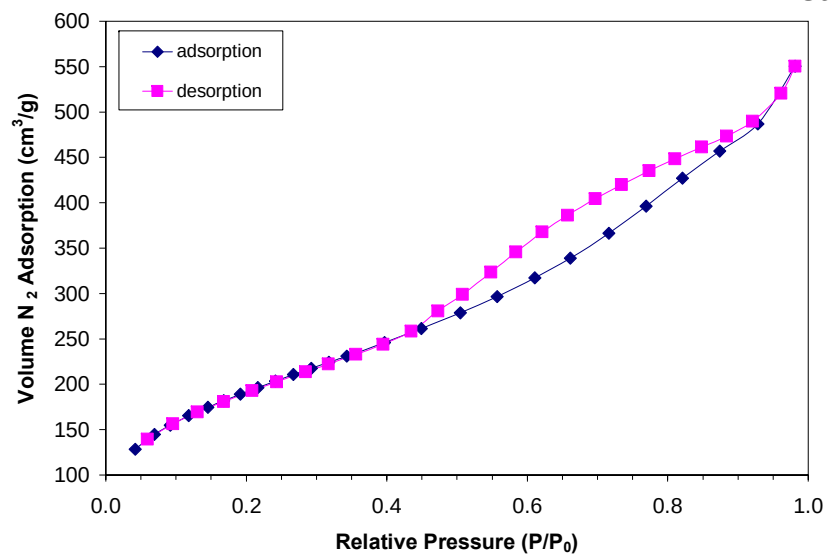
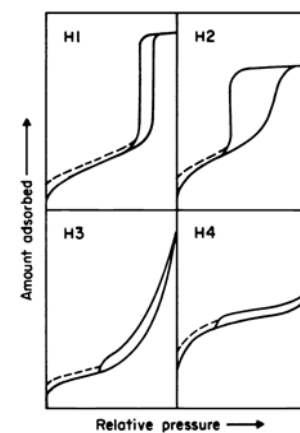


Figure 245: Nitrogen isotherm for the material following the reaction of ZrCl_4 and silicate building block support. Standard isotherms and hysteresis loops were obtained from literature.[131]

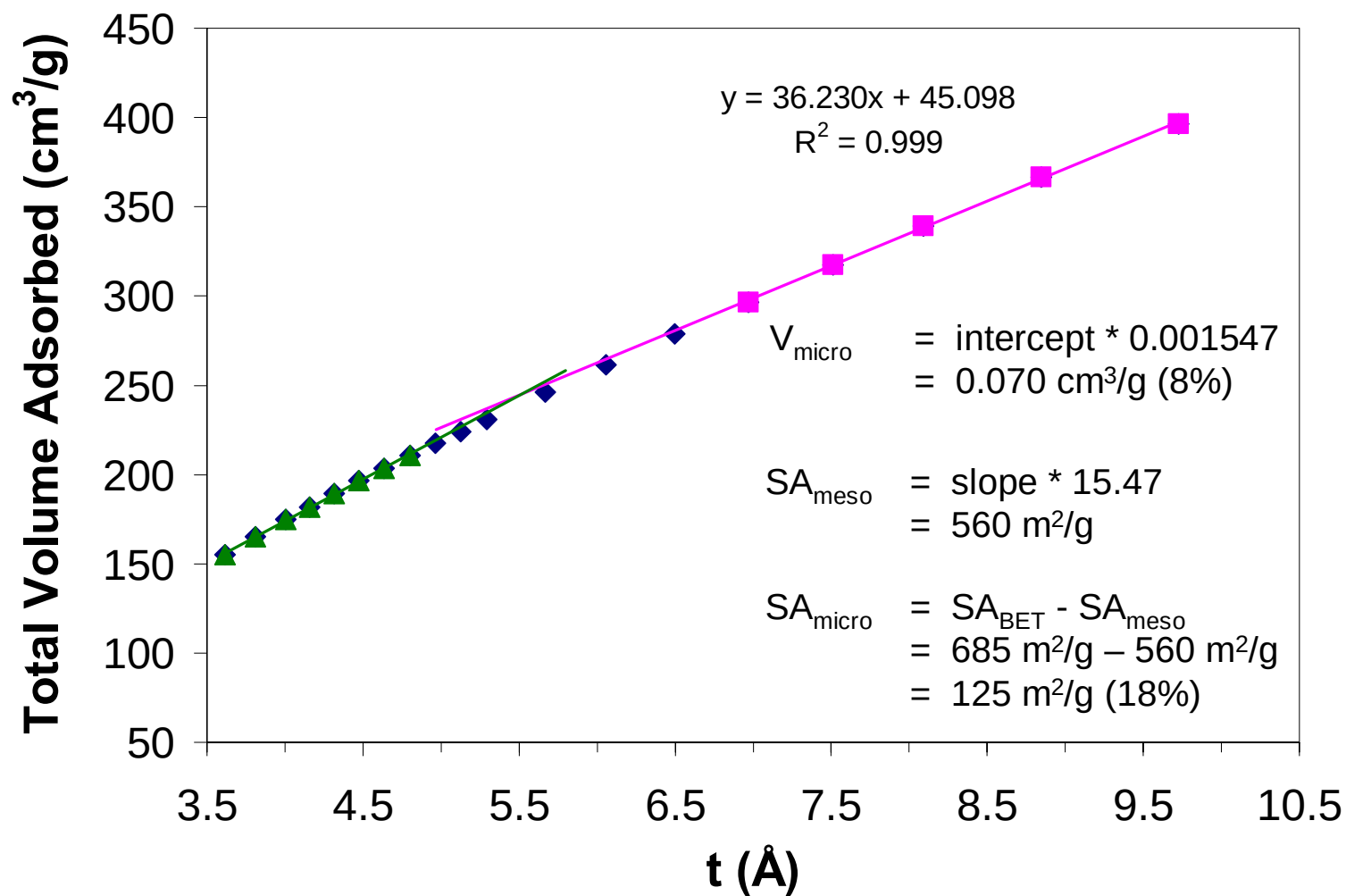


Figure 246: t-plot for the material following the reaction of ZrCl_4 and silicate building block support.

respect to pore volume (8%) and surface area (18%). The BET surface area of this material is $684 \text{ m}^2/\text{g}$ (Figure 247) and the total pore volume is $0.850 \text{ cm}^3/\text{g}$. The BJH plot (Figure 248) does display a maximum, which suggests the BJH average pore radius is $41.5 \text{ \AA}$.

XAS data were used to obtain more information about the coordination geometry and oxidation state of the zirconium centers (XANES) in addition to the connectivity of the zirconium centers (EXAFS).

XANES data for the zirconium K edge (17998 eV) provide information about the coordination geometry and oxidation state of the zirconium centers.[116,195] Figure 249 shows the XANES spectrum at the K edge of the material at this stage in the synthesis. The position of the K edge and the presence of a pre-edge feature provides information about the oxidation state and the coordination geometry respectively. Two features are observed in Figure 249. The first (17993 eV) is assigned to a pre-edge feature and the second feature (18000 eV) is assigned to the absorption edge. Table 12 summarizes the pre-edge and edge positions for each of the isolated zirconium(IV) catalyst ensembles discussed in this chapter as well as the edge position of the standard zirconium materials. The presence of a pre-edge feature ($1s \rightarrow 4d$ transition) provides evidence that the coordination geometry around the zirconium center is not octahedral and suggests the coordination geometry is tetrahedral. XAS studies on other transition metal chloride species (e.g. V and Ti) have identified an additional pre-edge feature that is superimposed on the adsorption edge but frequently not resolved from it.[96] The prominence of this additional feature relative to the adsorption edge increases with the number of chlorides bound to the transition metal. This feature can effect the selection of the adsorption edge position causing the adsorption edge position to appear at lower energy. While it is difficult to accurately measure the effect of this additional feature on the position of the absorption edge, the estimated edge position of the zirconium material supports the assignment of the oxidation state of zirconium centers as +4. The shape of the adsorption edge of the isolated zirconium centers appears to be similar to the shape of the absorption edge of c-ZrO_2 (T_d) and $\text{Zr(O}^n\text{Pr)}_4$ (O_h).[116] Therefore analysis of the shape of the adsorption edge of the material at this stage of the synthesis is inconclusive.

EXAFS data were used to obtain more information about the connectivity of the

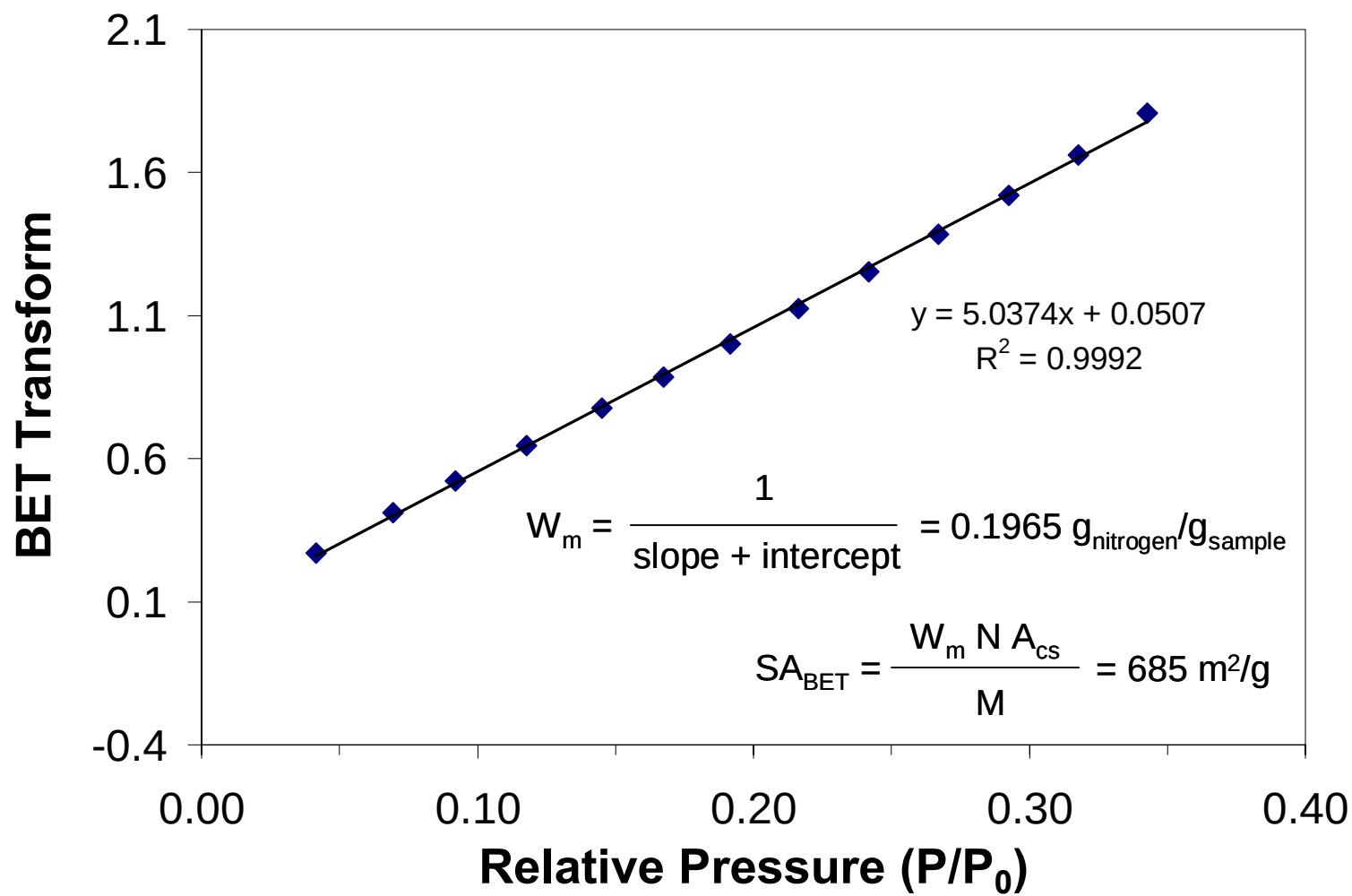


Figure 247: BET plot for the material following the reaction of ZrCl_4 and silicate building block support.

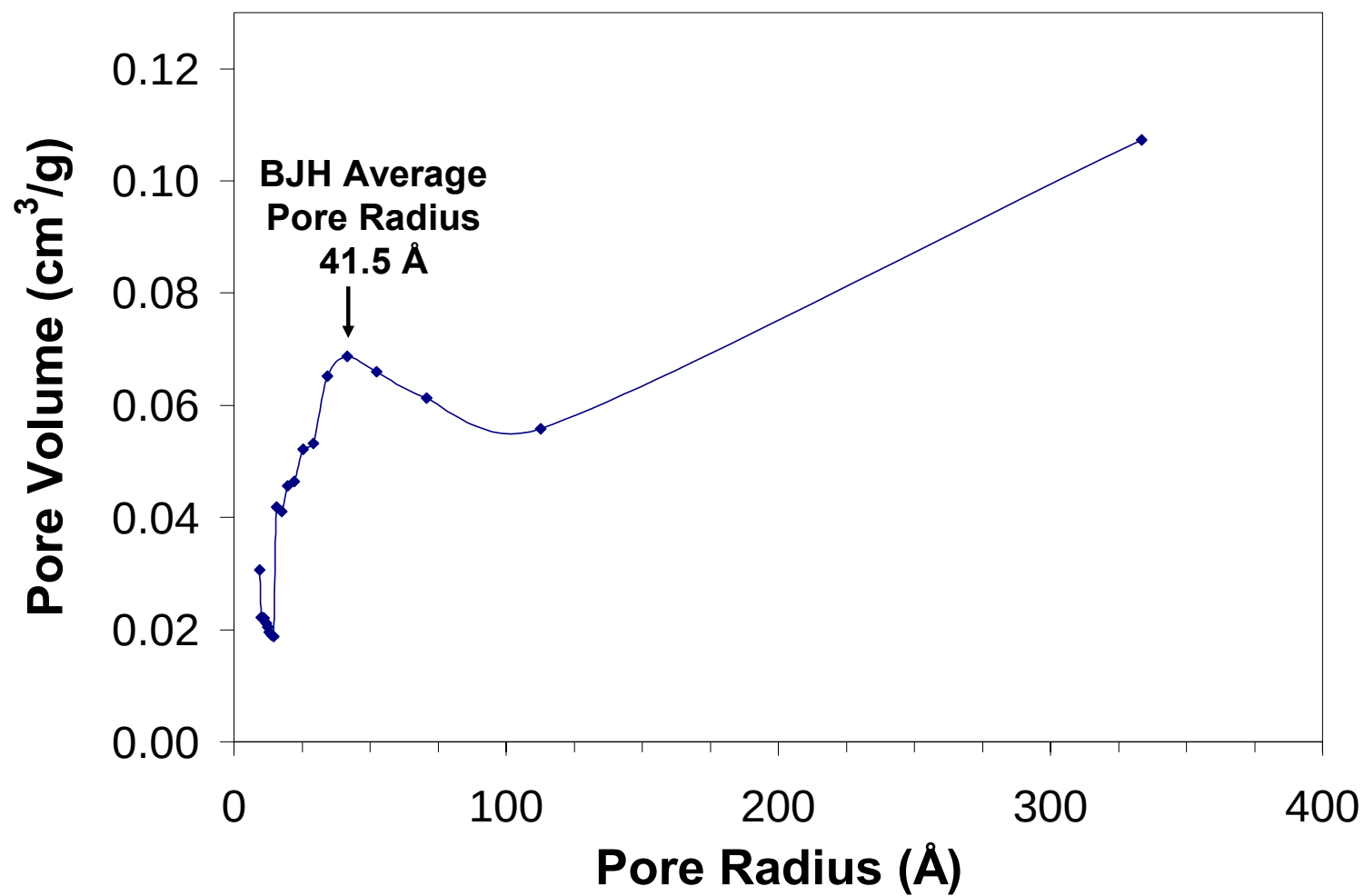


Figure 248: BJH pore size distribution plot for the material following the reaction of ZrCl_4 and silicate building block support.

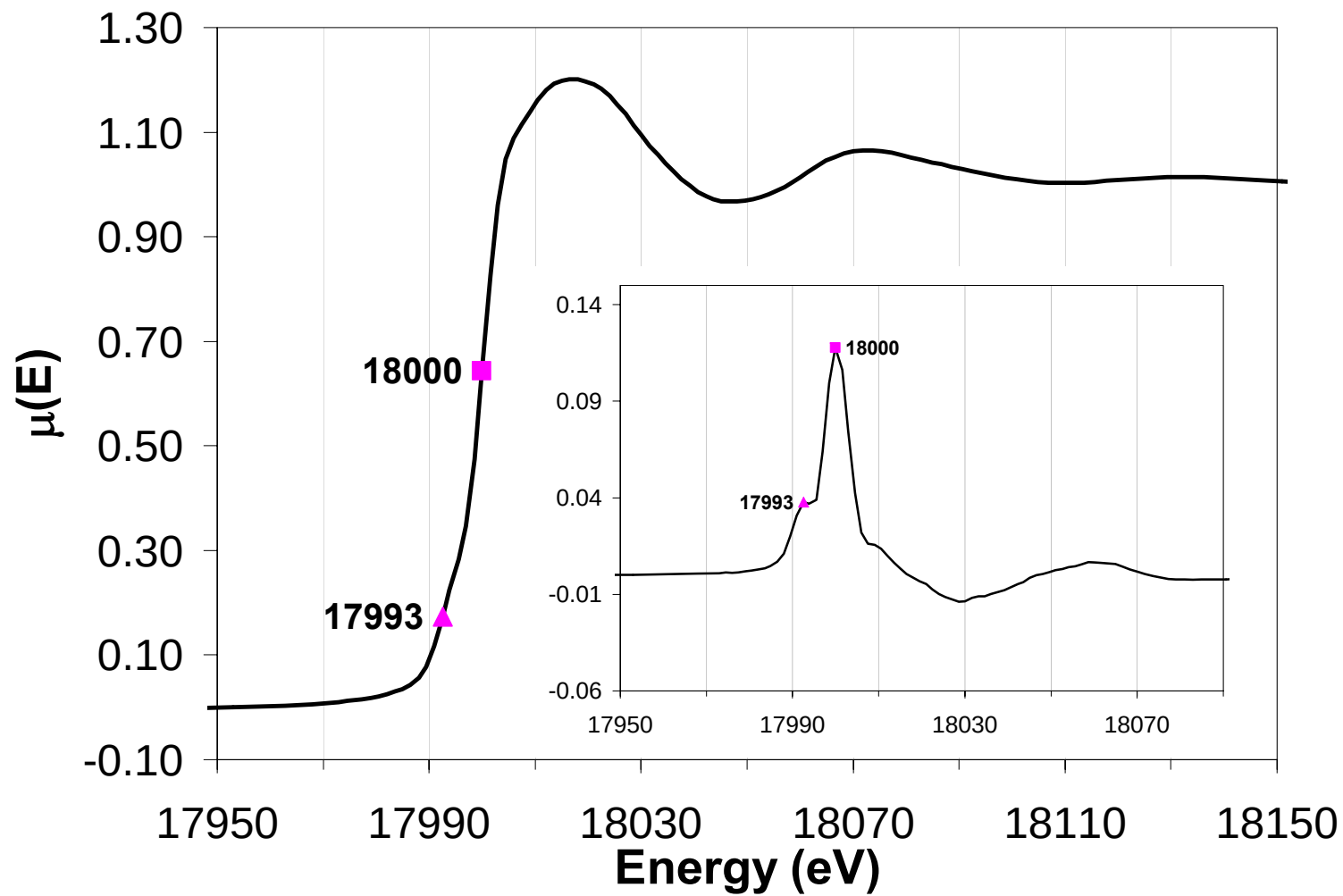


Figure 249: XANES spectrum (Zr K edge) following the reaction of ZrCl_4 and silicate building block support. The inset contains the derivative XANES spectrum which clearly shows the pre-edge feature (pink triangle) and the adsorption edge (pink square).

zirconium centers in the silicate building block matrix. The number of shells (i.e. atoms at different distances around zirconium) can be qualitatively determined by looking at the magnitude R-space plot (Figure 250). Based on the data already presented, three shells should be present around the zirconium centers after zirconium becomes attached to the surface of the silicate building block support: a shell of singly bound oxygen atoms (Zr-O), a shell of unreacted chlorine ligands (Zr-Cl), and a shell of nonbonded silicon atoms (Zr...Si) however only one feature was observed in the magnitude R-space plot. The one feature is tentatively assigned to the shell of singly bound oxygen atoms and the shell of unreacted chlorine ligands which are resolved.

Based on the qualitative analysis of the EXAFS data, the first coordination sphere (defined as atoms directly bound to the zirconium) of the surface zirconium centers should have at least one singly bound oxygen atom (Zr-O) and at least one singly bound chloride atom (Zr-Cl).

