

To the Graduate Council:

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Synthesis and Characterization of Atomically Dispersed,
Vanadosilicate Catalysts in Si_8O_{20} -Based Building Block Solids

A Dissertation

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Dedication

To my Parents (Shan-Nan Lee and Shou-Mon Fu),
Brother (Ming-Yeh Lee), Aunt Li-Hwa, and Uncle Chao-Ming Huang
who support and love me unconditionally

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Abstract

Silica supported vanadium complexes have attracted interest as catalysts for a variety of catalytic reactions in the past two decades. Although many strategies have been developed for incorporating vanadyl species on silica surfaces, controlling dispersion and loading while simultaneously producing single site catalysts remains a challenging goal in this context and in catalysis as well.

A simple strategy for producing single-site and site-isolated vanadyl species has been explored which allows for control of both the connectivity to the support as well as the local surface structure around a V=O group. The main elements of this strategy involve construction of the support from silicate building blocks linked by groups that both hold the matrix together and act as catalytically active sites. Controlled sequential dosing lead to catalysts in which control of the identity of the sites, their connectivity to the support and dispersion is maintained. The specific system that will be described involves the controlled reaction of vanadyl chloride (VOCl_3) and vanadium tetrachloride (VCl_4) with the tin functionalized spherosilicate cube, $(\text{SnMe}_3)_8\text{Si}_8\text{O}_{20}$. Labeled ^{17}O $(\text{SnMe}_3^*\text{O})_8\text{Si}_8\text{O}_{12}$ and $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule have also been synthesized successfully by using totally new synthetic methodologies. The physico-chemical properties of these vanadium catalysts were characterized by solid state ^{51}V and ^{17}O NMR, gravimetric analysis, EXAFS, and atomic absorption spectroscopy.

A quick survey of isopropanol dehydration and dehydrogenation with these vanadium (IV and V) catalysts has been studied. The acid-base property of these single-site and site-isolated catalysts has been assessed by the conversion of isopropanol. Preliminary results of highly selectivity (>97%) of isopropanol conversion to propene will be described.

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Chapter 1

Introduction

1.1 Catalysts in our life

In the science of catalysis a substance, called a catalyst, accelerates or slows down a chemical reaction without being consumed during the reaction. In chemistry, catalysts change the activation energy and provide another pathway that requires less energy to accomplish the reaction. Although the principles of catalysis were not recognized until relative recently, a variety of catalytic reactions were used in antiquity such as the fermentation of sugar to ethanol and the conversion of ethanol to acetic acid. The industry revolution in the 18th century accelerated the investigation and the usage of catalysts. Nowadays we understand that the application of catalysts in the industry can improve our environment and provide us a higher quality of life. The modern, industrialized world would be inconceivable without catalysts. Developing a new generation catalyst to reduce costs in the industry and control the pollution from industry will be one of the most important issues for chemists or chemical engineers in the future.

1.1.1 A brief history of catalysis

In 1746, a catalyst was used for the first time in the manufacture of sulfuric acid in lead condensing chambers by John Roebuck and Samuel Garbett.¹ At

that time, the word “catalysis” had not yet been used. Jöns Jakob Berzelius first described in 1835 how a reaction can be sped up via adding certain chemicals. About 30 years later, Deacon used CuSO_4 as a catalyst in chlorine production by HCl oxidation in 1867. In 1897, P. Sabatier and R. Senderen discovered that nickel was a good catalyst in the hydrogenation reaction. Pt, Rh, Fe, and Mo oxide were sequentially discovered to be catalysts between 1875 and 1927 such as nitric acid synthesis by NH_3 oxidation (Pt/Rh catalysts),² ammonia synthesis from N_2 and H_2 (Fe catalyst), and hydrogenation of coal to hydrocarbons (Fe, Mo, Sn catalysts). In 1930s, Brunauer and Emmett discovered a new methodology to measure the surface area and porous geometry of catalysts via physical adsorption. The availability of isotopes in 1933 provides a new route for chemists to identify a variety of catalysts and investigate the mechanism in catalytic reactions. In 1954, Ziegler and Natta discovered ethylene polymerization under low pressure by using Ti compounds as the catalyst and were awarded the Nobel Prize in Chemistry in 1963. Other significant developments of catalysts include the Mobil Oil Corporation discovery the family of ZSM zeolites in 1975 and Monsanto Company development of a methodology to convert methanol to acetic acid via carbonylation reactions. Nowadays a variety of catalysts has been developed from the academic research fields and applied to important industrial manufacturing process.

1.1.2 Catalyst in industry

The chemical industry has grown tremendously in recent decades and affects the economy and our life significantly. Although catalysts can be gases, liquids or solids, most industrial catalysts are liquids or solid because they are easier to be controlled and handled in the reaction. The industrial products made from catalytic reactions cover several areas and have a great impact on our life. Transportation (fuel, tires, and pollution control), construction (carpets, engineering plastic, and insulation), clothing (polyester, nylon, and rayon), and food (packaging, insecticides, and fertilizers), etc. are all related to our daily lives and these products are manufactured from different catalytic reactions in different industries. Deactivation and poisoning of catalysts are the two main problems during the manufacturing process. Overcoming these problems through the development of new catalytic reactions will be an important achievement in future industrial manufacturing.

1.1.3 Catalysts and the environment

Environmental pollution problems increased tremendously after the industry revolution. The application of catalysts has helped the development of the industry but has also caused significant damage to our environment. One of the most notable problems is global warming or the greenhouse effect. A fundamental part of the solution of this problem is to minimize or eliminate the release of carbon dioxide and methane to earth's atmosphere. Other chemicals such as carbon monoxide, nitrogen oxides, and hydrocarbons from waste and

exhaust gases also change the ecological balance and affect our environment. Nonpolluting processes in manufacturing are the ideal goal. One of the most important current missions of chemists is to find new generation catalysts to decrease pollution and protect our environment because we only have one earth.

1.1.4 Biocatalysts-Enzymes

Catalysis is not only the key in most industrial syntheses but also plays a critical role in many biological processes. Biocatalysis is an interdisciplinary area. It combines organic chemistry, molecular biology, enzymology, and protein chemistry. Its areas of application are very broad which include food, pharmaceuticals, agriculture, fine chemicals, medicine, etc. The discovery of enzymes illustrates how many biological functions are catalyzed chemical reactions. Enzymes are catalytic proteins and highly specific catalysts in biological systems. Human beings can be viewed as small catalytic machines in which numerous catalytic reactions occur in our body every second. It is generally held that biocatalysts such as enzymes are much more efficient than chemical catalysts and industrial catalysts. All of the metabolic pathways in our bodies depends upon specific contributions from the different functions of enzymes. The high selectivity of different enzymes is one of the most interesting properties that biochemists would like to understand. Enzymes in cells convert substrates into different molecules efficiently because they decrease the activation energy and accelerate the rate of the reaction. Nowadays approximately 4000 different enzymes have been identified. Only about 400

enzymes can be synthesized artificially by biochemists or chemists and commercially available. About 40 different enzymes are actually used for industrial processes.

1.2. Types of Catalysts

The impact and importance of catalysis have been described in the previous section. A brief classification of catalysts will be discussed following in order to understand their different applications.

1.2.1 Homogeneous catalyst

In homogeneous catalysis, starting materials, catalysts, and products are present in the same phase. Many homogeneous catalysts are organometallic complexes. The mechanism of homogeneous catalysis is easier to determine and understand because more is generally known about the reaction site. Having a single active site homogeneous catalyst generally leads to the important property of high selectivities. But having all of the materials in one phase also leads to a major disadvantage because it is difficult to separate the catalyst from the product after the reaction is complete. Lower thermal stability is another drawback of homogeneous catalysts that can restrict their applicability because they can be destroyed if higher reaction temperatures are applied in a reaction. Generally, homogeneous catalyst can perform catalytic reactions in a reasonable temperature range ($\sim < 200^{\circ}\text{C}$).

Acidic catalysts with H^+ or catalysts containing transition metal ions in high oxidation states such as Mo^{6+} , Ti^{4+} , and Zn^{2+} can be classified as “hard” catalysts. These catalysts can be used in oxidation, epoxidation, ester hydrolysis, etc. reactions. Low oxidation state, transition metal complexes such as Rh^+ , Ni^0 , and Cu^+ are classified as “soft” catalysts which can be used in carbonylation, hydrogenation, olefin oligomerization, etc. reactions. Many new transition metal catalysts have been developed in the last two decades. Discovering and synthesizing new homogeneous catalysts with higher tolerances in different reaction conditions will be a significant achievement in this research area.

1.2.2 Heterogeneous Catalysts

For heterogeneous catalysts, phase boundaries are always present between catalyst and reactants. This type of catalyst is generally more thermal stable and easier to recycle when the reaction is complete. But the mechanism of the heterogeneous catalytic reaction is more difficult to figure out because most of these catalysts lack uniformity in the active sites present. Most heterogeneous catalysts also involve porous materials with high surface areas. A catalyst with a higher surface area provides reactants a larger number of binding sites at which to enter into a catalytic cycle and be converted into products. In heterogeneous catalysis, the reaction begins with physical adsorption or chemical adsorption. If the substrate only interacts with catalytic centers via van der Waals forces, and no electron transfer occurs during the binding process, it is classified as physical adsorption. This type of the binding is

needed to lower activation energy and is highly reversible. If covalent bonds form between reactants and catalytic centers and electrons transfer during the reaction process, it is classified as chemical adsorption. The chemical adsorption reaction is normally temperature dependent and the activation energy is generally higher than the physical adsorption. Different types of surfaces influence the catalytic reactions because irregularities of surface in the structure can change the catalytic activity. How to develop single site and site isolated catalysts with well defined and predictable sites is one of the most challenging issue in this research area.

1.2.3 Current challenges in catalysis

Theoretically, an ideal catalyst would not be consumed and maintain its structure after any catalytic reaction. Actually, this goal is very difficult to achieve especially for the larger scale manufacturing in the industrial companies. Deactivation of catalysts always happens and requires that most catalysts must be regenerated or eventually replaced. Poisoning, coke formation, and sintering in supported metal system during the reaction are three major processes that lead to catalytic deactivation. Increasing the tolerance for the homogeneous catalysts in different reaction conditions and obtaining a higher selectivity for heterogeneous catalysis are key challenges in future catalytic processes. In order to maintain the advantage from different types of catalysts, single site and site isolated catalytic centers in a rigid material with high surface areas will be the fundamental principles involved in solving these problems.

1.3 Building block methodology to prepare new generation catalysts

The traditional methodologies of preparing heterogeneous catalysts include the sol-gel process, incipient wetness impregnation, and zeolite synthesis (natural and hydrothermal synthesis). The catalysts synthesized from each of these different methodologies have their own special properties but none of them can provide good selectivity because in most cases the catalysts lack uniformity in the active sites. Utilizing a building block strategy to synthesize new generation catalysts is a new approach to this challenge and is the major focus of this thesis.

1.3.1 Traditional methods of heterogeneous catalysts preparation

Methods of catalyst preparation are very diverse and each catalyst is produced via different routes. Many traditional catalysts involve metal catalysts in metal oxide supports such as SiO_2 , Al_2O_3 , MgO , TiO_2 , etc. One of the most common methods to prepare heterogeneous catalysts is the sol-gel process which is based on the hydrolysis-condensation of metal alkoxides and salts. This process converts simple molecular precursors into nanometer-sized particles which form colloidal suspensions. Three-dimensional solid networks are formed after the colloidal nanoparticles are linked with one another. Changing the pH of the reaction solution is the most convenient approach to transform the colloid to a gel. Although sol-gel process produces large scale materials in a short time, the distribution of catalytic sites or metal centers is a random distribution inside the

pores. Therefore it is very difficult to obtain uniform and isolated catalytic centers through this methodology.

Incipient wetness impregnation is another method to prepare heterogeneous catalysts in which the active metal precursor is dissolved in an aqueous or organic solution and then the metal-containing solution is added to a catalyst support. Normally, catalytic metal centers are deposited on the surface after the materials are dried and calcined to remove volatile components within the matrix. These methods provide quick routes to synthesis catalysts but the drawback of this methodology is, like sol-gel process, that multiple catalytic sites are generally spread randomly on the surface. Therefore it is not easy to identify which metal centers in the material provide better activity or selectivity in different catalytic reactions.

Zeolites with microporous and crystalline structures are one of the most important families of heterogeneous catalysts currently used in the petrochemical industry.³ One feature of zeolites is the active sites in these materials are easier to probe due to the crystalline nature of the material. Another feature is the regular pore structure of these materials provides of good selectivity in the catalytic reactions that take place in these materials. Most of the zeolites contain both Bronsted and Lewis types acid sites and perform very well in terms of reactivity of selectivity. But the microporous structure restricts the application of catalytic reactions. Some catalytic sites in the zeolites are not totally isolated and leaching of metal ions during the reaction are other drawbacks of these materials.

1.3.2. Building block methodology to prepare single-site and site-isolated catalysts

The synthesis of new generation heterogeneous catalysts relies on two major concepts which have not been used in the synthesis of traditional catalysts. First, well-defined molecular building blocks chosen as the reactants can provide a clearer structural picture of building block matrices that result. Second, nonhydrolytic, metathesis reactions result in matrices in which only building blocks are linked together to form cross-linked solids while maintaining the integrity of building blocks. Nanometer sized, spherosilicate building blocks combined with different transition metals present new opportunities to obtain nanostructured, metal oxides catalysts.

The derivatives of cubic spherosilicate, Si_8O_{20} (Figure 1-1), belong to the polyhedral oligomeric silsesquioxane (POSS) family. POSS chemicals are well defined three-dimensional shaped building blocks. These materials are larger than small molecules but smaller than macromolecules.

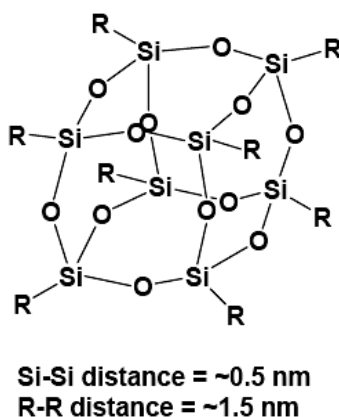


Figure 1 - 1 Si_8O_{20} spherosilicate

A variety of POSS chemicals has been synthesized in the past two decades and used in functionalized monomers, polymers, resins, silanols, and molecular silicates. These POSS chemicals are thermally and chemically more robust than silicones and their nanostructured shape provides unique opportunities for properties by controlling reaction at molecular level. Incompletely condensed Si_7O_{12} cage molecules are one of the branches in POSS chemistry which have different alkyl blocking groups on their corners. The single site model compound of metal on POSS silicate can be synthesized by reacting Si_7O_{12} molecule with different metal chlorides. (Figure 1-2)

The Si_8O_{20} spherosilicate with eight oxygen terminated corners has completely different synthetic properties compared with the incompletely condensed Si_7O_{12} cage molecules because all eight corners are all available for

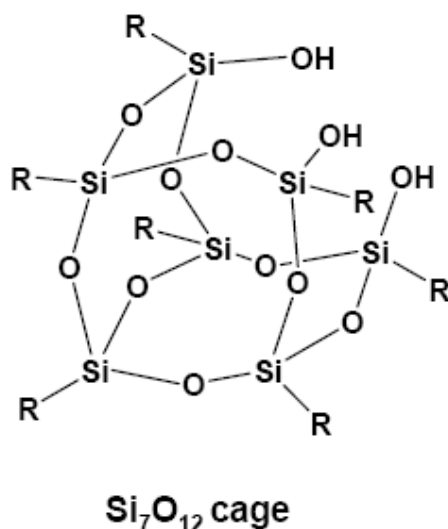


Figure 1 - 2 Si_7O_{12} molecule

further reaction. Feher and Weller reported the synthesis of octakis(trimethyl tin) spherosilicate $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$.⁴ This molecule is the main building block we use in this research project. All eight trimethyl tin corners in this molecule are available for reaction with different types of linking groups. The synthetic methodology is applicable to a wide variety of linking agents such as main group (Si, Sn, and P), transition metals (Ti, Zr, V, and W) and polynuclear metal oxides. The metal halide, linking agents will ultimately become the catalytic active sites. Main group halides such as SiCl_4 and Me_2SiCl_2 are used to maintain site isolation.

A building block approach to tailored catalysts is a totally new methodology to prepare a new generation of heterogeneous catalysts. The significant property of these catalysts is their single site and site isolated catalytic centers. The robust building block also provides a good environment to avoid metal centers leaching out when these materials are tested under catalytic reaction conditions. We show in this work that catalysts synthesized from the building block methodology will produce better catalysts than the traditional catalysts.

1.3.3 Characterization of heterogeneous catalysts and their application

The amorphous catalysts synthesized from our building block methodology lack long range order which makes it difficult to determine their structures. Thus several techniques such as gravimetric analysis, solid state

NMR, surface area measurement, and EXAFS spectroscopy will be discussed as the methods used to characterize these materials in this thesis.

The ultimate goal of this research is to apply these new synthetic materials in catalytic reactions. A variety of catalytic reactions such as dehydration, dehydrogenation, transesterification, epoxidation, and olefination can be tested by using these new generation catalysts. A higher selectivity is expected from different catalytic reactions because catalysts only contain single site. The thermal stability should also be higher due to chemically the robust environment of these building block materials.

1.4 Thesis overview

Single site and site isolated catalysts provide a clearer picture with which information to determine the mechanism of different catalytic reactions. Investigating novel and unique nanostructured metal oxide catalysts with single sites and site isolated centers via building block syntheses is the main goal in this thesis. These new catalysts are expected to provide not only better activities but also higher selectivities in a variety of catalytic reactions. Our original design of constructing single site and site isolated vanadium catalysts with silicate building block has been accomplished successfully and is described in this thesis.

The three major phases of this research, synthesis, characterization and catalytic application are discussed in this thesis. Optimizing reactions to obtain high yields of the silicate building block and recycling a toxic byproduct are part

of the goals of my work. Using different synthetic methodologies such as changing the stoichiometry and the additional order to obtain a single type of catalytic site and maintain sites isolation within the silicate matrix is a second important goal. Characterization of these materials covers how to utilize different techniques such as solid state NMR, surface area measurements, and EXAFS to identify and prove that the type of metal (vanadium) centers in these materials are indeed the ones we designed them to be. The section on catalytic applications of these materials describes preliminary results of a survey of the catalytic dehydrogenation and dehydration of isopropanol using these new generation vanadium catalysts.

Six different projects were accomplished and are described in Chapter two through seven. **Chapter 2** presents results of exploring an efficient methodology to separate large amounts of sphaerosilicate ($\text{H}_8\text{S}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$) mixtures which are the precursor silicate build blocks in this research. Functionalizing hydrogen corners of $\text{H}_8\text{S}_8\text{O}_{12}$ in an one-pot reaction to obtain a high yield $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ building block is also discussed in this chapter. Highly toxic tin materials are used in preparing the stannylated silicate building block. How to increase the yield and efficiently utilize the different tin compounds in each synthetic step are also very important issues addressed in this work. Successfully recycling the Me_3SnH byproduct and obtaining a crystal structure of trimethyltin peroxide, Me_3SnOOH , are also described. These new discoveries provided us new routes to utilize tin compounds efficiently while synthesizing $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$.

Chapter 3 describes how to react building blocks with different vanadium reagents (VOCl_3 and VCl_4) to obtain vanadium- Si_8O_{20} catalysts. The definition and the difference between “embedded” and “surface” vanadium (+4 and +5) samples will be discussed in this chapter. Different types of catalyst sites based on these vanadium samples are prepared from different reagent addition sequences while maintaining isolated vanadium centers in the silicate building block matrix. Gravimetric analysis is the first simple and quick method to provide information regarding the connectivity that exists in these vanadyl and vanadium materials. ^{29}Si , ^{51}V SSNMR spectra provide supporting information describing the silicon and vanadium environments present in these materials. The effect of changing the reaction temperature, reaction time, and solvent will also be discussed in this chapter. Surface area measurement (BET method) will be discussed last in this chapter and provide information on explain how the building blocks aggregate together and form porous materials when different linking reagents are used in the reaction.

Chapter 4 focuses on X-ray absorption near-edge spectrum (XANES) and extended X-ray absorption fine structure (EXAFS) experiments which are direct methods for probing the electronic and physical structure of metal sites at atomic scale. All of the data were collected from the National Synchrotron Light Source (NSLS) beam line X19A (focused beam) and X18B (unfocused beam). Data analysis was performed with the IFEFFIT⁵ data analysis software suite. The Athena and Artemis⁶ programs, which are used for data reduction and data modeling, will be described in this chapter. The different XANES spectra from

surface and embedded vanadium (+4 and +5) samples provide some interesting information on the effect of chloride ligands in the samples. EXAFS spectra of model compound, $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$, are analyzed first before examining different vanadium samples. Detailed EXAFS analysis procedures will be discussed in this chapter. The results of the analysis data strongly support NMR data that suggest these vanadyl and vanadium materials contain the vanadium sites we originally designed them to have.

Chapter 5 describes the application of these new generation vanadyl and vanadium silicates to actual catalysis. A quick survey of catalytic reactions has been performed. 2-propanol was used as the reactant and propene is the only product after catalytic dehydration. This preliminary result of the dehydration reaction indicates these vanadium catalysts are solid acid-catalysts. *Time on Stream* (TOS) and *Weight Hourly Space Velocity* (WHSV) will also be discussed in the chapter in order to obtain turnover numbers.

One of the most challenging projects in this thesis involved exploring to explore a totally new synthetic procedure to prepare ^{17}O labeled tin cube, $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$. This work is described in **Chapter 6**. The idea of putting labeled ^{17}O in the building block was based upon the desire to use ^{17}O solid state NMR measurements to identify and monitor the coordination environment of catalysis sites. The most significant achievement in this project is that ^{17}O labeled tin-cube has been synthesized in good yield using a limiting amount of extremely expensive starting material H_2^{17}O . Solution ^{29}Si , ^{119}Sn NMR spectra and mass spectra prove this labeled building block can be synthesized via this

new synthetic methodology. The measurement of ^{29}Si , ^{119}Sn , and ^{17}O SSNMR spectra were performed by Dr. Edward Hagaman and Dr. Jian Jiao in the Oak Ridge National Lab. The preliminary results of the ^{17}O spectra of hydrous and anhydrous labeled $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ building block are consistent with the different oxygen environments found in their crystal structures. These investigations are still ongoing and vanadium catalysts bound containing the labeled ^{17}O building block will eventually be synthesized and measured.

Chapter 7 presents a brief description of the synthesis and structure of octakis-(trichlorosiloxy)octasilsesquioxane, $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$. This new compound is synthesized by slowly adding $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ into excess SiCl_4 in CH_2Cl_2 solution. Due to the extreme air sensitivity of this compound, it was very difficult to obtain the crystal structure. The ^{29}Si NMR spectrum is the first line of the evidence to prove this compound has been synthesized successfully. Obtaining the crystal structure is a second achievement in this research project. This molecular structure provides information concerning Si-O, Si-Cl bond lengths and Si-O-Cl and Si-O-Si bond angles. It is another good model compound for the Si_8O_{12} building block family and has applications to future neutron and X-ray scattering research. The multiple active sites at each SiCl_3 group at each corner of this molecule allow this compound to be viewed as another type of building block which we call it as the “second generation building block”.

The final summary, conclusions and future work are described in **Chapter 8**. Several significant discoveries presented in this thesis open other windows of opportunity in this research area. A complete discussion of synthesis,

characterization and application indicates the importance of synthesizing single site and site isolated catalysts. The same procedure of synthesizing different type of catalysts via this building block methodology can be applied to a variety of high valence transition metals such as titanium, zirconium and tungsten. Future works will focus on investigating different catalytic reactions of single site and site isolated catalysts with different metal centers in building block matrices.

Chapter 2

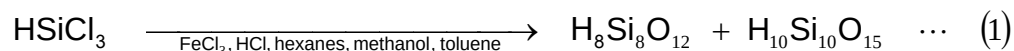
Efficient synthetic strategy for preparing and purifying functional spherosilicate building block molecules

2.1 Introduction

The chemistry of silicon has spread out into several domains of modern science and technology. Polyhedral oligomeric silsesquioxane (POSS) molecules have attracted much interest in the past two decades and are one of the important areas of active research among silicon-based molecules.⁷⁻¹⁰ These molecules are unique, nanometer-size inorganic/organic hybrid structures with chemical composition $(\text{RSiO}_{1.5})_n$ ($n = 6, 8, 10, \dots$) and the most studied member of this series is the cubic polyhedral octa-silsequioxane, $(\text{RSiO}_{1.5})_8$.

In the research described here, my investigations into potential building blocks for materials have focused primarily on developing efficient and high yield syntheses of the polyhedral octa-silsequioxane, $(\text{RSiO}_{1.5})_8$. The structure of this spherosilicate, $(\text{RSiO}_{1.5})_8$, is essentially a cube with eight silicon atoms on the corners, twelve oxygen atoms along the edges of the cube and eight R groups outside the corners. The simplest form of the cubic silsequioxanes is the octahydro analogue, $\text{H}_8\text{Si}_8\text{O}_{12}$, which has the R groups as hydrogen atoms. This compound was synthesized according to the procedure of Agaskar by the hydrolytic polycondensation of HSiCl_3 in a biphasic medium.¹¹ The total yield a mixture of the main product, $\text{H}_8\text{Si}_8\text{O}_{12}$, and byproduct, $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$, is ca. 25 ~

30% after crystallization (Eq.1). The ratio of the mixture of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is around 7: 2.

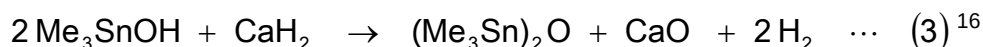
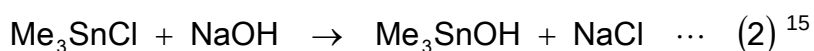


If the addition rate of the HSiCl_3 in the reaction is too fast, the amount of the product, $\text{H}_8\text{Si}_8\text{O}_{12}$, will decrease and the relative amount of the byproduct, $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$, will increase. These two major products are UV inactive with similar chemical properties. Therefore it is challenging to separate them via liquid chromatography on a large scale. In 1990, Buergy and Calzaferri reported a separation methodology of the oligomeric silsequioxanes $(\text{HSiO}_{1.5})_{8-18}$ by size-exclusion chromatography.¹² Marcolli et al. in 1997 reported a useful alternative approach of purification which was to remove $\text{H}_8\text{Si}_8\text{O}_{12}$ from the mixture by sublimation.¹³ Both of these reports were applied on very small scales (less than mg ~ 200 mg) mixture of the oligomeric silsequioxanes.

The first goal of this research project is to optimize the purification protocol which was described in Claudia's article to obtain large scale quantities of pure $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$. Large multi-gram amounts of $\text{H}_8\text{Si}_8\text{O}_{12}$ are needed as a starting material in our building block materials project via functionalization by replacing H atoms with Me_3SnO groups to get a new kind of the building block, $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$.

(Me₃SnO)₈Si₈O₁₂ was synthesized according to the procedures of Feher and Waller's reported in 1991.¹⁴ Although this compound, with eight trimethyltin groups on the corners, can be synthesized in reasonable amounts and in good yield (~80%) from H₈Si₈O₁₂, its synthesis involves the preparation and handling of very toxic and volatile trimethyltin reagents and byproducts which could pose a problem in incorporating this methodology into a technological setting. Therefore I developed an efficient synthetic strategy to increase the yield to 90% based on the trimethyltin reactant and simplify the synthetic procedure in a one-pot reaction to avoid dealing with trimethyl reagents throughout the synthetic steps leading to the final product. Furthermore, a highly efficient methodology of recycling the byproduct trimethyltin hydride, Me₃SnH, was successfully developed and a procedure of recycling the trimethyltin hydride is described below.

The reaction equations for preparing the trimethyltin building block compound, (Me₃SnO)₈Si₈O₁₂, are as follows:



From equation 4, it can be seen that only half of the trimethyltin groups in the reactant, bis(trimethyltin) oxide, are incorporated into the product, $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$. The other half ends up as the byproduct trimethyltin hydride, Me_3SnH . In previous synthetic processes, this toxic byproduct went to waste without recycling. Several different reactions were explored in an attempt to recycle Me_3SnH . Finally I developed an efficient procedure to convert the trimethyltin hydride into trimethyltin peroxide, Me_3SnOOH , by mixing 50% H_2O_2 with Me_3SnH . The crystal structure of Me_3SnOOH has also been obtained as apart of these investigations. This trimethyltin peroxide compound may be converted to bis(trimethyltin) oxide when exposed to CaH_2 and again be utilized to synthesize $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$. The entire synthetic and recycling schemes are summarized in the Figure 2-1.

2.2 Experimental

Diethyl ether and hexanes (Fisher Scientific) solvents were dried over Na/K alloy and distilled. Methylene chloride (Fisher Scientific) solvent was dried using calcium hydride and distilled. Calcium hydride, powder, ca. 0 - 20 mm, 90 ~ 95%, was obtained from Aldrich. Hydrogen peroxide, 50 wt% solution in water, was obtained from Acros. Trimethyltin chloride ($(\text{CH}_3)_3\text{SnCl}$) was obtained from Gelest, Inc. *Caution: Trimethyltin chloride is highly toxic and causes cerebral edema. It should be handled in the fume hood all the time. Trimethyltin containing products and byproducts such as trimethyltin hydroxide $(\text{CH}_3)_3\text{SnOH}$,*

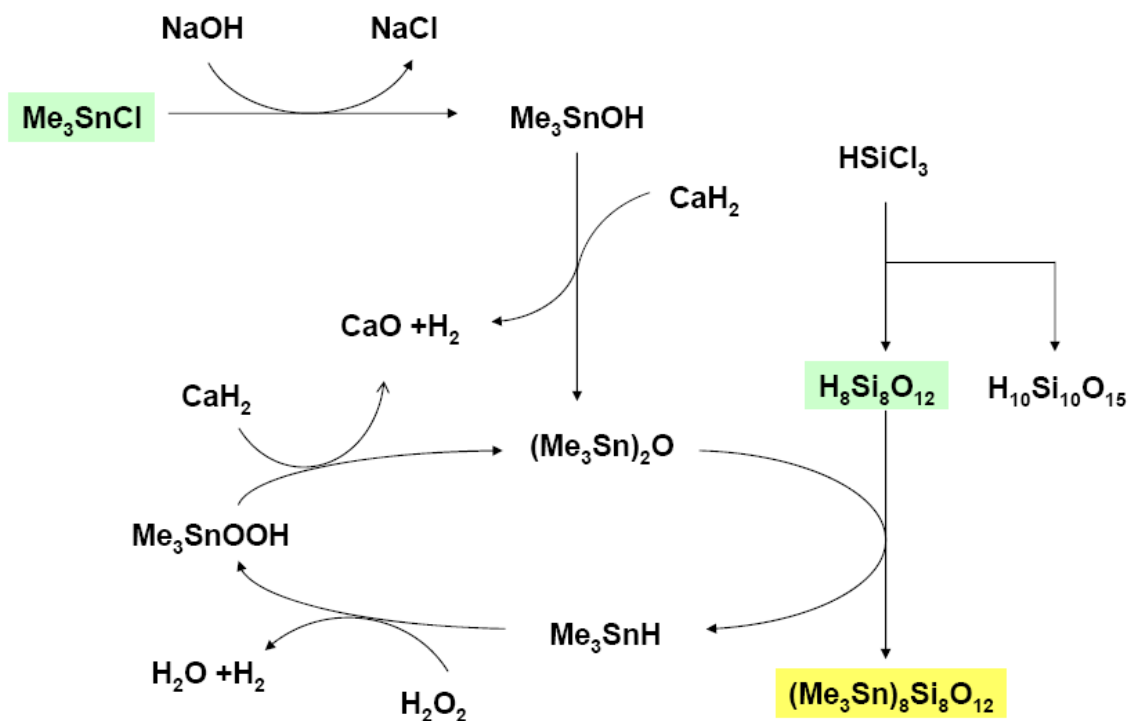


Figure 2 - 1 The procedures of synthesizing and recycling $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

trimethyltin hydride $(\text{CH}_3)_3\text{SnH}$, *bis(trimethyltin) oxide* $((\text{CH}_3)_3\text{Sn})_2\text{O}$, and *trimethyltin peroxide* $(\text{CH}_3)_3\text{SnOOH}$ are volatile and toxic and all of these compounds should also be handled in the fume hood at all times.

Solution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on Varian Mercury 300 MHz spectrometer. ^{29}Si and ^{119}Sn solution NMR spectra were acquired at 9.4 Tesla (400 MHz proton) on a Bruker Avance wide-bore system with micro-imaging accessory spectrometer. Chemical shifts were referenced internally to ^1H NMR δ (C_6D_6): 7.15 ppm; ^{13}C NMR δ (C_6D_6): 128.39 ppm; ^{29}Si δ $(\text{CH}_3)_4\text{Si}$: 0 ppm; and ^{119}Sn δ $(\text{CH}_3)_4\text{Sn}$: 0 ppm.

The single crystal structure of trimethyltin peroxide ((CH₃)₃SnOOH) was determined using a Bruker model AXS Smart 1000 X-ray diffractometer equipped with a CCD area detector with a graphite monochromated Mo source (K α radiation, λ = 0.71073 Å). X-ray intensity data from a colorless needle crystal were measured at -100°C. Raw data frame integration was performed with SAINT 6.02. The data were corrected for absorption effects with SADABS. Direct methods structure solution, difference Fourier calculations and full-matrix least-squares refinement against F² were performed with SHELXTL.

2.2.1 Efficient methodologies of separation H₈Si₈O₁₂ and H₁₀Si₁₀O₁₅

As described above, a mixture of H₈Si₈O₁₂ and H₁₀Si₁₀O₁₅ is obtained from the mother liquid then recrystallized as described by Agaskar's paper.¹¹ A dry sample (~ 10 grams) of this solid was put in a sublimator (Figure 2-2) and heated to 50 ~ 90°C under vacuum.

After several hours of heating, a crude residue consisting of pure H₁₀Si₁₀O₁₅ remained in the bottom of the flask while H₈Si₈O₁₂ and a small amount of H₁₀Si₁₀O₁₅ sublimed onto the cold finger (-10°C). Control of the temperature and the duration of heating determine what ratio of H₈Si₈O₁₂ and H₁₀Si₁₀O₁₅ will be obtained on the cold finger. Collecting the product from the cold finger and subliming this mixture a second time increases the ratio of H₈Si₈O₁₂ to H₁₀Si₁₀O₁₅ on the cold finger. As the ratio of the H₈Si₈O₁₂ and H₁₀Si₁₀O₁₅ reaches 9: 1 or higher, the mixture of H₈Si₈O₁₂ and small amount of H₁₀Si₁₀O₁₅ can be separated



Figure 2 - 2 A picture of the sublimator

successfully by dissolving in hot hexanes and crystallizing in the refrigerator for 24 hours. For large scale mixtures of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (40 ~ 60 grams), the sublimation step was repeated several times until the purity indicated above was reached (checked by ^1H 300 MHz NMR).

The large scale synthetic procedure consumes lots of hexanes in the crystallization step. Recycling hexanes then evaporating all solvent results in some insoluble silica polymer in the mixture of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$. The oligomeric silsequioxanes $(\text{HSiO}_{1.5})_{8-18}$ will slowly form a small amount of insoluble silica polymer in the high concentration solution. A quick and easy way to separate this insoluble silica polymer with the oligomeric silsequioxanes is to heat the dry mixture at 120°C for several hours until all $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$

are sublimed to the cold finger. The nonvolatile polymer and unknown compounds remain in the bottom of the flask.

2.2.2 Improved synthetic methodology of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

Trimethyltin hydroxide, Me_3SnOH , may be prepared by slowly adding a solution of 4.8 g (0.12 moles) of NaOH in 10 mL of deionized water to a solution of 24 g (0.12 moles) of Me_3SnCl in 10 mL of water while stirring (Eq. 2).



A white precipitate immediately formed upon the addition of the NaOH solution. After stirring for three hours, the precipitate was filtered by suction filtration (one hour in air to dry) and transferred to a 250 mL round bottom flask (Figure 2-3) with 100 mL distilled diethyl ether.



Figure 2 - 3 A picture of a 250 mL round bottom flask

The solvent and Me_3SnOH are then frozen with liquid nitrogen and excess (12 g) CaH_2 are added into the flask on the top of the frozen solvent. The solvent is thawed slowly in order to avoid uncontrolled reaction. *Caution: This step is an exothermic reaction and trimethyltin reactant and product are toxic. Be sure to set up the apparatus in the fume hood. If CaH_2 is added to the flask without cooling the solvent, vigorous reaction with residual water and Me_3SnOH will occur which produces large amounts of hydrogen gas and may cause the contents to exit out of the top of the Schlenk vessel.*

The solution was stirred for another 48 hours or longer at room temperature under a nitrogen atmosphere. Complete reaction can be accomplished within 12 hours at higher temperature (50°C). Due to the low boiling point of the diethyl ether, installing a reflux condenser to the round bottom flask (Figure 2-4) for the higher temperature reaction is necessary.



Figure 2 - 4 A picture of a round bottom flask with a condenser



Figure 2 - 5 A Schlenk tube with a fritted funnel

The solution is then quickly filtered in air through a fritted funnel into a Schlenk tube (Figure 2-5) by suction filtration. The product, bis(trimethyltin) oxide, and diethyl ether were filtered into the Schlenk tube and the excess CaH_2 , NaCl from the first step reaction, and byproduct calcium oxide-CaO were isolated by the fritted funnel. The filtered solution was purged with nitrogen as soon as the fritted funnel was removed and kept in the Schlenk tube under a nitrogen atmosphere during the rest of the reaction sequence.

A 2.0 g (4.71 mmol) portion of $\text{H}_8\text{Si}_8\text{O}_{12}$ (62% mole equivalents based on the initial scale of Me_3SnCl) was added to the bis(trimethyltin) oxide solution and stirred for 1 hour. Similar small doses of $\text{H}_8\text{Si}_8\text{O}_{12}$ were added to reaction and the residual bis(trimethyltin) oxide was monitored via ^1H 300 NMR until residual bis(trimethyltin) oxide was less than 3%. The solution was stirred at room

temperature for 1 more hours. After the reaction was complete, solvent and trimethyltin hydride were collected via vacuum transferring and recycled (see section 2.2.3). The white powder was dried at 80°C for 8 hours to remove small amount of unreacted bis(trimethyltin) oxide and obtained 95 ~ 98% pure $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ (yield: 95% based on Me_3SnCl). The resulting white powder was dissolved in boiling hexanes in air and needle shaped crystals formed upon cooling. The crystal $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$ yield was 90% based on Me_3SnCl .

2.2.3 Recycling Me_3SnH and converting to Me_3SnOOH

The reaction of $(\text{Me}_3\text{Sn})_2\text{O}$ with the octahydrido produces eight equivalents of trimethyltin hydride (Me_3SnH) based on the amount of $\text{H}_8\text{Si}_8\text{O}_{12}$ added in the reaction. An excess of 50 wt% H_2O_2 (~2.5-fold equivalents) was added to the solution in air and the beaker was covered with a watch glass to avoid diethyl ether evaporating too fast. After 10 ~ 20 minutes, the H_2O_2 started to react with Me_3SnH vigorously. The reaction was stirred for several hours until the white solid product, Me_3SnOOH , formed and precipitated in the solution. The diethyl ether and byproduct, water, were evaporated at room temperature in air in the fume hood after removing the watch glass. The product contained mostly Me_3SnOOH and small amount of Me_3SnOH . Trimethyltin hydroxide is a byproduct of the reaction due to trimethyltin peroxide and trimethyltin hydroxide can be attributed to a shift in the equilibrium if the system contains water (Eq. 5).

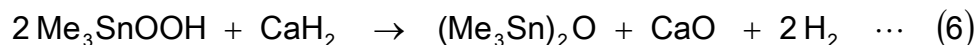


The yield of the reaction is around 80% based on $\text{H}_8\text{Si}_8\text{O}_{12}$. *Caution: Me_3SnOOH is not only toxic but also explosive. Do not sublime or heat the solid product. The white powder is reported to explode at 75°C quite reproducibly.*¹⁷

The precipitate was collected and put in a vial. Part of Me_3SnOOH slowly sublimed to the top of the vial to form crystals. Me_3SnOOH does not appear to be stable for long periods of time (two to three weeks). The yield of the bis(trimethyltin) oxide appear to decrease the longer the peroxide is stored as a solid.

2.2.4 Conversion of Me_3SnOOH to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

The white powder, Me_3SnOOH and small amount of Me_3SnOH , from section 2.2.3 were transferred to a round bottom flask. Diethyl ether solvent was added followed by CaH_2 . *Caution: The crystal structure of Me_3SnOOH shows one water of hydration is formed per molecule of peroxide in the solid. The water molecule react with CaH_2 warns up the solution and speeds up the reaction. Liquid nitrogen may be used to cool the solution intermittently in the first 30 minutes if the hydrogen generate too fast (bubbles come out too fast).* Me_3SnOOH and Me_3SnOH were transformed into $(\text{Me}_3\text{Sn})_2\text{O}$ in the reaction with CaH_2 (Eq 6).



The tin ether produced from the tin hydride may be used following the procedure described in section 2.2.2. The yield was 90% based on Me_3SnOOH .

2.3 Results and Discussion

2.3.1 Separation $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$

The spherosilioxane ($\text{H}_8\text{Si}_8\text{O}_{12}$) was prepared according to the method of Agaskar by controlled hydrolysis of trichlorosilane (HSiCl_3).¹¹ Previous approaches to the purification of octa-spherosilicate, $\text{H}_8\text{Si}_8\text{O}_{12}$, in our research group involved recrystallization of the crude product (the mixture of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$) from hot hexanes. $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is more soluble than $\text{H}_8\text{Si}_8\text{O}_{12}$ in hexanes. The mother liquid and washed hexanes from previous syntheses contained previously $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and a small amount of $\text{H}_8\text{Si}_8\text{O}_{12}$. If a concentrated mixture of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is stored in the air for a long period of time, a small amount of the polyhedral oligomeric silsesquioxane will polymerize and form insoluble compounds. These insoluble compounds can be separated from $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and $\text{H}_8\text{Si}_8\text{O}_{12}$ via sublimation. Transferring a mixture of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$, $\text{H}_8\text{Si}_8\text{O}_{12}$, and insoluble compounds into a sublimator and heating at 120°C for few hours (10 g mixture for 4 ~ 5 hours) under vacuum obtain a pure mixture of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and $\text{H}_8\text{Si}_8\text{O}_{12}$ on the cold finger. The insoluble compounds are unsublimable and remain in the bottom of the sublimator. The different ratios

of pure mixtures of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and $\text{H}_8\text{Si}_8\text{O}_{12}$ can be separated further in the following discussion.

Efficient methodologies for the separation $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ without insoluble compounds described above can be divided into three parts. *Part I:* When the ratio of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ is higher than 6 : 4 ($\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is more than 60% and $\text{H}_8\text{Si}_8\text{O}_{12}$ is less than 40%): The mixture can be separated efficiently via sublimation at 50°C to 90°C and obtain 97 ~ 100% pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ in the bottom of the sublimator. *Part II:* When the ratios of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ are between 6 : 4 and 2 : 8 ($\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is 60% to 20% and $\text{H}_8\text{Si}_8\text{O}_{12}$ is 40% to 80%): The mixture can be washed with hexanes. The hexane solution will contain higher ratios of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and the undissolved solid will contain higher ratios of $\text{H}_8\text{Si}_8\text{O}_{12}$. *Part III:* When the ratio of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ is lower than 2 : 8 ($\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is less than 20% and $\text{H}_8\text{Si}_8\text{O}_{12}$ is higher than 80%): The mixture can be separated via crystallization in hexanes and obtain pure $\text{H}_8\text{Si}_8\text{O}_{12}$ crystals (Figure 2-6).

Part I: Subliming the mixture of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ at higher temperature shortens the time to remove all of the $\text{H}_8\text{Si}_8\text{O}_{12}$ and obtains pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ in the bottom of the sublimator. More $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ accompanied with $\text{H}_8\text{Si}_8\text{O}_{12}$ are sublimed onto the cold finger at higher temperature during the same time. Adjusting the temperature and sublimation time (see below) are very important to optimize the separation of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and $\text{H}_8\text{Si}_8\text{O}_{12}$ and avoid too

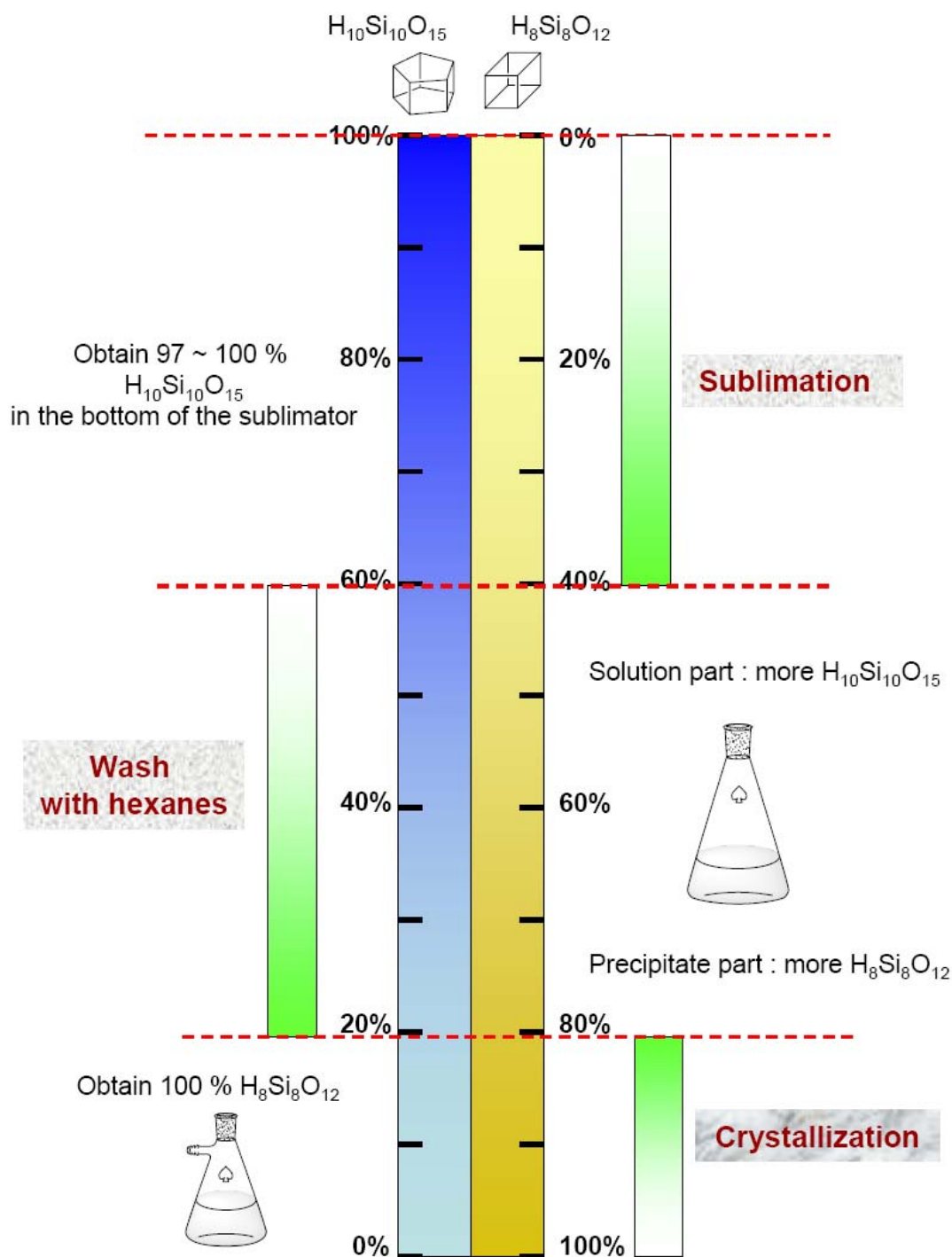


Figure 2 - 6 Overall purification scheme of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ and $\text{H}_8\text{Si}_8\text{O}_{12}$

much $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ being sublimed onto the cold finger before removing all of the $\text{H}_8\text{Si}_8\text{O}_{12}$ from the mixture.

As the amount of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ in the mixture (for 20 grams scale) increases above 85%, pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is obtained after subliming the mixture at 50°C for 12 to 48 hours. For higher ratios of $\text{H}_8\text{Si}_8\text{O}_{12}$ longer sublimation times will be needed. All of the $\text{H}_8\text{Si}_8\text{O}_{12}$ are sublimed onto the cold finger mixing with a small amount of the $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$. The white powder that remains in the bottom of the sublimator is pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$. If the ratio of the $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is around 70~85%, pure $\text{H}_8\text{Si}_8\text{O}_{12}$ with a small amount of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is obtained on cold finger at 80°C in 12 to 24 hours and pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is obtained in the bottom of the sublimator. As the ratios of the $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ decrease to 60 ~ 70%, all of the $\text{H}_8\text{Si}_8\text{O}_{12}$ in the mixture can be sublimed onto the cold finger at 90°C after 6 to 24 hours (Figure 2-7).

Part II: When the ratio of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ is between 6 : 4 and 4 : 6, washing the mixtures with hexanes initially is a efficient method to separate the mixture roughly and obtain higher ratios of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ in the solution part and $\text{H}_8\text{Si}_8\text{O}_{12}$ in the precipitate part. For a 20 gram scale, stirring the mixture in 500 ml hexanes for 30 mintues then filtering the solution gives approximately 70% $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ in the solution part. The components in the solution can be separated further via sublimation procedure described in the part I. The undissolved residue contains around 85% $\text{H}_8\text{Si}_8\text{O}_{12}$ and can be purified further via crystallization (Figure 2-8). When the ratio of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ to $\text{H}_8\text{Si}_8\text{O}_{12}$ is between

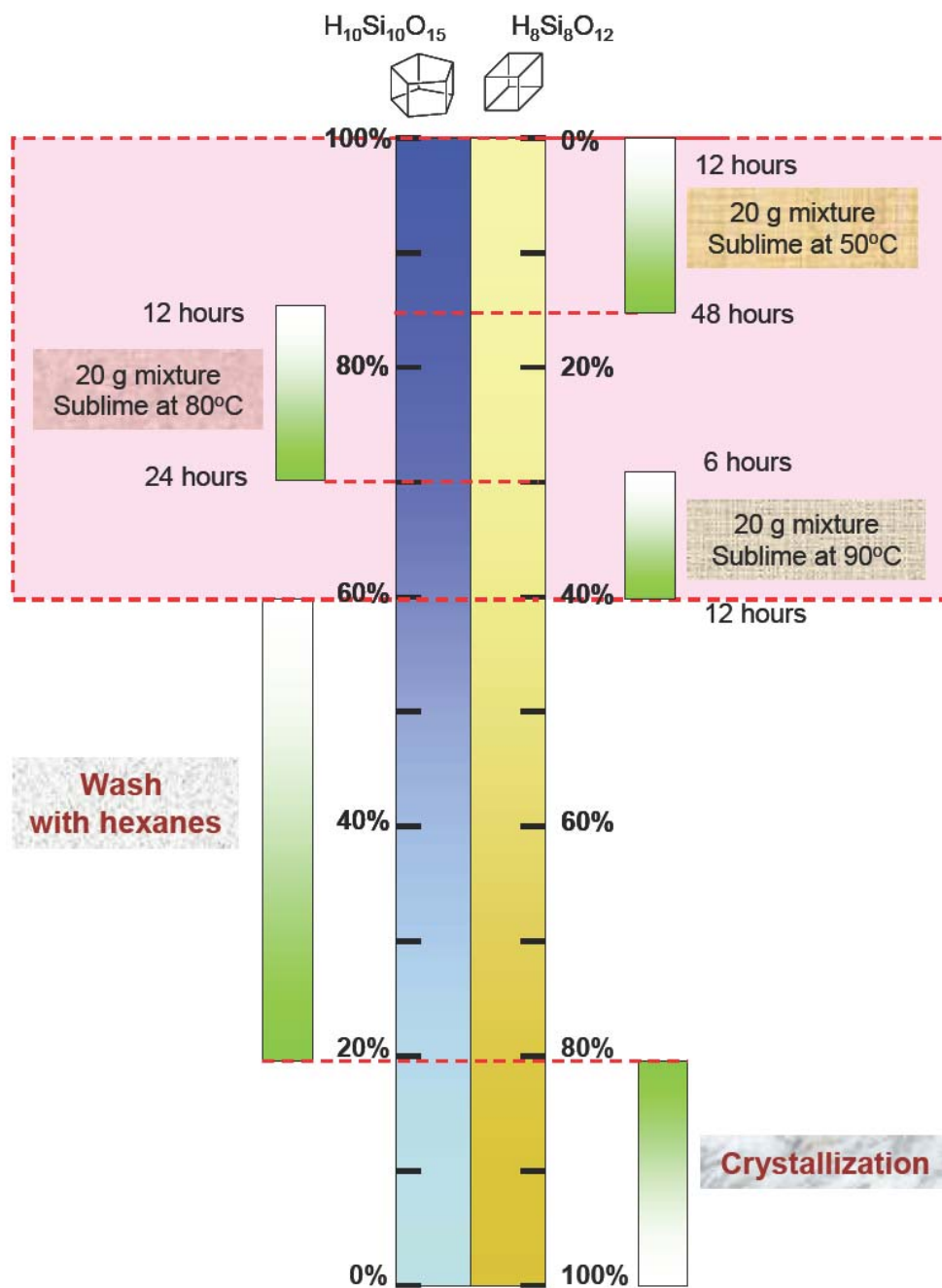


Figure 2 - 7 Sublimation of the mixture of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (60-100%) and $\text{H}_8\text{Si}_8\text{O}_{12}$ (0-40%)

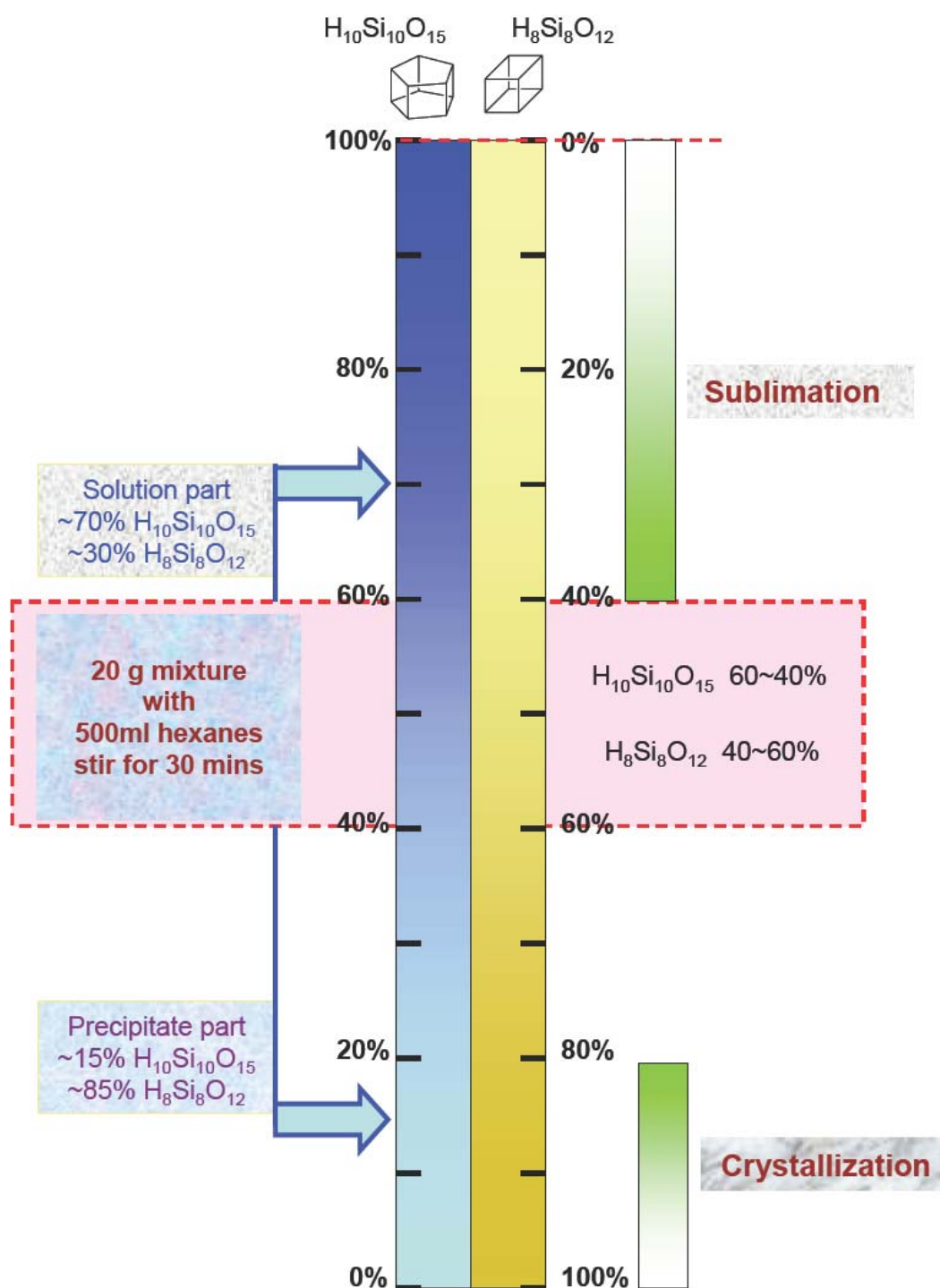


Figure 2 - 8 Separation of $H_{10}Si_{10}O_{15}$ (40-60%) and $H_8Si_8O_{12}$ (60-40%)

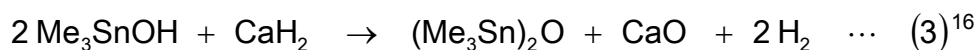
4 : 6 and 2 : 8, around 80% $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ is obtained in hexane the solution via the same washing procedure described above. The precipitate part contains around 90% $\text{H}_8\text{Si}_8\text{O}_{12}$ and can also be purified further via crystallization. (Figure 2-9)

Part III: When the ratios of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ are higher then 8 to 2, pure $\text{H}_8\text{Si}_8\text{O}_{12}$ are obtained after crystallizing from hexanes solution. For a 10 gram mixture of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (ratio is 8 : 2), 800 ml hot hexanes are used to dissolve the mixture and crystallize $\text{H}_8\text{Si}_8\text{O}_{12}$ from the solution. The amount of the hexanes decreases gradually from 800 ml to 400 ml while the mixture contains $\text{H}_8\text{Si}_8\text{O}_{12}$ increasing from 80% to 100%. (Figure 2-10)

2.3.2 Improved synthesis of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

The reaction procedures described in the literature were simplified to achieve a significant improvement in the synthesis of the tin cube, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. Additionally, contact with any tin compounds was minimized.

The traditional synthetic methodology involves reacting Me_3SnCl with NaCl in water solution following by subliming the product to remove byproduct NaCl to obtain pure Me_3SnOH (Eq. 2). The pure and dry trimethyltin hydroxide then transferred to a Schlenk tube and reacted with CaH_2 in toluene or benzene. (Eq. 3)



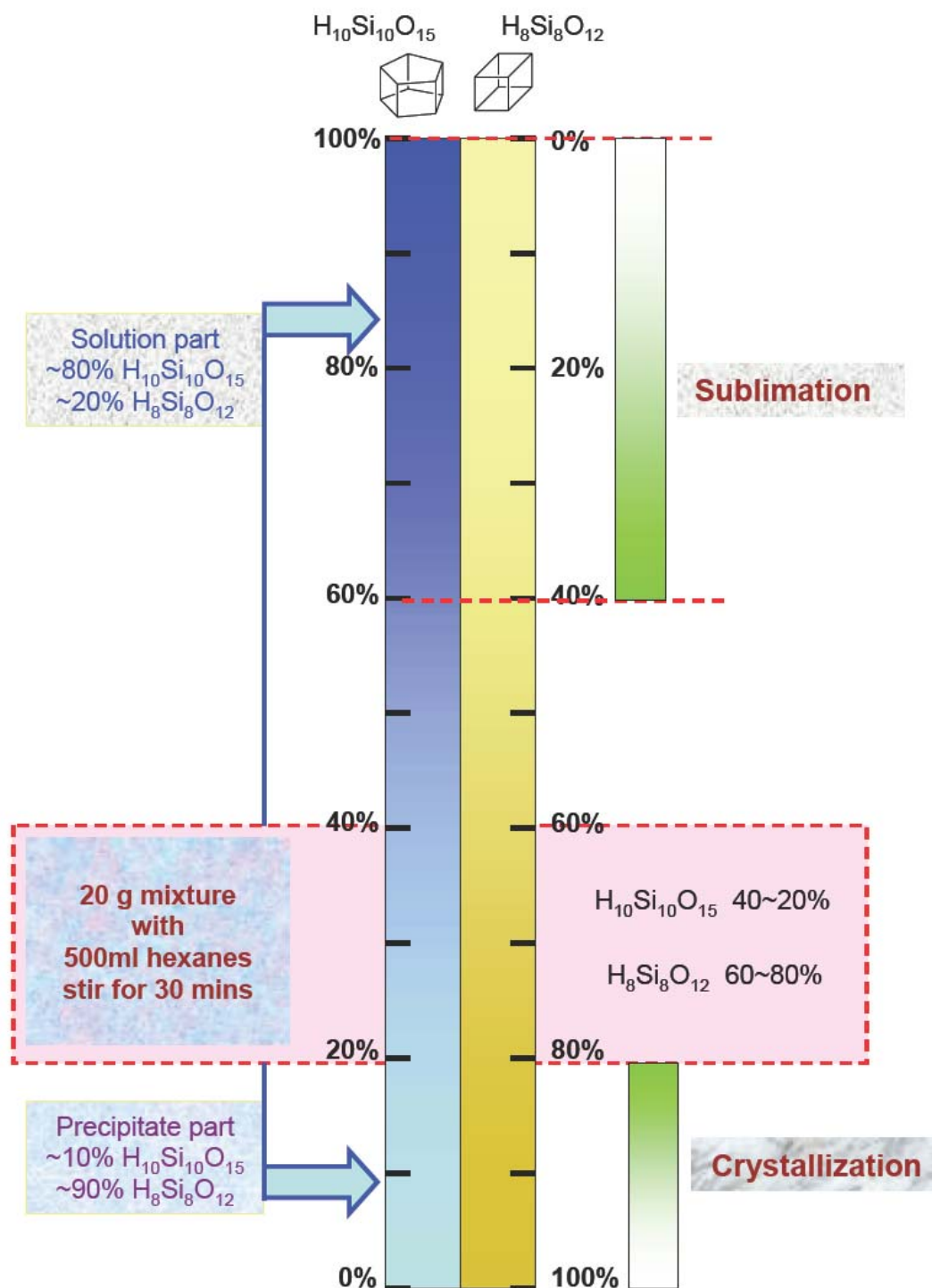


Figure 2 - 9 Separation of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (20-40%) and $\text{H}_8\text{Si}_8\text{O}_{12}$ (80-60%)

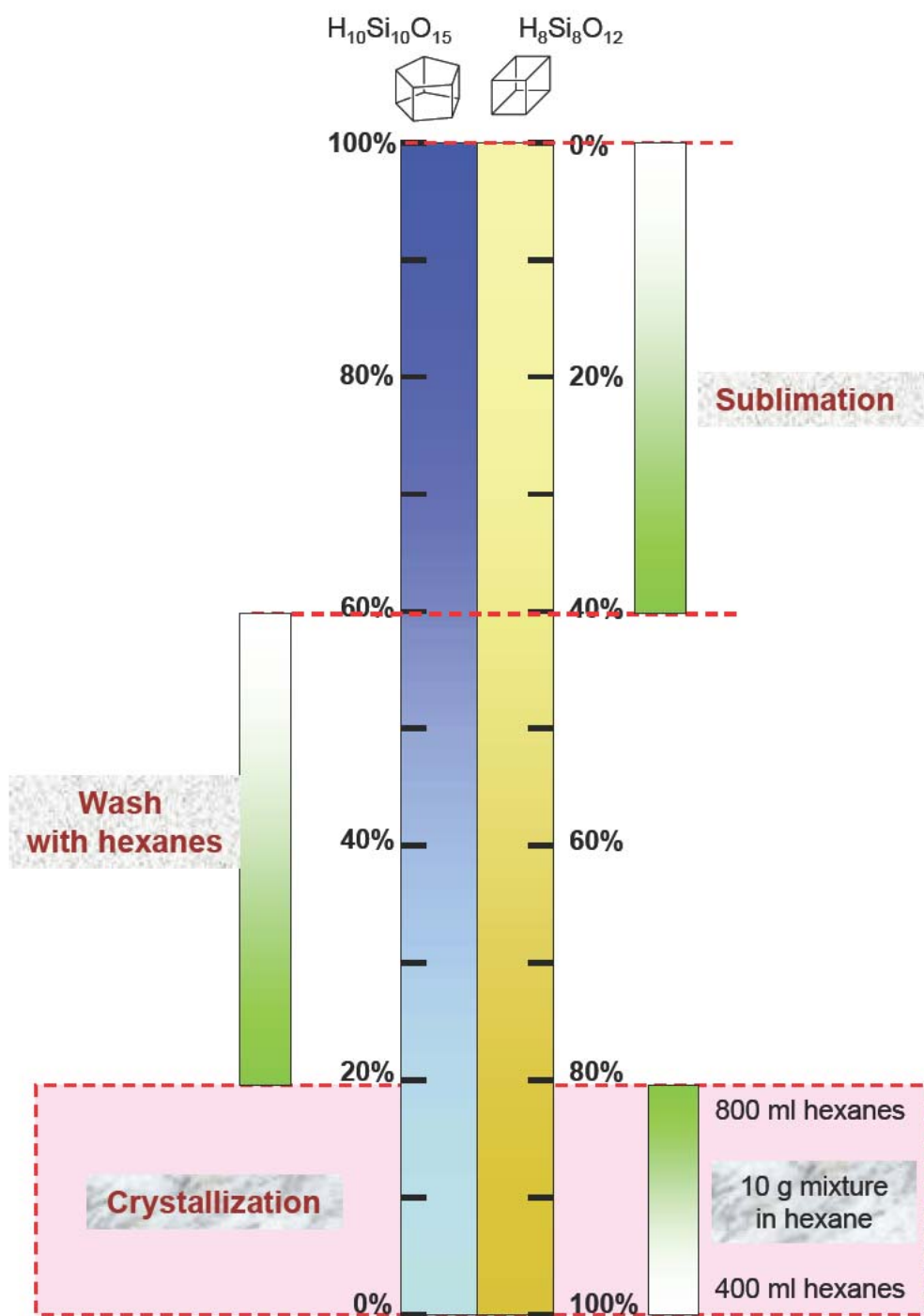


Figure 2 - 10 Crystallization of $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (0-20%) and $\text{H}_8\text{Si}_8\text{O}_{12}$ (100-80%)

The apparatus was set up under nitrogen instead of in the air because the bis(trimethyltin) oxide, $(\text{Me}_3\text{Sn})_2\text{O}$, is moisture sensitive. When the hydroxide reacts completely with CaH_2 , the product, $(\text{Me}_3\text{Sn})_2\text{O}$, was vapor transferred to another Schlenk tube via the freeze-thaw-degas method. A disadvantage of this procedure is that degassing and vapor transferring processes always requires several hours (more than 3 hours). Vapor transferring the product, $(\text{Me}_3\text{Sn})_2\text{O}$, also requires very good vacuum (pressure < 50 milli-torr). Warming up the solution to 90°C or higher temperature speeds up the vapor transferring process but an unknown white powder or crystals form in the T glass tube occasionally and the yield of the $(\text{Me}_3\text{Sn})_2\text{O}$ decreases significantly.

My first discovery in optimizing this procedure is that the byproduct, NaCl , doesn't affect reactions that follow. The crude product mixture from reaction in equation 1 reacts with CaH_2 directly in the Schlenk tube without sublimation to give the ether in high yield (Eq. 7).

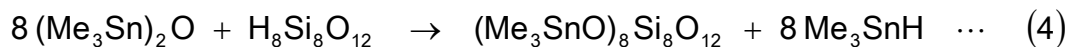


The reaction was stirred vigorously for 48 hours or longer at room temperature under a nitrogen atmosphere. Different solvents such as methylene chloride, diethyl ether, benzene, and toluene have been used and tested in this reaction. Similar yields of the final product indicate that different solvents don't affect the reaction. Another reaction parameter that was investigated is to change the temperature of the reaction. Complete reaction can also be

accomplished within 12 hours at 50°C in the diethyl ether or 6 hours at 80°C in toluene. In order to recycle the trimethyltin hydride, Me₃SnH, in the final step, the diethyl ether with a low boiling point is a better solvent. This step will be discussed in section 2.2.4 in more detail.

My second discovery is that pure (Me₃Sn)₂O can be obtained via brief suction filtration with a fritted funnel and quick washing with additional diethyl ether. The clean solution with pure (Me₃Sn)₂O was collected in a Schlenk tube after filtration. Excess CaH₂, byproduct-calcium oxide, and NaCl are trapped in the fritted funnel. This procedure should be done as quickly as possible and only take about THREE MINUTES. The Schlenk tube should be purged with nitrogen immediately after filtration. *Caution: If the reaction hasn't proceeded to completion, a product solution tends to form a gel with excess CaH₂ that slowly clogs the fritted funnel. The (Me₃Sn)₂O will then be exposed to air and will slowly decompose.*

The sphaerosilicate-H₈Si₈O₁₂ can then added to the solution and reacted with (Me₃Sn)₂O immediately. This reaction was complete within 30 minutes and produced the final product (Me₃Sn)₈Si₈O₂₀ (Eq. 4). The solvent with byproduct, Me₃SnH, was recycled and pure (Me₃Sn)₈Si₈O₂₀ will be obtained after crystallizing from hexanes solution.



In the reaction of the octahydrido with the tin ether, if the reaction isn't complete or if the amount of $\text{H}_8\text{Si}_8\text{O}_{12}$ in the reaction is overshoot, a signal consistent with unreacted hydrogen on sphaerosilicate- $\text{H}_8\text{Si}_8\text{O}_{12}$ will be observed in the NMR spectra with a different chemical shift than the starting octahydrido. The singlet peak of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ at 0.360 ppm will also be replaced by several peaks in same range because the product, $(\text{Me}_3\text{SnO})_x\text{H}_{(8-x)}\text{Si}_8\text{O}_{12}$, has a distribution of trimethyltin groups and hydrogen groups. The chemical shift of residual hydrogens on the $(\text{Me}_3\text{SnO})_x\text{H}_{(8-x)}\text{Si}_8\text{O}_{12}$ moves down field from 4.19 ppm to 4.69 ppm in C_6D_6 (Figure 2-11). The product from incomplete reaction is also stable in the air. It can be stored in the Schlenk vessel and reacted with more $(\text{Me}_3\text{Sn})_2\text{O}$ again to obtain pure final product, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$.

To summarize the improvements that have been made through this synthetic methodology, the total yield of the sequence reaction is greater than 90% based on the amount of trimethyltin chloride initially used. Skipping the sublimation process increases the yield and saves time. Different solvents in the reaction don't affect the results. The reaction process of synthesizing $(\text{Me}_3\text{Sn})_2\text{O}$ also can be reduced from 2 days to several hours if the reaction temperature is risen from room temperature to 50°C or higher. Shortening the reaction time and producing higher yield product are significant progress in this synthetic methodology. Doubling the scale of the reaction produces equally highly yield product but the reaction time needs to be increased about 50% in each step. This improved

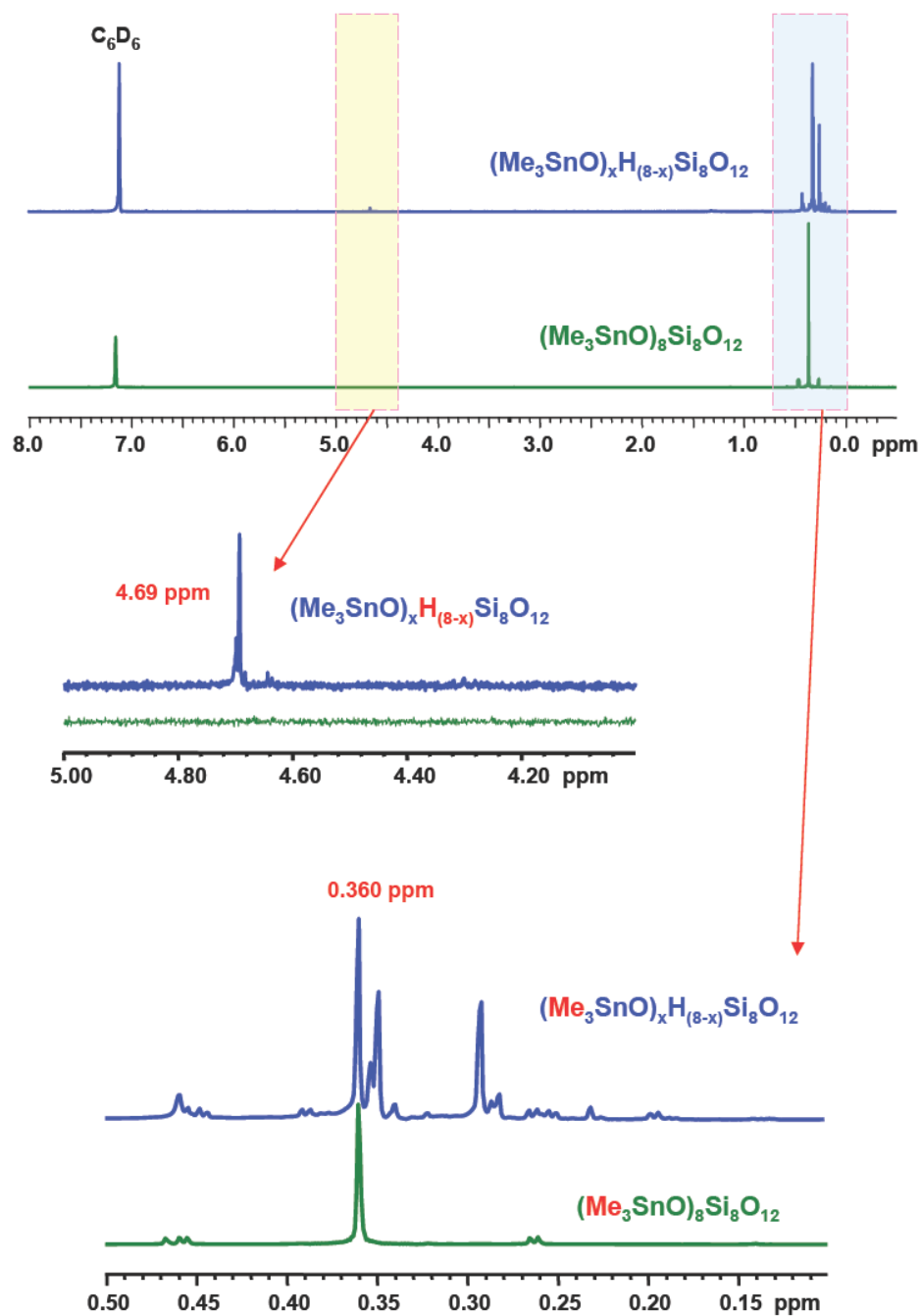
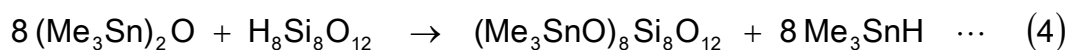


Figure 2 - 11 NMR spectra of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ and $(\text{Me}_3\text{SnO})_x\text{H}_{(8-x)}\text{Si}_8\text{O}_{12}$

synthetic methodology also helps us deal with toxic tin compounds and produces product efficiently.

2.3.3 Recycling byproduct Me₃SnH and converting to Me₃SnOOH

As described in the previous section, reaction of the sphereosilicates-H₈Si₈O₁₂ with the trimethyltin ether, (Me₃Sn)₂O, gives the trimethyltin cube (Me₃SnO)₈Si₈O₁₂. Half of the trimethyltin groups in (Me₃Sn)₂O are converted to the byproduct trimethyltin hydride, Me₃SnH (Eq 4).



In previous synthetic processes, this toxic byproduct goes to waste without recycling. Due to the fact that trimethyltin complexes are extremely toxic and the starting material, trimethyltin chloride, is very expensive, it was deemed worthwhile to explore ways to recycle trimethyltin hydride. Two approaches I have investigated as quick and efficient procedures for recycling the trimethyltin hydride are described below. One was successful and the other not.

The first involved reacting trimethyltin hydride (Me₃SnH) with I₂ and attempting to obtain Me₃SnI. The reaction of Me₃SnH with iodine was not successful. I didn't obtain desired product-Me₃SnI clearly after mixing stoichiometric amounts of (Me₃SnH) and I₂.

The second approach involved reacting trimethyltin hydride (Me₃SnH) with hydrogen peroxide. I found out the Me₃SnH can be converted to a white powder

when reacted with 30% H_2O_2 in a CH_2Cl_2 solution. When toluene was used as the solvent, the yield of white powder was lower. Our first guess as to the identification of the white product was trimethyltin hydroxide. After storing the white powder in a sealed small vial for one week, needle crystals were observed to have sublimed above the solid. An X-ray crystal structure determination was successful.

The crystal structure indicates that the white product is trimethyltin hydroperoxide (Me_3SnOOH) not that trimethyltin hydroxide, Me_3SnOH . Replacing 30% H_2O_2 with 50% H_2O_2 and choosing diethyl ether as the solvent increase the yield from 10% to 70%. The reaction in diethyl ether solution with 50% H_2O_2 is very slow for the first 10 minutes. Then a gas is observed to form and a white precipitate subsequently forms. Cooling the solution intermittently and covering the beaker with a watch glass prevents Me_3SnH from evaporating with diethyl ether in the beginning of the reaction and the yield increases (80%~85%).

The Me_3SnOOH was stored briefly in a vial (several days to week) and can be used as a replacement for Me_3SnOH in the previously described synthesis of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. Reducing the amount of waste toxic trimethyltin compounds is important from a green chemistry perspective. This development of a way to recycling Me_3SnH is important in our research project. All of Me_3Sn source can be utilized more efficiently in synthesizing $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ and the procedures to recycle byproduct are extremely simple and efficient.

2.3.4 Single crystal X-ray structure of Me₃SnOOH

Two different tin hydroperoxide compounds, trimethyltin hydroperoxide and triphenyltin hydroperoxide, have been synthesized and described in a 1965 publication from Ralph L. Dannley's group.¹⁷ Both of these compounds were synthesized from the tin hydroxide and structures of these hydroperoxide compounds have not been characterized.

From my investigation of recycling trimethyltin hydride, the trimethyltin hydroperoxide can be synthesized not only from tin hydroxide but also from tin hydride. The crystal structure of the trimethyltin hydroperoxide is a good example to compare the coordination environment with different trialkyltin hydroxide or triorganotin halides.¹⁸⁻²⁰ The crystal structure of trimethyltin hydroxide was reported in 1965.²¹ The structure of trimethyltin hydroxide consists of chains of trimethyltin groups and hydroxyl groups arranged alternately along the tin center. The trimethyltin group is nearly planar and oxygen atom lies on the axis between two tin atoms. Other trimethyltin compounds such as trimethyltin chloride¹⁹, triphenyltin fluoride²⁰, and [(Me₃Sn{ μ -(MeSO₂)₂N}Me₃Sn(μ -OH))]_n²² also have the similar linear or zigzag structures. These structures with five coordinate tin are the distinguishing feature of many trimethyltin compounds.

The "structure" of trimethyltin hydroperoxide is not like trimethyltin or triphenyltin hydroxide²³ which form linear polymers. It is a monomer with three different pairs of hydrogen bonds between molecules. But all of these tin compounds are bonded by two oxygen atoms with covalent bonds or weak Van

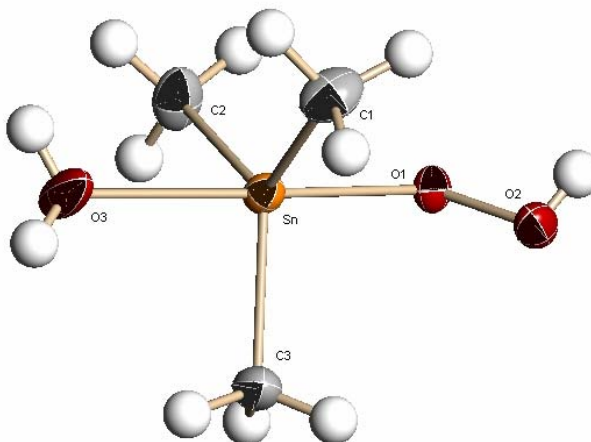


Figure 2 - 12 The crystal structure of $\text{Me}_3\text{SnOOH}\cdot\text{H}_2\text{O}$

der Waals forces and form a penta-coordinated tin center. The structure of an individual Me_3SnOOH molecule plus water is shown in Figure 2-12.