In order to obtain quantitative structural information about the local zirconium environment, a structural model must first be proposed. The structural model that was used to fit the data was constructed based on the gravimetric data. A structural model containing Zr-O (CN=1), Zr-Cl (CN=3), and Zr...Si (CN=1) single scattering paths was constructed (Figure 251). The inclusion of the Zr...Si single scattering path in the structural model improved the fit of the structural model to the data even though visually the presence of a feature assignable to a Zr...Si shell was not apparent. FEFF8[115] was used to independently estimate the value of S_0^2 . The value of S_0^2 obtained from FEFF8 was 0.928. The CN values based on the results of gravimetric analysis and S_0^2 , as determined by FEFF8, were initially fixed as the other structural parameters were iteratively refined. The EXAFS signal ($\chi(k) * k^3$) for the surface zirconium centers in a silicate building block matrix is presented in Figure 252 with the EXAFS data range that produced the best fit boxed (3.2 to 13.1 Å⁻¹). In R-space, the fit range is from 1.1 to 4.5 Å and the magnitude and real parts of the FT of the data and FEFF model are presented in Figure 250 and Figure 253 respectively. Table 13 summarizes the refined values of the structural parameters. As shown in Table 14 the refined bond lengths are in good agreement with values

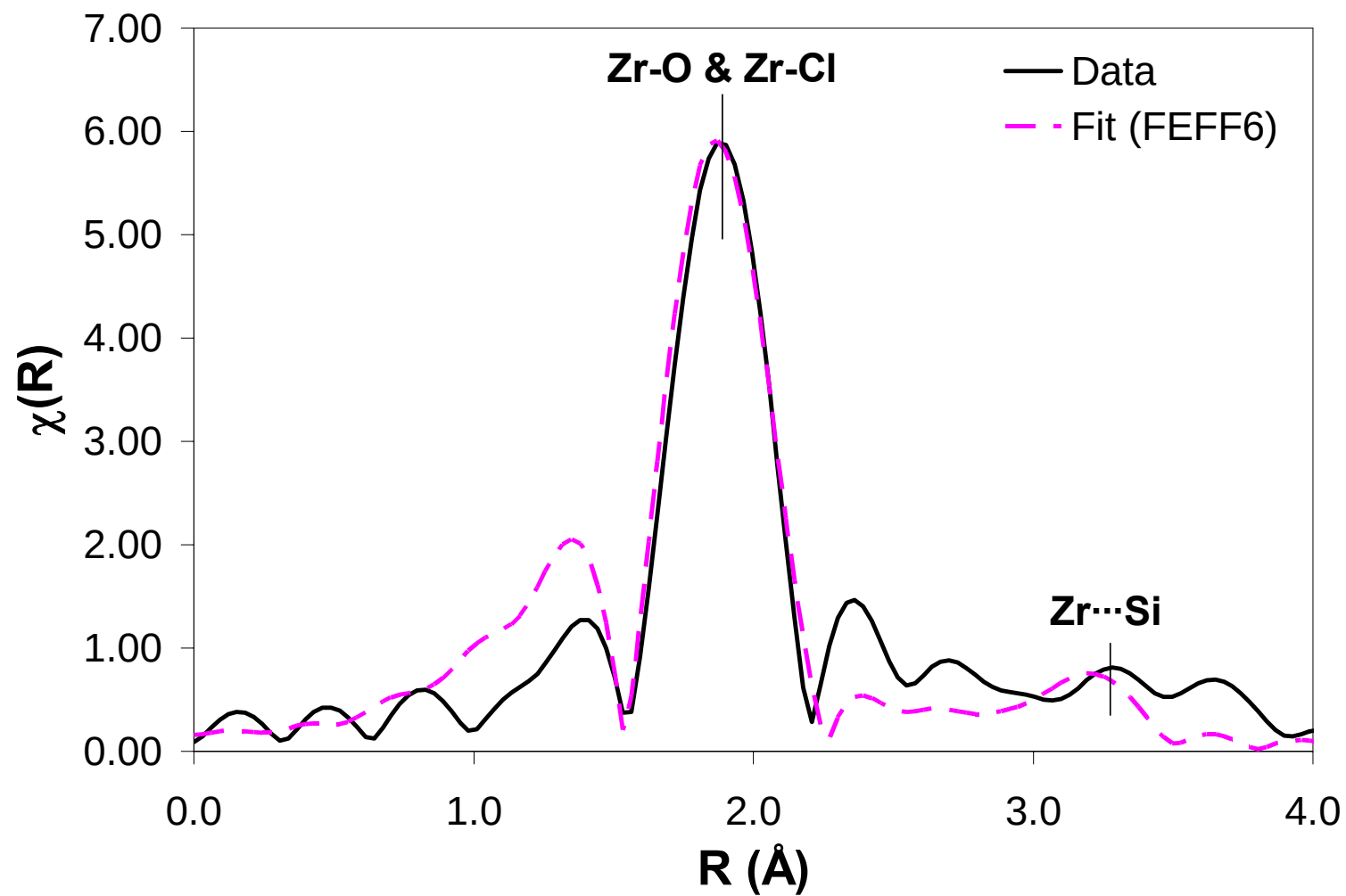


Figure 250: EXAFS R-space plot following the reaction of ZrCl_4 and silicate building block support. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

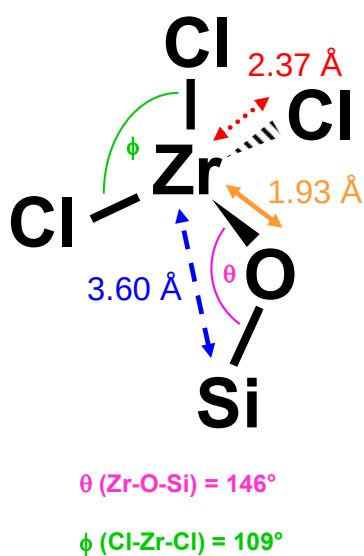


Figure 251: Structural model used for EXAFS data analysis of the isolated surface zirconium centers. The model contains a zirconium center with three singly bound chloride atoms (Zr-Cl), one singly bound oxygen atoms (Zr-O) and one nonbonded silicon atoms (Zr...Si).

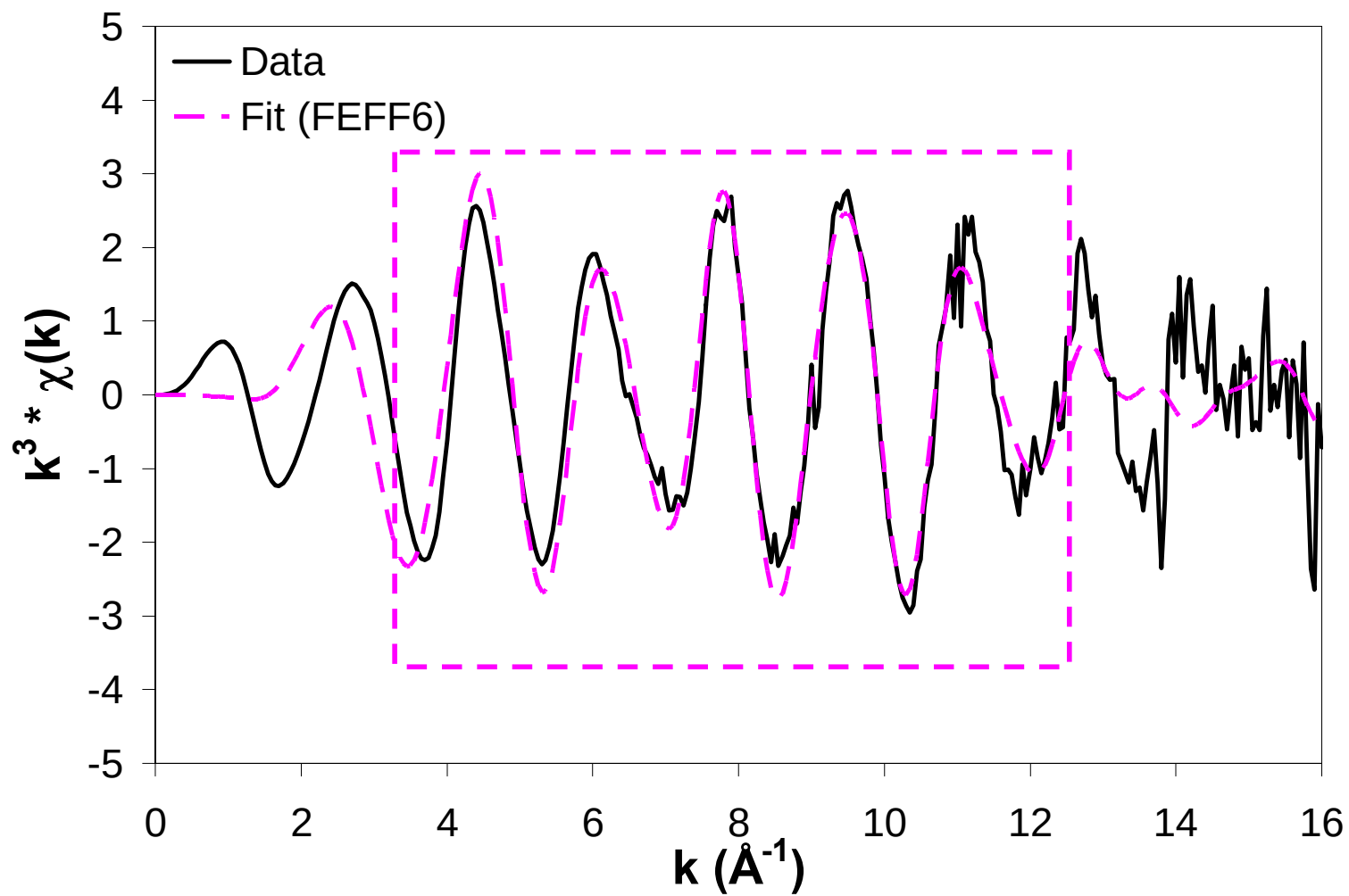


Figure 252: EXAFS k-space plot following the reaction of ZrCl_4 and silicate building block support.

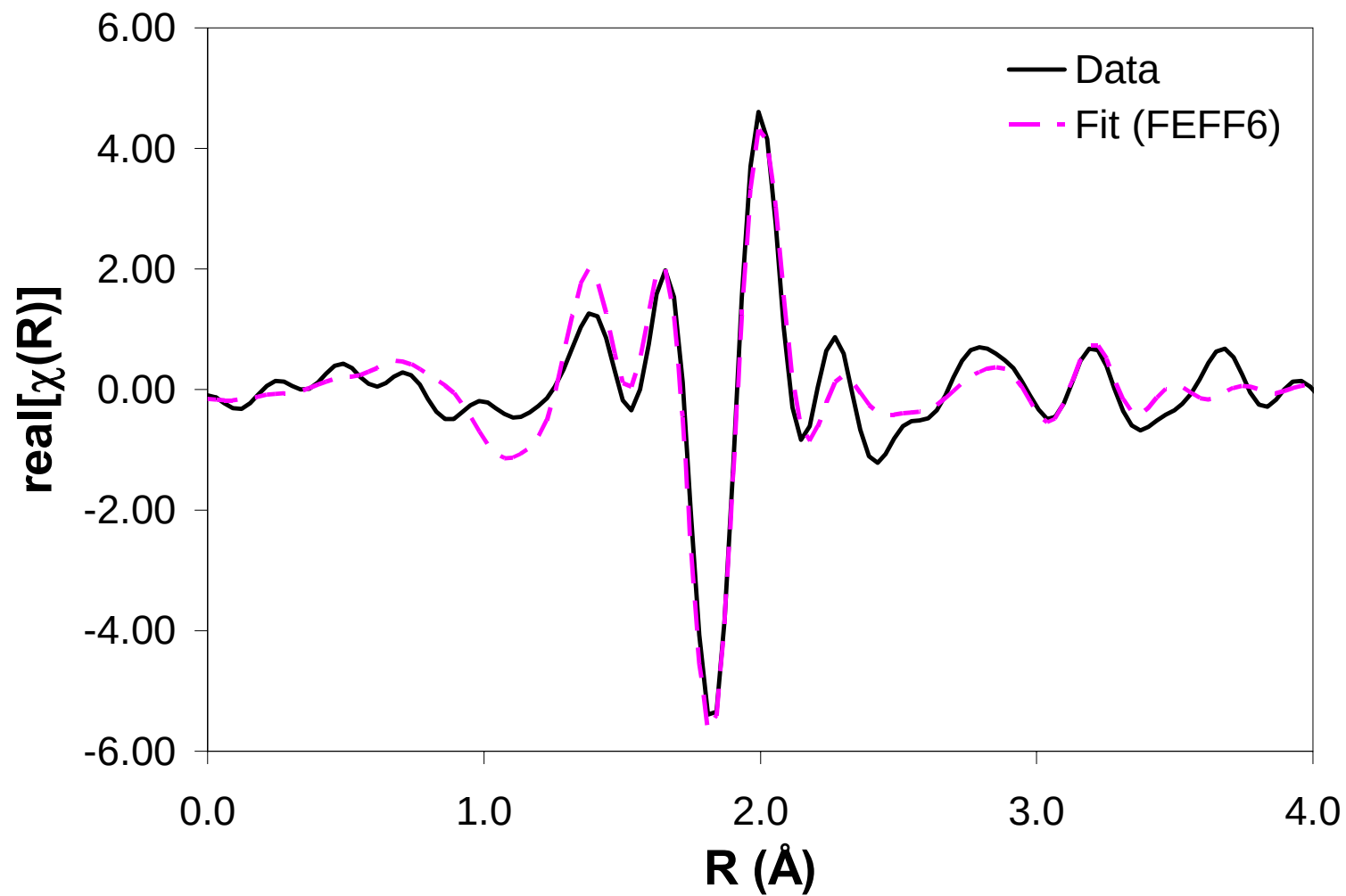


Figure 253: EXAFS real R-space plot following the reaction of ZrCl_4 and silicate building block support. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

found in the literature.[116,171,196,201-207] Fixing bond distances and atom separations and allowing coordination numbers to refine yielded the results summarized in Table 13. The refined values of the CNs are within 10% of the values determined by gravimetric analysis.

In summary, the EXAFS data analysis provides evidence that the immediate environment around the surface zirconium centers is as expected (1 Zr-O, 3 Zr-Cl and 1 Zr···Si). The structural model derived from EXAFS data are consistent with the conclusions drawn from both gravimetric and spectroscopic techniques, all of which support a model in which a single type of zirconium center that is atomically dispersed on the surface of the silicate material.

The combination of the techniques described above provides a reasonably clear picture of the products in the reaction of ZrCl₄ and the silicate building block support (Figure 254). The isolated surface zirconium centers were attached to the surface of a premade high surface area silicate support. Gravimetric analysis provided evidence that only one of the chloride ligands on the zirconium centers reacted with the trimethyltin functional groups on the premade silicate support (formation of Zr-O and preservation of Zr-Cl, control of the ligands). IR provided evidence of the formation of linkages between the zirconium centers and the premade silicate support (formation of Zr-O-Si, control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the zirconium centers remained unchanged during the cross-linking reaction (preservation of zirconium(IV) centers, control of the metal cation). A structural model based on EXAFS data confirms that the local environment around all zirconium centers in the matrix is identical and composed of a zirconium center surrounded by one oxygen atom and three chloride ligands. The building block approach and sequential dosing strategy provides control of all the necessary components to produce identical, surface zirconium catalyst ensemble.

Summary and Conclusions

The targeted synthesis of materials containing a single type of well-defined, isolated zirconium(IV) ensembles is demonstrated. Both the embedded and surface zirconium catalyst ensembles are readily synthesized using a targeted building block approach and sequential dosing synthetic strategy. Two unique catalyst ensembles containing zirconium(IV) centers were targeted and successfully synthesized.

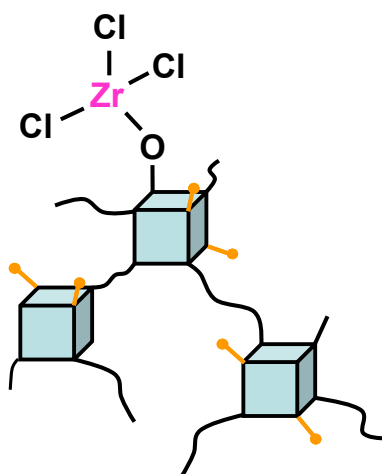


Figure 254: Proposed representation of the catalyst ensemble following the reaction of ZrCl_4 and silicate building block support.

Isolated embedded zirconium catalyst ensembles were synthetically targeted by reacting the silicate building block with a limiting amount of zirconium(IV) chloride, ZrCl_4 . The resulting material was further cross linked using SiCl_4 resulting in a high surface area silicate support containing isolated embedded zirconium catalyst ensembles (Figure 237). Gravimetric analysis provided evidence that all of the chloride ligands on the zirconium centers reacted with the trimethyltin functional groups on the silicate building block (control of the ligands). IR and SSNMR spectra provided evidence of the formation of linkages between the zirconium centers and the silicate building blocks (control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the zirconium centers remained unchanged during the cross-linking reaction (control of the metal cation). A structural model based on EXAFS data strongly supports a model in which the tetrahedral zirconium center is bound to four oxygen atoms.

Isolated surface zirconium catalyst ensembles were synthetically targeted by reacting a premade silicate building block support with a limiting amount of zirconium(IV) chloride, ZrCl_4 (Figure 254). Gravimetric analysis provided evidence that only one of the chloride ligands on the zirconium centers reacted with the trimethyltin functional groups on the premade silicate support (control of the ligands). IR provided evidence of the formation of linkages between the zirconium centers and the premade silicate support (control of the metal-to-support linkages). XAS data confirmed that the oxidation state of the zirconium centers remained unchanged during the cross-linking reaction (control of the metal cation). A structural model based on EXAFS data strongly supports a model in which the tetrahedral zirconium center is bound to one oxygen atom and three chloride ligands.

In both cases, the building block approach and sequential dosing strategy provided control of all the necessary components to target the desired zirconium catalyst ensemble.

The synthetic methodology illustrated here is broadly applicable to many high valent metals and main group elements. Analogous materials containing isolated metal centers (Ti, W, Al, Ga, and B) are being developed and characterized as above. Future work for these materials and the ones presented here includes the study of the correlation between site identity and activity in a number of solid acid and oxidation reactions.

Acknowledgments

I gratefully acknowledge the significant contributions made by Katherine P. Sharp in this chapter and the support of the U.S. Department of Energy-Office of Basic Energy Sciences, grant DE-FG02-01ER15259. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

CHAPTER 5. SYNTHESIS AND CHARACTERIZATION OF NANOSTRUCTURED SILICATE BUILDING BLOCK CATALYSTS WITH TARGETED POROSITY

Introduction

The incorporation of metal cations into the framework of mesoporous silica has been extensively studied.[36-39,41-53] The synthesis of these mesoporous materials typically requires the use of a sol-gel or hydrothermal approach in addition to templating agents and calcination. All of these procedures provide researchers with little synthetic control of the local environment around the metal cations. The development of synthetic methodologies for heterogeneous catalysts that provide researchers the ability to control the local environment around the metal cations and the porosity of the material has been part of our ongoing research program.

This chapter revisits the idea of tailoring the porosity of silicate building block supports and expands it to nanostructured heterogeneous catalysts. In this chapter, the synthetic methodology used to prepare embedded catalyst ensembles (originally presented in chapters three and four) was combined with the concept of generating silicate supports with targeted porosity (originally presented in chapter two). This combined approach allows one to control all of the necessary components of embedded ensembles and the porosity of the material containing the ensembles resulting in the preparation of nanostructured heterogeneous catalysts with targeted porosity.

Experimental

Information about the materials, general synthetic procedures, and instrumentation used in this chapter has already been presented in chapters two through four.

Results and Discussion

The surface area and porosity of nanostructured heterogeneous catalysts with isolated embedded metal cation centers (e.g. tungsten, zirconium, titanium) was investigated. As already discussed in chapters 3 and 4, the embedded centers are synthesized when a limiting amount of metal chloride (WOCl_4 , WCl_6 , ZrCl_4 , or TiCl_4) is reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. In all cases, the material following this first cross-linking reaction had no measurable surface area (Figure 255) and can be thought of as small oligomers that contain embedded metal cation centers. The

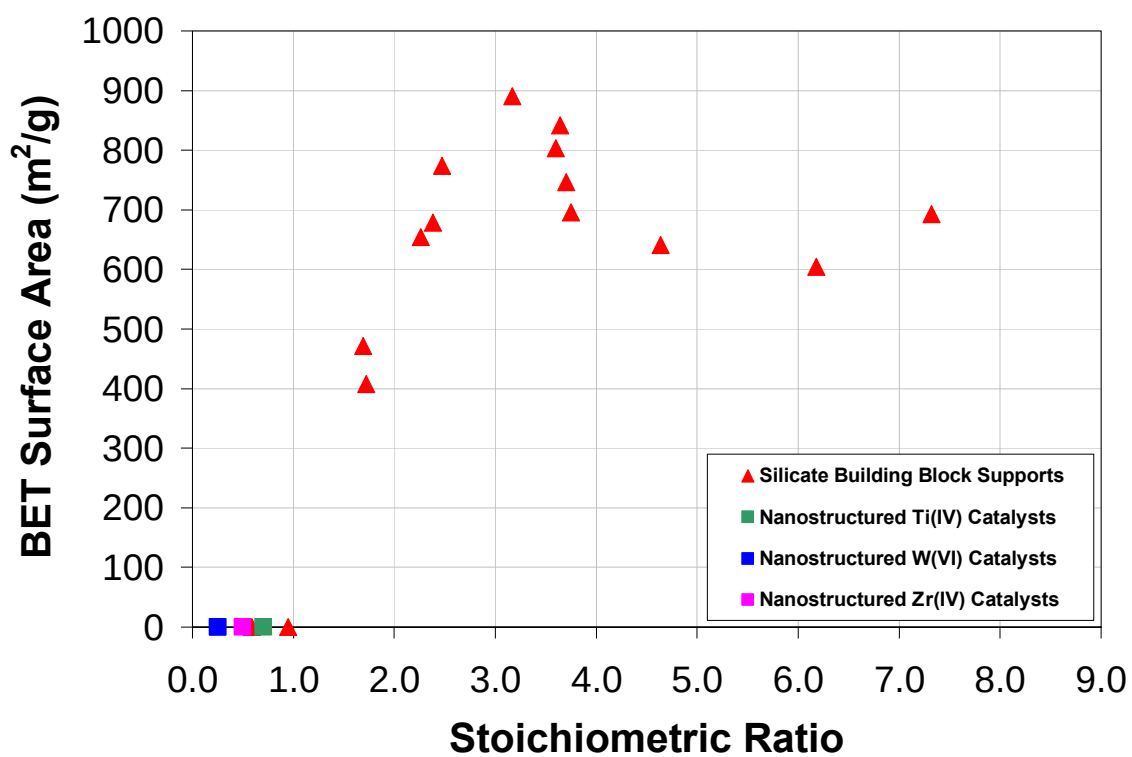


Figure 255: A plot of the BET surface area of the nanostructured materials versus the stoichiometric ratio of reactants, either $\text{MCl}_x : \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ or $\text{SiCl}_4\text{py}_2 : \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$.

oligomers were then linked together to form around the embedded centers a robust, high surface area, silicate support with targeted porosity. The growth of the silicate support with targeted porosity should not effect the local environment of the embedded centers.

The studies presented in chapter two which studied how the surface area of the silicate support changed as the SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ ratio was varied were expanded to include the sequential dosing strategy used to synthesize nanostructured heterogeneous catalysts. The total stoichiometric ratio of cross-linking agents, defined as the sum of the metal chloride to building block ratio and the silicon bispyridine to building block ratio, was used instead of the SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$ ratio. Figure 256 illustrates how the BET surface area changed as the total stoichiometric ratio was varied. One should immediately notice that the surface area of the nanostructured catalysts follows the trend presented in chapter two for the metal-free silicate supports. This means that the surface area of nanostructured heterogeneous catalysts can be synthetically targeted providing researchers with the ability to precisely control all of the necessary components of the catalyst ensemble and the surface area of the material containing the ensembles.

The rest of this chapter will focus on identifying the porosity of the materials and probing the immediate environment around the embedded centers in these materials.

Nanostructured W(VI) Catalysts with Embedded Ensembles and Targeted Mesoporosity

Isolated embedded tungsten(VI) centers, composed of a tungsten center surrounded by one oxo group and four linkages to building blocks, were prepared using the synthetic methodology presented in chapter three. The material containing the embedded tungsten(VI) centers was further cross linked with SiCl_4py_2 (3.0 SiCl_4py_2 : 1 $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$) in order to target the generation of a mesoporous silicate support around the embedded centers. The growth of the mesoporous silicate support should not disrupt the immediate environment of the embedded centers.

Qualitative analysis of the nitrogen adsorption/desorption isotherm (Type IV, Type H4 hysteresis loop) and t-plot suggests this material is primarily mesoporous (Figure 257 & Figure 258).[136] The t-plot method confirms the material is primarily mesoporous with respect to pore

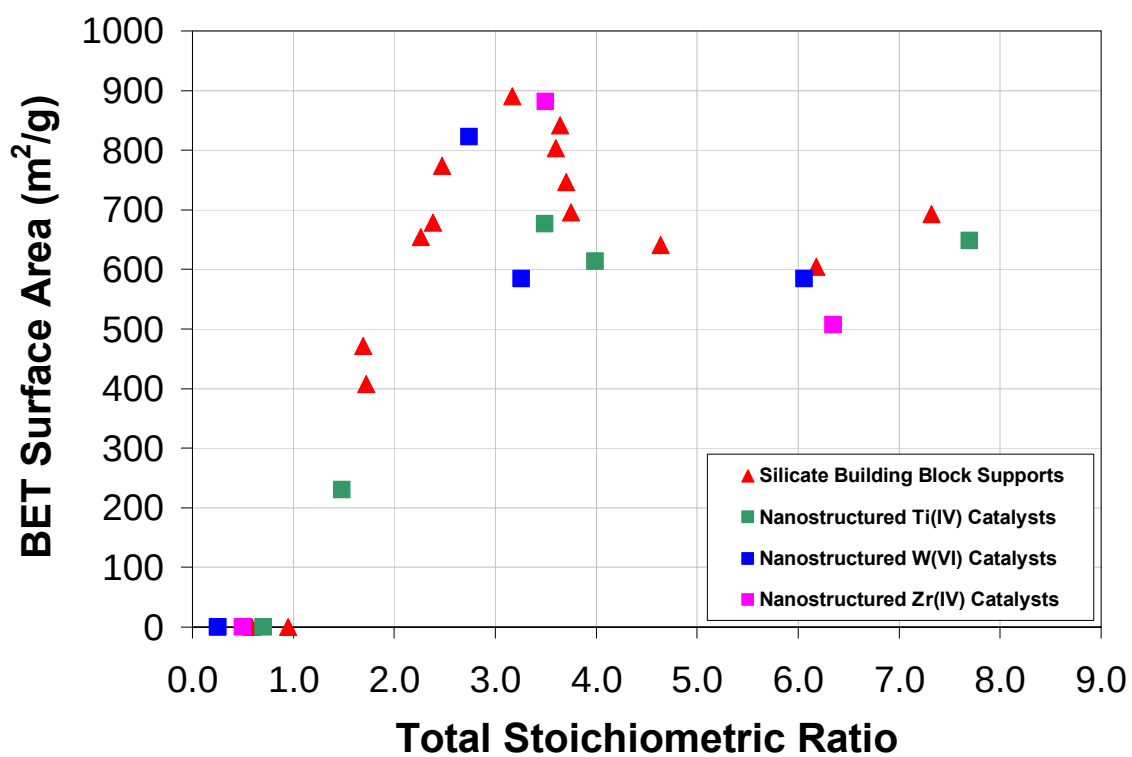
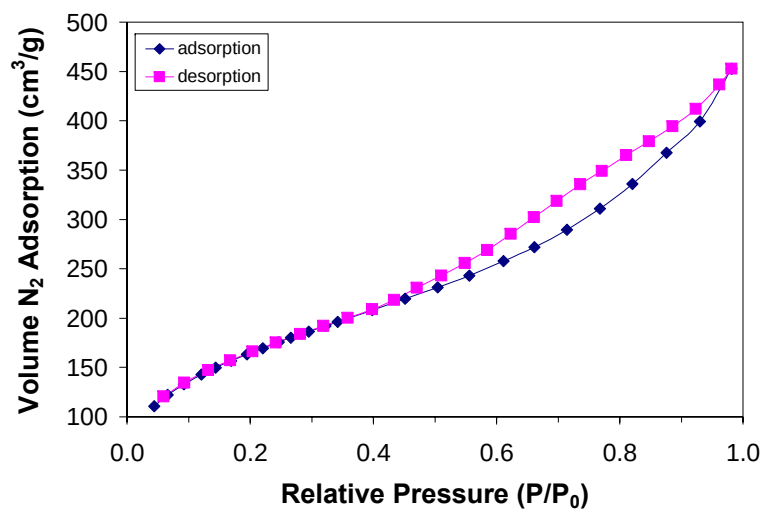
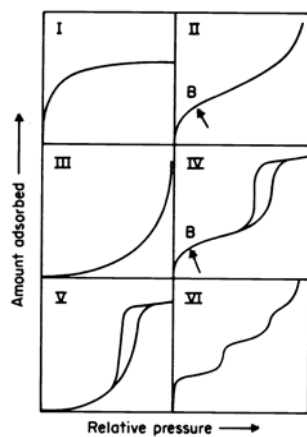


Figure 256: A plot of the BET surface area of the nanostructured materials versus the total stoichiometric ratio of the reactants ((MCl_x : Si₈O₁₂(OSnMe₃)₈) + (SiCl₄py₂ : Si₈O₁₂(OSnMe₃)₈)).

Standard Isotherms



Standard Hysteresis Loops

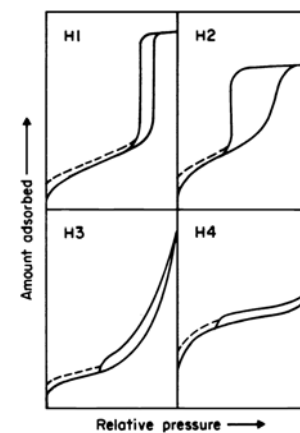


Figure 257: Nitrogen isotherm for a nanostructured tungsten(VI) catalyst with targeted mesoporosity. Standard isotherms and hysteresis loops were obtained from the literature.[131]

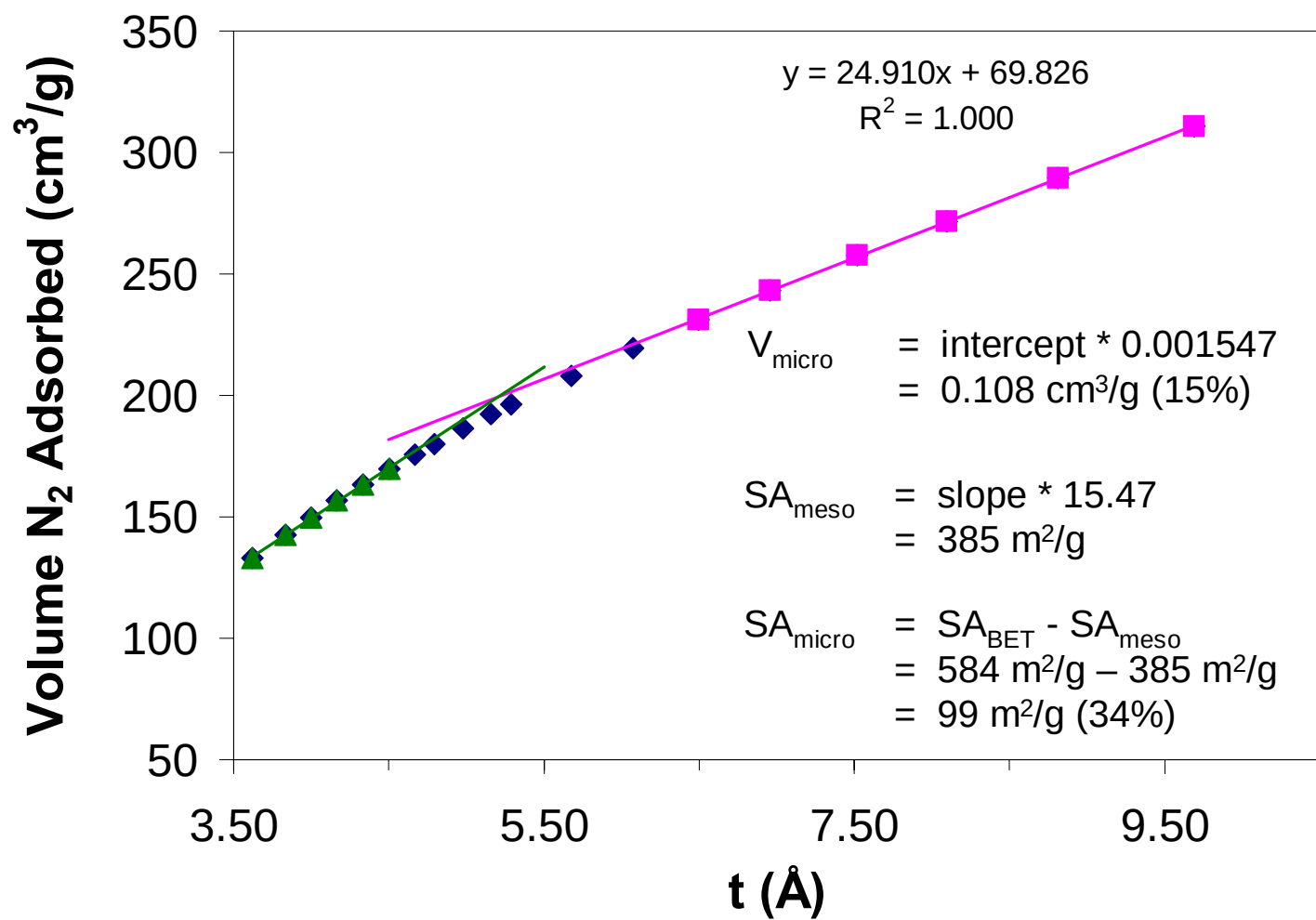


Figure 258: t-plot for a nanostructured tungsten(VI) catalyst with targeted mesoporosity.

volume (85%) and surface area (66%). The BJH average pore radius (71.5 Å, Figure 259) is consistent with the generation of a high surface area (584 m²/g, Figure 260), mesoporous, silicate support. Thus a mesoporous silicate support was generated with the use of templating agents.

Figure 261 and Figure 262 show the XANES spectra at the L_{III} and L_I edges of the material at this stage in the synthesis. The edge positions suggest the oxidation state of the tungsten centers is +6. The width of the white line at the L_{III} edge and the intensity of a pre-edge feature at the L_I edge suggest the coordination geometry is distorted octahedral.

EXAFS data were modeled using the same structural model (Figure 105), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.92), and refinement procedure presented in chapter three. The EXAFS signal ($\chi(k) * k^3$) for the material is presented in Figure 263 with the FT data range boxed (3.6 to 13.4 Å⁻¹). The fit range is from 1.0 to 4.0 Å and the magnitude and real part of the FT of the data and FEFF model are presented in Figure 264 and Figure 265 respectively. Table 15 summarizes the refined values of the structural parameters which are in agreement with values determined for the embedded tungsten(VI) centers presented in chapter three (Table 7 and Table 9).

Thus researchers have the ability to precisely control all of the necessary components of embedded tungsten(VI) ensembles and the surface area of the material containing the ensembles.

Nanostructured Zr(IV) Catalysts with Embedded Ensembles and Targeted Mesoporosity

Isolated embedded zirconium(IV) centers, composed of a zirconium center surrounded by four linkages to building blocks, were prepared using the synthetic methodology presented in chapter four. The targeted generation of a mesoporous silicate support around the embedded centers was accomplished by further cross-linking the material containing the isolated embedded zirconium(IV) centers with SiCl₄py₂ (3.1 SiCl₄py₂ : 1 Si₈O₁₂(OSnMe₃)₈). The growth of the mesoporous silicate support should not disrupt the immediate environment of the embedded centers.

Qualitative analysis of the nitrogen adsorption/desorption isotherm (Type IV, Type H4 hysteresis loop) and t-plot suggests this material is primarily mesoporous (Figure 266 & Figure 267).[136] The t-plot method confirms the material is primarily mesoporous with respect to pore

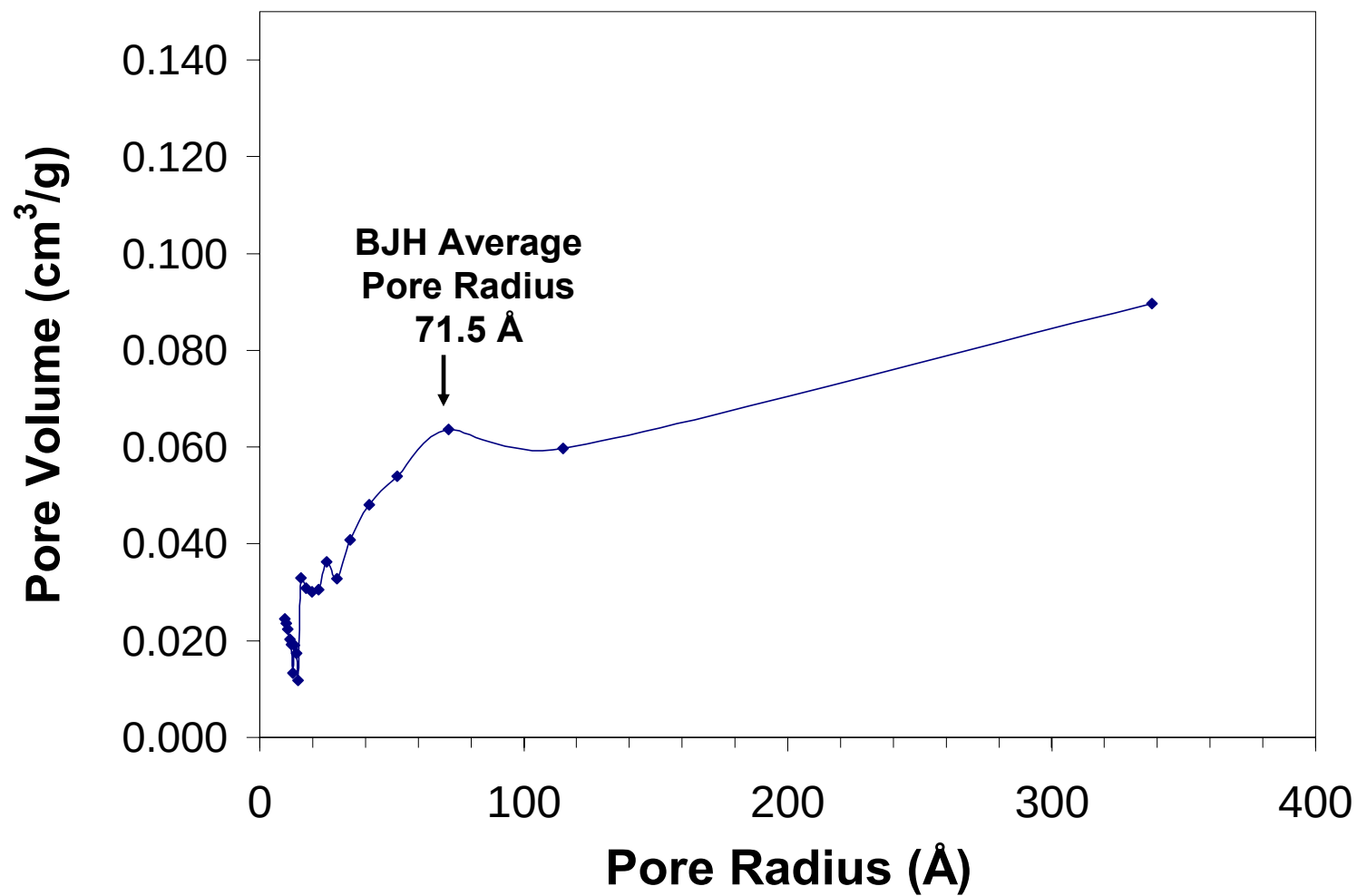


Figure 259: BJH pore size distribution plot for a nanostructured tungsten(VI) catalyst with targeted mesoporosity.

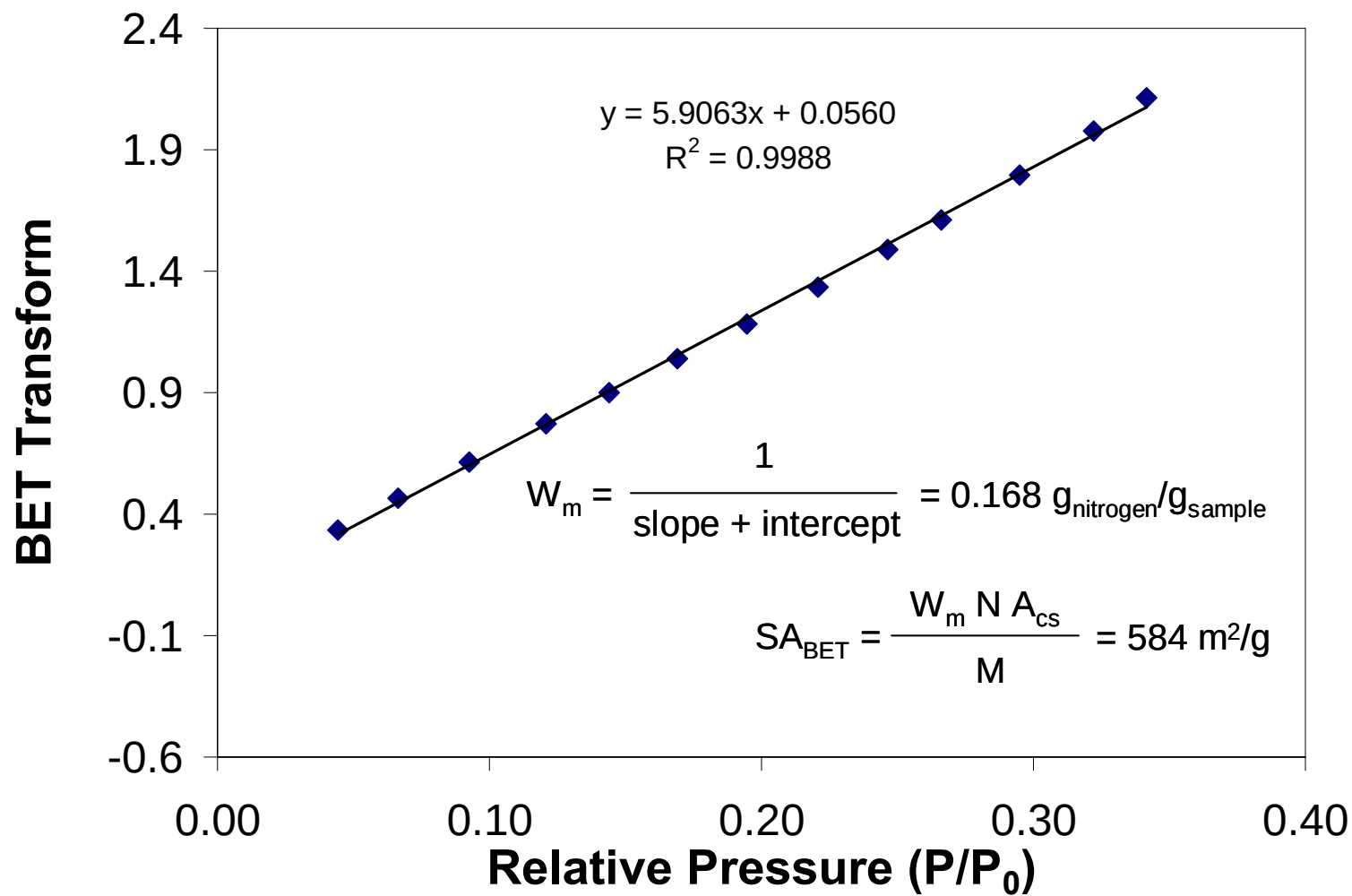


Figure 260: BET plot for a nanostructured tungsten(VI) catalyst with mesoporosity.

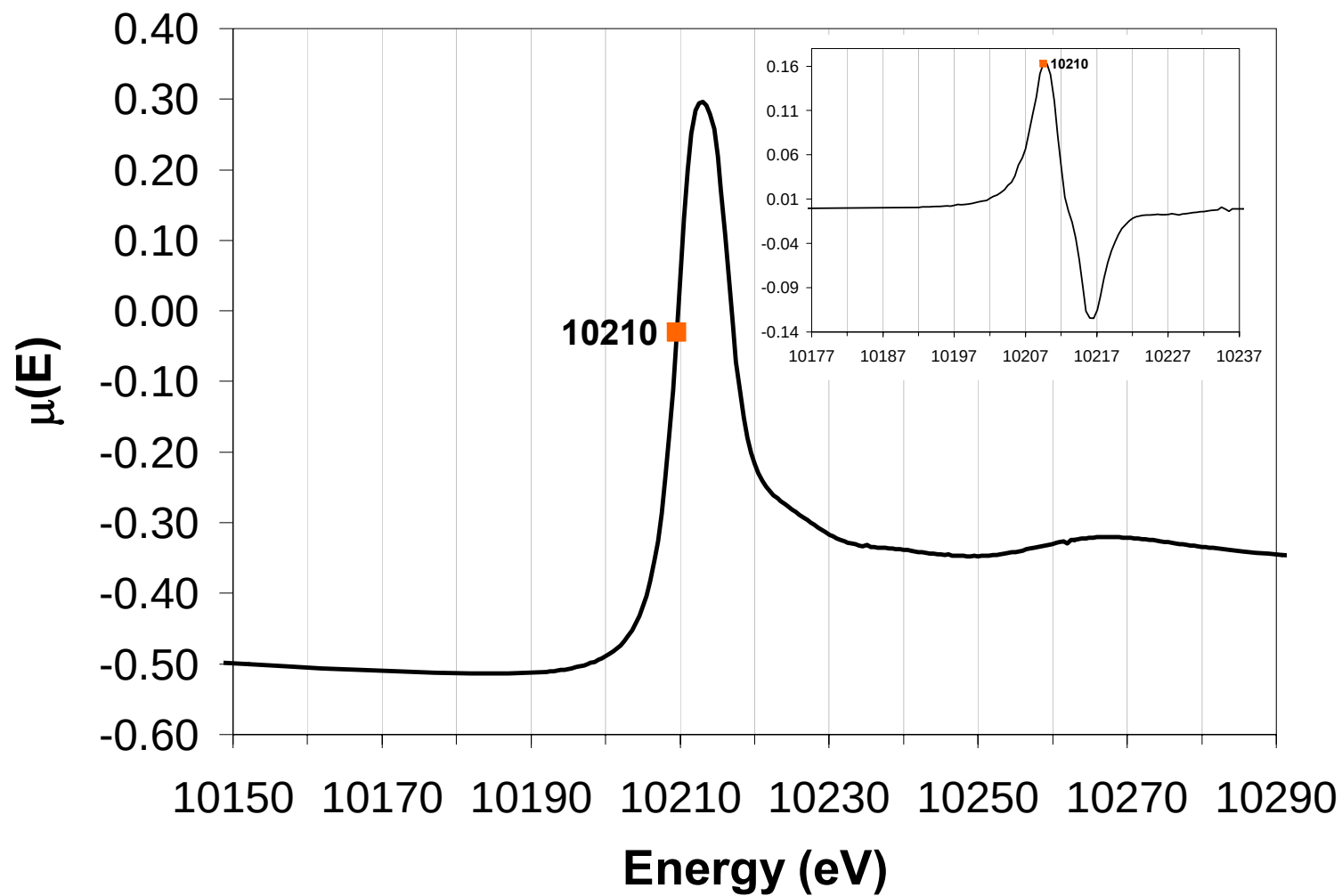


Figure 261: XANES spectra (W L_{III} edge) of a nanostructured tungsten(VI) catalyst with targeted mesoporosity. The inset contains the derivative XANES spectrum which shows the absorption edge position (orange square).