This compound consists of three methyl groups, one peroxide group and one water molecule. The geometry of groups bound to the tin atom form a distorted trigonal bipyramidal structure. The internuclear distance between water oxygen (O_3) and tin atom ($\text{Sn}-\text{O}_3$) is 2.361 Å. The bond distance between the peroxide and tin ($\text{Sn}-\text{O}_1$) is 2.167 Å. It is obvious the interaction between tin atom and water oxygen is weaker than interaction between tin and peroxide. The bond between peroxide and tin is a covalent bond and the bond between water and tin is a dative bond. Comparing the Sn-O bond length with other five-coordinated tin compounds, the Sn-O covalent bond of triethyltin hydroxide is 2.156(4) Å and triphenyltin hydroxide is 2.197(5) Å. The $\text{O}\rightarrow\text{Sn}$ dative bonds between oxygen and tin of triethyltin hydroxide (2.224 Å) and triphenyltin

hydroxide (2.255(5) Å) are shorter than that of trimethyltin hydroperoxide (2.361 Å). (Table 2-1) Therefore the interaction between water and tin is weaker than the interaction between hydroxide and tin.

There are three different pairs of intermolecular hydrogen bonds in the crystal. The hydrogen bond between the water molecule and the oxygen 1 in the peroxide is 1.883 Å. The hydrogen bond between water and the terminal oxygen of the peroxide is 1.987 Å (Figure 2-13). There is another pair of hydrogen bonds between peroxide with a distance 1.989 Å (Figure 2-14). These hydrogen bonds elongate the bond length between water molecule and tin center.

2.3.5 Conversion of Me_3SnOOH to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

Both of trimethyltin hydroxide and trimethyltin hydroperoxide can be transformed into $(\text{Me}_3\text{Sn})_2\text{O}$ in the reaction with CaH_2 . Due to the explosive nature of hydroperoxide compounds, trimethyltin hydroperoxide can't be purified

Table 2 - 1 Sn-O bond lengths

	Sn-O (Å)	O→Sn (Å)	O-Sn-O (Å)	Ref.
Et_3SnOH	2.156	2.244	177.9 (2)	24
Ph_3SnOH	2.197 (5)	2.255 (5)	177.6 (3)	25
Me_3SnOOH	2.167 (2)	2.361(3)	171.81 (9)	this work

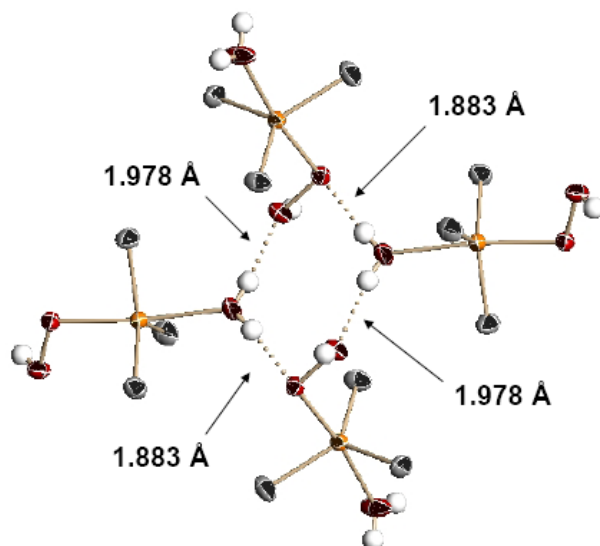


Figure 2 - 13 Hydrogen bonds in Me_3SnOOH molecule

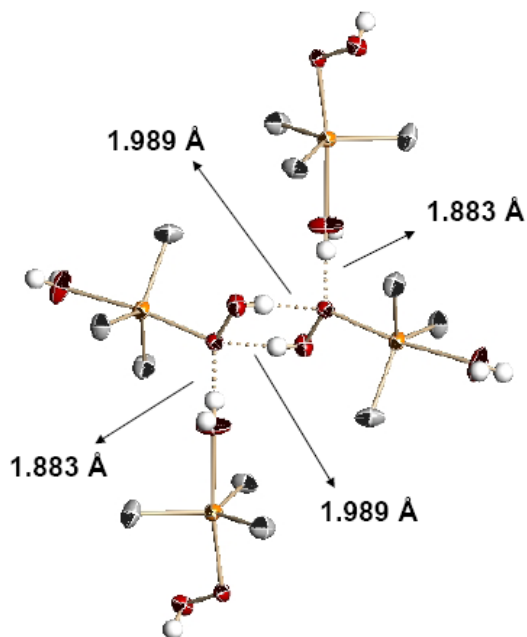


Figure 2 - 14 Other hydrogen bonds in Me_3SnOOH molecule

via high temperature sublimation. The residual water and water molecule bonds with trimethyltin hydroperoxide consume extra CaH_2 in the reaction. Hydrogen comes out vigorously for the first thirty minutes and it is important to cool the flask intermittently in the first half hour of the reaction. The reaction is complete within 12 hours at room temperature because the hydroperoxide compound is more reactive than hydroxide. After the reaction is finished, the same procedure as described in the 2.2.3 may be followed to obtain $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. Utilizing Me_3SnOOH to synthesize $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ successfully proves Me_3SnOOH can be converted to tin ether as Me_3SnOH . All of the trimethyl compound will be used efficient and the recycling procedure is simple and easy to be handled.

2.4 Summary and conclusions

Several efficient methodologies of preparing and purifying functional sphaerosilicate building block molecules have been explored. The ultraviolet inactive compounds, $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$, can be separated successfully via sublimation, washing with hexanes and crystallization in a large scale. Pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ separated from $\text{H}_8\text{Si}_8\text{O}_{12}$ can also be used as another new building block for the further reaction. The Improved synthetic methodology of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ not only save a lot of time through whole synthetic process but also increases the total yield of the reaction. How to deal with the toxic and expensive trimethyltin complexes is a challenging issue during these synthetic processes. Exploring a simple methodology to recycle trimethyltin hydride and

convert it to trimethyltin hydroperoxide is an important milestone in this research project. The crystal structure of Me_3SnOOH also provides another example of five coordinated tin compounds and can be compared with different trialkyltin complexes. The discoveries of reducing reaction steps, avoiding exposing ourselves to trimethyltin compounds and recycling trimethyltin compounds will be great achievement in green chemistry.

Chapter 3

Single site and site isolated vanadium (IV and V) complexes on Si_8O_{20} -based building block solids

3.1 Introduction

Silica supported vanadium complexes have recently attracted interest as catalysts for a variety of selective oxidation reactions.²⁶⁻³⁴ Although many strategies have been developed for incorporating vanadyl species on silica surfaces, controlling vanadium dispersion and loading while simultaneously producing single site catalysts remains a challenging goal for catalysis scientists.

In this chapter, a simple strategy will be described for producing single site, site isolated vanadyl and vanadium (+4) species in which not only the connectivity to the support may be varied by design but also the local surface structure around the vanadium is controlled. The main elements of the strategy involve construction of the support from silicate building blocks and a combination of linking groups that both hold the matrix together and become the catalytically active sites. Sequential dosing and changing of the stoichiometry lead to catalysts in which the site identity and the connectivity to the support can be controlled. The specific system that will be described involves the reactions of vanadium in oxidation states +4 and +5 with the tin functionalized spherosilicate cube, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. The physico-chemical properties of these vanadyl containing materials were characterized by gravimetric analysis, atomic

absorption/emission spectroscopy, solid state ^{51}V , ^{29}Si MAS-NMR, and surface area analysis.

3.1.1 “Embedded” vanadium complexes

The main goal of this research project is to prepare V-SiO₂ catalysts with atomically dispersed single vanadium atom centers which are isolated from one another in the silicate matrices. The fundamental reaction used to synthesize silicate matrices has been described in J. Clark’s thesis.³⁵ Reacting the (Me₃SnO)₈Si₈O₁₂ building block with a limiting amount of vanadyl trichloride (VOCl₃) results in exclusively three-connected vanadium (V) centers bound to silicate cubes. A similar synthetic procedure using limiting amount vanadium tetrachloride (VCl₄) as the vanadium source will result in all 4-connected vanadium (IV) centers bound to silicate cubes. These products contain “embedded” vanadyl or vanadium oligomeric species because each vanadium center is bound to the maximum number of Si₈O₁₂ building blocks which is determined by the original number of chloride ligands on the initial vanadium reagent. Figure 3-1 is an illustration describing embedded vanadyl oligomeric species that contain isolated vanadyl centers and Figure 3-2 shows an embedded vanadium (IV) oligomeric species that has isolated vanadium (IV) centers.

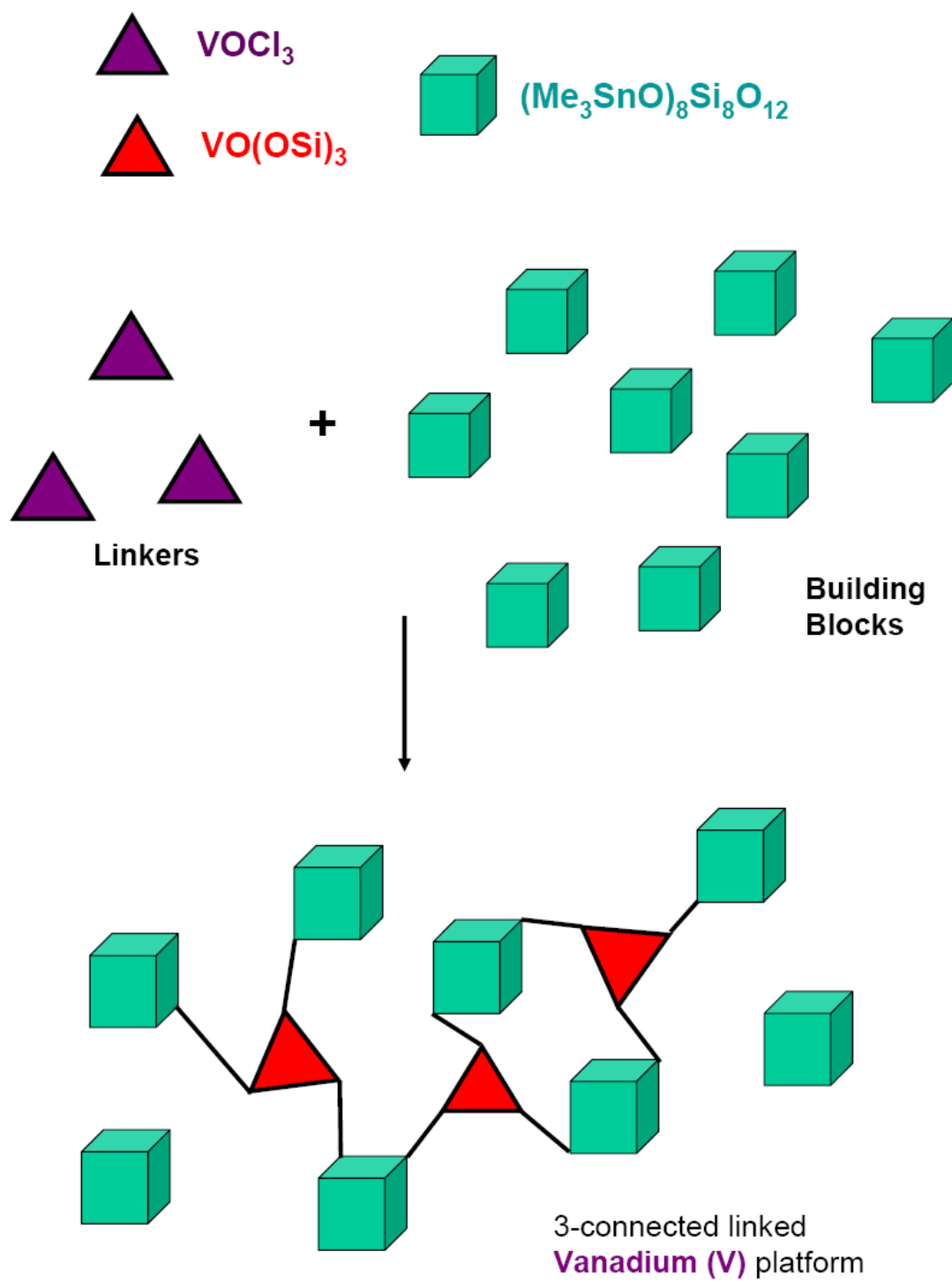


Figure 3 - 1 Three-connected vanadium (V) material

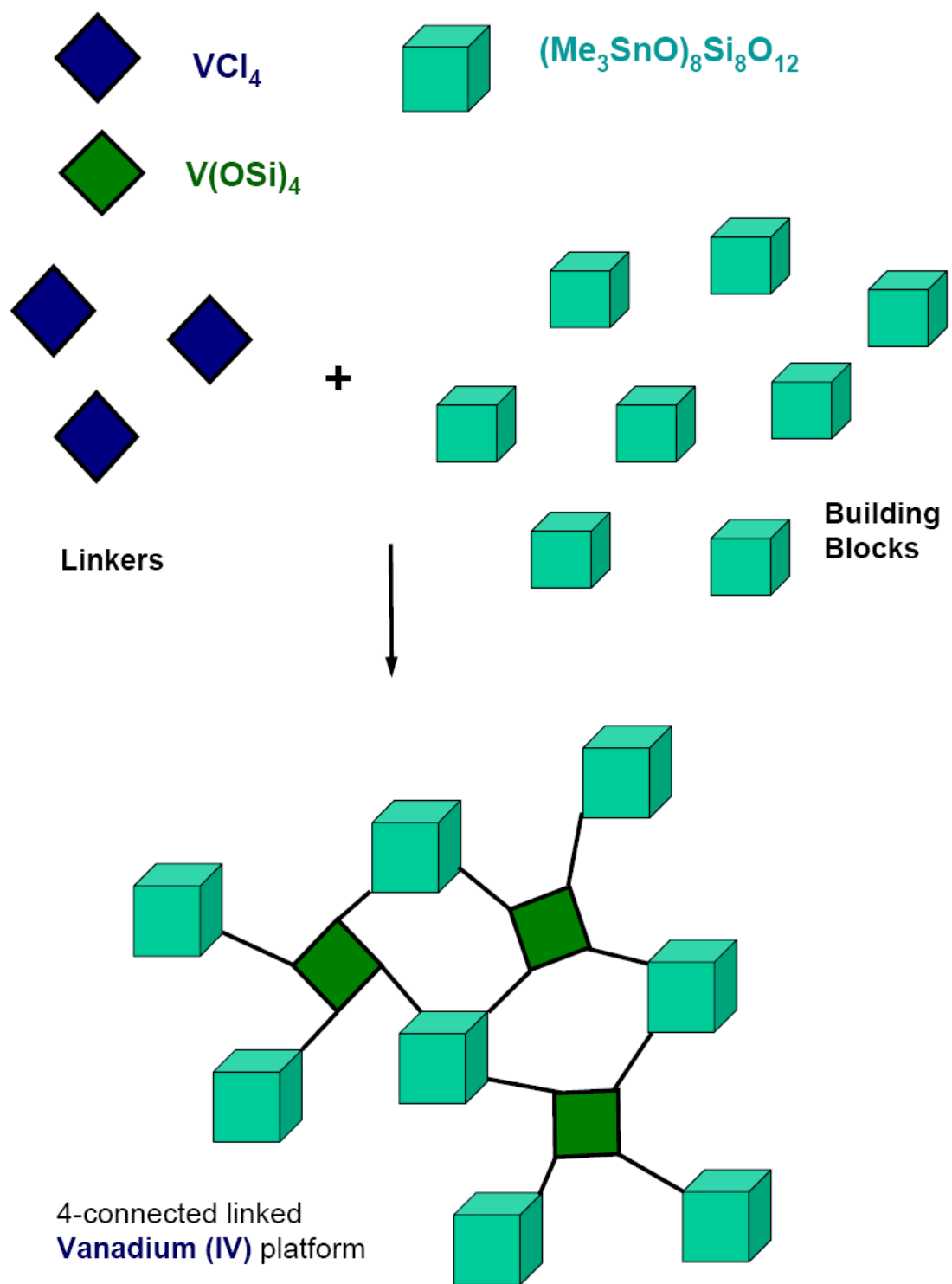


Figure 3 - 2 A Four-connected vanadium (IV) material

3.1.2 “Surface” vanadium complexes

Tailoring the matrix via different methods of sequential additions is the main technique used to vary the connectivity of either vanadium (IV) or vanadyl (V) to the Si_8O_{12} building block in the final matrix. Silicon tetrachloride (SiCl_4) is the first linking reagent that is reacted with a limiting amount of $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ to yield a silicate building block platform. This type of “synthetic silica” must have some unreacted trimethyltin groups left in the matrix. Treating this material with an excess VOCl_3 or VCl_4 should result in only 1-connected vanadyl or vanadium centers on the matrix. These products are referred to as “surface” vanadium catalysts because each vanadium center only has one V-O-Si bond linking it to the matrix. Figures 3-3 and 3-4 illustrate how to obtain the cross-linked silicate platform in the first step then react it with VOCl_3 or VCl_4 to obtain “surface” vanadium products.

The main purpose of synthesizing “embedded “ and “surface” catalysts is to compare how changes in connectivity to the matrix influence the stability, selectivity, and catalytic activity of different types of materials. Another advantage of using the building block strategy is that a higher weight percentage of catalytic centers in the silicate matrix is achievable while maintaining atomic dispersion on the support. Different reaction times, temperatures, and solvents have been investigated. Varying the loading ratios of the VOCl_3 and VCl_4 in the reaction will also be described in the following sections.

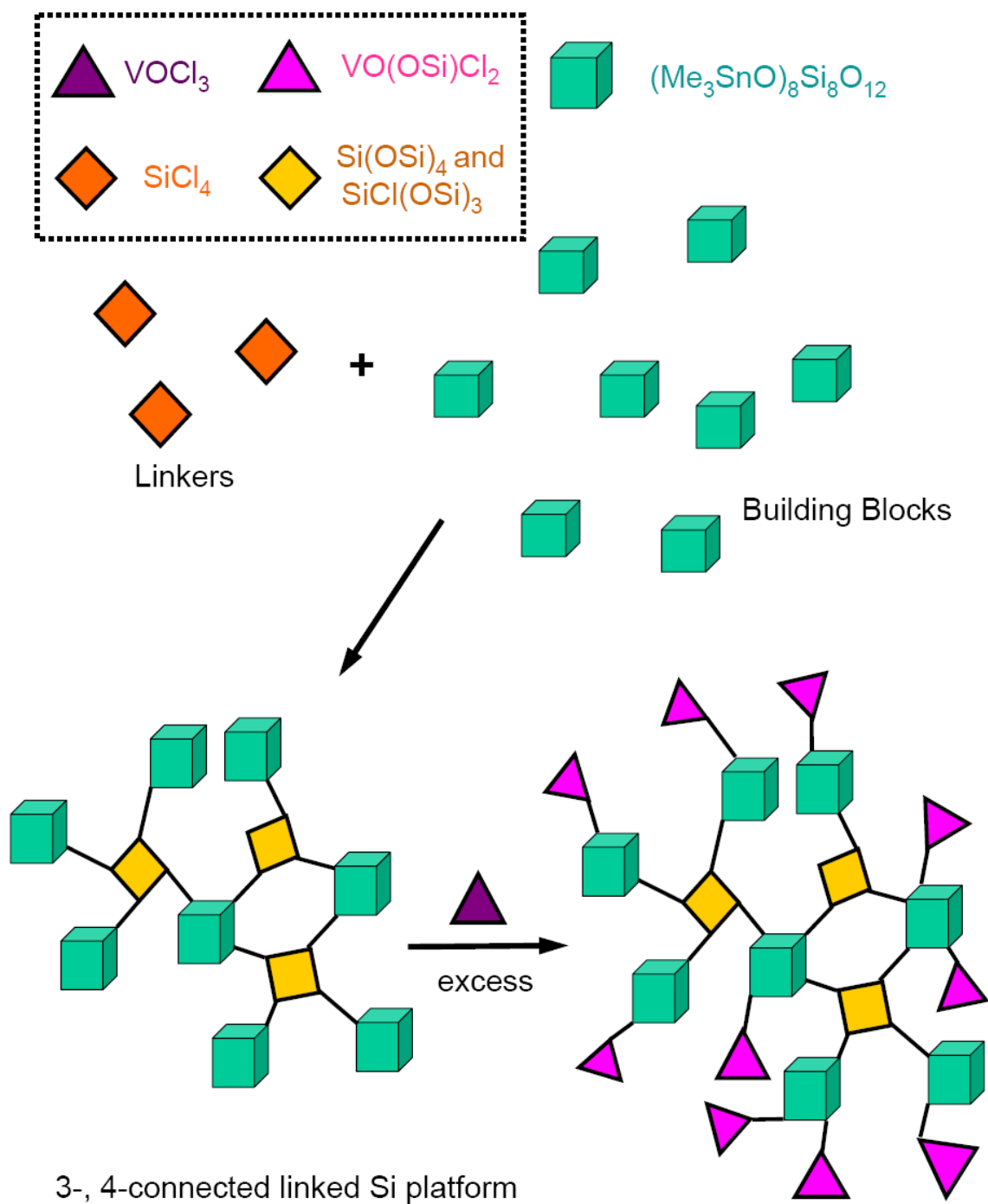


Figure 3 - 3 Surface vanadyl material

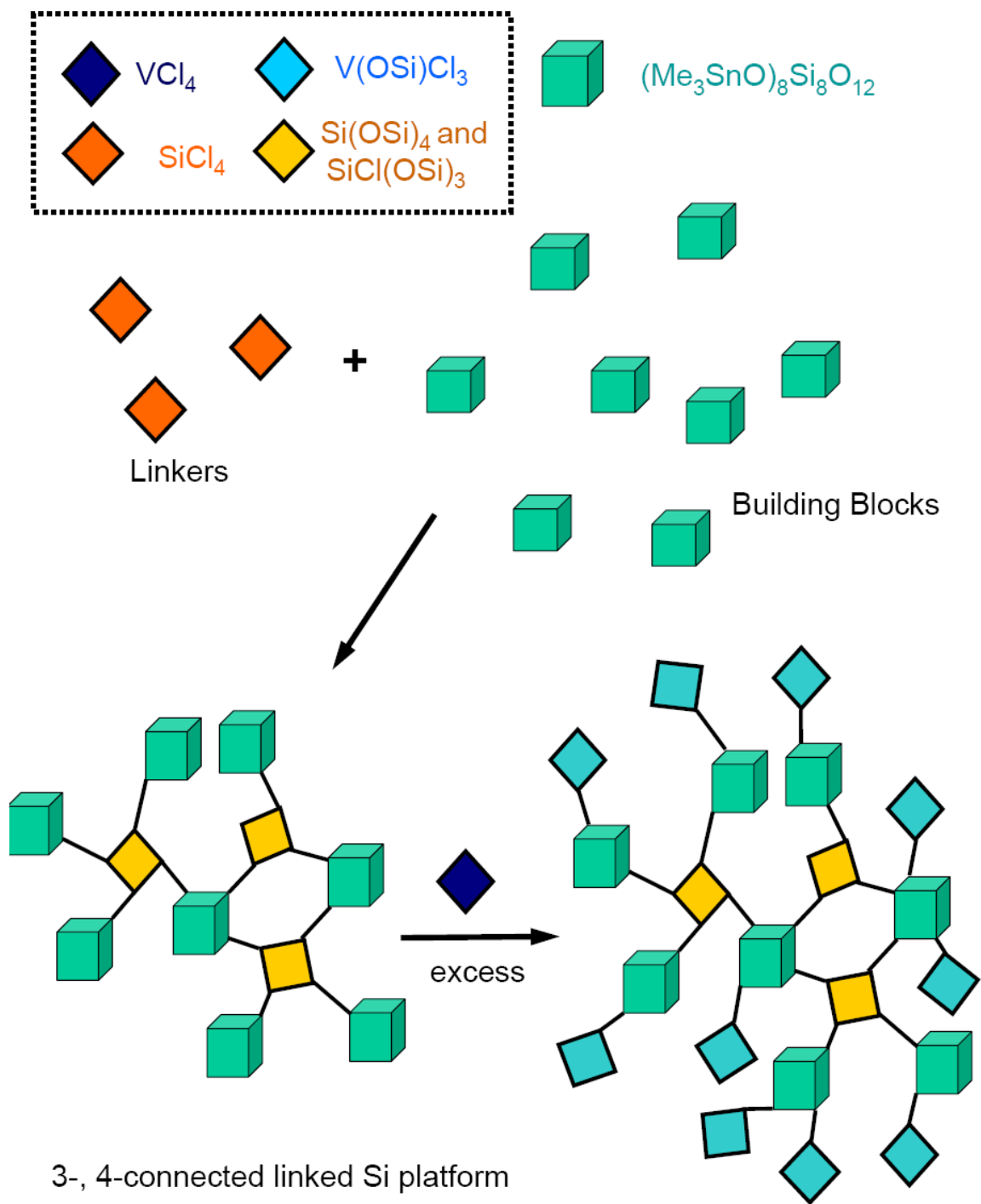


Figure 3 - 4 Surface vanadium material

3.2 Experimental

Diethyl ether, hexanes and toluene (Fisher Scientific) solvents were dried over Na/K alloy and distilled. Methylene chloride (Fisher Scientific) solvent was dried using calcium hydride and distilled. Calcium hydride, powder, ca. 0 - 20 mm, 90 ~ 95%, vanadyl trichloride (VOCl_3 - 99.995%), vanadium tetrachloride (VCl_4 - 99+%), chlorotrimethylsilane (Me_3SiCl - 98%), and dimethyldichlorosilane (Me_2SiCl_2 - 99%) were obtained from Aldrich. Tetrachlorosilane (SiCl_4 >99.5%) was obtained from Fisher Scientific. Chlorotrimethylsilane (Me_3SiCl or TMSCl), dimethyldichlorosilane (Me_2SiCl_2), and tetrachlorosilane (SiCl_4) were distilled and stored in solvent bulbs and capillaries under vacuum. Solvent and reactants were delivered using vapor transfer methods and a liquid nitrogen trap. All glassware was treated with TMSCl to remove hydroxyl groups on the glass surface. If the Schlenk reaction vessel is not silanized entirely, the VOCl_3 or VCl_4 will react with the hydroxyl groups and generate HCl in the Schlenk tube. If this reaction occurs, in the case of VOCl_3 , the color will change from gold yellow to orange; and in the case of VCl_4 , some precipitate will be observed in the dark black purple VCl_4 solution. Even though the glassware is silanized completely, VOCl_3 and VCl_4 still decomposed very slowly in the solvent bulbs or capillaries. Wrapping solvent bulbs and capillaries with aluminum foil and storing them in a dark and cool place slows degradation of these starting materials for long term storage.

Solution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on Varian Mercury 300 MHz spectrometer. ^{29}Si solution NMR spectra were acquired at 9.4 Tesla on a Bruker Avance wide-bore multinuclear NMR with a micro-imaging accessory.

^{51}V solid state NMR experiments were acquired at 105.4 MHz at spin rates of 5.555- 8.555 kHz, and ^{29}Si solid state NMR experiments were acquired at 79.48 MHz at spin rate 3.555 or 5.555 kHz on a Varian INOVA 400 wide-bore system spectrometer. Samples were placed in 5 mm pencil rotors in a nitrogen atmosphere dry box and sealed using paraffin wax. Solution chemical shifts were referenced internally to ^1H NMR δ (C_6D_6): 7.15 ppm; ^{13}C NMR δ (C_6D_6): 128.39 ppm; ^{29}Si δ ($(\text{CH}_3)_4\text{Si}$): 0 ppm; ^{51}V δ (VOCl_3): 0 ppm and ^{119}Sn δ ($(\text{CH}_3)_4\text{Sn}$): 0 ppm. Solid state chemical shifts were referenced internally to ^{29}Si δ ($(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$): 11.72 ppm; ^{51}V δ (VOCl_3): 0 ppm

Surface area measurements (Brunauer-Emmett-Teller (BET) method) were performed on a Quanta Chrome Corp. Nova 1000 High Speed Surface Area and Pore size Analyzer using nitrogen gas adsorption. The adsorption portion of the nitrogen gas adsorption/desorption isotherms was used to calculate the pore size distribution of the samples.

3.2.1 “Embedded” vanadyl trichloride (VOCl_3) and vanadium tetrachloride (VCl_4) complexes on Si_8O_{20} -based building block solids

For the embedded vanadium reactions, VOCl_3 which was stored in a thick-walled glass capillary was delivered to the reaction flask via vapor transfer

through a self-designed bent tee-shaped glass transfer piece (Fig. 3-5) to a Schlenk tube (Fig.3-6).

The mass of the VOCl_3 delivered to the Schlenk tube is estimated by the volume equation, $V = \pi r^2 h d$ which provides a rough idea of the amount of VOCl_3 that has been delivered into the reaction. In the equation above, h is the change in the height of the liquid column in the capillary, r is the radius of the capillary, and the d is the density of the VOCl_3 . Measuring the weight difference of the capillary before and after vapor transferring VOCl_3 to the Schlenk tube determines the exact amount of VOCl_3 added in the reaction. *Caution: If the total pressure of the vacuum system is higher than 50 milli-torr, the VOCl_3 will be difficult to deliver to the Schlenk tube via vapor transfer. Delivering VCl_4 requires an even better vacuum system. If the total pressure of the vacuum system is higher than 35 milli-torr, VCl_4 will not be delivered via vapor transfer efficiently.*



Figure 3 - 5 A picture of bent tee-shaped glassware

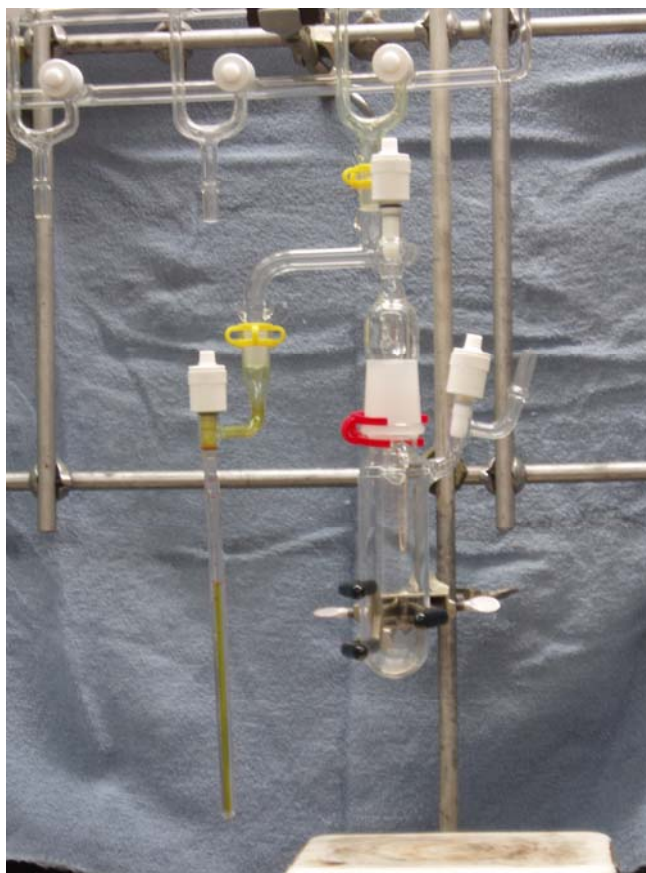


Figure 3 - 6 A capillary connects with a Schlenk tube via a tee-shaped glassware

The mass of the VOCl_3 delivered to the Schlenk tube is estimated by the volume equation, $V = \pi r^2 h d$ which provides a rough idea of the amount of VOCl_3 that has been delivered into the reaction. In the equation above, h is the change in the height of the liquid column in the capillary, r is the radius of the capillary, and the d is the density of the VOCl_3 . Measuring the weight difference of the capillary before and after vapor transferring VOCl_3 to the Schlenk tube determines the exact amount of VOCl_3 added in the reaction. *Caution: If the total pressure of the vacuum system is higher than 50 milli-torr, the VOCl_3 will be difficult to deliver to the Schlenk tube via vapor transfer. Delivering VCl_4 requires*

an even better vacuum system. If the total pressure of the vacuum system is higher than 35 milli-torr, VOCl_3 will not be delivered via vapor transfer efficiently.

The Schlenk tube was cooled to liquid nitrogen temperature and VOCl_3 was transferred and frozen at the bottom of the Schlenk tube. The solvent was then delivered to the reaction vessel via vapor transfer and covered the frozen VOCl_3 . The designated amount of $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ powder was poured into the Schlenk tube under a slow nitrogen purge while the solvent was frozen then a vacuum was reestablished. The solution was then thawed and the reaction allowed to proceed at 40°C . After the reaction was complete, the solvent was removed under vacuum and the volatile byproduct, Me_3SnCl , was removed via sublimation by heating the product at 40°C for at least 12 hours under vacuum.

An alternate procedure for the same reaction involves adding $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ to the Schlenk tube initially in a glove box and then delivering VOCl_3 to the Schlenk tube via vapor transfer. The amount of VOCl_3 needed in the reaction was estimated from the height of the capillary. The advantage of this procedure is to avoid opening the Schlenk tube when transferring reactants in the reaction vessel; but an approximate 5-10% error in the stoichiometric amount of the VOCl_3 which was designated to deliver to the Schlenk tube will occur because the height determination of the capillary visually has a small error. The calculated volume of the VOCl_3 from the height change is not as accurate as measuring the weight difference before and after delivering VOCl_3 to the Schlenk tube.

Caution: Vacuum must be maintained at all times except when adding $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ into the reaction vessel. If too much solvent is delivered into the Schlenk tube and the reaction temperature is higher than 45°C , the lower boiling point solvents such as CH_2Cl_2 will generate too much pressure. Pressures above ~ 1 atm inside the Schlenk tube should be avoided otherwise the solvent will slowly leak out from the joint of the Schlenk tube. For example, the reaction temperature should be set up no higher than 40°C for a 400 ml Schlenk tube with $\sim 15\text{-}20$ ml CH_2Cl_2 inside.

Reacting limited amounts of VOCl_3 or VCl_4 with $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ is expected to result in the formation of embedded vanadium (IV and V) centers in the silicate matrices. This is called a “first dose” reaction. After the first dose reaction is complete, the weight difference of the Schlenk tube before and after the reaction indicates the amount of Me_3SnCl formed. This in turn defines the average connectivity of the vanadium in the matrix. This concept will be described further in section 5.3.1. At this stage, there should still be unreacted trimethyltin groups on cube corners leftover in the silicate matrix. Solvent is again delivered to the Schlenk tube followed by delivering SiCl_4 or Me_2SiCl_2 via vapor transfer for the second dose treatment. The solution was allowed to react at 40°C for 12~24 hours followed by removal of the solvent and Me_3SnCl byproduct under vacuum. A pale purple solid product was obtained with only a small amount of unreacted trimethyltin groups still in the silicate matrix.

The final step of the reaction was to deliver trimethylchlorosilane, TMSCl , to the Schlenk tube to remove any residual trimethyltin groups. This was

achieved by adding an excess of TMSCl to the Schlenk tube (vapor transfer) without solvent and heating the reaction at 40~60°C for 6~12 hours. The gas phase reaction was more efficient than the liquid phase reaction; however solvents could be used in this step without differing the final result. *Caution: Using too much TMSCl in the reaction caused some unknown reactions including vanadium leaching. The color of the powder in the Schlenk tube changed from pale purple to greenish yellow when too much TMSCl was delivered to the Schlenk tube or the temperature of the reaction was too high (80°C in toluene). A 2~3 equivalent excess TMSCl (2~3 TMSCl : 1 unreacted trimethyltin groups) in the reaction is an appropriate ratio to use to avoid unwanted reactions or vanadium leaching out from the silicate matrix.*

3.2.2 “Surface” vanadyl trichloride (VOCl_3) and vanadium tetrachloride (VCl_4) complexes on Si_8O_{20} -based building block solids

“Surface” vanadyl or vanadium complexes were prepared by reversing the addition sequence described for “embedded” vanadium (VI and V) solids. The silicate platform is prepared first by reacting $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ building block with silicon tetrachloride (SiCl_4) or dimethyldichlorosilane (Me_2SiCl_2) followed by adding excess VOCl_3 or VCl_4 to yield only one connected vanadyl or vanadium centers in the silicate building block matrix. A general procedure for preparing surface vanadium catalysts is described as follows.

About ~4.00 grams (2.16 mmol) cube, $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$, were added to a 130 ml Schlenk tube followed by 15~20 ml distilled toluene via vapor transfer

under vacuum. After the $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ dissolves completely, different stoichiometric amounts of silicon tetrachloride (SiCl_4) (1 cube : $\sim 2 \text{ SiCl}_4$) or dimethyldichlorosilane (Me_2SiCl_2) (1 cube : $\sim 4 \text{ Me}_2\text{SiCl}_2$) were then delivered to the reaction vessel which was then stirred at 80°C for 48 hours. If the reaction time is shorter than 48 hours or the reaction temperature is lower than 80°C , incomplete crosslinking of cubes is observed leaving many unreacted Si-Cl bonds in the matrix and producing mainly small oligomers with low surface area. Precipitates were observed immediately if larger stoichiometric amounts of silicon tetrachloride (1 cube : 3 SiCl_4) or dimethyldichlorosilane (1 cube : 6 Me_2SiCl_2) are used. After the reaction was complete, all volatiles were removed under vacuum and the product was heated at 80°C for several hours until a fine, white powder was observed. The products were then transferred to a glove box and analyzed using multinuclear NMR techniques.

The silicate “platform” matrices described in the previous paragraph contained isolated, unreacted trimethyltin groups. A subsequent reaction was initiated at room temperature for 6 hours by delivering CH_2Cl_2 and excess VOCl_3 or VCl_4 (~ 5 -fold excess relative to the estimated unreacted trimethyltin groups) to the Schlenk tube. Due to excess amounts of VOCl_3 or VCl_4 in the reaction and the rigidity of the silicate platform, only one chloride ligand on each vanadyl or vanadium molecule is expected to react with each residual trimethyltin group. In this manner only one-connected (all capping) vanadyl or vanadium materials are obtained. A pale purple powder was observed after the reaction was complete

and all volatiles and excess VOCl_3 had been removed from the reaction. A deep purple powder was obtained in the case of surface VCl_4 samples.

3.3 Results and Discussion

3.3.1 Vanadium weight percentages and gravimetric analysis

A challenge in characterizing these vanadyl or vanadium solids is to be able to determine extent of reaction without having to resort to specialized techniques that are only accessible a couple of times a years (EXAFS) or require time consuming handling procedures (Solid State NMR). For this reason we developed a simple, quick, convenient method to follow reactions at the bench where average cross linking in products could be evaluated in minutes without exposing the sample to air. This technique involves simply weighting the sealed reaction flask both before and after the reaction and after the volatile byproduct Me_3SnCl was removed. The weight difference should be directly related to the number of coupling reactions that have occurred between the tin groups on the cube and the silane or vanadium chloride linking groups. The simple analysis can be used to follow initial dose reactions described above. For fully embedded samples (3-connected vanadyl and 4-connected vanadium materials), average cross linking or newly forming V-O-Si bonds should be equal to the total number of chlorides in the sample. In other cases such as 2- or 3- connected VCl_4 only average values of connectivity are obtained from weight changes. The only limitation of this technique is sequential weightings for multiple dose reactions are not accurate enough to give exact amounts of cross linking. In these cases

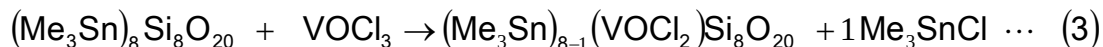
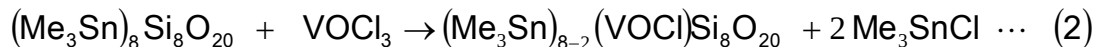
⁵¹V SSNMR and EXAFS measurements are necessary to characterize the number and types of linking groups that are present in such samples.

In the discussion that follows, a 1 to 1 ratio of VOCl₃ to (Me₃SnO)₈Si₈O₁₂ is used as an example to develop reaction equations describing the cross linking reactions that occur. Average molecular formulas derived from each equation are utilized to calculate the weight percentage of vanadium in each compound.

For a one-dose “embedded” VOCl₃ reaction, assuming all of the chloride ligands in the VOCl₃ react with trimethyltin groups, three equivalents trimethyltin chloride will be generated and the final product will contain all three connected vanadyl centers. The reaction is represented in equation 1.



If two or one chloride ligands in each VOCl₃ react with trimethyltin groups, the average connectivity of the final product should be two or one respectively. The reaction equations for these cases are given below (Eq. 2) and (Eq. 3).



The volatile byproduct, trimethyltin chloride, is easily removed via sublimation while the nonvolatile product remains in the reaction vessel after the reaction is complete. Tracking the weight loss observed in the reaction provides information on how many chloride ligands react with trimethyltin groups and this information can be converted to the average vanadyl connectivity of the product. As soon as the average connectivity is found, the average molecular formula may be derived and the weight percentage of the vanadium in the product calculated. Table 3-1 summarizes the theoretical vanadium weight % for different connectivities starting with a 1 : 1 ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VOCl}_3 = 1 : 1$ reaction.

Equations 1 - 3 can be combined and rewritten as equation 4.

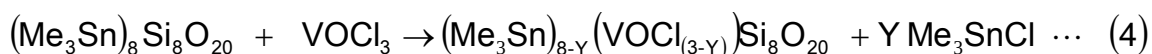
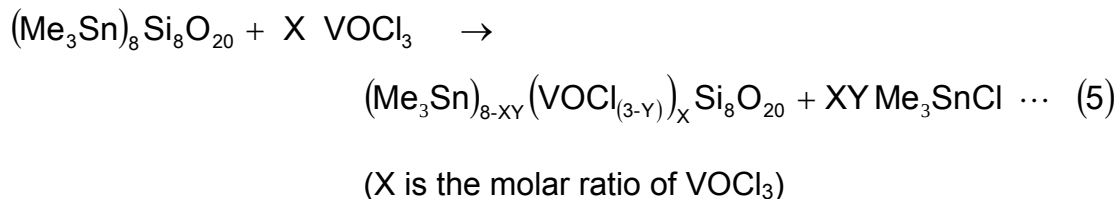


Table 3 - 1 Theoretical vanadium weight % for different connectivities starting with a 1 : 1 ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VOCl}_3$

$(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VOCl}_3$ = 1 : 1 (Sn : Cl = 8 : 3)	Average molecular formula	Weight %	Theoretical weight change for 1 gram $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ reaction
3 connected vanadyl	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	3.56 %	- 0.3222 g
2 connected vanadyl	$(\text{Me}_3\text{Sn})_6(\text{VOCl})\text{Si}_8\text{O}_{20}$	3.13 %	- 0.2148 g
1 connected vanadyl	$(\text{Me}_3\text{Sn})_7(\text{VOCl}_2)\text{Si}_8\text{O}_{20}$	2.79 %	- 0.1074 g

Y is the connectivity ($Y \leq 3$ in all VOCl_3 cases) which is determined by the moles of byproduct, trimethyltin chloride. If the initial ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ to VOCl_3 is different than 1 : 1, the equation 4 may be rewritten as equation 5 where the initial mole ratio is 1 : X (cube : VOCl_3).



The same concepts may also be applied to VCl_4 reactions. Equation 6 represents the stoichiometric formula for a one-dose “embedded” VCl_4 reaction where X represents moles of VCl_4 . Y represents the number of chlorides that react to form V-O-Si linkers which also demonstrates the average connectivity of the matrix. The connectivity can then be related to the initial moles of VCl_4 (X) in the reaction and the measured weight loss (XY). ($Y \leq 4$ in all VCl_4 cases)

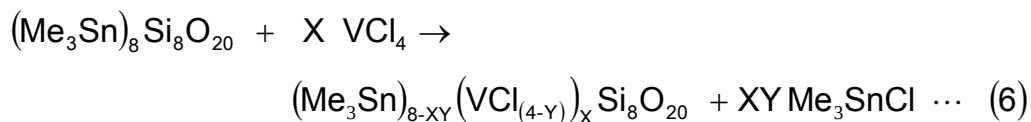


Table 3-2 is one example of the theoretical vanadium weight % for different connectivities starting with a 1: 0.75 ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$: VCl_4 .

Using limiting amounts of VOCl_3 or VCl_4 in these reactions lead to all three -connected vanadyl or all four-connected vanadium (IV) complexes. Each vanadyl or vanadium atom links with three or four $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ building blocks to form oligomeric species. Figure 3-7 is an illustration of a one-dose reaction of using a limiting amount of VOCl_3 with tin cube, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$.

If the ratio of VOCl_3 to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is higher than 1 (or $\text{Cl} : \text{Sn} > 3 : 8$), the average connectivity will be less than three and some unreacted chloride ligands will be leftover in the matrix. Increasing the reaction time or temperature can help to obtain a higher connectivity. These results provide some important information: (1) Rigid matrices or oligomers form after first and second chloride

Table 3 - 2 Theoretical vanadium weight % of different connectivities with a 1 : 0.75 ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VCl}_4$ reaction

$(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VCl}_4$ =1: 0.75 (Sn : Cl = 8 : 3)	Average molecular formula	Weight %	Theoretical weight change for 1 gram $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ reaction
4 connected vanadyl	$(\text{Me}_3\text{Sn})_4(\text{V})\text{Si}_8\text{O}_{20}$	2.73 %	- 0.3222 g
3 connected vanadyl	$(\text{Me}_3\text{Sn})_5(\text{VCl})\text{Si}_8\text{O}_{20}$	2.46 %	- 0.2417 g
2 connected vanadyl	$(\text{Me}_3\text{Sn})_6(\text{VCl}_2)\text{Si}_8\text{O}_{20}$	2.25 %	- 0.1611 g
1 connected vanadyl	$(\text{Me}_3\text{Sn})_7(\text{VCl}_3)\text{Si}_8\text{O}_{20}$	2.07%	- 0.0801 g

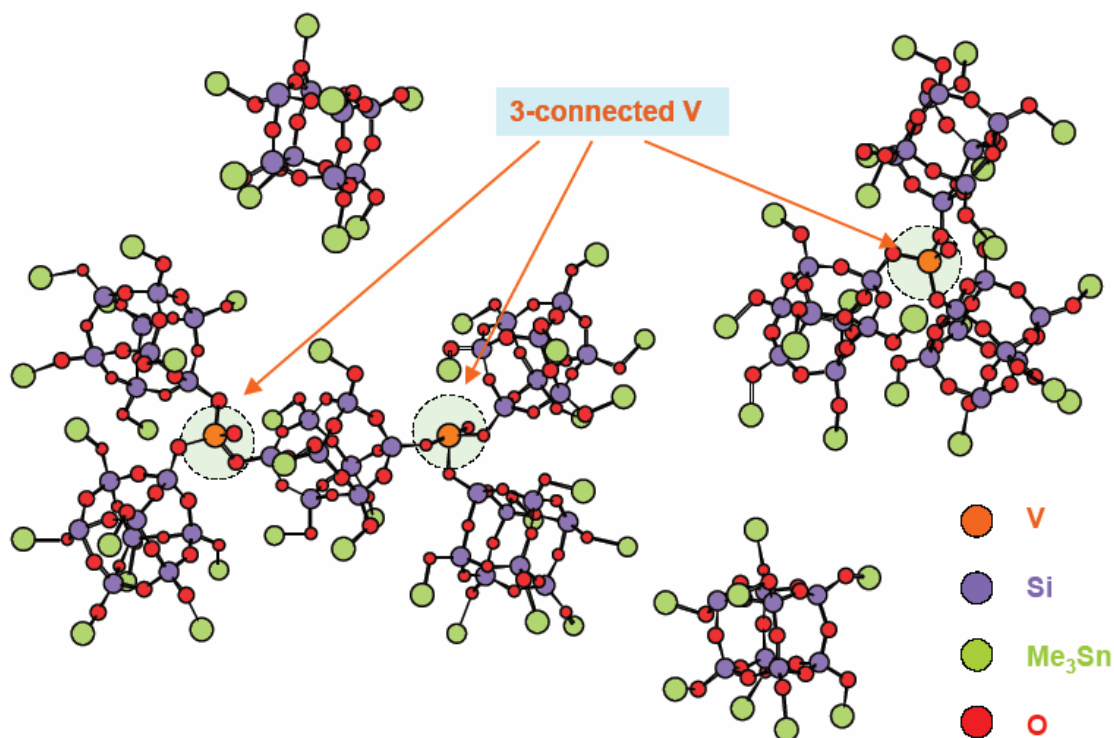
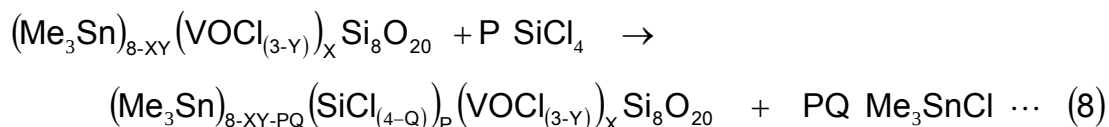
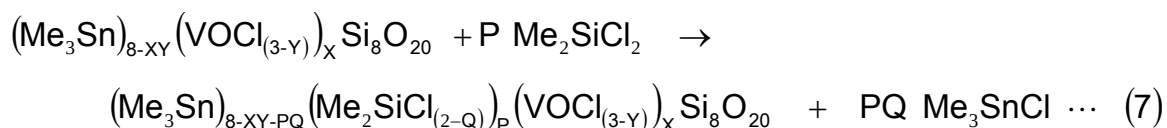


Figure 3 - 7 The molecular model of three-connected vanadyl compound

ligands react with building blocks. Residual trimethyltin groups in the building block matrix and unreacted chloride ligands become specially isolated from each other and can not react further. (2) The last chloride ligand in each vanadyl linker is the least reactive. Lengthening the reaction time and increasing the temperature force the last chloride ligand to react with residual trimethyl tin groups and form three-connected vanadyl centers. Similar situations are also observed in VCl_4 reactions. If the ratio of VCl_4 to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is higher than 0.75 (or $\text{Cl} : \text{Sn} > 3 : 8$), it is very difficult to react all chloride ligands with trimethyltin groups to obtain all 4-connected vanadium centers. In order to obtain only single types of vanadyl or vanadium materials the amounts of the VOCl_3 and

VCl₄ have to be limited otherwise the products will contain a mixture of different types of vanadyl or vanadium centers.

The product from the initial oligomeric vanadium species is subsequently exposed to a silane linking reagent such as Me₂SiCl₂ or SiCl₄ to yield cross-linking silicate materials. The function of these silane reagents is to glue the vanadyl or vanadium oligomeric species together with chemically robust bonds and form porous materials. These reactions are written in equations 7 and 8 where P represents the moles of Me₂SiCl₂ or SiCl₄ in the reaction and Q is the connectivity of Me₂SiCl₂ or SiCl₄ which is determined by the weight loss of the reaction.



The similar reactions for the VCl₄ oligomers are represented in equation 9 and 10 when one-dose embedded vanadium (IV) complexes react with Me₂SiCl₂ or SiCl₄.

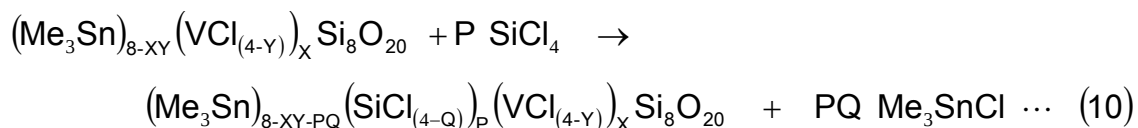
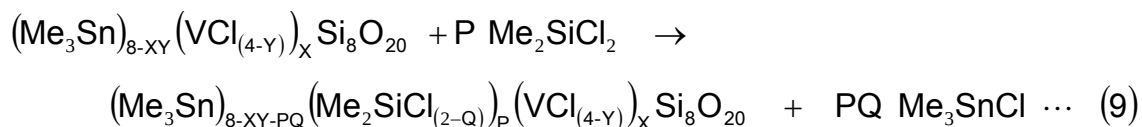


Figure 3-8 shows a molecular model to illustrate the proposed structure of the matrix after embedded VOCl_3 oligomers react with Me_2SiCl_2 . Each Me_2SiCl_2 molecule utilizes its chloride ligands to link two different $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ building blocks. The vanadyl atoms are still dispersed atomically in the silica matrix and the connectivity of each vanadyl center remains unchanged. If all chloride groups from Me_2SiCl_2 react with trimethyltin groups, the average connectivity of Me_2SiCl_2 should be two ($Q = 2$ in Eq 7) and the product will contain no chloride ligands. Replacing Me_2SiCl_2 with SiCl_4 yields a similar structure but more chloride ligands will remain in the matrix. Figure 3-9 shows a molecular model which uses SiCl_4 as a second dose reagent.

Figure 3-9 shows a vanadium-silicate cube matrix that contains different types of siloxane linking groups. Four-connected silicon has four building blocks connect to the silicon center through Si-O-Si bonds and has no chloride ligands leftover. The three-connected linkers have one chloride group remaining with three building blocks around the silicon center and so on. The chloride ligands left in the silicate matrix might affect the catalytic reaction when this material is

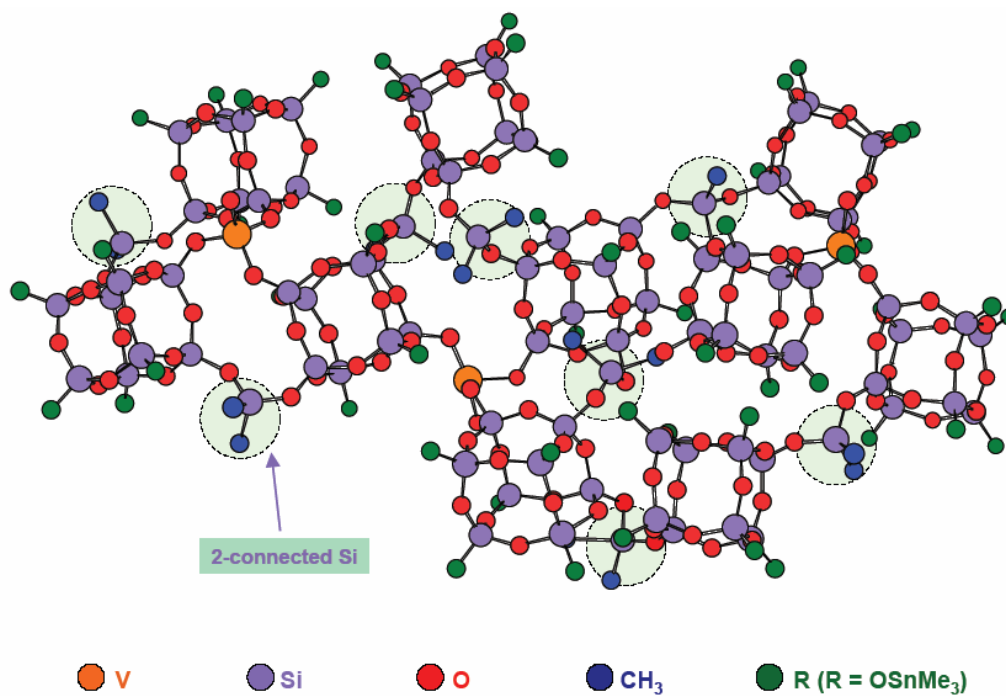


Figure 3 - 8 A molecular model of embedded VOCl₃ oligomers react with Me₂SiCl₂.

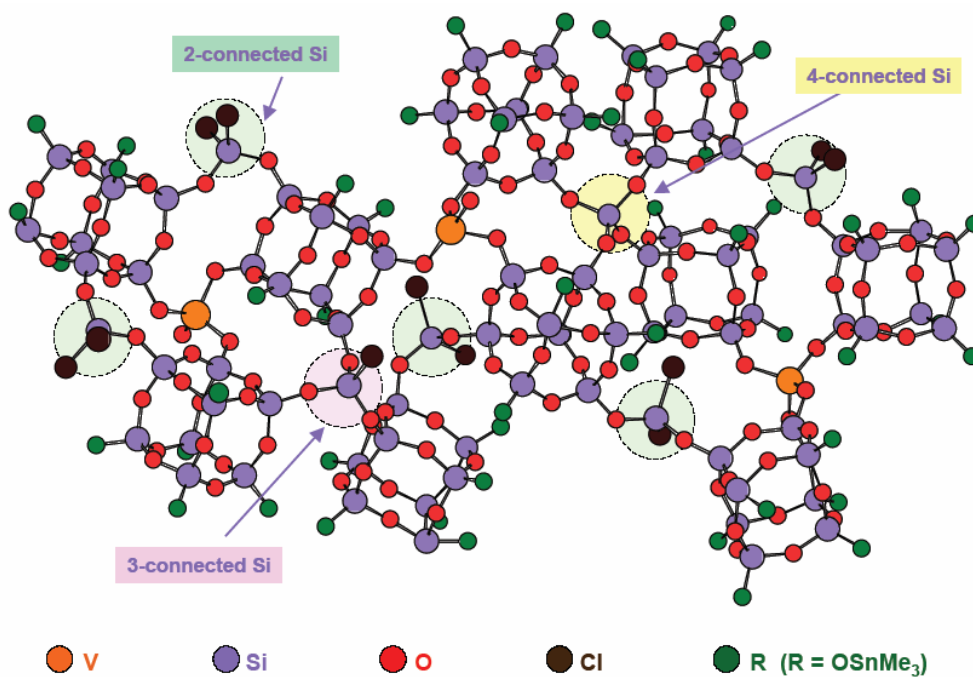
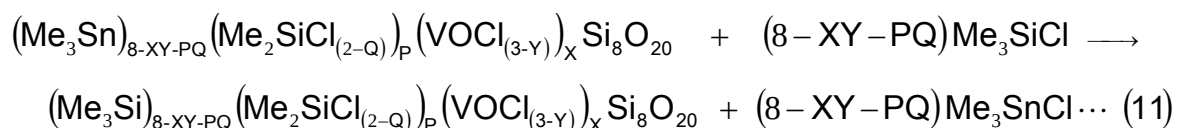


Figure 3 - 9 A molecular model of embedded VOCl₃ oligomers react with SiCl₄.

applied to different catalytic reactions. If this material is exposed to the air, moisture will react with Si-Cl ligands to form Si-OH groups and HCl. Long term exposure of the matrix to HCl should be avoided because strong acid might affect the results of catalytic reactions. This concern is the reason these materials need to be pretreated with alcohol to replace chloride with alkoxy groups before catalysis testing. This reaction will be described in more detail in Chapter 5.

When the second dose reaction is complete, some unreacted trimethyltin groups may still remain in the matrix. These tin groups might also play a role in the catalytic reaction. Removing all residual trimethyltin groups by treating the product with excess TMSCl is a very important final step in the preparation of a catalyst. Equation 11 illustrates the reaction of replacing trimethyltin groups with inert cappers, TMS groups.



The final embedded product should have no trimethyltin groups left before applying to catalytic reactions. Figure 3-10 illustrates an embedded vanadyl containing catalyst made by treating Me_2SiCl_2 as the second dose reagent and replacing all residual trimethyltin groups with TMS groups. Figure 3-11 is a similar molecular illustration for the product when SiCl_4 is used as the second dose reagent and no trimethyltin groups remain in the final product. All of the

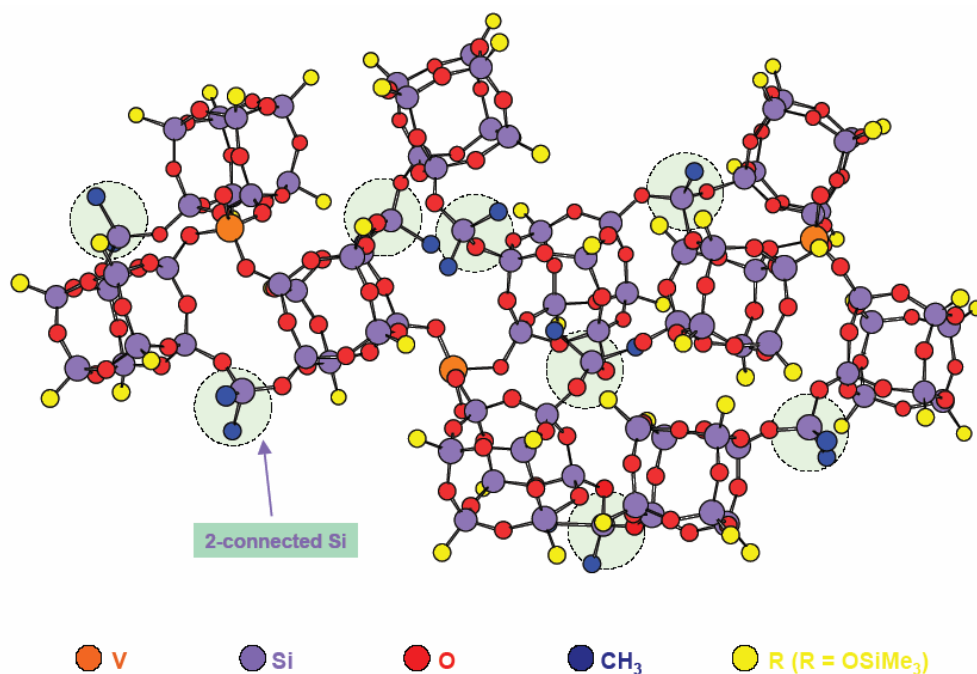


Figure 3 - 10 A three-vanadyl compound with all TMS groups

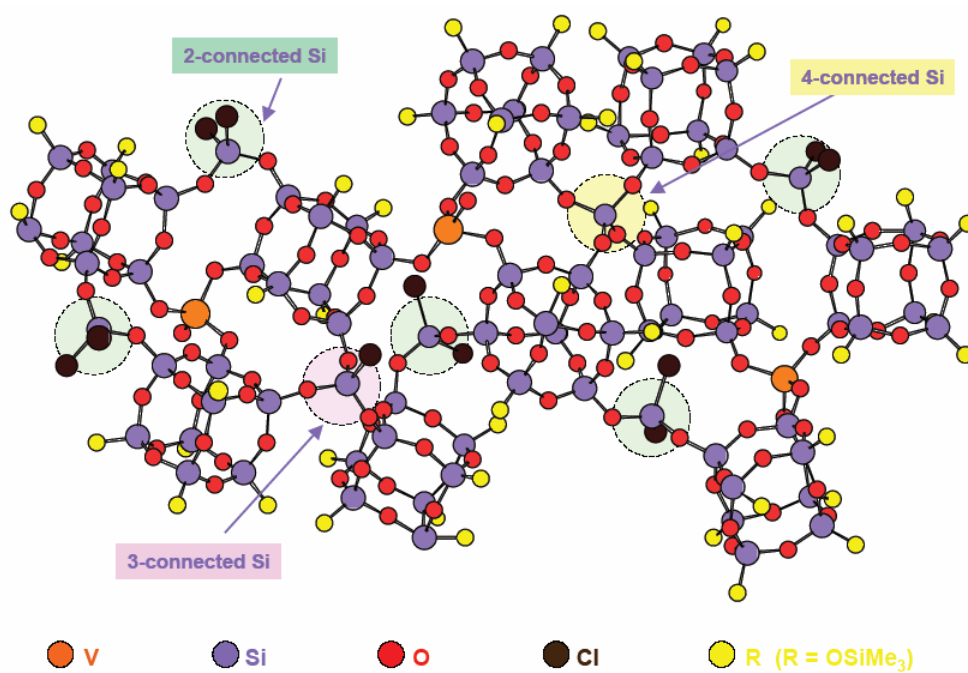


Figure 3 - 11 The three-vanadyl compound with all TMS groups (SiCl₄ is a second dose reagent)

vanadyl and vanadium centers are still very well isolated and the vanadyl and vanadium connectivity doesn't change in the second and third dose reactions.

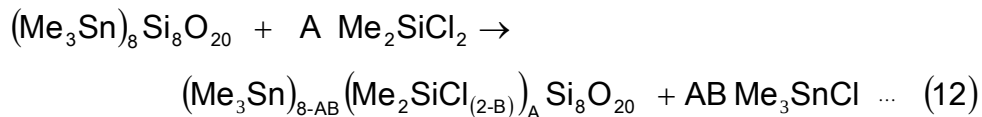
Different dose reactions produce different types of vanadyl and vanadium materials. The average molecular formulas in the final product will be different if different amount of reagents are used. To summarize these embedded vanadyl and vanadium materials from different reactions, average molecular formulas of final products are listed in Table 3-3.

Table 3 - 3 Average molecular formulas of embedded VOCl_3 and VCl_4 products

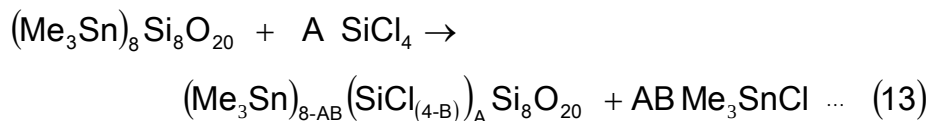
	reactants	Average molecular formula
VOCl_3	1st dose : VOCl_3	$(\text{Me}_3\text{Sn})_{8-\text{XY}}(\text{VOCl}_{(3-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	2nd dose: Me_2SiCl_2	$(\text{Me}_3\text{Sn})_{8-\text{XY-PQ}}(\text{Me}_2\text{SiCl}_{(2-\text{Q})})_{\text{P}}(\text{VOCl}_{(3-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	2nd dose: SiCl_4	$(\text{Me}_3\text{Sn})_{8-\text{XY-PQ}}(\text{SiCl}_{(4-\text{Q})})_{\text{P}}(\text{VOCl}_{(3-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	3rd dose: Me_3SiCl	$(\text{Me}_3\text{Si})_{8-\text{XY-PQ}}(\text{Me}_2\text{SiCl}_{(2-\text{Q})})_{\text{P}}(\text{VOCl}_{(3-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$ or $(\text{Me}_3\text{Si})_{8-\text{XY-PQ}}(\text{SiCl}_{(4-\text{Q})})_{\text{P}}(\text{VOCl}_{(3-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
VCl_4	1st dose : VCl_4	$(\text{Me}_3\text{Sn})_{8-\text{XY}}(\text{VCl}_{(4-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	2nd dose: Me_2SiCl_2	$(\text{Me}_3\text{Sn})_{8-\text{XY-PQ}}(\text{Me}_2\text{SiCl}_{(2-\text{Q})})_{\text{P}}(\text{VCl}_{(4-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	2nd dose: SiCl_4	$(\text{Me}_3\text{Sn})_{8-\text{XY-PQ}}(\text{SiCl}_{(4-\text{Q})})_{\text{P}}(\text{VCl}_{(4-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$
	3rd dose: Me_3SiCl	$(\text{Me}_3\text{Si})_{8-\text{XY-PQ}}(\text{Me}_2\text{SiCl}_{(2-\text{Q})})_{\text{P}}(\text{VCl}_{(4-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$ or $(\text{Me}_3\text{Si})_{8-\text{XY-PQ}}(\text{SiCl}_{(4-\text{Q})})_{\text{P}}(\text{VCl}_{(4-\text{Y})})_{\text{X}}\text{Si}_8\text{O}_{20}$

X is the molar ratio of VOCl_3 or VCl_4 , Y is the number of vanadyl or vanadium connectivity, P is the molar ratio of Me_2SiCl_2 or SiCl_4 , Q is the number of Me_2SiCl_2 or SiCl_4 connectivity.

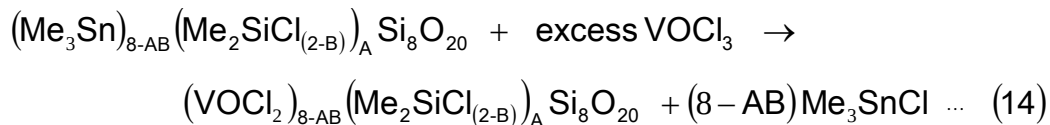
The average molecular formula of surface vanadyl and vanadium samples are derived from similar protocols as described in embedded samples. In the “surface” samples, silicate platforms have to be prepared in the first step before reacting with excess VOCl_3 or VCl_4 to yield all capping vanadyl or vanadium atoms around the silicate matrices. The reaction to prepare Me_2SiCl_2 platform is illustrated in equation 12 where A is the Me_2SiCl_2 molar ratio of the reaction and B is the number of the connectivity of the Me_2SiCl_2 which is determined by the weight loss of the reaction.



Equation 13 is the similar reaction but use SiCl_4 as the reagent.



Reacting excess VOCl_3 or VCl_4 with different silicate platform (products from Eq 12 or 13) yield all capping vanadyl or vanadium products. (Eq 14 to 17)



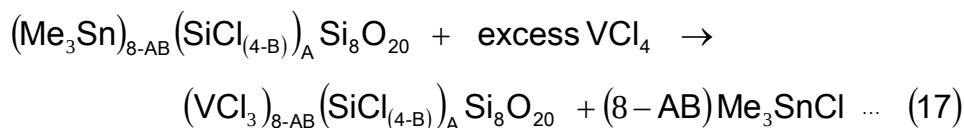
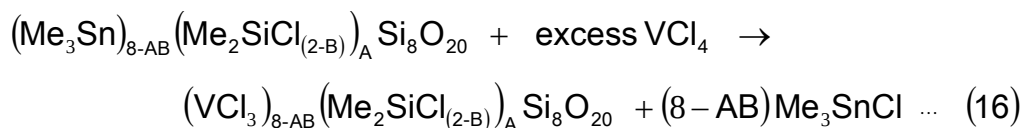
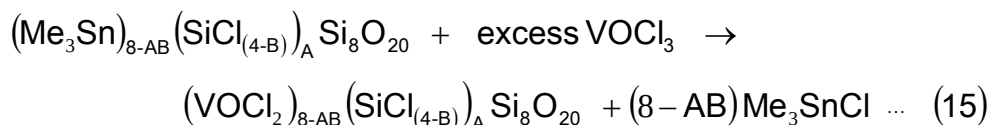


Table 3-4 lists average molecular formulas of one-connected all capping surface VOCl₃ and VCl₄ reactions with Me₂SiCl₂ or SiCl₄ platform.

The experimental data of synthesizing different weight percentage embedded VOCl₃ or VCl₄ samples are summarized in Tables 3-5 and 3-6. When

Table 3 - 4 Average molecular formulas of surface VOCl₃ and VCl₄ products

	Silicate platform	Average molecular formula
VOCl ₃	Me ₂ SiCl ₂	(VOCl ₂) _{8-AB} (Me ₂ SiCl _(2-B)) _A Si ₈ O ₂₀
	SiCl ₄	(VOCl ₂) _{8-AB} (SiCl _(4-B)) _A Si ₈ O ₂₀
VCl ₄	Me ₂ SiCl ₂	(VCl ₃) _{8-AB} (Me ₂ SiCl _(2-B)) _A Si ₈ O ₂₀
	SiCl ₄	(VCl ₃) _{8-AB} (SiCl _(4-B)) _A Si ₈ O ₂₀

A is the molar ratio of Me₂SiCl₂ or SiCl₄, B is the number of Me₂SiCl₂ or SiCl₄ connectivity.

Table 3 - 5 Summary of gravimetric analysis results from reactions of VOCl_3 with tin cube

	Code	*cube gram ± 0.005 (mmol)	VOCl_3 gram ± 0.005 (mmol)	Ratio Cube : VOCl_3	Weight loss Gram ± 0.005 (mmol)	con- nec- tivity	Average molecular formula $(\text{Me}_3\text{Sn})_{8-X}\text{Y}(\text{VOCl}_{(3-Y)})_X$ Si_8O_{20}	Time (hr)	Wt%
1	II-188	2.036 (1.097)	0.058 (0.3347)	1 : 0.31	0.203 (1.019)	3.04 $\pm$ 0.2	$(\text{Me}_3\text{Sn})_{7.1}(\text{VO})_{0.31}$ Si_8O_{20}	12	0.90
2	II-208	2.538 (1.368)	0.086 (0.4962)	1 : 0.36	0.315 (1.581)	3.19 $\pm$ 0.2	$(\text{Me}_3\text{Sn})_{6.92}(\text{VO})_{0.36}$ Si_8O_{20}	24	1.08
3	II-186	1.989 (1.072)	0.120 (0.6924)	1 : 0.65	0.415 (2.083)	3.01 $\pm$ 0.1	$(\text{Me}_3\text{Sn})_{6.04}(\text{VO})_{0.65}$ Si_8O_{20}	12	2.10
4	II-212	3.538 (1.907)	0.241 (1.391)	1: 0.73	0.819 (4.110)	2.95 $\pm$ 0.06	$(\text{Me}_3\text{Sn})_{5.85}(\text{VOCl}_{0.05})_{0.73}$ Si_8O_{20}	24	2.40
5	II-190	2.034 (1.096)	0.186 (1.073)	1: 0.98	0.638 (3.202)	2.98 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_{5.1}(\text{VO})_{0.98}$ Si_8O_{20}	12	3.47
6	II-206	2.532 (1.365)	0.234 (1.350)	1 : 0.99	0.812 (4.075)	3.02 $\pm$ 0.06	$(\text{Me}_3\text{Sn})_{5.01}(\text{VO})_{0.99}$ Si_8O_{20}	24	3.51
7	II-118	1.713 (0.9234)	0.160 (0.9233)	1 : 1	0.554 (2.780)	3.01 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	18	3.56
8	II-022	1.841 (0.9923)	0.172 (0.9925)	1 : 1	0.600 (3.011)	3.03 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	12	3.56
9	II-056	1.906 (1.027)	0.178 (1.027)	1 : 1	0.636 (3.189)	3.11 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	12	3.56
10	II-138	1.977 (1.066)	0.182 (1.050)	1 : 1	0.646 (3.242)	3.09 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	24	3.56
11	II-024	2.205 (1.189)	0.206 (1.189)	1 : 1	0.727 (3.649)	3.07 $\pm$ 0.08	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	12	3.56
12	II-010	3.670 (1.978)	0.342 (1.973)	1 : 1	1.184 (5.942)	3.01 $\pm$ 0.05	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	12	3.56
13	II-054	4.774 (2.573)	0.446 (2.574)	1 : 1	1.571 (7.885)	3.06 $\pm$ 0.03	$(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$	12	3.56
14	II-178	1.583 (0.853)	0.190 (1.096)	1 : 1.28	0.467 (2.344)	2.14 $\pm$ 0.09	$(\text{Me}_3\text{Sn})_{5.26}(\text{VOCl}_{0.86})_{1.28}$ Si_8O_{20}	12	4.26

*Cube represents $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$.

X is the molar ratio of VOCl_3 to tin cube, Y is the number of vanadyl or vanadium connectivity.
All of the reactions were completed in CH_2Cl_2 at 40°C .

Table 3 - 6 Summary of gravimetric analysis results from reactions of VCl_4 with tin cube

	Code	*Cube gram ± 0.005 (mmol)	VCl_4 gram ± 0.005 (mmol)	Ratio Cube : VCl_4	Weight loss gram ± 0.005 (mmol)	Con- nect- ivity	Average molecular formula $(\text{Me}_3\text{Sn})_{8-X}\text{Y}(\text{VCl}_{(4-Y)})_X$ Si_8O_{20}	Time (hr)	Wt%
1	II-198	2.498 (1.347)	0.064 (0.3320)	1 : 0.25	0.278 (1.395)	4.20 ± 0.32	$(\text{Me}_3\text{Sn})_7(\text{V})_{0.25}\text{Si}_8\text{O}_{20}$	24	0.75
2	II-204	3.499 (1.886)	0.174 (0.9027)	1 : 0.48	0.745 (3.739)	4.14 ± 0.12	$(\text{Me}_3\text{Sn})_{6.08}(\text{V})_{0.48}\text{Si}_8\text{O}_{20}$	24	1.56
3	II-194	1.993 (1.074)	0.106 (0.5499)	1 : 0.51	0.429 (2.153)	3.92 ± 0.15	$(\text{Me}_3\text{Sn})_{5.96}(\text{VCl}_{0.08})_{0.51}$ Si_8O_{20}	12	1.69
4	II-142	2.281 (1.230)	0.168 (0.8716)	1 : 0.71	0.697 (3.498)	4.01 ± 0.12	$(\text{Me}_3\text{Sn})_{5.2}(\text{V})_{0.71}\text{Si}_8\text{O}_{20}$	24	2.54
5	II-200	2.488 (1.341)	0.186 (0.9650)	1 : 0.72	0.794 (3.985)	4.13 ± 0.12	$(\text{Me}_3\text{Sn})_{5.12}(\text{V})_{0.72}\text{Si}_8\text{O}_{20}$	24	2.58
6	II-192	1.986 (1.071)	0.175 (0.9079)	1 : 0.85	0.696 (3.493)	3.88 ± 0.12	$(\text{Me}_3\text{Sn})_{4.7}(\text{VCl}_{0.12})_{0.85}$ Si_8O_{20}	12	3.18
7	II-180	1.733 (0.9341)	0.162 (0.8405)	1 : 0.9	0.563 (2.8256)	3.36 ± 0.12	$(\text{Me}_3\text{Sn})_{4.98}(\text{VCl}_{0.64})_{0.9}$ Si_8O_{20}	12	3.22
8	II-116	4.135 (2.229)	0.430 (2.231)	1 : 1	1.687 (8.467)	3.80 ± 0.03	$(\text{Me}_3\text{Sn})_{4.2}(\text{VCl}_{0.2})\text{Si}_8\text{O}_{20}$	24	3.95

*Cube represents $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. All of the reactions were performed in CH_2Cl_2 at 40°C

the loading ratio of VOCl_3 to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is lower than 1 to 1 (entry 1 to 13 in table 5), the connectivity is equal to 3 ± 0.2 and the weight percentages increase proportionally with the loading ratio of VOCl_3 . When the ratio of VOCl_3 to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is constrained to 1 to 1 while varying the amount of starting materials (Entry 7 to 13), the results are quite reproducible and the connectivity of these products is all equal to three. When the ratio of VOCl_3 to

(Me_3Sn) $_8\text{Si}_8\text{O}_{20}$ increases to higher than 1 (entry 14) , the connectivity decreases to 2.14 (lower than 3) and some V-Cl groups remained in the matrix.

The maximum number of the connectivity in the VOCl_3 reaction should be three and it consistent with the results in Table 3-5. Some other observations to note from the data in Table 5 are as follows. If the amount of starting material is too small such as entry 2, the error will be larger. When the ratio of VOCl_3 to tin-cube is larger than 1 (or the ratio of chloride ligands to trimethyltin groups is larger than 3 : 8), some of the chloride groups do not react with trimethyltin groups and the connectivity will be less than 3. It appears to be a limit to the vanadium wt% in the matrix while maintaining site homogeneity. As soon as the ratio is higher than one, sites with different connectivities will occur in the product and V-Cl groups will remain in the matrix.

All of the reactions in table 3-5 were accomplished in CH_2Cl_2 solution at 40°C and reaction times were controlled at 12, 18, or 24 hours. Other higher boiling point solvents such as benzene or toluene have also been considered but a danger in going to these solvents is that vanadyl chloride might decompose at high temperature in the reaction. From the results shown in Table 3-5, three-connected vanadyl compounds were synthesized within 12 hours. When the reaction time was increased from 12 to 24 hours, the connectivity was not observed to change. Thus 12 hour reaction times are sufficient. Scaling up the reaction does not appear to alter these conclusions (entries 7-13). These reactions also show that products are quite stable in solution at 40°C .

One-dose, embedded vanadium (IV) compounds were synthesized in the same manner as the one-dose, embedded vanadyl complexes. Table 3-6 lists the results for the reaction of VCl_4 with $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$. When the ratio of VCl_4 and $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is lower than 0.75 : 1 (or the ratio of chloride ligands to trimethyltin groups is less than 3 : 8), the average connectivity of the vanadium centers in the products is 4 ± 0.2 . If a smaller amount of VCl_4 is delivered to the reaction such as entry 1 in Table 6, a higher error of the weight difference determination will appear due to the limitation of the balance. When the VCl_4 : cube ratio is larger than 0.75 (or the ratio of chloride ligands to trimethyltin groups is larger than 3 : 8), some of the chloride ligands do not react with trimethyltin groups and remain in the product. One important observation of these reactions is the reaction time should be longer than 12 hours at 40°C in the vanadium (IV) system to force all of the chloride ligands to react with trimethyltin groups and obtain four-connected vanadium centers. At low loading ratio (entries 1, 2, 4 and 5), the products contained fully four-connected vanadium centers when reaction time was set for 24 hours. If the reaction time decreased to 12 hours (entry 3), some chloride ligands did not react with trimethyltin groups and the connectivity was less than four. When the ratio of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ to VCl_4 is close to 1 to 1 (entries 7 and 8), longer reaction times enabled more unreacted chloride ligands to react with trimethyltin groups and formed higher connectivity vanadium compounds. The average connectivities increased from 3.36 to 3.80 when the reaction time was doubled to 24 hours. These results are consistent with the fourth chloride ligand in the vanadium tetrachloride requiring longer times to fully

react with trimethyltin groups. The reaction time for synthesizing all four-connected vanadium compounds should be longer than synthesizing all three-connected vanadyl products.

The one-dose vanadyl complexes reacted with different amount of Me_2SiCl_2 or SiCl_4 produced silicate cross-linking materials and the results are summarized in Table 3-7. Liquid phase and gas phase reactions were explored. If the reaction was performed in gas phase without solvent, the byproduct, trimethyltin chloride, was observed to condense at the top of the reaction vessel while it was generated during the reaction and slowly formed crystals. Entries 1 to 5 in Table 3-7 used three-connected vanadyl as the starting material which were reacted with different amounts of Me_2SiCl_2 or SiCl_4 under different conditions. When the reaction times decreased from 24 hours to 12 hours (entries 1 and 2), the connectivities of Me_2SiCl_2 decreased from 1.72 to 1.54 even though a smaller amount of Me_2SiCl_2 was used. If the reaction condition was set in gas phase (entry 3), similar connectivity was observed after 12 hours at 50°C . When Me_2SiCl_2 was replaced with SiCl_4 , more chloride ligands remained in the silicate matrices under similar conditions in liquid or gas phase (entries 4 and 5). The highest connectivity in SiCl_4 reactions should be four and in Me_2SiCl_2 should be two. Entry 6 used 2.95 connected vanadyl starting material and set up the reaction in the gas phase for 24 hours, but the connectivity of silicate still did not reach two. From this data, all of the chloride

Table 3 - 7 Summary of gravimetric analysis results from second dose reactions
(vanadyl compounds with SiCl_4 and Me_2SiCl_2)

	Code	$^1\text{Vanadyl}$ gram ± 0.005 (mmol)	(Silane) gram ± 0.005 (mmol)	Ratio Cube : silane	Weight loss gram ± 0.005 (mmol)	Con- nec- tivity	Average molecular formula	Reaction condition	Wt%
1	II-028	1.413 (0.9877)	$(\text{Me}_2\text{SiCl}_2)$ 0.211 (1.635)	1:1.66	0.562 (2.821)	1.72 ± 0.04	$(\text{Me}_3\text{Sn})_{2.14}(\text{Me}_2\text{SiCl}_{0.28})_{1.66}(\text{VO})\text{Si}_8\text{O}_{20}$	40°C CH_2Cl_2 24hrs	3.62
2	II-058	3.240 (2.265)	$(\text{Me}_2\text{SiCl}_2)$ 0.393 (3.045)	1:1.34	0.932 (4.678)	1.54 ± 0.03	$(\text{Me}_3\text{Sn})_{2.94}(\text{Me}_2\text{SiCl}_{0.46})_{1.34}(\text{VO})\text{Si}_8\text{O}_{20}$	40°C CH_2Cl_2 12hrs	4.27
3	II-122	0.5710 (0.3992)	$(\text{Me}_2\text{SiCl}_2)$ 0.089 (0.6896)	1:1.73	0.218 (1.094)	1.59 ± 0.09	$(\text{Me}_3\text{Sn})_{2.25}(\text{Me}_2\text{SiCl}_{0.41})_{1.73}(\text{VO})\text{Si}_8\text{O}_{20}$	50°C Gas phase 12 hrs	4.61
4	II-012	0.900 (0.6291)	(SiCl_4) 0.063 (0.3708)	1 : 0.590	0.212 (1.064)	2.87 ± 0.23	$(\text{Me}_3\text{Sn})_{3.3}(\text{SiCl}_{1.13})_{0.59}(\text{VO})\text{Si}_8\text{O}_{20}$	40°C CH_2Cl_2 12hrs	4.27
5	II-146	0.8170 (0.5711)	(SiCl_4) 0.114 (0.6710)	1: 1.17	0.221 (1.109)	1.65 ± 0.07	$(\text{Me}_3\text{Sn})_{3.07}(\text{SiCl}_{2.35})_{1.17}(\text{VO})\text{Si}_8\text{O}_{20}$	60°C Gas phase 12 hrs	4.09
6	II-218	1.300 (0.8374)	$(\text{Me}_2\text{SiCl}_2)$ 0.317 (2.456)	1:2.93	0.723 (3.629)	1.48 ± 0.02	$(\text{Me}_3\text{Sn})_{1.51}(\text{Me}_2\text{SiCl}_{0.52})_{2.93}(\text{VOCl}_{0.05})_{0.73}\text{Si}_8\text{O}_{20}$	50°C Gas phase 24 hrs	3.49
7	II-228	0.8710 (0.6071)	$(\text{Me}_2\text{SiCl}_2)$ 0.217 (1.681)	1:2.77	0.488 (2.449)	1.46 ± 0.03	$(\text{Me}_3\text{Sn})_{0.99}(\text{Me}_2\text{SiCl}_{0.54})_{2.77}(\text{VO})_{0.99}\text{Si}_8\text{O}_{20}$	20°C CH_2Cl_2 24hrs	5.11

1. The average molecular formula of starting materials from entry 1 to entry 5 is $(\text{Me}_3\text{Sn})_5(\text{VO})\text{Si}_8\text{O}_{20}$ which were synthesized from one-dose reactions and the molecular weight is 1430.5 g/mol. The average vanadyl molecular formula of entry 6 is $(\text{Me}_3\text{Sn})_{5.85}(\text{VOCl}_{0.05})_{0.73}\text{Si}_8\text{O}_{20}$ which is the product from entry 4 in table 5 and the molecular weight is 1552.4 g/mol. The average vanadyl molecular formula of entry 7 is $(\text{Me}_3\text{Sn})_{5.01}(\text{VO})_{0.99}\text{Si}_8\text{O}_{20}$ which was the product from entry 6 in table 5 and the molecular weight is 1434.8 g/mol.

ligands in Me_2SiCl_2 or SiCl_4 do not appear to react with trimethyltin groups and obtain all two- or four-connected silicate products in a second dose reaction. Choosing Me_2SiCl_2 as the second dose reagent or increasing the reaction temperature helps the reaction goes further and avoids too many chloride ligands remaining in the products. When a second dose reaction was set at room temperature with the addition of Me_2SiCl_2 (entry 7), the reaction still proceeded well and a cross-linking silicate product with a similar connectivity was obtained.

Three different one-dose embedded vanadium (IV) compounds were reacted with Me_2SiCl_2 or SiCl_4 under different reaction conditions as summarized in Table 3-8. Some chloride ligands still remained in the products even though the reaction time was increased to 24 hours under gas phase reaction (entries 1 and 2). These results are similar to the results observed in the vanadyl cases. The connectivities were less than two in Me_2SiCl_2 cases and no two-connected Me_2SiCl_2 silicate cross-linking products can be produced. Running the reaction in the gas phase at 60°C for 12 hours and then vapor transferring toluene into the reaction vessel and continuing the reaction in the liquid phase for another 12 hours did not increase the connectivity (entry 3). The reaction time is an important factor in the second dose reaction. Higher reaction temperatures might be another possible factor to force more chloride ligands to react with trimethyltin groups.

Table 3 - 8 Summary of gravimetric analysis results from second dose reactions
(vanadium compounds with SiCl_4 and Me_2SiCl_2)

	Code	*Vanadium gram ± 0.005 (mmol)	Silane gram ± 0.005 (mmol)	Ratio Cube : silane	Weight loss gram ± 0.005 (mmol)	Con- nec- tivity	Average molecular formula	Reaction condition	Wt%
1	II-120	1.698 (1.316)	$(\text{Me}_2\text{SiCl}_2)$ 0.245 (1.898)	1:1.44	0.4350 (2.183)	1.15 ± 0.03	$(\text{Me}_3\text{Sn})_{2.54}(\text{Me}_2\text{SiCl}_{0.85})_{1.44}(\text{VCl}_{0.2})\text{Si}_8\text{O}_{20}$	50°C Gas phase 12 hrs	4.44
2	II-216	1.274 (0.8141)	$(\text{Me}_2\text{SiCl}_2)$ 0.335 (2.596)	1:3.19	0.6280 (3.152)	1.21 ± 0.02	$(\text{Me}_3\text{Sn})_{2.23}(\text{Me}_2\text{SiCl}_{0.79})_{3.19}(\text{V})_{0.48}\text{Si}_8\text{O}_{20}$	50°C Gas phase 24 hrs	2.02
3	II-144	0.9150 (0.6417)	(SiCl_4) 0.141 (0.8299)	1:1.29	0.2430 (1.220)	1.47 ± 0.05	$(\text{Me}_3\text{Sn})_{3.26}(\text{SiCl}_{2.53})_{1.29}(\text{V})_{0.71}\text{Si}_8\text{O}_{20}$	60°C Gas phase 12 hrs then toluene 12 hours	2.98

The average vanadium molecular formula of entry 1 is $(\text{Me}_3\text{Sn})_{4.2}(\text{VCl}_{0.2})\text{Si}_8\text{O}_{20}$ which is the product from entry 8 in table 6 and the molecular weight is 1290.6 g/mol. The average vanadium molecular formula of entry 2 is $(\text{Me}_3\text{Sn})_{6.08}(\text{V})_{0.48}\text{Si}_8\text{O}_{20}$ which is the product from entry 2 in table 6 and the molecular weight is 1564.9 g/mol. The average vanadium molecular formula of entry 3 is $(\text{Me}_3\text{Sn})_{5.2}(\text{V})_{0.71}\text{Si}_8\text{O}_{20}$ which is the product from entry 4 in table 6 and the molecular weight is 1426.0 g/mol.

The final step to prepare tin-free products is to treat the matrix with excess trimethylchlorosilane, TMSCl, with second-dosed vanadyl (entries 1 and 2 in Table 3-9) or vanadium (entries 3 and 4 in Table 3-9) products. One important issue of this final step reaction is avoiding adding too much TMSCl to the reaction otherwise disconnection of V-O-Si bonds appears to occur and vanadium leaches out of the matrix easily. When 20 equivalences (or more) Me_3SiCl are delivered to the reaction vessel and mixed with solvents such as CH_2Cl_2 or toluene, the solution changed color from pale purple to green. Gas phase reactions were better choices because the byproduct, trimethyltin chloride was generated and crystals were formed and visible in the top of the sealed Schlenk tube. As soon as the reaction completed, excess TMSCl and byproduct, Me_3SnCl , were removed from the Schlenk tube via vacuum.

For the surface materials, silicate platforms are prepared by reacting SiCl_4 or Me_2SiCl_2 with $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ building block. Longer reaction times and higher reaction temperatures were explored to attempt to obtain higher cross-linking products and have little chloride remaining in the silicate matrices. Table 3-10 shows two types of silicate platforms. Entry 1 was prepared from SiCl_4 with more residual trimethyl tin groups (3.75 trimethyltin groups remained in each building block) and entry 2 was prepared from Me_2SiCl_2 with less residual trimethyl tin groups (1.49 trimethyltin groups remained in each building block). Reacting different amount of Me_2SiCl_2 or SiCl_4 with tin cubes produces different types of silicate platforms with different amounts of residual trimethyl tin

Table 3 - 9 Third dose (TMSCI) reactions

	Code	Starting Material *Vanadyl or vanadium gram (mmol)	parameters	Reaction condition	Average molecular formula	Wt%
1	II-146	$(\text{Me}_3\text{Sn})_{3.07}(\text{SiCl}_{2.35})_{1.17}$ $(\text{VO})\text{Si}_8\text{O}_{20}$	X= 1 Y= 3 P= 1.17 Q= 1.65	50°C Gas phase 12 hrs	$(\text{Me}_3\text{Si})_{3.07}(\text{SiCl}_{2.35})_{1.17}$ $(\text{VO})\text{Si}_8\text{O}_{20}$	3.83
2	II-148	$(\text{Me}_3\text{Sn})_{2.25}(\text{Me}_2\text{SiCl}_{0.41})_{1.73}$ $(\text{VO})\text{Si}_8\text{O}_{20}$	X= 1 Y= 3 P= 1.73 Q= 1.59	50°C Gas phase 12 hrs	$(\text{Me}_3\text{Si})_{2.25}(\text{Me}_2\text{SiCl}_{0.41})_{1.73}$ $(\text{VO})\text{Si}_8\text{O}_{20}$	5.65
3	II-160	$(\text{Me}_3\text{Sn})_{2.54}(\text{Me}_2\text{SiCl}_{0.85})_{1.44}$ $(\text{VCl}_{0.2})\text{Si}_8\text{O}_{20}$	X= 1. Y= 3.8 P= 1.44 Q= 1.15	60°C Gas phase 8 hrs	$(\text{Me}_3\text{Si})_{2.54}(\text{Me}_2\text{SiCl}_{0.85})_{1.44}$ $(\text{VCl}_{0.2})\text{Si}_8\text{O}_{20}$	5.56
4	II-216	$(\text{Me}_3\text{Sn})_{2.23}(\text{Me}_2\text{SiCl}_{0.79})_{3.19}$ $(\text{V})_{0.48}\text{Si}_8\text{O}_{20}$	X= 0.48 Y= 4 P= 3.19 Q= 1.21	45°C Gas phase 21 hrs	$(\text{Me}_3\text{Si})_{2.23}(\text{Me}_2\text{SiCl}_{0.79})_{3.19}$ $(\text{V})_{0.48}\text{Si}_8\text{O}_{20}$	2.43

The starting material of entry 1 was from entry 5 in the table 7, entry 2 was from entry 3 in the table 7, entry 3 was from entry 1 in the table 8, and entry 4 was from entry 2 in the table 8.

Table 3 - 10 Me_2SiCl_2 and SiCl_4 platforms

	Code	*Cube gram ± 0.005 (mmol)	Silane gram ± 0.005 (mmol)	Ratio Cube : silane	Weight loss gram ± 0.005 (mmol)	Con- nec- tivity	Reaction condition	Average molecular formula
1	II-140	3.944 (2.126)	SiCl_4 0.683 (4.020)	1 : 1.89	1.803 (9.049)	2.25 ± 0.02	Toluene 80°C 48 hrs	$(\text{Me}_3\text{Sn})_{3.75}(\text{SiCl}_{1.75})_{1.89}$ Si_8O_{20}
2	II-202	4.578 (2.468)	Me_2SiCl_2 1.314 (10.18)	1 : 4.12	3.209 (16.11)	1.58 ± 0.02	Toluene 80°C 48 hrs	$(\text{Me}_3\text{Sn})_{1.49}(\text{Me}_2\text{SiCl}_{0.42})_{4.12}$ Si_8O_{20}

*Cube represents $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

groups in the matrices. The average molecular formula is determined from the gravimetric analysis. Both of these reactions were preformed at 80°C in toluene for two days.

Reacting silicate platforms with excess VOCl_3 or VCl_4 obtained all capping one-connected vanadyl or vanadium materials. The vanadium weight percentages are calculated and listed in Table 3-11. All of these reactions were performed at room temperature and unreacted VOCl_3 or VCl_4 was removed under vacuum. The final products were extremely air sensitive due to the residual chloride ligands around the vanadyl or vanadium center. The deep purple one-connected all capping vanadium materials changed color to yellow-orange immediately in the air and one-connected vanadyl samples also changed to orange color instantly in the air.

So far, different types of embedded and surface vanadyl and vanadium samples have been described. The average connectivity of these samples was determined carefully by gravimetric analysis. Vanadium weight percentage was

Table 3 - 11 All capping vanadyl and vanadium compounds.

	Code	Silicate platform	Excess	Average molecular formula	Wt%
1	II-156	$(\text{Me}_3\text{Sn})_{3.75}(\text{SiCl}_{1.75})_{1.89}\text{Si}_8\text{O}_{20}$	VOCl_3	$(\text{VOCl}_2)_{3.75}(\text{SiCl}_{1.75})_{1.89}\text{Si}_8\text{O}_{20}$	15.50
2	II-154	$(\text{Me}_3\text{Sn})_{3.75}(\text{SiCl}_{1.75})_{1.89}\text{Si}_8\text{O}_{20}$	VCl_4	$(\text{VCl}_3)_{3.75}(\text{SiCl}_{1.75})_{1.89}\text{Si}_8\text{O}_{20}$	14.63
3	II-224	$(\text{Me}_3\text{Sn})_{1.49}(\text{Me}_2\text{SiCl}_{0.42})_{4.12}\text{Si}_8\text{O}_{20}$	VOCl_3	$(\text{VOCl}_2)_{1.49}(\text{Me}_2\text{SiCl}_{0.42})_{4.12}\text{Si}_8\text{O}_{20}$	7.19
4	II-226	$(\text{Me}_3\text{Sn})_{1.49}(\text{Me}_2\text{SiCl}_{0.42})_{4.12}\text{Si}_8\text{O}_{20}$	VCl_4	$(\text{VCl}_3)_{1.49}(\text{Me}_2\text{SiCl}_{0.42})_{4.12}\text{Si}_8\text{O}_{20}$	7.00

also calculated after the connectivity had been determined. Another important line of evidence that may be used to determine the vanadium weight percentage in each sample is to use atomic absorption (AA) or atomic emission (AE) spectroscopy. Both of these spectroscopies are instrumental techniques used to measure the concentration of metal ions in solution. Vanadyl or vanadium liquid samples were aspirated via a nebulizer and burned in a flame. Three different samples had been measured and all of the results from AA and AE spectroscopies were consistent with the results from gravimetric analysis. Differences between these two techniques are less than 5% (Table 3-12).

The results from AA and AE spectroscopies are in good agreement with the results from gravimetric data. It proves the concept that the average connectivity in these materials is accurate and that the weight percent vanadium of each sample can be determined from the average molecular formula.

Table 3 - 12 wt % from AA and AE

	Code	Average molecular formula	mg	model	³ Average (ppm)	Wt%	Wt% (From ⁴ GA)
1	II-054	(Me ₃ Sn) ₅ (VO)Si ₈ O ₂₀	108	¹ AA	38.18	3.54	3.56
				² AE	40.36	3.74	3.56
2	II-060	(Me ₃ Sn) ₅ (VO)Si ₈ O ₂₀	97	AA	35.30	3.64	3.56
				AE	37.18	3.87	3.56
3	II-058	(Me ₃ Sn) _{2.94} (Me ₂ SiCl _{0.46}) _{1.34} (VO)Si ₈ O ₂₀	100	AA	45.96	4.60	4.27
				AE	47.30	4.73	4.27

All of the samples were digested in 100 ml solution. 1. AA: represents atomic absorption, 2. AE: represents atomic emission, 3. The number in the column were the average number from three consecutive injections. 4. GA: represents gravimetric analysis.

3.3.2 Solid state NMR

3.3.2-1 Reaction time, temperature, and solvents

Section 3.3.1 described how to synthesize three-connected “embedded” vanadyl and four-connected “embedded” vanadium materials. As more V-O-Si links are formed, more V-Cl bonds are lost and more of the byproduct, Me_3SnCl , is generated. Vanadyl trichloride reacts with $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ at room temperature to form a cloudy solution. If the ratio of VOCl_3 to tin cube is higher than 2 to 1, precipitates form immediately after the two reagents are mixed together. The color of the vanadyl (V) trichloride dissolved in the methylene chloride is orange. After the addition of $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$, the transparent orange solution changes to yellow with the formation of a precipitate instantly. Upon standing for 30 minutes, color of the reaction mixture changes from yellow to pale yellow followed by a change to pale purple after one to two hours. In this section, ^{51}V solid state NMR spectra of vanadyl samples are presented and analyzed. No analogous spectra for vanadium (IV) materials were obtained because paramagnetic vanadium (IV) (d^1) samples can not be observed in ^{51}V NMR.

The isotropic ^{51}V chemical shifts for 1-, 2-, 3-connected vanadyl centers in the matrix were predicted to appear at 0 ppm for VOCl_3 , approximately -290 ~ -310 ppm for $(\text{O=})\text{VOCl}_2$ (cappers), -530 ~ -560 ppm for $(\text{O=})\text{VO}_2\text{Cl}$ (dilinkers), and -640~700 ppm for $(\text{O=})\text{VO}_3$ (trilinkers).^{ref} Figure 3-12 illustrates the chemical shifts from different types of vanadyl compounds. The wavy lines observed in ^{51}V SSNMR spectra are spinning side bands. A higher spinning

^{51}V -Solid State NMR

Isotropic peaks

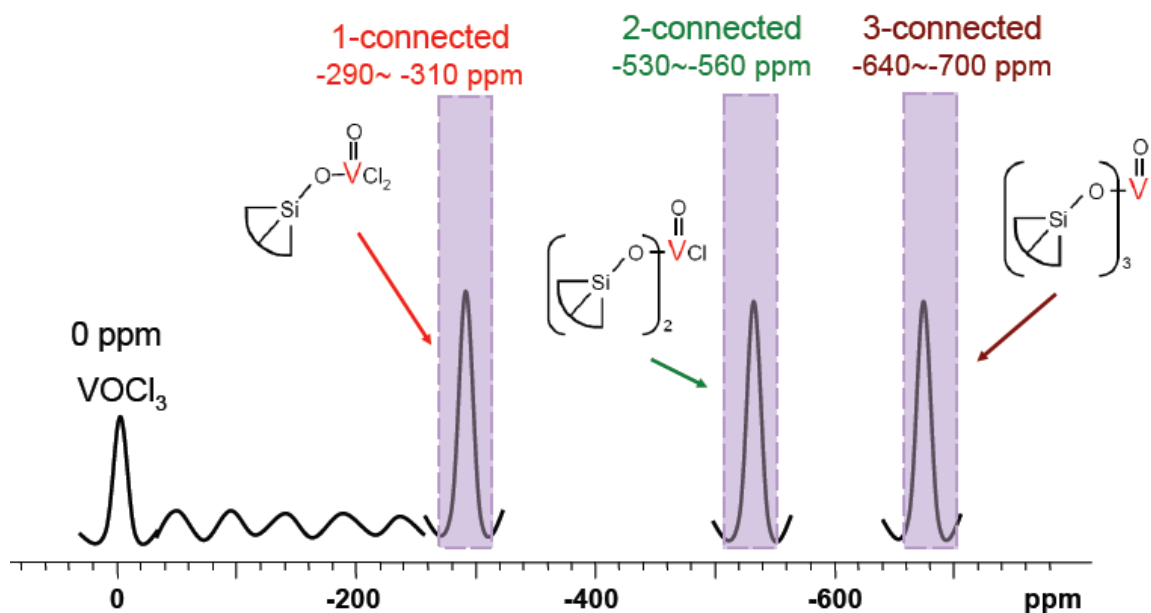


Figure 3 - 12 Isotropic peaks of ^{51}V SSNMR

speed produces larger line width between each side-band. The positions of the spinning side bands change as the spinning rate changes but the isotropic peak does not move under different spinning rate. The spinning side bands and isotropic peaks might overlap if the material contains more than one type of vanadyl. Isotropic peaks are finally identified by changing the spinning rate and identifying the undrifted peak. The highest spinning rate of the SSNMR instrument in the Department of Chemistry at the University of Tennessee is around 8.5 KHz. This is not sufficient to unambiguously separate the spinning sideband patterns for two- and three-connected vanadyl linkers from one

another. The two- and three-connected species would be resolved if 10 KHz or higher spinning rate was available.

The ^{51}V solid state NMR spectra of the products from the reaction of 1.33 VOCl_3 : 1.0 tin cube show that a mixture of di- and tri-linkered oligomeric species was formed (Figure 3-13).

Spectra A and B in figure 3-13 show that extending the reaction time from 15 hours to 24 hours at room temperature (around 20°C) does not affect the results. Increasing the temperature to 40°C and varying the reaction time (6 hours, 12 hours and 24 hours), did not cause the ^{51}V SSNMR spectra to change significantly (spectra C D, and E). The distribution of peaks at the chemical shift ranges expected for three-connected and two-connected vanadyl also doesn't change if the temperature is increased to 60°C for 12 hours (spectrum F).

Samples of spectra A to F were synthesized in CH_2Cl_2 solutions which have a boiling point of $39\text{--}40^\circ\text{C}$. It is not possible to run the reaction at higher temperature with methylene chloride in sealed reaction vessels. In order to investigate higher reaction temperatures, other higher boiling point solvents such as toluene (boiling point: 110°C) were used. When VOCl_3 (gold yellow) was added to toluene, the solution changed to dark orange consistent with the formation of a charge transfer complex between vanadium atoms and π -bonds of the aromatic solvent. Once VOCl_3 reacts with $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ and forms V-O-Si bonds the interaction between vanadium and solvent decreases and the color changes from deep dark orange to orange immediately and subsequently to

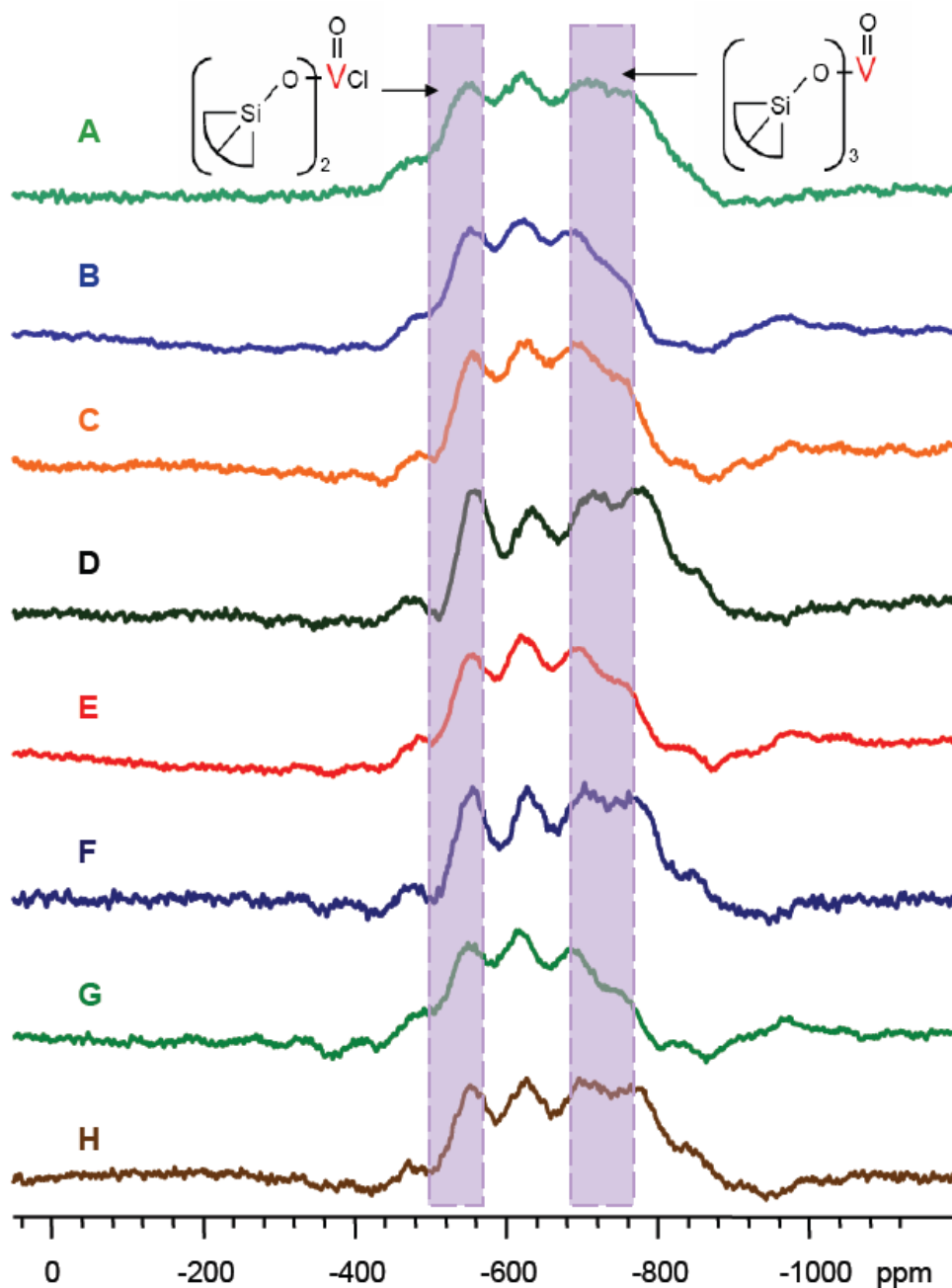


Figure 3 - 13 ^{51}V SSNMR, V51-MAS, spinning rate = 6.555 KHz, $I_b = 200$, $d1 = 0.2$ sec, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} : \text{VOCl}_3 = 1:1.33$ (Sn : Cl= 1 : 0.5)

A: MYL-I-200, room temperature, 15 hours in CH_2Cl_2 , B: MYL-I-236, room temperature, 24 hours in CH_2Cl_2 , C: MYL-I-242, 40°C , 6 hours in CH_2Cl_2 , D: MYL-I-246, 40°C , 12 hours in CH_2Cl_2 , E: MYL-I-250, 40°C , 24 hours in CH_2Cl_2 , F: MYL-I-252, 60°C , 12 hours in CH_2Cl_2 , G: MYL-I-256, 60°C , 6 hours in Toluene, H: MYL-I-258, 80°C , 6 hours in Toluene

yellow-orange. The ^{51}V SSNMR spectra G and H were obtained from the samples which were synthesized in the toluene at 60°C and 80°C for 6 hours. Both of these spectra are similar to spectra A to F which were synthesized from CH_2Cl_2 . This observation is consistent with the vanadyl environments in these materials being similar regardless of which solvent is chosen. Gravimetric analyses of samples when the ratio of the VOCl_3 to $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is higher than 1 to 1 such as 1.33 : 1 give an average connectivity of the vanadyl centers of less than three consistent with a mixture of two and three-connected vanadyl centers. The ^{51}V SSNMR data support gravimetric analysis results under variable reaction solvents, temperatures and times.

^{29}Si solid state NMR (Figure 3-14) spectra show that a significant number of trimethyltin groups remained in these materials. The chemical shifts of silicon atoms for Si-O-Sn and Si-O-V groups are slightly different. The peak at around -100 ppm in ^{29}Si NMR is assigned to the residual trimethyltin groups in Si-O-Sn groups. The peak at ~ -105 ppm is assigned to silicon atoms engaged in Si-O-V groups. The small peak at around -24 ppm arises from silicon grease which was used to seal the NMR rotor.

Cross polarization magic angle spinning (CPMAS) NMR spectra (Figure 3-15) show the same chemical shifts as the spectra in Figure 3-13. The cross polarization from silicon to protons occurs through dipolar interactions between these two nuclei. CPMAS experiments can be used to observe silicon signals having hydrogen atoms around. The relative intensity of Si-O-Sn peak at ~ -100

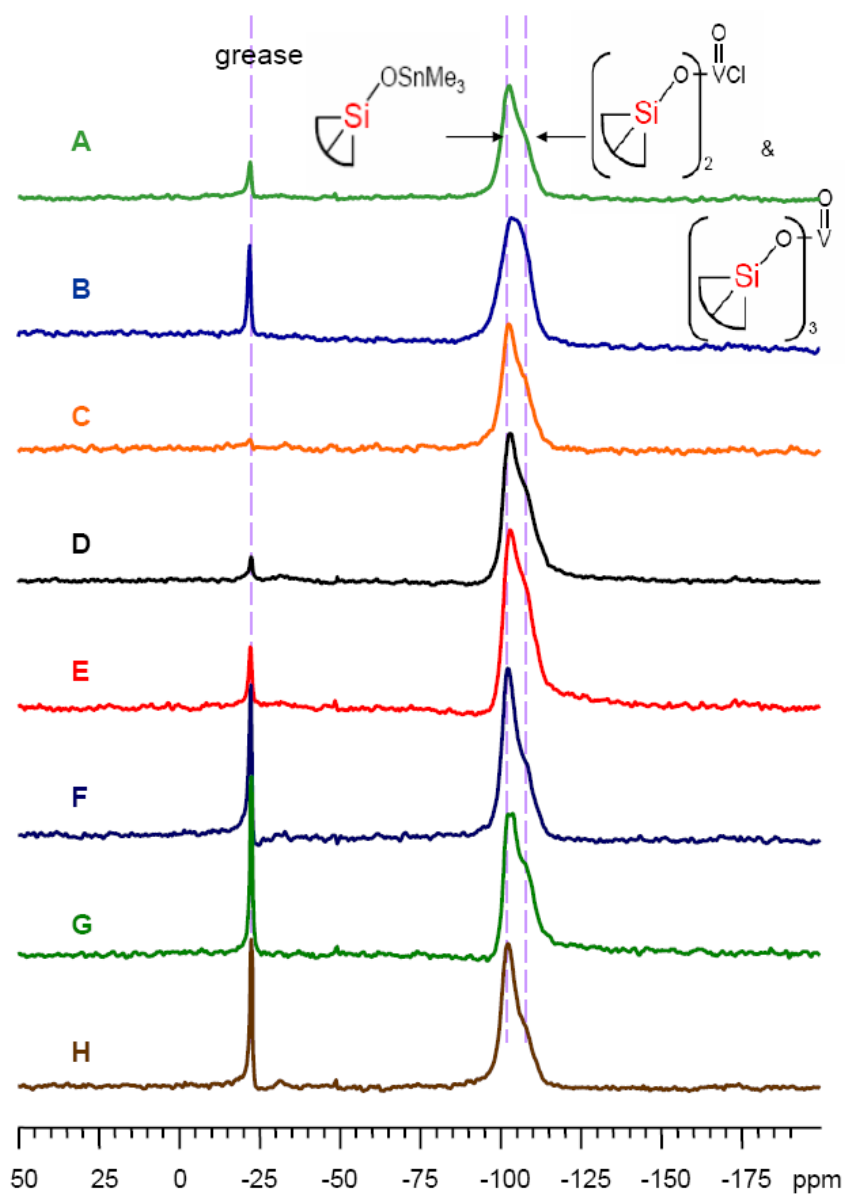


Figure 3 - 14 ^{29}Si SSNMR A: MYL-I-200, room temperature, 15 hours in CH_2Cl_2 , B: MYL-I-236, room temperature, 24 hours in CH_2Cl_2 , C: MYL-I-242, 40°C , 6 hours in CH_2Cl_2 , D: MYL-I-246, 40°C , 12 hours in CH_2Cl_2 , E: MYL-I-250, 40°C , 24 hours in CH_2Cl_2 , F: MYL-I-252, 60°C , 12 hours in CH_2Cl_2 , G: MYL-I-256, 60°C , 6 hours in Toluene, H: MYL-I-258, 80°C , 6 hours in Toluene

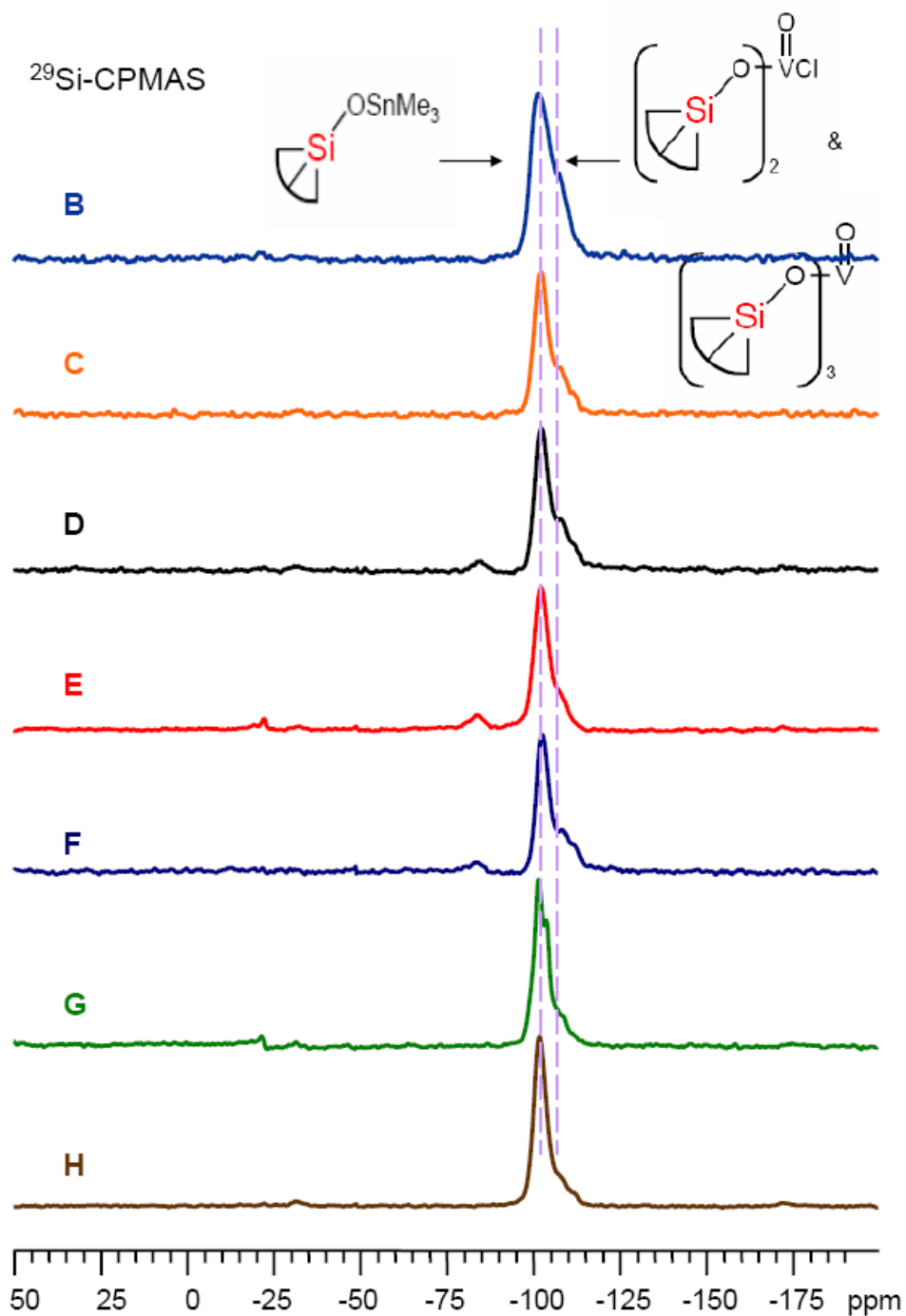


Figure 3 - 15 ²⁹Si CPMAS SSNMR

B: MYL-I-236, room temperature, 24 hours in CH₂Cl₂, C: MYL-I-242, 40°C, 6 hours in CH₂Cl₂, D: MYL-I-246, 40°C, 12 hours in CH₂Cl₂, E: MYL-I-250, 40°C, 24 hours in CH₂Cl₂, F: MYL-I-252, 60°C, 12 hours in CH₂Cl₂, G: MYL-I-256, 60°C, 6 hours in Toluene, H: MYL-I-258, 80°C, 6 hours in Toluene

ppm is larger than Si-O-V peak at $\sim$ -105 ppm in Figure 3-15 because protons in trimethyltin groups near Si-O-Sn groups generate stronger dipolar interactions and therefore greater peak enhancements.

3.3.2-2 Different ratios of VOCl_3 to $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ reactions

Changing the loading ratio of VOCl_3 to $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ resulted in different distributions of vanadium centers in the matrix. Higher vanadyl loading ratios produce more one-connected or two-connected vanadium centers. A lower vanadyl loading ratio yields only two and three-connected vanadium centers but no one-connected vanadium centers (“capping” vanadyl). ^{51}V SSNMR spectra show that when the ratio of vanadium to cube is 1.33 to 1, the product has a mixture of di- and tri-linkers (spectrum M in Figure 3-16). When the ratio of vanadium to cube increases to 2.66 : 1 (Cl : Sn = 1 : 1), the spectrum shows 2-connected vanadium centers dominate the spectrum (spectrum N in Figure 3-16). When the ratio is raised to 5.33 VOCl_3 : 1 cube (Cl : Sn = 2 : 1), the product contains predominately 1-connected vanadium centers (spectrum O in Figure 3-16).

From ^{29}Si SSNMR spectra, lower vanadyl loadings yield materials containing a larger percentage of unreacted trimethyltin groups based on the relative intensity of the peak at $\sim$ -100 ppm (Si-O-Sn groups) compared to the peak at $\sim$ -105 ppm (spectrum I in Figure 3-17). As the ratio of VOCl_3 to cube

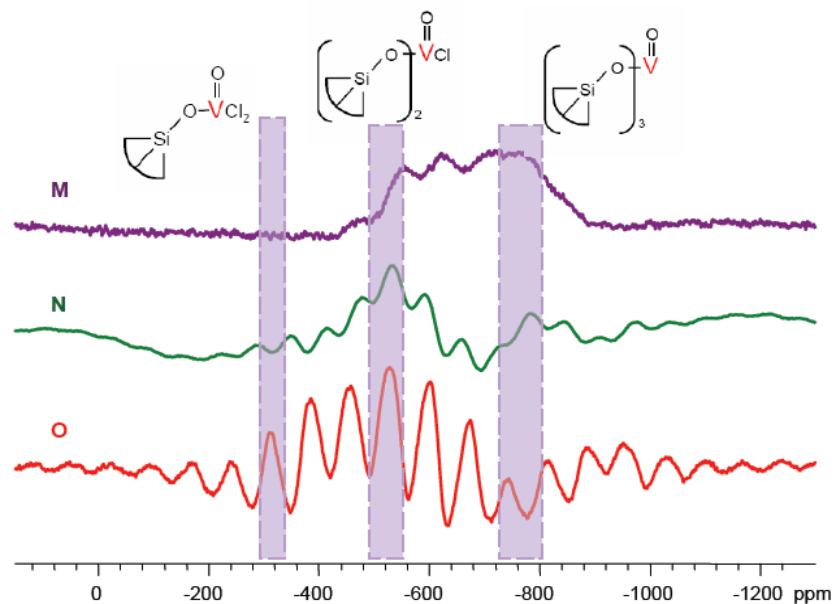


Figure 3 - 16 ^{51}V MAS spectra, spinning rate = 6.555 KHz, $t_b = 150$, $d_1 = 0.2$ sec,
M: MYL-I-200, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1), N: MYL-I-218, VOCl_3 : cube = 2.66 : 1
(Cl : Sn = 1 : 1), O: MYL-I-228, VOCl_3 : cube = 5.33 : 1 (Cl : Sn = 2 : 1)

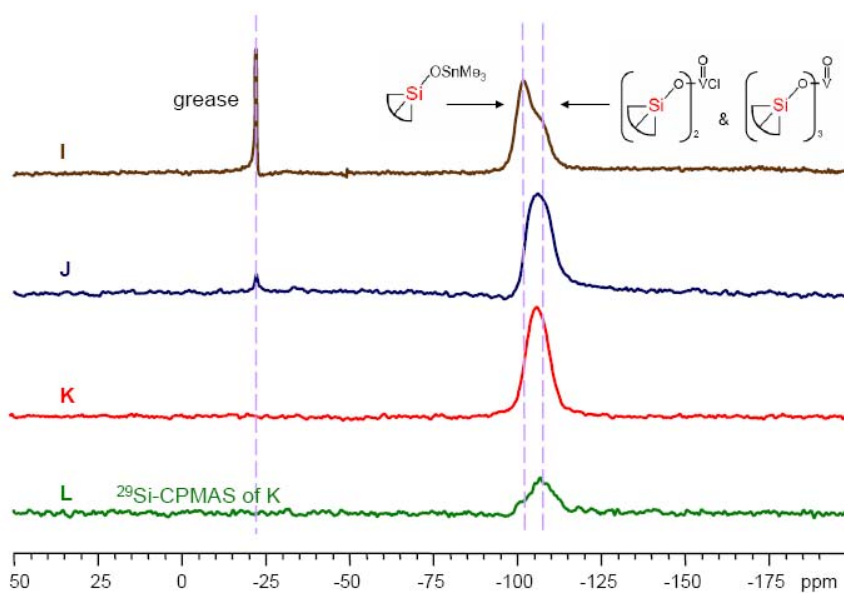


Figure 3 - 17 ^{29}Si SSNMR spectra, room temperature, 15 hours in CH_2Cl_2 .
I: MYL-I-200, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1), J: MYL-I-218, VOCl_3 : cube = 2.66 : 1 (Cl :
Sn = 1 : 1), K: MYL-I-228, VOCl_3 : cube = 5.33 : 1 (Cl : Sn = 2 : 1), L: MYL-I-228, VOCl_3 : cube =
5.33 : 1 (Cl : Sn = 2 : 1), CPMAS

increases to 2.66 : 1 or 5.33 : 1, the ^{29}Si spectra show that the intensity of Si-O-Sn peak at ~ 100 ppm decreases and Si-O-V peak at ~ 105 ppm increases. (spectra J and K in Figure 3-17). These results indicate more Si-O-V groups were formed and less Si-O-Sn groups remained in higher VOCl_3 loading reactions. Spectrum L in Figure 3-17 is the result of a cross-polarization experiment for a VOCl_3 : cube = 5.33 : 1 reaction. Due to the high loading ratio of VOCl_3 in the reaction, only small amounts of trimethyltin groups remain in the product. Weak dipole interactions between silicon and protons in the matrix result in weak signals in the ^{29}Si CPMAS spectrum.

3.3.2-3 The second dose and the third dose reactions

The purpose of using SiCl_4 or Me_2SiCl_2 as the second dose reagents is to chemically “glue” the vanadyl containing oligomeric species together and form cross linking matrices. Figure 3-18 shows the ^{29}Si SSNMR spectra of two-dose reactions in which the precursor was the product from a 1.33 : 1 (VOCl_3 : tin cube) reaction. The sample of spectrum P in Figure 3-18 was synthesized by adding excess SiCl_4 (20 equivalents) to the reaction and reacting with vanadyl oligomeric precursor for 15 hours at room temperature. Most of trimethyltin groups have been lost through reaction with silicon tetrachloride. But the ^{29}Si SSNMR spectrum (spectrum P) shows that some unreacted trimethyltin groups remain in the material. The product also contains a majority of one-connected Si centers (-45 ppm) and a small number of two-connected Si centers (~ -70 ppm).

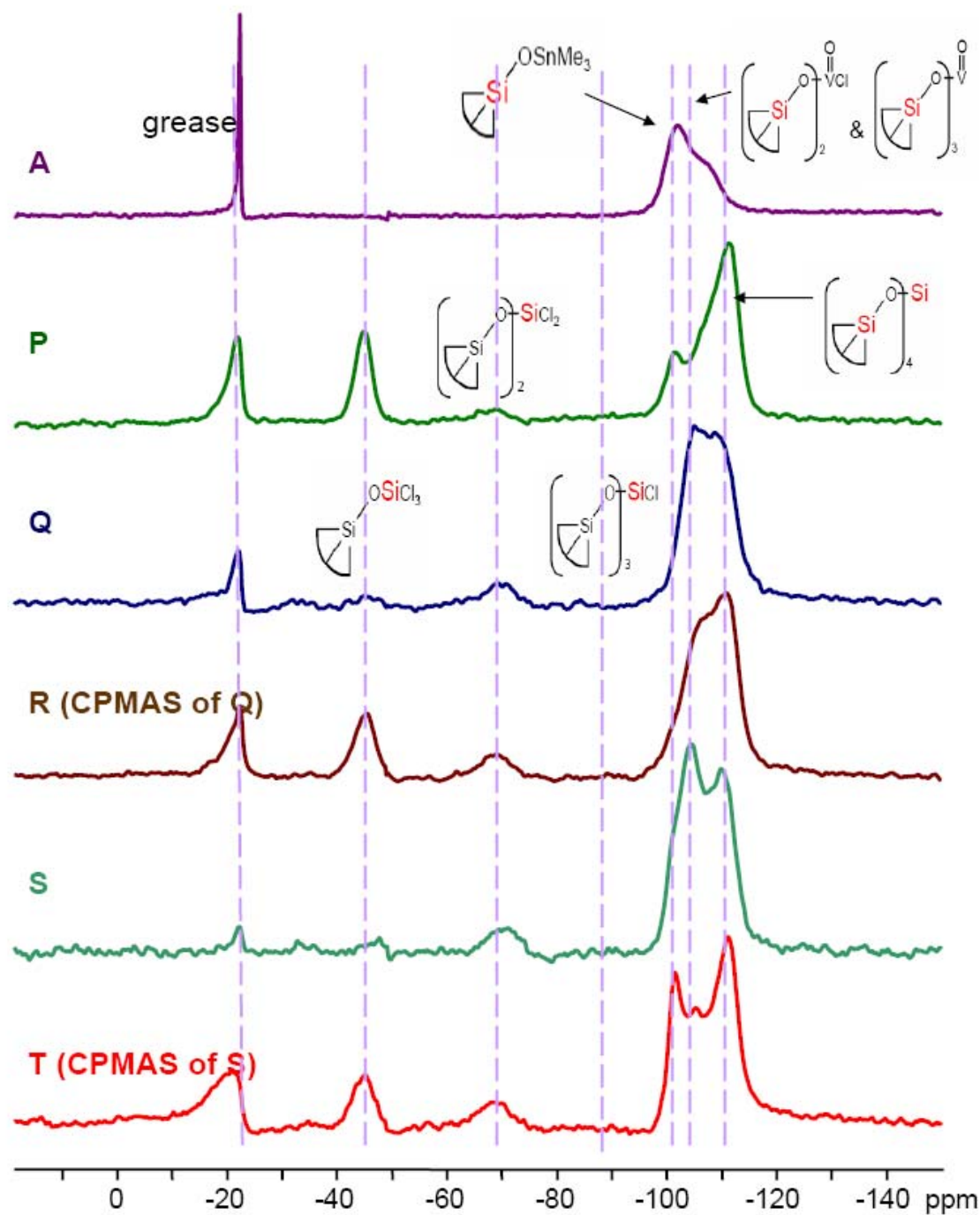


Figure 3 - 18 ^{29}Si NMR, precursor: VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1)
 A: MYL-I-200, precursor, P: MYL-I-206, excess SiCl_4 15 hrs, Q: MYL-I-244, cube: Si=1:1.1 SiCl_4
 40°C 7 hrs, R: MYL-I-244, CPMAS of Q, S: MYL-I-254, cube: Si=1:2.6 SiCl_4 40°C 6 hrs, T: MYL-I-
 254, CPMAS of S

The interpretation of this spectrum indicates that the reaction did not proceed efficiently at room temperature even after 15 hours. Observation of a major one-connected Si peak at -45 ppm indicates that only one chloride ligand in most of the SiCl_4 groups reacted with a tin group.

If a limiting amount of SiCl_4 is used in the second dose reaction (cube : Si = 1 : 1.11) at 40°C for 7 hours, the amount of two-connected Si centers increases and fewer one-connected Si centers are formed (Spectra Q and R). Some trimethyltin groups remained in this case and a new peak was formed at -110 ppm representing Si-O-Si groups which derived from tetra-linked silicon centers between cubes. Raising the ratio of SiCl_4 : cube to 2.6 : 1 and running the reaction at 40°C for 6 hours results in a matrix containing a similar ratio of one and two-connected linkers with some unreacted trimethyltin groups.

If a precursor derived from a higher vanadyl loading (VOCl_3 : tin cube = 2.67 : 1) is reacted with excess SiCl_4 at room temperature for 15 hours, only one-connected Si centers are formed (Spectra U and V in Fig 3-19). It is difficult to interpret whether trimethyltin groups still remain in the product from MAS spectrum alone (spectrum U) because the signal at -100 ppm is not observed clearly. But the CPMAS experiment (spectrum V) indicates that some trimethyltin groups are present.

The ^{51}V SSNMR spectrum W in Figure 3-20 was obtained from a sample with a 1:33 :1 ratio of VOCl_3 : tin cube. When excess SiCl_4 reacted with this material, the ^{51}V SSNMR spectrum changed dramatically and a significant

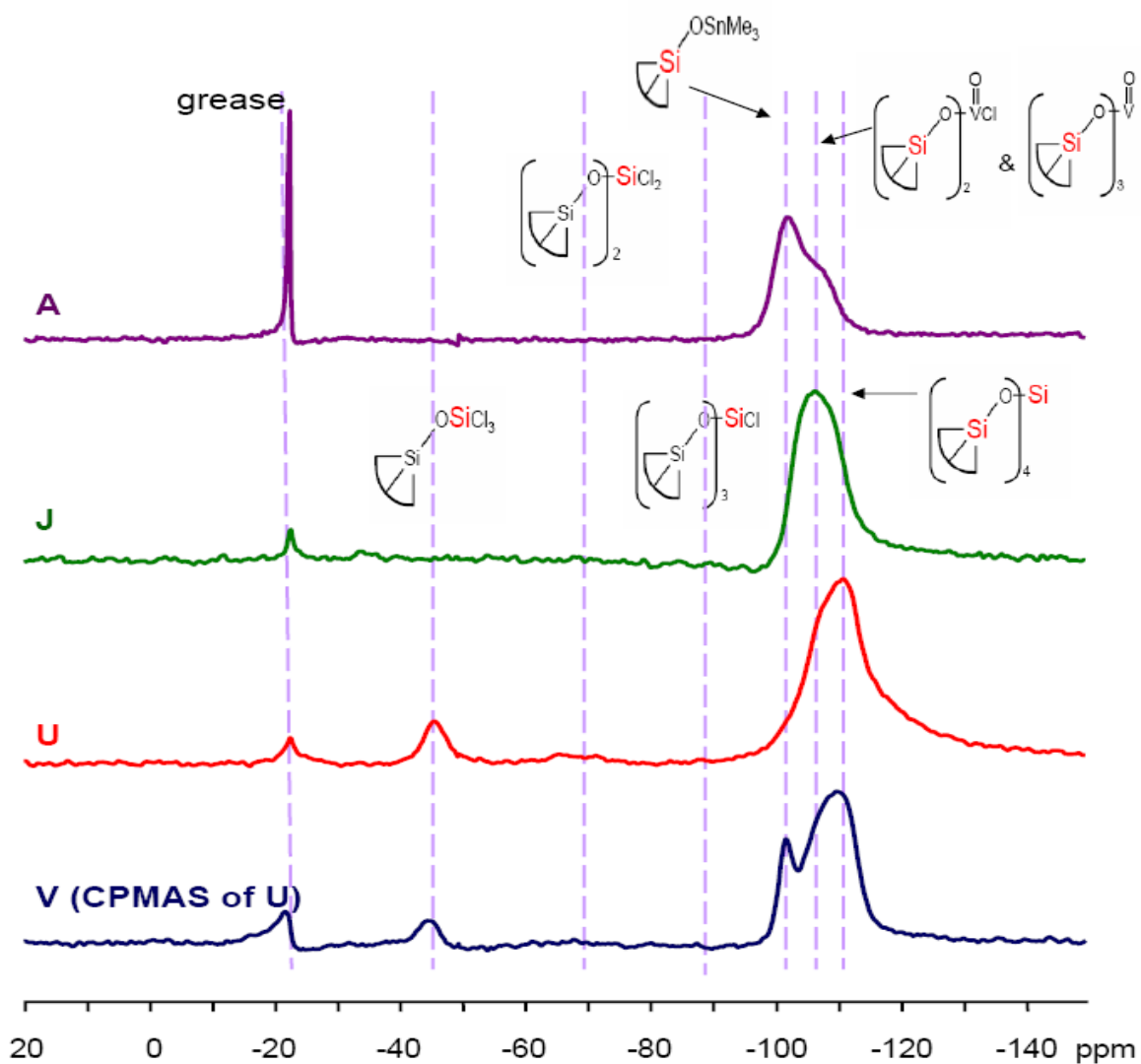


Figure 3 - 19 ^{29}Si NMR, room temperature in CH_2Cl_2

A: MYL-I-200, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1), J: MYL-I-218, VOCl_3 : cube = 2.66 : 1 (Cl : Sn = 1 : 1), U: MYL-I-224, MYL-I-218 +second dose: excess SiCl_4 for 15 hrs, V: MYL-I-224, CPMAS of U

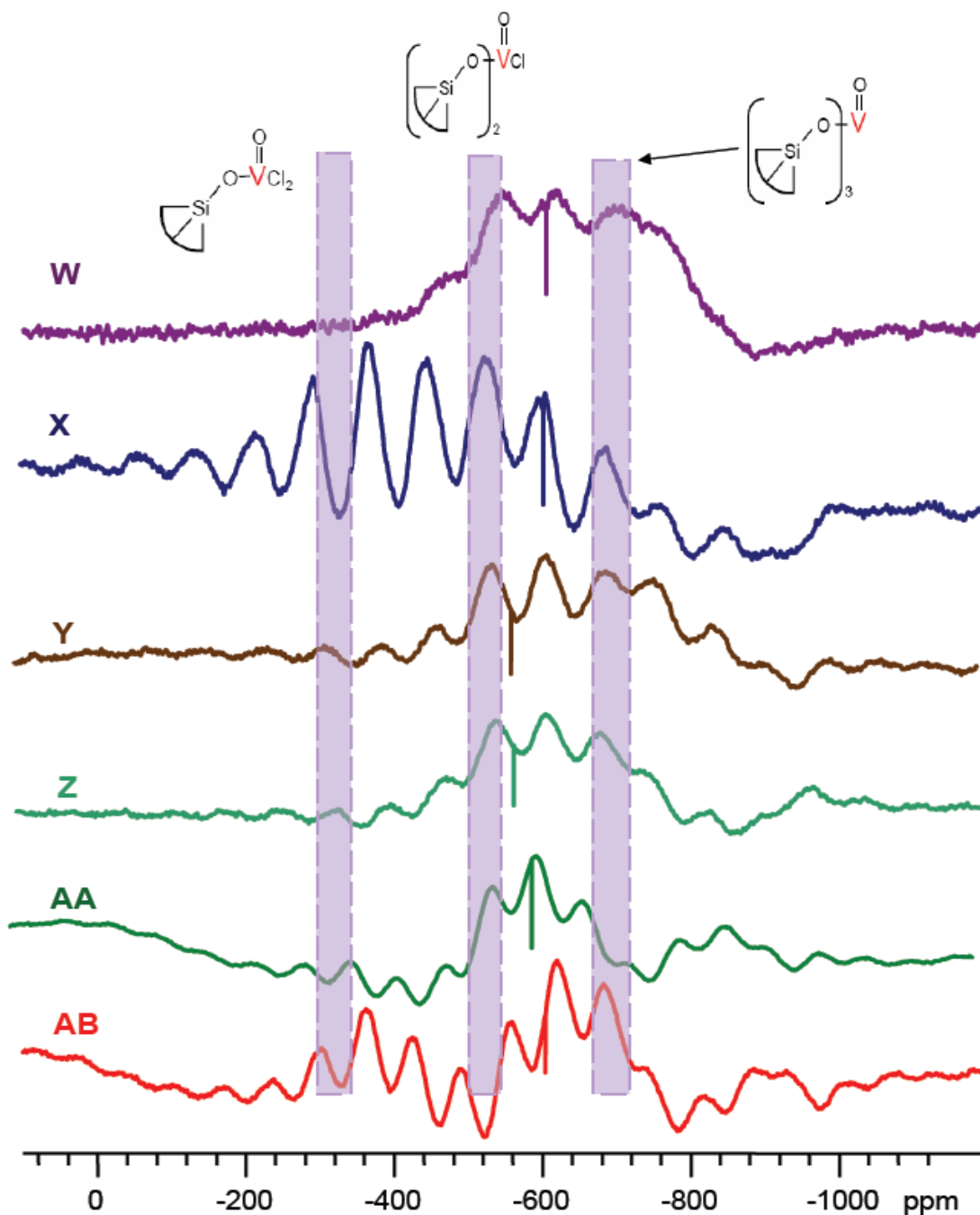
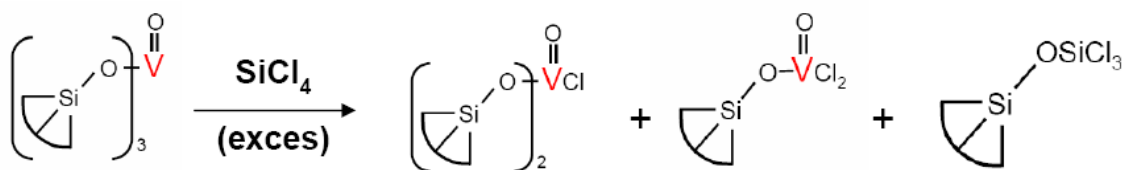


Figure 3 - 20 ^{51}V -MAS spectra, spinning rate = 6.555 KHz, $I_b = 150$, $d1 = 0.2$ sec, W: MYL-I-200, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1), X: MYL-I-206, VOCl_3 : cube = 1.33 : 1 then excess SiCl_4 15 hrs, Y: MYL-I-244, VOCl_3 : cube = 1.33 : 1 then SiCl_4 : cube = 1.1 : 1 at 40°C 7 hrs, Z: MYL-I-254, VOCl_3 : cube = 1.33 : 1 then SiCl_4 : cube = 2.6 : 1 at 40°C 6 hrs, AA: MYL-I-218, VOCl_3 : cube = 2.66 : 1 (Cl : Sn = 1 : 1), AB: MYL-I-224, VOCl_3 : cube = 2.66 : 1 then excess SiCl_4 for 15 hrs,

number of one-connected vanadyl centers were observed. When smaller amounts of SiCl_4 were used in the reaction (SiCl_4 to cube ratios of 1.1 : 1 and 2.6 : 1), the spectra were not significantly different (spectra Y and Z). Similar results were observed when a higher loading vanadyl precursor (VOCl_3 : tin cube = 2.66 : 1) was reacted with excess SiCl_4 (spectra AA and AB represent before and after adding excess SiCl_4 respectively).

From these experiments, it appears that excess SiCl_4 in the reaction can alter the vanadyl environment and connectivity in the matrix. The color of one-dosed vanadium oligomer is pale purple. After reacting with excess SiCl_4 , the material changes to a gray-white color. The color of the material changes to green (emerald) immediately when the material is exposed to the air.

Based on the experiments described to this point, exposure of vanadyl linked oligomers in excess SiCl_4 appears to disrupt V-O-Si linkages and form V-Cl groups. A reaction that could explain these observations is given in equation 18. The three-connected vanadyl centers change to two or one-connected center and form a new Si-O-Si group after excess SiCl_4 add to the reaction.



Equation 18

Other tests of this reaction were to use excess PCl_3 or TMSCl as reaction reagents. The spectra AD and AE in the Figure 3-21 indicate both excess PCl_3 and TMSCl also changed the vanadyl environment in a manner similar to what was observed in the case of SiCl_4 .

At this stage, several different reaction conditions were tried. ^{51}V and ^{29}Si SSNMR spectra were used to characterize the vanadyl and silicate linkers' distributions in different materials which were prepared from different loading ratios, reaction temperatures, solvents, times, and reagents. In the following discussion, the embedded vanadyl samples were prepared by using small

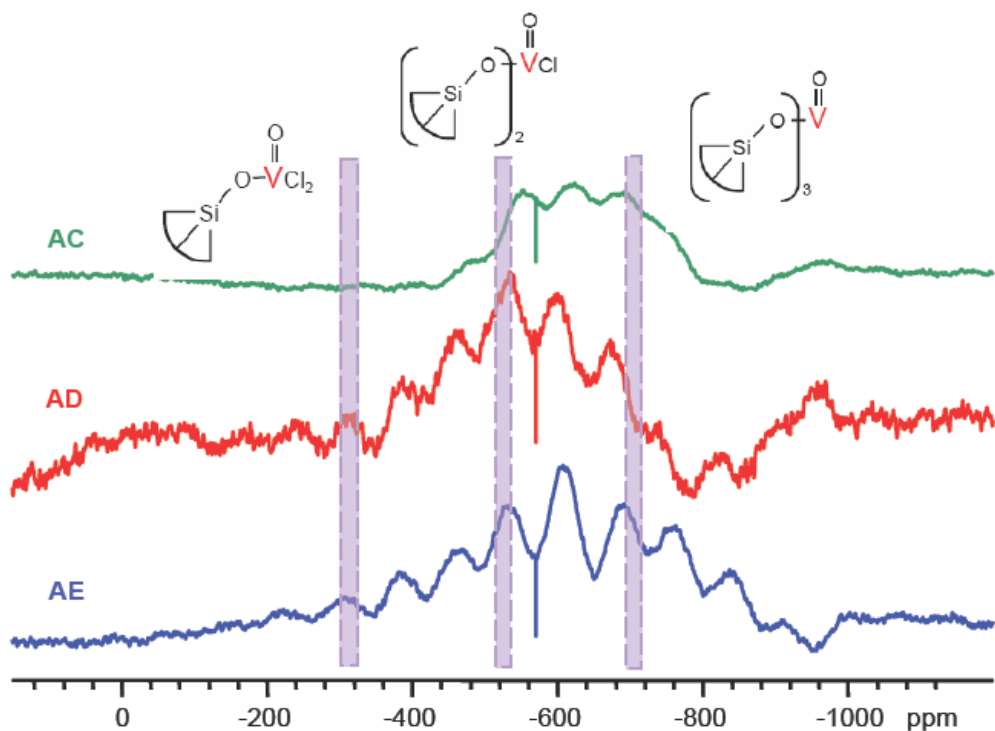


Figure 3 - 21 ^{51}V SSNMR, spinning rate = 6.555 KHz, $I_b = 150$, $d_1 = 0.2$ sec,
 AC: MYL-I-236, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1), AD: MYL-I-238, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1) then excess PCl_3 , AE: MYL-I-240, VOCl_3 : cube = 1.33 : 1 (Cl : Sn = 0.5 : 1) then excess TMSCl

amount of VOCl_3 in the first dose reaction (VOCl_3 : tin cube < 1 : 1). A limiting amount of SiCl_4 or Me_2SiCl_2 was used in the second dose reaction to avoid altering the vandyl connectivity or environment. Then TMSCl was added in the final step to remove residual trimethyltin groups.

Figure 3-22 shows spectra at three different spinning rates for the same embedded vanadyl sample (VOCl_3 : tin cube is 0.33 : 1). The spinning rates of ^{51}V SSNMR spectra AF, AG, and AH were 5555, 6555, and 7555 Hz respectively. The isotropic peak at ~ -675 ppm indicates that only one type of vanadyl group (three-connected $\text{VO}(\text{OSi})_3$) exists in this material. Changing the spinning rate only alters the spinning side bands' positions but does not change

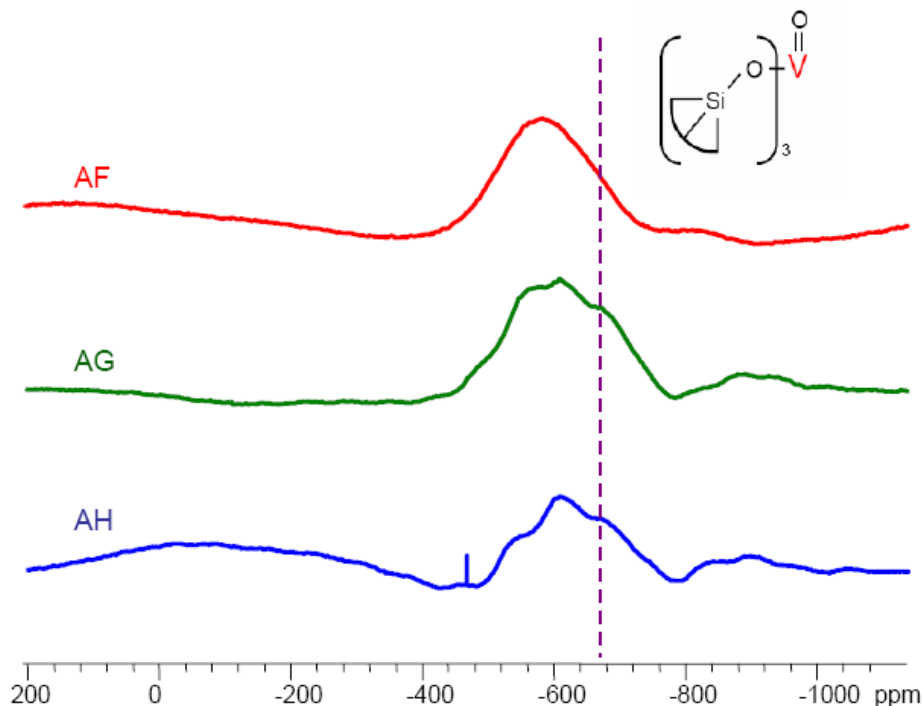


Figure 3 - 22 ^{51}V SSNMR spectra, From MYL-II-208, VOCl_3 : tin cube= 0.33 : 1 spinning rate = 5555 (AF), 6555 (AG), 7555 (AH) KHz

the chemical shift of the isotropic peak. The isotropic peak was identified by comparing the spectra at different spinning rates. A higher spinning rate gives better resolution because the spinning side bands are better separated from one another. The loading ratio of this vanadyl sample is very low and the weight % is only 0.99 % (from gravimetric analysis). The signals in these spectra were very weak. More than 10 thousand scans were required to obtain acceptable signal to noise.

Increasing the vanadyl to cube ratio to 0.67 : 1 gave clearer spectra at a higher spinning rate. ^{51}V SSNMR spectra AI, AJ, and AK in Figure 3-23 were collected under 5555, 6555, and 7555 Hz respectively from one-dosed embedded vanadyl sample. Reacting this one-dosed embedded vanadyl sample with Me_2SiCl_2 followed by the addition of TMSCl gave spectra AL (5555 Hz), AM (6555 Hz), and AN (7555 Hz). Only one type of vanadyl center was observed in these spectra. The isotropic peak at ~ -675 ppm was not affected by the addition of limiting amounts of Me_2SiCl_2 or by the removal of residual trimethyl tin groups via the addition of three equivalents excess TMSCl .

When the ratio of VOCl_3 to tin cube increased to 1 : 1, a single type of 3 connected vanadyl remained in the product (Figure 3-24). ^{51}V SSNMR Spectra AO, AP, and AQ were collected at 5555, 6555 and 7555 Hz from one-dosed embedded vanadyl sample. Adding Me_2SiCl_2 and TMSCl in the second and third dose reaction produced a trimethyl tin free sample. Spectra AR (5555 Hz), AS (6555 Hz), AT (7555 Hz) and AU (8555 Hz) indicate three connected vanadyl

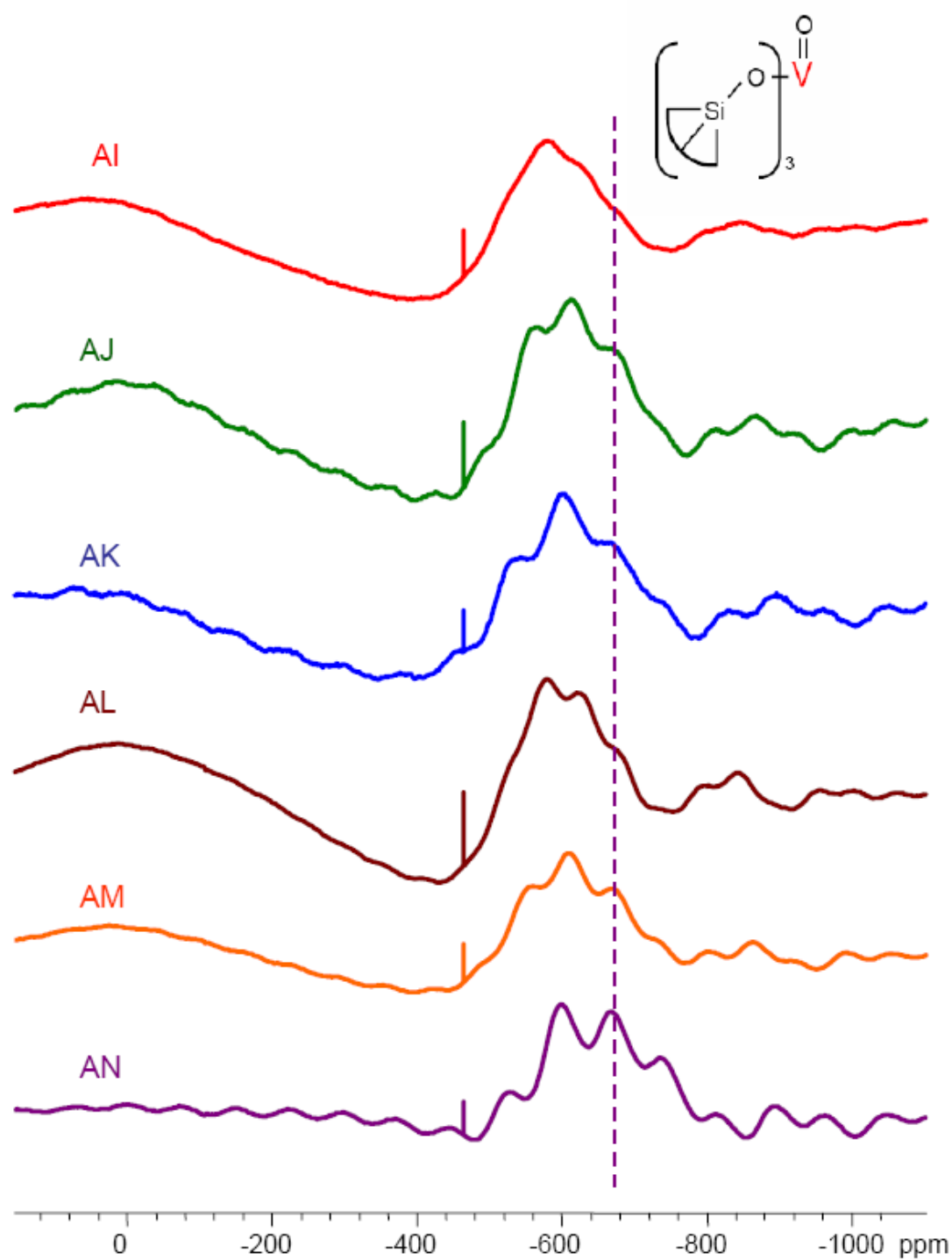


Figure 3 - 23 ^{51}V SSNMR, From MYL-II-212 and 218, VOCl_3 : tin cube= 0.67 : 1
 spinning rate = AI and AL 555Hz, AJ and AM 655 Hz, AK and AN 755 HZ

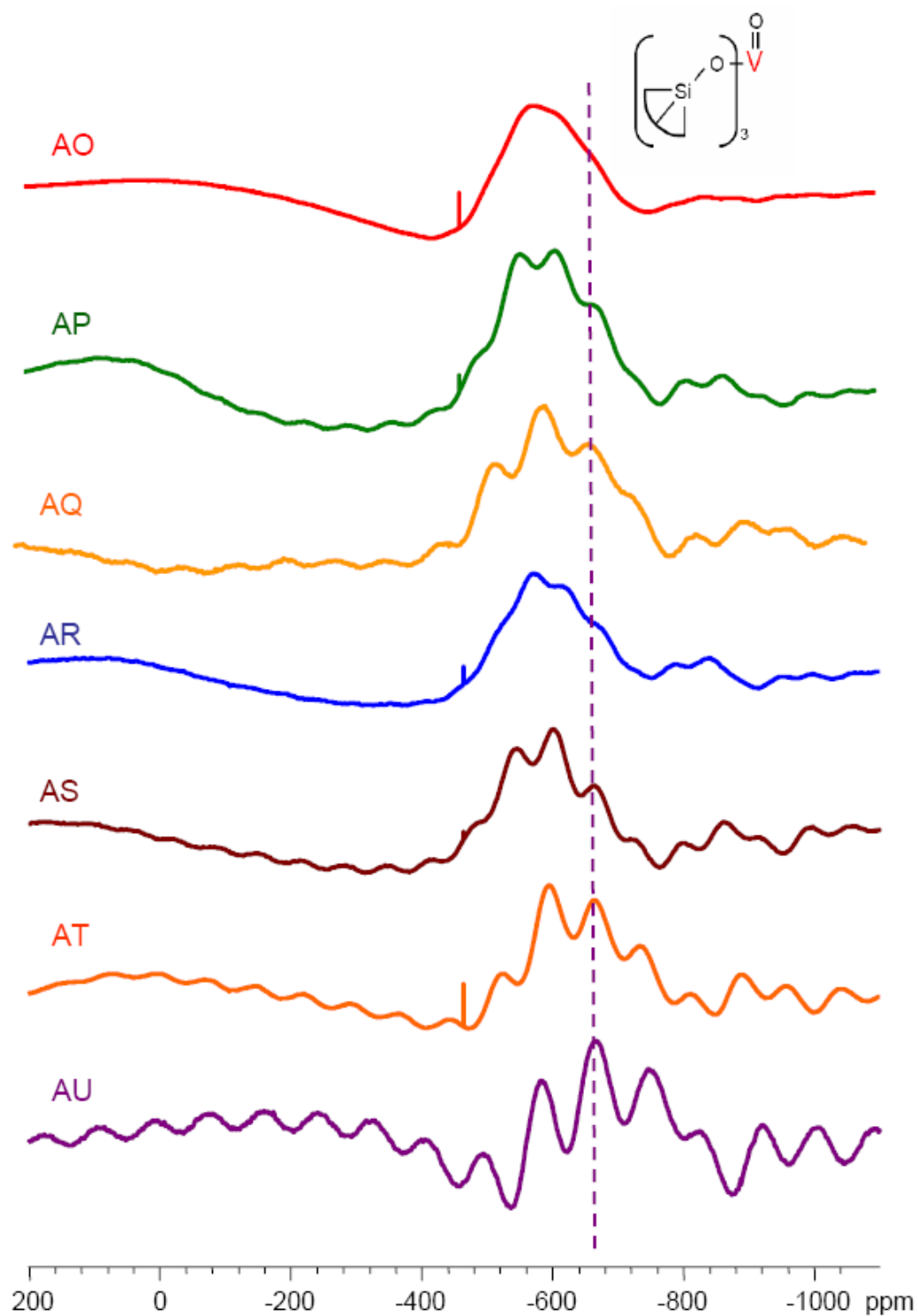


Figure 3 - 24 ^{51}V SSNMR, From MYL-II-206 and 228, VOCl_3 : tin cube= 1 : 1 spinning rate = AO and AR 5555Hz, AP and AS 6555 Hz, AQ and AT 7555 HZ, AU 8555 Hz.

remained in the matrix after adding Me_2SiCl_2 and TMSCl to cross link vanadyl oligomeric species and remove tin groups. The highest spinning rate (8555 Hz) in spectrum AU provided the clearest observation of the isotropic peak (~ 675 ppm) and spinning side bands.

Different low loading ratios of VOCl_3 to tin cube are compared in figure 3-25. ^{51}V SSNMR spectra AH, AK, and AQ were collected at 7555 Hz and only one isotropic peak at ~ 675 ppm was observed. Spectrum AQ is the clearest spectrum in figure 24 because the sample was prepared from the highest vanadyl loading ratio and has highest vanadyl weight percentage (3.51%). No two-connected (~ 540 ppm) or one-connected (~ 300 ppm) vanadyl centers were observed in these spectra. It strongly proves that when the ratio of VOCl_3 to tin cube is 1 : 1 or lower (or Cl : Sn ratio is 3 : 8 or lower), all of the vanadyl centers are three-connected “embedded” sites in the silicate building block matrix.

^{29}Si SSNMR MAS spectra from different vanadyl loading ratios of one-dose vanadyl samples are shown in Figure 3-26. The peak at ~ 100 ppm is assigned to residual trimethyltin groups in the material and the peak at ~ 105 ppm is assigned to newly formed Si-O-V groups after vanadyl reacted with the building blocks. The spectrum AV was collected from the lowest vanadyl loading sample (VOCl_3 : tin cube = 0.33 : 1) and the intensity of the peak at ~ 105 ppm is weaker than the other two spectra. When a higher VOCl_3 ratio was added in the reaction (spectrum AX), the relative intensity of the peak at ~ 105 ppm which

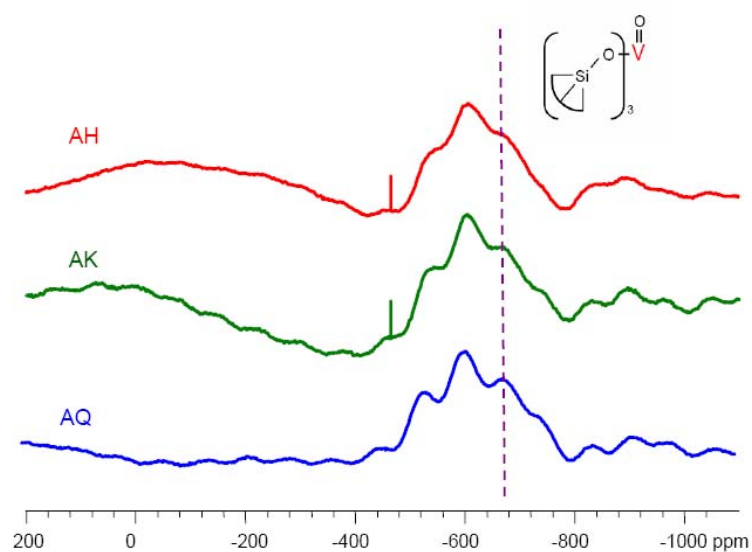


Figure 3 - 25 ^{51}V SSNMR spectra, VOCl_3 : tin cube= 0.33 : 1 (AH) , 0.67 : 1 (AK), 1 : 1 (AQ) spinning rate = 7555 HZ

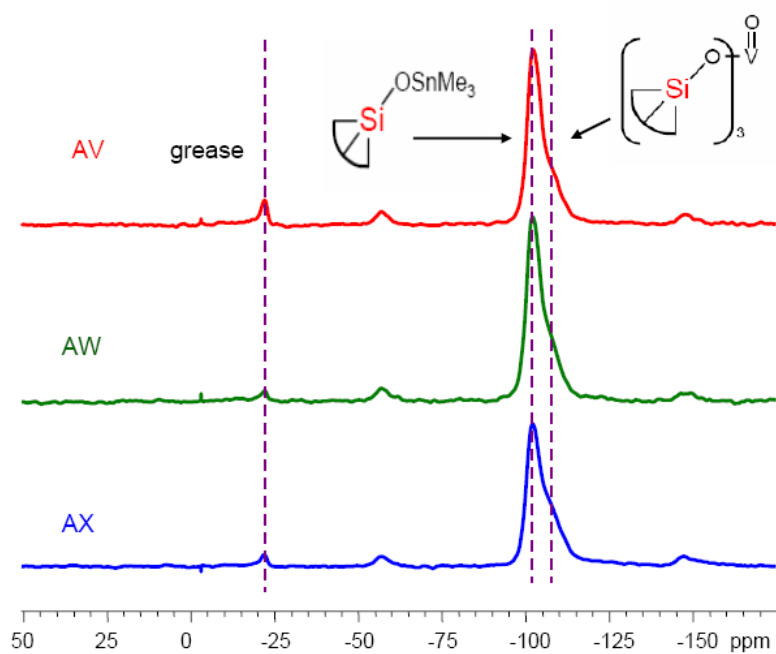


Figure 3 - 26 ^{29}Si SSNMR, (MYL-II-208, 212, 206), VOCl_3 : tin cube= 0.33 : 1 (AV) , 0.67 : 1 (AX), 1 : 1 (AX) spinning rate = 3555 HZ

represents the amount of Si-O-V groups increased because more Si-O-V groups were formed and less trimethyl tin groups remained in the product.