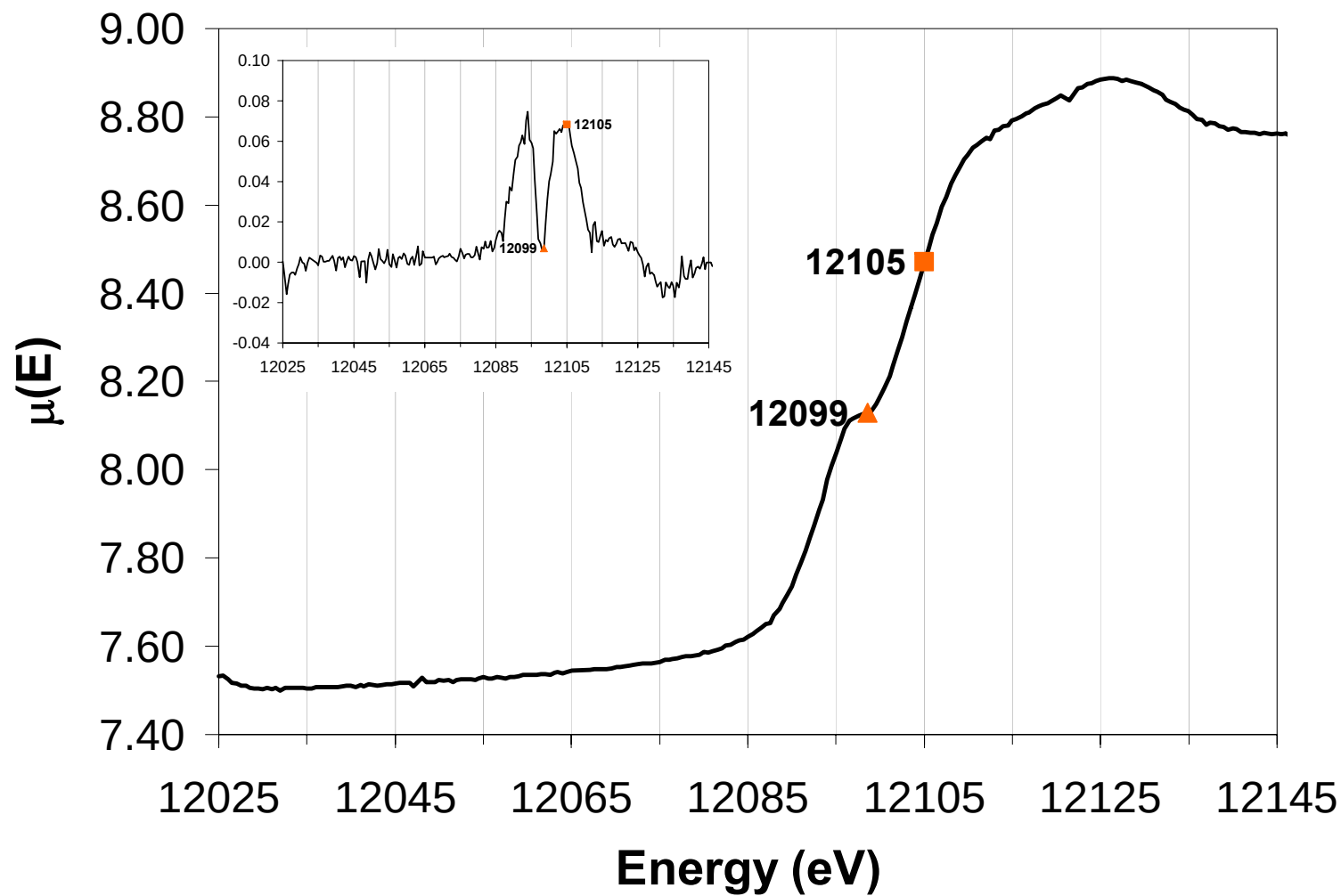


Figure 262: XANES spectra (W L_1 edge) of a nanostructured tungsten(VI) catalyst with targeted mesoporosity. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (orange triangle) and the absorption edge (orange square) labeled.

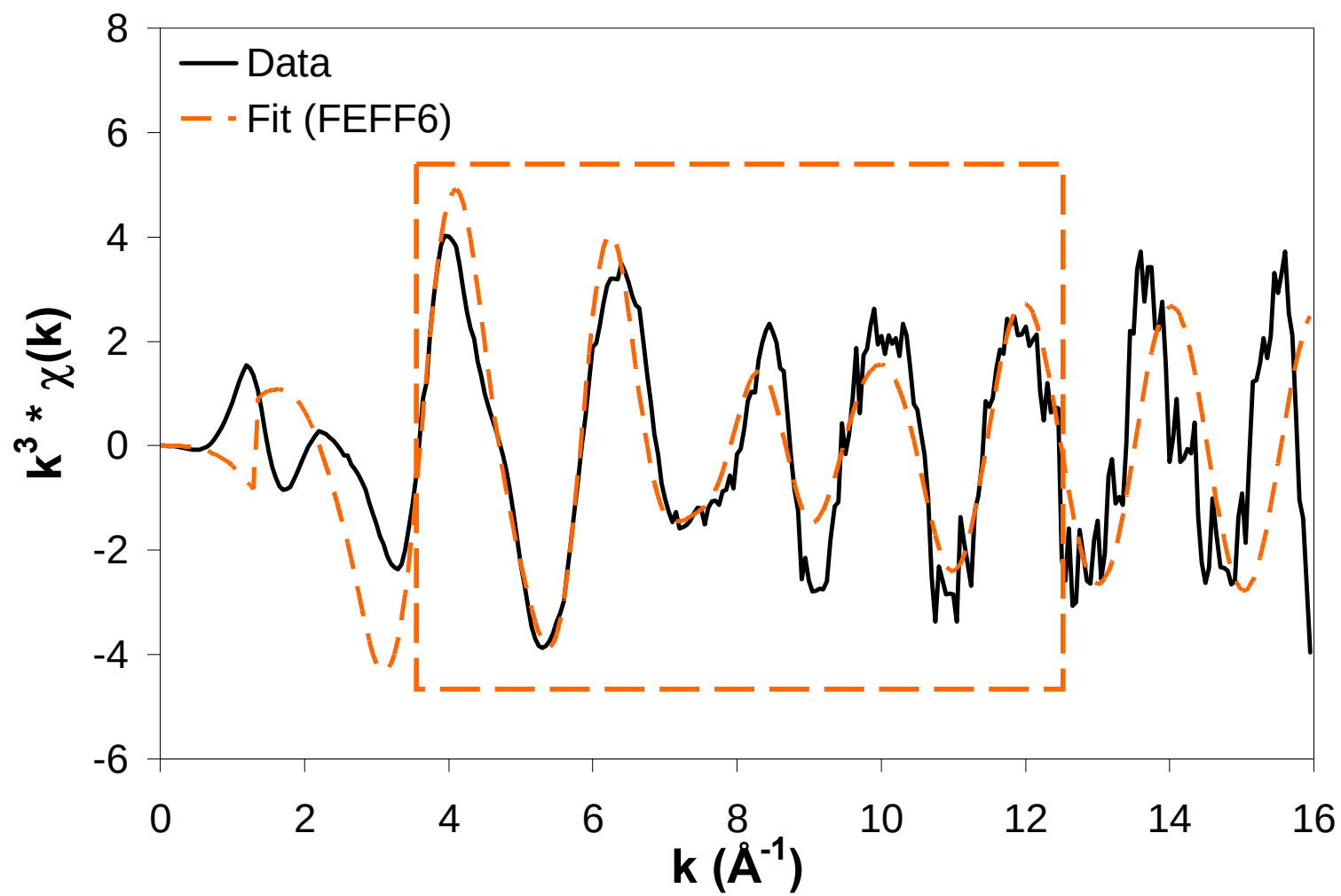


Figure 263: EXAFS k-space plot for a nanostructured tungsten(VI) catalyst with targeted mesoporosity.

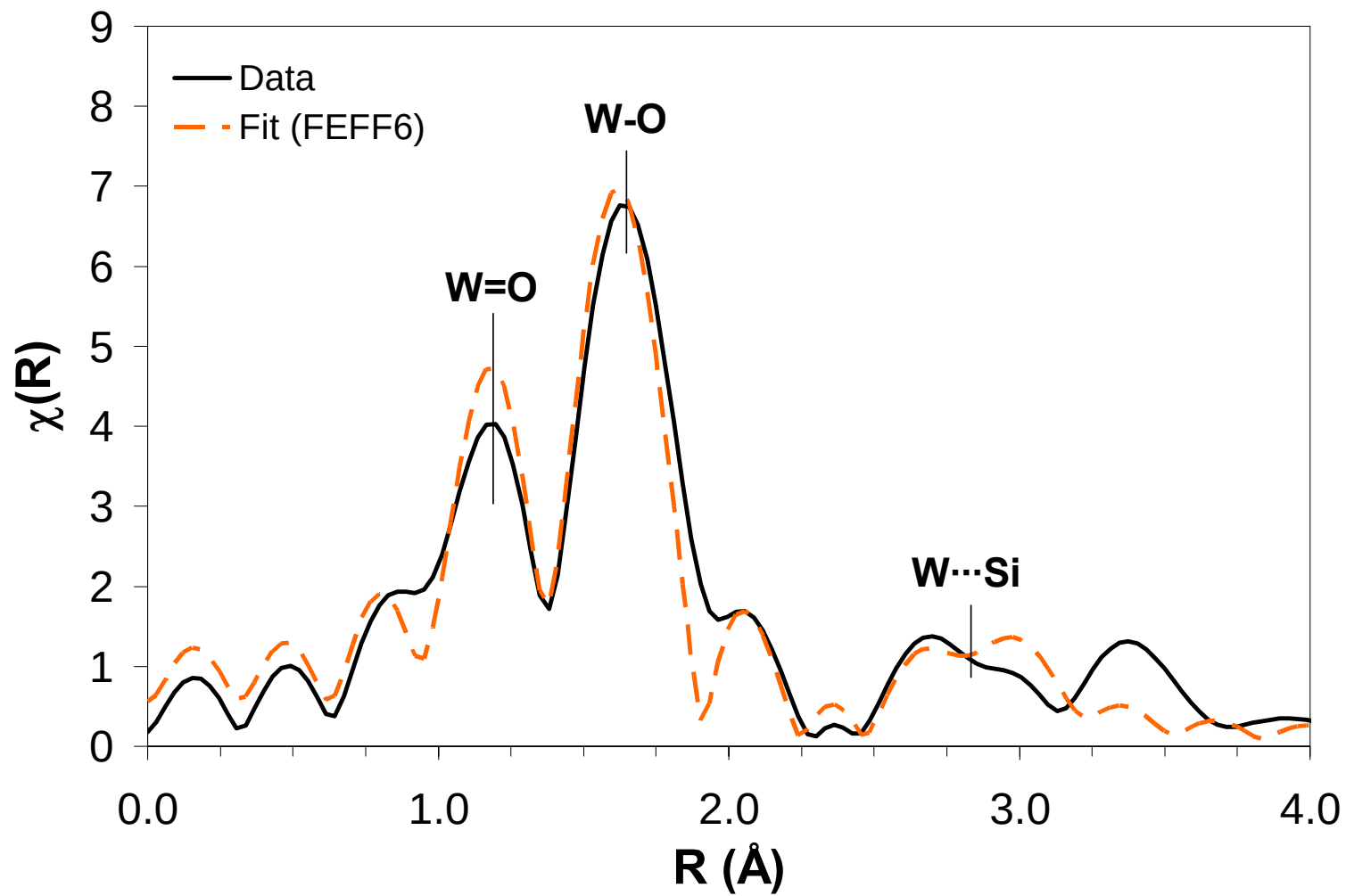


Figure 264: EXAFS R-space plot for a nanostructured tungsten(VI) catalyst with targeted mesoporosity. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

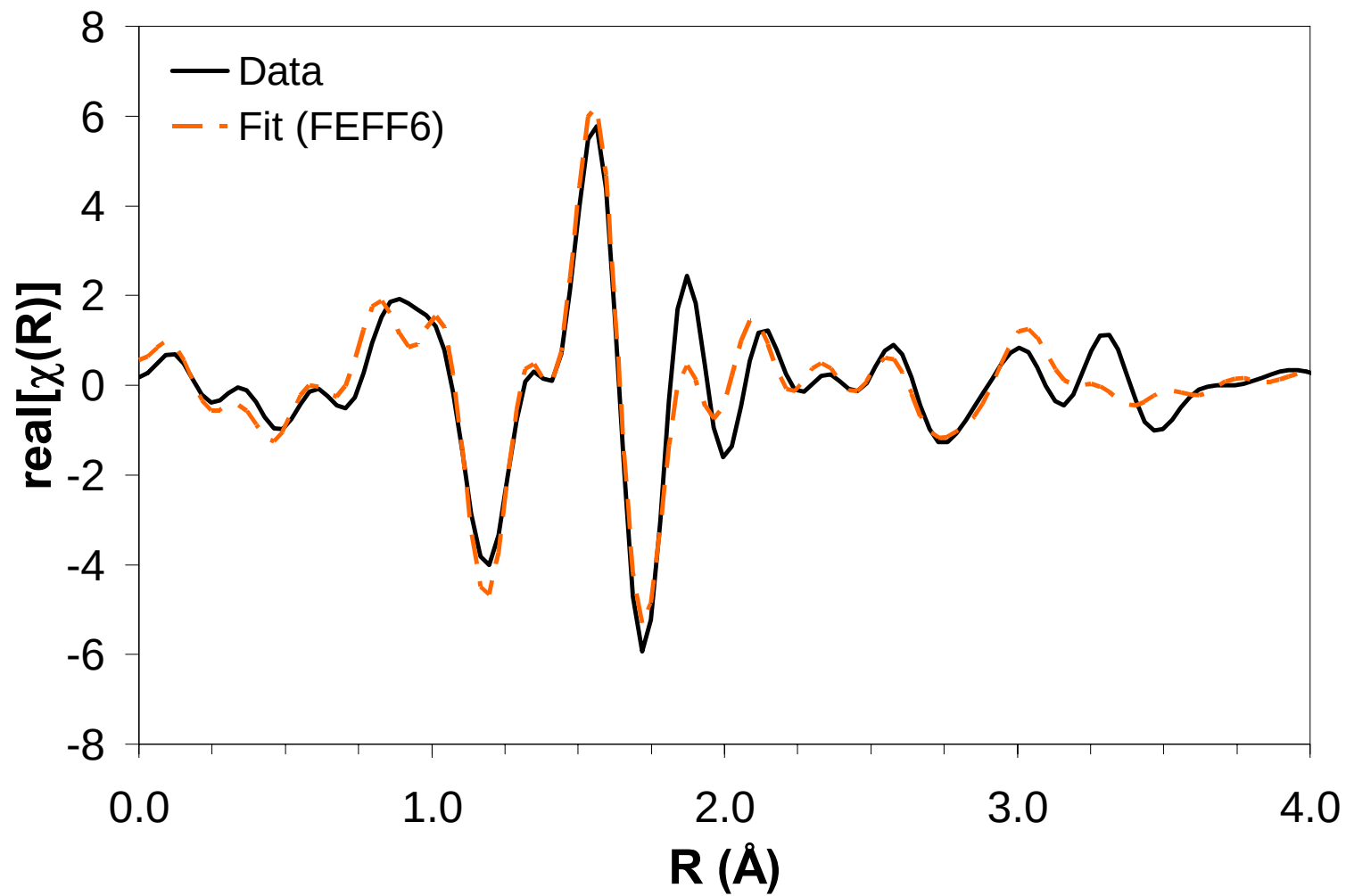
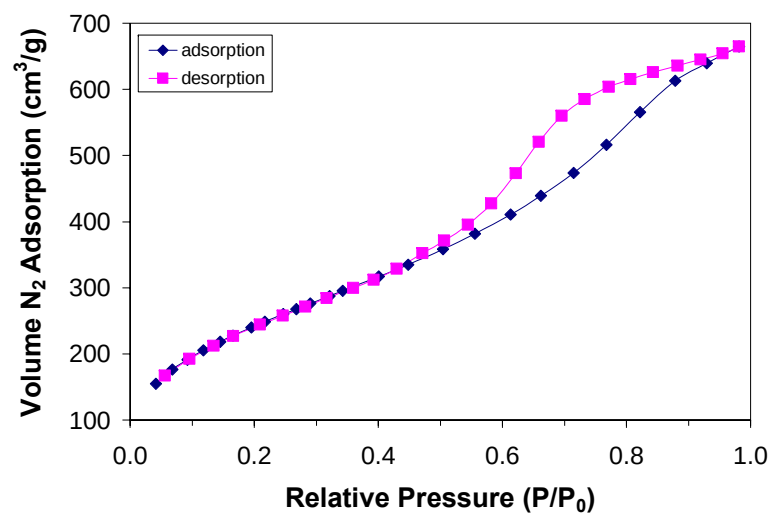
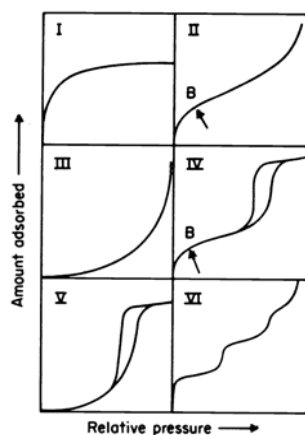


Figure 265: EXAFS real R-space plot for a nanostructured tungsten(VI) catalyst with targeted mesoporosity. The distances on the x-axis are not phased corrected and will appear shorter than “real” bond/separation distances.

Table 15: EXAFS fit values for a nanostructured tungsten(VI) catalyst with targeted mesoporosity

Embedded W(VI) Centers with Targeted Mesoporosity				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.687	1.890	---	3.209
σ^2 (Å ²)	0.12 x 10 ⁻³	5.11 x 10 ⁻³	---	16.30 x 10 ⁻³
E ₀ (eV)	6.6 ± 2.7	6.6 ± 2.7	---	6.6 ± 2.7
CN	0.95 ± 0.13	3.76 ± 0.31	---	3.76 ± 0.31
$S_0^2 = 0.92$ (set), $N_{\text{idp}} = 18.5$, $N_{\text{var}} = 7$, $\chi^2 = 558$, reduced $\chi^2 = 49$, R-factor = 0.108, FT k region = 3.558 – 13.365 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

Standard Isotherms



Standard Hysteresis Loops

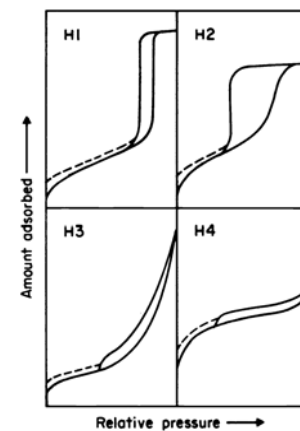


Figure 266: Nitrogen isotherm for a nanostructured zirconium(IV) catalyst with targeted mesoporosity. Standard isotherms and hysteresis loops were obtained from the literature.[131]

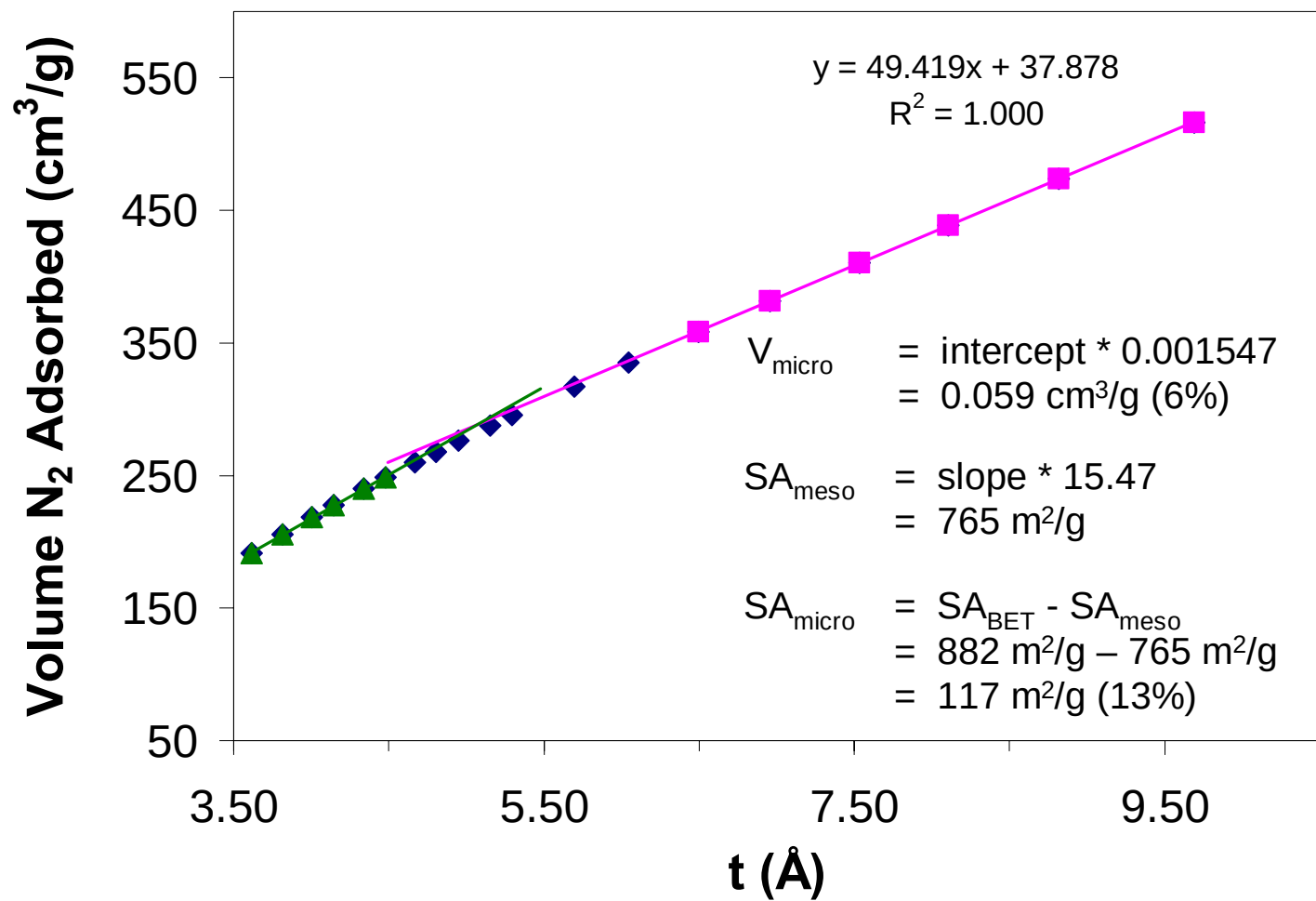


Figure 267: t-plot for a nanostructured zirconium(IV) catalyst with targeted mesoporosity.

volume (94%) and surface area (87%). The BJH average pore radius (52.3 Å, Figure 268) is consistent with the generation of a high surface area (882 m²/g, Figure 269), mesoporous, silicate support. Thus a mesoporous silicate support was generated with the use of templating agents.