When the one-dose vanadyl oligomeric materials are reacted with Me_2SiCl_2 , different types of silicon bonds are formed. If only one chloride from Me_2SiCl_2 reacts with one trimethyltin group, a $\text{Si-O-SiMe}_2\text{Cl}$ group is formed and the chemical shift of this type silicon in ^{29}Si NMR is ~ 10 ppm. If both chloride ligands from Me_2SiCl_2 react with two trimethyltin groups, a $(\text{SiO})_2\text{-SiMe}_2$ group is formed and the chemical shift of this type silicon in ^{29}Si NMR is ~ -15 ppm. ^{29}Si MAS spectrum AW was collected from a one-dosed vanadyl sample (VOCl_3 : tin cube = 0.67 : 1) and lots of trimethyltin groups (~ -100 ppm) remained in this sample. ^{29}Si MAS spectrum AY and ^{29}Si CPMAS spectrum AZ in Figure 3-27 were collected on same vanadyl sample (VOCl_3 : tin cube = 0.67 : 1) after treating it with Me_2SiCl_2 and TMSCl . The peak at -15 ppm in spectra AY and AZ is assigned to $(\text{SiO})_2\text{-SiMe}_2$ groups. The smaller peaks at 10 ppm in spectra AY and AZ represent a small amount of one-connected SiMe_2 centers in this sample. The peak at ~ 15 ppm in spectra AY and AZ represents TMS group in the matrix. Spectrum AX was collected from a higher loading vanadyl sample (VOCl_3 : tin cube = 1 : 1). ^{29}Si MAS spectrum BA and ^{29}Si CPMAS spectrum BB (Figure 3-27) were collected from this higher loading vanadyl sample after treating with Me_2SiCl_2 and TMSCl . Spectra BA and BB indicate this sample contains more one-connected silicon linkers (10ppm) and less two-connected silicon centers (-15 ppm) after adding Me_2SiCl_2 in the reaction. TMS groups replaced most

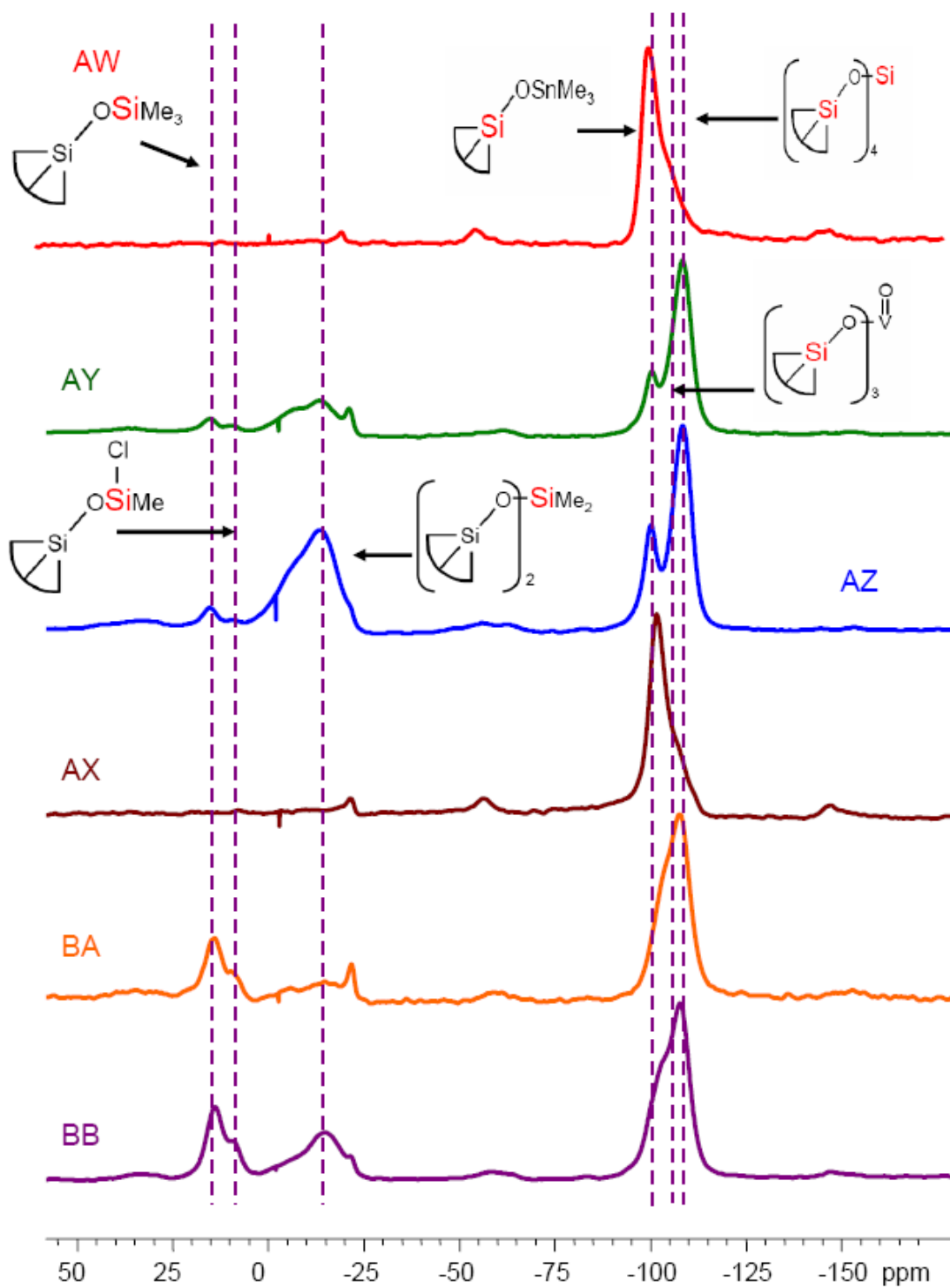


Figure 3 - 27 ^{29}Si MAS and CPMAS NMR (From MYL-II-212,218,206,228)
 AW, AY, AX, BA are MAS, AZ and BB are CPMAS

remaining trimethyl tin groups in this sample and resulted in a significant peak at 15 ppm. The peak at -100 ppm in spectra BA and BB is smaller than in spectra AY and AZ and indicates few if any residual trimethyltin groups remain in this sample. ^{29}Si CPMAS NMR spectra (AZ and BB) provide stronger peaks at -15 ppm (two-connected silicon), 10 ppm (one-connected silicon) and 15 ppm (TMS groups) because methyl groups around these silicon atoms enhance dipole interactions and increase the intensity of these peaks.

Spectra characterizing the three-connected vanadyl samples have been described thus far. Before focusing on the topic of surface vanadyl ^{51}V SSNMR spectra, the ^{29}Si SSNMR spectra of the silicate platform precursors will be discussed briefly. Two different silicate platforms were prepared by using SiCl_4 as the reagent. One was synthesized with a 0.75 :1 ratio of SiCl_4 : tin cube at 80°C for 24 hours in toluene. The other one was prepared from a 2 : 1 ratio of SiCl_4 : tin cube at 80°C for 24 hours in toluene. Figure 3-28 shows both ^{29}Si MAS and CPMAS spectra of these materials.

When the low loading ratio of SiCl_4 -to-tin cube was used, only one type of silicon center was formed (four-connected silicon). The ^{29}Si MAS spectrum BC and ^{29}Si CPMAS spectrum BD show there are no one-, two-, or three- connected silicon in the sample. All of chloride ligands in each SiCl_4 molecule reacted with trimethyl tin groups to form four-connected silicon centers. The peak at $\sim$ -110 ppm represents newly formed $\text{Si}(\text{O-Si})_4$ groups and the peak at $\sim$ 100 ppm represent residual trimethyl tin groups. There is no evidence for chlorine

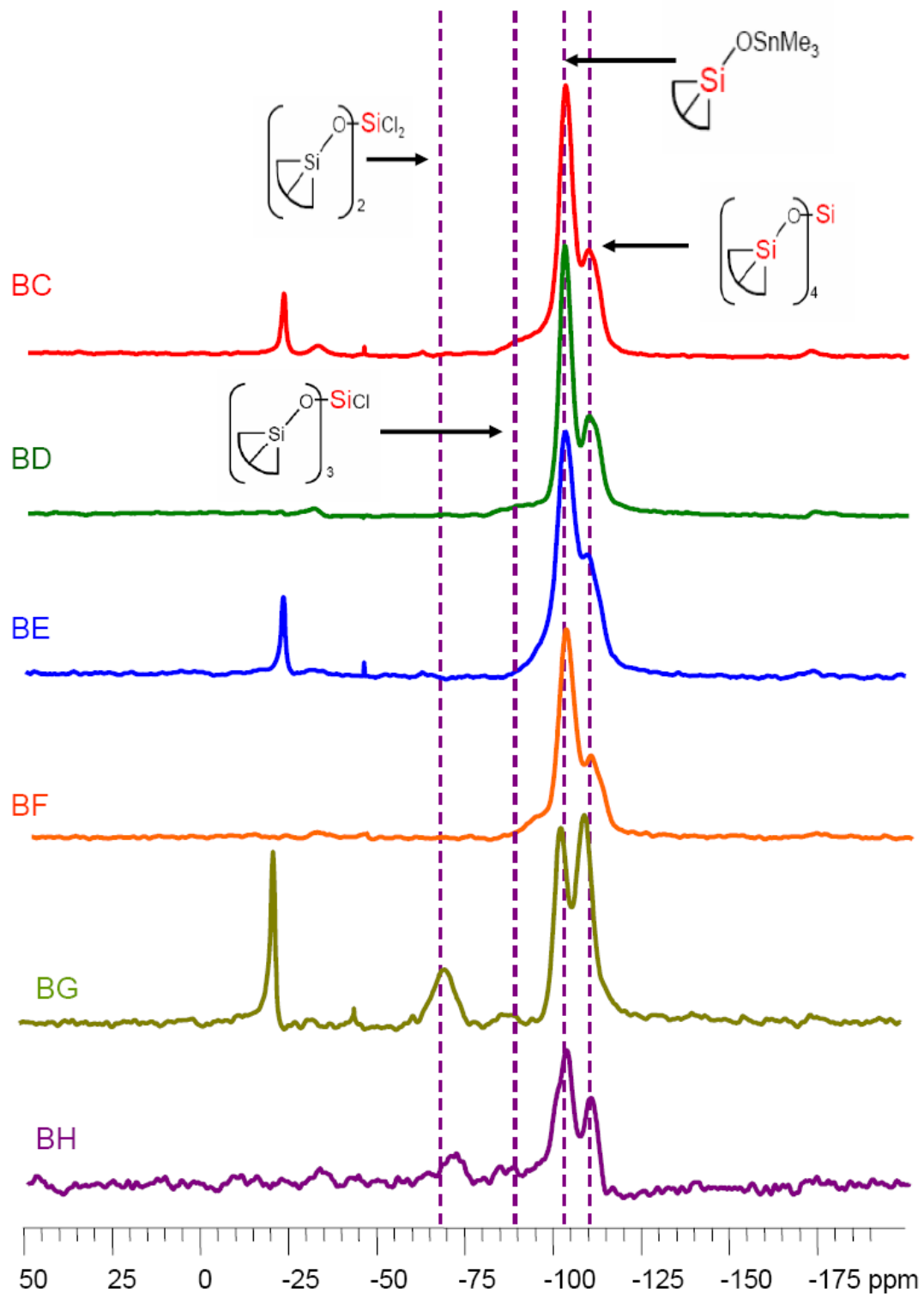


Figure 3 - 28 ^{29}Si MAS and CPMAS (MYL-II-124, 128) spinning rate : 5555Hz

containing Si linking groups in the sample and it should be stable in the air. After exposing this sample in the air for two days and recollecting ^{29}Si spectra, no extra peaks were observed in spectrum BE (^{29}Si MAS) and spectrum BF (^{29}Si CPMAS) in Figure 3-28. These observations are further evidence that all of the chloride ligands reacted with trimethyl tin groups and formed fully embedded silicate oligomeric species under this low loading ratio reaction. When the ratio of SiCl_4 : tin cube increased to 2 : 1, two- and three-connected silicon centers were observed at ~ 70 ppm and -90 ppm in ^{29}Si MAS spectrum BG and ^{29}Si CPMAS spectrum BH. The reaction was set at 80°C for 24 hours. Longer reaction times or reducing the SiCl_4 loading ratio are two choices to avoid leaving chloride ligands in the silicate platform.

Other silicate platforms were prepared using Me_2SiCl_2 as the linking reagent. A sample was synthesized with a 4.13 : 1 ratio of Me_2SiCl_2 : tin cube at 80°C for 48 hours in toluene. ^{29}Si MAS spectrum BI and ^{29}Si CPMAS spectrum BJ in Figure 3-29 indicate some Me_2SiCl_2 formed two connected silicate centers (~ -15 ppm) and others formed one connected silicate centers (~ 10 ppm). This silicate platform contained some residual trimethyl tin groups (~ -100 ppm). After adding excess VOCl_3 (10~15 equivalents) into the reaction vessel (room temperature for 8 hours in CH_2Cl_2), the intensity of the peak at ~ -100 ppm decreased significantly and almost disappeared (^{29}Si MAS in spectrum BK and ^{29}Si CPMAS in spectrum BL). Little change was observed in peaks at -15 ppm and 10 ppm and no new peaks were observed in these spectra (BK and BL).

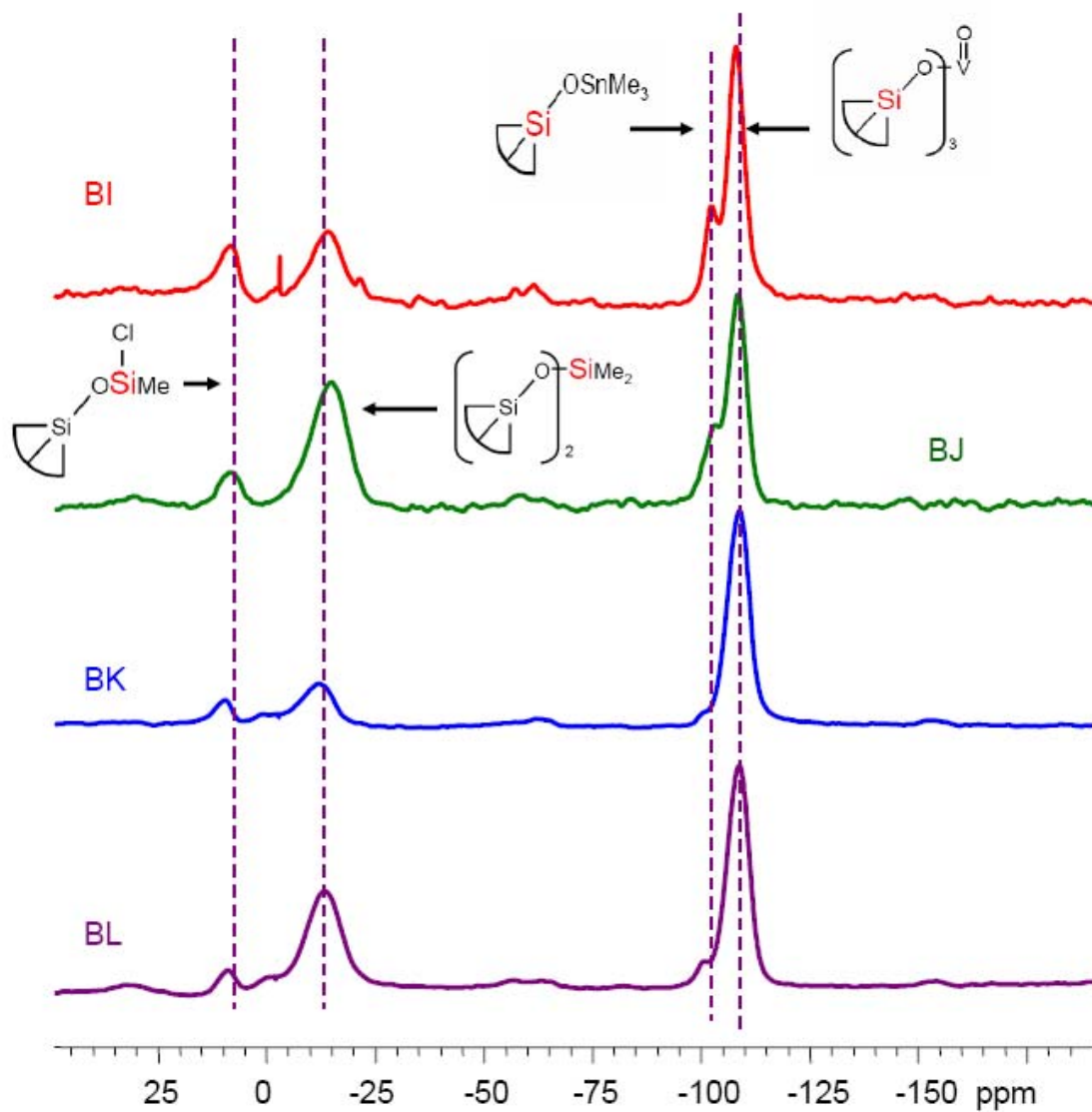


Figure 3 - ^{29}Si SSNMR (MYL-II-202, 224)

Me_2SiCl_2 : tin cube = 4.13 : 1 at 80°C 48 hours in toluene. BI and BK: ^{29}Si MAS, BJ and BL: ^{29}Si CPMAS.

This result indicates excess VOCl_3 does not alter the connectivity of silicate centers. It only reacts with residual trimethyl tin groups to form Si-O-V links to the platform.

The final step in the characterization of these samples was to identify what types of vanadyl were present via ^{51}V SSNMR data. After reacting excess VOCl_3 with a silicate platform, only one type of vanadyl has been observed in the spectra. Figure 3-30 illustrates ^{51}V SSNMR spectra at four different spin rates. The spinning rates are 3555, 4555, 5555, and 6555 in spectra BM, BN, BO, and BP respectively. The isotropic peak at ~ 305 ppm is assigned to one-connected vanadyl groups ($\text{VOCl}_2(-\text{OSi})$). No other isotropic peaks are observed in these spectra as the spinning rate was changed. These spectra indicate to that the VOCl_3 reacted with only one trimethyl tin group to form a single (SiO)-V bond linking the vanadyl group to the surface. The weight percentage of this single type of one connected vanadyl material can be adjusted by reacting excess VOCl_3 with different types of silicate platforms which have different amount of residual trimethyl tin groups.

Paramagnetic vanadium (IV) centers can not be observed in ^{51}V NMR. But the ^{29}Si SSNMR spectra of low loading vanadium (IV) materials in silicate matrices were measured. If the vanadium (IV) weight percentage is too high ($>10\sim 15\%$), too many paramagnetic vanadium (IV) atoms are in the matrix and broaden the silicon signals to the extent that no signal can be observed. Figure 3-31 provides one example of ^{29}Si SSNMR spectra from a low loading vanadium

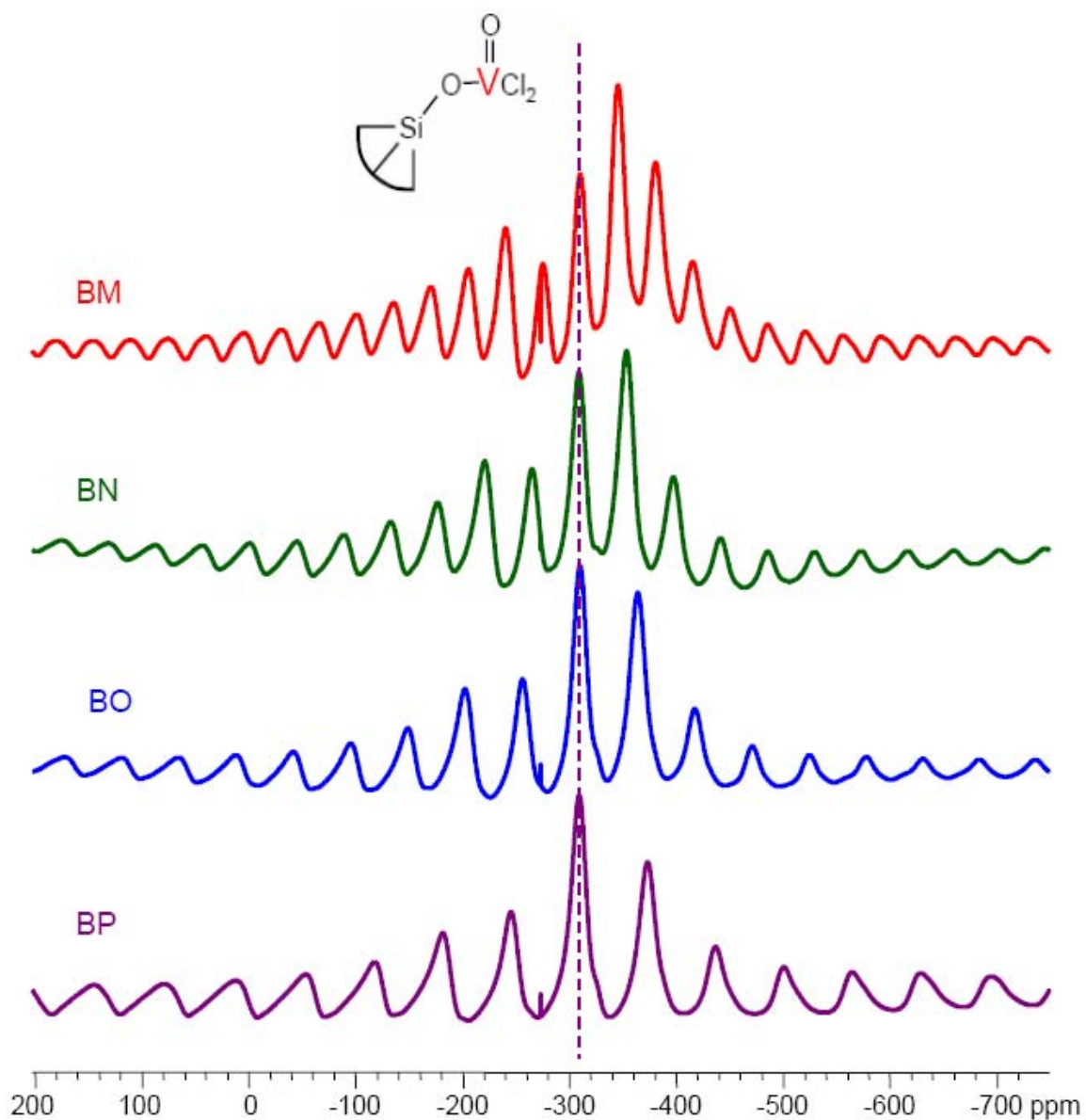


Figure 3 - ^{51}V SSNMR (MYL-II-224) Spinning rate : 3555 Hz(BM), 4555 Hz (BN), 5555 Hz (BO), 6555 Hz (BP)

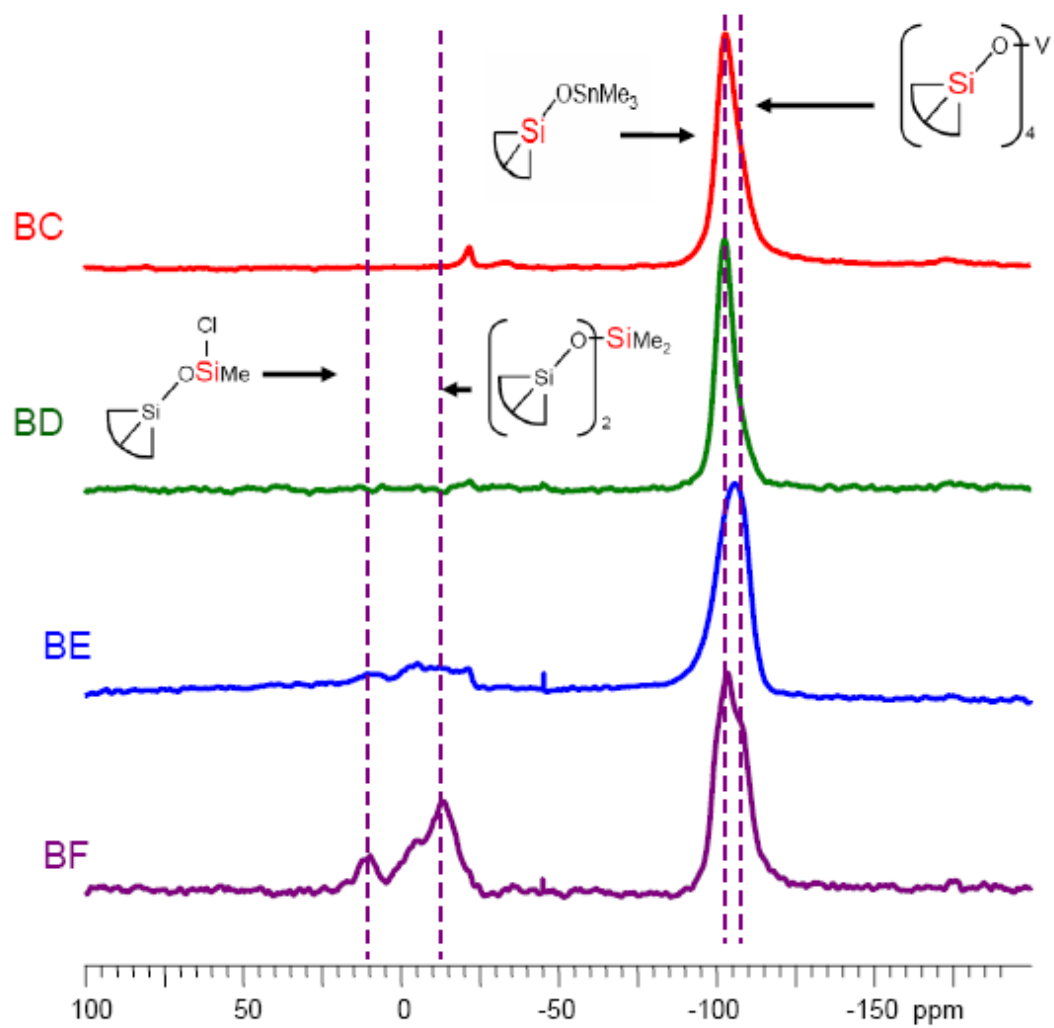


Figure 3 - 31 ^{29}Si SSNMR (MYL-II-116 ,120)
 VCl_4 : tin cube = 1 : 1 . BC and BE : MAS, BD and BF : CPMAS

(IV) sample. The sample was prepared from a 1 : 1 ratio of VCl_4 -to-tin cube reaction. ^{29}Si MAS spectrum BC and ^{29}Si CPMAS spectrum BD in Figure 3-31 are collected from one-dosed vanadium (IV) sample. The peaks at around -102 ppm and -107 ppm represent residual trimethyl tin groups and newly formed Si-O-V groups, respectively. Chemical shifts of these signals from this vanadium (IV) sample are consistent with those peaks in vanadyl materials. After delivering limiting amount of Me_2SiCl_2 into the reaction, one- and two-connected silicon centers formed and two new peaks (-15 ppm and 10 ppm) were observed in ^{29}Si MAS spectrum BE and ^{29}Si CPMAS spectrum BF. ^{29}Si SSNMR spectra provide useful information of the vanadium (IV) sample. The other technique to identify the connectivity of vanadium (IV) is EXAFS which will be discussed in chapter 4.

3.3.3 Surface area determination and porous size distribution

The Brunauer-Emmett-Teller (BET) method is the mostly widely used procedure for determining surface area of solid materials.³⁶ Materials with higher surfaces are generally better catalysts because more collisions, absorption or desorption among molecules occur, which increases the reaction rate. Surface area measurements collected from different vanadyl or vanadium samples provide some information or clues as to whether the products are oligomeric species or cross linked materials. Generally higher surface areas materials exhibit high cross linking and lower surface area materials are compounds that are better described as small oligomeric species.

Samples in Table 3-13 (entries 1-4) were prepared from one-dose vanadyl reactions. When the ratio of VOCl_3 to tin cube is lower than 2:66 to 1, the surface areas of these materials are very small no matter what temperature, solvent or reaction time is used. These results indicate the products only form oligomeric vanadyl species. When a larger amount of VOCl_3 was added in the reaction (entry 4), the surface area increased to $197 \text{ m}^2/\text{gram}$ even though the reaction was set at 0°C for 12 hours. The vanadyl groups appear to have generated enough cross links to produce porous, high surface area materials.

Low loading vanadyl materials (entry 5 and 6) (VOCl_3 : tin cube < 1 : 1) subsequently reacted with Me_2SiCl_2 in the gas phase also form very low surface area materials. When the ratio of VOCl_3 to tin cube increased to 1 : 1 and the products were then reacted with a small amount of SiCl_4 , PCl_3 , or Me_2SiCl_2 (entries 7 to 9), the products still appeared to be oligomeric species with very low surface areas. When the reaction time in the second dose reaction increased to 24 hours or the reaction temperature increased to 80°C , high surface area materials were obtained (entries 10 and 11). These results provide very important information about the growth processes that this linking chemistry follows on the way to form the designed high surface area materials. Higher reaction temperature did help oligomeric species to cross link each other and form porous materials. This conclusion also applies to silicate platforms. Entries 12 and 14 in Table 13 represent two different types of silicate platforms. When the silicate platform was prepared from a 1 : 1 ratio of SiCl_4 : tin cube at 20°C for

Table 3 - 13 Surface area measurement by BET method

	Code	ratio	solvent	Temp. (°C)	Time (Hours)	Surface area (m ² /gram)
1	II-010	VOCl ₃ : cube = 1 :1	CH ₂ Cl ₂	40	12	1.3
2	I-258	VOCl ₃ : cube = 1.20 :1	Toluene	80	6	2.2
3	I-218	VOCl ₃ : cube = 2.66 :1	CH ₂ Cl ₂	20	24	1.5
4	I-184	VOCl ₃ : cube = 64 : 1	CH ₂ Cl ₂	0	12	200
5	II-216	VCl ₄ : cube = 0.48 :1 then Me ₂ SiCl ₂ : cube = 3.19 : 1	CH ₂ Cl ₂ gas phase	40 then 50	24 24	0.5
6	II-218	VOCl ₃ : cube = 0.73 :1 then Me ₂ SiCl ₂ : cube = 2.92:1	CH ₂ Cl ₂ Gas phase	40 then 50	24 24	13
7	II-012	VOCl ₃ : cube = 1 :1 then SiCl ₄ : cube = 0.59 : 1	CH ₂ Cl ₂ CH ₂ Cl ₂	40 then 40	12 12	1.6
8	II-014	VOCl ₃ : cube = 1 :1 then PCl ₃ : cube = 0.74 : 1	CH ₂ Cl ₂ CH ₂ Cl ₂	40 then 40	12 12	4.1
9	II-228	VOCl ₃ : cube = 1 :1 then Me ₂ SiCl ₂ : cube = 2.77 : 1	CH ₂ Cl ₂ CH ₂ Cl ₂	40 then 20	24 24	17
10	II-028	VOCl ₃ : cube = 1 :1 then Me ₂ SiCl ₂ : cube = 1.65 : 1	CH ₂ Cl ₂ CH ₂ Cl ₂	40 then 40	12 24	196
11	II-030	VOCl ₃ : cube = 1 :1 then SiCl ₄ : cube = 1.78 : 1	CH ₂ Cl ₂ toluene	40 then 80	12 10	235
12	I-202	SiCl ₄ : cube = 1 : 1	CH ₂ Cl ₂	20	15	<1
13	I-208	SiCl ₄ : cube = 1:1 then excess VOCl ₃	CH ₂ Cl ₂	20 then 20	15 15	2
14	II-202	Me ₂ SiCl ₂ : cube = 4.13 :1	toluene	80	48	249
15	II-224	Me ₂ SiCl ₂ : cube = 4.13 :1 then excess VOCl ₃	Toluene CH ₂ Cl ₂	80 then 20	48 8	246
16	II-226	Me ₂ SiCl ₂ : cube = 4.13 :1 then excess VCl ₄	Toluene CH ₂ Cl ₂	80 then 20	48 8	375

15 hours in CH_2Cl_2 , the solution was transparent and no gel material formed in the reaction vessel. The low surface area ($<1 \text{ m}^2/\text{g}$) measured for these samples also indicates this material only formed oligomeric silicate species. Reacting excess VOCl_3 with this low surface area silicate precursor at 20°C for 15 hours does not appear to effectively cross link these silicate oligomeric species. The final surface area of this surface vanadyl product is still low.

When the silicate platform was prepared from a 4.13 : 1 ratio of Me_2SiCl_2 : tin cube at 80°C for 48 hours in toluene, a gel solution was formed with a much higher surface area ($240 \text{ m}^2/\text{g}$). This shows again that high reaction temperature and long reaction time help silicate oligomeric species cross link and form porous materials. Reacting excess VOCl_3 or VCl_4 with this high surface area material at 20°C yielded all capping, one-connected vanadyl or vanadium products. These one-connected vanadium compounds still exhibit high surface areas because each VOCl_3 or VCl_4 molecule only reacts with one trimethyl tin group in the silicate matrix and the high surface silicate structure stays the same.

Figure 3-32 to 3-43 show plots of surface area measurement by BET method and porous size distribution from sample MYL-I-184, MYL-II-028, MYL-II-030, MYL-II-202, MYL-II-224, MYL-II-226 and the surface areas of these samples are higher than $196 \text{ m}^2/\text{g}$. The porous sizes of these materials are in the mesoporous range (2-50 nm) and porous size distributions are broad.

MYL184 isotherm Surface Area 200 m²/gm

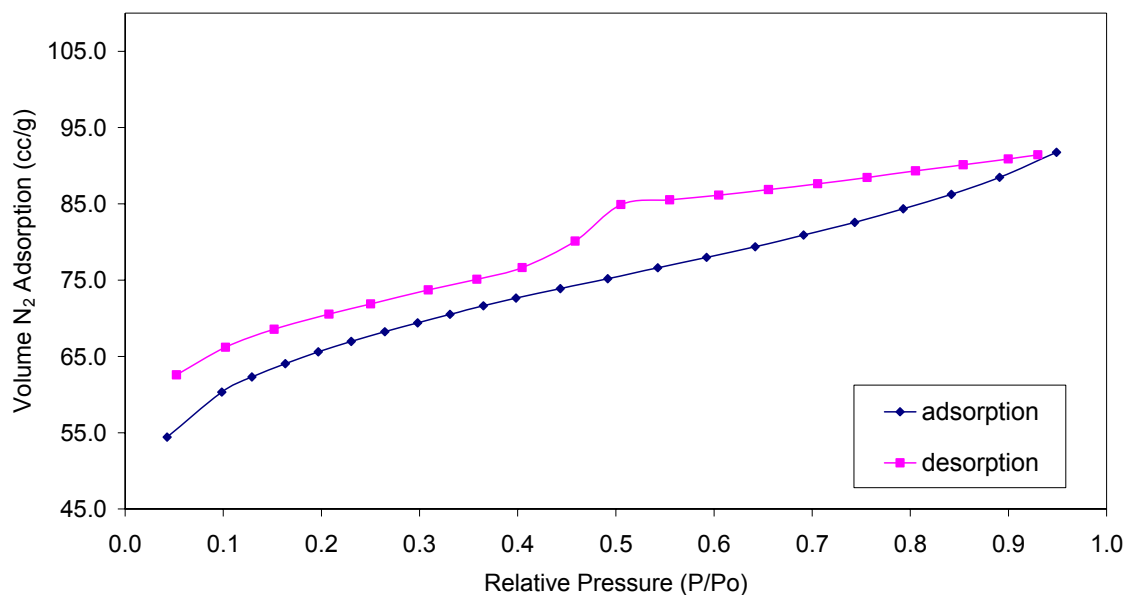


Figure 3 - 32 Entry 4 MYL-I-184 (BET)

MYL184 porous size distribution

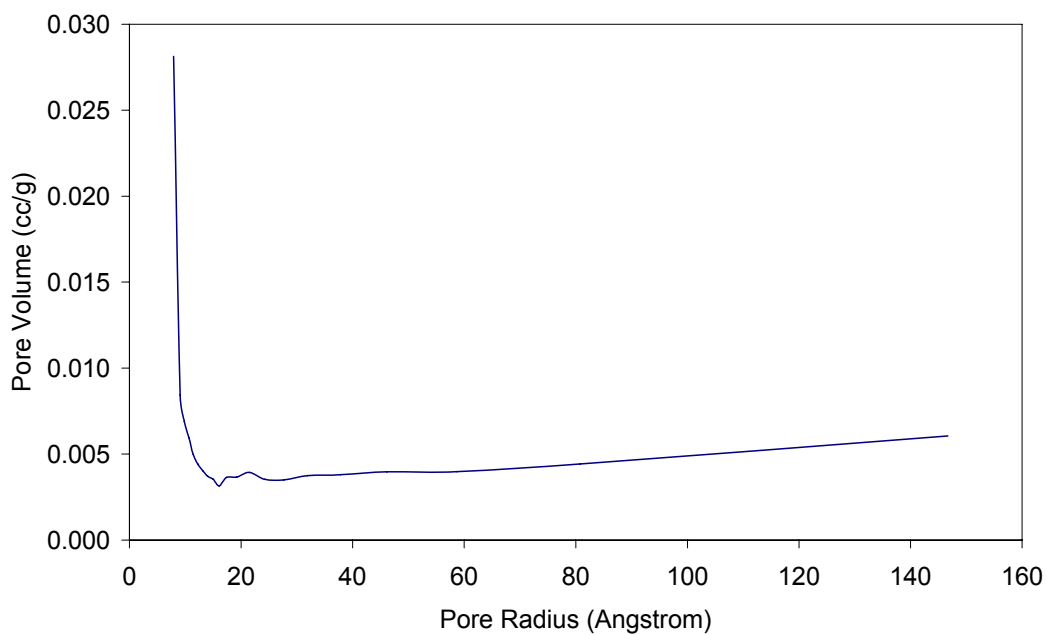


Figure 3 - 33 Entry 4 MYL-I-184 (BJH)

MYL-II-028 isotherm Surface Area 196 m²/gm

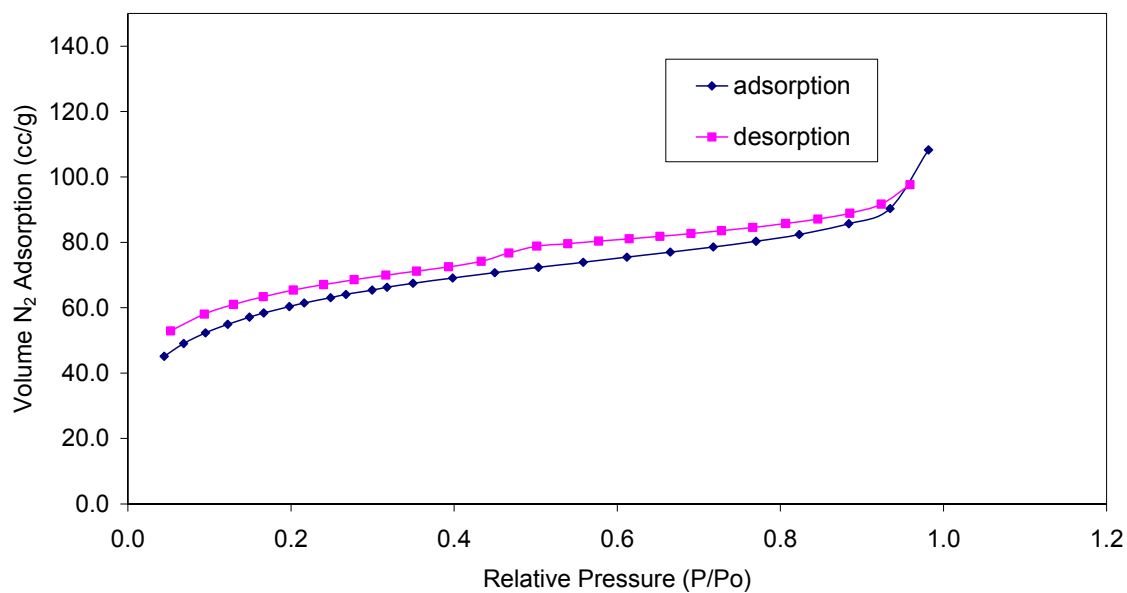


Figure 3 - 34 Entry 10 MYL-II-028 (BET)

MYL-II-028 porous size distribution

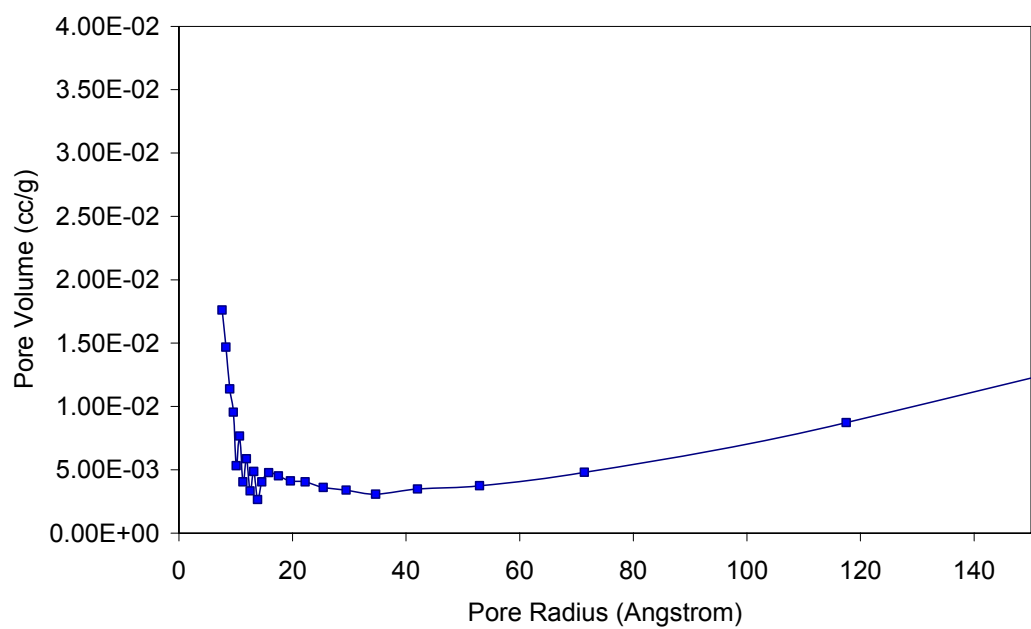


Figure 3 - 35 Entry 10 MYL-II-028 (BJH)

MYL-II-030 isotherm Surface Area 235 m²/gm

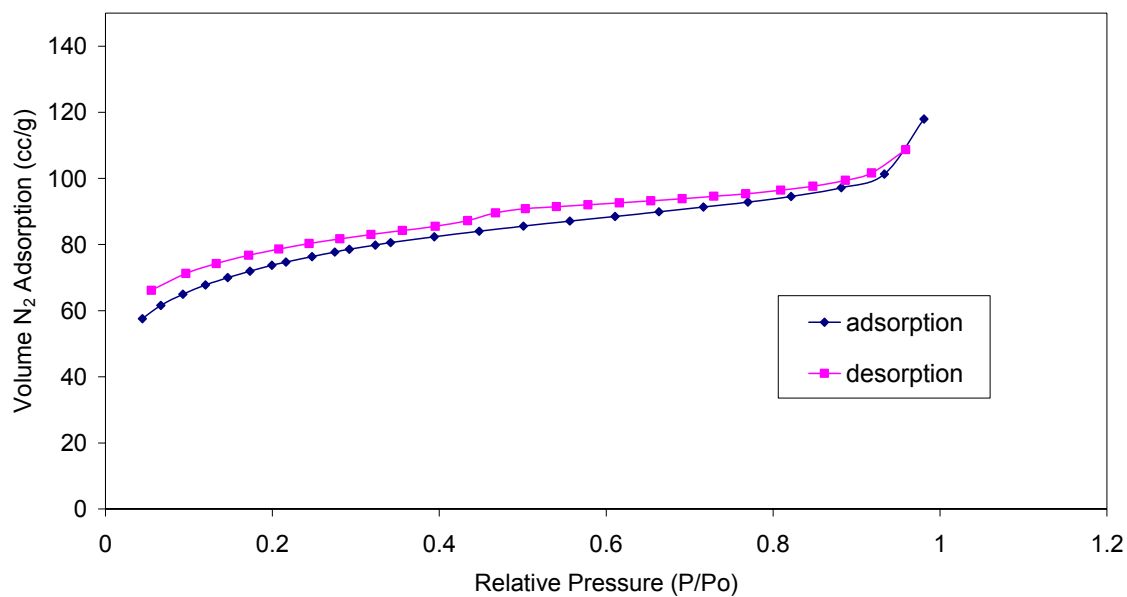


Figure 3 - 36 Entry 11, MYL-II-030 (BET)

MYL-II-030 porous size distribution

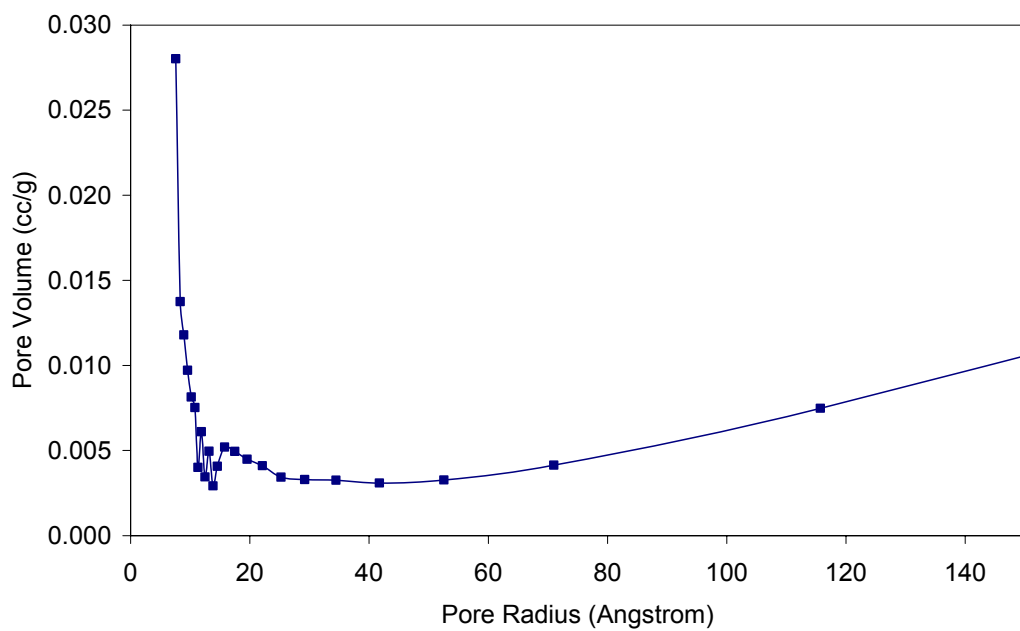


Figure 3 - 37 Entry 11, MYL-II-030 (BJH)

MYL-II-202 isotherm Surface Area 249 m²/gm

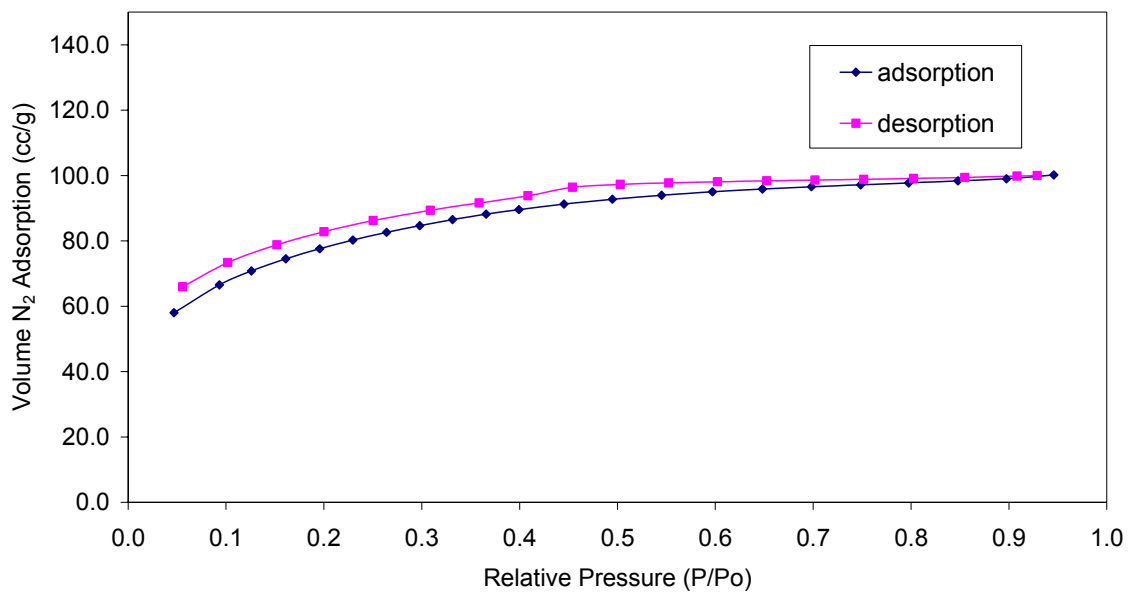


Figure 3 - 38 Entry 14, MYL-II-202 (BET)

MYL-II-202 porous size distribution

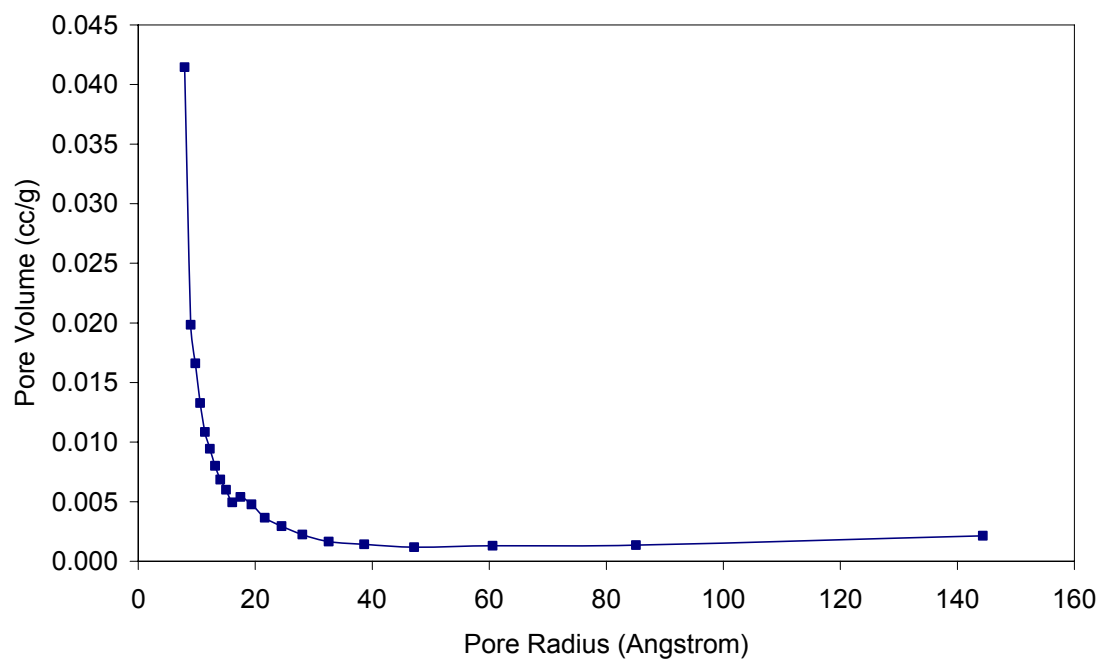


Figure 3 - 39 Entry 14, MYL-II-202 (BJH)

MYL-II-224 isotherm Surface Area 246 m²/gm

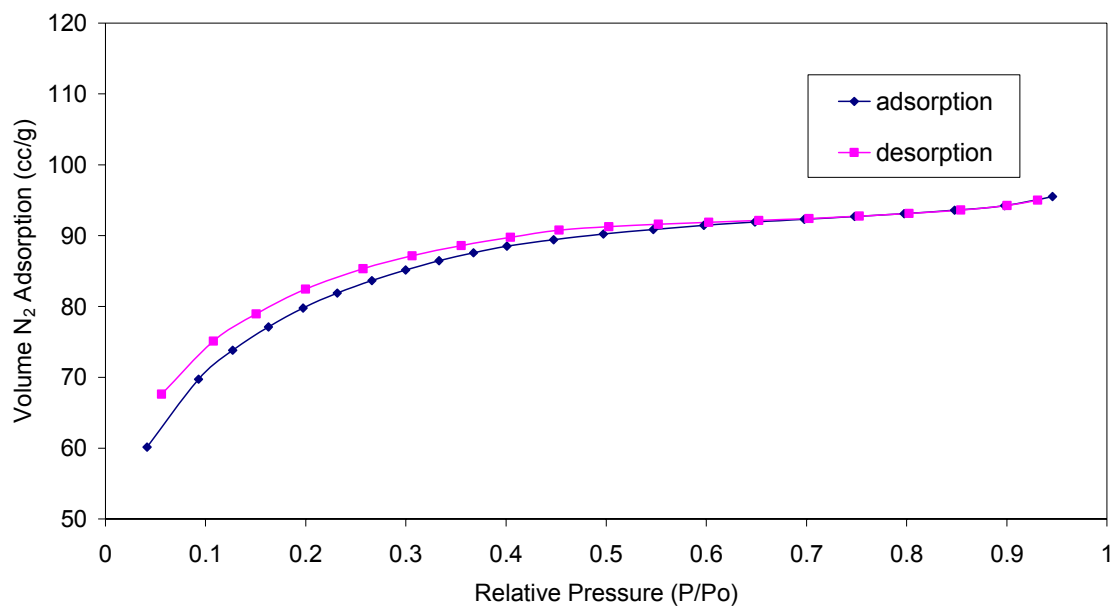


Figure 3 - 40 Entry 15, MYL-II-224 (BET)

MYL-II-224 porous size distribution

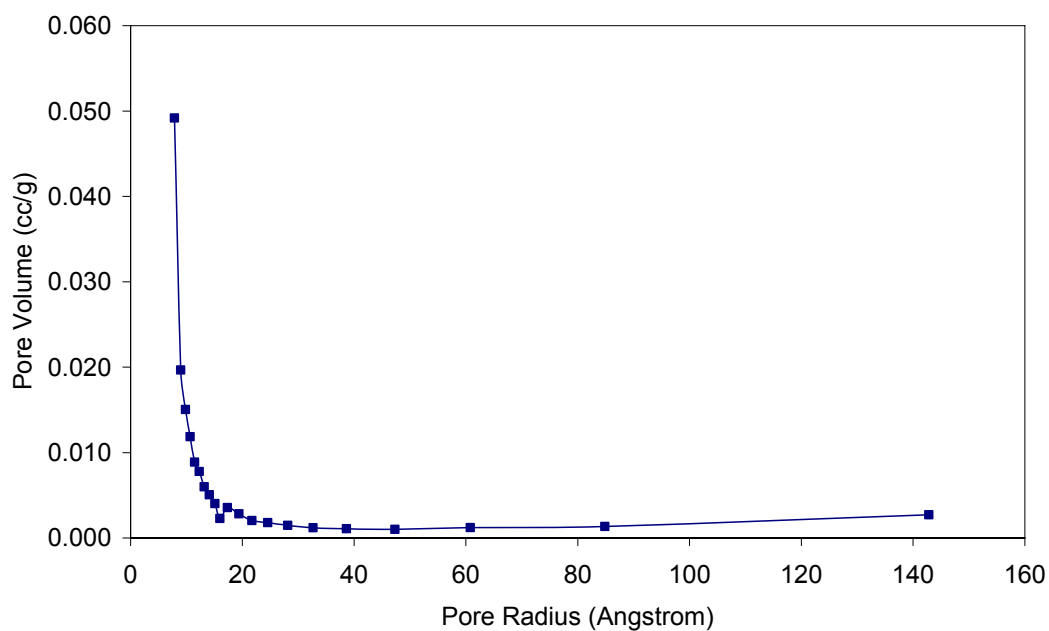


Figure 3 - 41 Entry 15, MYL-II-224 (BJH)

MYL-II-226 isotherm Surface Area 375 m²/gm

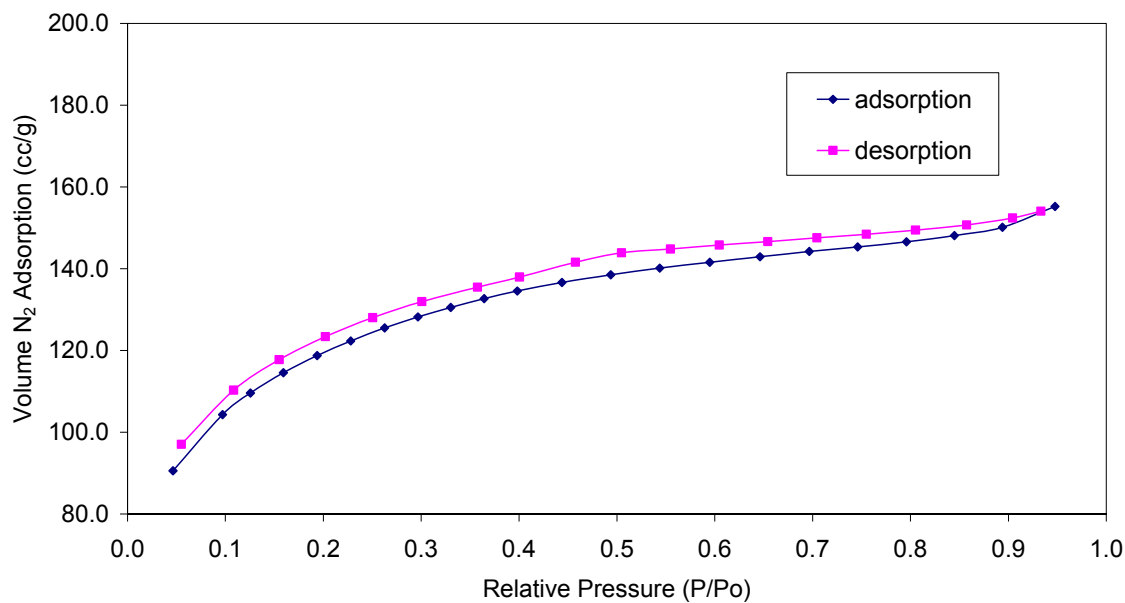


Figure 3 - 42 Entry 16, MYL-II-226 (BET)

MYL-II-226 porous size distribution

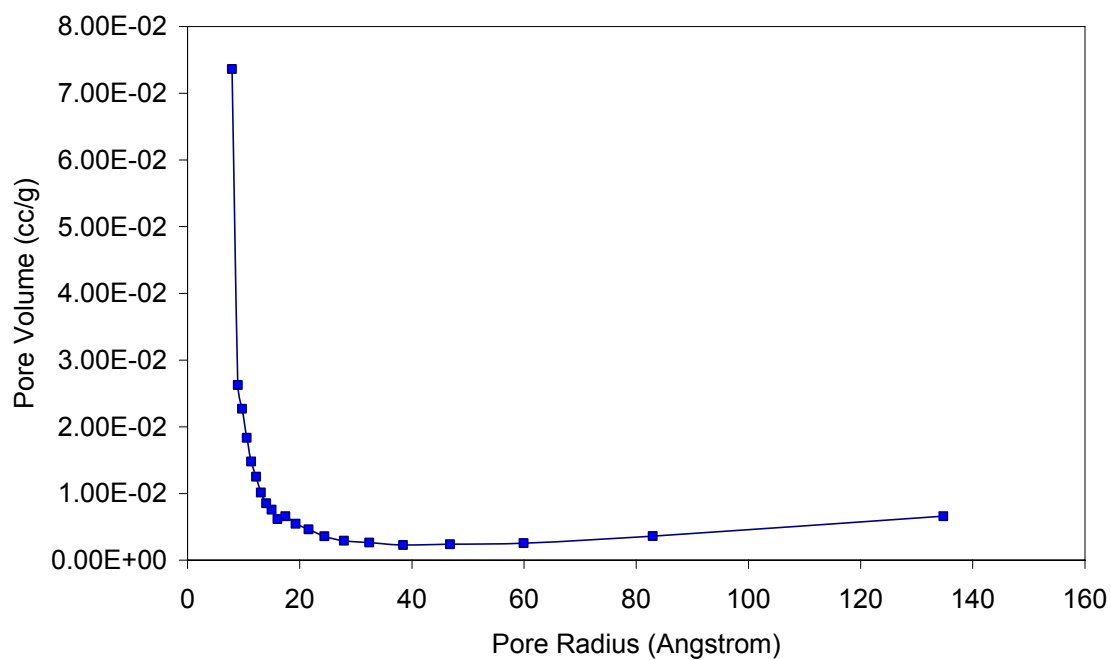


Figure 3 - 43 Entry 16, MYL-II-226 (BJH)

3.4 Conclusions

Atomically dispersed, vanadosilicate materials in Si_8O_{20} -based building block solids have been successfully synthesized. Different addition sequences of vanadyl and vanadium chlorides react with the tin cube building block to produce different types of isolated, vanadium centers in the silicate matrix. The three-connected embedded vanadyl and four-connected vanadium (+4) samples contain no chlorides in the metal center. These samples are synthesized using a limiting amount of VOCl_3 or VCl_4 in the first dose reaction which is followed by multiple doses of silyl chloride reagents to further crosslink the matrix and remove all tin. Changing the synthetic strategy by preparing a silicate platform first, followed by reaction with excess vanadium reagents produces materials containing atomically dispersed surface vanadium species. The volatility of the trimethyltin chloride provides an easy route remove this byproduct from the reaction mixture. Simply connecting the reaction vessel to a vacuum line and heating the product at 60 to 80°C for several hours will remove trimethyltin chloride and leaving a pure nonvolatile product.

Gravimetric analysis provides information about average connectivity of the linking groups. The results from gravimetric analysis indicate that all of chloride ligands in the embedded vanadyl and vanadium samples react with trimethyltin groups and generate three or four equivalents trimethyltin chloride respectively. Average molecular formulas can also be determined after the connectivity is known. Vanadium weight percentages may be calculated from

the average molecular formulas and these results are consistent with the atomic absorption and emission measurements.

^{29}Si and ^{51}V SSNMR spectra indicate that the use of different solvents, reaction temperatures, and reaction times does not affect the connectivity results when synthesizing embedded vanadyl samples. ^{29}Si SSNMR spectra indicate that second or third dose reagents (SiCl_4 , Me_2SiCl_2 or TMSCl) react with trimethyltin groups and are incorporated into the matrix. The ^{51}V SSNMR spectra indicate that a single type of vanadyl species was synthesized successfully using the sequential addition strategy outlined above. Too much TMSCl reacts with embedded vanadyl or vanadium materials at high temperature should be avoided because the different ^{51}V SSNMR spectra indicate the vanadyl environments have been changed after the reaction and the metals may leach out from the silicate matrix.

Surface area measurements indicate the first dose reaction produces only small oligomeric species with low surface areas. These small oligomeric species are cross linked together after reaction with SiCl_4 or Me_2SiCl_2 to form porous materials with higher surface areas. Longer reaction times or higher reaction temperatures may force the chloride ligands to react with residual trimethyltin groups to further increase the rigidity of the building block matrix and increase the surface area.

Several lines of evidence show that the building block methodology produces single-site and site-isolated vanadosilicates. Different connectivities of vanadyl or vanadium centers in the silicate matrices can be synthesized by

simply changing the stoichiometry and addition sequence. These materials will be applied to the catalytic reactions and the studies will be described in chapter 5.

Chapter 4

XANES and EXAFS of Vanadium (IV and V) complexes on Si_8O_{20} -based building block solids

4.1 Introduction

X-ray absorption fine-structure spectroscopy (XAFS)³⁷⁻³⁹ is a direct method for experimentally probing the electronic and physical structure of metal complexes at atomic scale. In an XAFS experiment, an energy-tunable x-ray source is scanned through the binding energy of a particular core electronic level of a metal atom. The X-ray absorption near-edge spectrum (XANES) is a term used to describe the energy region just above ($\sim 50\text{eV}$) the absorption edge and focuses on the pre-edge and edge features of the absorbing atom. Before the ionization absorption edge, pre-edge features contain information about core electron excitations into bound states in valence molecular or atomic orbitals. XANES spectra are dominated by intramolecular resonances of π or σ symmetry. When the symmetry of the ligands around the metal center is lowered from octahedral symmetry (O_h), the inversion center is lost. The $1s \rightarrow 3d$ transition is not strictly dipole forbidden any more and gives rise to the intense pre-edge feature in the XANES spectra. The information about electronic configuration, vacant orbitals, and the site symmetry of the absorbing atom can be obtained by analyzing the near-edge spectrum. The absolute position and intensity (with

respect to the absorption edge) of the pre-edge feature also provides information of the oxidation state of the absorbing atom.

Extended X-ray Absorption Fine Structure (EXAFS) is another term used to describe the oscillatory part of the X-ray absorption spectrum near the absorption edge of a particular element and extends to about 1000 eV above the edge. The coordination environment of a selected atom can be obtained by analyzing the oscillating part of the spectrum after the edge.

Herein both XANES and EXAFS spectra for different vanadyl and vanadium based heterogeneous catalysts will be discussed. VOCl_3 (V^{5+}) and VCl_4 (V^{4+}) were used as the starting materials and different types of vanadyl and vanadium species in the silicate matrix were synthesized for XAFS measurement. The products derived from each vanadium reagent may be divided into two parts. The first is referred to as the “embedded” sites. In embedded vanadyl samples (oxidation state is +5), there should be four oxygen ligands around each vanadium center. Three of the oxygens form V-O single bonds while the other oxygen forms a V=O double bond as shown in the Figure 4-1a. The second type of site is referred to as “surface” vanadyl samples where in two chloride ligands, one oxygen in the form of a V=O double bond and one oxygen in the form of a V-O single bond around the vanadium as shown in the Figure 4-1b. The cubes in all the figures below represent cubic Si_8O_{20} building blocks.

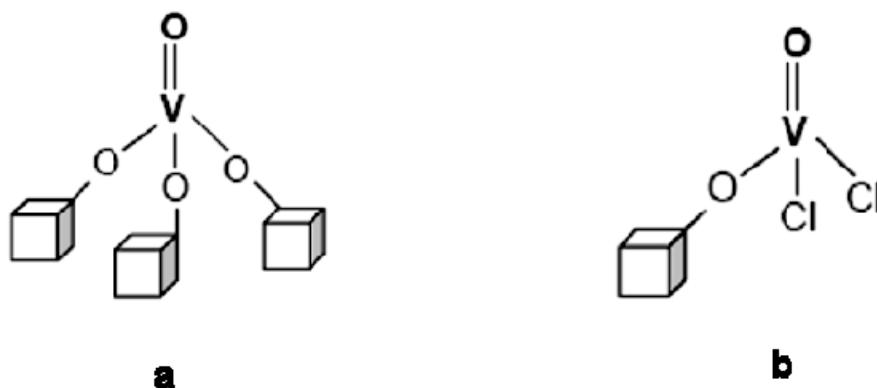


Figure 4 - 1 embedded and surface vanadyl models

In “embedded” vanadium (IV) samples, isolated vanadium centers are put into an amorphous SiO_2 building block matrix. Four oxygen ligands are around the vanadium with four V-O single bonds as shown in Figure 4-2a. In “surface” vanadium samples, one V-O single bond and three chloride ligands are around the vanadium atom as shown in the Figure 4-2b.

A number of independent “indirect” techniques such as gravimetric analysis and SSNMR are used to predict what we should see in the EXAFS. In the following discussion, the K-edge XANES spectra and EXAFS spectra of several different vanadium samples with oxidation states four and five in the silicate matrix will be described and analyzed.

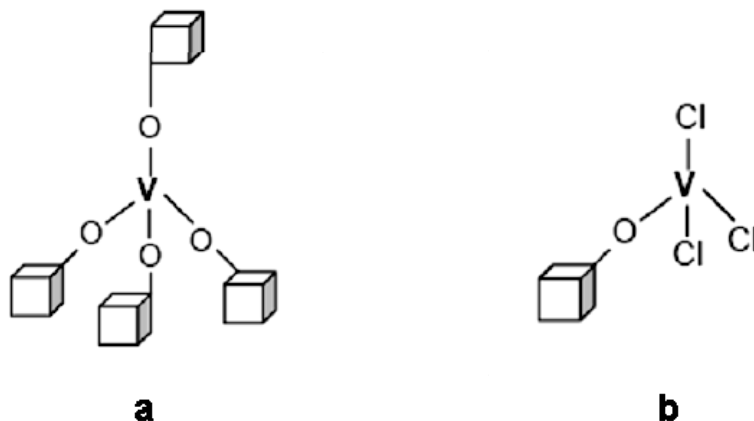


Figure 4 - 2 embedded ad surface vanadium models

4.2 Experimental

4.2.1 Samples preparation

4.2.1-1. Model compound: $OV[OSi(O^tBu)_3]_3$ ^{40, 41}

Vanadyl oxytrichloride (0.482 g, 2.78 mmol) was delivered via vapor transfer to a Schlenk tube with a solution of $HOSi(O^tBu)_3$ (2.299 g, 8.69 mmol) and pyridine (0.655g, 8.28 mmol) in 80 ml distilled benzene. The reaction was set at 40°C for 24 hours and stirred vigorously. The pyridinium hydrochloride byproduct formed and precipitated from the solution immediately. The product and unreacted $HOSi(O^tBu)_3$ were separated by filtration and washed with 30 ml hexanes. The resulting white solid was dried under vacuum for 12 hours at RT and during this time volatile, unreacted $HOSi(O^tBu)_3$ was removed. Some $HOSi(O^tBu)_3$ crystals were sublimed to the top of the Schlenk tube and 99% pure product was collected after removed unreacted $HOSi(O^tBu)_3$.

4.2.1-2 “Embedded” vanadyl and vanadium compounds

Three-connected vanadyl and four-connected vanadium samples were prepared as described in the experimental section to chapter 3. Different ratios of VOCl_3 to cube were prepared in the first dose reaction followed by adding Me_2SiCl_2 or SiCl_4 as the second dose reagent and then three-fold excess TMSCl to remove residual trimethyl tin groups.

4.2.1-3 “Surface” vanadyl and vanadium compounds

Me_2SiCl_2 was reacted with tin cube to form silicate platforms. Detailed procedures are described in Ch3. Excess VOCl_3 and VCl_4 were reacted with silicate platforms to form one-connected vanadyl and vanadium products. The vanadium weight percentages of these samples are determined by gravimetric analyses.

4.2.2 XAS spectra acquisition and data analysis³⁹

All of the vanadyl and vanadium samples were prepared in sealed aluminum or polycarbonate sample cells with polypropylene windows sealed with two-sided transparent tape. Data were collected in fluorescence mode at the National Synchrotron Light Source (NSLS) beam line X19A (focus beam) with a 12-channel solid-state Ge detector (Figure 4-3) and beam line X18B (unfocus beam) with a solid-state passivated implanted planar silicon (PIPS) detector. X-rays were monochromatized via reflection from Si (111) crystals. The incident

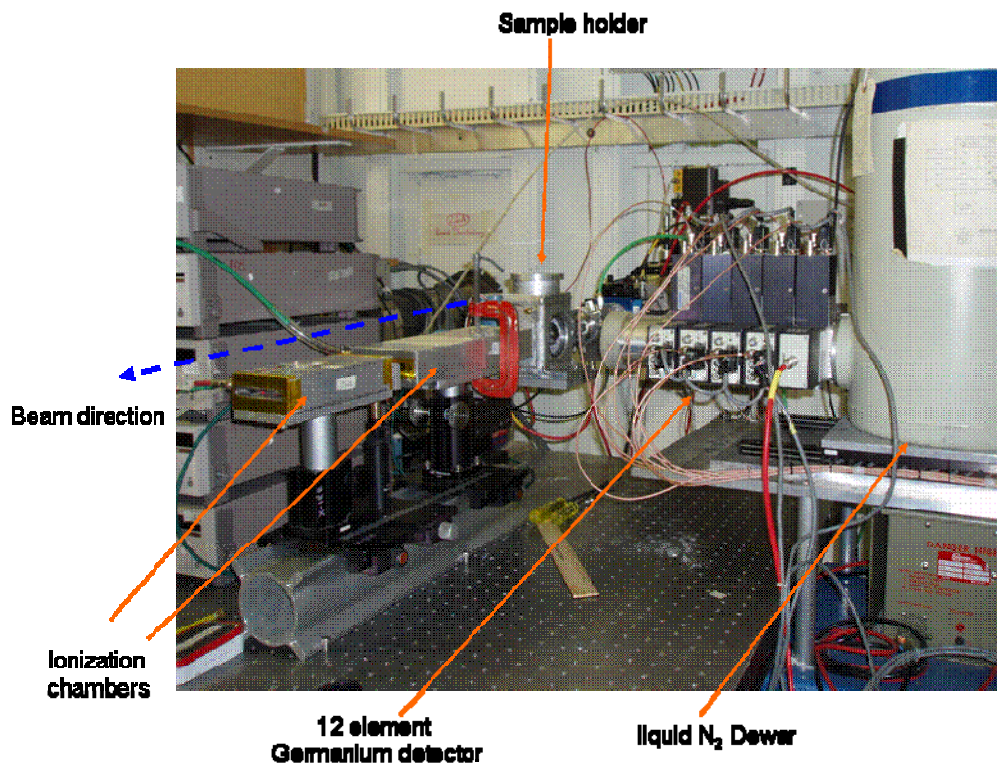


Figure 4 - 3 Germanium detector

beam was detuned 30% to suppress harmonics. Samples were mounted at 45° to the beam (Figure 4-4).

Spectra were recorded in four energy regions about the V K edge at 5465.0 eV: -150 to -20 eV (below the edge) in 5-eV steps (1 second integration time per step), -20 to 30 eV (through the edge) in 0.1-eV steps (1 second integration time per step), 30 to 12 k in 0.05-k steps (2 seconds integration time per step), and 12k to 16k or 18k in 0.05-k steps (4 seconds integration time per step). Calibration runs during each scan were not performed in the experiments on beam line X19A because no significant energy shifts were observed between each scan. The energy shifts of the standard, vanadium-metal foil were less

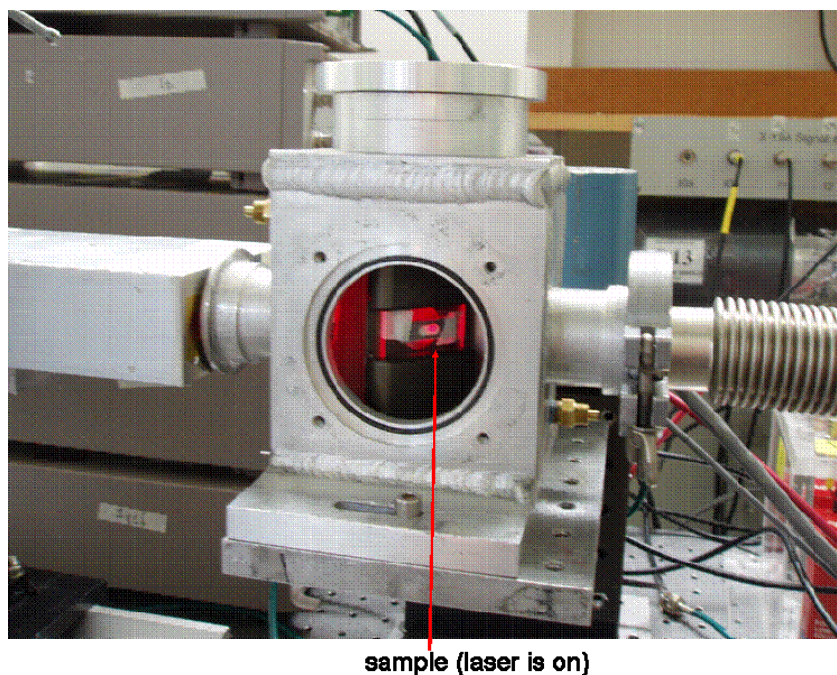


Figure 4 - 4 A sample is mounted at 45°C on the beam

than 0.3 eV in beam line X19A before and after scanning various vanadium compounds and this small value of the energy shift was smaller than the inherent resolution of the monochromator on the beam line. Spectra collected from beam line X18B were calibrated to vanadium metal foils (K-edge 5465.0 eV) before and after data collection. The energy shifts in beam line X18B were less than 0.2 eV before and after each vanadium sample.

Three to six scans were collected for each sample and energy shifts between these scans were determined to be only 0.02~0.03 eV. Data analysis was performed with the IFEFFIT⁵ data analysis software suite. The Athena⁶ program was used for data reduction. Merged files were generated after auto aligning several scans in Athena program. The Artemis⁶ program was used for data

modeling. The theoretical phase and amplitude functions were generated from FEFF6L.

4.3 Result and Discussion

4.3.1 XANES analysis⁴²

4.3.1-1 Vanadium (5+) sites

Glitches in the low energy range do not appear in all collected data but arise significantly at high k value in most of the vanadium samples in beam line X19A. Removing glitches at high k range does not affect the XANES spectra because the energy range for the XANES is chosen between 5460 and 5500 eV and the glitches appear at an energy higher than 6000eV. Individual XANES scans overlapped perfectly to the eye. In the following discussion, all of the XANES spectra are generated from merged files and required no deglitching. The edge-jumps of all spectra were normalized to one and then used to generate absorption spectra.

The three spectra in the figure 4-5 represent three different vanadyl embedded samples. Sample “MYL-II-138” is synthesized via a one-dose reaction which denotes the sample was prepared by reacting $\text{Me}_3\text{Sn-cube}$ with limiting amount of VOCl_3 to obtain a three-connected vanadyl product (Fig 4-1a). Sample “MYL-II-146” was prepared via a “three dose” reaction sequence in which the product from the first dose was treated with a second dose of SiCl_4 and then a third dose of TMSCl . Sample “MYL-II1-48” was synthesized with the

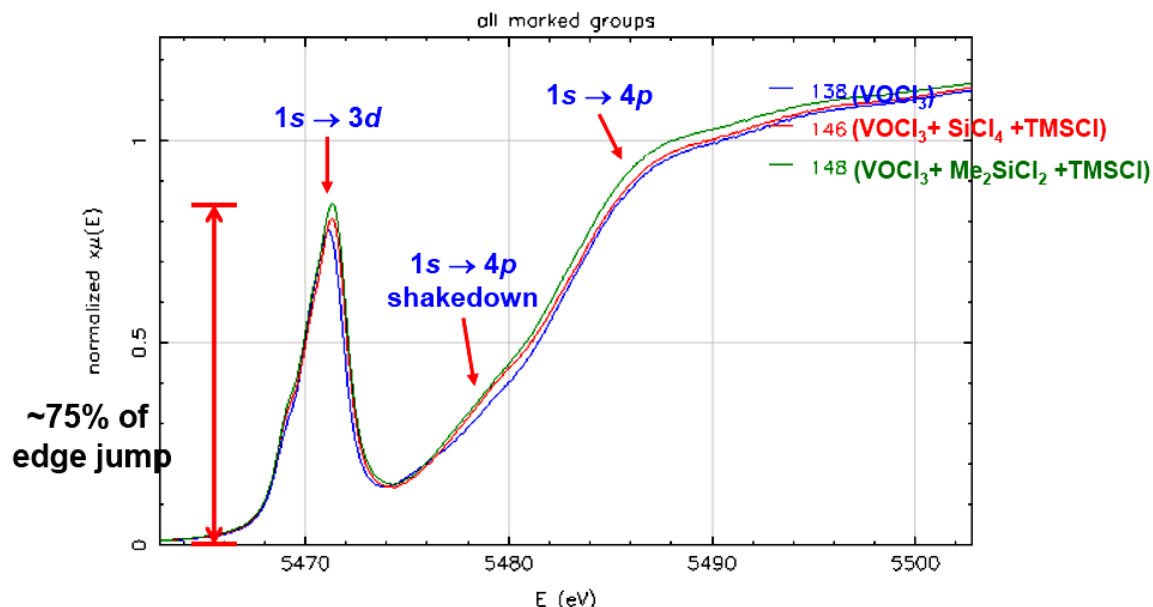


Figure 4 - 5 XANES spectra of different embedded vanadyl samples

same three-dose procedure as described in MYL-II-146 except that Me₂SiCl₂ was used as the second dose reagent.

The K-edge XANES of these three samples exhibit an intense pre-edge absorption feature followed by a weak shoulder on a rising absorption curve. The sharp pre-edge peak has been assigned to an allowed $1s \rightarrow 3d$ transition in the vicinity of 5470.5 ± 0.2 eV.⁴³ The small shoulder at 5479 ± 0.5 eV has been assigned as the $1s \rightarrow 4p$ shakedown transition⁴⁴ (a group of transitions involving $1s \rightarrow 4p$ simultaneous with ligand-to-metal shakedown). The hump around 5487 eV has been assigned as the dipole-allowed transition $1s \rightarrow 4p$. XANES spectra of these three samples are quite similar. They indicate the electronic environments around the vanadium centers of these three samples are very

similar. They also provide indirect evidence that second and third dose reagents in the synthetic procedures did not change the connectivity of the vanadyl centers to the cube matrix and the vanadium atoms stay embedded in the silicate matrix.

The XANES spectra of surface and all-capping vanadyl samples are shown in Figure 4-6. Sample “MYL-II-156” was prepared by exposing VOCl_3 to a silicate matrix in which the silicate matrix was synthesized by reacting Me_3Sn -cube with limiting amount of SiCl_4 . The rigid silicate platform has some trimethyltin group left over which should be widely separated from one another thereby preventing cross linking from occurring. Each trimethyltin group reacts with VOCl_3 to form one-connected VOCl_2 species on the surface of the matrix (Fig. 4-1b). MYL-II-162 was also synthesized by reacting VOCl_3 with a building block matrix. But the silicate matrix in the sample MYL-II-162 was synthesized by reacting Me_3Sn -cube with a limiting amount of Me_2SiCl_2 . MYL-II-168 is the all-capping vanadyl molecular species which was synthesized by reacting excess VOCl_3 with Me_3Sn -cube and obtained eight VOCl_2 groups in the corners of the cube.

The weight percentage of the surface vanadyl samples (MYL-II-156 and MYL-II-162) are around 8% and of the all capping molecular vanadyl sample (MYL-II-168) is around 14%. Even though the weight percentage of these vanadyl samples are higher than the vanadyl embedded samples (3~5%), the data collected in the fluorescence mode still appear to provide clear undistorted XANES spectra in beam line X19A.

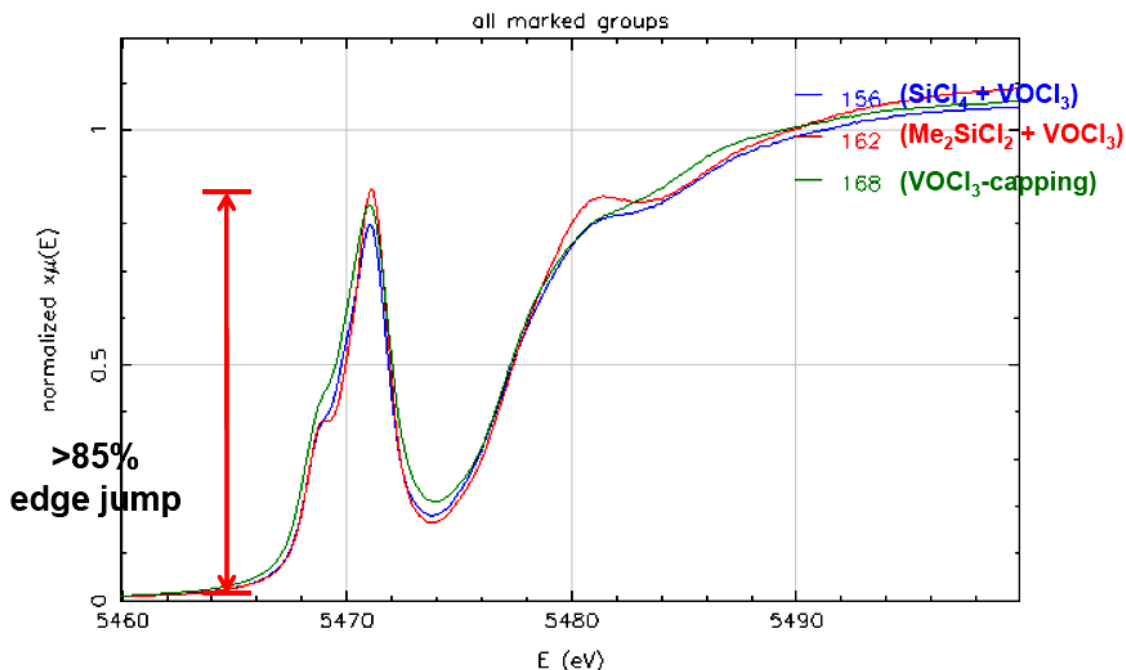


Figure 4 - 6 XANES spectra of different surface vanadyl samples

The XANES spectra of the surface and all-capping vanadyl samples also have strong pre-edge features in the vicinity of 5471 ± 0.5 eV. The similar pre-edge features of these spectra show the vanadyl products in different silicate matrices (from SiCl_4 and Me_2SiCl_2) have similar electronic environments and coordination geometry.

The $1s \rightarrow 4p$ shakedown transition in the 5479 ± 0.5 eV of the surface and all-capping vanadyl samples is much more intense than that observed in vanadyl embedded samples. Figure 4-7 shows the difference between embedded and surface vanadyl samples. The small hump in the edge appears to correlate with the presence of at least one chloride ligand around the vanadium center.

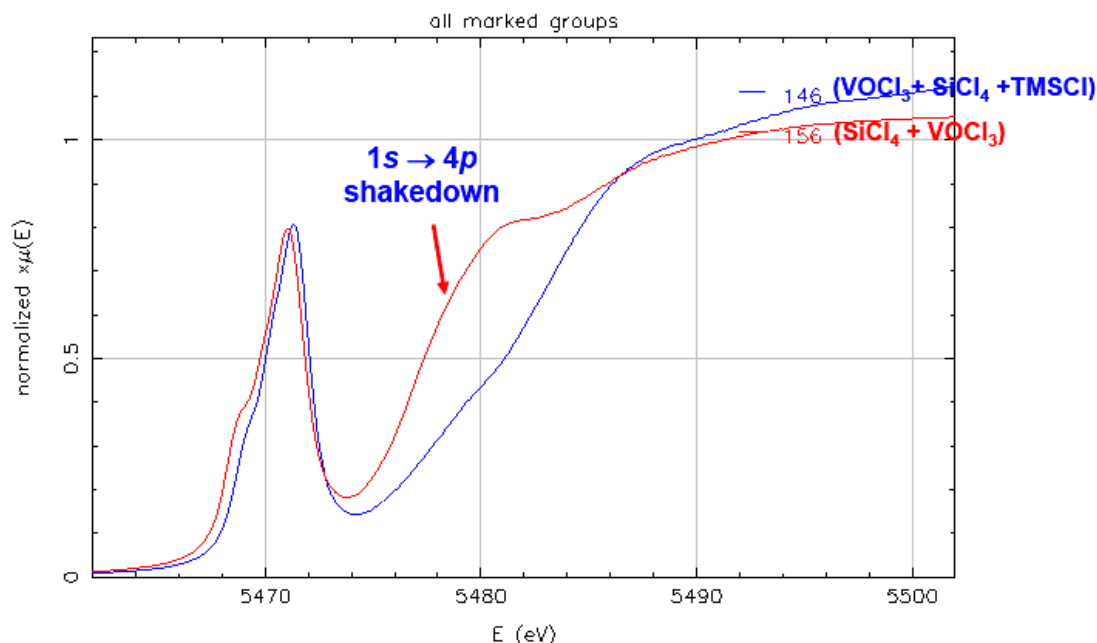


Figure 4 - 7 XANES spectra of embedded and surface vanadyl samples

4.3.1-2 Vanadium (+4) sites

The vanadium (+4) embedded samples also have a clear pre-edge feature (Fig. 4-8). MYL-II-120 represents a vanadium sample prepared via a two-dose reaction sequence starting with VCl_4 and followed by Me_2SiCl_2 as the second dose reagent. MYL-II-160 is a sample derived from MYL-II-120 by exposing it to a third dose of TMSCl. Both of these samples have a pre-edge feature at 5471 ± 0.5 eV. The feature is similar in appearance and energy to the pre-edge feature observed in the vanadyl (+5) embedded samples described previously.

MYL154 in Figure 4-9 is the surface vanadium (+4) sample prepared by exposing VCl_4 to a silicate matrix which the silicate matrix was synthesized by reacting $\text{Me}_3\text{Sn-cube}$ with limiting amount of SiCl_4 . This “surface” vanadium (+4)

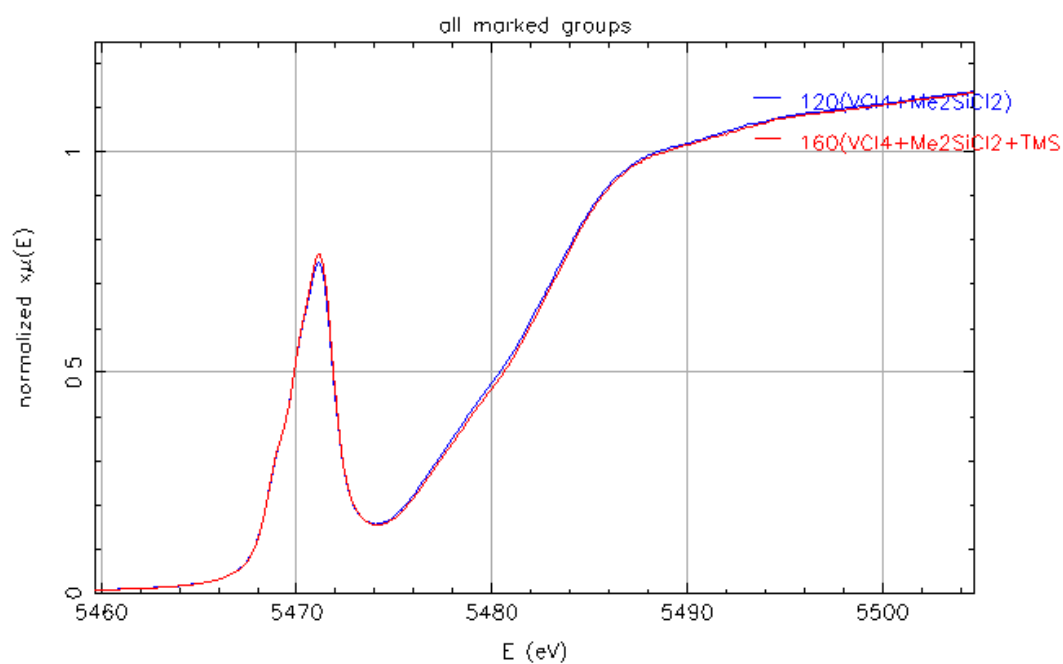


Figure 4 - 8 XANES spectra of embedded vanadium samples

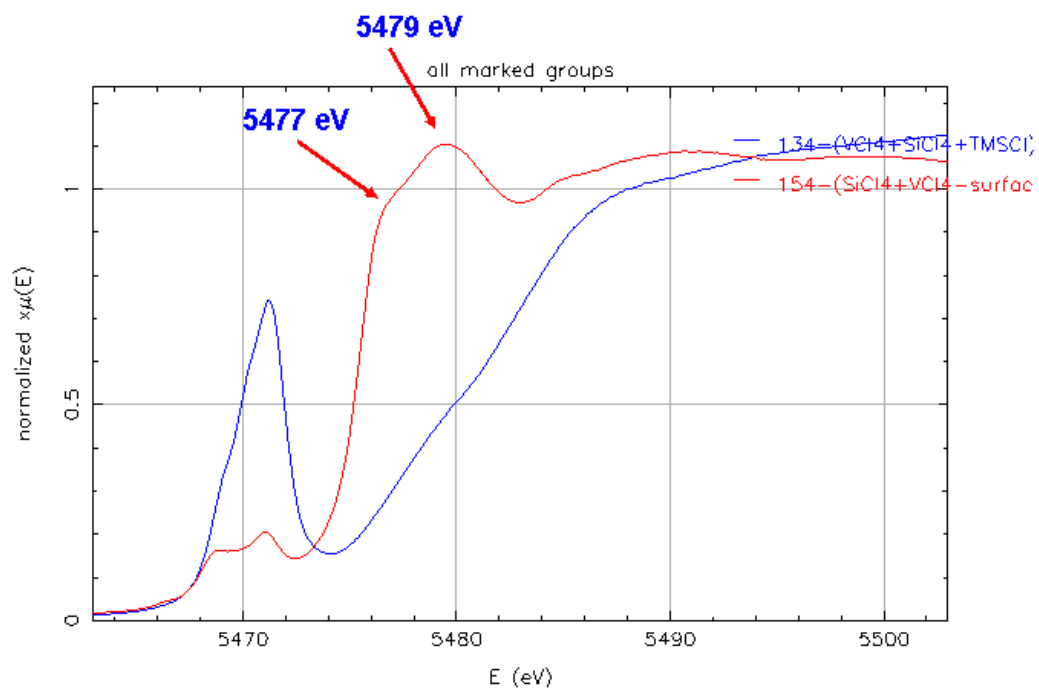


Figure 4 - 9 XANES spectra of embedded and surface vanadium samples

sample (Fig 4-2b) has a very weak pre-edge feature and at least two new absorption edge features superimposed on the edge at approximately 5477 and 5479 eV. We interpret these notable edge features of the surface vanadium (+4) sample as features induced by ligand-to-metal transitions from residual chloride ligands around the vanadium (+4) atom. A vanadium (+4) atom with three chloride ligands as in the surface vanadium (+4) sample has stronger edge feature than vanadyl (+5) atom around with two chloride ligands ($-\text{VOCl}_2$) in the surface vanadium (+4) sample. More chloride ligands around the vanadium atom provide more ligand-to-metal transitions and generate a stronger edge feature. This might be a factor to explain why the edge feature of the surface vanadium (+4) sample is stronger than all other vanadium (+4 and +5) samples.

Figure 4-10 compares the XANES spectra for embedded and surface vanadium samples with different oxidation states. The purple curve is the surface vanadium (+4) sample. The red curve is the surface vanadyl (+5) sample. Both of these samples have stronger edge features than the embedded vanadyl or vanadium samples. The pre-edge features in the vicinity of 5471 eV are significant in these samples except surface vanadium (+4) sample. Distorted octahedral, distorted square-pyramidal or distorted square-planer coordination geometries don't have the inversion center. These structures apply to the embedded vanadyl samples because the $\text{V}=\text{O}$ double bond of the vanadium (+5) center breaks the symmetry and doesn't have an inversion center. The significant difference between these samples is the low pre-edge feature of the surface vanadium (+4) sample. We currently do not have a clear understanding

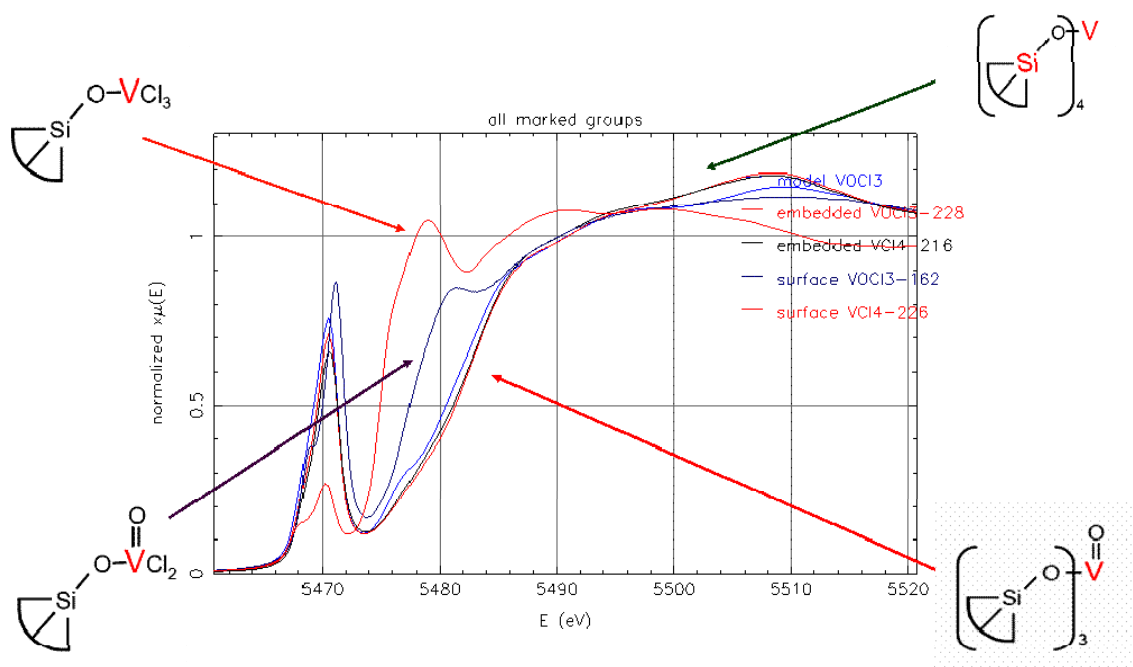


Figure 4 - 10 XANES spectra of embedded and surface vanadyl and vanadium samples

for the low intensity of this feature in this sample. The vanadium species of this sample might have higher symmetry structure because it shows a much weaker $1s \rightarrow 3d$ transition ($1s \rightarrow 3d$ transition dipole forbidden) and decreases the intensity of the pre-edge feature in the XANES spectra.

Different oxidation states of vanadium have different energy shifts in the pre-edge. From the literature, the pre-edge energy value of vanadium monoxide (VO) (oxidation state: +2) is 5468.0 eV, V₂O₃ (oxidation state: +3) is 5468.4 eV, V₄O₇ (average oxidation state: +3.5) is 5469.1 eV, V₂O₄ (oxidation state: +4) is 5470.4 eV, and V₂O₅ (oxidation state: +5) is 5470.6 eV. Higher oxidation states

of the vanadium oxide compound give rise to higher pre-edge energies. Applying this approximate correlation of oxidation states and pre edge energies to our vanadium (+4 and +5) samples provides some useful information to identify the oxidation state of each vanadium sample. The pre-edge energy of the vanadium samples is between 5470.4 and 5470.6 eV. It is difficult to identify if the oxidation states of our vanadium samples is +4 or +5 by looking at the pre-edge energy values without calibrating the energy more exactly because the energy difference between vanadium +4 and vanadium +5 compounds is only 0.2 eV. But at least we are sure all of our samples are not reduced to vanadium +3 or +2.

4.3.2 EXAFS analysis

4.3.2-1 Model compound: $OV[OSi(O^tBu)_3]_3$

Three scans were acquired in NSLS beam line X18B (PIPS detector) for this sample. The merged file was obtained by aligning three $\mu(E)$ spectra in Athena followed by merging these spectra to improve the signal-to-noise ratio. The parameter panel used in the Athena program is shown in Figure 4-11.

The pre-edge range was set at -145 eV to -30 eV (relative to vanadium K-edge, 5464.0 eV). It is the range in energy of pre-edge line regression (green line in Figure 4-12). Post-edge range was set at 150 eV to ~929 eV which represents the range of the post-edge normalization (purple line in Figure 4-12). These two ranges decide how to normalize the E-space spectrum and the value of the edge jump. Edge jump is the change in the absorption coefficient through the edge which is evaluated by taking the difference of the pre-edge and post-

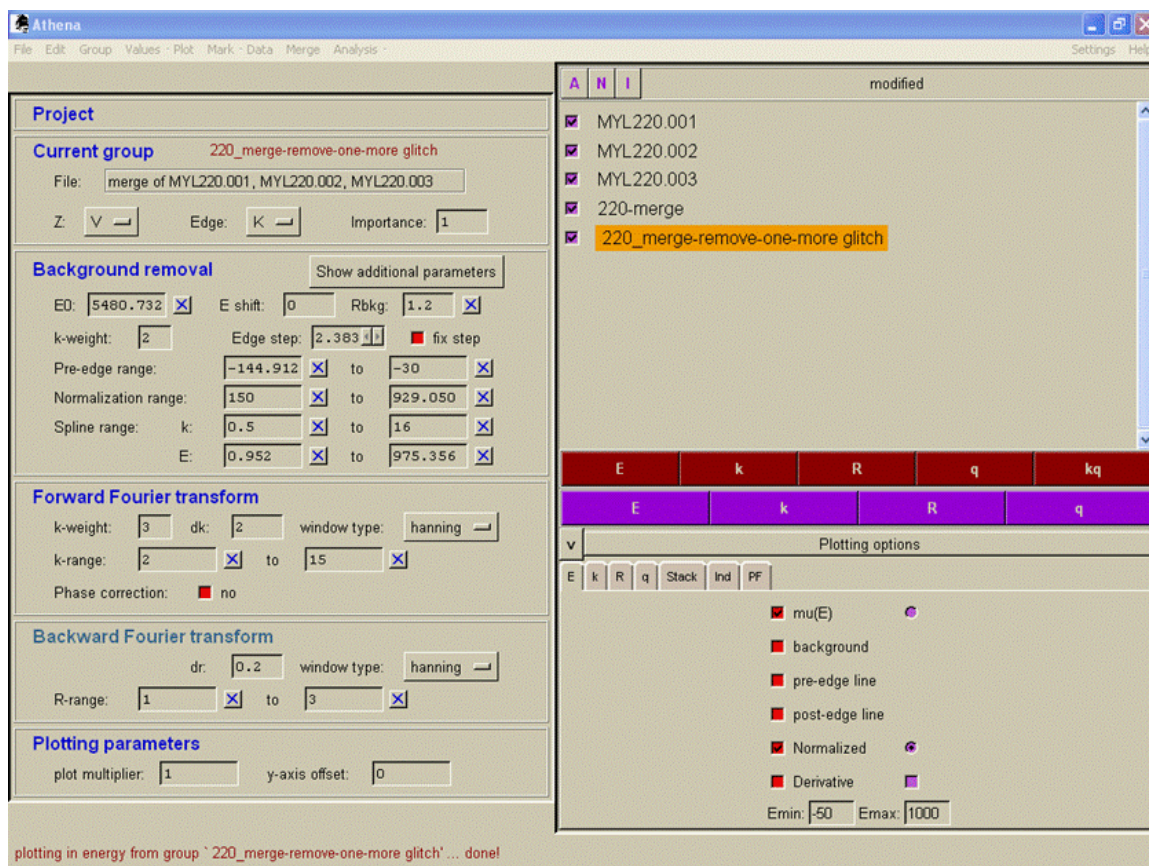


Figure 4 - 11 Parameter panel in Athena

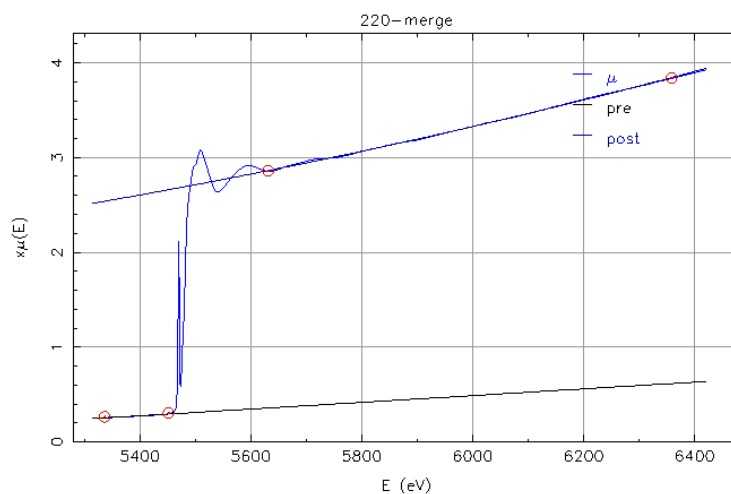


Figure 4 - 12 The E-space spectrum before normalization

edge lines at E_0 , the energy at the absorption edge. The edge jump is ~ 2.38 in this sample and the normalized $\mu(E)$ spectrum is shown in Figure 4-13.

The more useful XAFS formation, $k\chi(k)$, is a function of the photoelectron wave factor k and the k -space plot is derived from the E -space plot by using equation 1 where M_e is the mass of the electron, E is the incident photon energy in electron volts, E_0 is the threshold energy, and $\hbar$ is $h/2\pi$ (h is Planck's constant). The equation can be rewritten to ΔE , $(E-E_0) = \sim 3.81 k^2$.

$$\kappa^2 = \frac{2M_e(E - E_0)}{\hbar^2} \dots\dots(1)$$

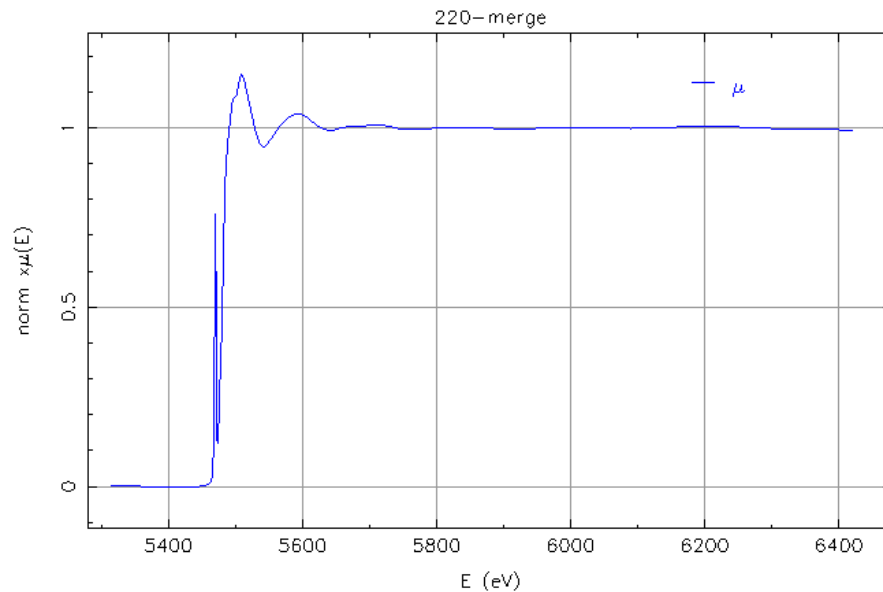


Figure 4 - 13 The normalized E-space spectrum

The $\chi(k)$ data is often weighted by k^2 or k^3 . Different k-weighting emphasize different regions of the data. A higher k-weight value magnifies the spectra in the high k region. Figure 4-14 shows k-space plots with different k-weight. When the k-weight value changes from one to three, the relative intensity of the signal in the high k region increases significantly. One glitch was seen in the k-space plot at around $k = 10.5$ when k-weights of two and three are used. The glitch can be removed from the raw data in Athena to improve the k-space plot before FT.

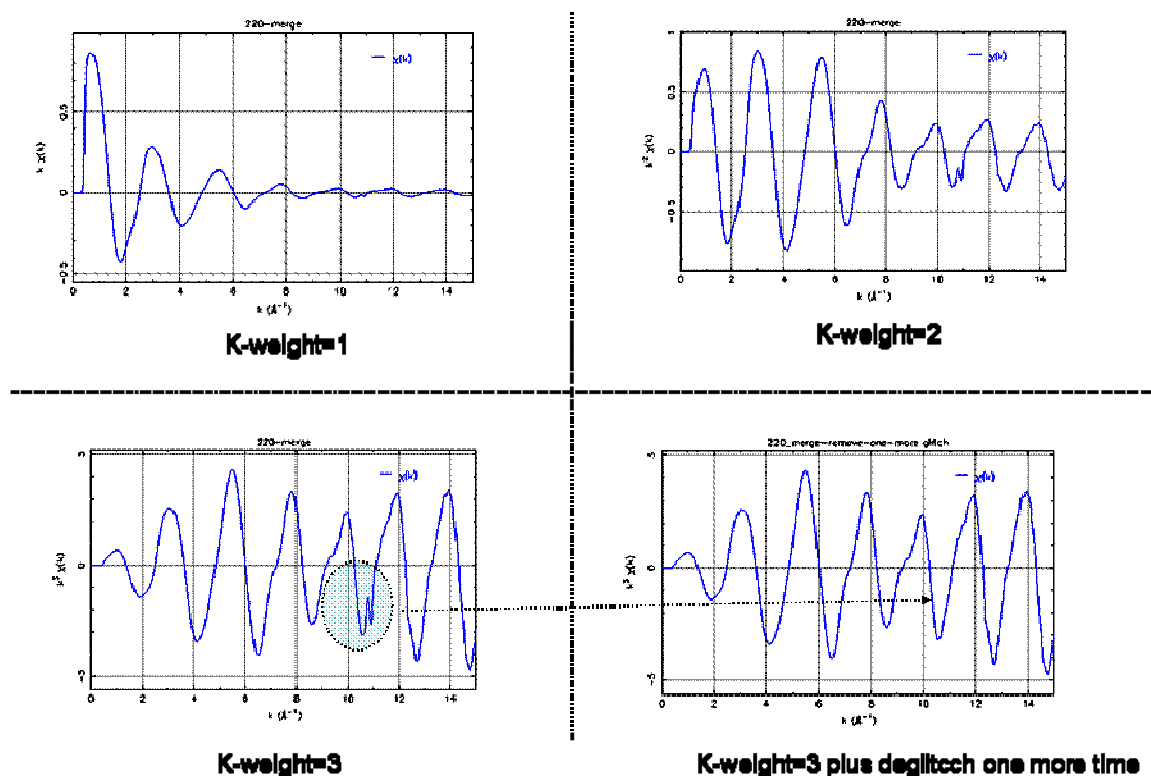


Figure 4 - 14 k-space plots with different k-weighting

A Hanning window was applied to the data before Fourier transformation to R-space. Fourier transform is a frequency filter that converts the frequencies in k-space into localized signals in R-space. Before Fourier transformation of the k-space plot, the R background (R_{bkg}) value should be discussed. A good background function removes low frequency oscillations from $\chi(k)$. These low frequency oscillations appear as peaks in the low-R region of the Fourier Transform. Figure 4-15 shows different R-space plots with different R_{bkg} values. When the R_{bkg} is 1.0, one peak at low R range ($R < 1\text{\AA}$) is shown in the spectrum. This model compound, $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$, should contain only one V=O double bond at $\sim 1.57\text{\AA}$ and three V-O single bonds at $\sim 1.78\text{\AA}$ of the first coordination sphere. The peaks at $\sim 1.2\text{\AA}$ and $\sim 1.6\text{\AA}$ represent V=O double and V-O single bonds, respectively, before phase correction of the R-space spectra. Any peak lower than $1\text{\AA}$ in R-space spectrum is physically unrealistic and are artifacts of the background removal and should either be reduced or removed from the plot without affecting the other peaks near them. When the R_{bkg} value is set for 1.1 and 1.2, the intensity of the low-R peak at around $0.8\text{\AA}$ is reduced significantly. When the R_{bkg} value increases to 1.3, the peak at $1.2\text{\AA}$ is also removed and only one peak remains in the first coordination sphere.

The finally reasonable R_{bkg} value should be 1.2 in this model compound by comparing these spectra with different R_{bkg} values and finding the best spectra with no unreal low-R feature.

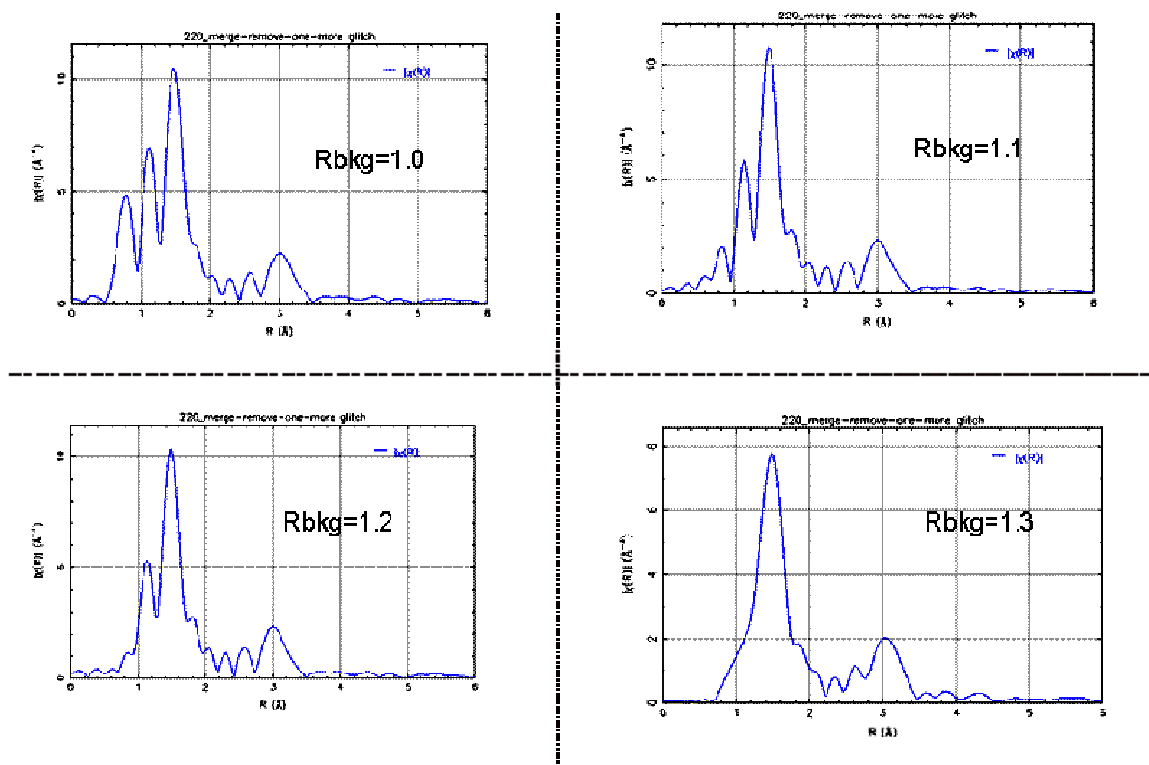


Figure 4 - 15 R-space spectra with different R_{bkg} values

In a fluorescence experiment, the depth into the sample that the incident beam penetrates is modulated as the beam energy changes. The edge jump and the fine structure oscillations are also modulated as the penetration depth changes, thus attenuating the amplitude of the measured $\chi(k)$. This effect is commonly called "self absorption". Booth⁴⁵ and Pfalzer⁴⁶ describe how to account for self-absorption effects from fluorescence measurements. Athena contains four functions to correct the spectra for self absorption effects. EXAFS (Booth) function was chosen due to the function accounting for sample thickness. Figure 4-16 shows R-space spectra before (blue spectrum) and after (red

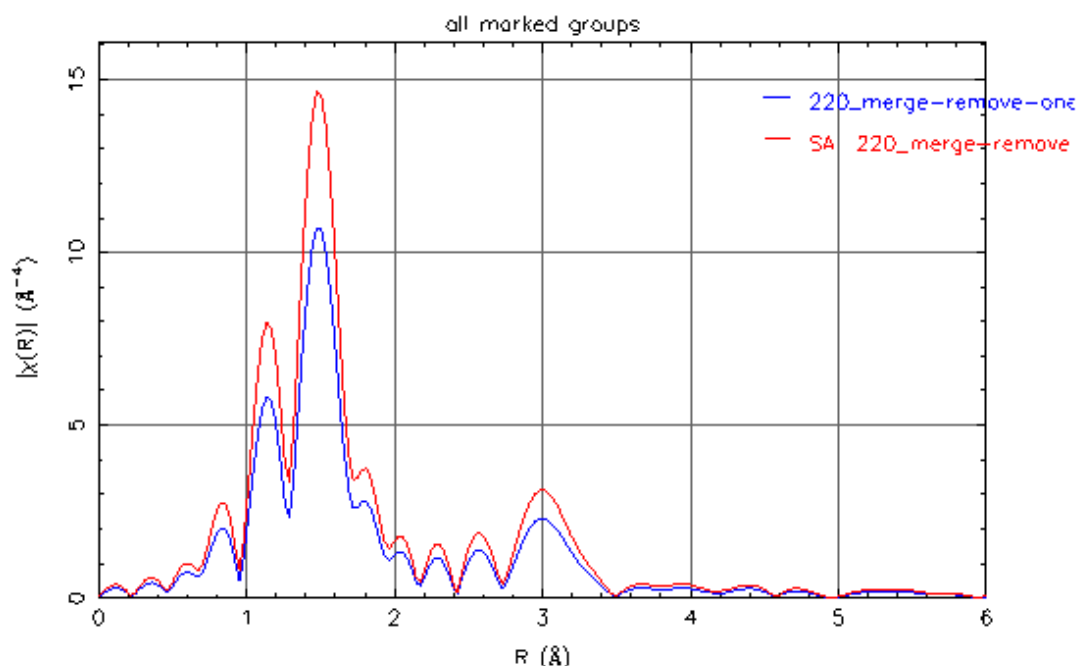


Figure 4 - 16 R-space spectra before and after self absorption correction

spectrum) a self absorption correction. It is obvious the relative intensity of signals in the spectra improves significantly without changing the signal-to-noise ratio. This final spectrum is saved as a “prj” file and used to model the data with Artemis program.

A “prj” file which is generated from Athena is imported into Artemis and used to generate an “apj” file. The k-space spectra were fitted to single-scattering paths with use of the EXAFS equation (2) where N_i is the degeneracy of the path, S_0^2 is the passive electron reduction factor⁴⁷, $F_i(k)$ is the effective scattering amplitude, $\phi_i(k)$ is effective scattering phase shift, λ is the mean free path of the photoelectron, and σ_i^2 (Debye-Waller factor) is the root-mean-squared displacement.

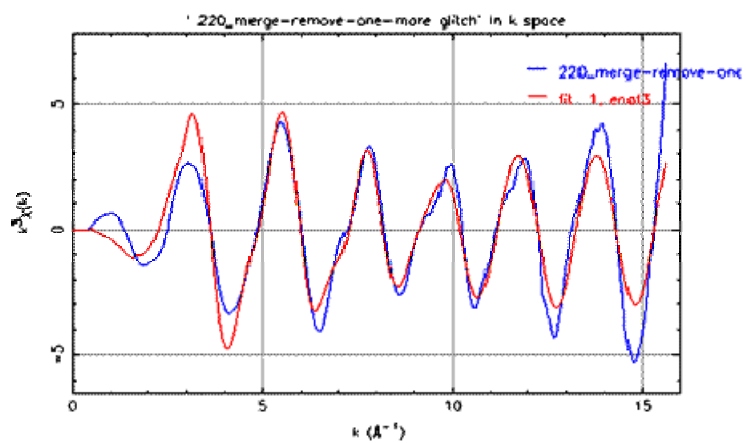
$$\chi(k) = \sum_i \frac{N_i S_o^2 F_i(k)}{k R_i^2} \exp(-2k^2 \sigma^2) \exp\left(\frac{-2R_i}{\lambda}\right) \sin(2kR_i + \phi_i(k)) \quad \dots(2)$$

The residual R is define in Equation 3 where $\chi_{\text{obs}}(k_i)$ is the experimental data and $\chi_{\text{calc}}(k_i)$ is the calculated EXAFS.

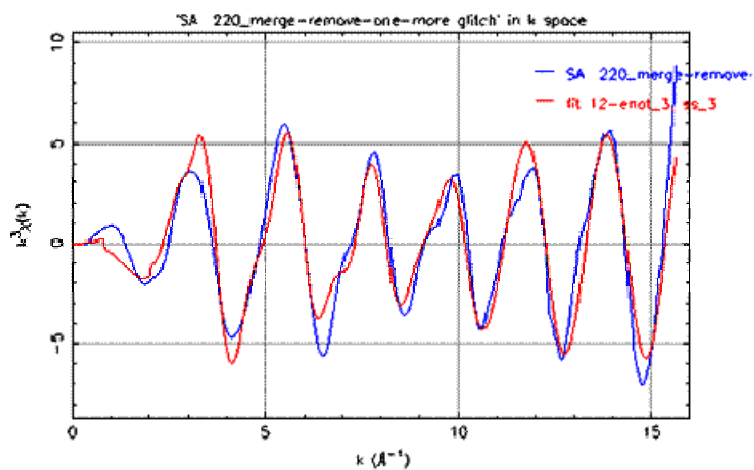
$$R = \frac{\sum_{i=1}^N |\chi_{\text{obs}}(k_i) - \chi_{\text{calc}}(k_i)|}{\sum_{i=1}^N |\chi_{\text{obs}}(k_i)|} \times 100\% \dots\dots(3)$$

The k^3 -weighted $\chi(k)$ -space spectra of the model compound, $\text{OV}[\text{OSi}(\text{O}^t\text{Bu})_3]_3$, are shown in Figure 4-17. The red curves represent the theoretical fit and blue curves represent experimental spectra which are generated from Athena program. It can be seen here that the spectra at high k range ($k > 10$) are fit better after processing self absorption correction.

The FT spectra of the imaginary part also show some differences (Figure 4-18) before and after SA correction. The parameters were set up using a priori knowledge of the sample. The CN number for V=O is set to one, for V-O is set to 3 and for V... Si is set to 3 (Figure 4-19). For each path, the following free variables “path length (R)”, “Debye-Waller factor (σ^2)”, and “inner potential energy (E_0)” were then refined sequentially. Fit Parameters are summarized in Table 4-1. The amplitude reduction factor is 0.93 ± 0.06 after SA correction and 0.83 ± 0.05 before SA correction.

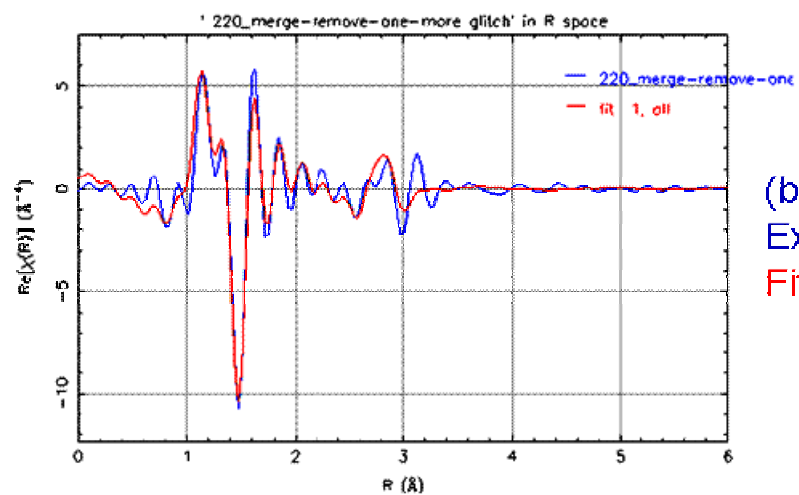


(before SA correction)
Experimental data
Fitting data

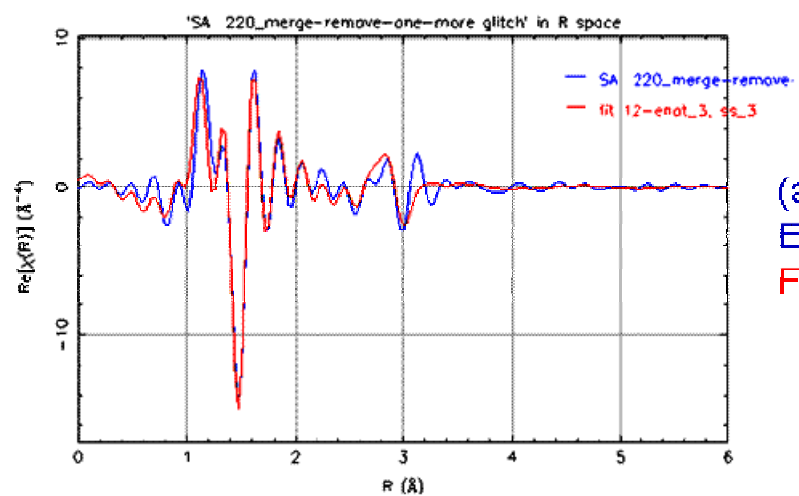


(after SA correction)
Experimental data
Fitting data

Figure 4 - 17 Experimental and fitting spectra before and after self absorption (SA) correction



(before SA correction)
Experimental data
Fitting data



(after SA correction)
Experimental data
Fitting data

Figure 4 - 18 FT of imaginary part before and after SA correction

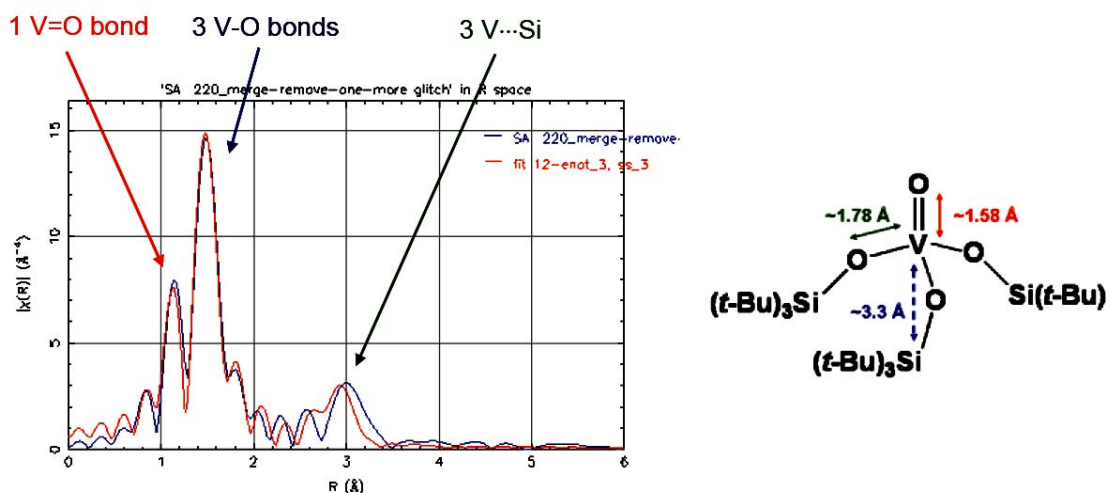


Figure 4 - 19 A R-space spectrum of experimental and fit data

Table 4 - 1 EXAFS Fit parameters for model compound before and after SA correction

path	CN	R(Å)	σ^2		ΔE_0 (eV)	
			Before SA	After SA	Before SA	After SA
V=O	1	1.57	0.0015 ± 0.0015	0.0001 ± 0.0012	1.3 ± 2.5	2.7 ± 3.3
V-O	3	1.78	0.0012 ± 0.00069	0.0012 ± 0.0006	1.3 ± 2.5	2.7 ± 3.3
V...Si	3	3.25	0.0114 ± 0.0032	0.024 ± 0.013	10.2 ± 1.9	11.0 ± 3.7

4.3.2-2 Three-connected embedded vanadyl samples⁴⁸

“MYL-II-218” is an embedded vanadyl sample prepared with a ratio of 0.73 VOCl_3 : 1 cube followed by further cross linking with Me_2SiCl_2 and then removal of any residual trimethyltin groups with TMSCl . The vanadium content of this sample is $4.0 \pm 0.3 \%$ which is determined from gravimetric analysis. ^{51}V SSNMR spectra indicate that this sample should contain only three-connected, vanadyl centers. The bond length of the $\text{V}=\text{O}$ double bond and $\text{V}-\text{O}$ single bond of this type of the material is shown in figure 4-20.

The E-space plot with pre- and post-edge ranges is shown in Figure 4-21. Different k-weighting of k-space plot is shown in Figure 4-22, with and without SA correction. The spectra before (blue curves) and after (red curves) SA correction seems similar in different k-weighted k-space spectra. The plots indicate that fluorescence data for this sample with $\sim 4 \%$ vanadium exhibit only a small SA effect. A k^3 -weighting with SA correction is then chosen in the following fitting processes.

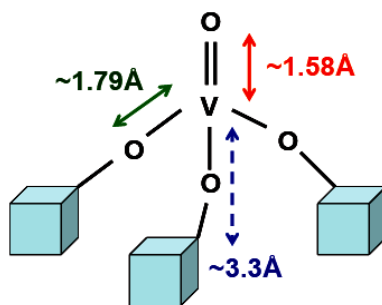


Figure 4 - 20 A model of the embedded vanadyl sample

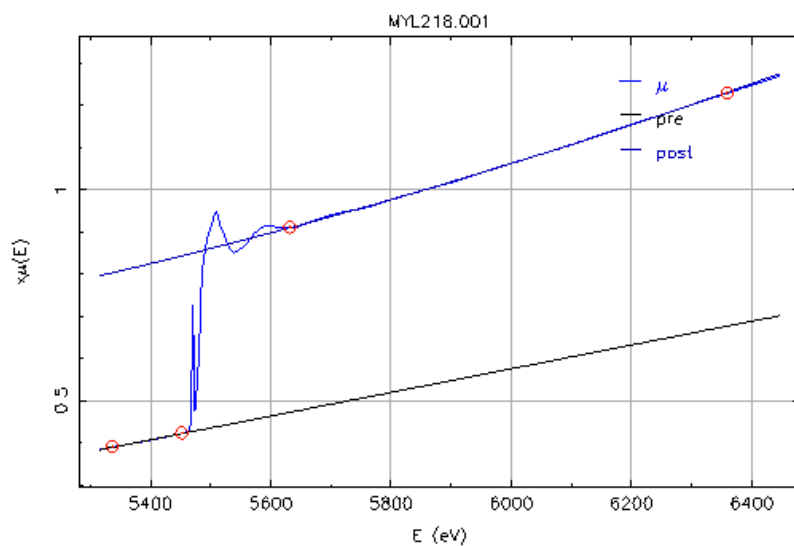


Figure 4 - 21 E-space plot of embedded vanadyl sample-MYL-II-218

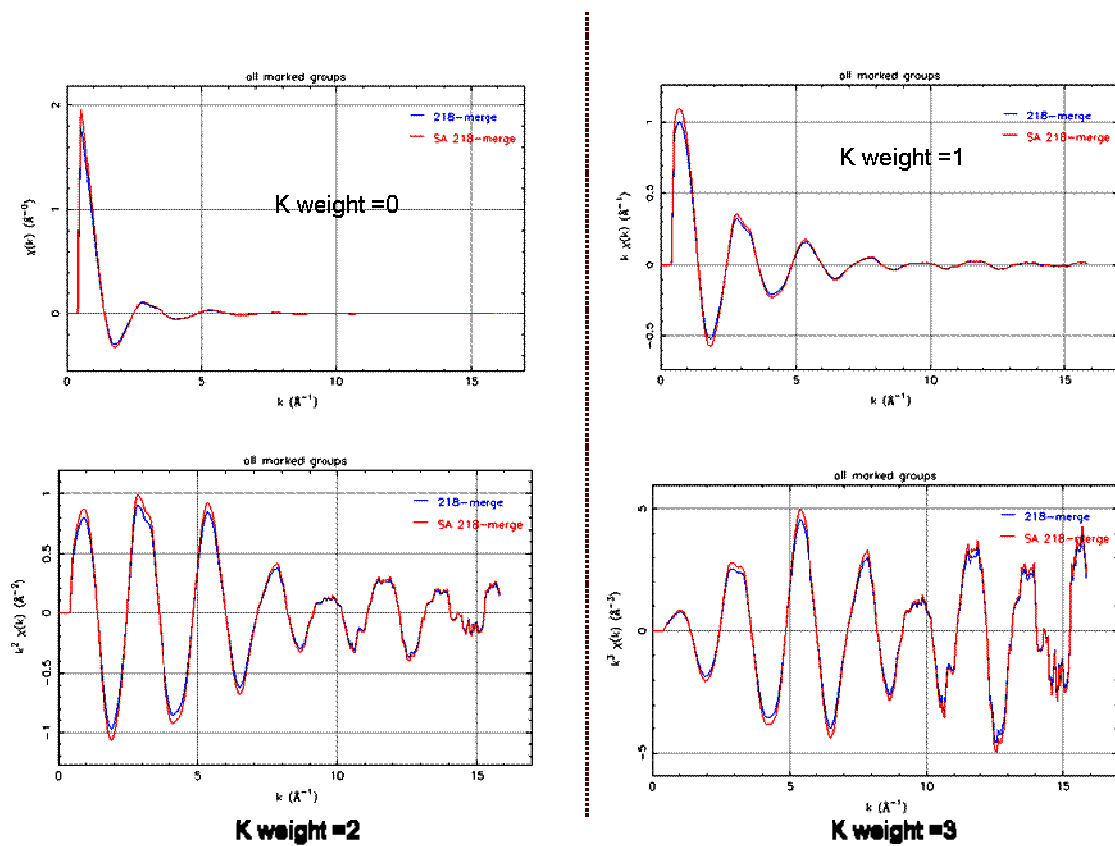


Figure 4 - 22 Different k-weight of embedded vanadyl sample-MYL-II-218

Different R_{bkg} values change R-space spectra tremendously. When $R_{\text{bkg}} = 1.0$, one prominent physically unrealistic peak in the low R region appears in the spectra in Figure 4-23. A reasonable spectrum is generated by choosing the R_{bkg} value equal to 1.2. When the R_{bkg} value is set to 1.3, the V=O peak at $\sim 1.2 \text{ \AA}$ is altered. Fixing the R_{bkg} to 1.2 and changing the k range yield the different R-space spectra as shown in Figure 4-24. When a smaller k range is applied ($k = 2\sim 10$), the two distinct features between $R = 1$ and 2 are unresolved. The V=O double bond and V-O single bonds features are not distinguished from each

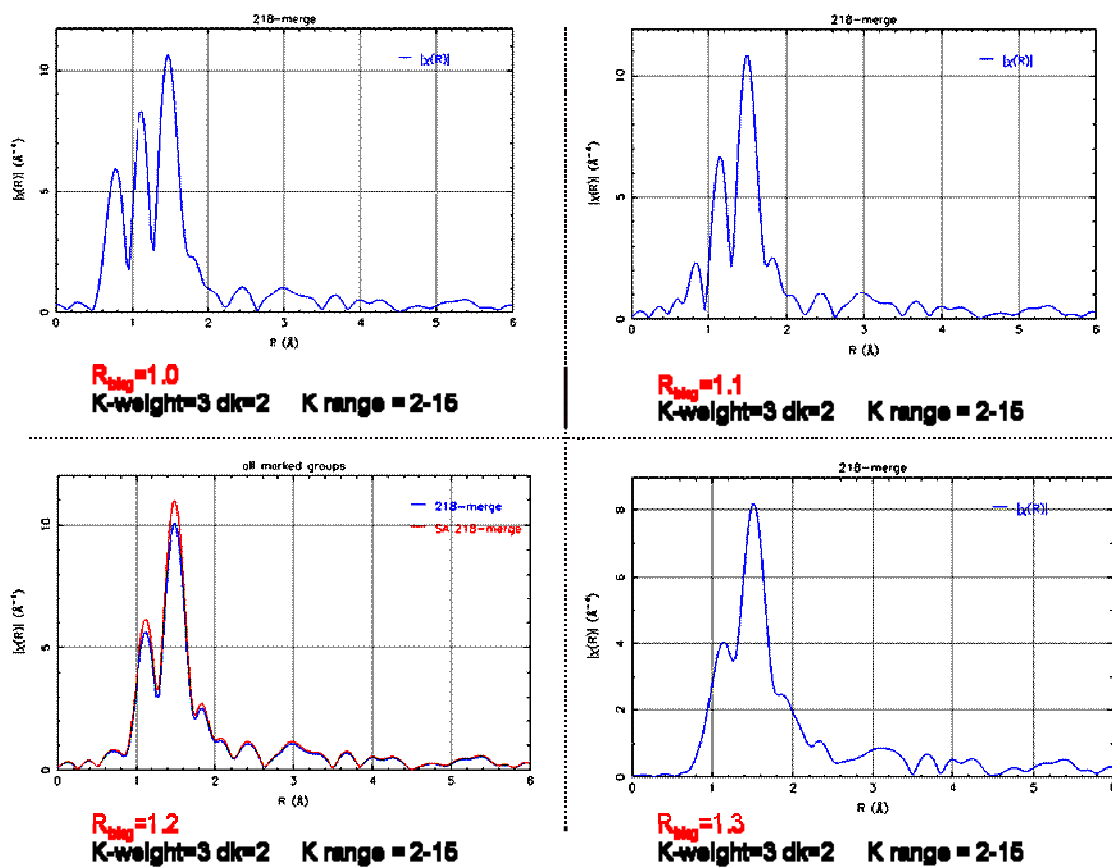


Figure 4 - 23 R-space plots with different R_{bkg} value (MYL-II-218)

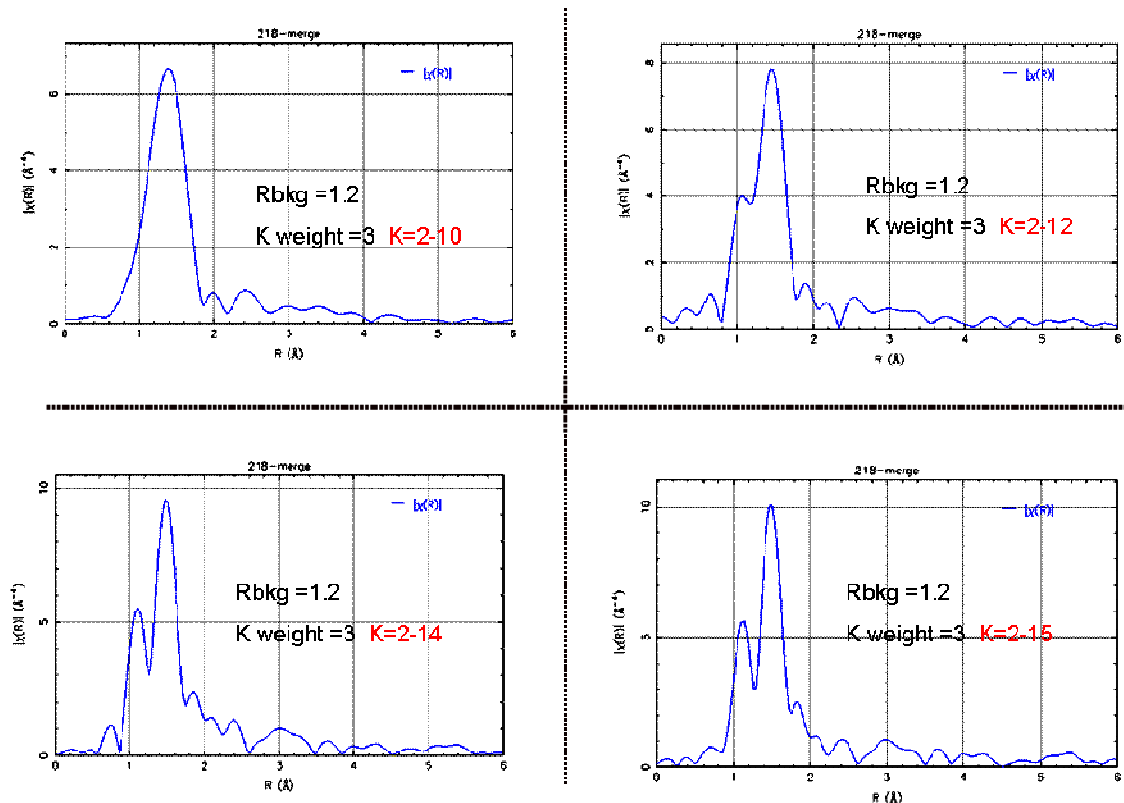


Figure 4 - 24 R-space plot with different k range (MYL-II-218)

other when the k range is smaller than 10. As the k range increases to 12 to 13, these two different types of oxygens in the first coordinate sphere of vanadium are well resolved in the spectra. Normally higher quality samples provide clearer k-space spectra at high k and better resolution in the R-space spectrum. The parameter $R_{bkg} = 1.2$ and $k = 2-15$ are finally chosen and saved as prj file.

“MYL-II-228” is also an embedded vanadyl sample but prepared with a different ratio $VOCl_3$: cube (0.99 : 1) followed by exposure to Me_2SiCl_2 and then $TMSCl$. The weight percentage of this sample is 5.6 %, determined from gravimetric analysis. ^{51}V SSNMR spectra indicate that this sample also contains only three-connected vanadyl centers.

The E-space plot with pre-edge and post-edge ranges (Figure 4-25) and k-space plot (Figure 4-26) of this sample are similar to the spectra observed in the 4.0 wt% vanadyl sample MYL-II-218.

The parameters $R_{\text{bkg}} = 1.2$ and $K = 2-15$ are chosen to FT k-space plot and the R-space spectrum (Figure 4-27) is obtained. The red curve is the spectrum after processing SA correction. The SA correction here exhibits only a small effect in the R-space spectrum. The results from two different three-connected vanadyl samples indicate the SA effect is small when the vanadyl loading ratio is low in the silicate matrix.

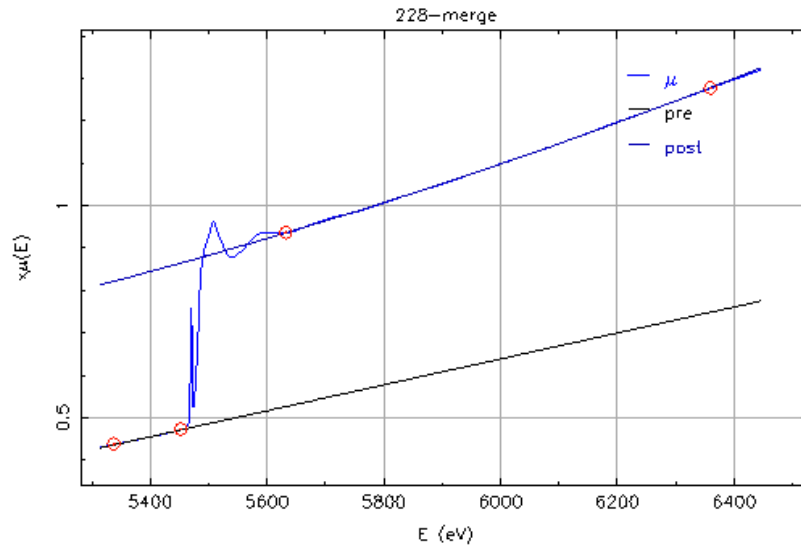


Figure 4 - 25 E-space plot of embedded vanadyl sample-MYL-II-228

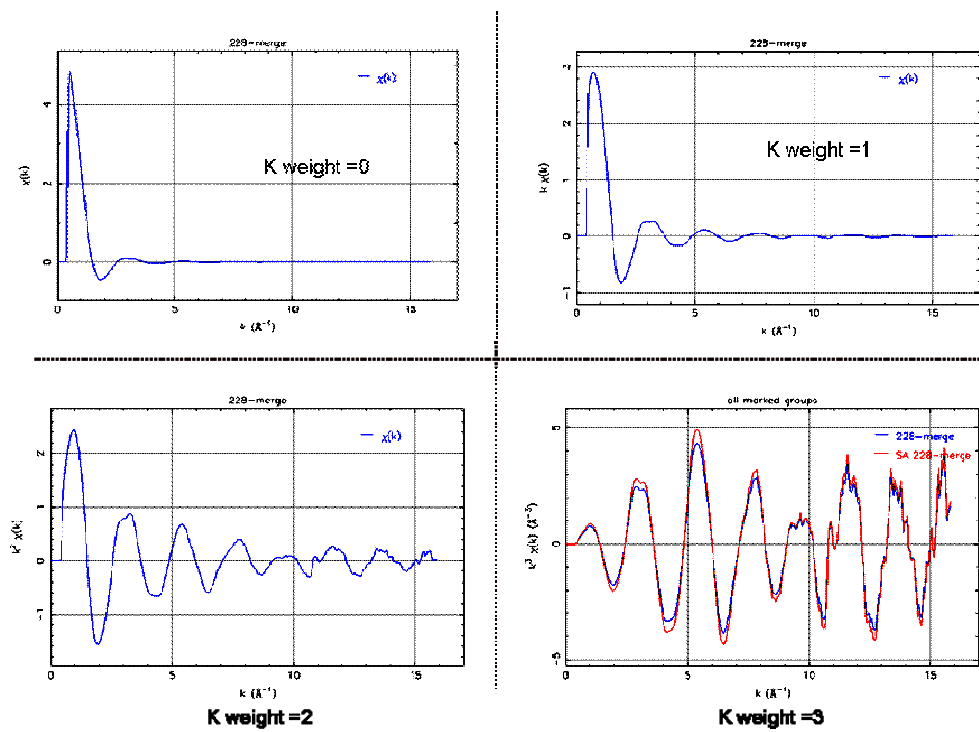


Figure 4 - 26 Different k-weight of embedded vanadyl sample-MYL-II-228

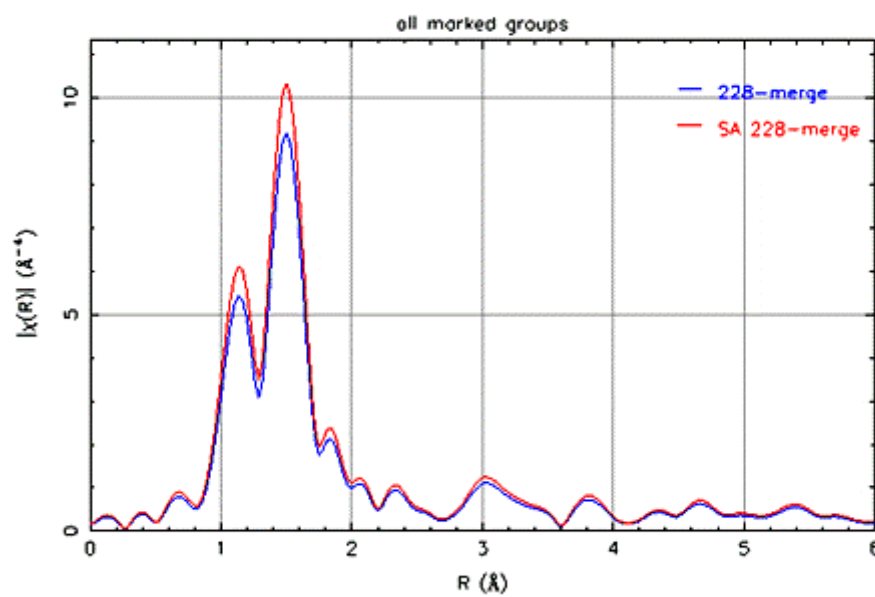


Figure 4 - 27 R-space plots with $R_{\text{bkg}} = 1.2$ and $K = 2-15$ (MYL-II-228)

Both of these embedded vanadyl samples provide similar EXAFS spectra. In Artemis, the amplitude reduction factor is set at 0.93 which is obtained from the model compound. The coordination number of V=O double bond is set at 1. The single-scattering modeling of the MYL-II-228 sample in k^3 -weighted EXAFS k-space and R-space spectra is shown in Figure 4-28 and 4-29. The final EXAFS fit data are summarized in Table 4-2. The R factor of sample MYL-II-218 is 0.063 and MYL-II-228 is 0.054.

The refined V-O coordination numbers of these two samples are very close to three and there are no chlorine features ($\sim 2.15\text{\AA}$) observed in the R-space spectra. The fitted V=O and V-O distances, at 1.60 and 1.79 $\text{\AA}$, respectively, are consistent with those for VOCl_3 and other vanadyl silanolates ($\text{VO}(\text{OSiPh}_3)_3$ and $[\text{VOCl}(\text{O}_2\text{Si}^t\text{Bu}_2)]_3$). The EXAFS results agree with the information from gravimetric analyses and ^{51}V SSNMR data. These samples should contain only three connected vanadyl centers without any remaining chlorine ligands, just as was targeted in the synthetic scheme.

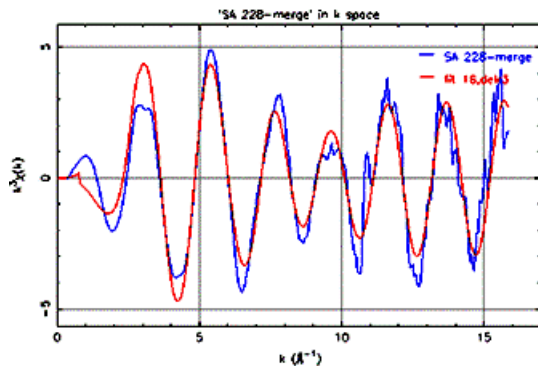


Figure 4 - 28 Single scattering refinement of the MYL-II-228 sample in k^3 -weighted EXAFS k-space

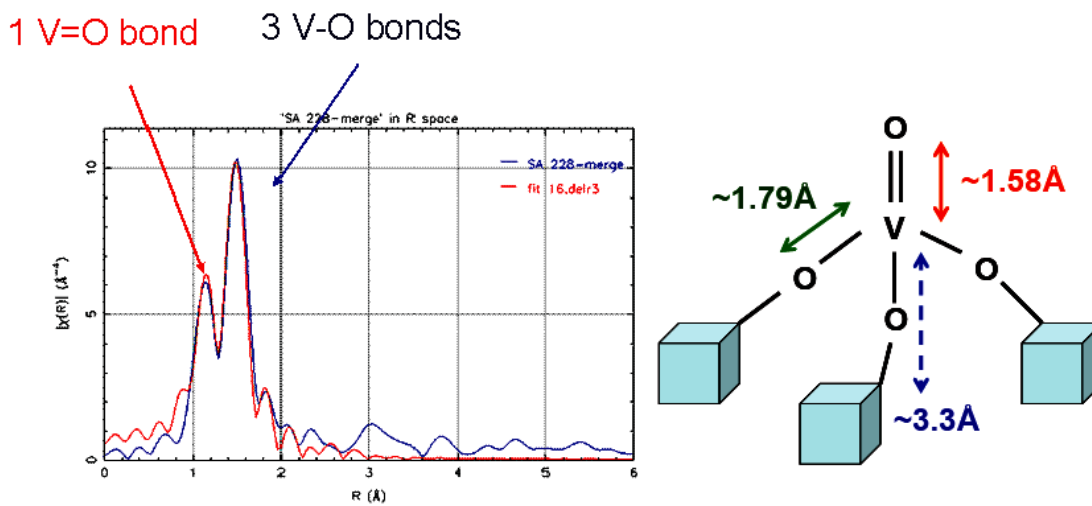


Figure 4 - 29 Single scattering refinement of the MYL-II-228 sample in R-space

Table 4 - 2 EXAFS fits for single scattering path in embedded vanadyl samples

path	CN		R ($\text{\AA}$)		σ^2		ΔE_o (eV)	
	MYL-II-218	MYI-II-228	MYL-II-218	MYI-II-228	MYL-II-218	MYI-II-228	MYL-II-218	MYI-II-228
V=O	1	1	1.60 ± 0.015	1.60 ± 0.005	0.0006 ± 0.0008	0.0012 ± 0.0013	0.62 ± 0.86	2.18 ± 2.3
V-O	2.87 ± 0.13	2.95 ± 0.12	1.78 ± 0.005	1.79 ± 0.008	0.0018 ± 0.0010	0.0024 ± 0.0007	0.62 ± 0.86	2.18 ± 2.3

4.3.2-3 Four-connected embedded vanadium⁴⁹

A four-connected vanadium sample was prepared from a ratio of 0.48 VCl_4 to 1 cube reaction followed by adding Me_2SiCl_2 and then TMSCl . The model of this type of compound is shown in Figure 4-30. The weight percentage of this sample is $2.7 \pm 0.3 \%$ from the gravimetric analysis. A significant glitch in the EXAFS data was observed at $k = \sim 10.5 - 10.9$ in k^3 -weighted k -space plot (Figure 4-31). The relative energy of this k range is 5905-5930 eV (Figure 4-32). In order to find out the source of this glitch in the data, comparison with spectra from different samples is necessary. Figure 4-33 shows k -space spectra for different vanadyl samples. When the vanadium weight percentage is low ($< 3.5 \%$) or if the sample contains residual trimethyl tin groups (blue curve in Figure 4-33), the relative intensity of this glitch is large with respect to the EXAFS oscillations spectra. When the vanadium weight percentage in these samples is

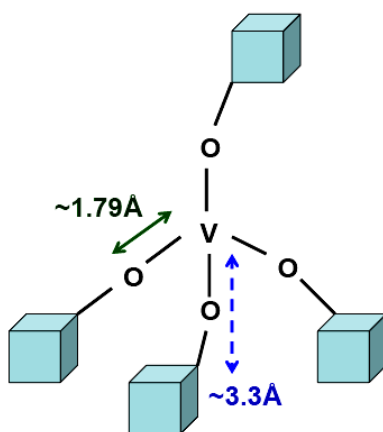


Figure 4 - 30 A model of the embedded vanadium (+4) sample

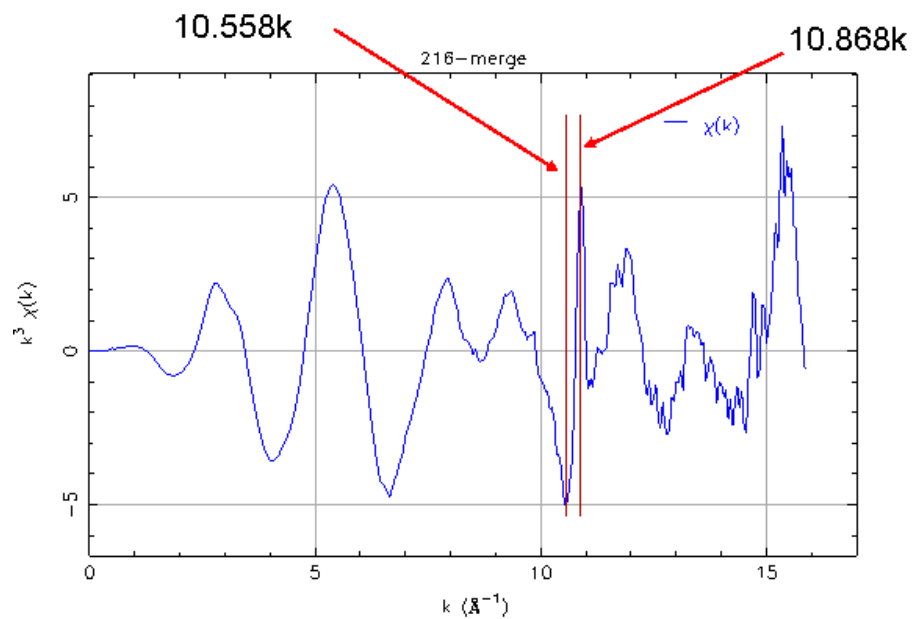


Figure 4 - 31 A glitch in k^3 -weighted k-space plot

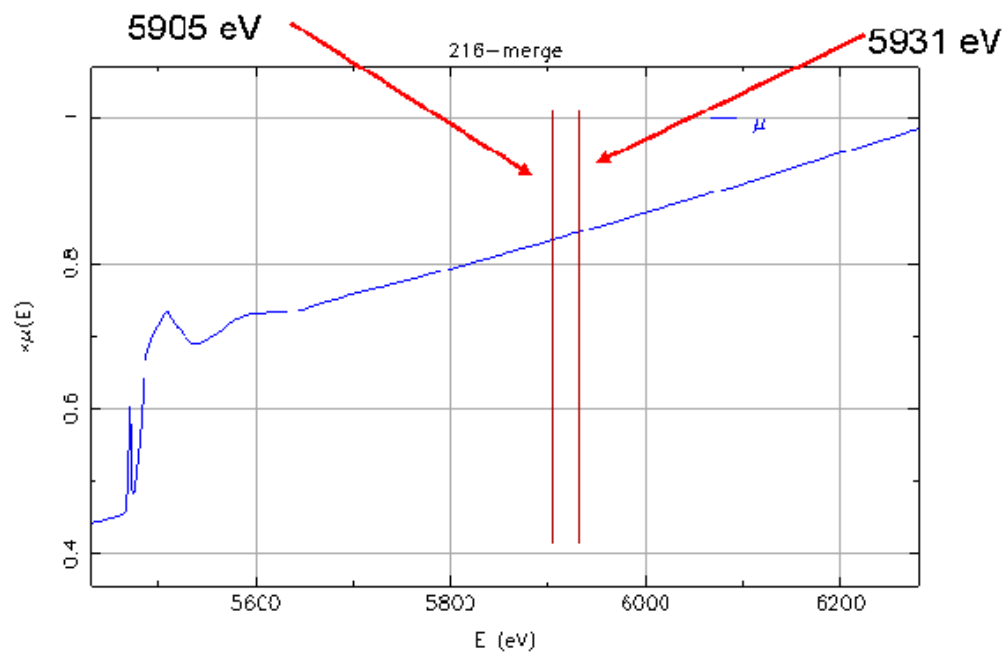


Figure 4 - 32 Relative energy of the glitch

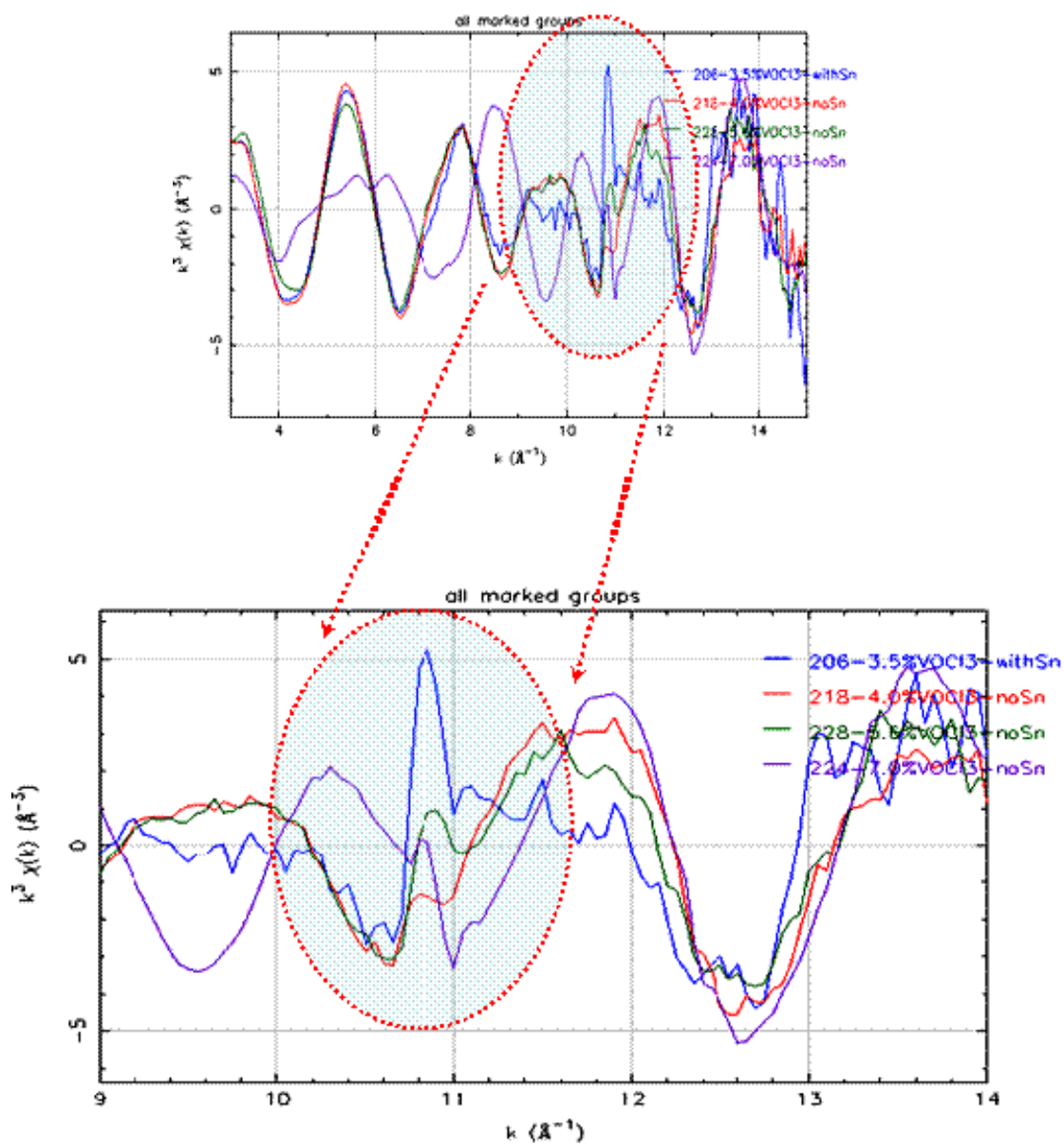


Figure 4 - 33 k-space spectra for different vanadyl samples

4.0 or 5.6 and without trimethyl tin groups (red and green curves), the relative intensity of the glitch is small. For a surface vanadyl sample with 7 wt%, the glitch still exists in the same position with a relatively small intensity. The same observations are also apparent in vanadium (+4) samples (Figure 4-34). When the vanadium wt% is 1.6~2.8 %, the glitch is significant in the k^3 -weighted $\chi(k)$ plot (blue, red, and green curves). When the vanadium weight percentage is 7% (surface vanadium sample), the relative intensity of the glitch is small in the spectra. This information indicates the glitch should not be from the contamination of vanadyl (+5) or vanadium (+4) precursor but from the monochromator associated with beam line X18B at ~5900 eV. If the vanadium concentration of the sample is too low (<3%), it will not provide good data especially in the $k > 10$ region.