XAS data for this material are in agreement with the data presented in chapter four. The position of the ionization edge (18002 eV) suggests the oxidation state of the zirconium centers is +4 and the presence of a pre-edge feature (17991 eV) suggests the coordination geometry around the zirconium center is tetrahedral (Figure 270). EXAFS data were modeled using the the same structural model (Figure 221), theoretical phase and amplitude factors, single scattering paths, amplitude reduction factor (0.928), and refinement procedure presented in chapter four. The EXAFS signal ($\chi(k) * k^3$) for the material is presented in Figure 271 with the FT data range boxed (4.1 – 15.4 Å⁻¹). The fit range is from 1.0 to 4.5 Å and the magnitude and real part of the FT of the data and FEFF model are presented in Figure 272 and Figure 273 respectively. Table 16 summarizes the refined values of the structural parameters which are in agreement with values determined for the embedded zirconium(IV) centers presented in chapter four (Table 13).

Thus researchers have the ability to precisely control all of the necessary components of embedded zirconium(IV) ensembles and the surface area of the material containing the ensembles.

Nanostructured Catalysts with Targeted Macroporosity

Researchers do not have the ability to precisely control all of the necessary components of embedded ensembles and the surface area of the material containing the ensembles when targeting macroporosity. The use of stoichiometric ratios greater than 5 (SiCl₄py₂ : Si₈O₁₂(OSnMe₃)₈) results in the local environment around the embedded centers significantly changing. This is most evident in the EXAFS R-space plot. Figure 274 shows the R-plots for nanostructured tungsten(VI) and zirconium(IV) catalysts that were synthesized using both a stoichiometric ratio greater than 5 and less than 5. One should immediately notice the features that have been assigned to M-Cl (M = W, Zr). The presence of M-Cl bonds suggests that M-O-Si linkages were cleaved during the second cross-linking reaction. Both tungsten(VI) and zirconium(IV) centers appear to leach when large stoichiometric ratios of SiCl₄py₂ are used.

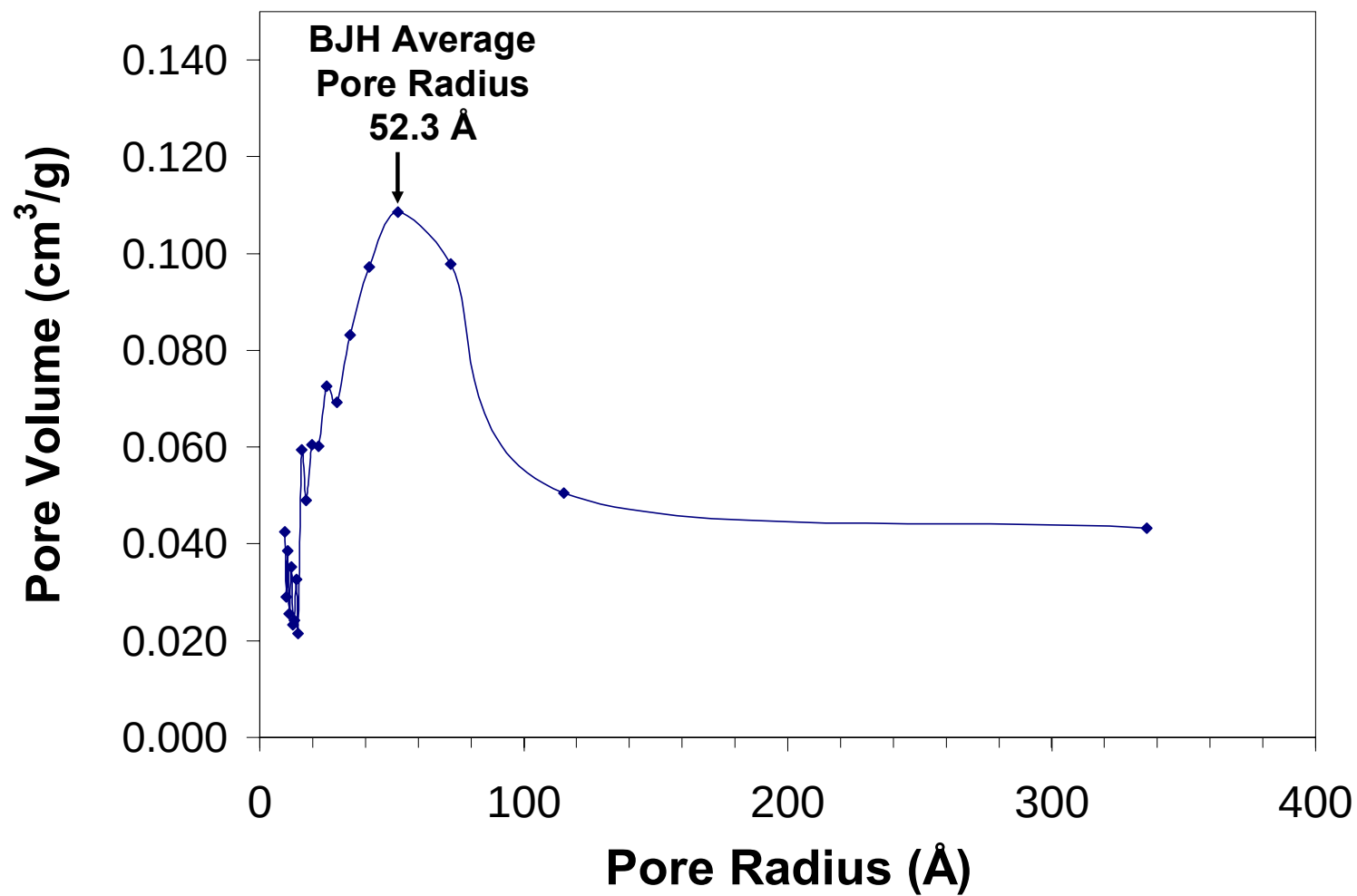


Figure 268: BJH pore size distribution plot for a nanostructured zirconium(IV) catalyst with mesoporosity.

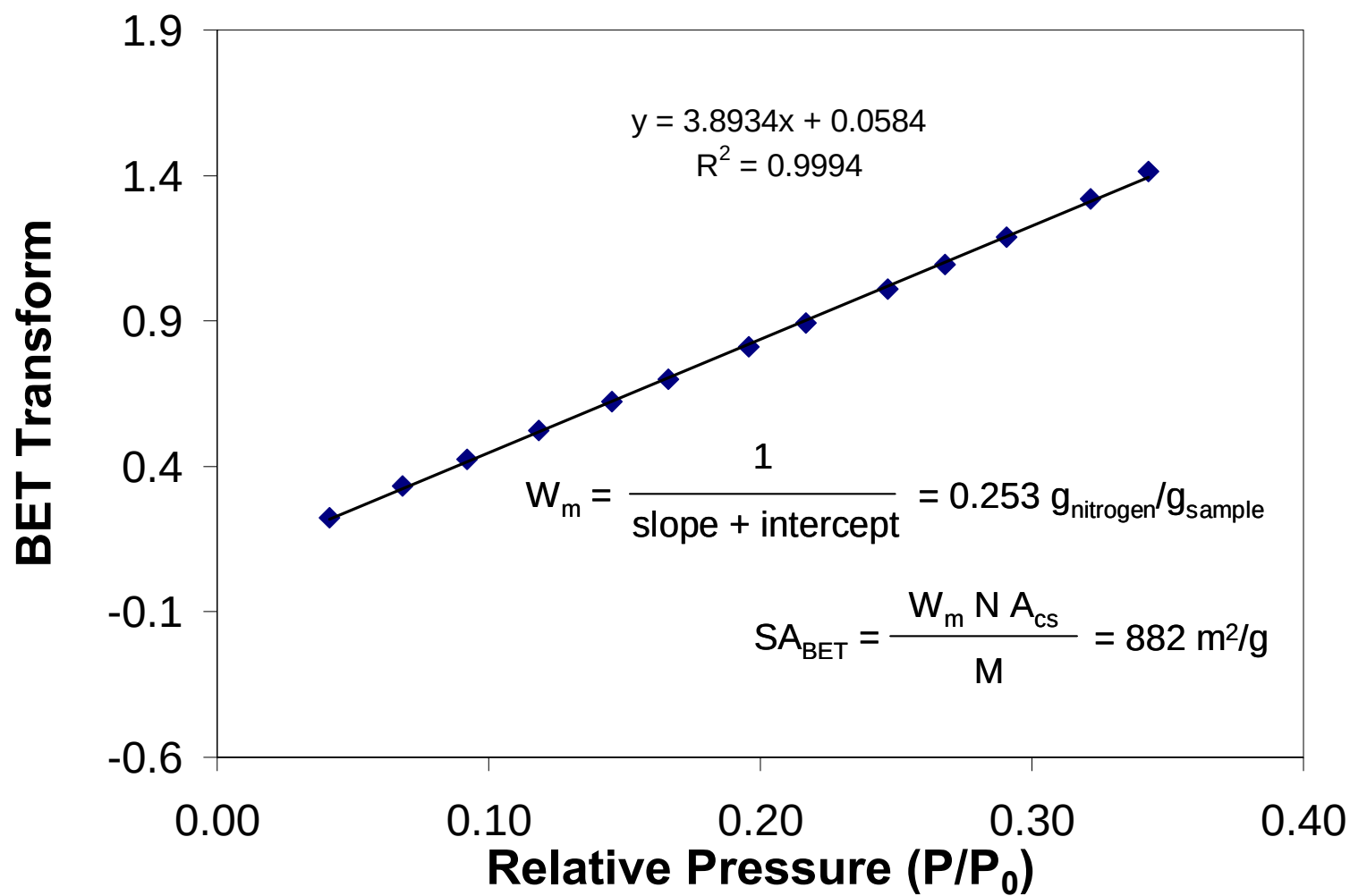


Figure 269: BET plot for a nanostructured zirconium(IV) catalyst with targeted mesoporosity.

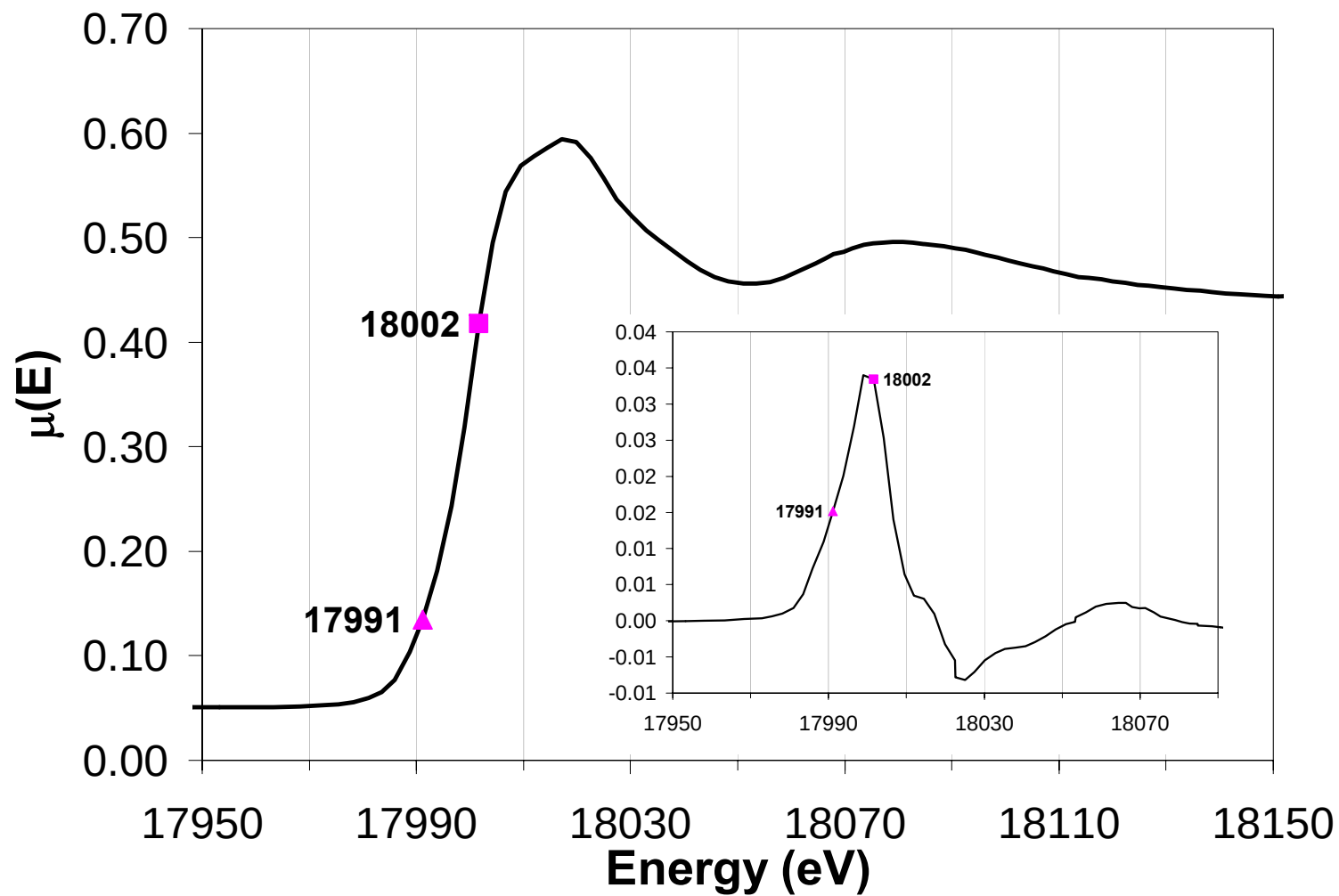


Figure 270: XANES spectra (Zr K edge) of a nanostructured zirconium(IV) catalyst with targeted mesoporosity. The inset contains the derivative XANES spectrum with the position of the pre-edge feature (pink triangle) and the absorption edge (pink square) labeled.

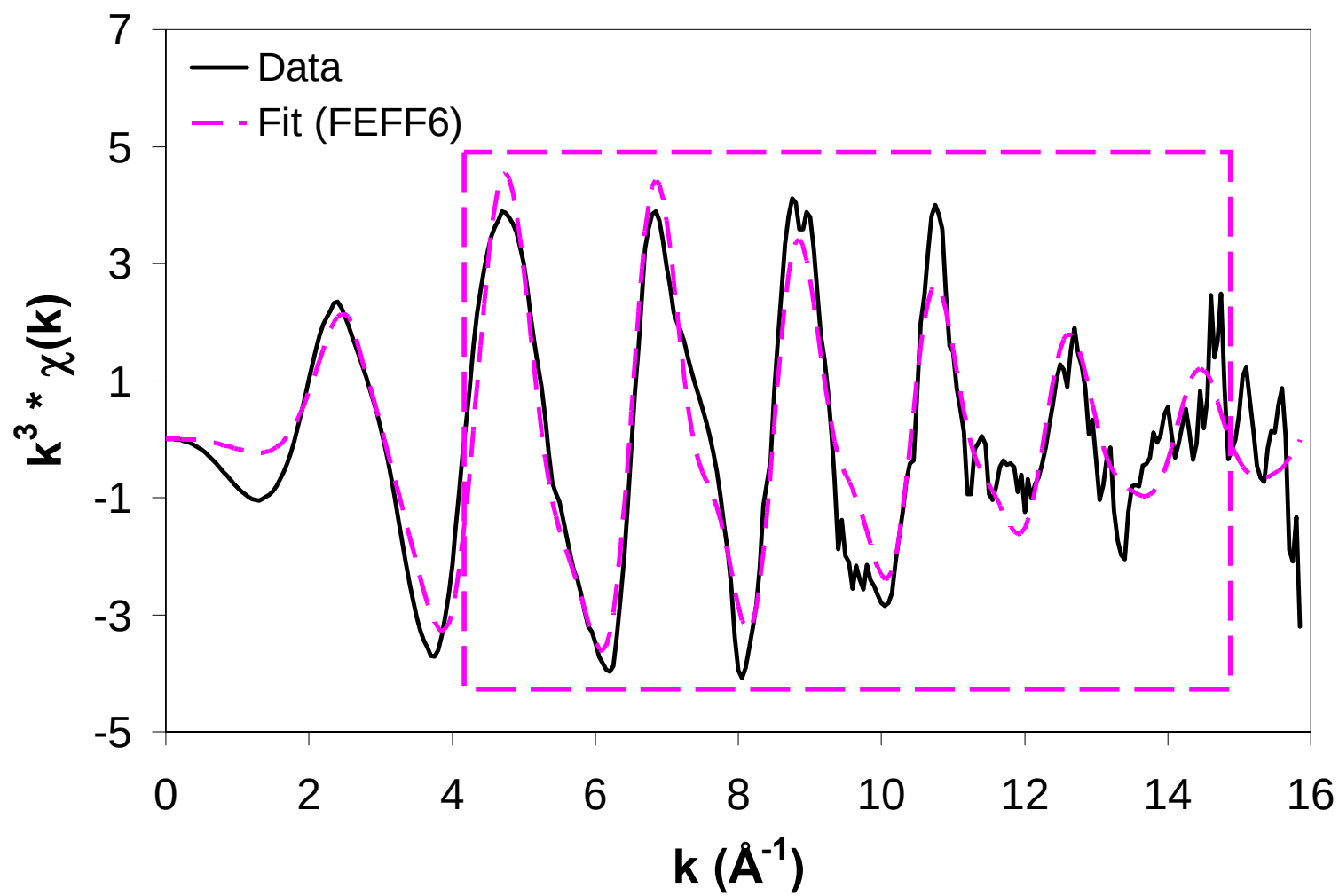


Figure 271: EXAFS k-space plot for a nanostructured zirconium(IV) catalyst with targeted mesoporosity.

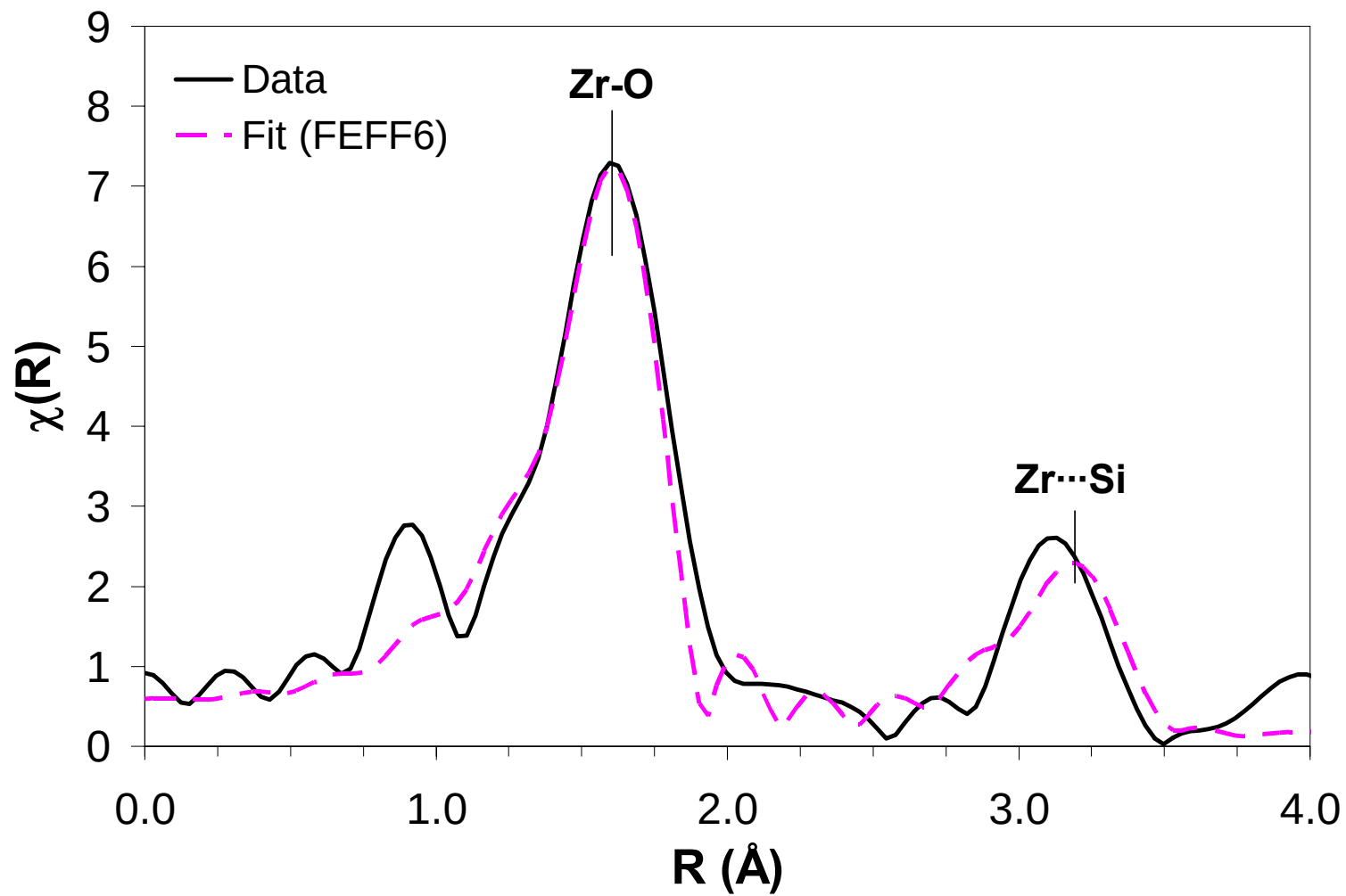


Figure 272: EXAFS R-space plot for a nanostructured zirconium(IV) catalyst with targeted mesoporosity. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