After removing the glitch from the raw data, the spectrum improved significantly (red curve in Figure 4-35). This sample was designed to contain only one type of vanadium with four V-O single bonds. The R-space spectrum (blue curve in Figure 4-36) shows only one peak at ~1.5Å (not phase corrected) after FT of the k range from 2 to 10. A small peak at ~ 1.0 Å appears when a larger k range is applied ($k = 2 - 11$ red curve, $k = 2 - 12$ green curve, and $k = 2 - 13$ purple curve in Figure 4-36). Gleeson et al. discussed a titanium model compound with a similar small by fitting the data with a small k range ($k = 4 \sim 11$). Comparing our data with this precious literature reports indicate that the vanadium data are still usable if a smaller k range is used in the FT step. The

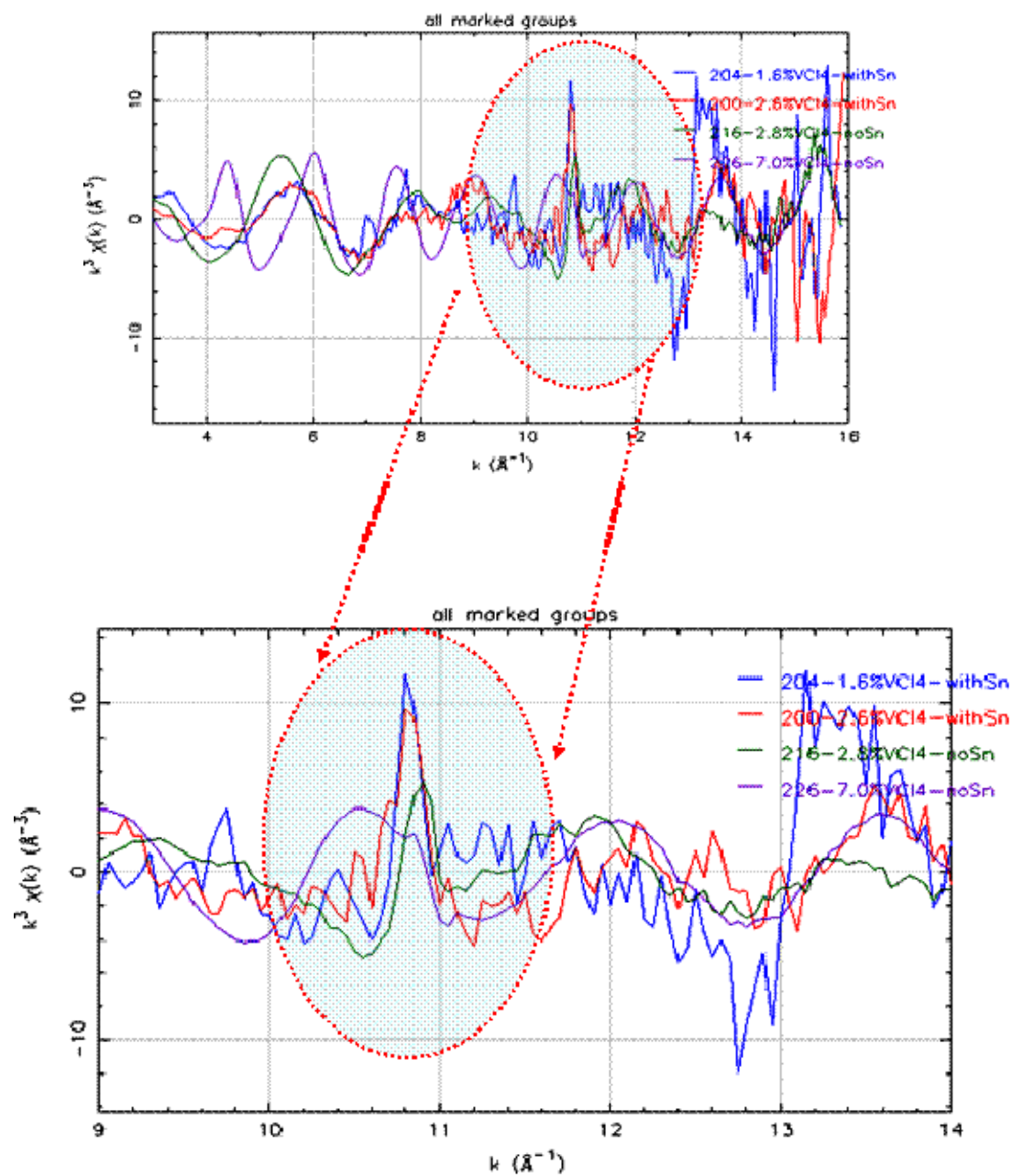


Figure 4 - 34 k -space spectra for different vanadium samples

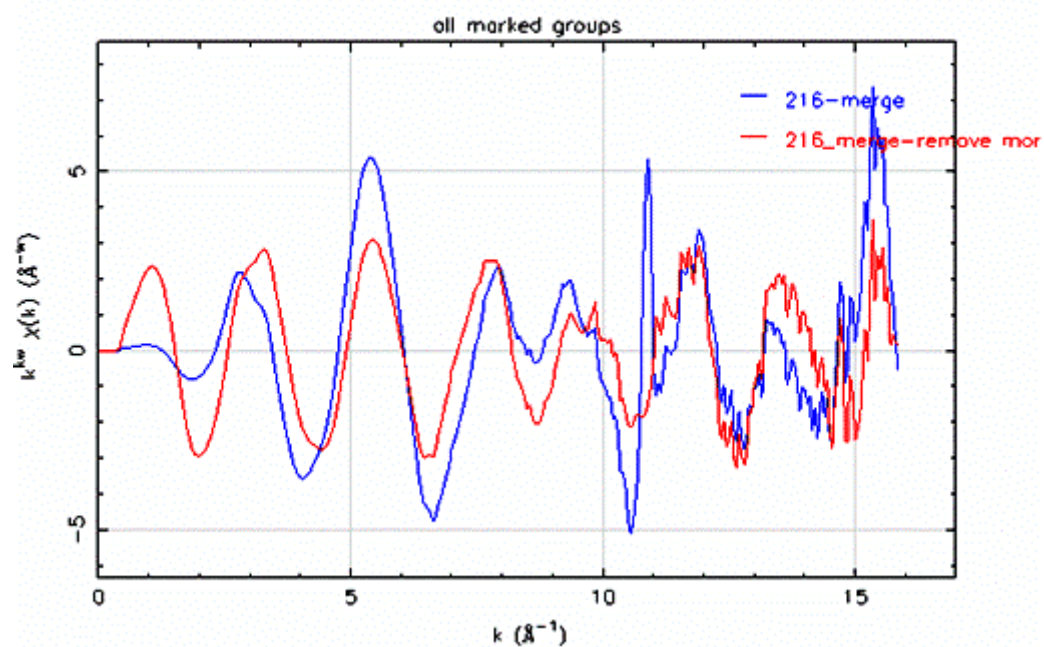


Figure 4 - 35 k^3 -weighted EXAFS k-space plot with and without deglitch

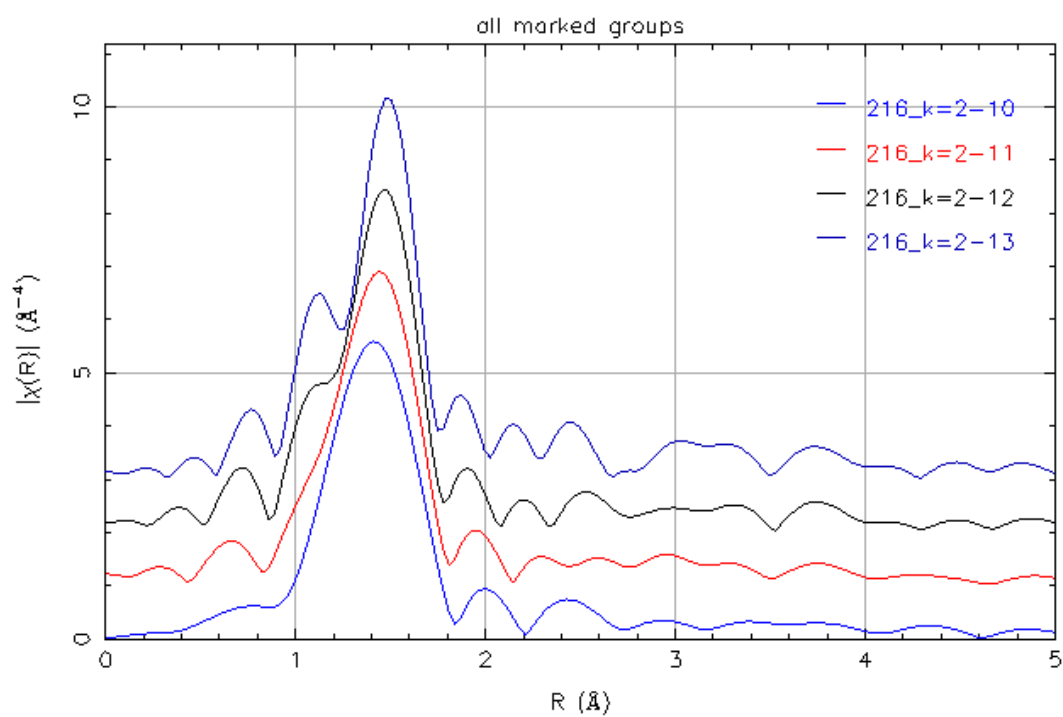


Figure 4 - 36 R-space spectra with FT from different k range

glitch observed at high k range ($k > 10$) at NSLS beam line X-18B causes problems especially when measuring low weight percentage vanadium samples and should be avoided in the future measurement.

The fitted spectrum is shown in Figure 4-37 (red curve), and the parameters are summarized in Table 4-3. This sample should contain only 4 V-O single bonds without any chlorine ligands. The coordination number (3.99 ± 0.46) is consistent with the result from the gravimetric analysis and no chlorine feature is observed in the R-space spectrum which is consistent with this embedded vanadium sample containing one type of vanadium center as designed.

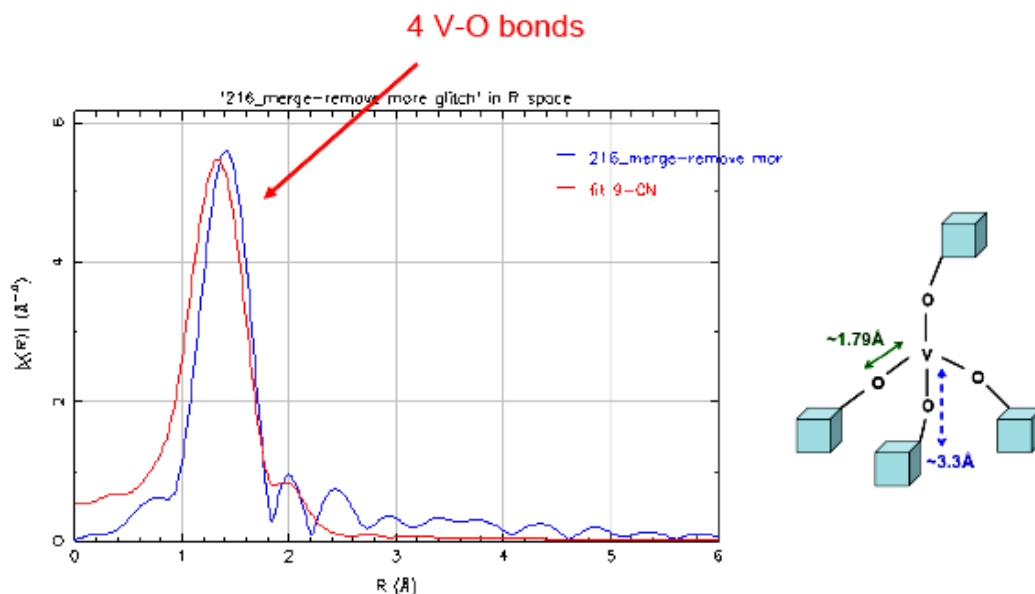


Figure 4 - 37 R-space spectrum of four-connected vanadium sample

Table 4 - 3 Refined EXAFS parameters for an embedded vanadium sample

path	CN	R(Å)	σ^2	ΔE_o (eV)	S_o^2
V-O	3.99 ± 0.46	1.78 ± 0.028	0.012 ± 0.002	5.13 ± 3.74	0.793

4.3.2-4 One-connected surface vanadyl sample⁵⁰

For a surface vanadyl sample, three different types of bonds to the vanadium center be observed in the spectra. One is a V=O double bond at $\sim 1.57\text{\AA}$, another is the V-O single bond at $\sim 1.78\text{\AA}$, and a final V-Cl single bond at $\sim 2.16\text{\AA}$. The model of this type of surface sample is illustrated in Figure 4-38.

This surface vanadyl sample is extremely air sensitive. V-Cl bonds will quickly react with water and be replaced with V-OH groups. Furthermore we have seen evidences (discolorations) that these samples will react slowly with the aluminum sample holders. The best way to obtain good data of the surface sample is to pack a fresh sample in a polycarbonate sample cell just before the measurement to avoid the sample decomposition. The E-space plot is shown in Figure 4-39 and the chloride ligands in this surface vanadyl sample change the edge feature as describe in the XANES section.

Different k-weighted k-space plots are shown in Figure 4-40. When the k-weight is zero or one, the peaks at high k range are very weak. When the k-weight increases to two, the intensity of peaks at high k range is modulated to the intensity similar to that of peaks at low k range. When the k-weight is equal to

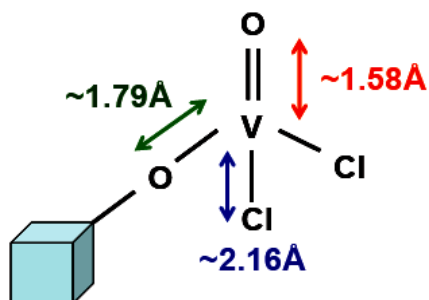


Figure 4 - 38 A model of the surface vanadyl (+4) sample

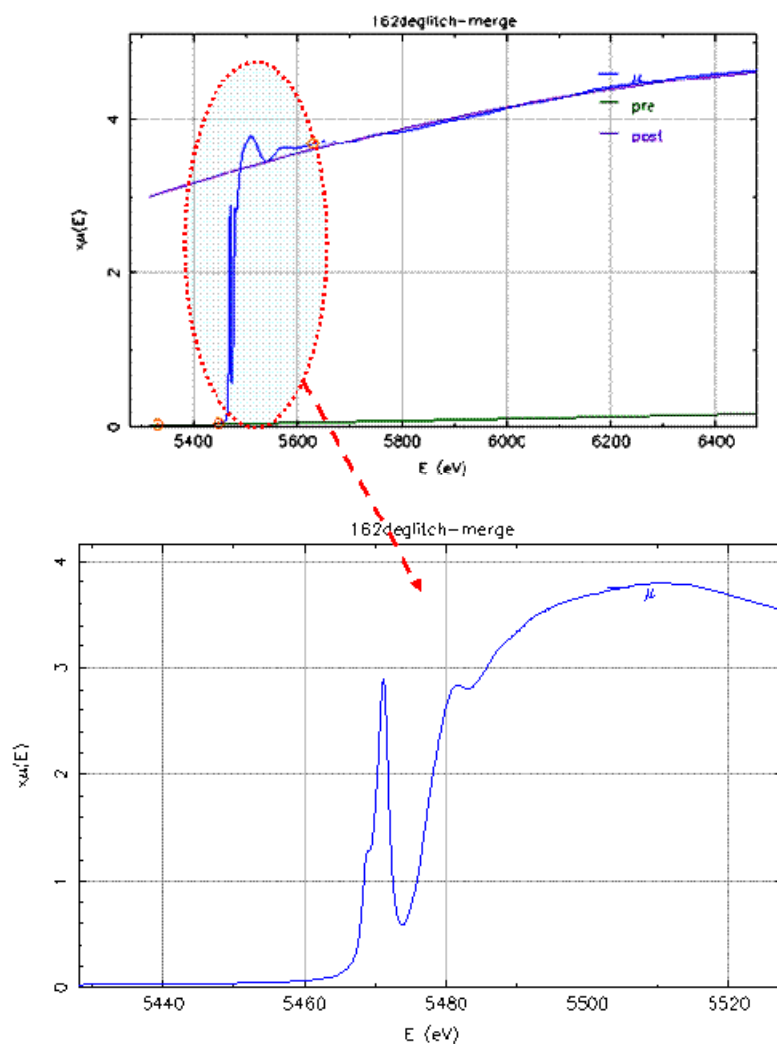


Figure 4 - 39 E-space plot of surface vanadyl sample (form X19A-Ge detector)

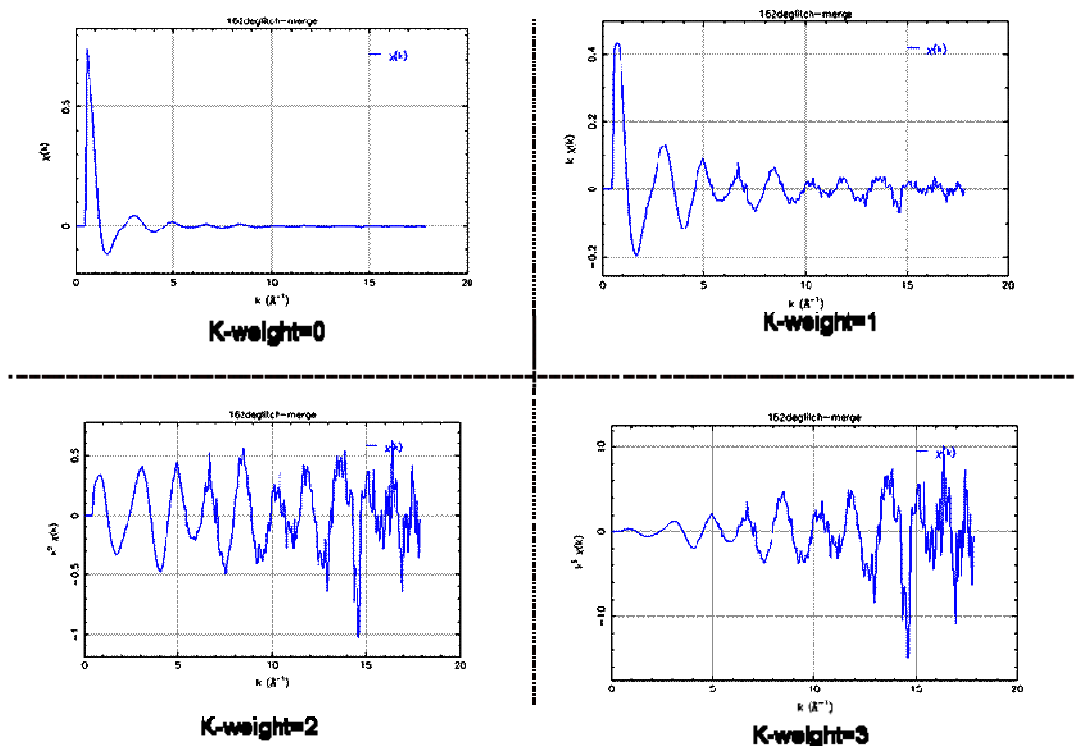


Figure 4 - 40 K-space plots with different k-weight

three, peaks at high k are more intense than peaks at low k . The k^3 - weighting is not suitable to be used for these data. Therefore a k -weight equal to two was chosen for this sample.

Fixing the k -weight to two and Fourier Transforming the k -space spectra with different k ranges results in different R -space spectra (Figure 4-41). When a smaller k range ($k = 2 - 12$) was used, only one peak was observed at the $1.0\sim 1.5$ Å in the R -space plot. The V=O double and V-O single bonds can not be distinguished with this small k range. As the k range is increased to 15, two features which represent V=O and V-O bonds appear in the R -space spectrum

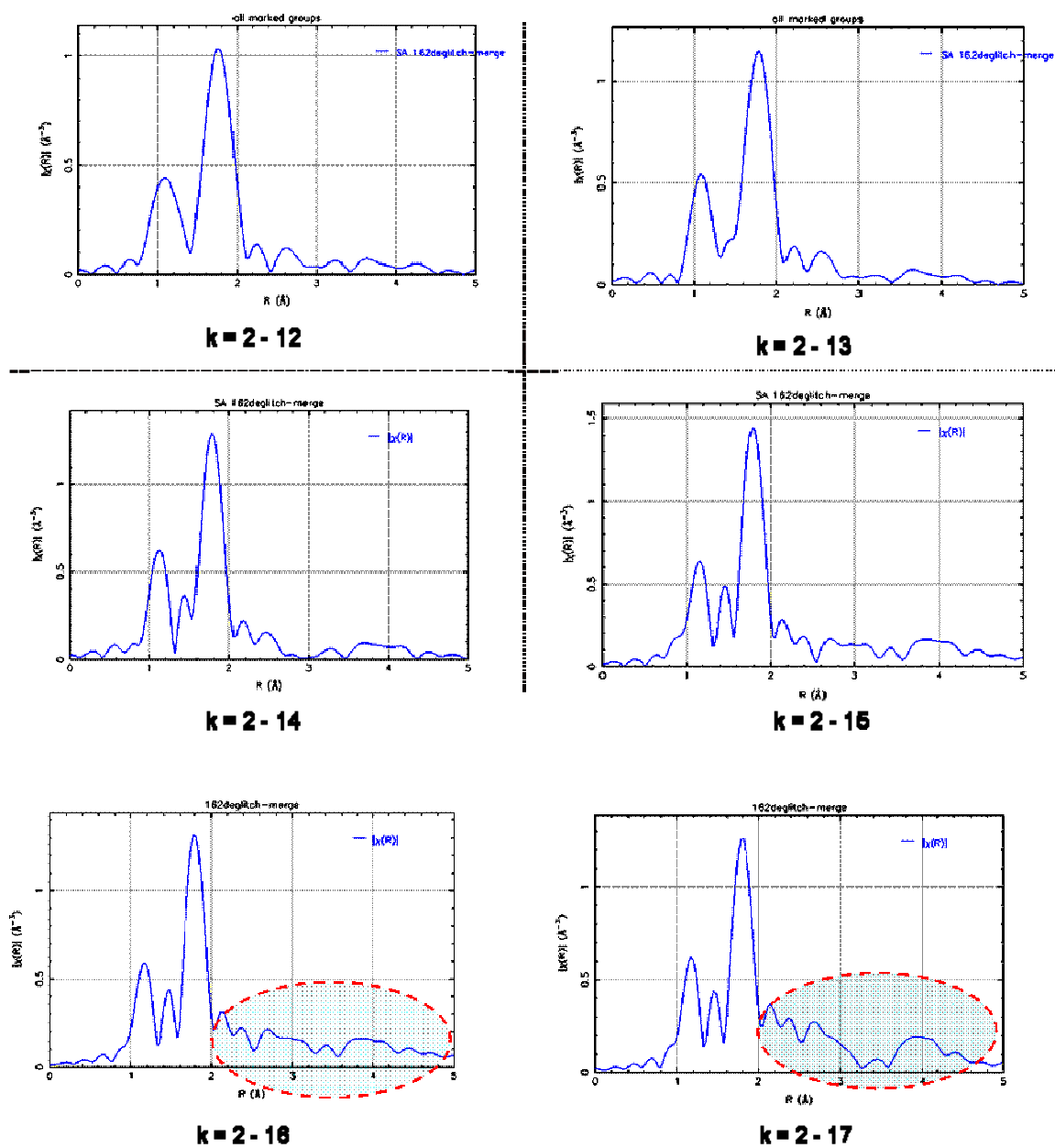


Figure 4 - 41 R-space plots with different k-range

and the feature at ~ 1.8 Å narrows. This feature represents V-Cl does not change in intensity while altering the k range. The background noise is smaller when a smaller k range is applied but increases significantly without changing the intensity of V=O, V-O, and V-Cl feature when Fourier transforming the k-space spectra with a larger k range ($k = 2 - 16$ or 17). These results indicate that Fourier transforming a k-space plot with a higher k range provides a better spectrum but the noise in the background also increases. Finding the balance between the quality of the spectrum and the noise in the background is very important before fitting the EXAFS spectrum. A good data reduction in Athena helps to produce better fit parameters in Artemis.

In Artemis, only single scattering path were included in the model for refinement in this sample. Path lengths of V=O, V-O and V-Cl were refined first. The refined V=O, V-O, and V-Cl distances are consistent with those of VOCl_3 . The Debye-Waller factor and inner potential energy were then refined sequentially for each path. The two V-Cl groups are constrained to be equivalent. The amplitude reduction factor is 0.75 and the R factor is 0.20. The coordination number of the V-Cl bond is 1.91 ± 0.17 Å which is consistent with one-connected vanadyl center. The calculated fit curve (red) and experimental data (blue) of k-space and R-space spectra are shown in Figure 4-42 and 4-43, respectively. EXAFS fit parameters are summarized in Table 4-4.

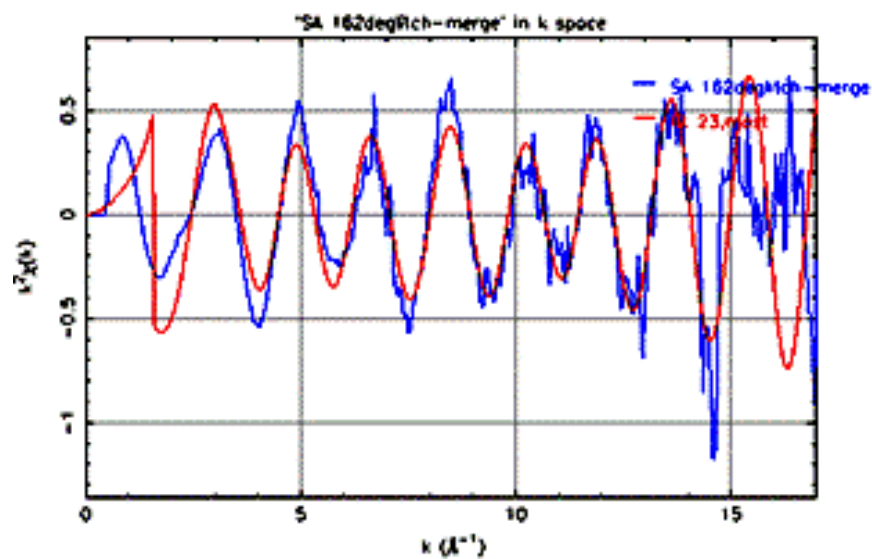


Figure 4 - 42 k^3 -weighted k -space of single-scattering refinement of the one-connected vanadyl sample

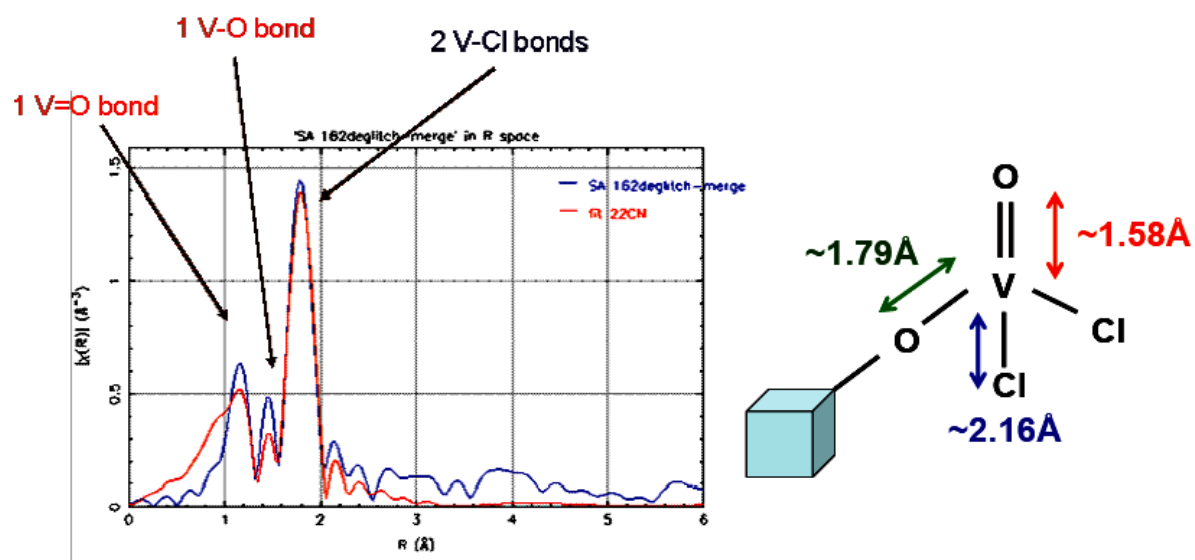


Figure 4 - 43 R -space of single-scattering refinement of the one-connected vanadyl sample

Table 4 - 4 EXAFS fits for single scattering path in the surface vanadyl sample

path	CN	R (Å)	σ^2	ΔE_o (eV)
V=O	1	1.57 ± 0.037	0.0005 ± 0.0020	9.78 ± 2.48
V-O	1	1.79 ± 0.024	0.0011 ± 0.0020	9.78 ± 2.48
V-Cl	2	2.16 ± 0.008	0.0032 ± 0.0010	-1.62 ± 1.35

4.3.2-5 One-connected surface vanadium sample

For the surface vanadium sample, two types of vanadium bond should be observed. One is the V-O single bond at ~ 1.78 Å and the other one is V-Cl single bond at ~ 2.16 Å. The model of this type of compound is shown in Figure 4-44. This surface vanadium sample has a small pre edge feature in XANES spectrum as was described in the previous section (Figure 4-45). The k-space plots before (blue) and after (red) SA correction with different k weight are shown in Figure 4-46. The k^3 and k^2 -weighted k-space spectra shows the spectra do not change too much after processing the SA correction and the oscillations at high k region are still very clear.

The first coordination sphere around vanadium should include one V-O single bond and three V-Cl bonds. EXAFS analysis of V-O and V-Cl bonds show the bond distances are longer than those for other vanadyl samples. The refined coordination number of V-Cl bond is 3.00 ± 0.12 which is consistent with one-

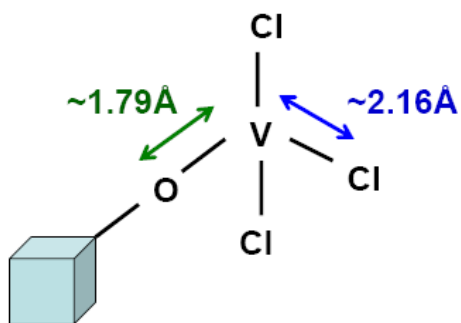
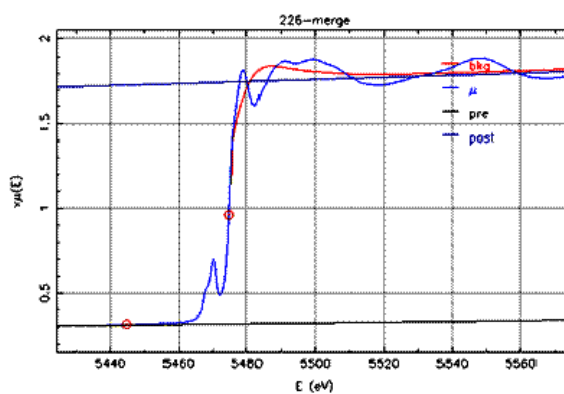
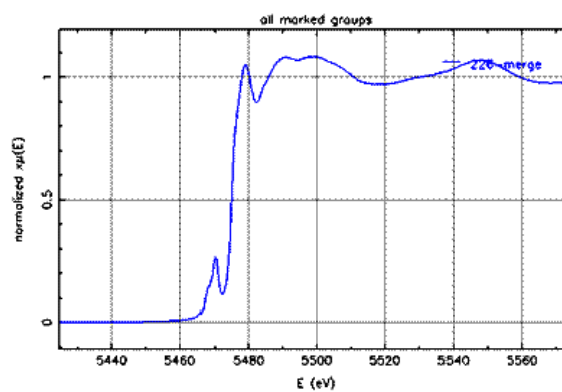


Figure 4 – 44 A model of the surface vanadyl (+4) sample



before normalize



after normalize

Figure 4 - 45 E-space spectrum

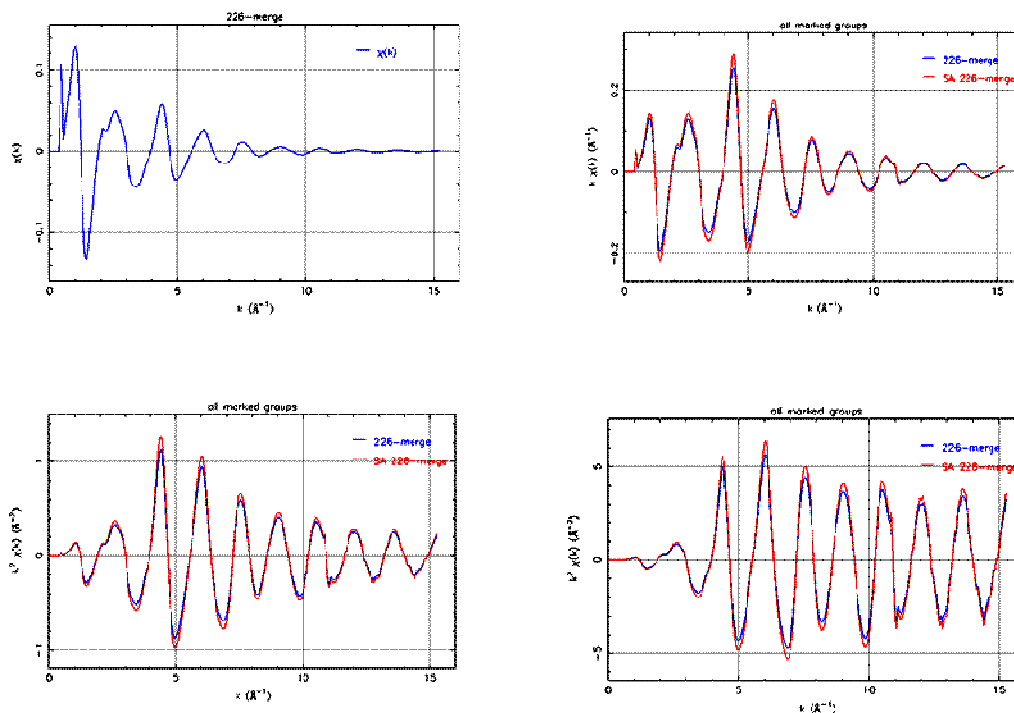


Figure 4 - 46 Different k-weighted k-space spectra

connected vanadium centers. The second coordination sphere analysis shows the V...Si bond distance is around 3.38 Å which is longer than in other vanadyl samples. The single-scattering refinement in R-space spectra is shown in Figure 4-47. The low R feature at 1.35 Å is a Fourier ripple and not a real peak. EXAFS fit parameters are summarized in Table 4-5. The amplitude reduction factor is 0.92 and the R factor is 0.038. When the coordination numbers of V=O double bond and V-O single bond are set to one, the fitted coordination number of V-Cl bond is 3.00 ± 0.12 . This result is consistent with only one-connected vanadium center in the matrix.

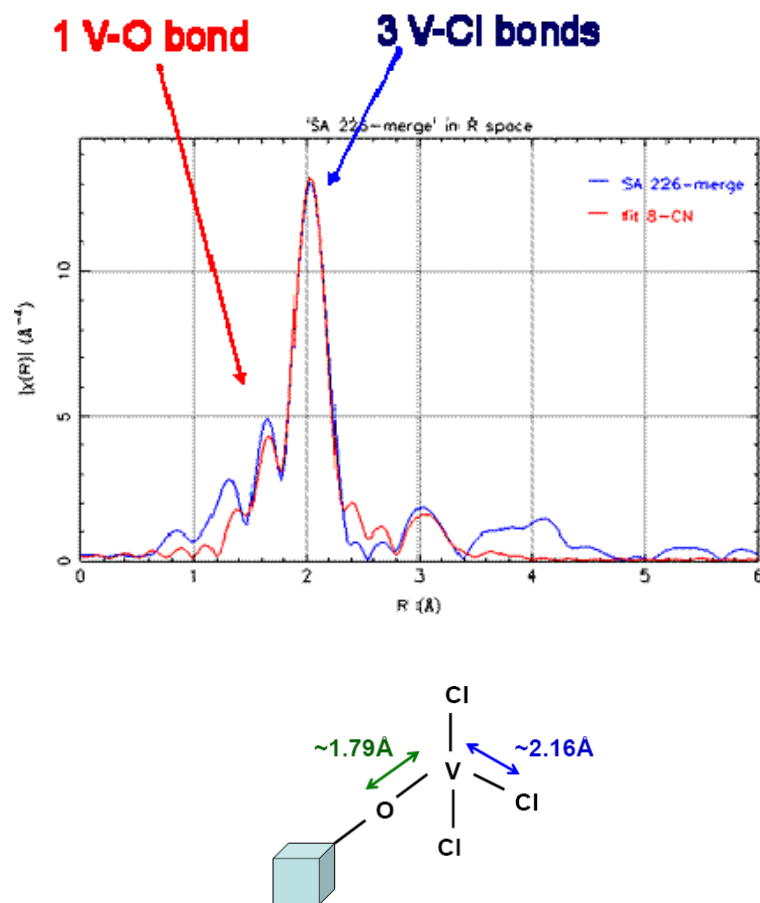


Figure 4 – 47 R-space of single-scattering refinement of the one-connected vanadium (+4) sample

Table 4 - 5 EXAFS fits for single scattering path in the surface vanadium (+4) sample

path	CN	R (Å)	σ^2	ΔE_o (eV)
V-O	1	2.00 ± 0.019	0.0019 ± 0.0014	16.2 ± 3.1
V-Cl	3.00 ± 0.12	2.37 ± 0.006	0.0030 ± 0.0003	-0.91 ± 1.35
V...Si	1	3.38 ± 0.046	0.0040 ± 0.0028	12.7 ± 5.87

4.3.2 Edge jumps and weight percentages

The edge jump is the change in the absorption coefficient at the edge which is evaluated by taking the difference of the pre-edge and post-edge lines at E_0 . Different pre-edge and post-edge lines might change the edge jump slightly but generally the value of the edge jump should be proportional to the number of absorber atoms in the sample. A sample with a higher wt% should have a larger edge jump theoretically. Therefore recording the edge jump for each sample is another indirect technique to identify the wt% of the sample. Table 4-6 summarizes all of the samples that were measured at NSLS beam line X18B. Entries 1 to 5 are vanadium samples with different wt% from different preparations. Entries 6 to 10 are vanadyl samples with different wt%. Entry 11 is the model vanadyl compound. The weight percentages of all samples are determined from gravimetric analyses.

Figure 4-48 contains three different one-dosed four-connected vanadium samples (entries 1 to 3). The weight percentage determined from gravimetric analyses is closely proportional to the edge jump. When the data for a three dose vanadium sample (entry 4 in Table 4-6) and surface vanadium (entry 5 in Table 4-6) are plotted, the R^2 value of the plot decreases to ~84% (Figure 4-49). It indicates the gravimetric analysis data of the samples with one dosed reaction are reliable and the accuracy of the gravimetric analyses for samples with multiple doses reactions is not as good as for samples with single dose reactions.

Table 4 - 6 Edge jump and wt% of different vanadyl and vanadium samples

		sample	Wt%	Edge jump (befor normalization)
1	198	embedded - VCl_4	0.81	0.029
2	204	embedded - VCl_4	1.56	0.11
3	200	embedded - VCl_4	2.58	0.182
4	216	embedded-204 + Me_2SiCl_2 + TMSCl	2.7	0.224
5	226	Me_2SiCl_2 -platform + VCl_4	7	1.427
6	212	embedded- VOCl_3	2.41	0.129
7	206	embedded- VOCl_3	3.51	0.204
8	218	embedded-212 + Me_2SiCl_2 + TMSCl	4.04	0.424
9	228	embedded-206 + Me_2SiCl_2 + TMSCl	5.6	0.395
10	224	Me_2SiCl_2 -platform + VOCl_3	7.19	1.545
11	220	VOCl_3 model compound $\text{VOCl}_3 + 3 \text{HOSiOR}_3 + \text{Py}$	5.95	2.383

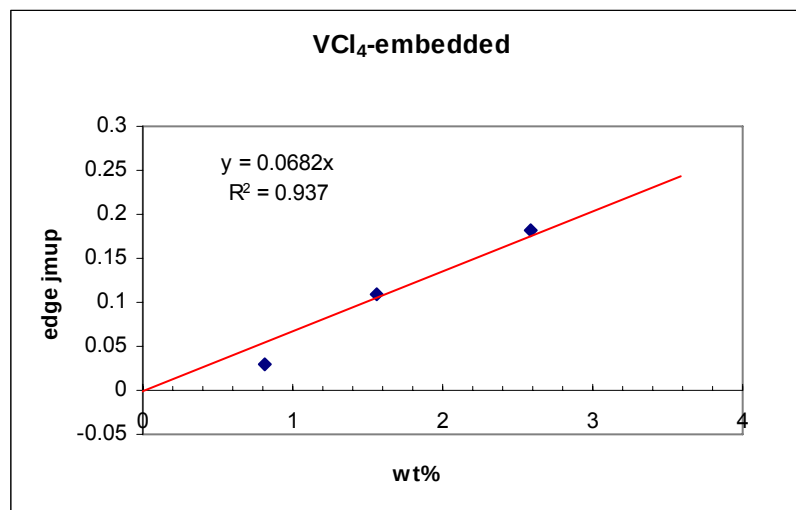


Figure 4 - 48 edge jumps vs. wt% of three embedded vanadium (+4) samples

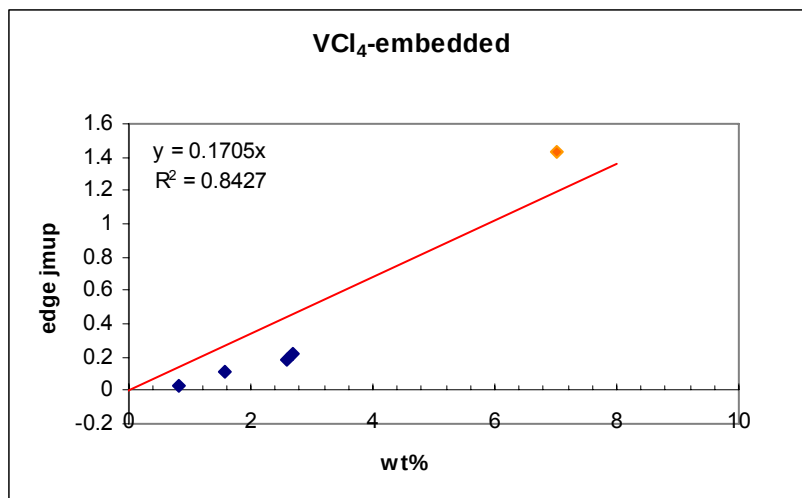


Figure 4 - 49 edge jumps vs. wt% of all embedded vanadium (+4) samples

Similar results are observed in vanadyl samples. Figure 4-50 shows two data points from one dosed vanadyl reaction. Figure 4-51 shows all of the data points including different doses vanadyl samples and the model compound. The edge jump of the surface vanadyl sample (green spot) and the model compound (orange spot) are not quite proportional to the number of the wt% because the surface vanadyl sample is synthesized from a silicate platform with a higher error of wt% determination and the composition of the model compound (orange point) is not like other vanadyl or vanadium samples which contain much more silicon.

If different one-dosed vanadium samples with different oxidation state are chosen in the edge jump-wt% plot, the result shows wt% is still proportional to the edge jump (green spots are from vanadyl samples and blue spots are from vanadium samples, Figure 4-52). It indicates the gravimetric analyses of one-dosed reactions are more accurate and different oxidation states of the vanadium samples do not affect the edge jump.

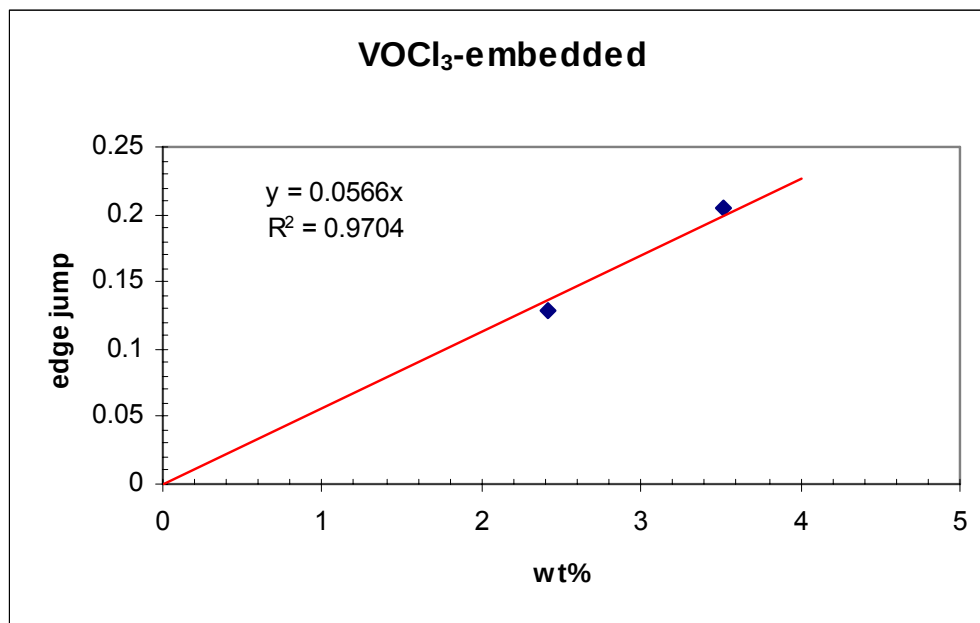


Figure 4 - 50 edge jumps vs. wt% of two one-dosed embedded vanadyl samples

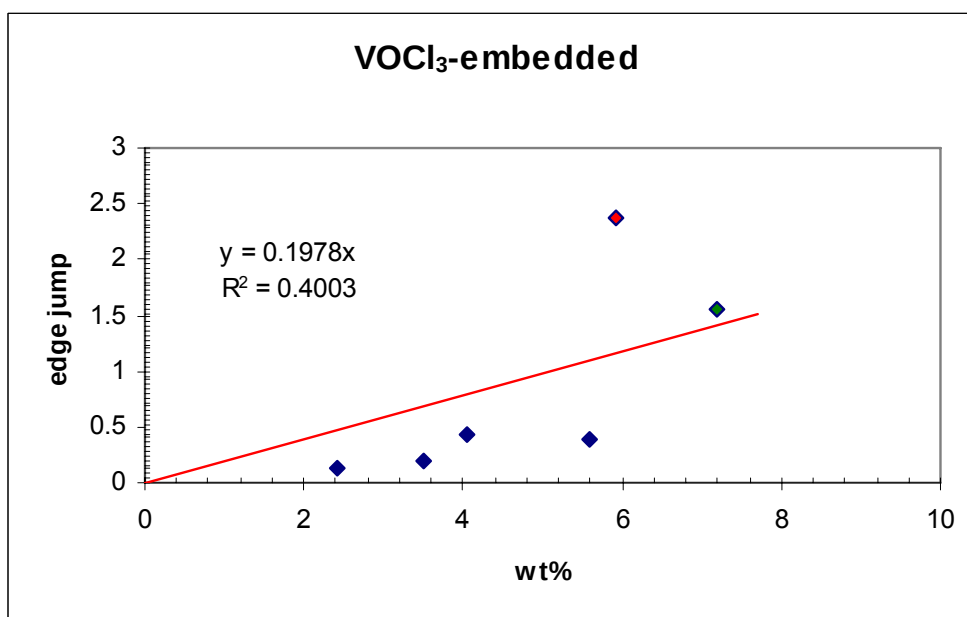


Figure 4 - 51 edge jumps vs. wt% of all embedded vanadyl samples

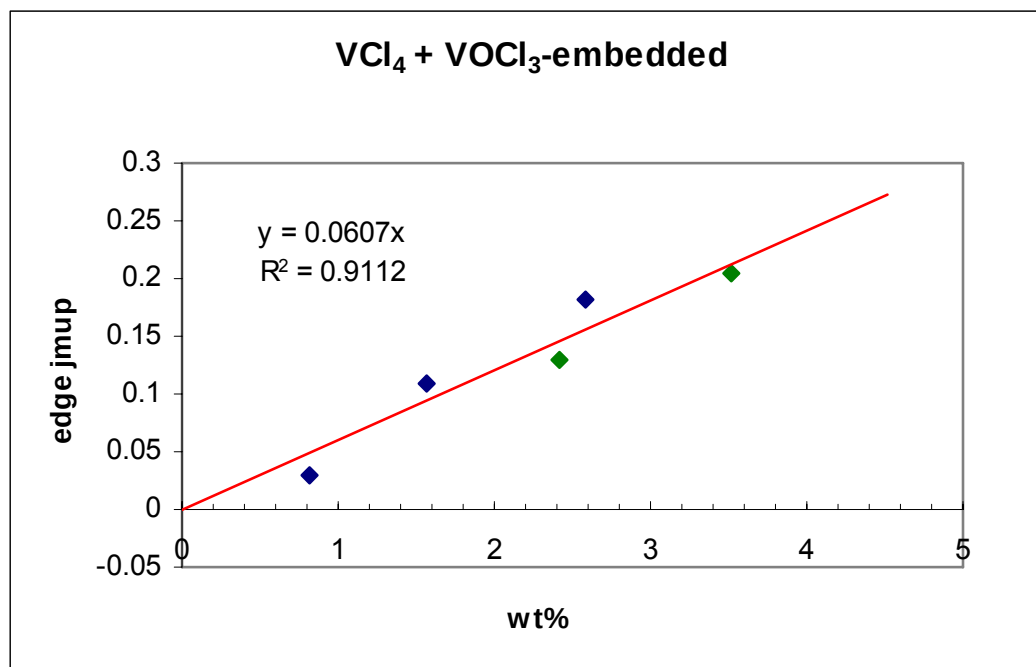


Figure 4 - 52 edge jumps vs. wt% of one-dosed embedded vanadyl and vanadium (+4) samples

To conclude the measurement from two different beam lines, the beam line X19A with a focused beam provides better data for low weight percentage vanadium samples with a Germanium detector. But some of the samples changed color after exposing the samples under the focused beam for a long time. If the sample is too concentrated, it has to be diluted with BN to obtained better signals. The beam line X18B is an unfocused beam and it provides better spectra for high weight percentage vanadium samples with a PIPS detector. When the wt% is lower than 3%, the noise is larger and the quality of k-space spectra is not good at high k range.

4.4 Conclusions

The results of a XANES and EXAFS analysis of vanadium (+4) and vanadyl (+5) containing building block matrixes are described. The surface vanadium (+4) sample provides a XANES spectrum with a low pre-edge feature which is different from other vanadyl or vanadium (+4) samples. It indicates the vanadium (+4) environment in the surface sample with three chloride ligands should have a higher symmetry structure and weakened $1s \rightarrow 3d$ transitions. A higher intensity pre-edge peak superimposed on the absorption edge at approximately 5479 eV is another feature of both surface vanadyl and vanadium samples which correlates with the number of chloride ligands coordinated to the vanadyl or vanadium centers.

In EXAFS spectra, the results from all of the data analysis using theoretical phase and amplitude functions generated from FEFF6L are consistent with the other indirect lines of experimental evidence that had been collected for these samples. For an embedded vanadyl sample, no evidence of a V-Cl feature has been observed in the spectra and the coordination number of V-O single bonds is three. For an embedded vanadium (+4) sample, only one peak which represents V-O single bonds with a four-coordinate number is observed in the EXAFS spectra. For surface vanadyl and vanadium (+4) samples, a V-Cl feature with two- and three-coordinate number respectively have been obtained after the data analysis.

Chapter 5

Highly selective catalytic reaction of Vanadium-Si₈O₂₀ catalysts

5.1 Introduction

Catalysis is a multidisciplinary area of chemistry and plays a key role on many useful chemical transformations. In a chemical reaction, reactants interact with one another to create products. A catalyst for a chemical reaction may not, by definition, be consumed during the reaction but converts reactants to the products through a pathway with lower activation energy. New chemical bonds frequently are formed during a catalyzed reaction. A key step in many catalyzed reactions is the binding of a reactant which is transformed into product and then released. A simple illustration of catalytic cycle is shown in Figure 5-1.

For heterogeneous catalysis^{51, 52}, most of the intermediates involved in a cycle are difficult to detect because of their high reactivity. This challenge can be compounded when multiple catalytic sites are present in a system. Single-site

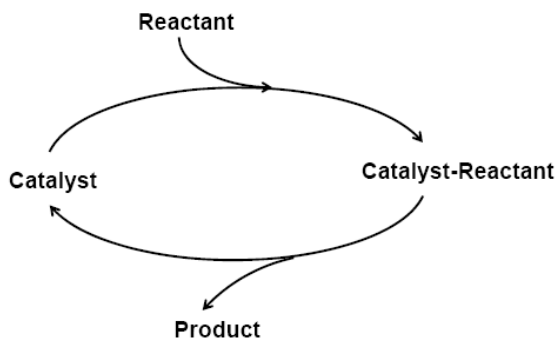


Figure 5 - 1 Catalytic cycle

heterogeneous catalysts synthesized from a building block methodology we have developed may potentially provide clearer catalytic information than traditional catalysts especially for determining reaction mechanisms.⁵³⁻⁵⁶ From our investigations, atomically dispersed and site-isolated vanadyl and vanadium sites in Si_8O_{20} -based building block solids have been synthesized successfully and described in previous chapters. The ultimate goal of this research is to relate the “nano structuring” of these catalytic sites to their activity and selectivity.

A gas phase catalysis micro-reactor was built by Richard Mayes which consisted of five mass flow controllers (MFCs), two multi-port switching valves, a computer controlled gas chromatograph, residual gas analyzer (0-300 amu quadrupole mass spectrometer), hydrogen generator, and split-tube furnace (Figure 5-2). Several different protocols for using the micro-reactor were tested in order to understand how to operate this newly built system efficiently and correctly.

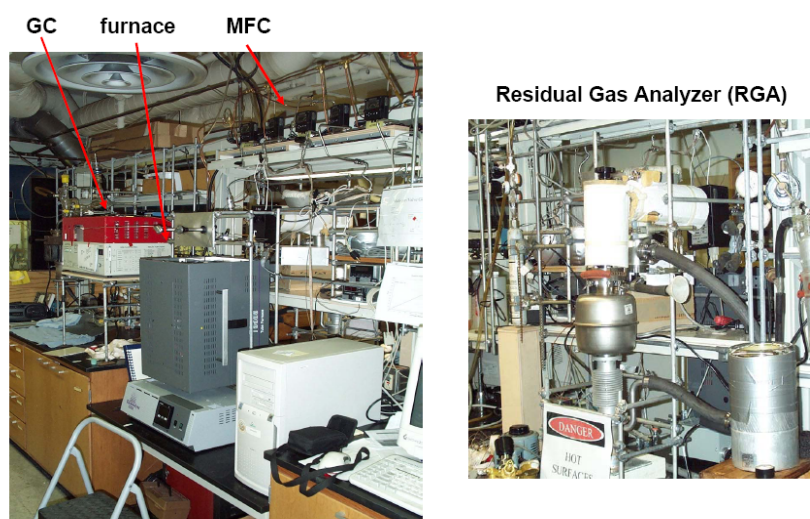


Figure 5 – 2 Micro-reactor

In this project, we did a quick survey to determine whether the vanadyl and vanadium materials were good catalysts for a series of well known reactions described in the literature. Zhao et al. reported that lightly dispersed isolated silica-supported vanadia based catalysts are less reducible and are selective for acid catalyzed catalysis.⁵⁷ The basicity or acidity characteristics of the catalyst are the major factors that control the catalytic reactivity. The conversion of isopropanol to acetone or propene is a common method to test the acid-base properties of such catalysts.^{58, 59} The samples we prepared contain low loading vanadyl (+5) or vanadium (+4). The preliminary results indicate these materials have reasonable activity and are highly selective from the production of propene from isopropanol.

5.2 Experimental

5.2.1 Sample preparation

Six different vanadyl and vanadium samples were tested. In order to avoid complicating reactions due to residual trimethyl tin groups in the samples (tin oxide is also a well known heterogeneous catalyst), all of the embedded samples investigated were treated with TMSCl to remove any residual trimethyltin groups. MYL-II-144 is an embedded vanadium (+4) sample which was prepared from a ratio of 0.71 VCl_4 to 1 tin cube followed by adding SiCl_4 and TMSCl as the second and third dose reagents. MYL-II-146 is an embedded vanadyl sample which was synthesized from a ratio of 1 VOCl_3 to 1 tin cube

followed by SiCl_4 as the second dose reagent and TMSCl as the third dose reagent. MYL-II-164 is a surface vanadium (+4) sample which was synthesized by adding excess VCl_4 to a silicate platform containing SiMe_2 linking groups. MYL-II-216 is an embedded vanadium (+4) sample which was synthesized from a ratio of 0.48 VCl_4 to 1 tin cube followed by adding Me_2SiCl_2 and TMSCl reagents in the second and third dose reactions. MYL-II-228 is an embedded vanadyl sample which is prepared from a ratio of 1 VOCl_3 to 1 tin cube followed by adding Me_2SiCl_2 and TMSCl . MYL-II-218 is also an embedded vanadyl sample which is prepared from a ratio of 0.73 VOCl_3 and 1 tin cube reaction followed by adding Me_2SiCl_2 and TMSCl . Details concerning synthetic procedures for preparing these samples are described in chapter 3. Only one surface catalyst was chosen in this investigation because surface samples contain more chloride ligands and a significant amount of HCl is generated at the beginning of the catalytic reaction. To begin to understand how to operate micro-reactor and GC correctly, embedded samples were tested first. Therefore the survey in this project mostly focuses on embedded vanadyl and vanadium samples. The sample list and sample abbreviations are summarized in Table 5-1.

5.2.2 Instrumentation

The gas chromatograph (GC) used in these investigations is “SRI GC Model 8620 Multiple Gas Analyzer”. The GC is equipped with 3 columns (6 m 13x Mol. Sieve and 3 m Hayesep-D packed columns, 30 m MXT-1 capillary column) and 3 detectors (Thermal conductivity detector (TCD), helium ionization

Table 5 - 1 Sample list and abbreviation

sample	type	First dose vanadium : tin cube ratio	Vana dium wt%	Second dose reagent	Thesis abbreviation
MYL-II-164	Surface V(+4)	Me ₂ SiCl ₂ silicate platform	NA	VCl ₄	V4-surf
MYL-II-144	Embedded V (+4)	0.71 VCl ₄ : 1 tin cube	2.9	SiCl ₄	V4A-emb
MYL-II-216	Embedded V (+4)	0.50 VCl ₄ : 1 tin cube	2.7	Me ₂ SiCl ₂	V4B-emb
MYL-II-146	Embedded V(+5)	1 VOCl ₃ : 1 tin cube	3.8	SiCl ₄	V5A-emb
MYL-II-218	Embedded V(+5)	0.73 VOCl ₃ : 1 tin cube	4.0	Me ₂ SiCl ₂	V5B-emb
MYL-II-228	Embedded V(+5)	0.99 VOCl ₃ : 1 tin cube	5.6	Me ₂ SiCl ₂	V5C-emb

detector (HID), and flame ionization detector (FID)). Herein, we report the data collected from the FID detector because we obtained the best signal to noise ratio from this detector. The FID detector is a destructive detector that burns substrates in a hydrogen-air flame.

A 0-50 cc/min helium mass flow controller (MFC) is dedicated to the gas saturators. A 0-100 cc/min helium MFC regulates the make up gas to the micro-reactor. A 6-port switching valve diverts the gas flow in the micro-reactor from bypass mode to reactor mode. Make-up helium is provided to the reaction tube when the catalyst is not exposed to the substrate gas. A 4-port switching valve is used to divert the product stream from the RGA to the GC.

Catalyst samples were put in a pyrex U-tube sandwiched between plugs of quartz wool.

5.3 Result and Discussion

5.3.1 Weight Hourly Space Velocity (WHSV)

Catalysts are often investigated in continuously operated test reactors. The space velocity is defined as the volumetric flow rate V_o , relative to the catalyst mass, m_{cat} . (Eq 1)

$$\text{Space velocity} = \frac{V_o}{m_{cat}} \dots\dots (1)$$

Liquid hourly space velocity (LHSV) and weight hourly space velocity (WHSV) are most commonly used terms to represent the space velocity. Herein, all of our reactions were gas phase reactions. Thus, we only use weight hourly space velocities with units of per hour on stream relative to one gram catalyst to describe our reactions. In order to determine the volumetric flow rate V_o , the partial pressure of the reactant and the moles of the reactant (isopropanol) need to be calculated first.

The equation of partial pressure (P_{iPrOH}) is shown in eq 2 where P_{iPrOH} = torr, t = °C, A = 8.11778, B = 1580.92, C = 219.61 for isopropanol.

$$\log P_{iPrOH} = A - \frac{B}{t + C} \dots\dots (2)$$

The moles of isopropanol in 1cc/min flow rate (0.001 L/min) is shown in equation 3 with the unit of “mol/min” where n = moles of isopropanol in 1 cc/min flow, P_{iPrOH} = partial pressure of isopropanol in atmosphere, R = gas constant (0.0820574 L·atm/mol·k), and T = temperature in Kelvin

$$n = \frac{P \times 0.001}{R \times T} \dots\dots (3)$$

Total volumetric flow rate V_0 in the reactor is shown in Eq 4 with units of “mol/min” where V_0 = moles of isopropanol per total isopropanol flow, n = moles of isopropanol in 1 cc/min flow, F_{sat} = flow of isopropanol through the saturator. The total mass of the isopropanol, m_{iPrOH} is equal to $V_0 \times m.w$ where $m.w$ represents the molecular weight of isopropanol.

$$m_{iPrOH} = V_0 \times m.w = n F_{sat} \times m.w \dots\dots (4)$$

The final WHSV equation is shown in Eq 5 with the unit of “hr⁻¹”

$$WHSV = \frac{m_{iPrOH} \times 60 \text{ min/hr}}{m_{cat}} \dots\dots (5)$$

For example, assuming 3 cc/min of isopropanol flow through the saturator at 26°C mixed with a 95 cc/min of helium flow over 50 mg catalyst, the calculation of WHSV will be as follows.

$$\log P_{i\text{PrOH}} (26^{\circ}\text{C}) = 8.11778 - (1580.92/(26+219.61)) = 1.681$$

$$P_{i\text{PrOH}} (26^{\circ}\text{C}) = 10^{1.681} \text{ torr} = 47.97 \text{ torr} = (47.97 / 760) \text{ atm} = 0.0631 \text{ atm}$$

$$n = 0.0631 \times 0.001 / (0.082 \times (26+273)) = 2.57 \times 10^{-6} \text{ mol/min}$$

$$V_o = 2.57 \times 10^{-6} \text{ mol/min} \times (3) = 7.71 \times 10^{-6} \text{ mol/min}$$

$$m_{i\text{PrOH}} = 7.71 \times 10^{-6} \text{ mol/min} \times 60 \text{ g/mol} = 4.63 \times 10^{-4} \text{ g/min}$$

$$\text{WHSV} = 4.63 \times 10^{-4} \times 60 / 0.05 = 5.55 \times 10^{-1} \text{ hr}^{-1}$$

The WHSV for six samples are summarized in Table 5-2

5.3.2 Response factor

The FID detector responds to many different compounds with differing levels of sensitivity. A correction factor called a “response factor” is normally

Table 5 - 2 WHSV of different vanadyl and vanadium samples

Thesis abbreviation	sample	Isopropanol Flow rate (cc/min)	Weight (gram)	Vanadium wt%	WHSV (hr ⁻¹)
V4-surf	MYL-II-164	3	20	NA	1.39
V4A-emb	MYL-II-144	3	40	2.9	6.94 x 10 ⁻¹
V4B-emb	MYL-II-216	3	50	2.7	5.55 x 10 ⁻¹
V5A-emb	MYL-II-146	3	40	3.8	6.94 x 10 ⁻¹
V5B-emb	MYL-II-218	3	50	4.0	5.55 x 10 ⁻¹
V5C-emb	MYL-II-228	3	50	5.6	5.55 x 10 ⁻¹

used to transform raw peak integrations from the detector to absolute or relative mole equivalents for each species. Two common response factor formats are “response factor multiplier” and “relative response factor”

The response factor multiplier is equal to “actual concentration divided by measured response. Using this method one needs to know the actual concentration of the compound of interest before calculating the response factor. For example, if a 50 ppm compound produces a 20 ppm FID reading on an analyzer calibrated with methane, then the FID response factor for that compound would be 2.5 (50 / 20).

The relative response factor is expressed as a percent or a ratio of a compound’s response to that of a calibration gas. In our investigations, we used the relative response factor to obtain conversion percentages. The reactant in our catalytic system is isopropanol and the major product is propene. The calculation of relative response factor between isopropanol and propene is described below.

The GC provides the integrated area for each peak which is proportional to the actual moles of compound as shown in equation 6 where r is a constant factor.

$$\text{Actual mole} = \text{Area number from GC} \times r \dots (6)$$

If only one reactant and one product are observed in the reaction, the relative areas of the unreacted reactant and product recorded by in the GC are

proportional to A% and (100-A)%. The mole % can be represented in Equations 7 and 8 where r_1 and r_2 are constant factors.

$$\text{Unreacted reactant} = A\% \quad \text{product} = (100-A)\%$$

$$\text{Mole \% of unreacted reactant} = A\% \times r_1 \dots (7)$$

$$\text{Mole \% of product} = (100-A)\% \times r_2 \dots (8)$$

$$(\text{mole\% of unreacted reactant} + \text{mole\% of product} = 100\%)$$

Assuming the response factor for the reactant is 1, the relative response factor for the product is RF (or $r_1 : r_2 = 1 : \text{RF}$). Equations 7 and 8 can be rewritten as equations 9 and 10 and the actual mole ratio of unreacted reactant to product obtained.

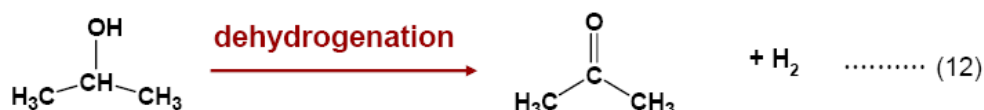
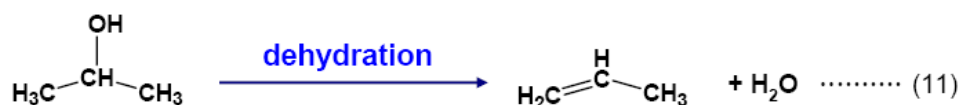
$$\text{Mole \% of unreacted reactant} = (A\% \times 1) / [A \times 1 + (100-A) \times \text{RF}] \dots (9)$$

$$\text{Mole \% of propene} = (100-A)\% \times \text{RF} / [A \times 1 + (100-A) \times \text{RF}] \dots (10)$$

5.3.3 Reactivity studies of isopropanol with vanadyl and vanadium building block catalysts

The reaction chosen to investigate the catalytic activities of our surface and embedded vanadium (IV and V) catalysts was the high temperature decomposition of isopropanol to propene and acetone. This reaction has been studied by many other groups in the context of both solid acid and oxidation

chemistry. The two major products that are usually observed are propene via acid-catalyzed dehydration and acetone from the oxidative dehydrogenation of isopropanol. These two reactions are illustrated in Equations 11 and 12.



In our investigations of the isopropanol conversion with vanadyl and vanadium catalysts, propene is the major product observed from the dehydration reaction and acetone is a minor product produced from an oxidative dehydrogenation reaction. Another peak (total <1%) appearing when the catalytic reaction is run at high temperature (>300°C) may be isopropyl ether. This product has not been conclusively identified. The following discussion will include the descriptions of control experiment studies, selectivity, and activity with different catalysts.

5.3.3-1 Control samples: Building block matrices containing only silicon

A vanadium free silicon building block matrix with a small amount of residual trimethyltin groups, (Me₂SiCl₂ silicate platform) and a separate sample of

TMS cube, $((\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20})$, were tested as control samples to determine if the support was active in the decomposition of isopropanol. For TMS cube, over a temperature range of 100°C to 350°C (Table 5-3), only the starting material was observed with a constant area of integration. The silicon building block matrix with a small amount of trimethyltin groups also shows no activity at temperatures lower than 300°C. Trace amounts of unknown decomposition products are observed when the temperature is ramped to 350°C or higher. (Figure 5-3) These results indicate that the tin free silicate material without any metal in the matrix has no activity in the dehydration reaction when the temperature is lower than 350°C.

Table 5 - 3 Area number vs. Temp for TMS-cube and Me_2SiCl_2 platform

Temperature (oC)	TMS-cube		Me ₂ SiCl ₂ platform (with some trimethyl tin groups: 7 wt% Sn)	
	Isopropanol	others	isopropanol	others
100	17596	0	NA	NA
150	16859	0	18927	0
200	18070	0	18712	0
250	17991	0	18889	0
300	18294	0	18938	0
350	18421	0	17438	~300
400	18938	267	16681	~1500

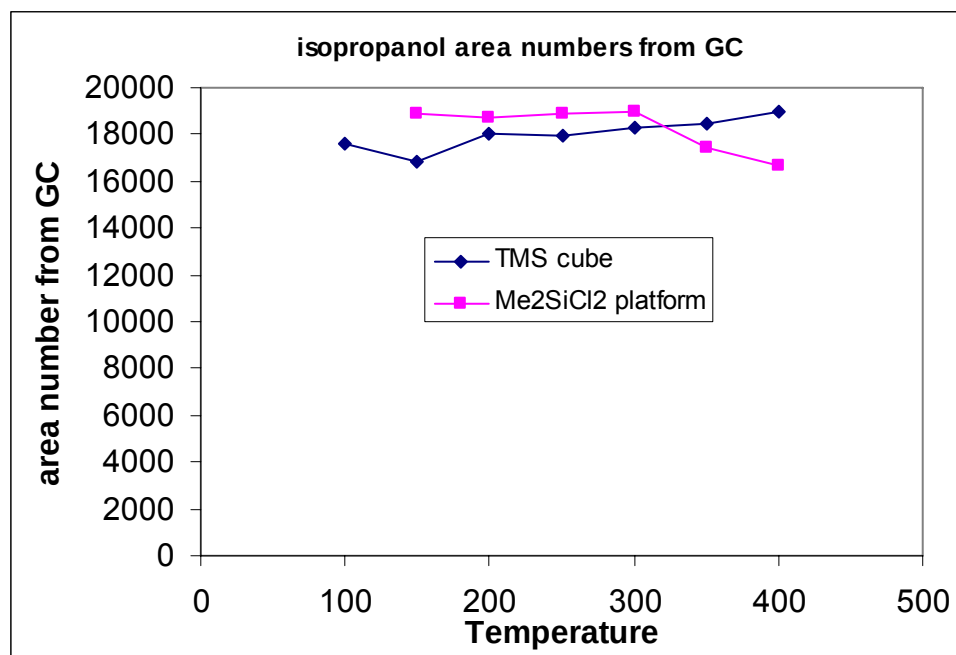


Figure 5 - 3 area number vs. Temp for TMS-cube

5.3.3-2 Selectivity

The selectivity of a reaction is the fraction of the reactant that is converted to the desired product relative to other unwanted byproduct. Two general reaction profiles that explain multiple products are parallel and sequential reactions (Figure 5-4).

Before starting the catalytic reaction, the embedded catalyst was treated in situ with isopropanol flowing at 3 cc/min helium through isopropanol and with 95 cc/min helium for 20 minutes because a small amount of chloride ligands still remain in the SiCl_4 or Me_2SiCl_2 derived linkers from the second dose reaction when the samples were prepared. The surface sample was treated with same flow rate for 40 minutes at room temperature in order to remove all of the chloride ligands from ≡Si-O-VCℓ_3 groups and convert them to alkoxy groups.

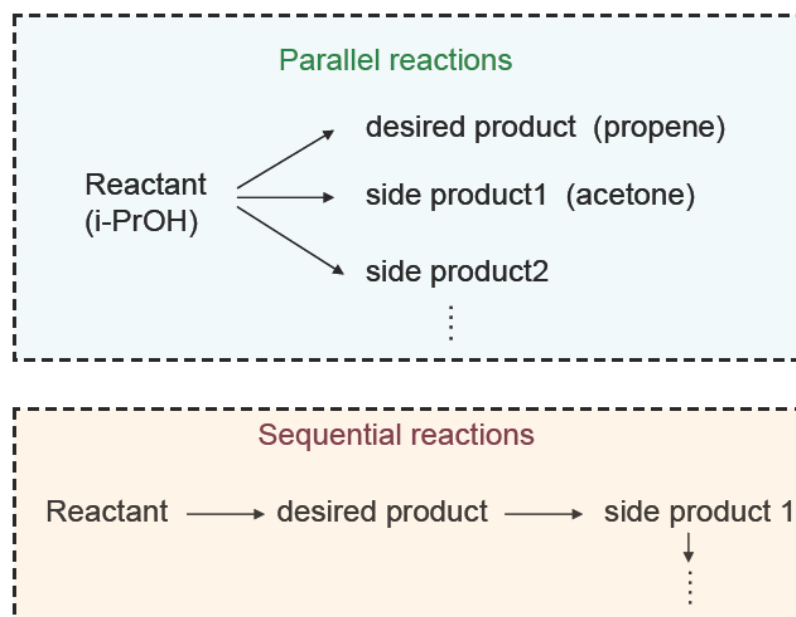


Figure 5 - 4 Two types of reactions

The preliminary results from different catalytic reaction for the using six different vanadyl and vanadium catalysts all show propene is the major product and the amount of acetone is less than 4% for the "V4-surf" surface sample and less than 2% for other five embedded samples. Both vanadium (oxidation state +4) and vanadyl (oxidation state +5) samples that have been studied exhibit almost exclusive dehydration chemistry when the reaction temperature is lower than 350°C. Therefore we conclude these atomically dispersed vanadyl and vanadium materials are solid acid catalysts.⁶⁰⁻⁶³

5.3.3-3 V4-surf catalyst and response factor discussion

When “V4-surf” (MYL-II-164) is used as the catalyst, isopropanol is converted in high yield to propene (> 95 %) and a small amount of acetone (< 3.8 %) at low temperature (~ 300°C). Because the reaction cleanly converts isopropanol to propene the area numbers from GC which represent reactant and product can be used to calculate an approximate relative response factor for these two compounds. The area numbers and ratios obtained from GC are summarized in Table 5-4.

The area number for 125°C is out of the range because the sample was not injected into the GC correctly. Therefore this data point was not used in the calculation of relative response factor. The relation between area number and ratio % of isopropanol and propene is shown in Figure 5-5.

The equation derived from Figure 5-5 for isopropanol is $y = 95.378x + 10642$. The intercept of y axis is 10642 when the ratio of propene is 0% and is 20179 when the ratio of propene is 100%. The relative response factor is derived as $20179.8/10642 = 1.896 \approx 1.9$. The linear relation between isopropanol and propene indicates that we can use the relative response factor method to obtain the relative amount of isopropanol and propene at any temperature and conversion. The conversion percentages after correcting the GC integrations with the relative response factor of 1.9 are calculated from equation 11 and 12 summarized in Table 5-5 and Figure 5-6.

$$\text{Mole \% of unreacted reactant} = A\% / (190 - 0.9 A) \dots (11)$$

$$\text{Mole \% of propene} = (190 - 1.9A)\% / (190 - 0.9A) \dots (12)$$

Table 5 – 4 Area number from GC (sample: V4-surf)

Temperature (°C)	Area i-PrOH	i-PrOH (%)	Area propene	propene (%)	Area acetone	Acetone (%)	Area (total)
105	19368	100.0	0	0.0	0	0	19368
125	27086	99.6	107	0.4	0	0	27193
175	18757	97.3	520	2.7	0	0	19277
180	19459	97.6	481	2.4	0	0	19939
210	16181	83.0	3311	17.0	0	0	19492
240	6104	42.0	8243	56.7	185	0	14532
270	320	3.0	9966	93.8	342	3.2	10628
300	92	0.9	10225	95.7	365	3.4	10682
330	53	0.5	9756	94.8	395	3.8	10289
300	822	7.5	9867	89.4	345	3.1	11034
270	5240	35.9	9119	62.5	240	1.6	14599
240	12863	67.6	6160	32.4	0	0	19023
210	17418	90.2	1882	9.8	0	0	19301
180	18719	97.7	439	2.3	0	0	19158

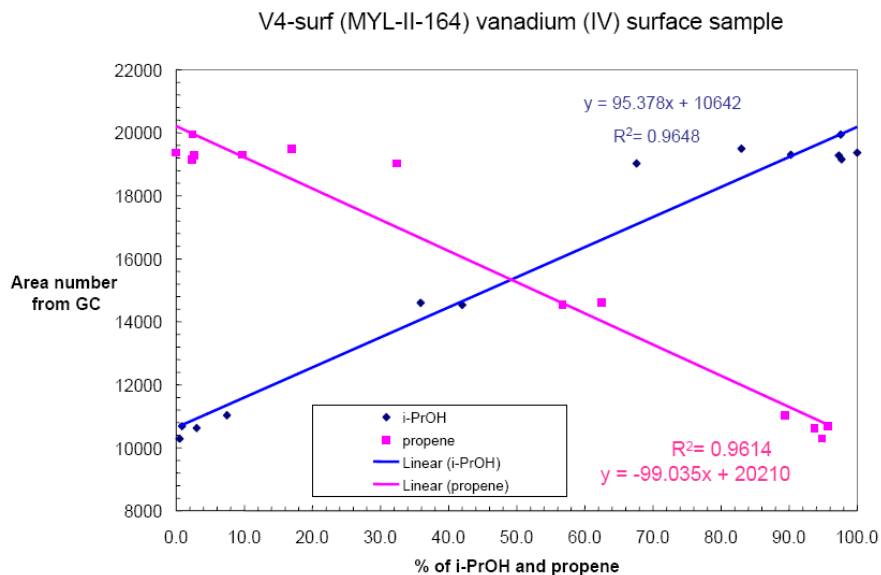


Figure 5 - 5 Area number vs. conversion %

Table 5 - 5 Conversion % before and after RF

	Before RF		After RF	
Temperature (°C)	Ratio of i-PrOH (%)	Ratio of propene (%)	Ratio of i-PrOH (%)	Ratio of propene (%)
105	100.0	0.0	100.0	0.0
125	99.6	0.4	99.3	0.7
175	97.3	2.7	95.0	5.0
180	97.6	2.4	95.5	4.5
210	83.0	17.0	72.0	28.0
240	42.0	56.7	28.0	72.0
270	3.0	93.8	1.7	98.3
300	0.9	95.7	0.5	99.5
330	0.5	94.8	0.3	99.7
300	7.5	89.4	4.2	95.8
270	35.9	62.5	23.2	76.8
240	67.6	32.4	52.4	47.6
210	90.2	9.8	83.0	17.0

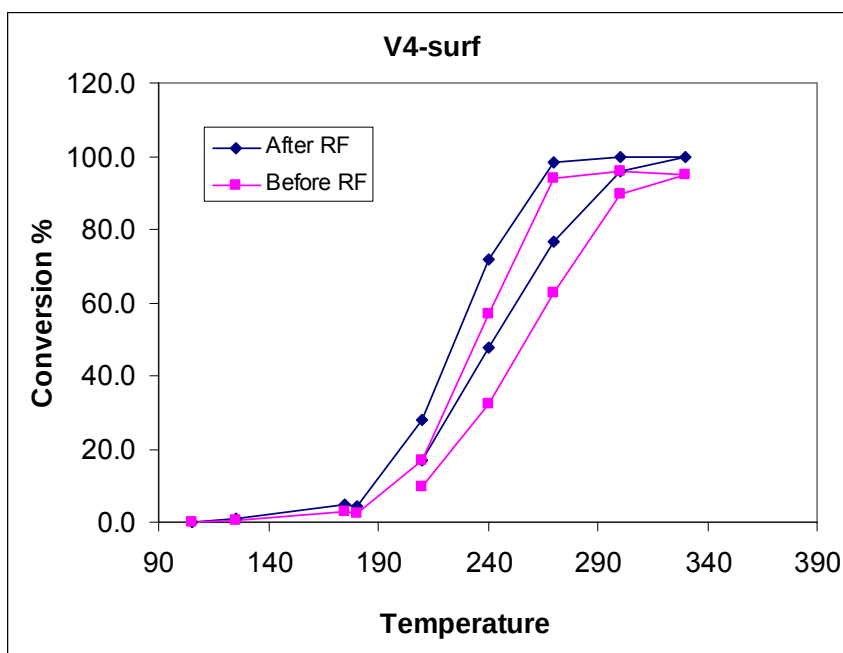


Figure 5 - 6 Calibration of isopropanol conversion of V4-surf sample

In the following discussions, all of the results from FID are calibrated by a relative response factor of 1.9.

5.3.3-4 Behavior of vanadium (+4) catalysts

The sample V4-surf (surface vanadium (+4)) provides very high conversion of isopropanol to propene. Only 20 mg catalyst were used in this reaction and a high conversion percentage at low temperature. When the temperature is approximately raised to 220°C, 50% isopropanol is converted to propene with no side products observed. When the temperature is raised to 270°C, more than 99% isopropanol is converted to propene. The plot of conversion percentage as a function of temperature is shown in Figure 5-7.

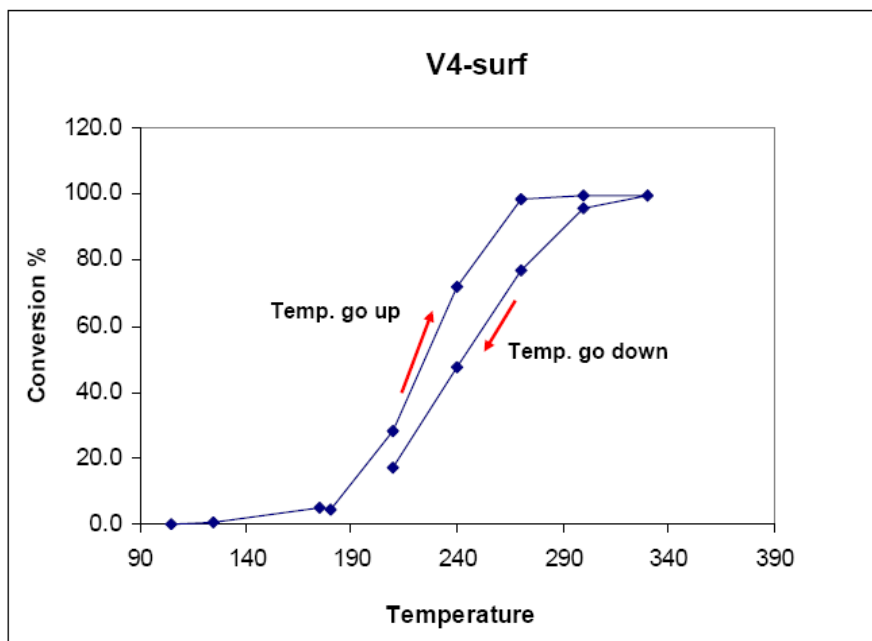


Figure 5 - 7 isopropanol conversion of V4-surf sample

Each data point was collected after the sample was maintained at the target temperature for 30 minutes.