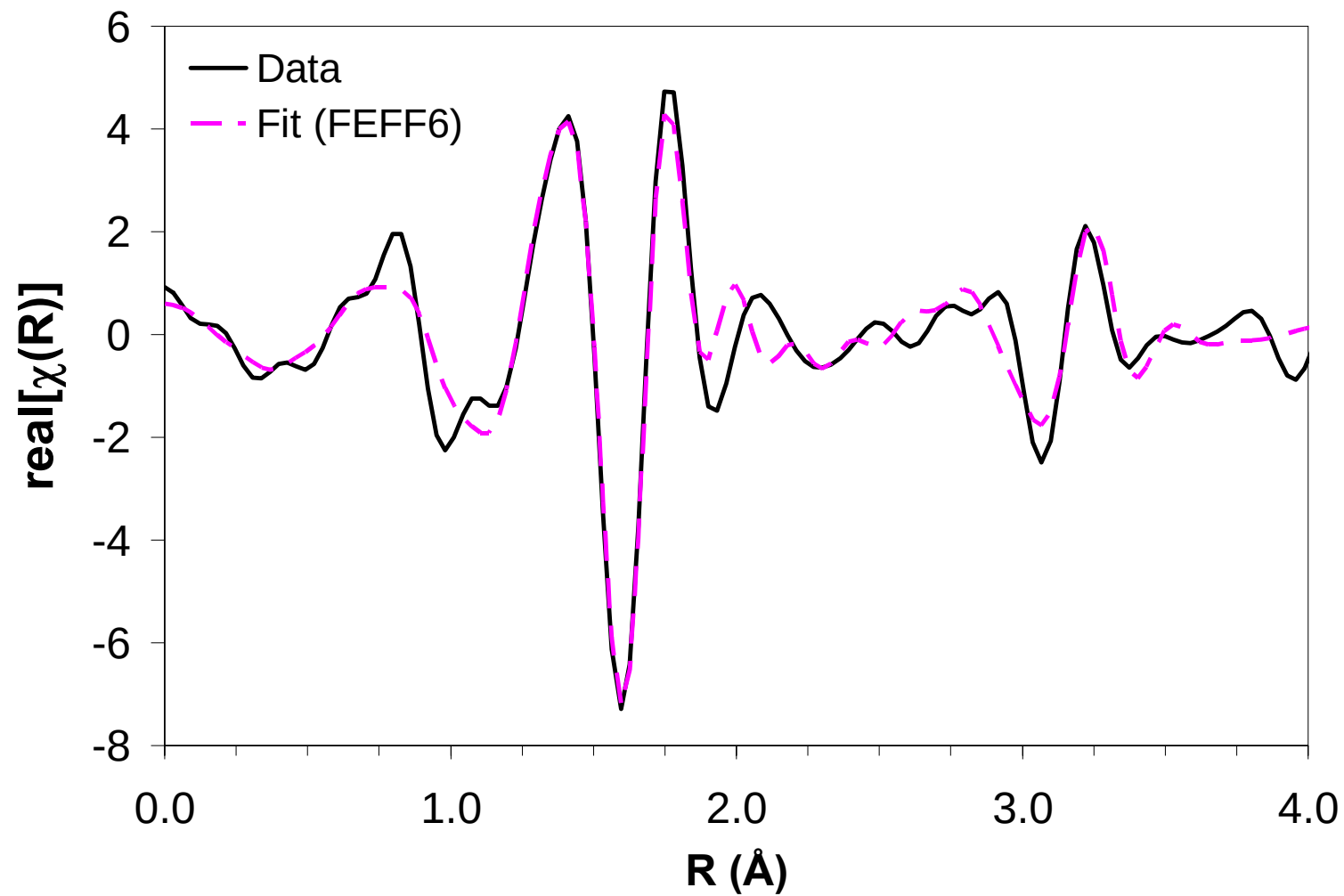


Figure 273: EXAFS real R-space plot for a nanostructured zirconium(IV) catalyst with targeted mesoporosity. The distances on the x-axis are not phased corrected and will appear to be shorter than “real” bond/separation distances.

Table 16: EXAFS fit values for a nanostructured zirconium(IV) catalyst with targeted mesoporosity

Embedded Zr(IV) Centers with Targeted Mesoporosity			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	2.014	---	3.665
σ^2 (Å ²)	4.16×10^{-3}	---	6.36×10^{-3}
E ₀ (eV)	-0.9 ± 2.0	---	-0.9 ± 2.0
CN	3.97 ± 0.24	---	3.97 ± 0.24
$S_0^2 = 0.928$ (set), $N_{\text{idp}} = 24.6$, $N_{\text{var}} = 5$, $\chi^2 = 1065$, reduced $\chi^2 = 54$, R-factor = 0.079, FT k region = $4.159 - 15.396 \text{ Å}^{-1}$, Fit range = $1.0 - 4.5 \text{ Å}$			

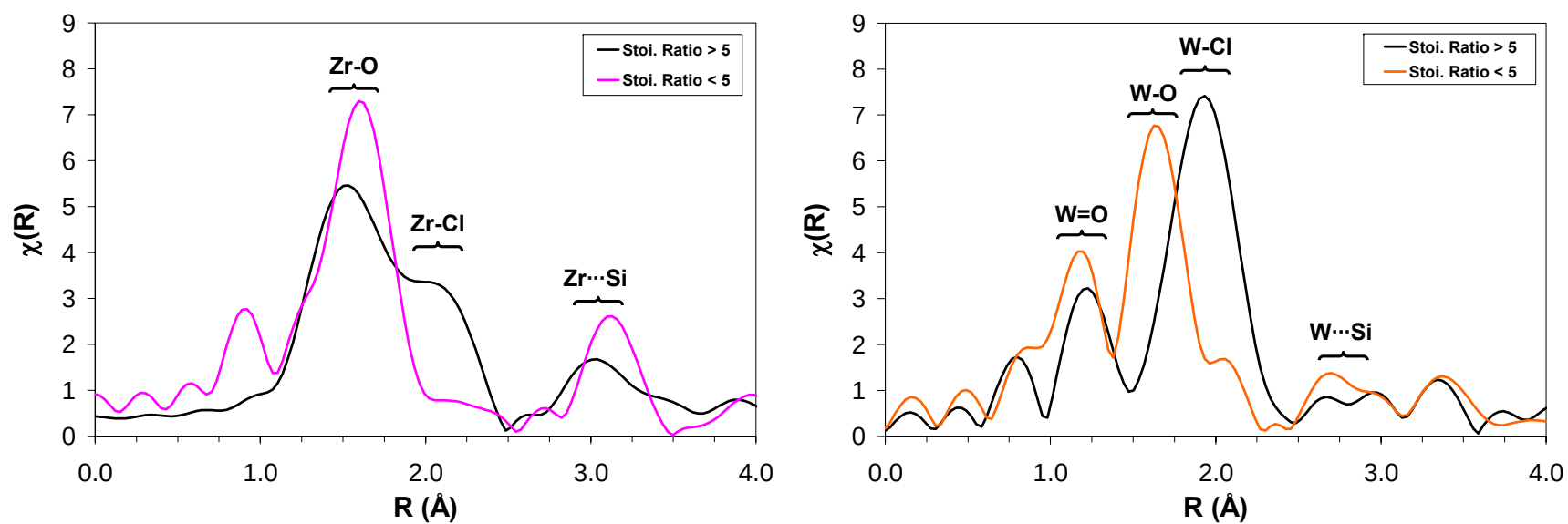
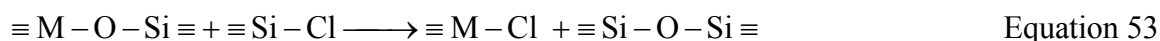


Figure 274: EXAFS R-space plots for nanostructured zirconium(IV) and tungsten(VI) catalysts that were prepared using stoichiometric ratios greater than 5.

Therefore embedded tungsten(VI) or zirconium(IV) centers should not be further cross linked with SiCl₄py₂ when using stoichiometric ratios greater than 5.

A possible explanation as to why the embedded centers leach requires one to consider the stability of the bonds involved. If SiCl₄py₂ attacks M-O-Si linkages then one M-O bond ($\Delta H_{Zr-O} = 760$ kJ/mol, $\Delta H_{W-O} = 653$ kJ/mol) and one Si-Cl bond ($\Delta H_{Si-Cl} = 456$ kJ/mol) must break while one M-Cl bond ($\Delta H_{Zr-Cl} = 491$ kJ/mol, $\Delta H_{W-Cl} = 423$ kJ/mol) and one Si-O bond ($\Delta H_{Si-O} = 798$ kJ/mol) must form (Equation 53).



The stability of the bonds was gauged by determining the enthalpy of reaction (Equation 54). If the enthalpy of reaction is positive then it is assumed that the bonds that would be broken (M-O and Si-Cl) are more stable than the bonds that would be formed (M-Cl and Si-O).

$$\Delta H_{rxn} = \Delta H_{bonds\ broken} - \Delta H_{bonds\ formed} \quad \text{Equation 54}$$

However the bonds formed appear to be more stable than the bonds broken for both tungsten ($\Delta H_{rxn} = -112$ kJ/mol) and zirconium ($\Delta H_{rxn} = -73$ kJ/mol).

This fact should not be of concern except in the limited case when stoichiometric ratios greater than 5 are used. One is reminded of Figure 71 in chapter two which illustrates that in general at least five Me₃Sn groups remain in the material following the generation of embedded centers. Therefore a limiting amount of SiCl₄py₂ is being used when the second cross-linking stoichiometric ratio is less than 5. Also the enthalpy of reaction for SiCl₄py₂ reacting with Me₃Sn groups is -200 kJ/mol ($\Delta H_{Sn-O} = 548$ kJ/mol, $\Delta H_{Sn-Cl} = 406$ kJ/mol) which suggests that the Sn-O-Si linkages are weaker than M-O-Si linkages. Therefore one might conclude SiCl₄py₂ is more likely to react with Me₃Sn groups then cleave M-O-Si linkage when stoichiometric ratios less than 5 are used. The cleavage of M-O-Si linkages appears to only occur when an excess of SiCl₄py₂ is used (i.e. stoichiometric ratios greater than 5).

Summary and Conclusions

The synthesis of nanostructured heterogeneous catalysts with targeted porosity is demonstrated. The surface area of the nanostructured heterogeneous catalysts can be synthetically targeted by varying the stoichiometric ratios used for each cross-linking reaction. Mesoporous silicate supports can be grown around embedded ensembles without disrupting the

local environment around the ensembles. The local environments around the ensembles can be altered when excess SiCl_4py_2 is used. Therefore it is important that one understands the limitations of the synthetic methodology presented in this chapter. The work presented here provides researchers with the ability to control both the local environment of embedded ensembles and the porosity of the material containing the ensembles.

Acknowledgments

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CHAPTER 6. CONCLUSIONS AND FUTURE WORK

Conclusions

This dissertation describes work aimed at synthesizing and characterizing nanostructured silicate building block supports and heterogeneous catalysts. This work was part of an ongoing research program to develop new synthetic methodologies for the targeted preparation of heterogeneous catalysts. The challenge of preparing high surface area supports while maintaining control of surface functionality that is crucial in obtaining single site catalysts was one of the areas where significant attention was focused. This work also aimed at demonstrating how a building block approach to constructing single site heterogeneous catalysts can be applied to tungsten and zirconium silicate catalysts.

Targeting Nanostructured Supports

One of the primary focuses of this dissertation was the preparation of nanostructured supports where surface areas, porosities, and specific densities of isolated surface functionalities were targeted. The use of a molecular building block helped keep the surface functionality (i.e. Me_3Sn groups) isolated as the silicate support was generated. Specific densities of Me_3Sn groups were targeted by varying the stoichiometric ratio of reactants (SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$). In general, as the stoichiometric ratio increased, the density of surface functionality decreased.

The stoichiometric ratio of reactants also controls the surface area and porosity of the resulting material. The use of a molecular building block aids in the the generation of porous materials without requiring the use of templating agents. In most cases, as the stoichiometric ratio is increased, the surface area of the material and/or the size of the pores in the material increased.

The nanostructured silicate supports presented in chapter two not only represent new materials but also aided in the development of new single site heterogeneous catalysts.

Targeting Nanostructured Catalysts

Another primary focus of this dissertation was the preparation of nanostructured catalysts where one can control all of the necessary components of the catalyst ensembles in the material. Isolated metal cation centers, specifically tungsten(VI) and zirconium(IV), were incorporated into the framework and on the surface of silicate building block matrices.

Embedded catalyst ensembles, those incorporated in the framework of the support, were synthetically targeted by reacting the molecular building block with a limiting amount of metal chloride (WOCl_4 , WCl_6 , ZrCl_4). The local environment around all of the metal cation centers in the matrix is identical which means the nanostructured catalysts contain only one type of metal cation center. These materials were further cross linked using a silyl chloride linking agent which resulted in the generation of a high surface area material around the embedded ensembles. The local environment around the embedded ensembles remained unchanged during the generation of the high surface area support and therefore the catalysts still contain only one type of metal cation center and can be classified as single site catalysts. Embedded ensembles were successfully targeted using WOCl_4 and ZrCl_4 . The reaction between WCl_6 and the building block did not result in the preparation of the targeted ensemble however the resulting ensemble was thoroughly characterized.

Surface catalyst ensembles, those incorporated on the surface of the support, were synthetically targeted by reacting a premade silicate building block support with a limiting amount of metal chloride (WOCl_4 , WCl_6 , ZrCl_4). The premade support initially contained spatially isolated surface functionalities which insured that the generated surface catalyst ensembles were also spatially isolated. The local environment around all of the metal cation centers in the matrix is identical which means the nanostructured catalysts again can be classified as single site catalysts. Surface ensembles were successfully targeted using ZrCl_4 . The reaction between the tungsten chlorides (WOCl_4 and WCl_6) and the premade support did not result in the preparation of the targeted ensembles however the resulting ensembles were thoroughly characterized.

The synthetic methodology presented in chapters three and four provides researchers with the ability to target specific catalyst ensembles.

Targeting Nanostructured Catalysts with Specific Porosity

The central themes just mentioned were combined in order to prepare nanostructured catalysts where one has complete control of the ensemble components in addition to the surface area and porosity of the material. The porosity of the support generated around embedded ensembles was controlled by varying the stoichiometric ratio of reactants (SiCl_4py_2 : $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$). Problems arose when stoichiometric ratios greater than 5 were used.

However mesoporous supports were generated around the ensembles without disrupting the local environment of the ensembles when stoichiometric ratios less than 5 were used.

The synthetic methodology presented in chapter five provides researchers with the ability to target specific catalyst ensembles and pore structures.

Future Work

Incorporation of Polyoxo Metal Clusters

One of the areas which future work could be devoted focuses on incorporating polyoxo metal clusters into the silicate building block supports. This would allow researchers to address such questions as whether isolated single metal cation centers are more or less active than isolated collections of metal cations (i.e. polyoxo metal clusters). An example of a possible polyoxo metal cluster that could be incorporated into the building block matrices was reported in the literature by Ma et al.[179] The tetrameric tungsten-oxo complex $[\text{WO}_2\text{Cl}_2(\text{THF})]_4$ contains crystallographically equivalent tungsten centers that have two chloride ligands which could result in the formation of two linkages to the support.

Catalysis Test Reactions Using Heterogeneous Catalysts with Different Pore Sizes

Another area which future work involves conducting catalysis test reactions using nanostructured catalysts with varying pore sizes. One could study how the size of the pores affects the observed catalytic activity of the nanostructured catalysts in selective oxidation reactions. For example, the epoxidation of 1-hexene, cyclohexene, and norbornene could be used to probe the pore structure of the nanostructured catalysts. The synthetic methodology presented in this dissertation allows one to synthetically target nanostructured catalysts that contains pore which might only allow certain substrates to be catalytically converted.

Development of Methods to Remove Residual Trimethyltin Groups

The development of a method for the removal of residual Me_3Sn groups from the silicate matrices is an ongoing challenge facing our research program. In both the tungsten(VI) and zirconium(IV) systems discussed in this dissertation the removal of residual Me_3Sn groups was complicated by the fact that M-O-Si linkages started to cleave before all the Me_3Sn groups were removed. The approach used in this dissertation was to remove as much Me_3Sn groups as possible without cleaving M-O-Si bonds. One of the risks of leaving Me_3Sn groups in the matrices is that the groups could be catalytic active or be transformed into active species and

therefore our “single site” catalysts would really become “multisite” catalysts. Therefore the development of a method for the removal of residual Me_3Sn groups is needed.

Development of Methods to Remove Unreacted Chloride Ligands

The development of a method for the removal of unreacted chloride ligands is another ongoing challenge facing our research program. The removal of unreacted chloride ligands cannot result in the generation of HCl because HCl is known to attack M-O-Si linkages. One approach that could be explored is using an alcohol in the presence of a noncoordinating base like triethylamine. The triethylamine would immediately neutralize the acid generated by the reaction of the alcohol and unreacted chloride ligand which possibly could result in the complete removal of unreacted chloride ligands without disrupting the metal cation centers.

Development of New Building Block Approach

The development of a new building block approach could solve the two challenges just mentioned (Me_3Sn and unreacted chloride removal). A new building block approach would require the discovery of a new building block, new linking agents, and new cross-linking reaction. Some exploratory work has been conducted trying to use other nonhydrolytic sol-gel reactions (e.g. alkyl halide elimination and ester elimination) however these tests did not provide enough synthetic control to target specific catalyst ensembles. The development of a Me_3Sn -free building block approach would reduce the cost and health hazard that are currently associated with the building block approach discussed in this dissertation.

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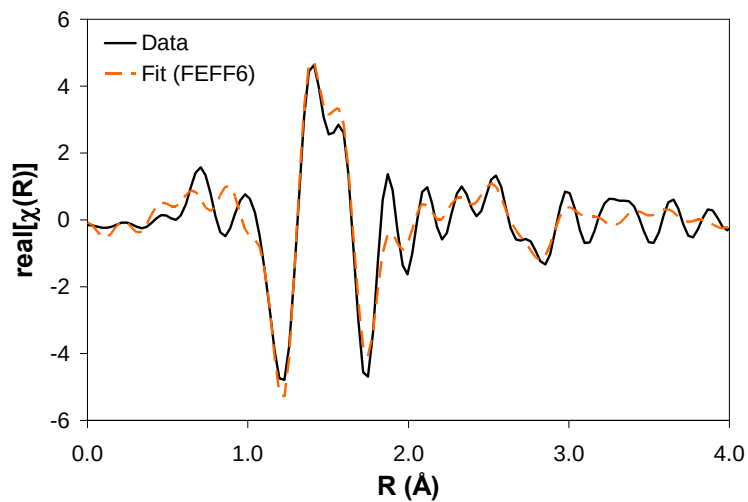
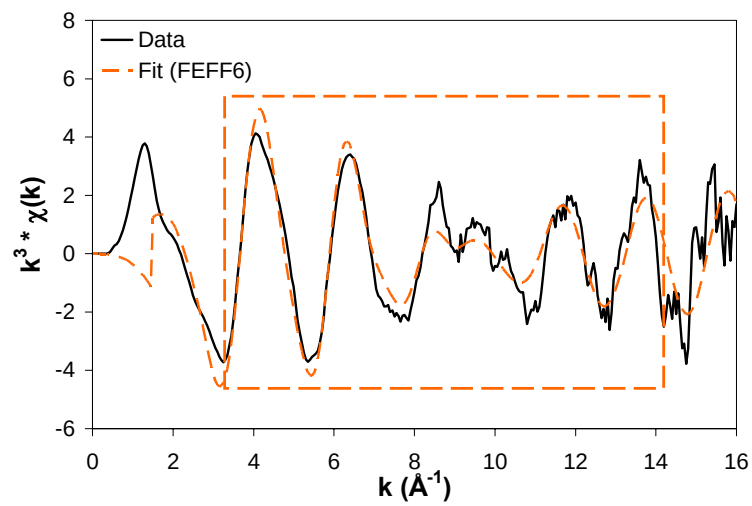
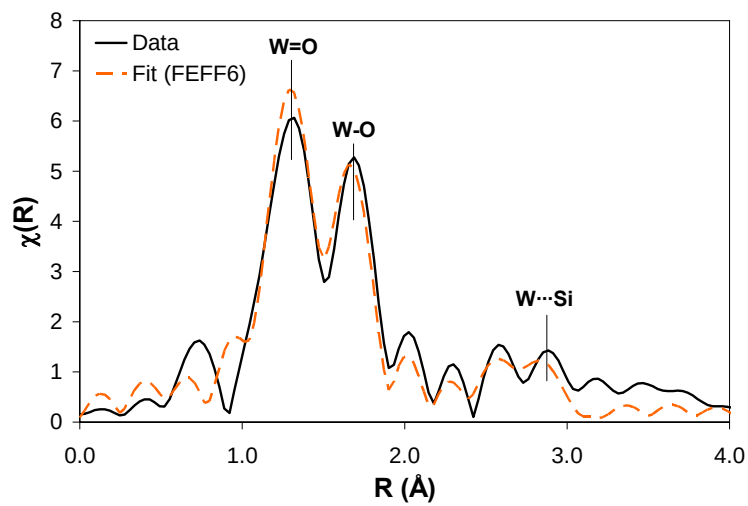
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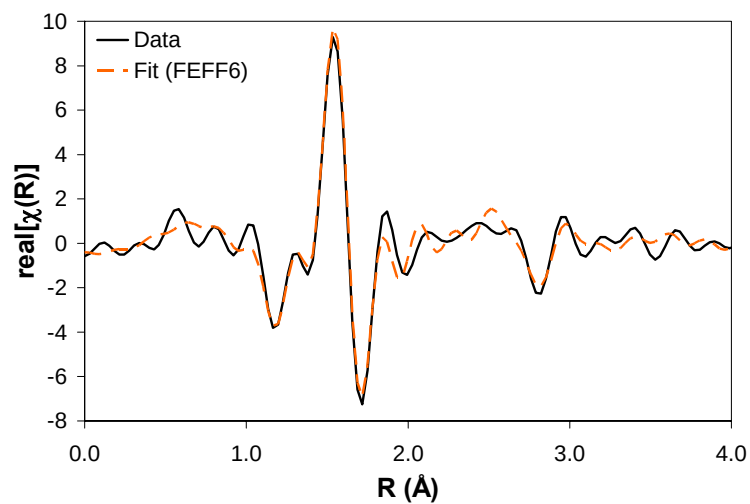
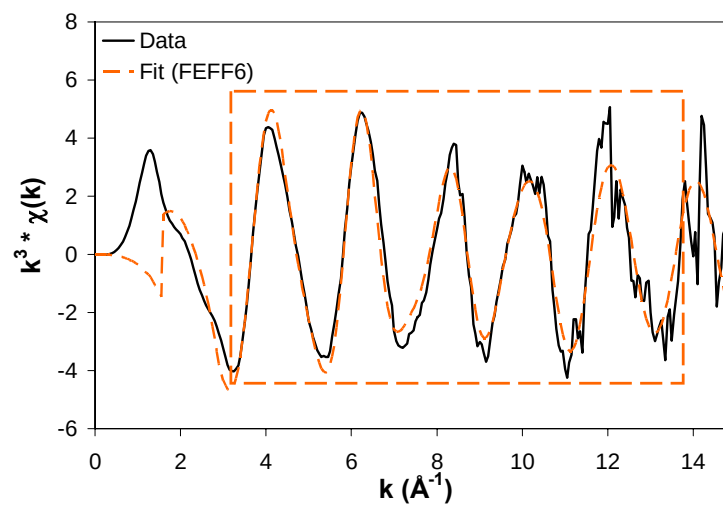
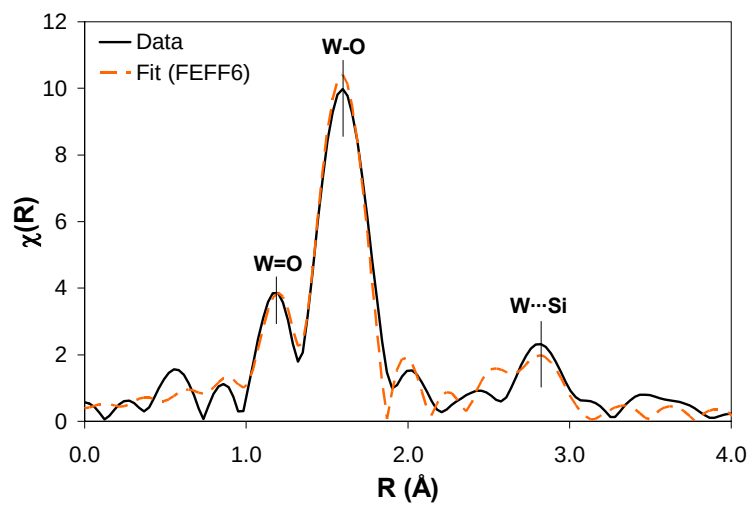
APPENDIX

1st Cross-Linking Reaction: $\text{WOCl}_4 + \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$



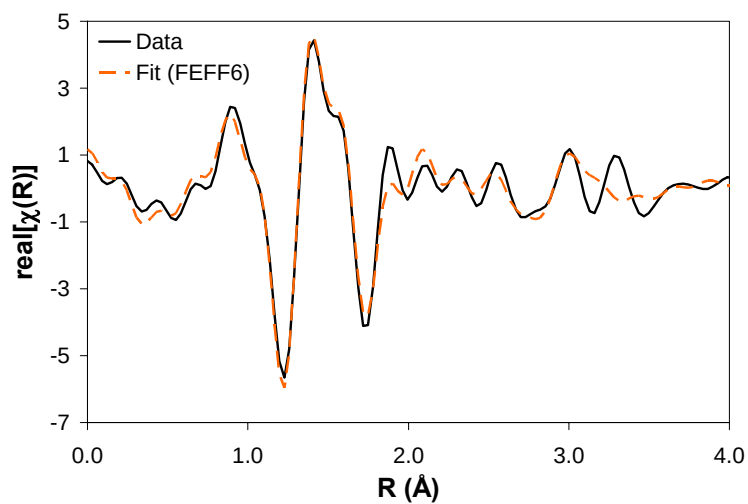
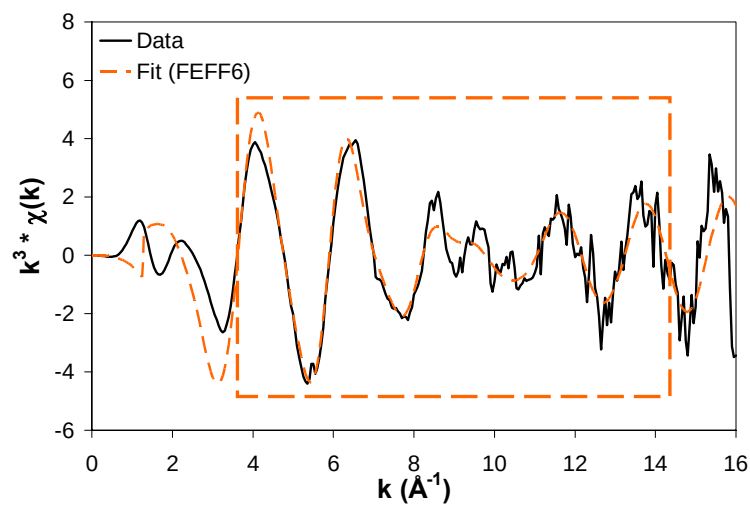
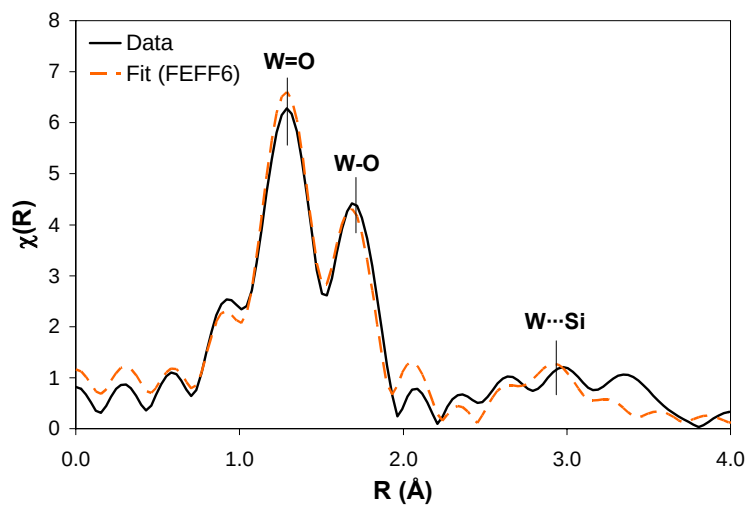
Embedded WOCl_4 1 st dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.715	1.890	---	3.222
σ^2 (Å ²)	1.50×10^{-3} (set)	9.09×10^{-3}	---	19.00×10^{-3}
E_0 (eV)	8.1 ± 2.7	8.1 ± 2.7	---	8.1 ± 2.7
CN	0.95 ± 0.09	3.66 ± 0.27	---	3.66 ± 0.27
$S_0^2 = 0.92$ (set), $N_{\text{idp}} = 20.0$, $N_{\text{var}} = 6$, $\chi^2 = 1999$, reduced $\chi^2 = 143$, R-factor = 0.117, FT k region = $3.377 - 13.973$ Å ⁻¹ , Fit range = $1.0 - 4.0$ Å				

2nd Cross-Linking Reaction: WOCl₄ + Si₈O₁₂(OSnMe₃)₈; SiCl₄



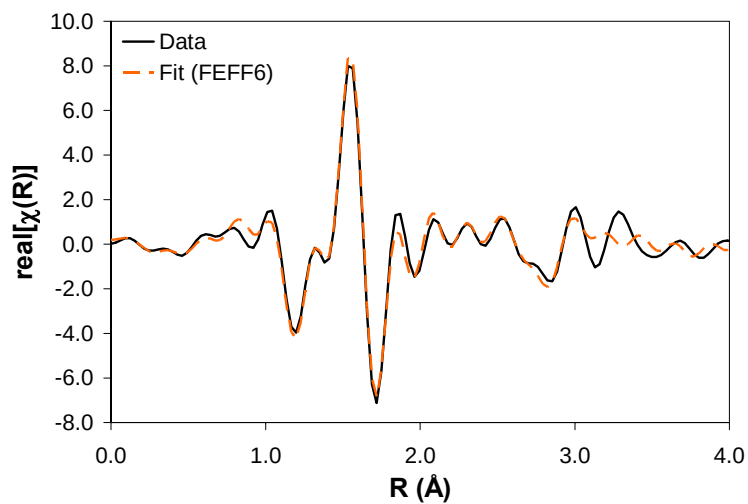
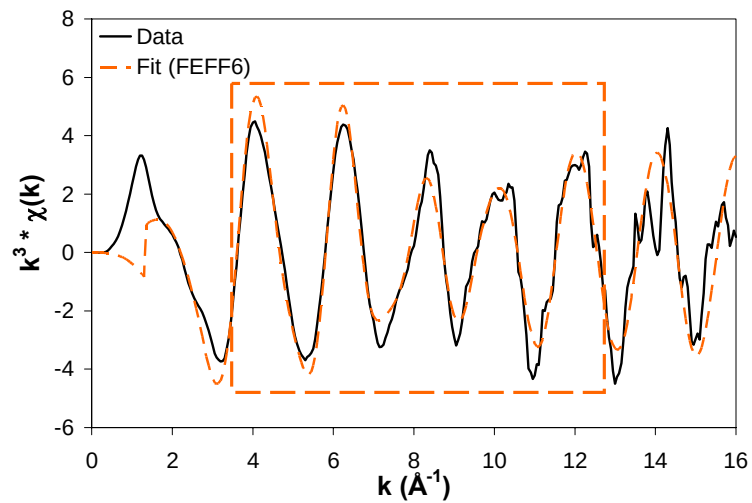
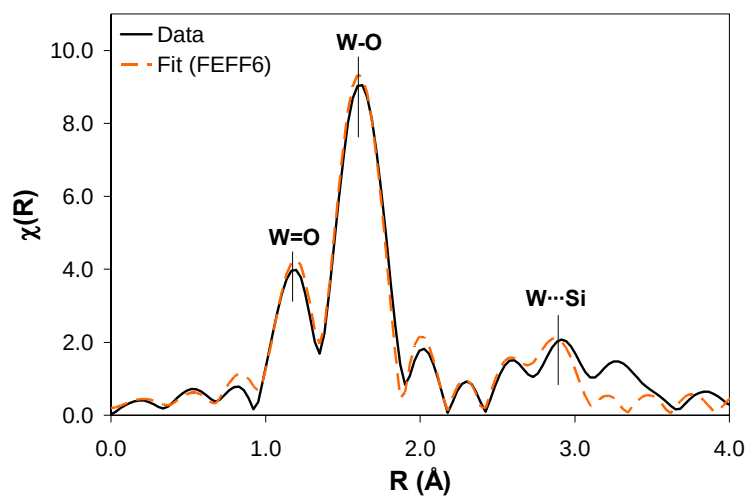
Embedded WOCl ₄ 2 nd dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.690	1.898	---	3.203
σ ² (Å ²)	2.02 x 10 ⁻³	3.29 x 10 ⁻³	---	12.78 x 10 ⁻³
E ₀ (eV)	9.3 ± 1.9	9.3 ± 1.9	---	6.6 ± 5.4
CN	0.93 ± 0.14	3.85 ± 0.21	---	3.85 ± 0.21
S ₀ ² = 0.92 (set), N _{idp} = 19.4, N _{var} = 8, χ ² = 559, reduced χ ² = 49, R-factor = 0.049, FT k region = 3.348 – 13.623 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				

1st Cross-Linking Reaction: $\text{WCl}_6 + \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

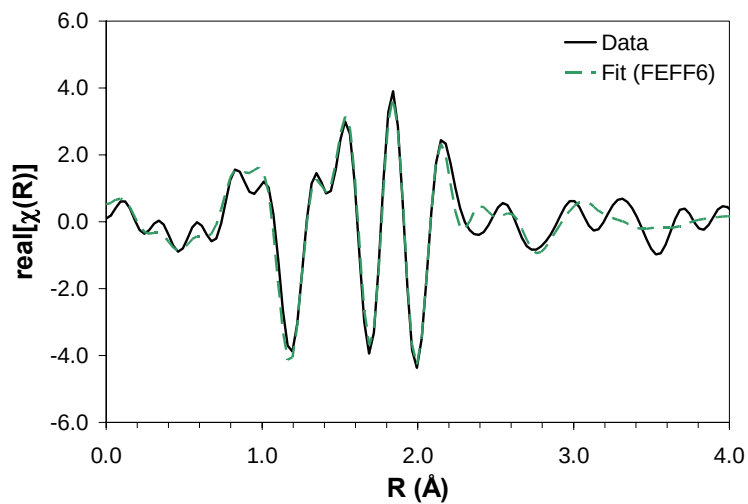
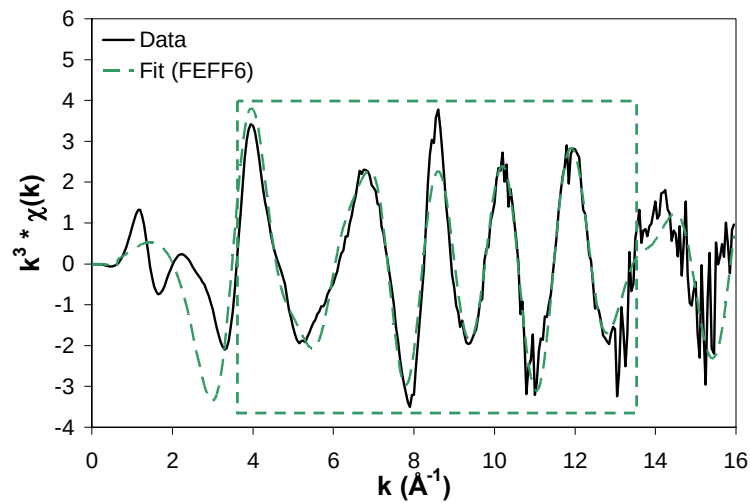
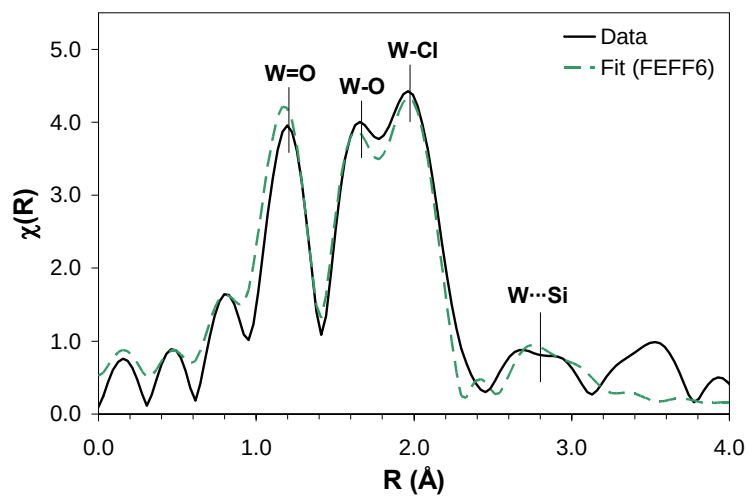
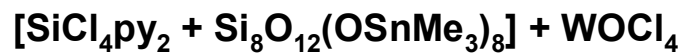


Embedded WCl_6 1 st dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.713	1.876	---	3.205
σ^2 (Å ²)	0.18×10^{-3}	8.16×10^{-3}	---	18.36×10^{-3}
E_0 (eV)	6.4 ± 2.1	6.4 ± 2.1	---	6.4 ± 2.1
CN	0.96 ± 0.08	3.79 ± 0.25	---	3.79 ± 0.25
$S_0^2 = 0.92$ (set), $N_{\text{idp}} = 19.9$, $N_{\text{var}} = 7$, $\chi^2 = 427$, reduced $\chi^2 = 33$, R-factor = 0.064, FT k region = $3.587 - 14.149 \text{ Å}^{-1}$, Fit range = $1.0 - 4.0 \text{ Å}$				

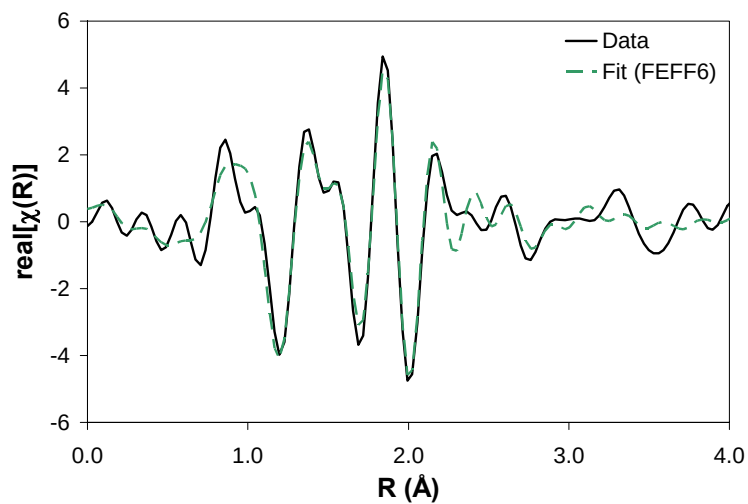
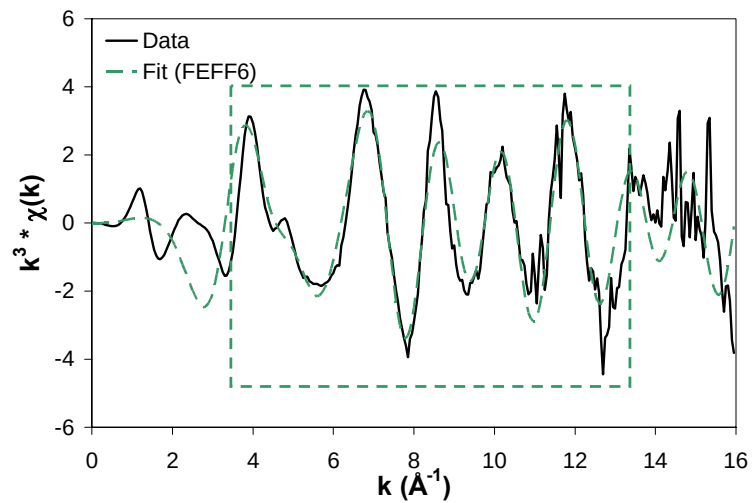
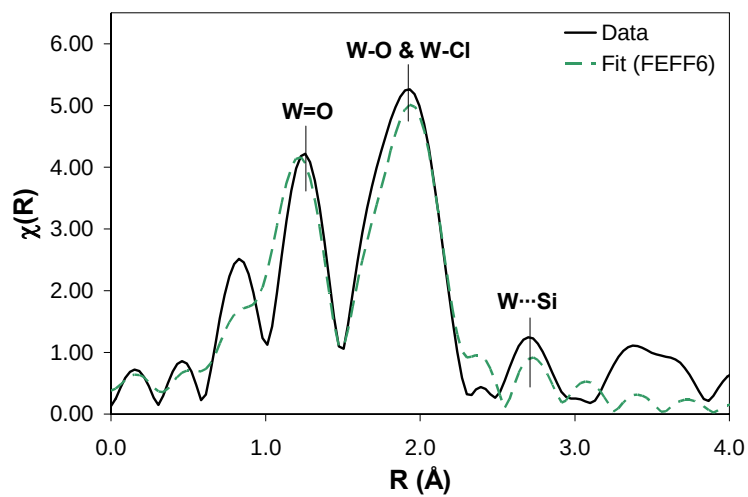
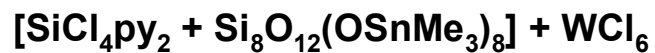
2nd Cross-Linking Reaction: $\text{WCl}_6 + \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$; SiCl_4



Embedded WCl_6 2 nd dose				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.691	1.890	---	3.207
σ^2 (Å ²)	0.23×10^{-3}	3.25×10^{-3}	---	13.77×10^{-3}
E_0 (eV)	6.9 ± 1.6	6.9 ± 1.6	---	6.9 ± 1.6
CN	0.96 ± 0.08	3.79 ± 0.25	---	3.79 ± 0.25
$S_0^2 = 0.92$ (set), $N_{\text{idp}} = 18.6$, $N_{\text{var}} = 7$, $\chi^2 = 1261$, reduced $\chi^2 = 109$, R-factor = 0.045, FT k region = $3.614 - 13.485 \text{ Å}^{-1}$, Fit range = $1.0 - 4.0 \text{ Å}$				

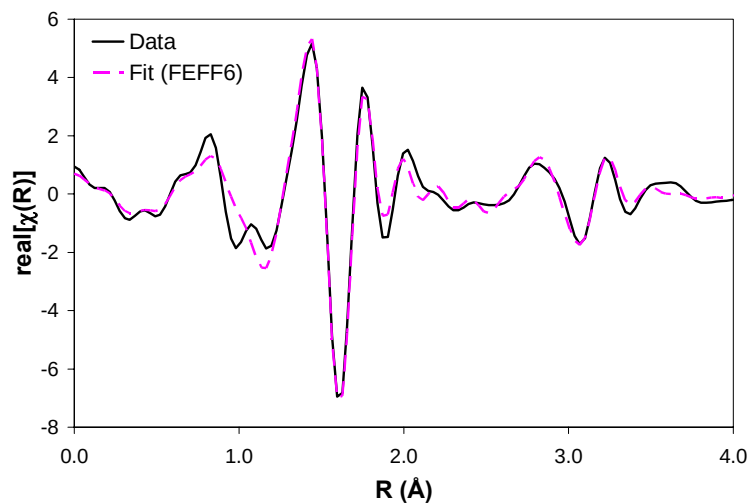
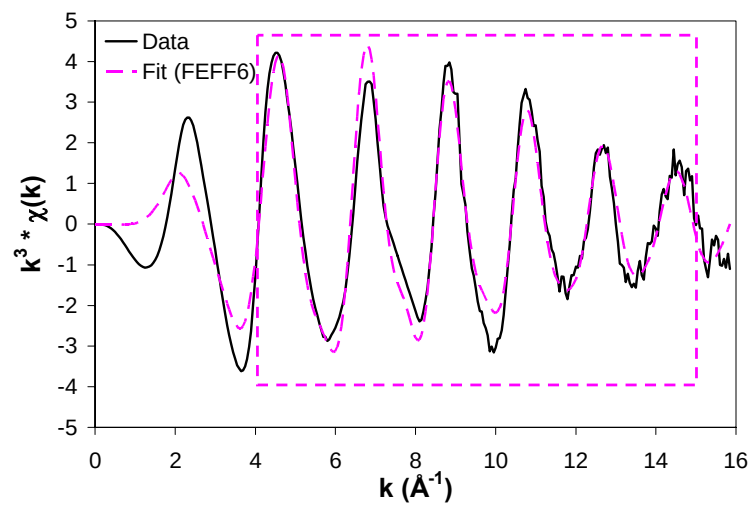
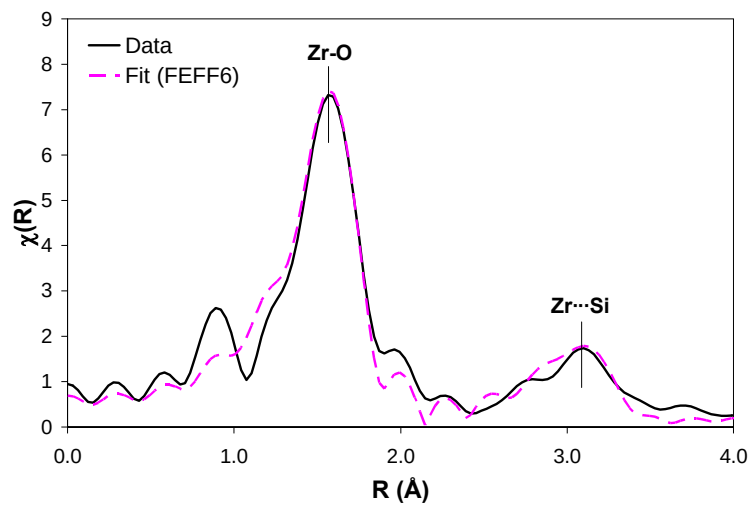