For a 40 mg V4A-emb sample (embedded vanadium (+4)), 50% isopropanol is converted to propene at a temperature of 240°C and about 80% conversion occurs when the temperature is raised to 290°C (Figure 5-8).

For a 50 mg V4B-emb sample, 50% conversion also occurs at around 235°C and ~85% conversion occurs when the temperature was raised to 300°C (Figure 5-9). A comparison of the temperature vs. conversion curves for all vanadium (+4) samples is shown in Figure 5-10. The high conversion percentage at low temperature condition (<300°C) indicates these materials are strong solid acid catalysts for dehydration of alcohols to olefins.

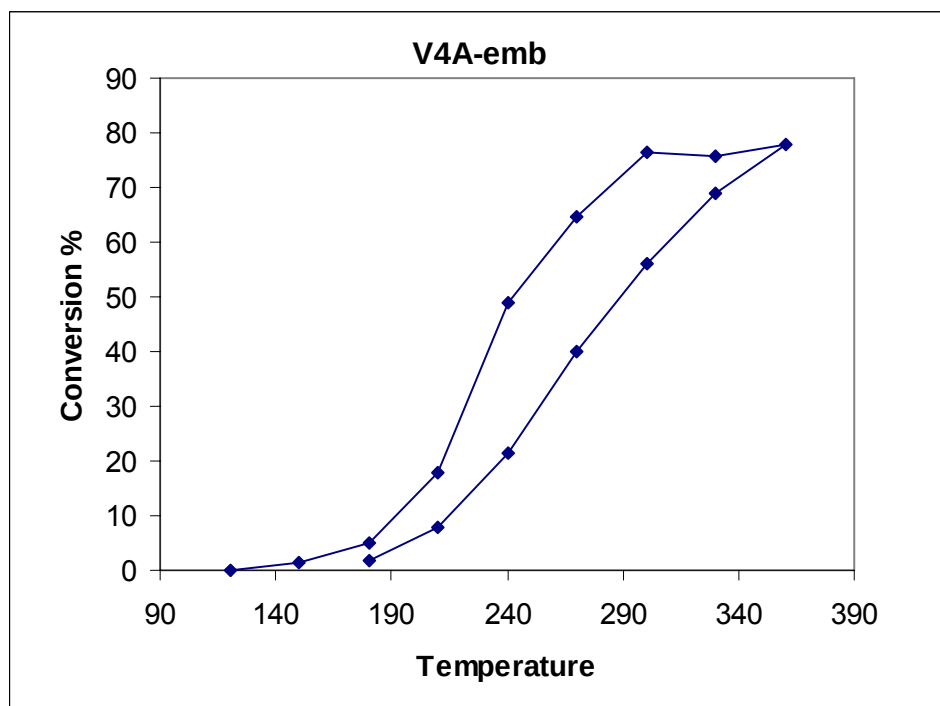


Figure 5 - 8 isopropanol conversion of V4A-emb sample

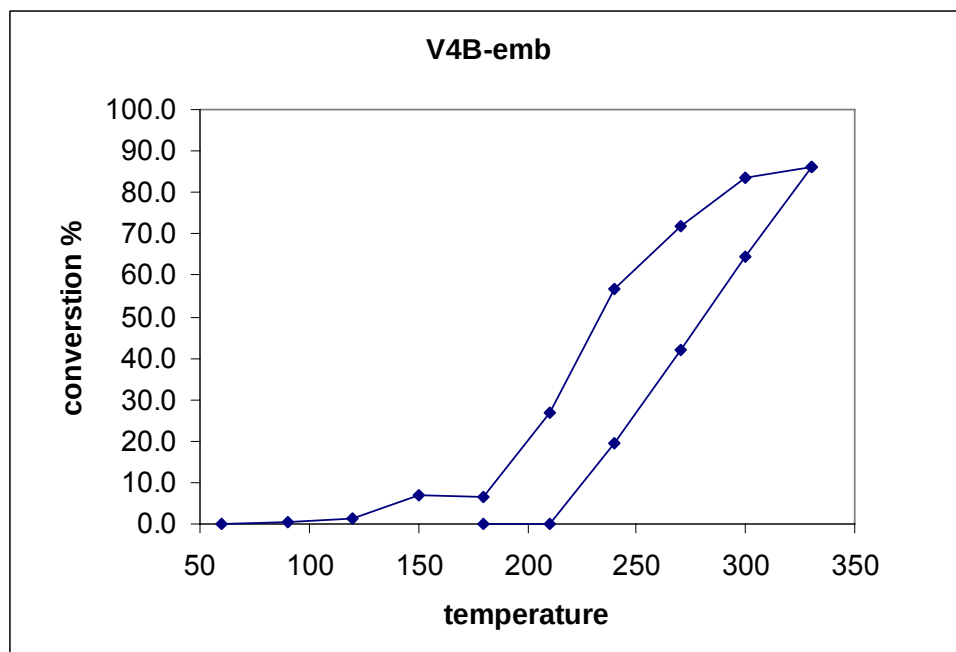


Figure 5 - 9 isopropanol conversion of V4A-emb sample

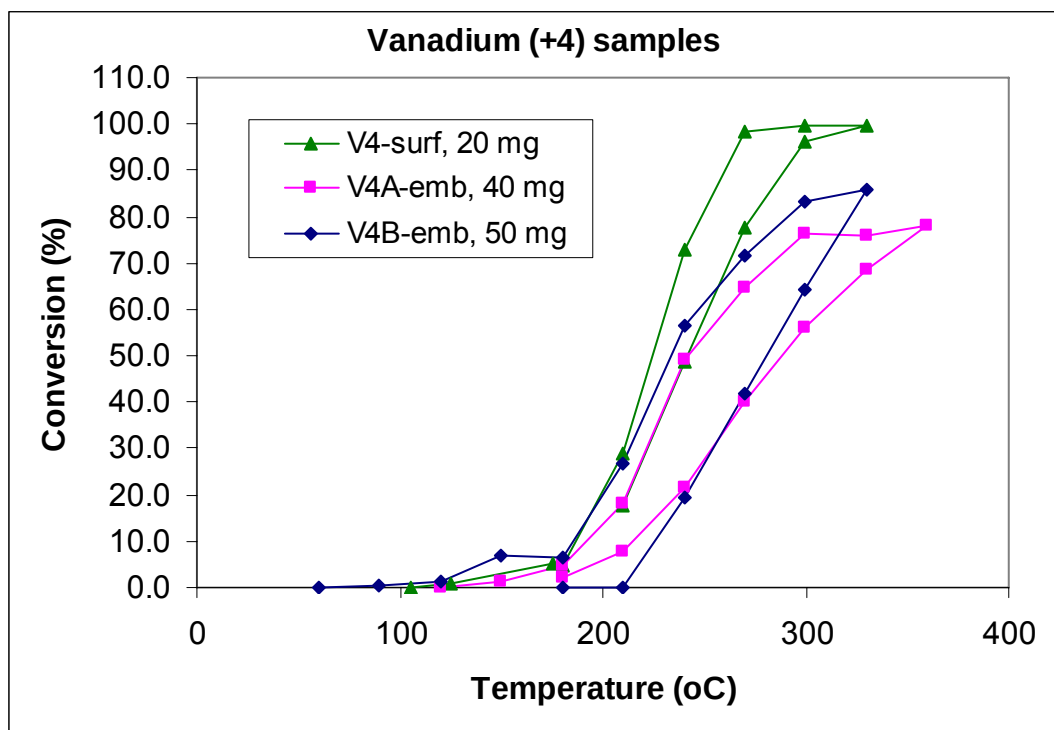


Figure 5 - 10 isopropanol conversion with all vanadium (+4) samples

In all of the temperature studies just presented, the catalyst deactivates⁶⁴ slowly and the conversion percentage drops as a function of time on stream. In order to probe the stability of our catalyst, the effect of time on stream (TOS) on conversion to propene was investigated briefly. Figure 5-11 illustrates how the activity slowly drops as TOS increased at different reaction temperatures for sample V4B-emb. When the temperature is lower than 200°C, the conversion percentage only drops about 5% in the first 30 minutes. As the temperature is increased above 250°C, the conversion percentage drops more than 10% after 30 minutes. It is important to note, however, that the activity stabilizes after isopropanol flows through the catalyst at target temperature for 30 to 60 minutes.

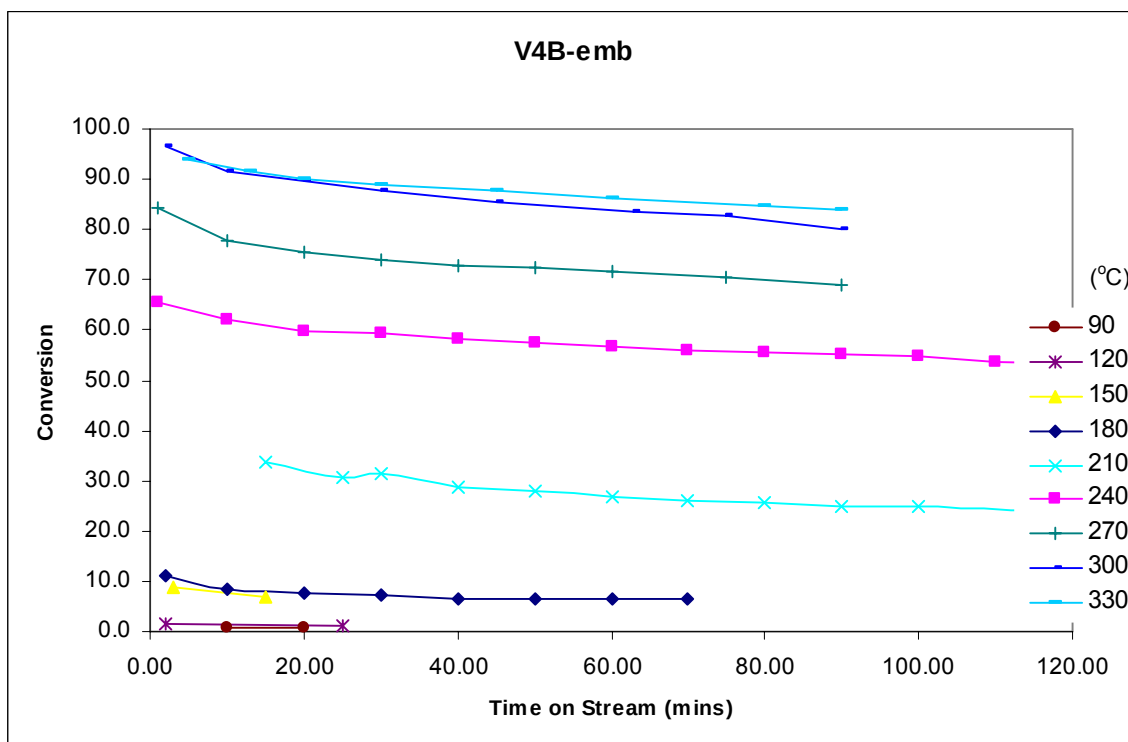


Figure 5 - 11 Effect of TOS for V4b-emb

Possible reasons of deactivation might be sites become less accessible due to annealing of the silicate support matrix and collapse of a small number of pores and / or coke formation. Another possible explanation for the initial deactivation of the catalysts is that a small amount of HCl may still reside in the matrix that is desorbed as the temperature increases. A strong acid such as HCl would facilitate dehydration reactions until it is leached from the matrix at longer times at higher temperatures. In the discussions that follow, only catalyst activities after initial deactivation will be considered.

5.3.3-5 Behavior of vanadyl catalysts

For vanadyl samples, V5A-emb produces similar results as vanadium samples. But 50% conversion occurs at higher temperature (around 290°C) than vanadium (+4) samples and the 75% conversion occurs at ~330°C (Figure 5-12). Each data point was collected after the temperature was maintained at the set point for 30 minutes.

Two temperature cycles were tested for sample V5B-emb and the results are shown in Figure 5-13. The first cycle shows the deactivation phenomena is observed. When the catalyst is kept in the furnace overnight at 90°C in a 10cc/min helium flow following by a second cycle, the activity of the catalyst is stable and its activity is essentially the same as the second leg of the temperature ramp in the first cycle.

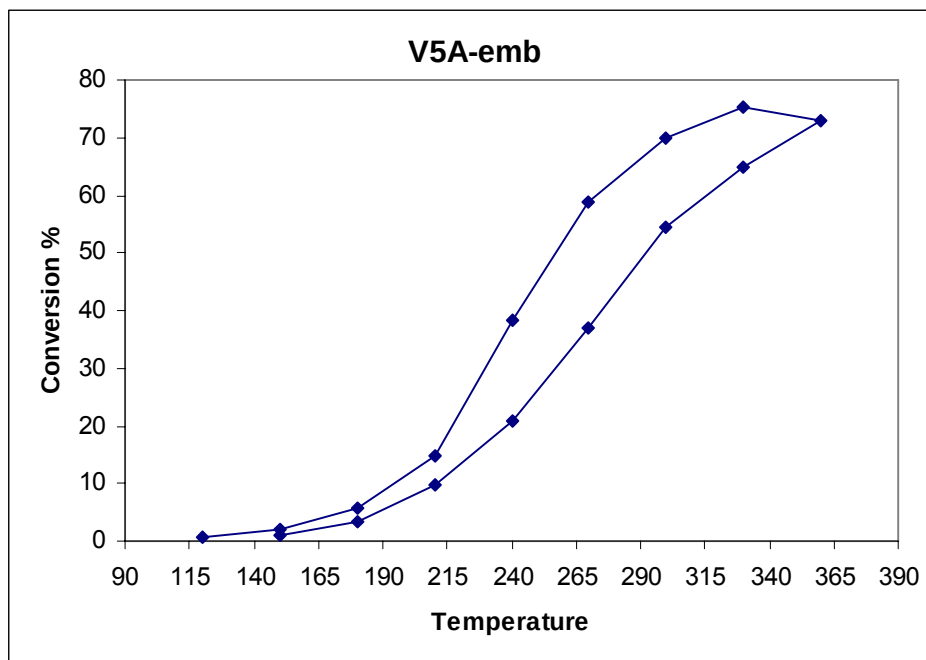


Figure 5 - 12 isopropanol conversion of V5A-emb sample

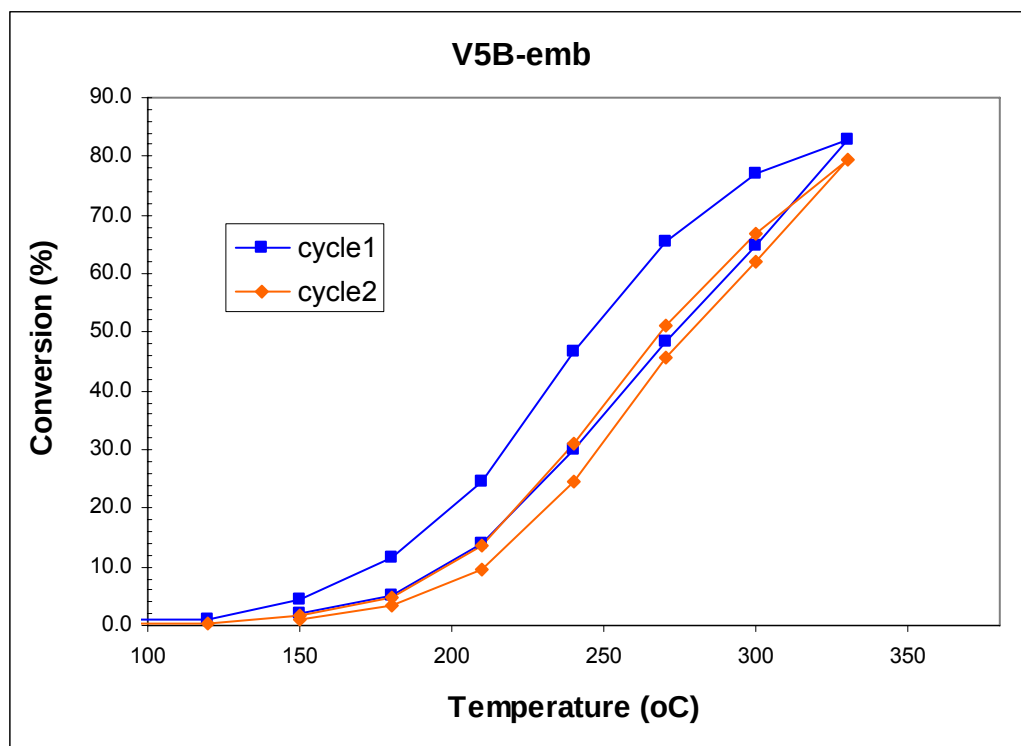


Figure 5 - 13 isopropanol conversion of V5B-emb sample

For sample V5C-emb, the effect of time on stream was also investigated in order to compare the differences between vanadium (+4) and vanadyl (+5) samples. After doing a quick survey, the effect of TOS on the embedded vanadyl sample is similar to the vanadium (+4) sample. The conversion drops about 10% in the first 30 minutes at each set temperature point then stabilizes. The protocols of collecting TOS data between the vanadium (+4) sample (Figure 5-11) and the vanadyl sample (Figure 5-14) are a little bit different. For V4B-emb sample, isopropanol was kept flowing through the catalyst all the time during the reaction before injecting the sample to GC. For V5C-emb sample, the 6-port switching valve was rotated so the substrate stream did not pass over the

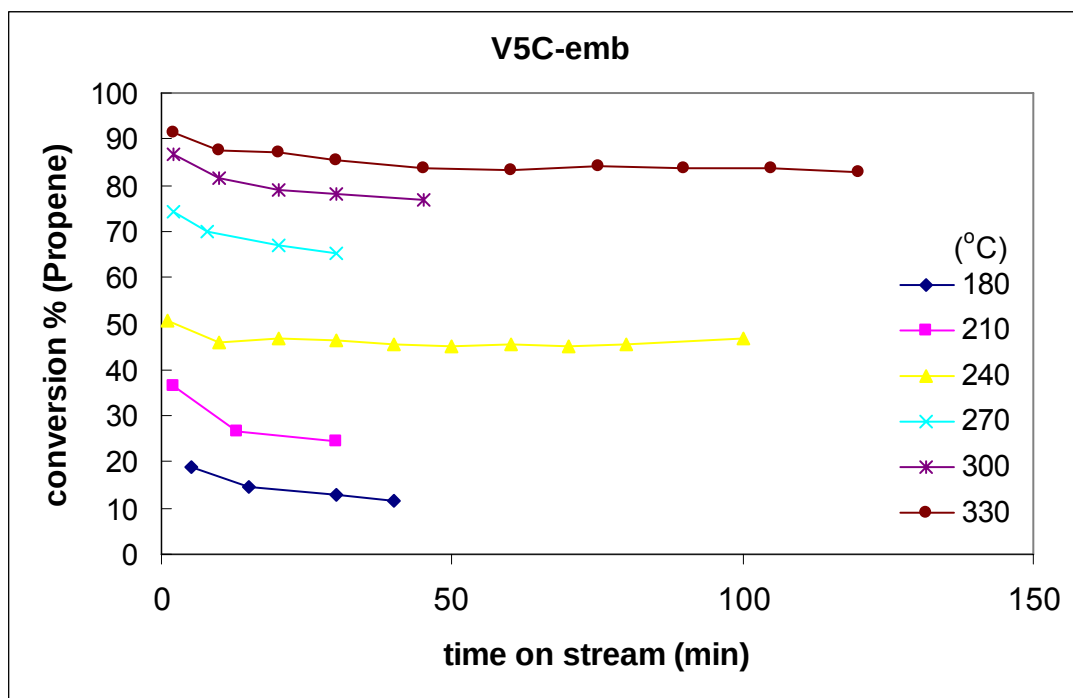


Figure 5 - 14 Effect of TOS for V5C-emb

catalyst during temperature equilibrations. The substrate, isopropanol in helium, was allowed to contact the catalysts for 2 minutes before injecting a sample into the GC and then switched back to the bypass mode. The purpose of using this protocol is to investigate whether isopropanol or the byproduct, water, binds to the catalytic sites and prohibits the reaction. The results of the TOS study show no significant change between these two protocols and the activity stabilizes after one hour. Therefore, we speculate the deactivation of each sample is not caused from the competitive binding of isopropanol or water on the catalysis sites. Further investigation of the causes of dehydration involved treating the catalyst with water at certain temperatures and observing changes in activity. For V5C-emb sample, when the temperature is ramped to 390°C, the conversion of

isopropanol drops from 87% to 82 % in the first 30 mins (Figure 5-15). After 30 minutes, 3 cc/min of helium through water was flowed into the system mixing with 3 cc/min of isopropanol (pink region in Figure 5-15) and continued for 45 minutes. The conversion did not change significantly when catalyst was exposed to additional water and alcohol simultaneously. After 45 minutes, the water was turned off and isopropanol flowed through the catalyst again and the conversion of isopropanol was still around 80~85%. The change of conversion is less than 5% when water flows through the system. This result indicates the byproduct, water, from the isopropanol dehydration does explain the catalyst deactivation that is observed.

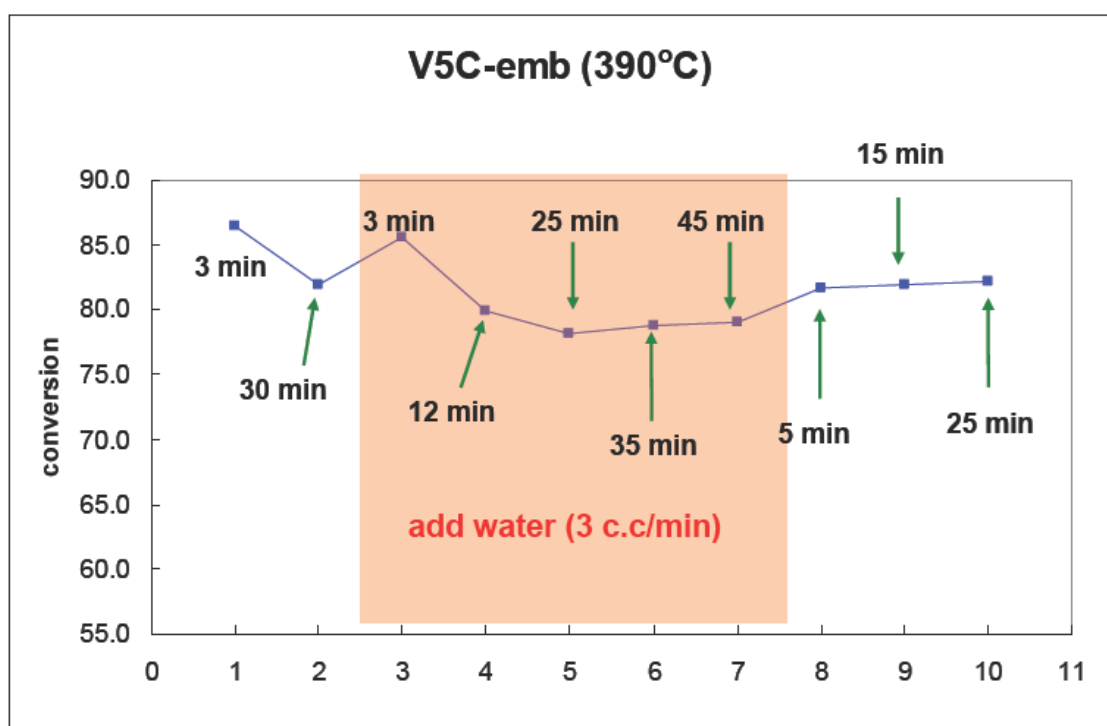
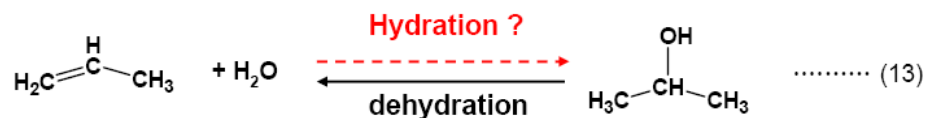


Figure 5 - 15 add water at 390°C for V5c-emb

In order to investigate whether the reaction is reversible, a mixture of 5 cc/min propene and 3 cc/min of helium through water stream were flowed over the catalyst at 390°C (Eq 13).



No isopropanol was formed under these conditions even after increasing the helium flow rate to 10 cc /min through water. This result indicates that the reaction is not reversible under these conditions.

The V5C-emb catalyst was tested for long term stability over three temperature cycles (Figure 5-16). Each cycle has 50% isopropanol conversion at around 270°C. The conversion percentages of isopropanol are similar among these cycles. This indicates the activity of the catalyst is very stable and does not decay when the reaction time increases.

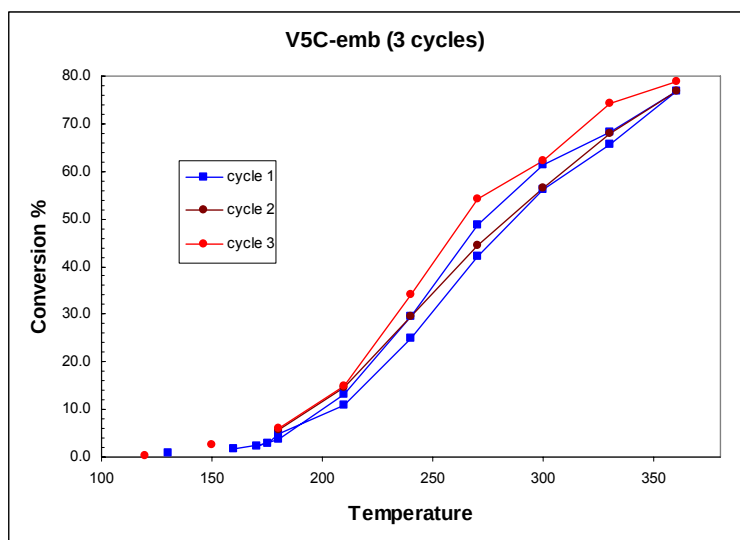


Figure 5 - 16 Three cycles of V5C-emb

A comparison of the activities of all vanadyl samples is shown in figure 5-17. Sample V5A-emb used SiCl_4 as the second dose reagent and the other two samples used Me_2SiCl_2 as the second dose reagent. All of these materials produce similar activity no matter what types of silane compounds are chosen as the cross-linking reagents. These vanadyl catalysts produce 50% isopropanol conversion at around 270°C which is about 30°C higher than vanadium (+4) samples to obtain the same conversion. Different oxidation states of the vanadium active sites should have different activation energies. Because similar amounts of catalysts were used along with the same flow rate in each reaction, these preliminary results indicate vanadium (+4) samples have a lower activation energy toward isopropanol dehydration. Ongoing studies are currently focused on relating the activities of the catalysts on a per site basis and will be presented in the future.

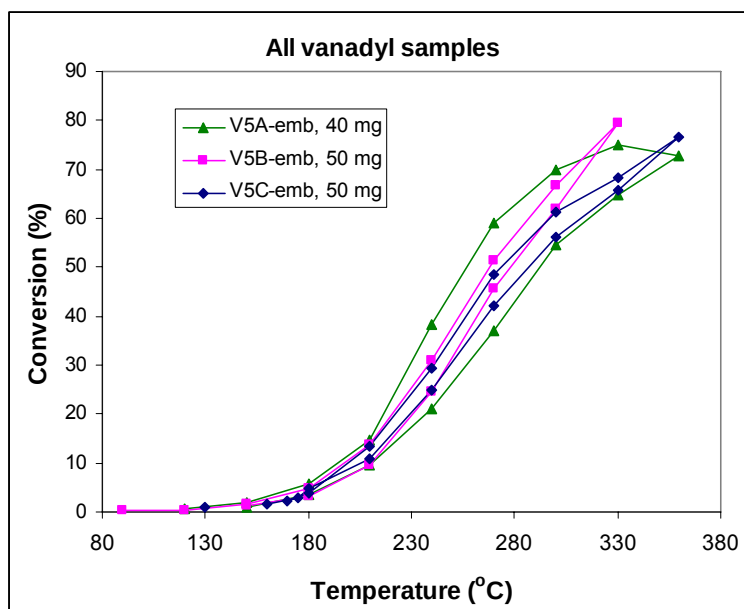


Figure 5 - 17 A comparison of the activities of three vanadyl samples

5.4 Conclusion

Several different protocols have been tested to investigate the reactivity of different vanadyl and vanadium samples in the dehydration of isopropanol to form propene. All of the vanadosilicates samples function primarily as solid acid catalysts in converting isopropanol to propene with high selectivity and reasonable activity. The studies of time on stream with different measurement protocols and flowing water through the catalysts indicate the deactivation of the catalysts is not caused from the interference of the byproduct water. The reaction reached steady state after the stream flows over the catalyst for about 30 minutes. The materials are capable of withstanding very high temperatures while maintaining stable activity.

Further catalytic studies are ongoing. Although these preliminary results indicate both vanadyl and vanadium exhibit reasonable activities in the dehydration of isopropanol, the actual activation energies for each catalyst have not been investigated yet. Applying different space velocities in the reaction will provide information about the reaction mechanism. The dependence of the reaction rates on temperature will allow an analysis of the reaction energetics through the Arrhenius equation ($k = A \cdot \exp(-E_a/RT)$).

Chapter 6

A newly synthetic approach of labeled ^{17}O Si_8O_{20} building block

6.1 Introduction

Oxygen-17 (^{17}O) is the only NMR active oxygen isotope and efforts to exploit ^{17}O in solid-state NMR have increased greatly in last two decades.⁶⁵⁻⁷⁶ It has been routinely applied for the determination of the coordination geometry in crystalline and amorphous materials. However, there are two major challenges associated with ^{17}O NMR spectroscopy which must be overcome. First is the low natural abundance (0.037%) of the ^{17}O isotope which results in low sensitivity and complex spectra. Second is the anisotropic quadrupolar interactions of ^{17}O spins (5/2 nuclear spin) which result in broad lines. The first problem can be solved by using enriched ^{17}O compounds such as H_2^{17}O and $^{17}\text{O}_2$ as starting materials but the costs of these ^{17}O labeled compounds can be extremely high. The second problem can be overcome by applying high magnetic fields and new multipulse experiments to enhance the resolution and sensitivity.

Herein, we have attempted to use ^{17}O solid state NMR data to identify and monitor the coordination environment of catalysis sites described in earlier chapters. Although ^1H , ^{13}C , and ^{29}Si NMR spectroscopies have been applied to study the structure of the sphaerosilicates, to our knowledge no ^{17}O NMR studies have been published on this family of compounds. If oxygen-16 can be replaced with oxygen-17 at terminal positions around the cube, then the labeled ^{17}O

building block, $(\text{Me}_3\text{Sn}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$, will be obtained (Figure 6-1). Using different transition metals such as V, Ti, W, and Zr as linking groups and reacting them with this labeled ^{17}O building block will yield labeled ^{17}O building block solids as illustrated in Figure 6-2. These transition metals will be the potential catalytically active metal centers in the system. The eventual goal of this project is to use the ^{17}O spin to indirectly monitor changes in the identity and environment of catalyst nuclei that are difficult or impossible to detect via NMR.

The first step in considering a ^{17}O SSNMR project is to develop an efficient synthesis of the tin cube that is enriched in ^{17}O in the terminal positions. The high cost of ^{17}O enriched starting materials (\$960 USD for 1 gram 40~45% H_2^{17}O) is the initial problem we faced. A new synthetic methodology had to be developed using a limiting amount of ^{17}O enriched water. After investigating several different synthetic strategies, an efficient way to synthesize labeled $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ was successfully developed. This procedure involved first

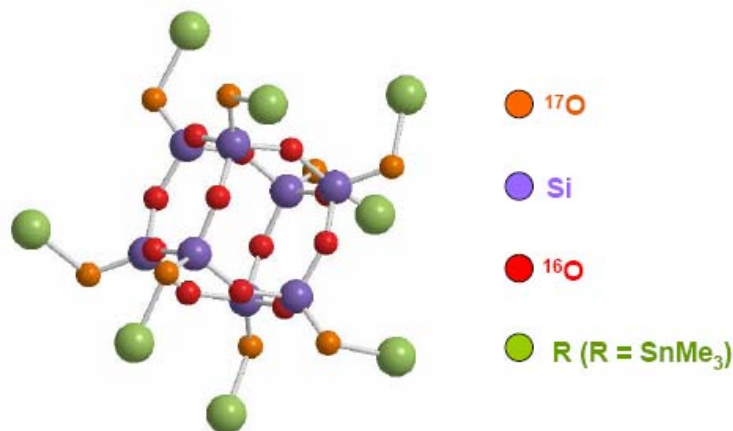


Figure 6 - 1 Molecular model of labeled $(\text{Me}_3\text{Sn}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$

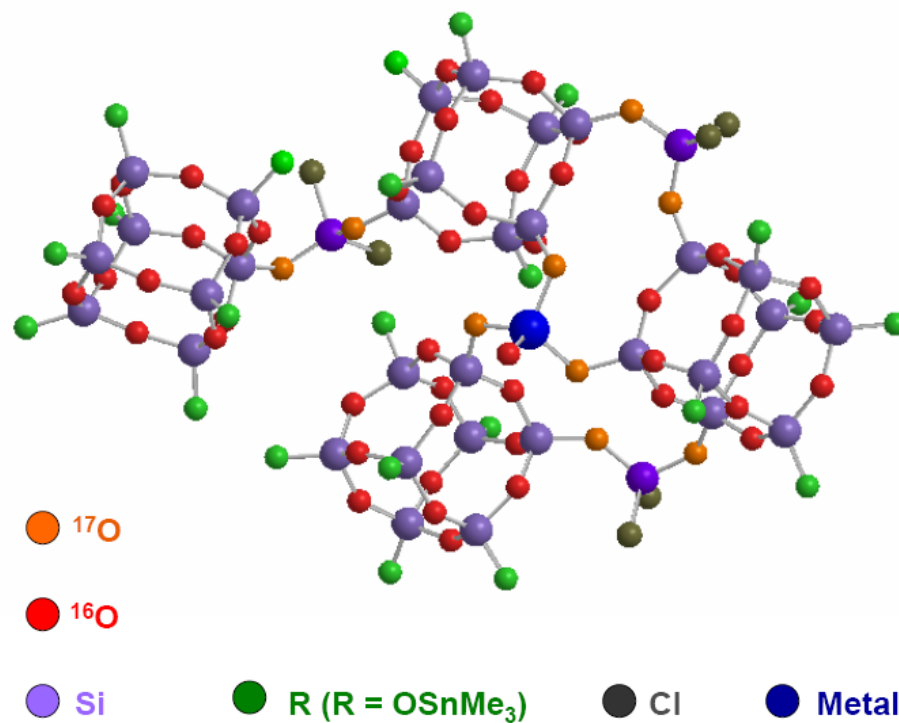


Figure 6 - 2 Molecular model of amorphous crossing-link labeled ^{17}O building block with a transition metal

reacting MeLi with labeled water to obtain labeled Li^*OH . By replacing NaOH with LiOH and following the same procedure described in the Chapter 2 we were able to obtain labeled $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$. The detailed experimental part of this effort will be described in the following sections.

The crystal structures of hydrous and anhydrous $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ have been discussed and published by J. Clark et al.⁷⁷ Several changes in the coordination environments between hydrous and anhydrous $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ are observed due to the hydrogen-bonding interactions in the tetrahydrate tin cube. In agreement with the crystal structure of the tetrahydrates tin cube, several

different ^{119}Sn signals are observed for the tin atoms in the solid state. ^{29}Si SSNMR spectra of crystalline and amorphous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ also reveal the different distortions in the edge Si-O-Si angles connecting SiO_4 tetrahedral units. Finally the different coordination environment of O-SnMe₃ groups in the hydrous $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ provide different chemical shifts in ^{17}O SSNMR spectra and the effect of the different bond angle, bond length and hydrogen-bonding interactions between hydrous and anhydrous $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ will be discussed.

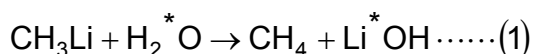
Note: All of the ^{17}O , ^{29}Si and ^{119}Sn SSNMR spectra were collected by Dr. Edward Hagaman and Dr. Jian Jiao in the Oak Ridge National Lab except where noted.

6.2 Experimental

Methyl lithium (1.6M in diethyl ether) was obtained from Aldrich. 1 gram ^{17}O water (40~45% labeled) was purchased from Isotec, Inc (\$ 950 USD / g). Trimethyltin chloride $((\text{CH}_3)_3\text{SnCl})$ was obtained from Gelest, Inc. Solution ^1H and ^{13}C nuclear magnetic resonance (NMR) spectra were acquired on Varian Mercury 300 MHz spectrometer. ^{29}Si solution NMR spectra were acquired at 9.4 Tesla on a Bruker Avance wide-bore multinuclear NMR. ^{17}O , ^{29}Si and ^{119}Sn SSNMR measurements were collected by Dr. Edward Hagaman and Dr. Jian Jiao in the Oak Ridge National Lab. Mass spectra were recorded on a JEOL-DART MA instrument. All of the reactions were accomplished under nitrogen without further notification.

6.2.1 Labeled ^{17}O $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ building block

Fresh 1.6 M methyl lithium (34 mL, 54.4 mmole) of was injected to a Schlenk tube and frozen under liquid nitrogen ambient. Labeled ^{17}O water (1.00 mL, 55.6 mmol) was then quickly injected to the Schlenk tube following by 20 mL of dry diethyl ether. The ice was melted and the reaction was allowed to proceed (Eq. 1).

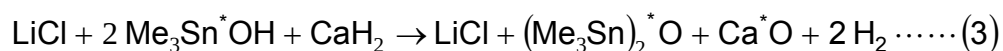


The byproduct, methane, was generated immediately when the temperature of the solution reached to $\sim 0^\circ\text{C}$ and was vented through a nitrogen line. Keeping the solution between $0\text{--}5^\circ\text{C}$ in an ice bath for the first hour and stirring the solution vigorously resulted in the formation of a fluffy white powder. The temperature increased to $5\text{--}10^\circ\text{C}$ in the next 4 hours and then the ice bath was removed. 10.98 g (55.1 mmole) of Me_3SnCl was added in the Schlenk tube and stirred for another 2 hours to obtain a colorless solution with a large amount of white precipitate (Eq 2).



Calcium hydride (8 g, 190 mmol) was then added to the solution and connected the Schlenk tube with a condensor to avoid diethyl ether evaporation

(Eq 3). The LiCl in the solution did not affect the reaction and can be filtered out in the next step. Fifty percent of the ^{17}O formed CaO and the other 50% was incorporated into the tin ether, $(\text{Me}_3\text{Sn})_2^*\text{O}$.



The solution was stirred for 3 days and quickly filtered into another Schlenk tube followed by addition of 1.334g (3.14 mmol) $\text{H}_8\text{Si}_8\text{O}_{12}$ and stirred for 4 hours (Eq 4).

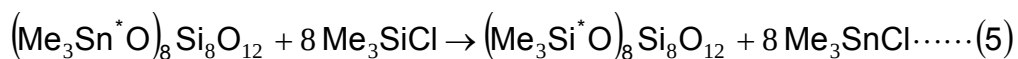


The solvent and byproduct, Me_3SnH , were removed under vacuum and the white product, $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$, was heated at 60°C and dried under vacuum for 12 hours (5.2 g, yield: 80%). The product was crystallized from hexanes and 4.5 g crystals were obtained. The yield of crystals is 70% based on the labeled water. After heating the crystals at 80°C under vacuum for 12 hours, waters of hydration were removed from the solid.

6.2.2 Labeled TMS-cube, $(\text{Me}_3\text{Si}^*\text{O})_8\text{Si}_8\text{O}_{12}$

Anhydrous $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ (0.649g, 0.350 mmol) was reacted with excess Me_3SiCl (1.20 g, 11.05 mmol) at room temperature for 6 hours. Pure

$(\text{Me}_3\text{Si}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ was obtained after removing the byproduct Me_3SnCl and unreacted Me_3SiCl (Eq 5). The crude yield of the powder $(\text{Me}_3\text{Si}^*\text{O})_8\text{Si}_8\text{O}_{12}$ is 98% (crystal yield is 64%).

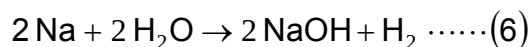


6.3 Results and discussion

6.3.1 A new methodology of synthesizing $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$

An efficient synthetic methodology to prepare a high yield $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ building block (tin cube) has been discussed in Chapter 2. The precursor, Me_3SnOH , is prepared in water by reacting Me_3SnCl with NaOH . In order to synthesize labeled ^{17}O tin cube using a limiting amount of labeled ^{17}O water, a totally different synthetic methodology had to be explored. Initial investigations focused on synthesizing NaOH via using a limiting amount of labeled water. As soon as a new methodology of synthesizing a high yield, pure labeled NaOH is discovered, this labeled NaOH could be used in the synthesis of labeled $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$. Several different approaches were investigated and is described as follows.

Before using ^{17}O enriched water as the reactant, normal distilled water was tested in different reactions. The first attempt to discover a new synthetic procedure was to synthesize labeled precursor, NaOH , by reacting a limiting amount of water with sodium (Eq 6).

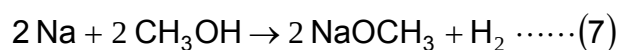


The problem with this reaction is that the sodium did not react totally with limiting amount of water when the molar ratio of Na to water is 1 to 1. Some sodium pieces were coated with product NaOH which prevented further reaction. Newly formed NaOH also hydrogen-bonded with some water and reduced the amount of reactive water. "Sodium sands" were then used in order to improve to reactivity by increasing the sodium surface area. (*"Sodium sands" were prepared in a hot distilled toluene solution by heating the solvent at 100°C and stirring the sodium chunks vigorously under nitrogen. Big sodium pieces were broken into tiny sodium powders after stirring for a few minutes at 100°C.*) When the ratio of H₂O to Na was increased to 3~4 : 1, the sodium did react totally with water to form NaOH. But three to four-fold excess of water in the reaction is not atom-efficient and this approach was not a good choice to synthesize labeled ¹⁷O NaOH.

Adding 18-Crown-6-ether (1,4,7,10,13,16-hexaoxacyclooctadecane) to complex the Na⁺ ion in the reaction was also investigated. Crown-ethers are cyclic polyethers that are capable of binding alkali metal cations. When a small amount of 18-Crown-6-ether was added into a ratio of 1 : 1 of Na : water reaction, more hydrogen formed immediately. It indicated Na cations from NaOH were complexed by crown-ether and the reaction proceeded further. This methodology did reduce the amount of excess water in the reaction, but a two-

fold excess of water was still needed and problems were encountered when using this synthesized NaOH in following reactions. Pure trimethyltin ether, $(\text{Me}_3\text{Sn})_2\text{O}$, could not be obtained using NaOH prepared in this manner.

Dissolving Na in methanol to form sodium methoxide, NaOCH_3 , as the precursor was another approach investigated (Eq 7). NaOCH_3 is an air sensitive compound and capable of reacting with water to form NaOH immediately. (Eq 8).



Na dissolved in the methanol solution entirely and formed NaOCH_3 . A white powder was obtained after removing unreacted methanol. The advantage of this synthetic methodology is that only one equivalent of water is needed in the reaction of sodium methoxide with water. The disadvantage of this methodology is the reaction is reversible and the byproduct, methanol, reacts with NaOH to reduce the yield of NaOH. The unreacted NaOCH_3 caused some problems in the following reactions involving tin. Some unknown products were always seen in the ^1H NMR spectra after reacting Me_3SnCl with the synthesized NaOH and therefore this methodology can not be used to obtain pure NaOH without contamination with NaOCH_3 .

The best procedure discovered so far involved the use of methyl lithium, MeLi, as the deprotonating reagent to form lithium hydroxide (LiOH) instead of sodium hydroxide (NaOH). It was found that LiOH also reacts with Me₃SnCl and forms Me₃SnOH cleanly. Commercially available MeLi is dissolved in the diether ether and is a good reagent for a homogeneous reaction. The byproduct LiCl is air sensitive (easily absorbs water in air) and all of the reactions were performed under nitrogen. It can be filtered out after the formation of (Me₃Sn)O without affecting the yield (Eq 3). Combining this new discovery with the one-pot synthetic methodology described in Ch2, a high yield and pure product was eventually obtained successfully using a smallest amount of labeled water as the reactant.

This new synthetic methodology provided us with the following important information. First, the reactivity of LiOH is similar to NaOH and it can be chosen to react with Me₃SnCl to form Me₃SnOH. Second, neither LiCl nor NaCl byproduct in the reaction affect the yield of (Me₃Sn)₂O. Third, the reaction in which (Me₃SnO)₈Si₈O₁₂ is formed can be accomplished in the diethyl ether solution in high yield. Fourth, labeled oxygen successfully incorporating into the (Me₃SnO)₈Si₈O₁₂ building block supports the mechanism underlying the synthetic procedures as presented in Ch2 (Ch2-Figure 1). It is a very important milestone in our research projects because labeled ¹⁷O building block provides us another opportunity to track the reactions as the Si₈O₂₀ building block reacts with different metal chlorides.

One drawback of this synthetic methodology is only 50% of the ^{17}O labeled reactant is theoretically converted to $(\text{Me}_3\text{Sn})_2\text{O}$, the other 50% of the ^{17}O label is lost, presumable as a mixture of CaO and CaOH . If the labeled CaO can be recycled, this synthetic methodology would be even more efficient

6.3.2 Mass spectra

The first line of the evidence to prove that ^{17}O was incorporated into $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ is mass spectra for this sample. The initial concentration of the commercially available labeled water is 40~45% and the products from each synthetic step such as Li^{17}OH , $\text{Me}_3\text{Sn}^{17}\text{OH}$, and $(\text{Me}_3\text{Sn})_2^{17}\text{O}$ should also contain 40~45% labeled oxygen. 40~45% labeled oxygen in the $(\text{Me}_3\text{Sn})_2^{17}\text{O}$ reacts with $\text{H}_8\text{Si}_8\text{O}_{12}$ should obtain a labeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ with 40~45% labeled Me_3SnO groups in the eight corners of the building block. The molecular weight of the labeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ should increase 3.2 - 3.6 g/mol (8 corners x 40 - 45%).

The labeled and unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ were analyzed by dipping the outside surface of the sealed end of melting point tube into liquid solutions or by picking up dry crystals with a melting point tube. Isotope pattern matching was used to support elemental composition assignments based on exact mass. The mass spectrum of unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ is shown in Figure 6-3. The theoretical isotope pattern $[\text{M}+\text{H}]^+$ and theoretical isotope distribution is shown in Figure 6-4. The peak at 1856.5 m/z represent the most intense peak in the envelop of the parent ion of $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$.

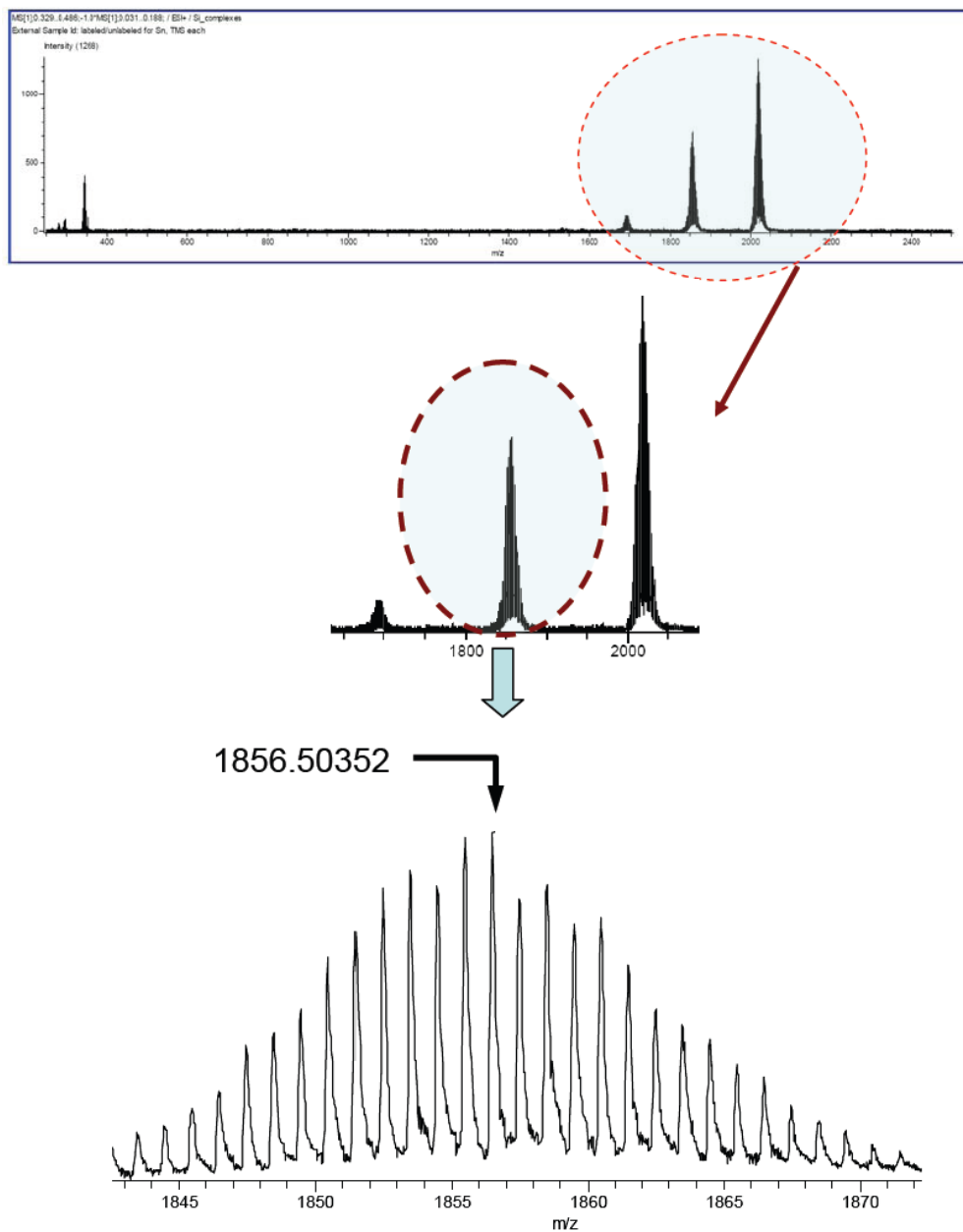


Figure 6 - 3 The mass spectrum of unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

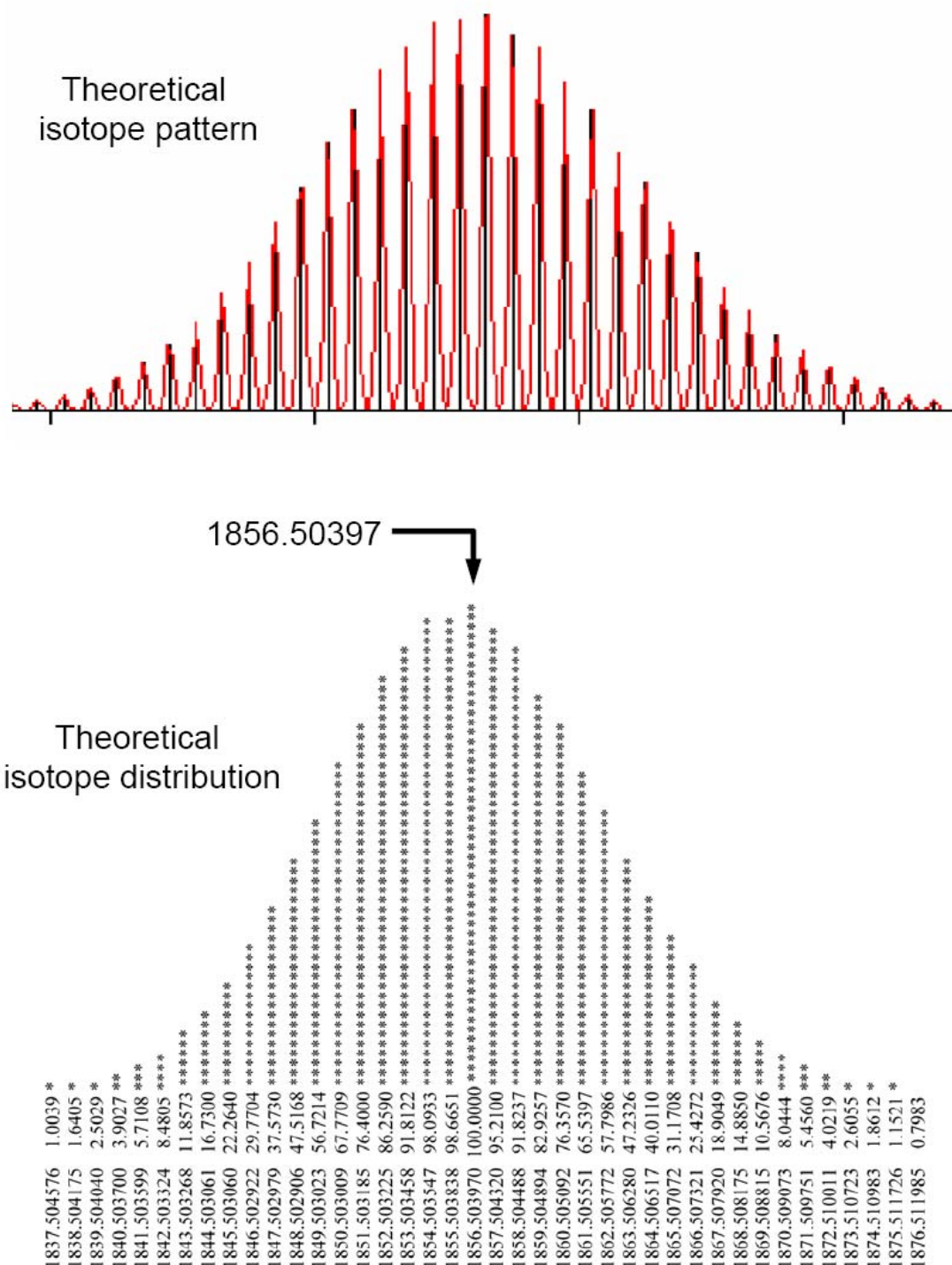


Figure 6 - 4 The theoretical isotope pattern $[M+H]^+$ and theoretical isotope distribution

The envelop of peaks at ~2019 g/mol represents the parent $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ with an additional Me_3Sn group attached. The mass spectrum with an enlarged pattern of unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ is shown in Figure 6-5. The theoretical isotope pattern $[\text{M}+\text{H}+\text{Me}_3\text{Sn}]^+$ and theoretical isotope distribution of $[(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12} + \text{Me}_3\text{Sn}]$ is shown in Figure 6-6. Comparing these mass spectra with labeled $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$, the parent peak increases from 1856.5 m/z to 1860.5 m/z (Figure 6-7). The molecular weight of the measured and theoretical parent peaks in each envelop are summarized in Table 6-1.

This information from the mass spectra indicates labeled ^{17}O was successfully incorporated into the building block. Around 4 m/z increment of the labeled tin cube is consistent with what we expect when we used 40~45% labeled water as the starting material. The intensity of the envelop at ~2020 m/z which represents $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ with an additional Me_3Sn group attached is stronger than the envelop at ~1856 m/z which represents $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ in both labeled and unlabeled tin cube mass spectra. It indicates the Me_3Sn fragment quickly attached to the tin cube and formed a $[(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}+\text{Me}_3\text{Sn}]$ complex during the MS measurement.

Table 6 - 1 Measured and theoretical mass of labeled and unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

	Measured mass (m/z)	Theoretical mass (m/z)
$(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$	1856.50352	1856.503970
$(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12} + \text{Me}_3\text{Sn}$	2019.46802	2019.476737
$(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$	1860.51693	
$(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12} + \text{Me}_3\text{Sn}$	2023.48502	

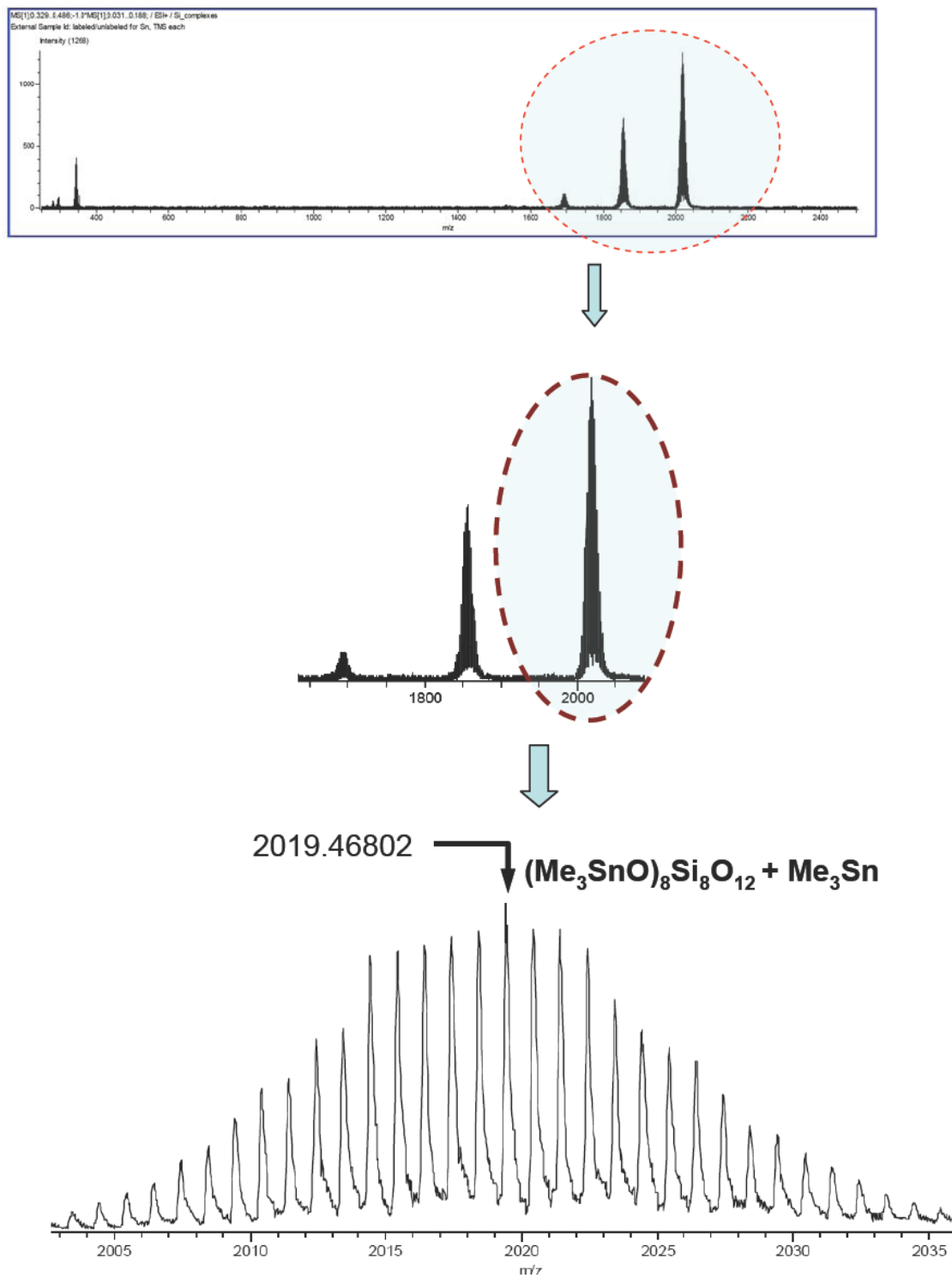


Figure 6 - 5 The mass spectrum of unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12} + \text{Me}_3\text{Sn}$ group

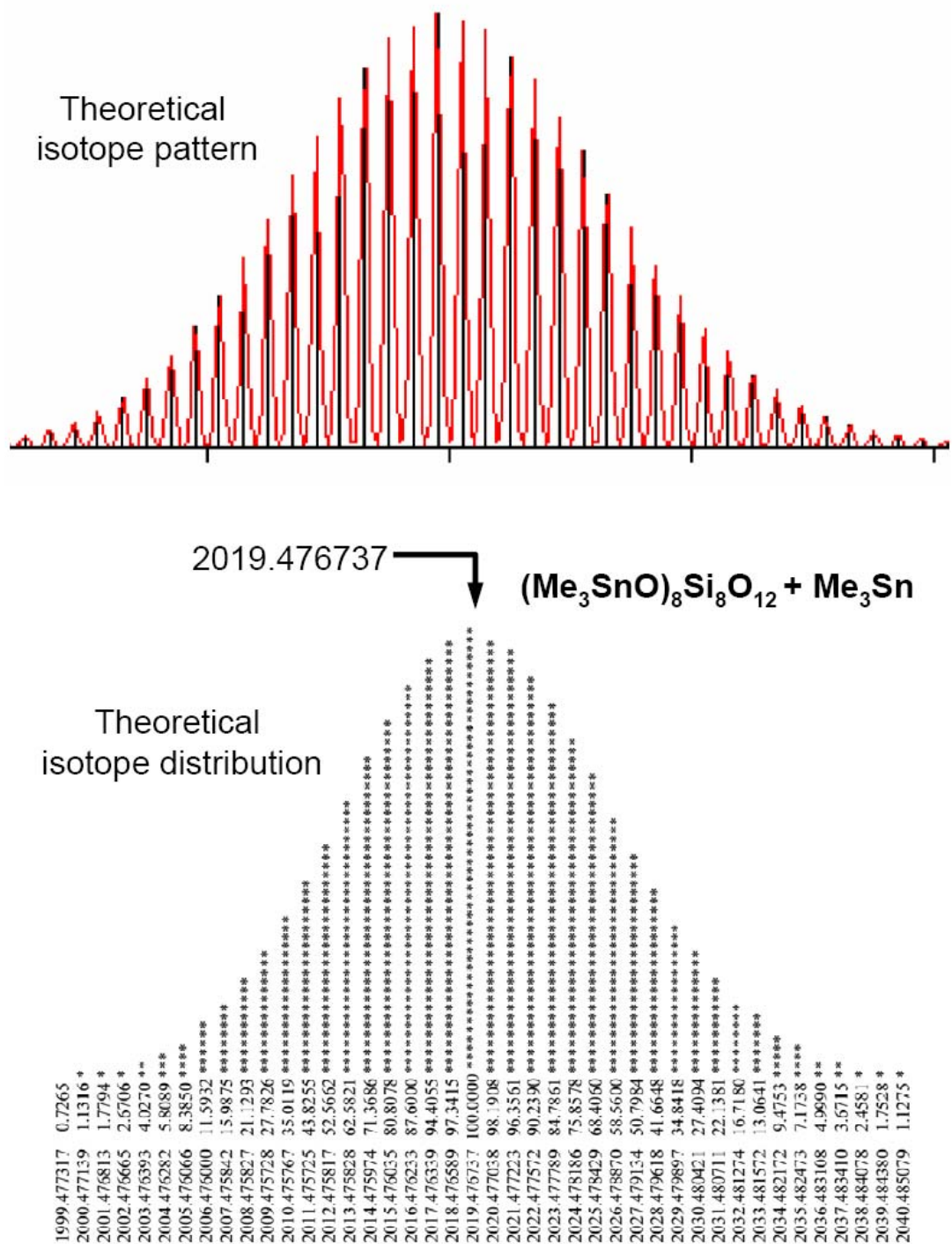


Figure 6 - 6 The theoretical isotope pattern $[\text{M} + \text{Me}_3\text{Sn} + \text{H}]^+$ and theoretical isotope distribution

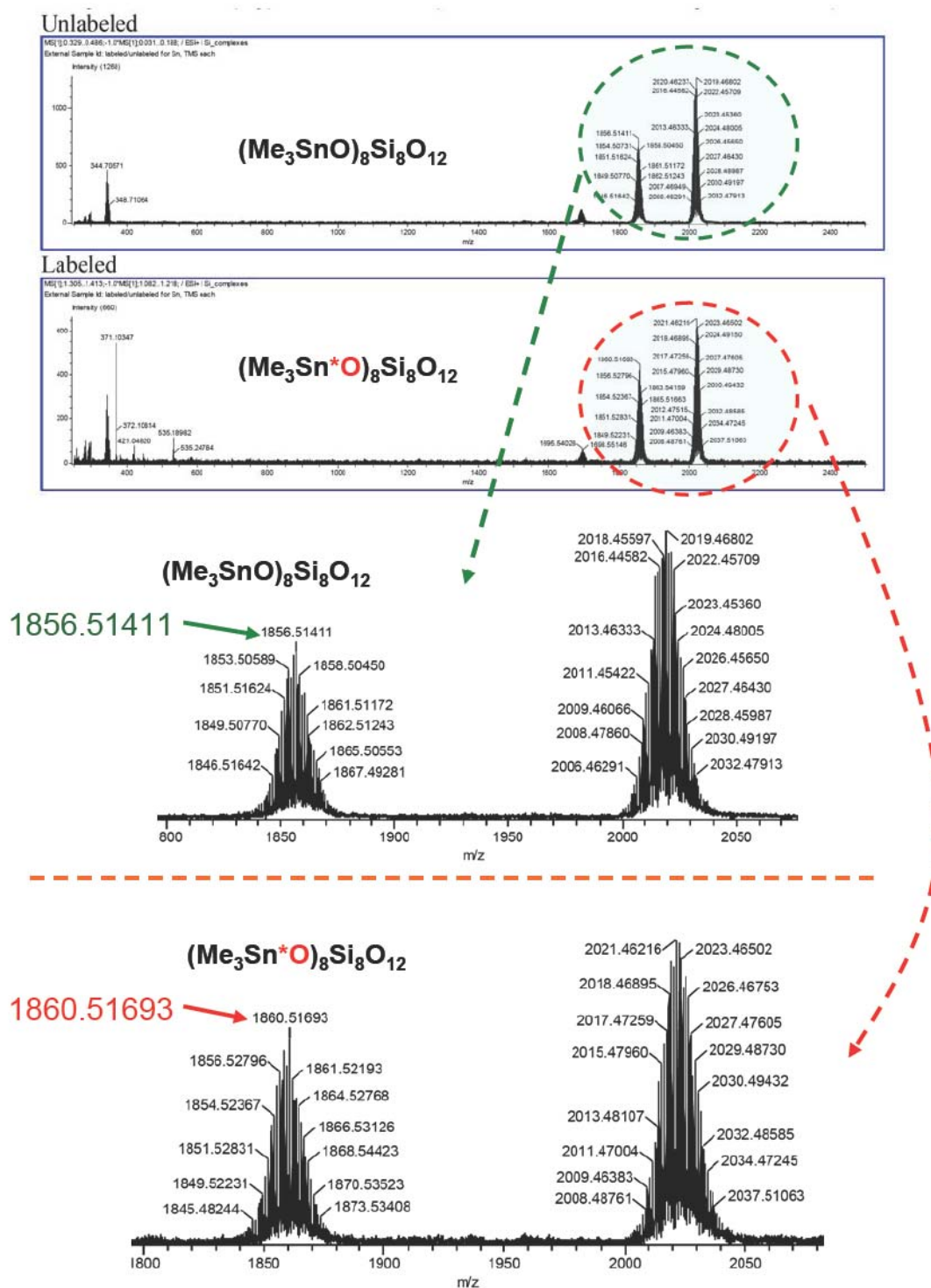


Figure 6 - 7 The mass spectrum of labeled and unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

The labeled $(\text{Me}_3\text{Si}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ (TMS-cube) was synthesized after reacting excess TMSCl with labeled $(\text{Me}_3\text{Sn}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ building block. The molecular weight of the unlabeled TMS-cube is 1131 g/mol and is ~ 1135 g/mol for the labeled TMS-cube. More fragments attached with $(\text{Me}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$ are observed in the mass spectra (Figure 6-8). The envelop with the strongest intensity of peaks at 1131 m/z represents the parent $(\text{Me}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$. The envelop with the second strongest intensity of peaks at 1176 m/z represents the parent tin cube attached with three additional methyl groups $([(\text{Me}_3\text{SiO})_8\text{Si}_8\text{O}_{12} + 3 \text{CH}_3])$. The mass spectrum of labeled $(\text{Me}_3\text{Si}^*\text{O})_8\text{Si}_8\text{O}_{12}$ contains an envelop with the strongest intensity of peaks at around 1136 m/z (Figure 6-9). The observation of approximately a 4 m/z increment in the mass of labeled TMS-cube is consistent with Me_3Si groups from TMSCl reagent only reacted with Me_3Sn groups and formed new $\text{Si}^{17}\text{O-Si}$ groups in the building block. The labeled ^{17}O atoms in the building block after the reaction indicate that the Si^*O bond in each corner of the building block is very stable and ^{17}O atoms remain associated with the Si_8O_{12} cage in the reaction.

6.3.3 ^{29}Si and ^{119}Sn SSNMR

The observation of identical chemical shifts of ^1H NMR spectra of labeled $(\text{Me}_3\text{Sn}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ and unlabeled $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ is another line of the evidence supporting the successful synthesis of labeled tin-cube. Both of these samples exhibit the same chemical shift at 0.359 ppm in deuterated benzene. ^{29}Si CPMAS SSNMR spectrum collected from the University of Tennessee

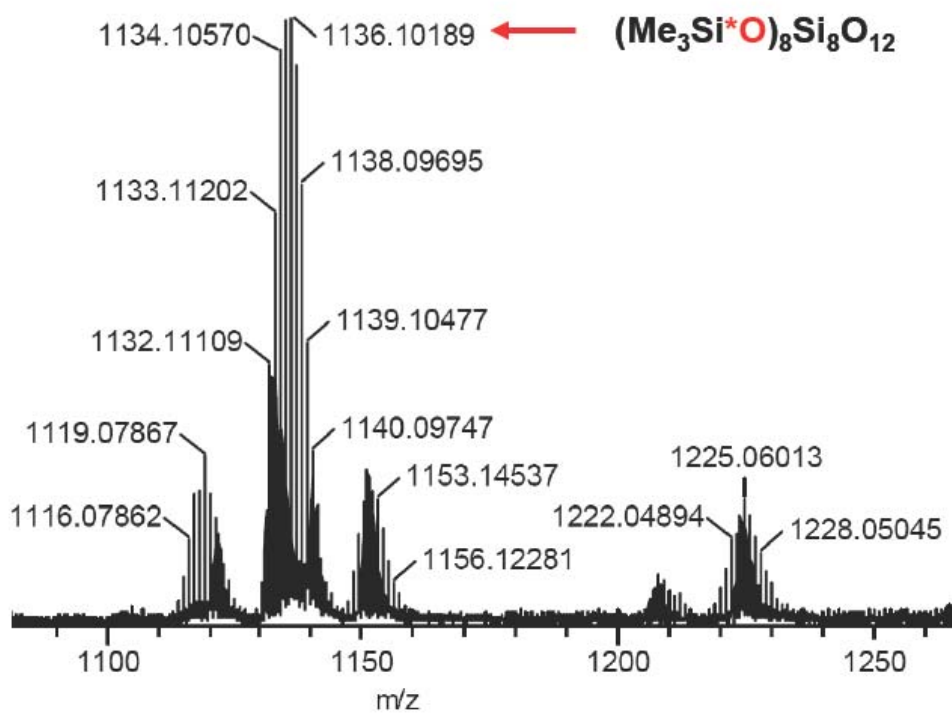
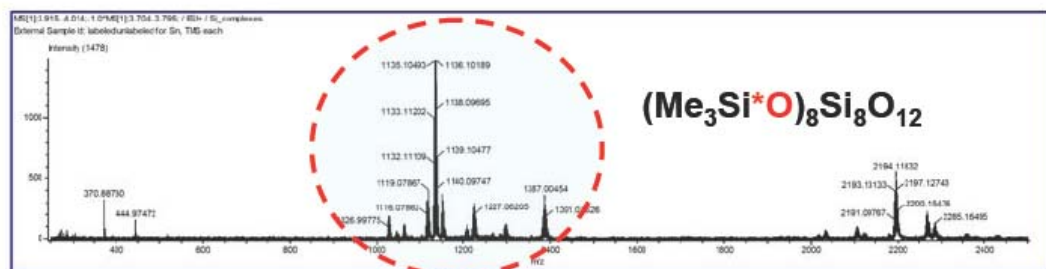


Figure 6 - 9 Mass spectrum of labeled TMS-cube

shows two sets of silicon environments in the anhydrous crystalline $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ molecule. One set is at ~ -101 to -102 ppm and the other set is at ~ -104 to -105 ppm (Figure 6-10).

Dr. Edward Hagaman and Dr. Jian Jiao from the Oak Ridge National Lab repeated the ^{29}Si SSNMR measurement of crystalline labeled and unlabeled anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ samples and obtained similar results (Figure 6-11). The simulated spectrum and deconvoluted peaks indicate there are four different types of silicon centers in one tin-cube molecule. Both labeled and unlabeled tin-cubes provide the same chemical shifts and the same distribution of different Si sites. The parameters are summarized in Table 6-2. Slightly different ^{29}Si chemical shifts of the anhydrous tin-cube sample indicate that the tin-cube should have distorted Si sites with different Si-O bond lengths and Si-O-Si bond angles which are consistent with the results observed in the crystal structure (Figure 6-12).

Table 6 - 2 ^{29}Si SSNMR parameters of labeled and unlabeled tin cubes

Sample	Signals	Assignment	δ / ppm	FWHP /ppm	I /%
$(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ crystalline	Signal1	Si1 site	-102.1	0.7	24
	Signal2	Si2 site	-102.8	0.8	25
	Signal3	Si3 and Si4 sites	-104.5	1.1	51
$(\text{Me}_3\text{Sn}^{17}\text{O})_8\text{Si}_8\text{O}_{12}$ crystalline	Signal1	Si1 site	-101.7	1.6	26
	Signal2	Si2 site	-102.6	1.3	25
	Signal3	Si3 and Si4 sites	-104.5	2.1	49

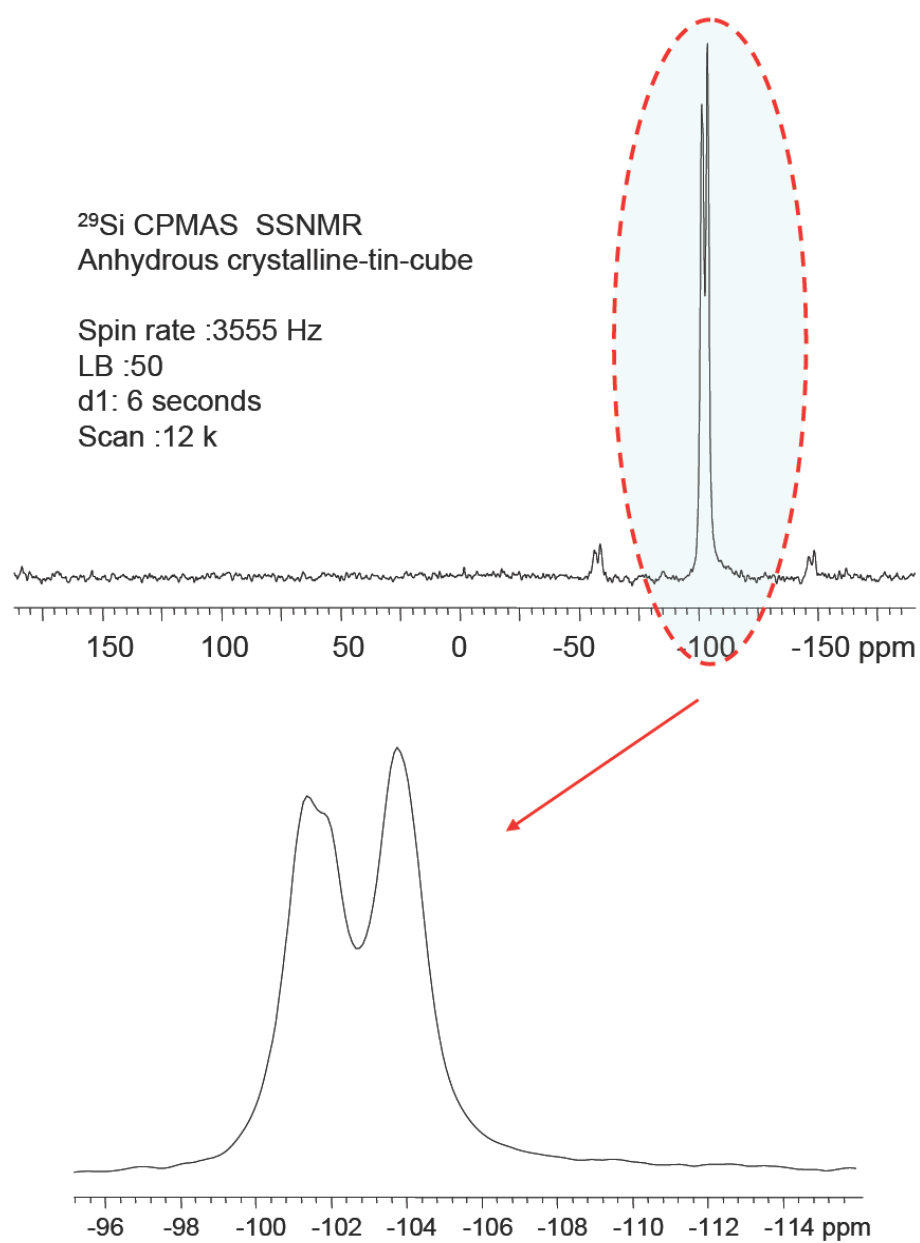


Figure 6 - 10 ^{29}Si CPMAS SSNMR of anhydrous crystalline tin cube

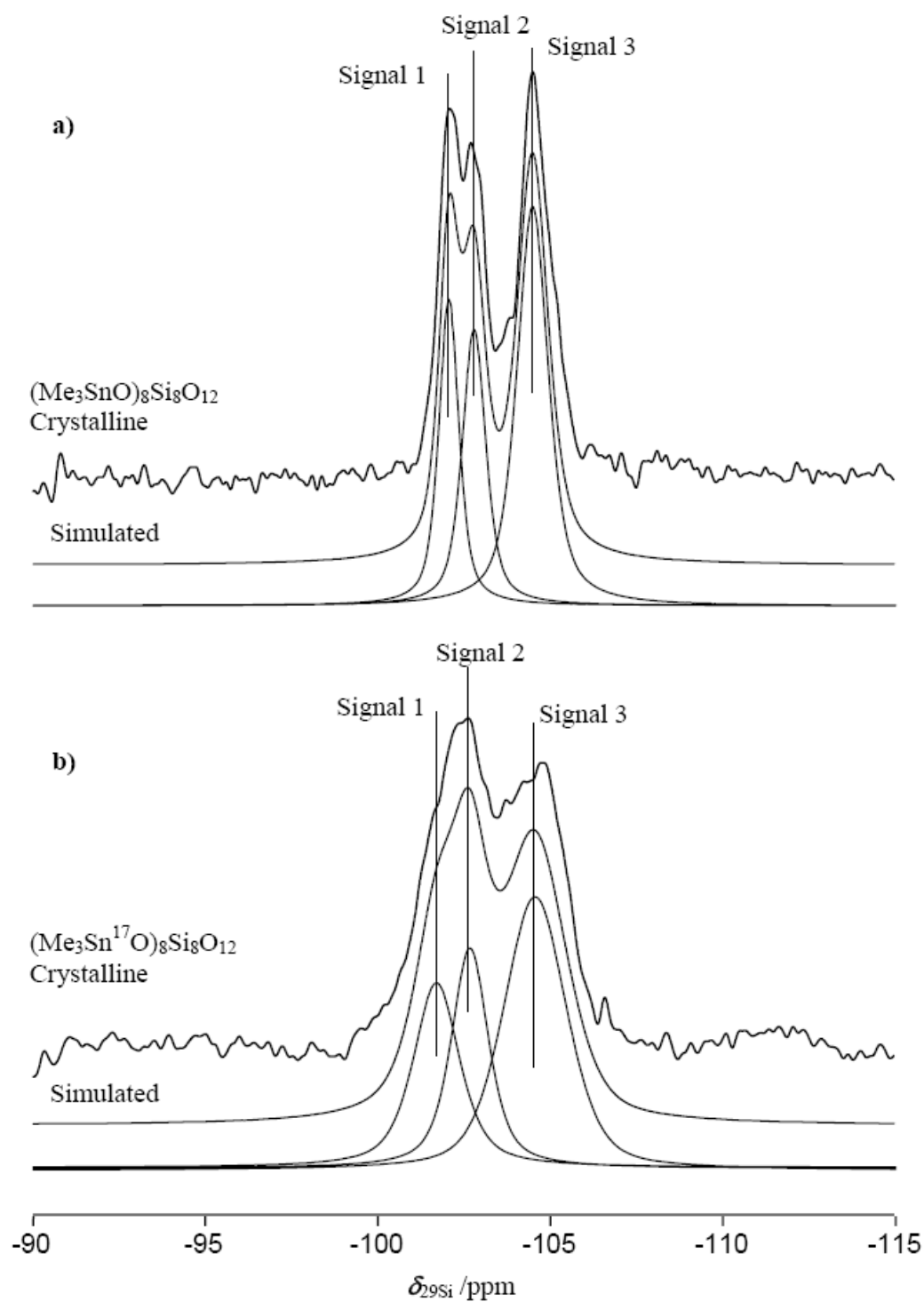


Figure 6 - 11 ^{17}O SSNMR of crystalline label and unlabeled anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

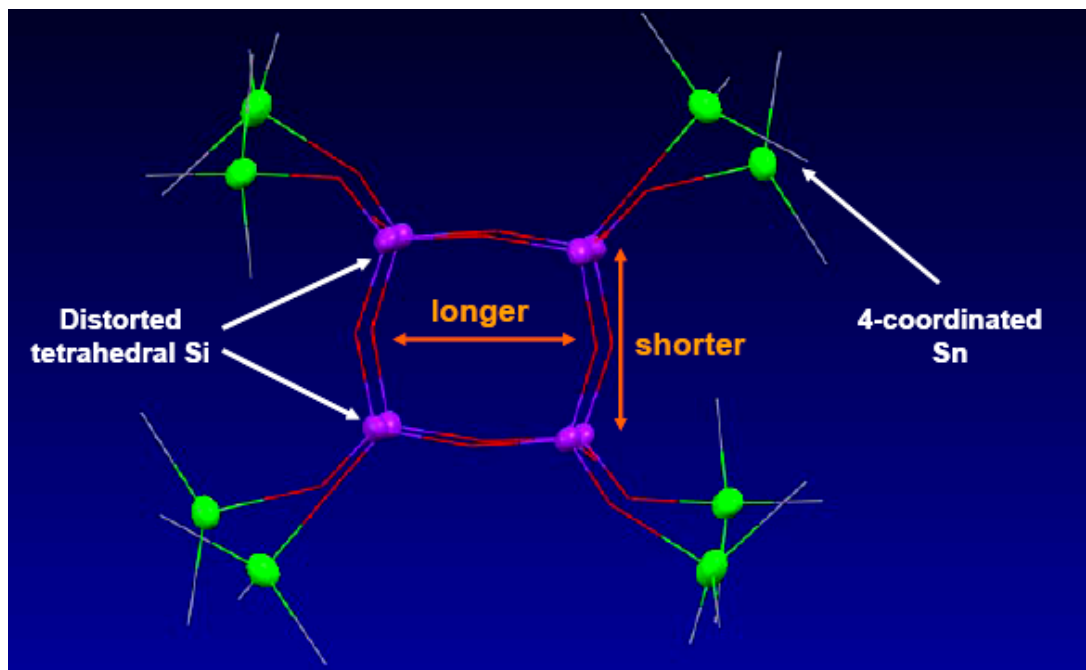


Figure 6 - 12 Crystal structure of anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

The ^{119}Sn SSNMR spectrum of crystalline anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ is shown in Figure 6-13. There is only one type of Sn atom in the molecule with a chemical shift at 117.7 ppm because all of the Sn sites are four-coordinated. When four water molecules coordinate to the tin-cube, the Lewis base and hydrogen bonds between water and trimethyl tin groups change the coordinate environment of tin centers and provide different chemical shifts in ^{119}Sn SSNMR spectrum (Figure 6-14). Four different types of Sn centers are present in the crystalline hydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ with isotropic chemical shifts of 148.6, 137.3, 57.9, and -31.8 ppm based upon simulations of the raw spectrum. The tin atoms coordinated with water change to a five-coordinate environment and change the chemical shifts from low field to high field (more negative chemical shift).