Surface Tungsten Oxo Centers				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.665	1.851	2.327	3.189
σ² (Å²)	0.66 x 10 ⁻³	5.56 x 10 ⁻³	2.16 x 10 ⁻³	17.95 x 10 ⁻³
E ₀ (eV)	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8	1.4 ± 2.8
CN	1 (set)	3 (set)	1 (set)	3 (set)
S ₀ ² = 0.92 (set), N _{idp} = 18.7, N _{var} = 9, χ² = 383, reduced χ² = 40, R-factor = 0.055, FT k region = 3.570 – 13.491 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				



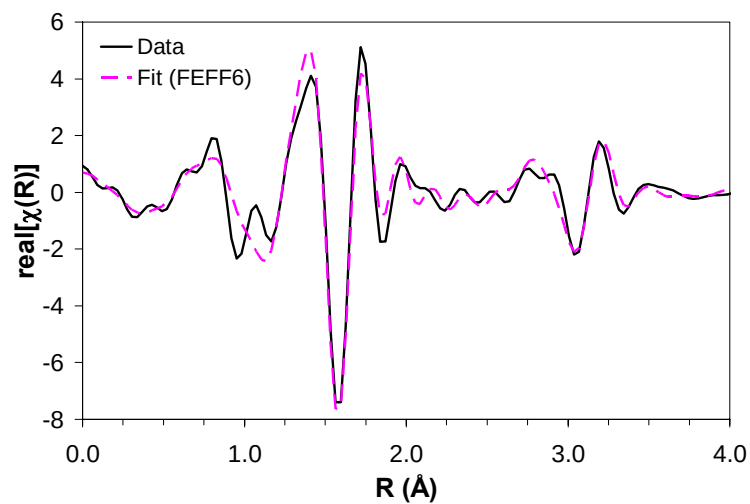
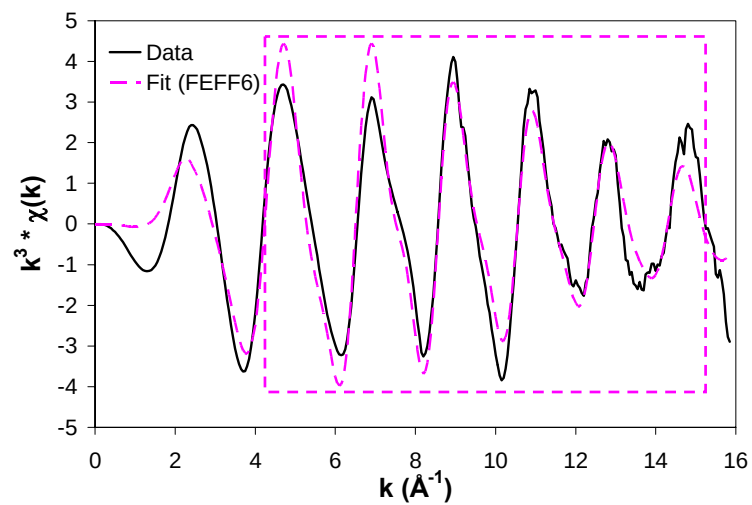
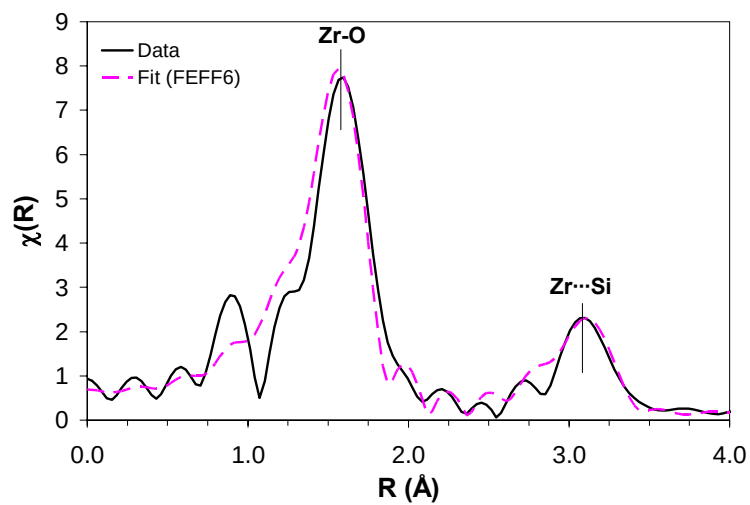
Surface Tungsten Centers				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.661	1.823	2.317	3.156
σ^2 (Å ²)	2.28×10^{-3}	9.85×10^{-3}	0.85×10^{-3}	22.97×10^{-3}
E ₀ (eV)	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0	-5.2 ± 5.0
CN	1 (set)	3 (set)	1 (set)	3 (set)
$S_0^2 = 0.92$ (set), $N_{\text{idp}} = 18.4$, $N_{\text{var}} = 9$, $\chi^2 = 377$, reduced $\chi^2 = 40$, R-factor = 0.078, FT k region = $3.544 - 13.274$ Å ⁻¹ , Fit range = $1.0 - 4.0$ Å				

1st Cross-Linking Reaction: $\text{ZrCl}_4 + \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

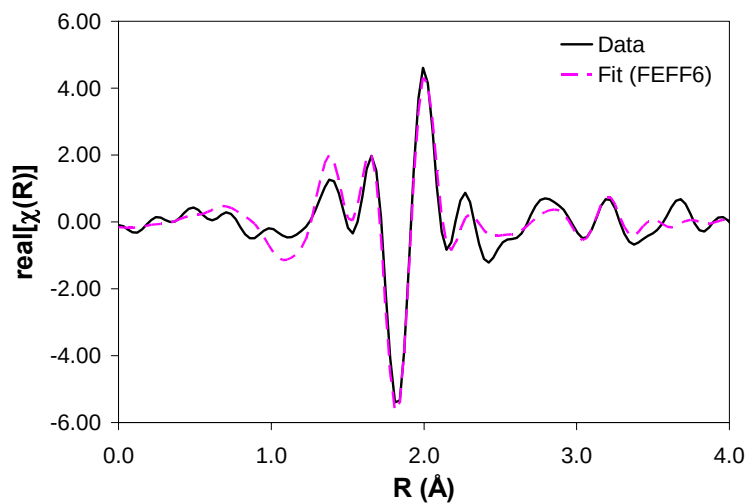
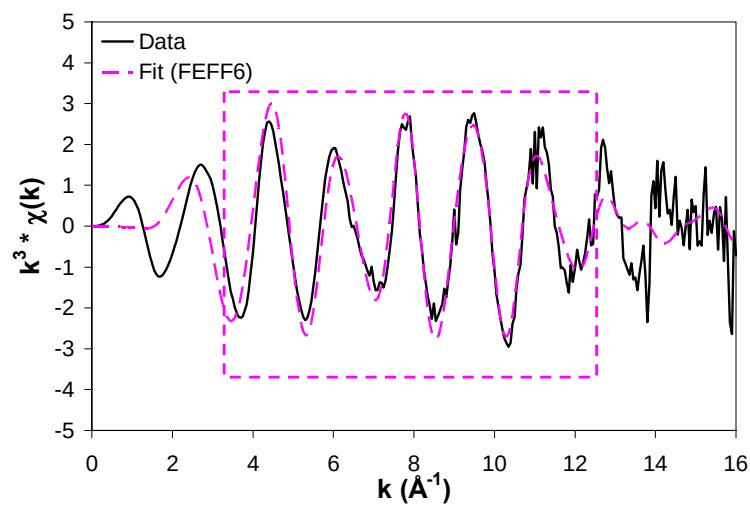
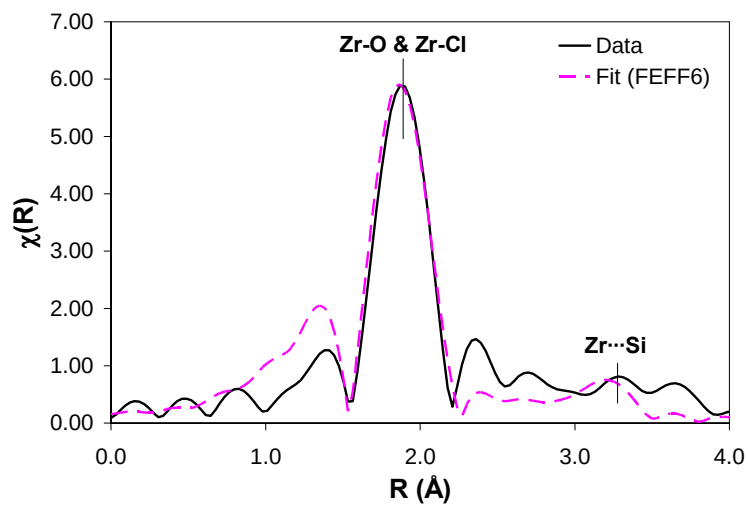
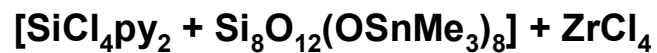


Embedded ZrCl_4 1 st dose			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	2.002	---	3.615
σ^2 (Å ²)	3.66×10^{-3}	---	7.37×10^{-3}
E_0 (eV)	-9.1 ± 1.4	---	-9.1 ± 1.4
CN	3.82 ± 0.15	---	3.82 ± 0.15
$S_0^2 = 0.928$ (set), $N_{\text{idp}} = 24.3$, $N_{\text{var}} = 5$, $\chi^2 = 1366$, reduced $\chi^2 = 71$, R-factor = 0.038, FT k region = $4.057 - 15.141 \text{ Å}^{-1}$, Fit range = $1.0 - 4.5 \text{ Å}$			

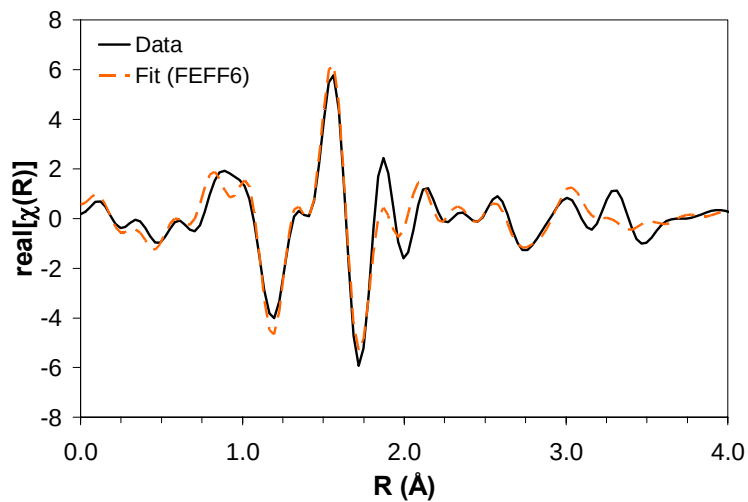
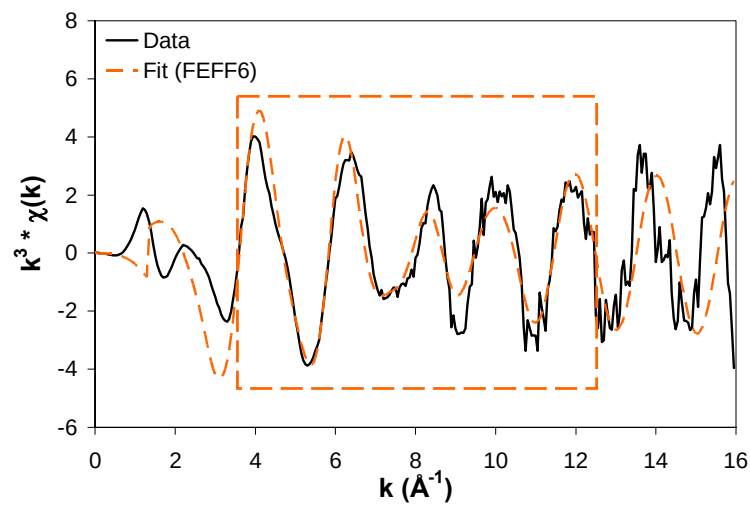
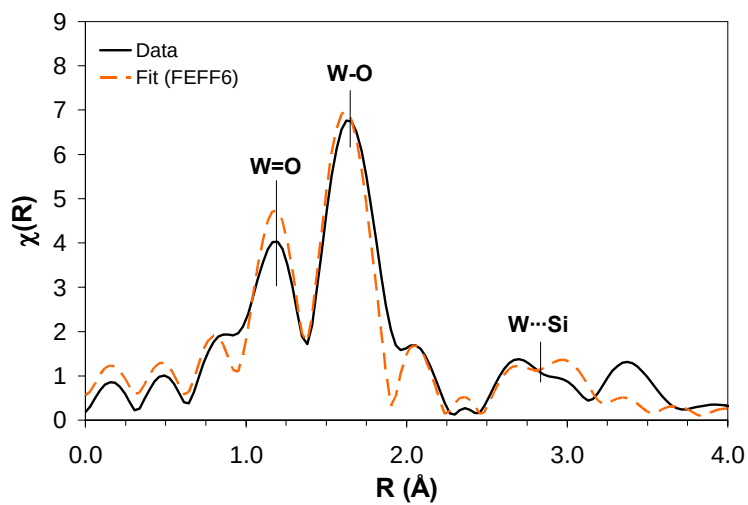
2nd Cross-Linking Reaction: $\text{ZrCl}_4 + \text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8; \text{SiCl}_4$



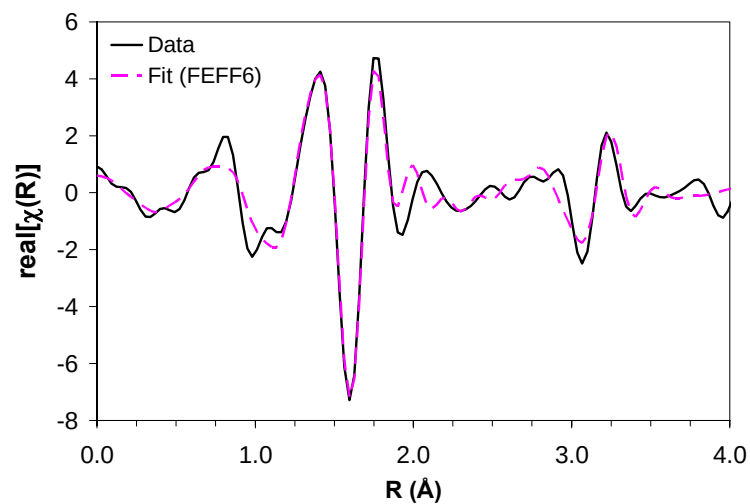
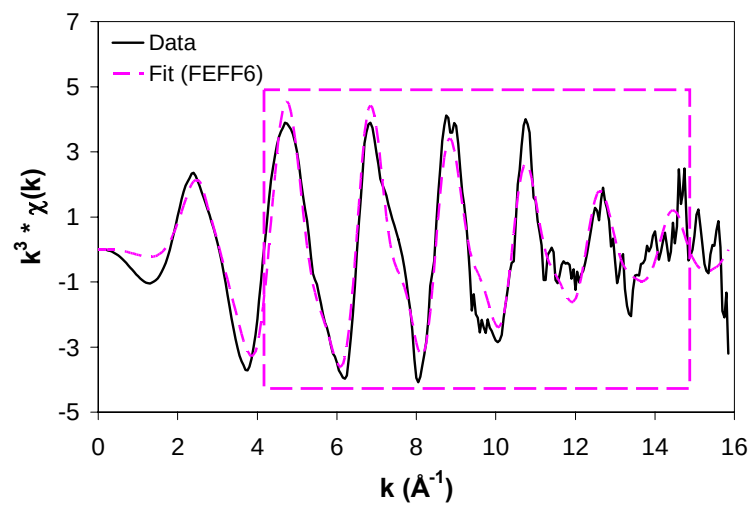
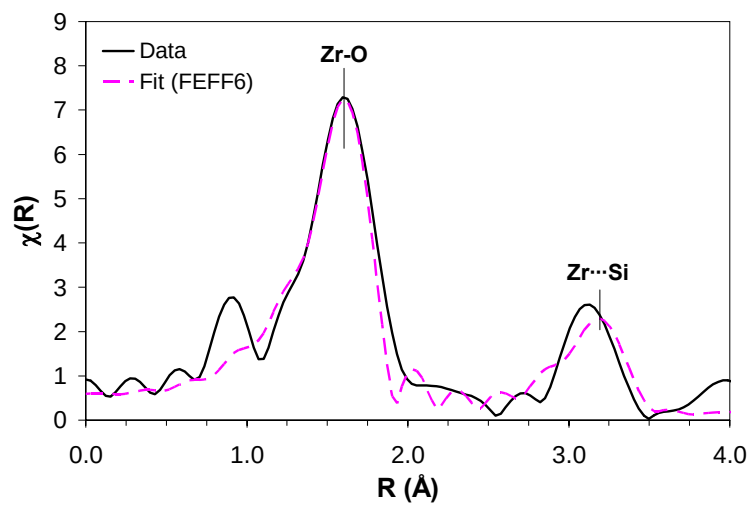
Embedded ZrCl_4 2 nd dose			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	1.977	---	3.609
σ^2 (Å ²)	3.55×10^{-3}	---	6.32×10^{-3}
E_0 (eV)	-6.6 ± 1.9	---	-6.6 ± 1.9
CN	3.62 ± 0.19	---	3.62 ± 0.19
$S_0^2 = 0.928$ (set), $N_{\text{idp}} = 25.0$, $N_{\text{var}} = 5$, $\chi^2 = 7737$, reduced $\chi^2 = 386$, R-factor = 0.076, FT k region = $4.159 - 15.590 \text{ Å}^{-1}$, Fit range = $1.0 - 4.5 \text{ Å}$			



Surface Zirconium Centers			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	1.929	2.376	3.606
σ^2 (Å ²)	2.45×10^{-3}	7.55×10^{-3}	3.80×10^{-3}
E ₀ (eV)	-9.1 ± 2.0	-9.1 ± 2.0	-9.1 ± 2.0
CN	1.07 ± 0.10	2.93 ± 0.10	1.07 ± 0.10
$S_0^2 = 0.928$ (set), $N_{\text{idp}} = 21.3$, $N_{\text{var}} = 7$, $\chi^2 = 1009$, reduced $\chi^2 = 71$, R-factor = 0.080, FT k region = $3.180 - 13.127 \text{ Å}^{-1}$, Fit range = $1.1 - 4.5 \text{ Å}$			



Embedded W(VI) Centers with Targeted Mesoporosity				
	W=O	W-O	W-Cl	W...Si
R (Å)	1.687	1.890	---	3.209
σ ² (Å ²)	0.12 x 10 ⁻³	5.11 x 10 ⁻³	---	16.30 x 10 ⁻³
E ₀ (eV)	6.6 ± 2.7	6.6 ± 2.7	---	6.6 ± 2.7
CN	0.95 ± 0.13	3.76 ± 0.31	---	3.76 ± 0.31
S ₀ ² = 0.92 (set), N _{idp} = 18.5, N _{var} = 7, χ ² = 558, reduced χ ² = 49, R-factor = 0.108, FT k region = 3.558 – 13.365 Å ⁻¹ , Fit range = 1.0 – 4.0 Å				



Embedded Zr(IV) Centers with Targeted Mesoporosity			
	Zr-O	Zr-Cl	Zr...Si
R (Å)	2.014	---	3.665
σ^2 (Å ²)	4.16×10^{-3}	---	6.36×10^{-3}
E ₀ (eV)	-0.9 ± 2.0	---	-0.9 ± 2.0
CN	3.97 ± 0.24	---	3.97 ± 0.24
$S_0^2 = 0.928$ (set), $N_{\text{idp}} = 24.6$, $N_{\text{var}} = 5$, $\chi^2 = 1065$, reduced $\chi^2 = 54$, R-factor = 0.079, FT k region = 4.159 – 15.396 Å ⁻¹ , Fit range = 1.0 – 4.5 Å			

VITA

Michael E. Peretich grew up in Fredericksburg, VA and graduated from Stafford Senior High School in June of 2002. He then enrolled at James Madison University and completed his B.S. in chemistry (with distinction and ACS certified) and mathematics in May 2006. At JMU he conducted research with Prof. Thomas DeVore on the kinetics of the reactions between copper based catalysts and 1-propanol. His honor thesis was titled “The Kinetic Studies of the Reactions Between Copper Based Catalysts and 1-Propanol” and was selected as one of the top honors theses at JMU and received the Phi Beta Kappa Award for Outstanding Honors Project. He completed a summer research internship at Oak Ridge National Laboratory (ORNL) and the University of Tennessee in 2004, where he conducted research with Dr. Robert Shaw and Prof. Charles Feigerle on the synthesis and characterization of corrugated thin diamond stripper foils for the Spallation Neutron Source at ORNL. The following summer he worked with Dr. R. Gregory Downing at the National Institute of Standards and Technology (NIST) analyzing a wide variety of samples using a unique nondestructive analytical technique, Neutron Depth Profiling (NDP).

In August 2006, he joined the Chemistry Department at the University of Tennessee – Knoxville where he began work on a doctoral degree in chemistry under the guidance of Prof. Craig E. Barnes. His research was part of an ongoing research program to develop new synthetic methodologies for the targeted preparation of heterogeneous catalysts. He completed the requirements for the Doctor of Philosophy in chemistry in December 2011.