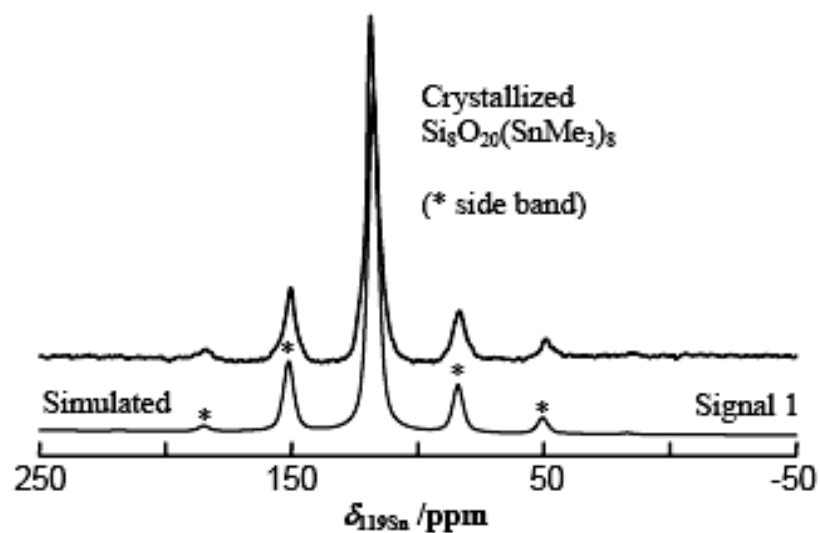


Figure 6 - 13 ^{119}Sn SSNMR of crystalline anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

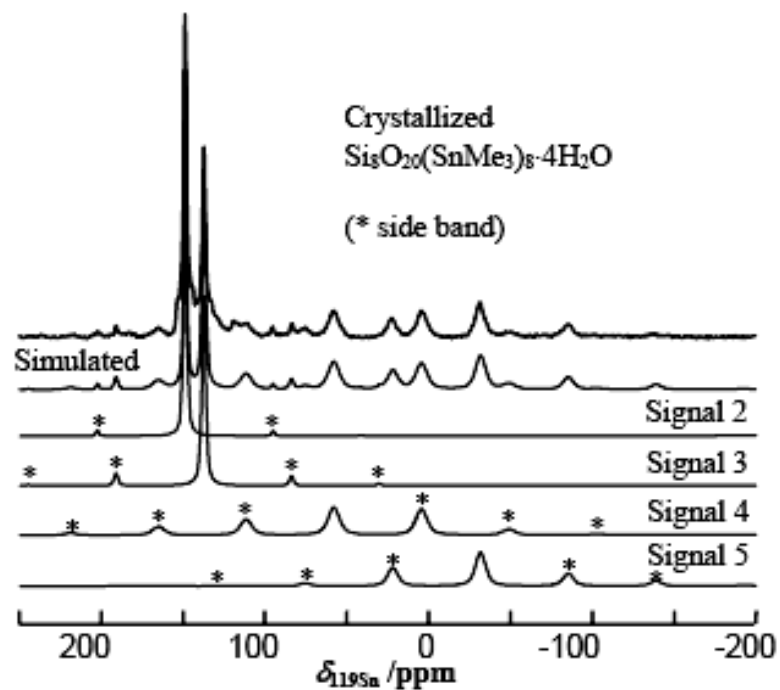


Figure 6 - 14 ^{119}Sn SSNMR of crystalline hydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

The hydrous crystal structure in Figure 6-15 shows both four- and five-coordinated Sn atoms exist simultaneously in one $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ molecule. The hydrogen bonds between the protons of water and the oxygen bonded to Si and Sn (Si-O-SnMe_3 groups) change the Si-O-Sn bond angles. One hydrogen bond is formed to the oxygen bound to a four-coordinate Me_3Sn group and the other hydrogen bond is formed between the same water molecule and the oxygen bound to a five-coordinated Me_3Sn group (Figure 6-16). Four-coordinated Sn sites in the hydrous crystalline $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ sample result in low field ^{119}Sn chemical shifts (148.6, 137.3 ppm). Five-coordinate Sn sites result in high field ^{119}Sn chemical shifts (57.9, and -31.8 ppm).

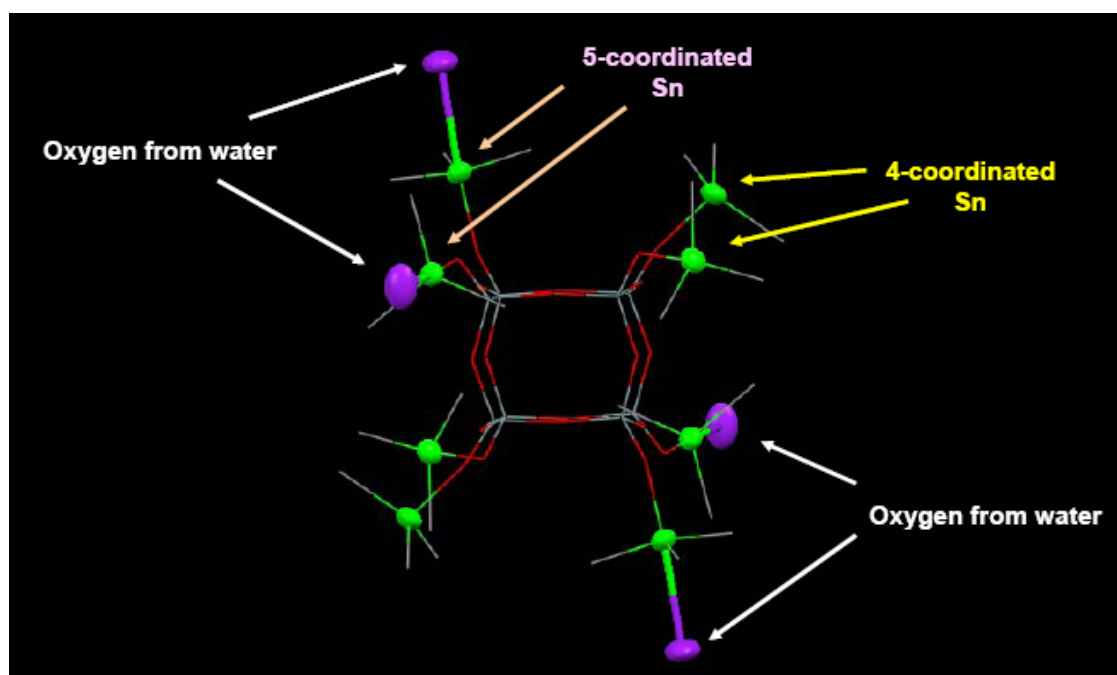


Figure 6 - 15 four and five-coordinated Sn atoms in hydrous tin cube

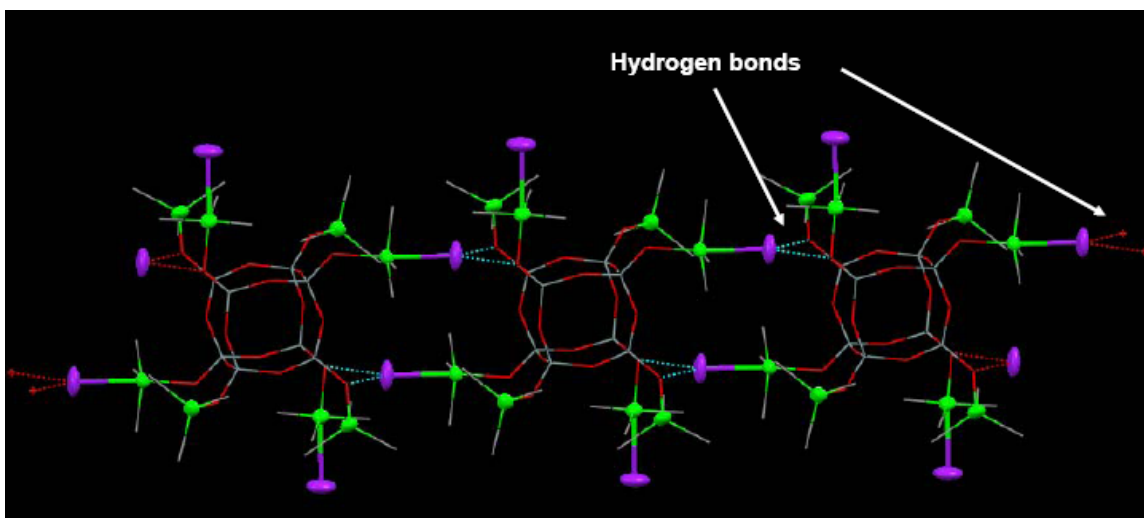


Figure 6 - 16 hydrogen bonds in hydrous tin cube

When amorphous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ was measured in ^{119}Sn SSNMR, only two types of Sn sites are shown in the spectrum, and is similar to the spectrum of the crystalline anhydrous tin-cube (Figure 6-17). Different O-Sn bond lengths and O-Sn-C bond angles change the ^{119}Sn chemical shifts in comparison with those in hydrous crystalline $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$.

6.3.4 ^{17}O SSNMR

Two sets of oxygen sites with different Si-O-Sn bond angles are observed in the crystal structure of the anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ (Figure 6-18). One set of the Si-O-Sn bond angle is $\sim 140^\circ$ (140.1° and 140.2°), the other set is $\sim 130^\circ$ (129.1° and 132.4°). The different bond angles result in small chemical shift differences in the ^{17}O MAS SSNMR spectrum. The spectrum in Figure 6-19 was collected from amorphous anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$. The anhydrous

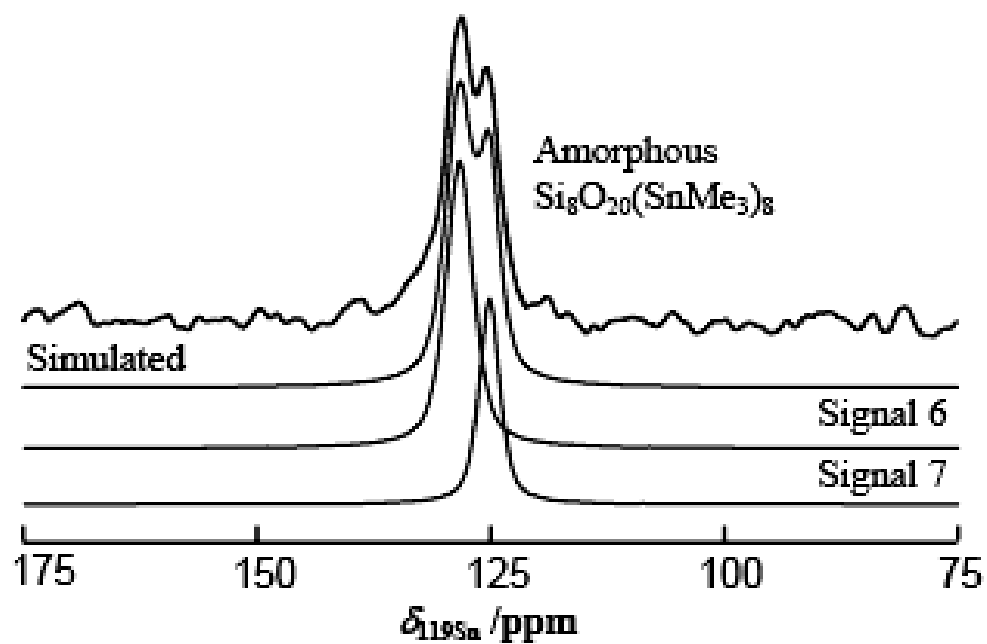


Figure 6 - 17 ^{119}Sn SSNMR of amorphous anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

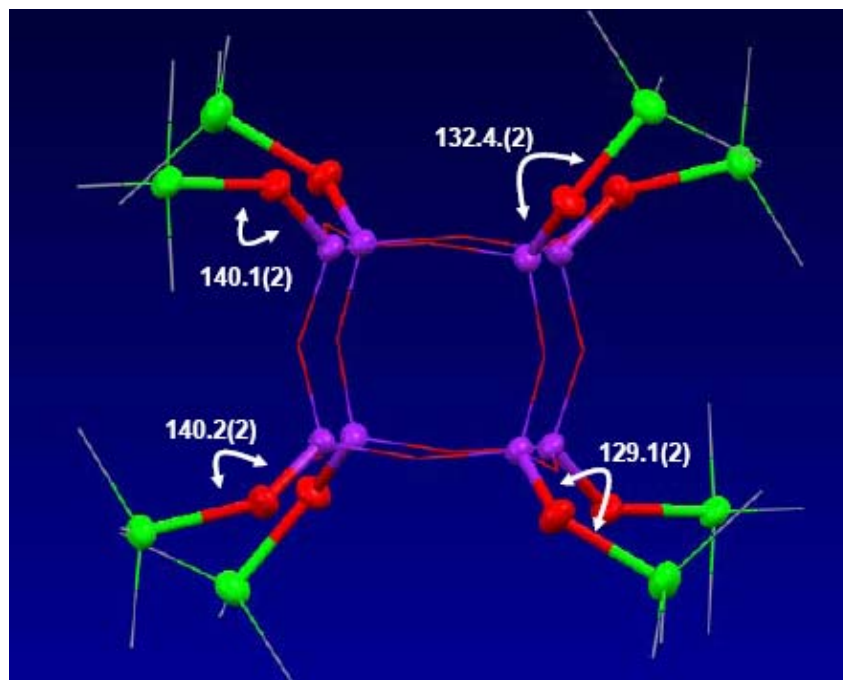


Figure 6 - 18 Crystal structure of anhydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

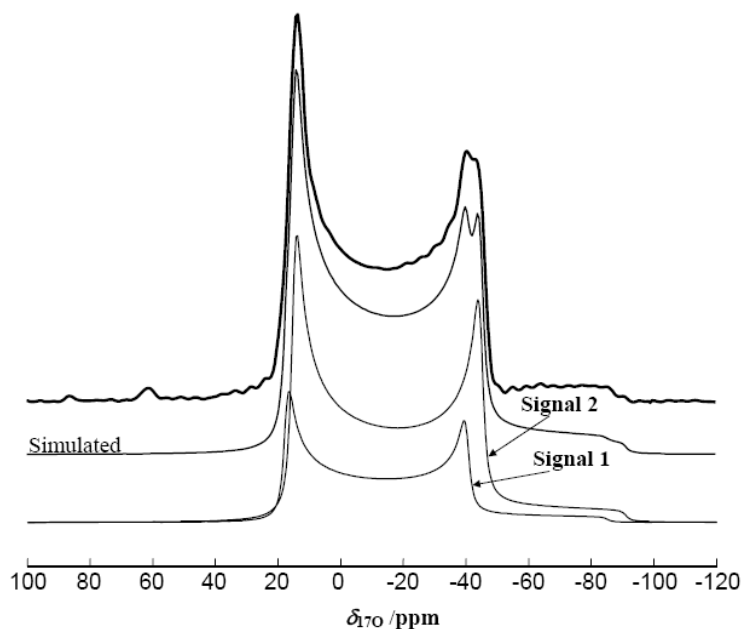


Figure 6 - 19 ^{17}O SSNMR MAS spectra of the anhydrous tin cube

crystalline tin-cube sample will be examined soon from ORNL and then can be compared with the results from the amorphous sample.

In this amorphous material, two resonances with almost identical parameters are present in the area ratio of 2:1. In the anhydrous form there is high local symmetry at the labeled oxygen sites. This distribution may change if we look at the anhydrous crystalline material. The splitting in the spectrum may be due to a distortion in the crystal upon dehydration. The parameters are summarized in Table 6-3 where δ represents the chemical shift, η represents the asymmetry parameter, SOQE represents the Second Order Quadrupole Effect from the equation $\text{SOQE} = Q_{cc}\sqrt{(1 + \eta^{1.5})}$, and Q_{cc} is the quadrupole coupling constant.

When four water molecules are incorporated into the lattice of $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ cubes, the bond angle of Si-O-Sn and the bond lengths of O-Sn change significantly. The crystal structure in Figure 6-20 shows there are smaller Si-O-Sn bond angles and longer O-Sn bond lengths when the Sn atom in the SnMe_3 group coordinates with a water molecule and changes the coordination number to five. The O-Sn bond length increases about 0.05 Å in the five-coordinate O-SnMe₃ groups and the Si-O-Sn bond angle decreases from ~130° to ~128°.

Table 6 - 3 ^{17}O SSNMR parameters of anhydrous tin cube

	δ_{CS} /ppm	η	SOQE / MHz	I /%
Signal 1	35 ± 2	0.02 ± 0.02	4.8 ± 0.2	31 ± 2
Signal 2	33 ± 2	0.02 ± 0.02	4.9 ± 0.2	69 ± 2

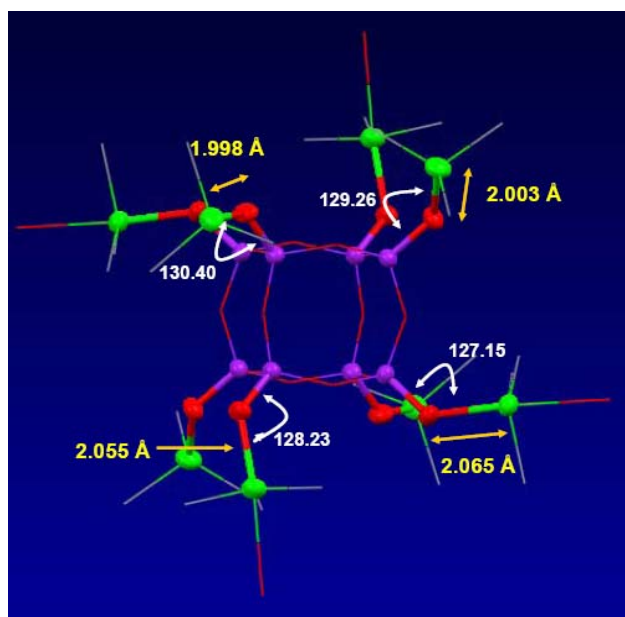


Figure 6 - 20 Bond angles and bond lengths in the Crystal structure of hydrous $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$

The ^{17}O MAS SSNMR spectrum in Figure 6-21 shows multiple resonances and prominent singularities. Two resonances are very similar at high field (signal 3') and two resonances at low field are resolved nicely (signals 1' and 2') in the amorphous hydrous $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$ cubes. Signal 3' is split into two peaks when a crystal hydrous labeled tin cube is measured. (Figure 6-22)

The fit intensities of signals 1', 2', and 3' are in the ratio: 1 : 1 : 2. All of parameters are summarized in Table 6-4. The effect of the hydrogen bonded water is to increase η (from ~ 0.02 to ~ 0.5) and to decrease SOQE (from ~ 4.8 to $\sim 4.0, 4.2$, and 4.6) for all sites compared to the anhydrous form. In the hydrate, all enriched oxygen sites participate in hydrogen bonding with a single water molecule bridging two sites. The oxygen atom from each water molecule bonds to a Sn atom to form a five-coordinate Sn center and two hydrogen atoms from each water molecule form two hydrogen bonds with two different O-Me₃Sn

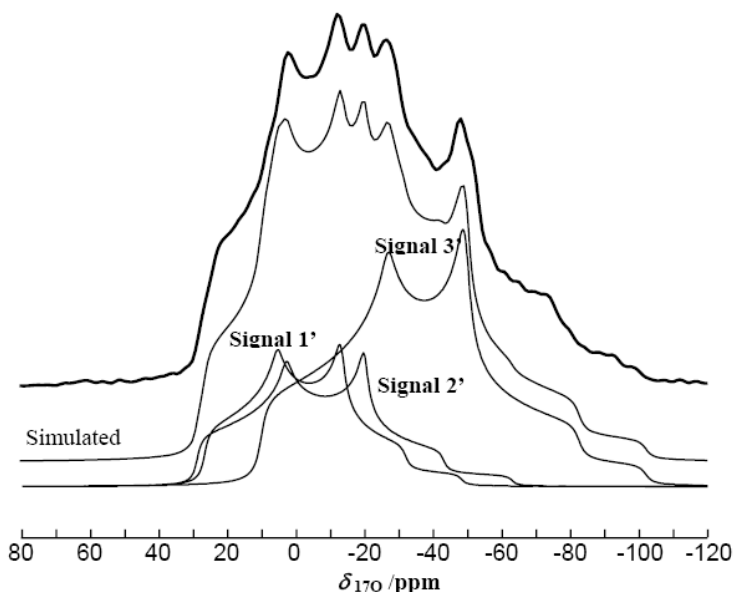


Figure 6 - 21 ^{17}O MAS spectra of the amorphous hydrous material

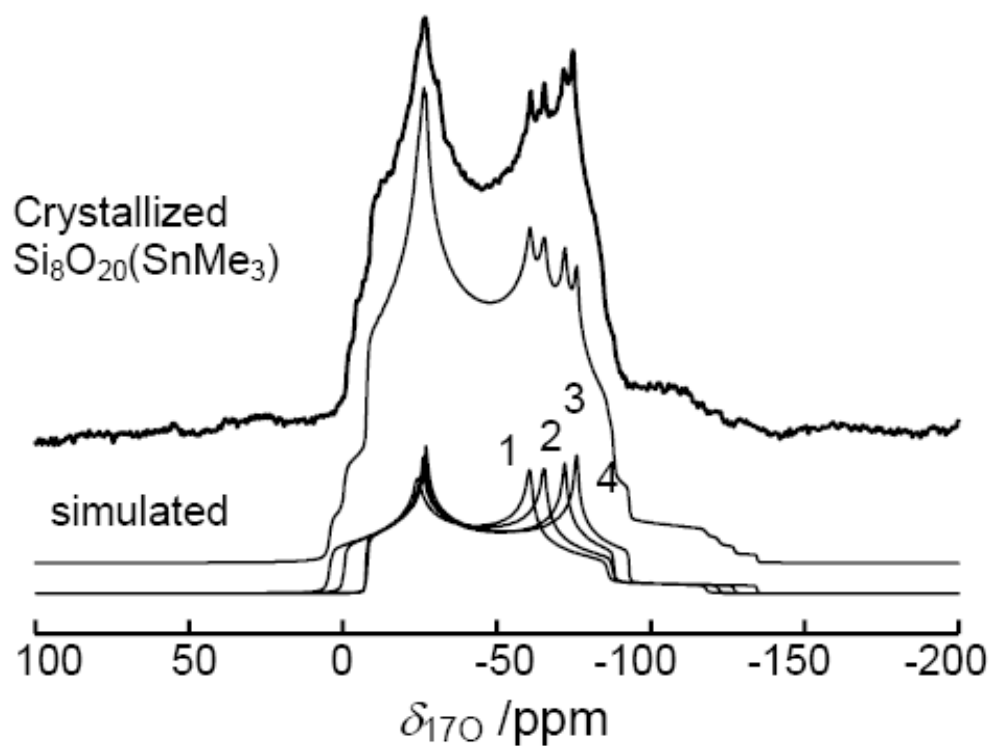


Figure 6 - 22 ^{17}O MAS spectra of the crystalline hydrous material

Table 6 - 4 ^{17}O SSNMR parameters of hydrous amorphous tin cube

	$\delta_{\text{cs}} / \text{ppm}$	η	SOQE / MHz	$I / \%$
Signal 1'	30 ± 2	0.5 ± 0.05	4.0 ± 0.2	22 ± 2
Signal 2'	28 ± 2	0.5 ± 0.05	4.2 ± 0.2	24 ± 2
Signal 3'	9 ± 2	0.6 ± 0.05	4.6 ± 0.2	54 ± 2

groups. Four sets of hydrogen bonds are shown in the crystal structures which are 2.178, 2.189, 2.194, 2.216 Å respectively (Figure 6-23). The hydrogen bonds to five-coordinate O-SnMe₃ groups are longer (2.216 and 2.194) than to four-coordinate O-SnMe₃ groups. Different coordination environments of the Sn centers result in the change of Sn-O-Si bond angle and Sn-O bond length. The signals 1' and 2' represent one type of oxygen bond with four- or five-coordinate Me₃Sn groups. The signal 3' represents the other type of O-SnMe₃ sites. The complete assignments of the oxygen signals have not been made and both measurement and analysis are ongoing. The preliminary results from the ¹⁷O SSNMR indicate subtle changes in bond angles and length control the NMR parameters and change the spectrum.

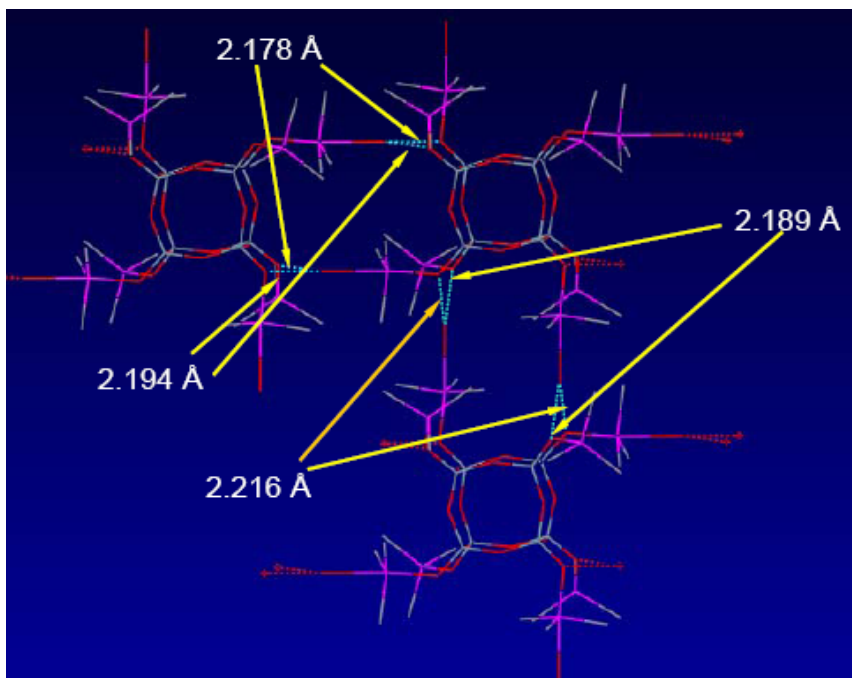


Figure 6 - 23 hydrogen bonds in hydrous tin cube

6.4 Conclusions

One of the most important achievements in this research project is to develop an efficient synthetic procedure to prepare the tin cube, $(\text{Me}_3\text{Sn}^*\text{O})_8\text{Si}_8\text{O}_{12}$, specifically labeled ^{17}O in the terminal Si-O-Sn positions. The results from mass spectra indicate that the labeled ^{17}O atoms are successfully incorporated into the trimethyltin analogue and TMS substituted building blocks. ^{119}Sn SSNMR spectra indicate the different coordinated environments of Sn atoms in the hydrated analogue change the spectra tremendously. The hydrogen-bonding interactions between water and tin groups affect the chemical shift of both ^{29}Si and ^{17}O SSNMR signals assigned to silicon atoms in the cube and Si- $^*\text{O}$ -Sn oxygen atoms. Different Si and O environments in the hydrous and anhydrous tin cube provide slightly different ^{29}Si and ^{17}O SSNMR spectra and all of these results are consistent with the crystal structure.

The TMS labeled tin cube and an embedded vanadium sample with labeled ^{17}O building block have been prepared and will be investigated further. This project is an ongoing collaboration with Dr. Edward Hagaman and Dr. Jian Jiao at ORNL. If ^{17}O SSNMR spectra do present good results to distinguish different V- ^{17}O -Si environments, the reactions of other metal chlorides such as TiCl_4 or WCl_6 will be investigated and ^{17}O SSNMR data collected.

Chapter 7

All capping $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ and its analogues

7.1 Introduction

Understanding the structure of a catalyst is one of the most important issues in catalysis science. For homogeneous catalysts, single crystal X-ray diffraction analysis is one of the most powerful techniques to determine the structure of the catalyst. In the case of heterogeneous catalysts, many of these materials are amorphous and their structures are difficult to determine. Solid state NMR, EXAFS, and XANES are techniques frequently used to determine the physical structure around metal centers (catalytic centers) in the heterogeneous catalysts. Preparing a model compound in which the coordination environment of the catalytic centers is similar to the heterogeneous catalysts is another method to indirectly probe how the catalytic reaction happens in these catalytic centers.

In our research, we developed a new synthetic methodology to obtain single site and site isolated vanadosilicate catalysts in Si_8O_{20} -based building block solids and these materials provide reasonable activity and high selectivity in the dehydration of isopropanol in the gas phase. For *surface* vanadyl and vanadium compounds, the catalytic centers attached to corners of each Si_8O_{20} building block are $\equiv\text{Si-O-VOCl}_2$ or $\equiv\text{Si-O-VCl}_3$ groups. Other nonactive corners contains different types of silane groups such as $(\equiv\text{Si-O})_2\text{SiCl}_2$, $(\equiv\text{Si-O})_3\text{SiCl}$,

and $(\text{Si-O})_2\text{SiMe}_3$. If a model compound which contains all the same functional groups at eight corners in each Si_8O_{20} building block can be synthesized successfully, it will be very helpful for us to understand the properties of the catalytic centers through a comparison of the catalytic reactions of the model compound and these heterogeneous materials.

These new model compounds, which contain same functional groups at eight corners around a Si_8O_{20} building block are called “all capping” molecular species. They should crystallize into solids that have long range ordered structures. Figure 7-1 shows some possible all capping building blocks (only one function group at one corner is shown) which are related to our research projects. Different main group halides such as SiCl_4 , Me_2SiCl_2 , and PCl_3 can be used to synthesize these materials which may be considered nonactive catalyst models. Different metal halides such as VOCl_3 , TiCl_4 and ZrCl_4 can be used as active catalyst models.

All of these new materials have multiple chloride ligands at each corner. These chloride ligands are very active and can be applied to numerous reactions as illustrated in Figure 7-2. The multiple functional groups at each corner are different than what is found on the tin cube build block for which each corner only has one active site. Therefore we call these materials “second generation building blocks”.

In this study, we describe a new synthetic methodology to prepare an all-capping compound. Octakis-(trichlorosiloxy)octasilsesquioxane, $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, has been successfully synthesized and its crystal structure has been obtained.

New Building Blocks

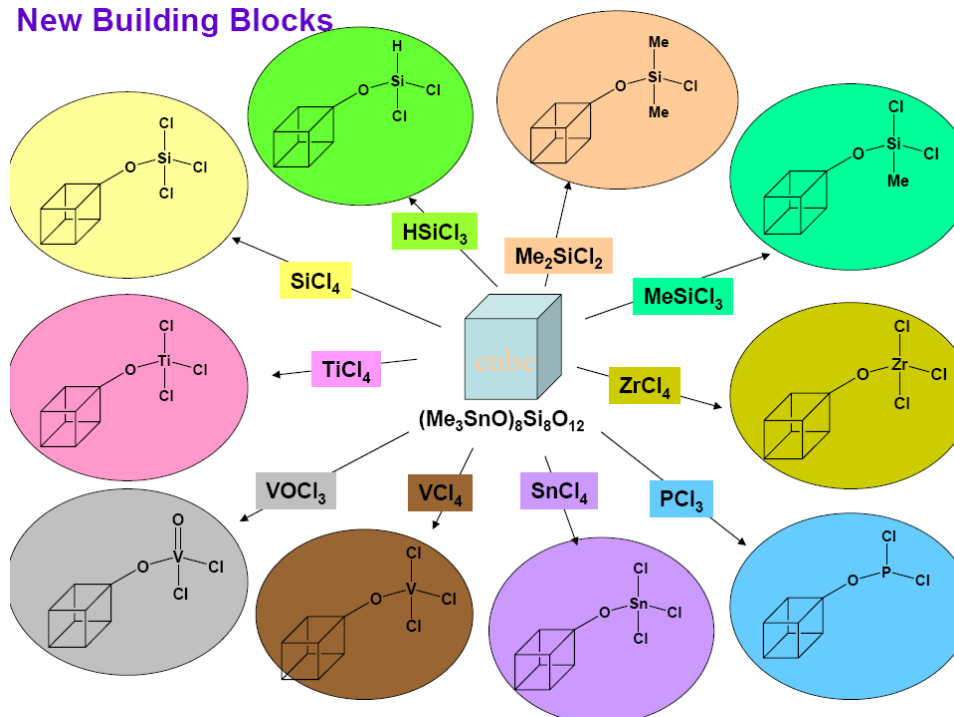


Figure 7 - 1 Different $R_8Si_8O_{20}$ new building blocks

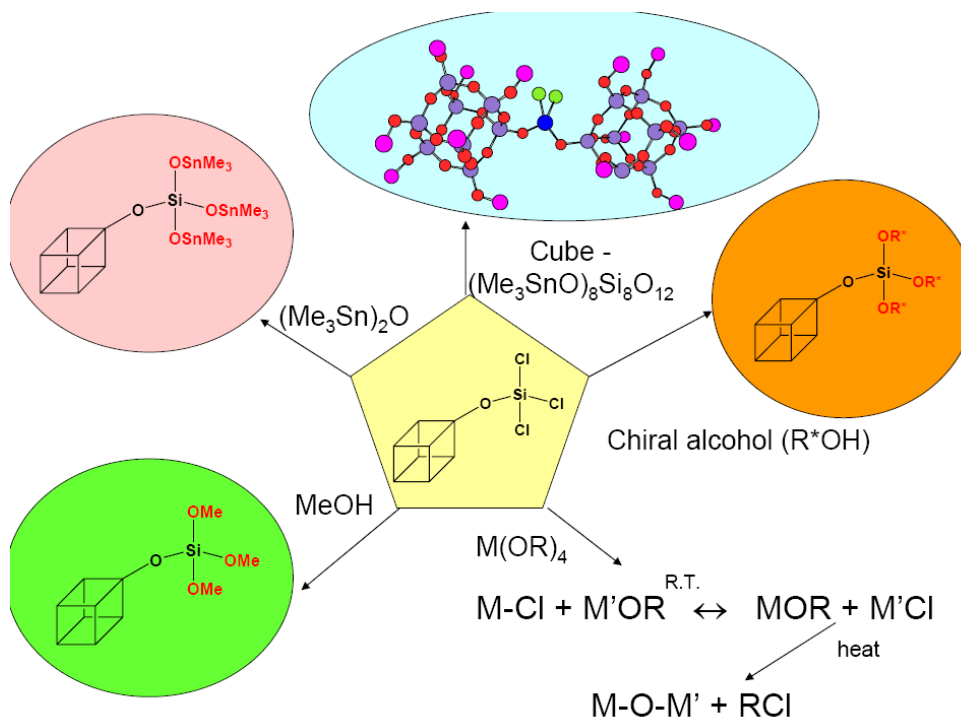


Figure 7 - 2 Possible applications of all capping compounds

Similar methodology to prepare all-capping VOCl_3 compound has been investigated and will also be described.

7.2 Experimental

The sources and purification of solvents (hexanes, methylene chloride, and diethyl ether) and reagents (SiCl_4 , and vanadyl trichloride) are the same as described in Chapter 3.2. All glassware was treated with TMSCl to remove hydroxyl groups on the glass surface. ^{29}Si solution NMR and ^{51}V and ^{29}Si solid state NMR spectra were also acquired as the same procedure which described in Chapter 3.2.

SiCl_4 (10.83g , 63.74 mmol) was delivered from a SiCl_4 solvent bulb to a Schlenk tube via vapor transfer followed by mixing with ~10ml CH_2Cl_2 and kept the Schlenk tube in a ice bath ($0-5^\circ\text{C}$). Anhydrous tin cube (2 g, 1.078 mmol) was dissolve in another Schlenk tube with 15 mL CH_2Cl_2 and transferred to a 20 mL syringe which was connected to a syringe pump. The tin cube solution in the syringe was slowly injected to the SiCl_4 solution drop by drop with a 10 mL/hr additional rate. Transparent solution without any precipitate was observed during the addition process. When tin cube solution was totally injected into the SiCl_4 solution (~ 1.5 hours), the solution was kept stirring for another 30 minutes then removed from the ice bath and stirred for another hour. The solvent and unreacted SiCl_4 liquid were removed through a vacuum line and collected in a trap after the reaction was complete. The reaction vessel was then heated at 80°C for 6 hours under vacuum to remove the volatile trimethyltin chloride

byproduct and obtained pure product $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$. This white, pure product is extremely air sensitive and has to be stored under nitrogen at all times.

Similar procedures have been used in the attempted preparations of the all capping VOCl_3 molecular species.

7.3 Results and Discussion

7.3.1 All-capping $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$

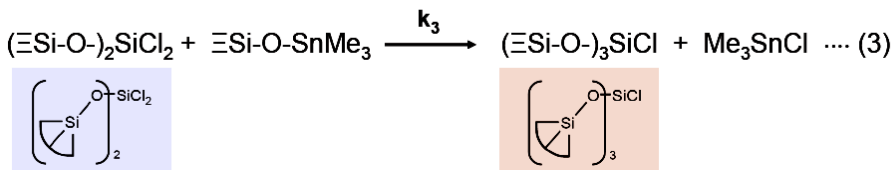
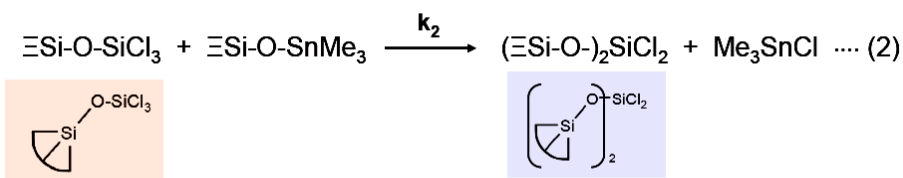
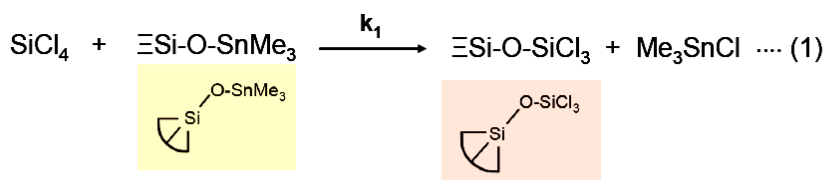
7.3.1-1 sample preparation

Previous procedures to prepare materials with a tin cube building block involved adding the reagents such as main group halide or metal halide into a tin cube solution. A new synthetic methodology used here is called an "inverse addition" which means tin cube building block is slowly added to an excess main group halide solution. This method provides an efficient way to control the reaction and avoids side reactions to occur.

Different reaction temperatures and additional rates to prepare this all-capping molecule have been investigated. A pure $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecular species can be obtained at lower reaction temperatures and slow additional rates. If the reaction temperature is higher than 30°C or the tin cube solution is injected to the SiCl_4 solution too fast (>20 ml/hr), a gel and cloudy solution will form and be observed during the additional process. Keeping the SiCl_4 solution in an ice bath is a suitable choice to start the reaction. These conditions avoid the vaporization of SiCl_4 at the top of the Schlenk tube where it may react with tin cube on the tip of the needle in the syringe and form gel compounds. How much

of an excess of SiCl_4 is another factor that must be determined in preparing this all-capping molecule. If the ratio of SiCl_4 to tin cube is lower than $\sim 32 : 1$ (or the ratio of SiCl_4 to trimethyltin groups is lower than $4 : 1$) some cross linked product such as linked cube dimmers will form.

The reaction equations of each trimethyltin group in a tin cube with SiCl_4 are shown in Equation 1 to 3 with different reaction rate k_1 , k_2 , and k_3 .



Our investigations into the preparation of the all-capping SiCl_4 molecule under different reaction conditions indicate the first chloride ligand in a SiCl_4 molecule reacts with a trimethyl tin group faster than the second chloride ligand and therefore only one-connected “capping” groups may be formed exclusively if conditions are correct. Therefore k_1 (one-connected silicate) must be larger than k_2 (two-connected silicate) at low temperatures. The differences between k_1 and

k_2 might become smaller at higher reaction temperatures. Under these conditions more two-connected silicates are formed and a gel is obtained. A kinetic study of these reactions will help us to understand the reactivity of chloride ligands when they react with different numbers of trimethyltin group. A knowledge of these reaction rates would help us define the conditions necessary to produce species or materials with single types of linking groups (one-, two-, and three-connected).

7.3.1-2 ^{29}Si NMR

Both solution and solid state ^{29}Si NMR data have been obtained for this new all-capping silicate molecule. The solution ^{29}Si NMR spectrum is shown in Figure 7-3. The peak at -113 ppm is assigned to the internal silicon atoms in the Si_8O_{20} cage and the peak at -45 ppm is assigned to the terminal SiCl_3 groups at each corner.

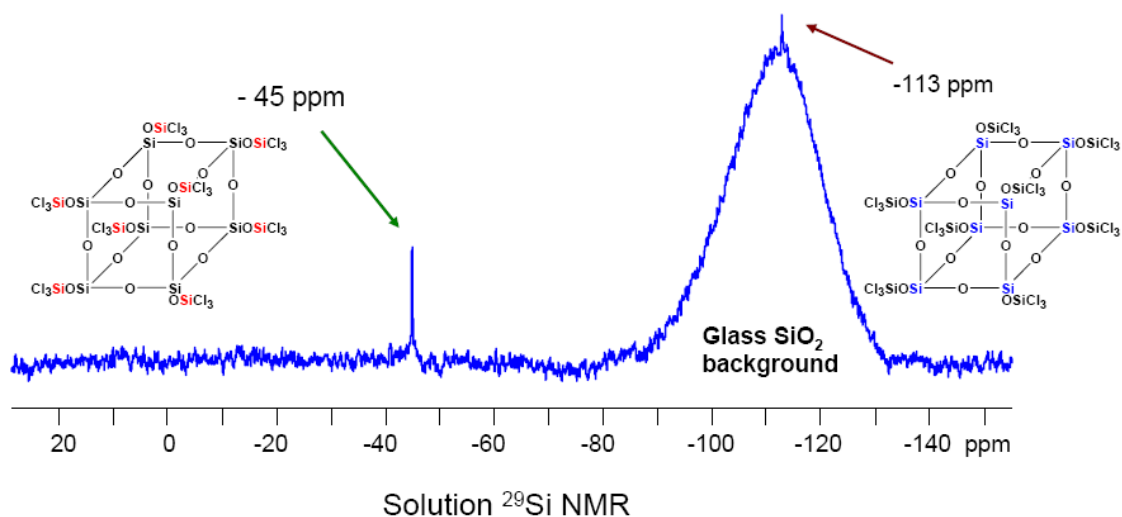


Figure 7 - 3 Solution ^{29}Si NMR of $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$

The broad signal at -100~-130 ppm region is derived from the NMR glass tube. The peak at -113 ppm and the glass SiO_2 background overlap and therefore it is difficult to obtain accurate relative integrations for the two peaks in the spectrum. But the spectrum clearly shows only two peaks and strongly supports assignment to the all-capping molecule.

For the ^{29}Si Solid State NMR spectrum (Figure 7-4), a sample is packed in a ZrO_2 rotor and therefore the spectrum does not contain the glass background signal. The chemical shifts of internal silicon atoms and SiCl_3 group are the same as observed in the solution ^{29}Si NMR. A theoretical integration value of these two peaks should be 1 to 1 but a ratio of 1 SiCl_3 group to 0.6 internal Si is observed in the spectrum due to the different relaxation times of the different types of silicons in this molecule. Adding different amounts of $\text{Cr}(\text{acac})_3$ might help to reduce the relaxation time and change the relative intensity of these peaks. This sample might be a good model to investigate how much $\text{Cr}(\text{acac})_3$ is needed to obtain the expected 1 to 1 ratio for the peaks in the spectrum.

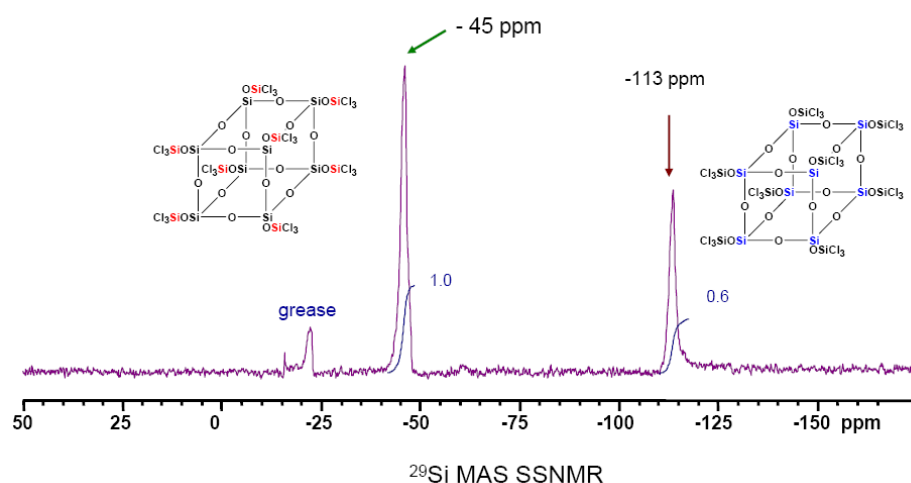


Figure 7 - 4 Solid state ^{29}Si NMR of $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$

7.3.1-3 Crystal structure

The $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule is extremely air sensitive and quite soluble in most organic solvents. Several different crystallization methodologies were investigated. Crystals were only obtained from concentrated hexanes solution. Other methods such as diffusing diethyl ether to CH_2Cl_2 solution with high concentrated $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ or two layers solution crystallization were not successful. The picture of crystals formed in the concentrated hexanes solution is shown in Figure 7-5.

A high symmetric crystal structure is shown in Figure 7-6 with a R-3 space group and a rhombohedral crystal system. All of the SiCl_3 groups are disordered and the Oak Ridge Thermal Ellipsoid Plot (ORTEP) structure is shown in Figure 7-7. Data collection and refinement parameters are summarized in Appendix B

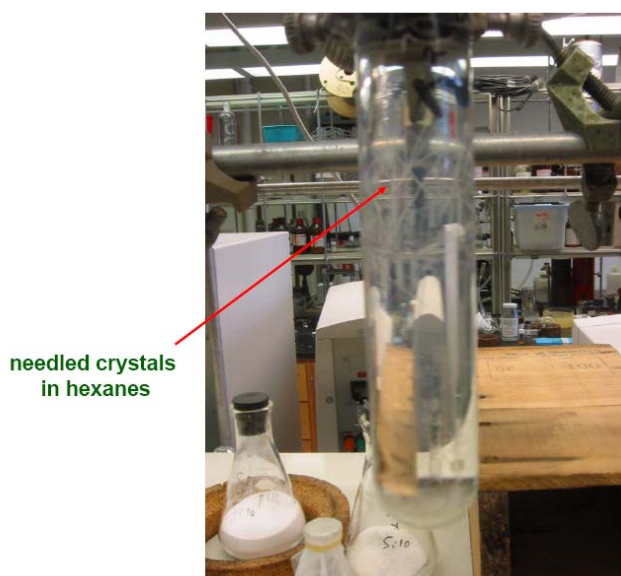


Figure 7 - 5 $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ crystals in a hexanes solution

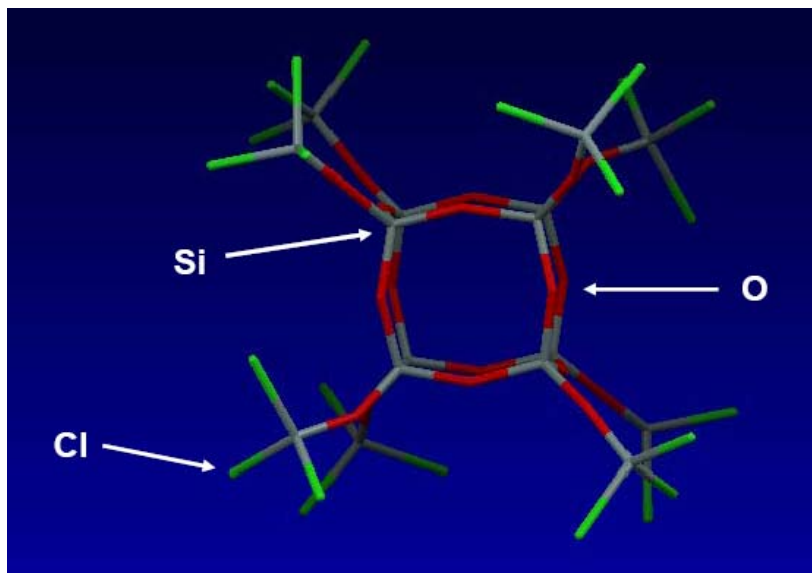


Figure 7 - 6 Crystal structures of $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$

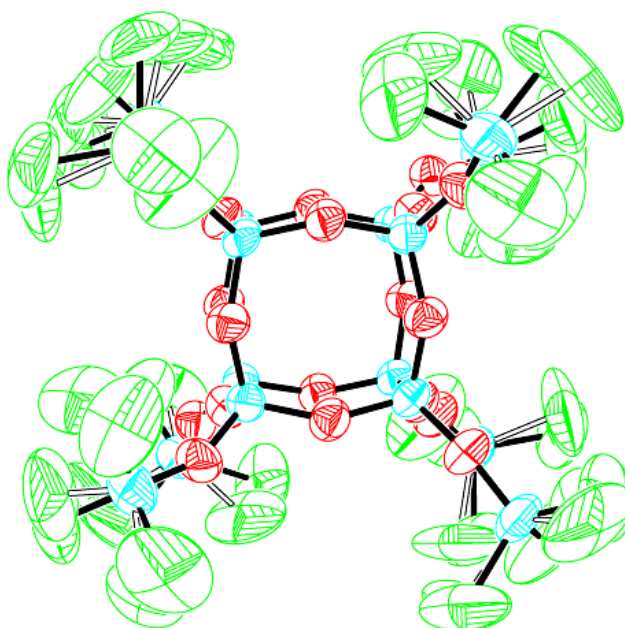


Figure 7 - 7 ORTEP of $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ with disordered SiCl_3 groups

The labeled ORTEP structure without chloride ligands is shown in Figure 7-8 and a whole crystal structure with a unique set of Si, O, Cl atom labels is shown in Figure 7-9 in order to provide a clearer view of this structure. The combination of C_3 rotation symmetry and inversion symmetry at the center of the Si_8O_{20} cube reduce the number of unique atoms in the structure to two $-\text{OSiCl}_3$ groups and two Si-O-Si edges in the cube.

Selected bond lengths and angles are summarized in Table 7-1. All of the Si-O bond lengths are around 1.55-1.56 Å except $\text{Si}_3\text{-O}_3$ and $\text{Si}_4\text{-O}_4$ which belong to O-SiCl₃ groups (~0.05 Å shorter). All of the internal Si-O-Si bond angles inside the Si_8O_{12} cage are around 148°. The external Si-OSiCl₃ bond angles may be

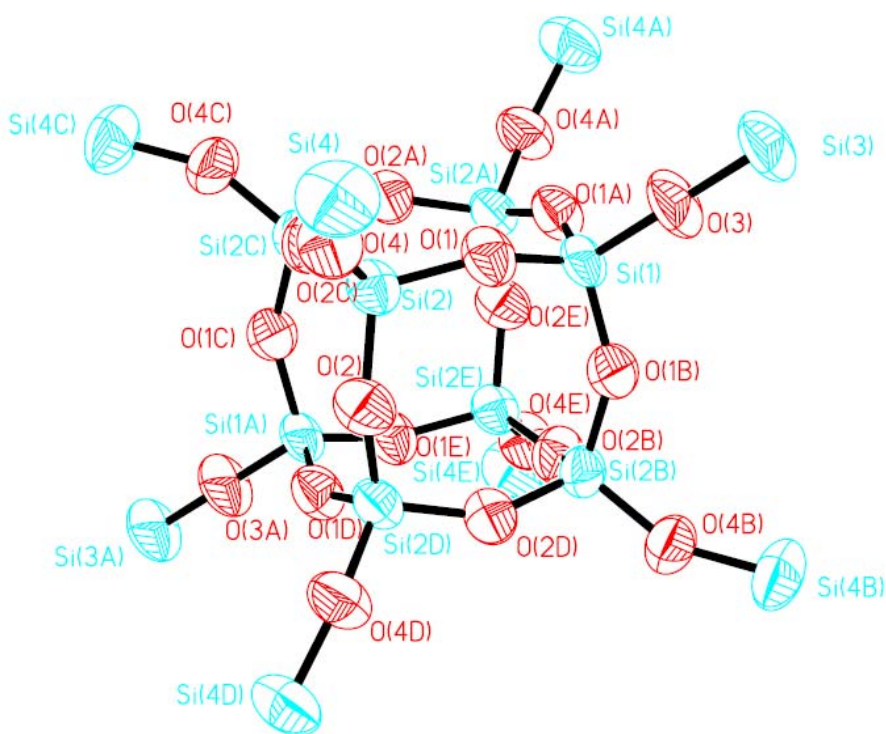


Figure 7 - 8 labeled ORTEP structure without chloride ligands

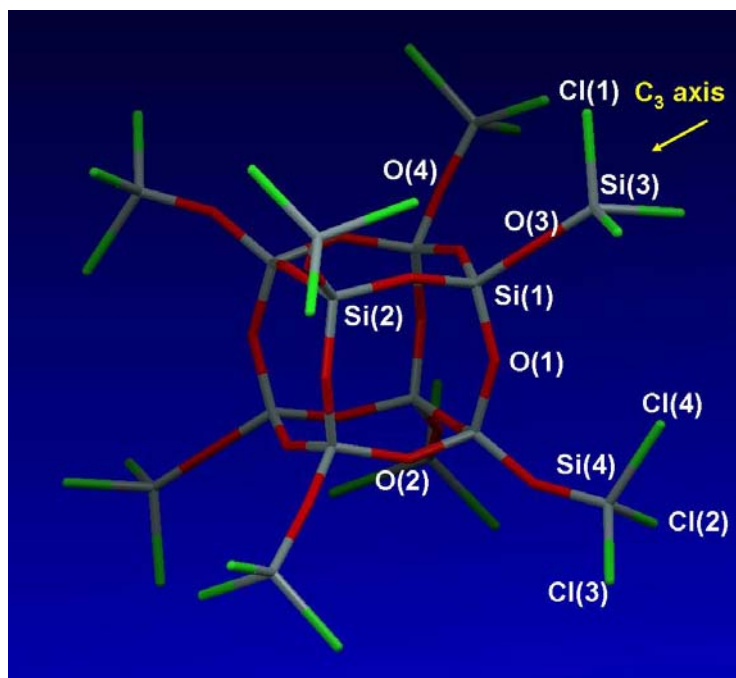


Figure 7 - 9 crystal structure with one set of Si, O, Cl labels

Table 7 - 1 Selected bond lengths and bond angles for $(\text{Cl}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$

	Bond length (Å)		Angle (°)
Si(1)-O(3)	1.549(5)	Si(1)-O(1)-Si(2)	148.2(2)
Si(1)-O(1)	1.556(3)	Si(2)#4-O(2)-Si(2)	148.3(3)
Si(1)-O(1)	1.556(3)	Si(3)-O(3)-Si(1)	180.000(1)
Si(2)-O(4)	1.553(4)	Si(4)-O(4)-Si(2)	155.6(3)
Si(2)-O(2)	1.560(4)	O(4)-Si(4)-Cl(2)	110.0(3)
Si(2)-O(1)	1.561(3)	O(4)-Si(4)-Cl(4)	109.4(5)
Si(3)-O(3)	1.496(5)	O(4)-Si(4)-Cl(3)	109.1(6)
Si(4)-O(4)	1.510(4)	O(3)-Si(3)-Cl(1)	118.0(4)
Si(4)-Cl(3)	1.861(12)	O(3)-Si(3)-Cl(1')#2	99.9(6)
Si(4)-Cl(4)	1.929(12)	Cl(1)-Si(3)-Cl(1')#2	111.6(10)
Si(4)-Cl(2)	1.996(7)	O(3)-Si(3)-Cl(1')#1	99.9(6)
Si(3)-Cl(1)	1.851(10)		

divided into two groups: six that are close to $\sim 155^\circ$ (eg. $\text{Si}_4\text{-O}_4\text{-Si}_2$) and two which are rigorously linear (eg. $\text{Si}_3\text{-O}_3\text{-Si}_1$). All of the SiO_4 units are basically tetrahedral with only slightly distortions observed. These results indicate SiCl_3 groups affect the external Si-O-Si bond angles and Si-O bond lengths significantly. The Si-O bonds from the O- SiCl_3 groups significantly shorter than Si-O bonds associated with the Si_8O_{20} cage.

Crystal structures for as $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$,⁷⁷ $(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, and $(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$ ⁷⁸ have been reported by J. Clark et al. and N. Aumer et al. The Si_8O_{20} cages attached with silyl groups at 8 corners (compounds $(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, and $(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$) are highly symmetric and each Si_4O_4 face has similar Si...Si distances (squared structure) without any elongated feature. The Si_8O_{20} cages attached with trimethyltin groups have different Si...Si distances. Two opposite Si_4O_4 faces are close to square while the other four Si_4O_4 faces connecting these are elongated with different Si-O-Si angles especially in the hydrous tin cube structure. Figure 7-10 to 7-14 illustrate different Si...Si distances and Si-O-Si angles in $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}\cdot 4\text{H}_2\text{O}$, $(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, and $(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$ molecules, respectively. The comparisons of Si...Si bond distances and Si-O-Si bond angles are summarized in Table 7-2.

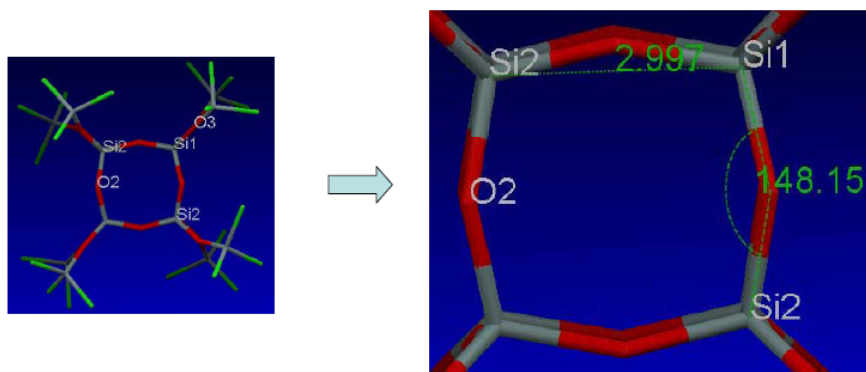


Figure 7 - 10 Si...Si bond distance and Si-O-Si bond angle in Si_8O_{20} cage of $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule

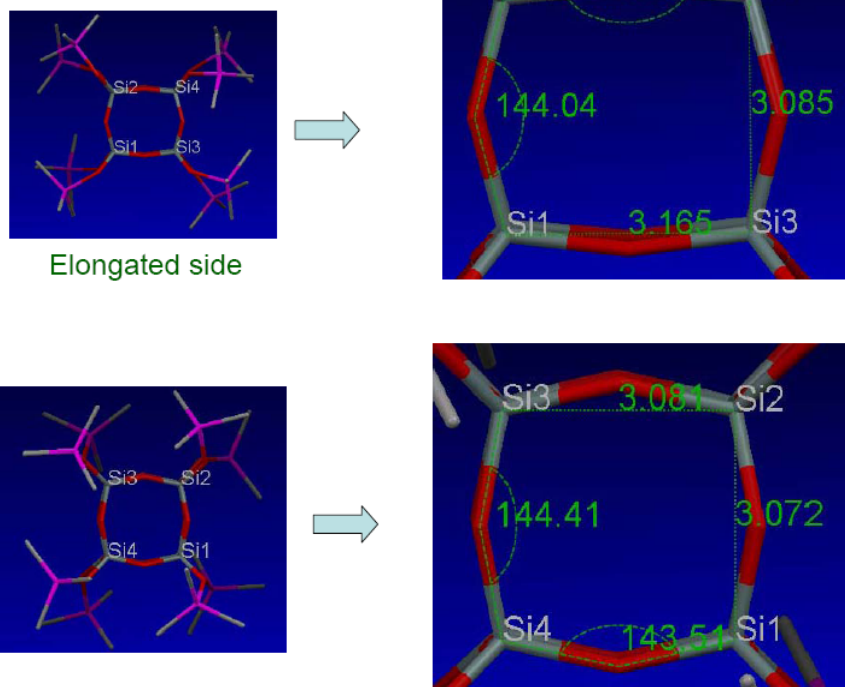
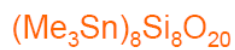
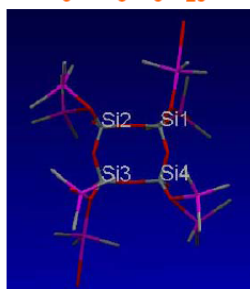


Figure 7 - 11 Si...Si bond distance and Si-O-Si bond angle in Si_8O_{20} cage of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ molecule



Elongated side

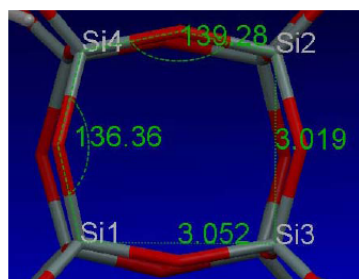
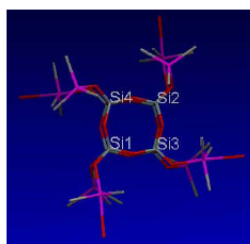
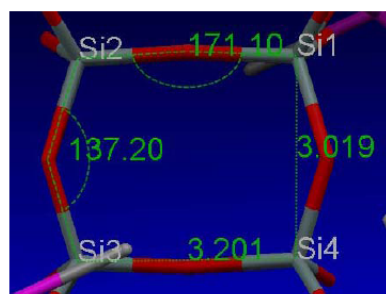
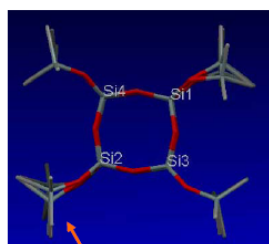


Figure 7 - 12 Si...Si bond distance and Si-O-Si bond angle in Si_8O_{20} cage of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ molecule



Disordered
 Me_3Si groups

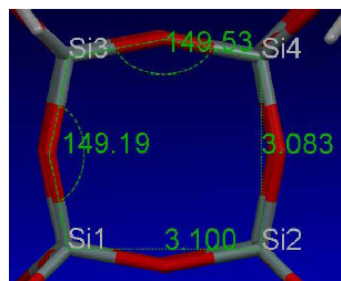
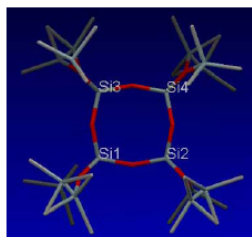
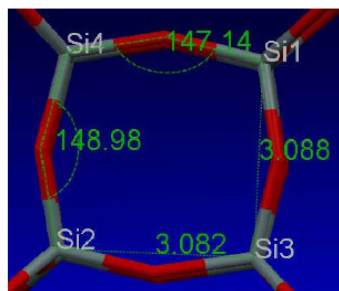


Figure 7 - 13 Si...Si bond distance and Si-O-Si bond angle in Si_8O_{20} cage of $(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule

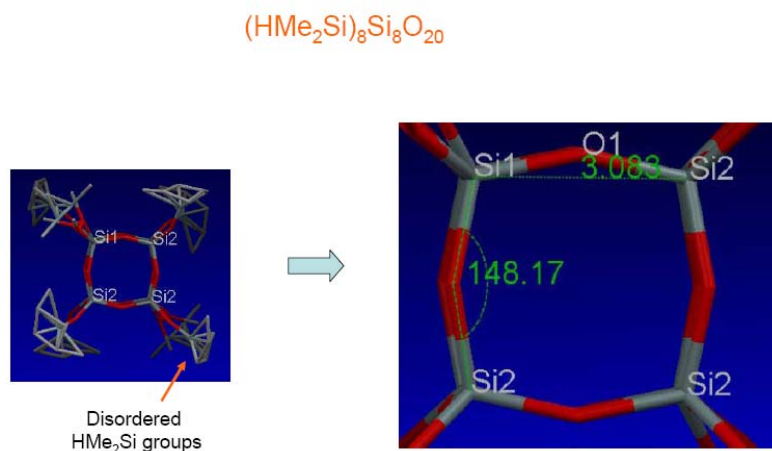


Figure 7 - 14 Si...Si bond distance and Si-O-Si bond angle in Si_8O_{20} cage of $(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule

Table 7 - 2 Si...Si bond distances and Si-O-Si bond angles of different Si_8O_{20} building blocks

	$(\text{SiCl}_3)_8\text{Si}_8\text{O}_{20}$	$(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$	$(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20} \cdot 4\text{H}_2\text{O}$	$(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$	$(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$
Crystal system	rhombohedral	triclinic	triclinic	triclinic	rhombohedral
Space group	R-3	P-1	P-1	P-1	R-3
Si...Si (Å) (enlogated Si_4O_4 face)	NA	3.165 3.085	3.201 3.019	NA	NA
Si...Si (Å) (squared Si_4O_4 face)	2.997	3.081 3.072	3.052 3.019	3,082 - 3.100	3.083
Si-O-Si angle ($^\circ$) (enlogated Si_4O_4 face)	NA	161.18 144.04	171.10 137.20	NA	NA
Si-O-Si angle ($^\circ$) (squared Si_4O_4 face)	148.15	144.41 143.51	139.28 136.36	147.14 – 149 .53	148.17
Reference	This work	J. Clark et al. ⁷⁷	J. Clark et al. ⁷⁷	N. Aumer at al. ⁷⁸	N. Aumer at al. ⁷⁸

The Si_8O_{20} building block carrying trimethyltin groups is distinctive by having elongated Si_8O_{20} cages in which four Si_4O_4 faces have longer Si...Si distances in the molecule. When the trimethyltin groups coordinate with water (hydrous tin cube molecule), the effect of the elongation is even more significant. The sphaerosilicates with silyl groups do not exhibit this elongated feature. Six Si_4O_4 faces in $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, $(\text{HMe}_2\text{Si})_8\text{Si}_8\text{O}_{20}$ and $(\text{Me}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecules are close to square with similar Si...Si distances and Si-O-Si bond angles. The $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule has the smallest Si_8O_{20} cage with the shortest average Si...Si distances observed among these molecules.⁷⁷ The significant elongated feature in the hydrous trimethyltin cube may be due to the presence of Lewis base and hydrogen-bonding interactions of stannylated sphaerosilicates and exocage oxygen atoms.

7.3.2 All-capping Vanadyl (V) complexes

We also attempted to synthesize the all-capping $(\text{VOCl}_2)_8\text{Si}_8\text{O}_{20}$ molecule by using a similar synthetic methodology. Unfortunately, the product always contained some two-connected vanadyl groups $((\equiv\text{Si}-\text{O})_2\text{VOCl})$. Several different reaction temperatures such as 25°C (room temp.), 0°C (ice bath), -10°C (ice bath with salts), -42 °C (CH_3CN with dry ice), and -77 °C (acetone with dry ice) have been studied. But ^{51}V SSNMR spectra from all of these reactions are similar (Figure 7-15) which indicate majority one-connected vanadyl and minority of two-connected vanadyl centers exist in the product simultaneous.

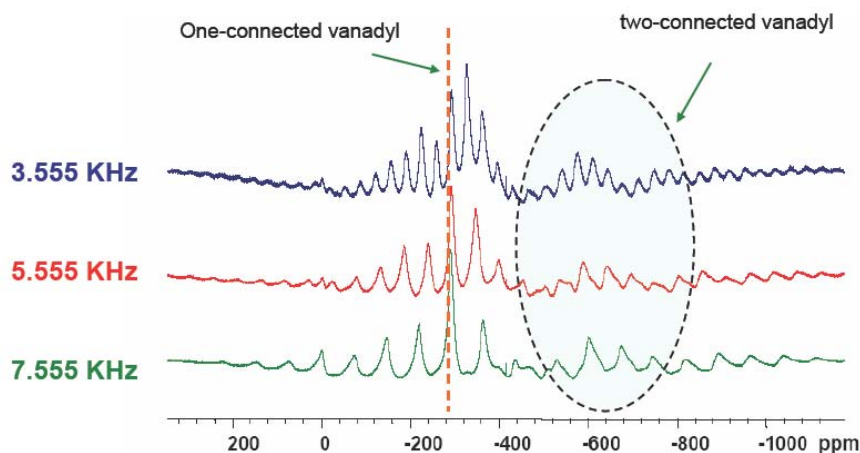


Figure 7 - 15 ^{51}V SSNMR spectra (-42°C synthesis)

The melting point of the VOCl_3 is -77°C . Therefore the lowest temperature we can study is above -77°C before VOCl_3 frozen in the solution. The first chloride ligands react with trimethyltin groups immediately and form Si-O-VOCl_2 group as soon as tin cube is added to the VOCl_3 solution. A small amount of two-connected $(\text{Si-O})_2\text{VOCl}$ groups appears to also form even though the reaction is conducted at low temperature. These results indicate the values of k_1 and k_2 for the first and second chloride ligand in VOCl_3 molecule react with trimethyltin groups are close no matter the reaction is run at what temperature.

A ^{29}Si SSNMR spectrum was collected for a sample of the capping vanadyl which was synthesized at -77°C . Only one signal appears at ca. -110 ppm in the ^{29}Si SSNMR spectrum which represents different Si-O-V groups and no residual trimethyltin groups are observed (Figure 7-16). This result indicates

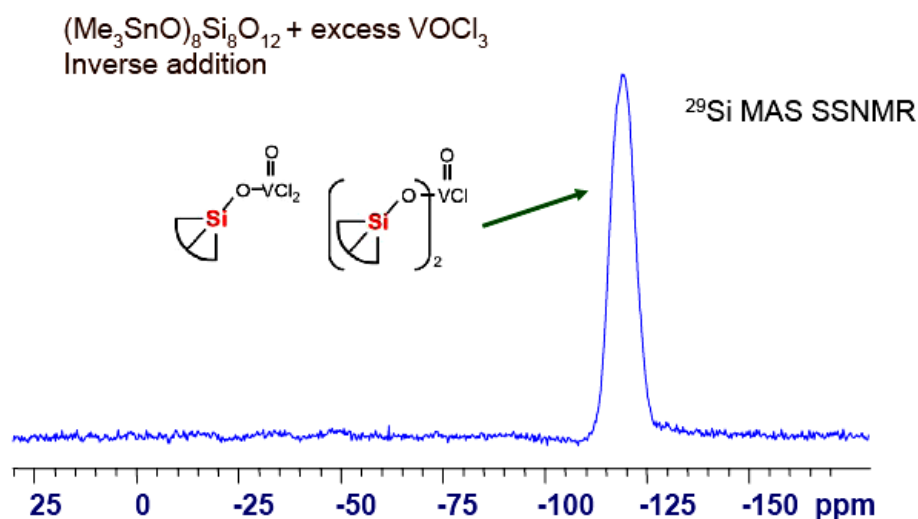


Figure 7 - 16 ^{29}Si SSNMR spectrum

that all trimethyltin groups can react with VOCl_3 and form one or two-connected vanadyl groups even though the reaction temperature is low. Although the targeted all-capping $(\text{VOCl}_2\text{O})_8\text{Si}_8\text{O}_{12}$ molecule was not obtained in pure form, these materials with a majority of one-connected vanadyl center can still be applied to catalytic reactions and their activities studied.

7.4 Conclusion

An all capping $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule has been synthesized successfully. A new synthetic methodology which we call “inverse addition sequence” can be used to control the reaction rate efficiently when $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ reacts with excess SiCl_4 at low temperature. The multiple active sites of each SiCl_3 group at each corner in the Si_8O_{20} cage allow this compound to be viewed as another type

of building block which we call the “second generation building block”. The crystal structure of this extremely air sensitive molecule has been obtained. The new molecule is a very good model compound for the Si_8O_{12} building block family and has applications to future neutron and X-ray scattering research.

Investigations into the preparation of different types of all-capping metal halides (VOCl_3 , VCl_4 , or TiCl_4) molecules are still ongoing. Changing the reaction temperature and the stoichiometries of reactants are two major factors that might help us to achieve the goal in the future.

Chapter 8

Conclusions and Future work

8.1 Conclusions

A new synthetic methodology to synthesize single-site and site-isolated catalysts via a building block approach has been successfully developed. The preliminary results of using vanadyl and vanadium (IV) building block materials in gas phase catalytic dehydration of isopropanol are very encouraging from the standpoint of product selectivity. The conclusions from the work described in this thesis are divided into three parts: synthesis, characterization, and application of new building block catalysts and are described as follows.

8.1.1 Synthesis

An efficient method to separate large scale mixtures of $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ (20~30 g), which requires no more than sublimation, washing the mixture with hexanes, and crystallization, provides us with a rapid way to obtain a large amount of pure sphaerosilicate from the mixture in a short amount of time. A one-pot procedure for preparing the critical stannylated building block, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ not only optimizes the large scale synthesis of $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$, but also lessens the contact with toxic tin byproducts and shortens the reaction time for the synthesis. Recycling trimethyltin hydride, Me_3SnH , and successfully converting it to trimethyltin peroxide in high yield are important achievements in

this research project. Trimethyltin peroxide, Me_3SnOOH , can also be used to synthesize the trimethyltin-ether, $(\text{Me}_3\text{Sn})_2\text{O}$.

An efficient methodology to obtain high yields and large amounts of the “tin cube”, $(\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{20}$ is an important first step in constructing a new generation catalyst utilizing the Si_8O_{20} cubic building block. “Embedded” and “surface” vanadyl and vanadium materials which were described in chapter 3 are successfully prepared via different sequences of linking reagent additions with different stoichiometries. The stoichiometric ratio to obtain fully embedded three-connected vanadyl and four-connected vanadium catalysts under a mild condition (reaction temperature lower than 60°C) is a ratio of Cl to Sn of no more than 3 to 8 (1 VOCl_3 : 1 tin-cube or 0.75 VCl_4 : 1 tin-cube). If the ratio of Cl to Sn is higher than 3 to 8, some of the chlorides from VOCl_3 or VCl_4 will not react completely with the trimethyltin groups and will remain in the product. Furthermore, some vanadyl centers will be less than three-connected or some vanadium centers less than four-connected in the matrix.

For the “surface” catalysts, one-connected vanadyl or vanadium centers exist in the silicate matrix with lots of VOCl_2 or VCl_3 groups around the surface. Therefore surface compounds are much more air sensitive than the embedded compounds. The vanadium weight percentage in the surface compounds can be adjusted by preparing different types of silicate platforms which contain a different amount of residual trimethyl groups around the silicate matrices.

Successfully synthesizing labeled ^{17}O tin-cube provides us with the opportunity to use ^{17}O SSNMR to identify the coordination environment near the

catalytic centers which we can not observe from other SSNMR nuclei. Reacting a limiting amount of labeled water with one equivalent of methyl lithium to obtain labeled Li^*OH is the key reaction in this new synthetic methodology. The same procedure also can be used to synthesize unlabeled tin-cube.

The slow addition methodology to synthesize all-capping Si molecular species, $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$, not only provides an important new building block synthon but also provides information about the reaction rates of chloride ligands in each SiCl_4 molecule as they react with trimethyltin groups. The ability to cleanly prepare the trichlorosiloxy analogue indicates that the first chloride reacts much faster than the other chloride ligands. We have also attempted to synthesize all-capping vanadyl and vanadium molecule species utilizing the same procedure but have not succeeded yet. Mixtures of multiple vanadyl or vanadium sites have always been formed in the products irrespective of the reaction temperature. This synthetic methodology may be used to prepare second generation building blocks which have multiple functional groups on each corner if the differences in the reactivities of the chloride ligands are large.

8.1.2 Characterization

8.1.2-1 Gravimetric analysis

Gravimetric analysis is one of the simplest and fastest methods to obtain the information of average connectivities of the linking groups by tracking the weight change due to the loss of trimethyltin chloride. The average molecular formula derived from different stoichiometric reactions provides useful weight

percentage information for each sample. Another method to determine the vanadium weight percentage is atomic absorption and atomic emission spectroscopy. Atomic absorption and emission measurements are consistent with the results which were obtained from gravimetric analyses. For the embedded materials, the vanadium weight percentage can be adjusted by using different amount of VOCl_3 or VCl_4 in the first dose reaction. For the surface materials, different types of silicate platform with different amount of residual trimethyltin groups will determine the final vanadium weight percentage.

8.1.2-2 Multinuclear Solid State NMR

Solid state NMR spectroscopy is one of the most powerful methods of structure determination in the solid state. For the embedded materials, ^{29}Si SSNMR spectra provide information about the silicate environment in each vanadyl sample. The chemical shifts of Si-O-Sn, Si-O-Si, and Si-O-V groups are slightly different and can be used to understand whether trimethyltin groups still remain in the product. For second dose reactions, a mixture of differently connected silicate centers exist in the sample when SiCl_4 or Me_2SiCl_2 are used as linking reagents. For the third dose (TMSCl) reaction, trimethyl silyl groups were shown to completely replace trimethyl tin groups in the ^{29}Si SSNMR spectra.

For ^{51}V SSNMR spectra, identification of the isotropic peak requires collecting spectra using different spinning rates. For the embedded samples, higher spinning rates are needed to identify two and three-connected vanadyl centers. The low vanadium weight percentage embedded samples also need a

longer collection times (about 12~24 hours) to obtain good quality spectra. The surface vanadyl samples contain higher vanadium loadings and are easier to obtain clear ^{51}V SSNMR spectra for identifying isotropic peaks. Three-connected vanadyl centers were observed in the embedded vanadyl samples. One-connected vanadyl centers were observed in the surface vanadyl samples. These ^{51}V SSNMR spectra results are consistent with the design goals of the project and prove that single-site vanadyl materials were successfully synthesized via sequential additional techniques.

8.1.2-3 Mass spectra and ^{17}O SSNMR

Mass spectra of enriched ^{17}O samples of the tin cube and TMS cube proved that the ^{17}O label had been successfully incorporated into the final product. ^{17}O SSNMR spectra of tetrahydrate and anhydrous labeled building block materials indicate the hydrogen bonds in the hydrate change the ^{17}O chemical shift slightly. ^{119}Sn SSNMR spectra of the hydrous and anhydrous crystalline tin cube prove four and five coordinated tin center did change the chemical shifts tremendously. The different chemical shifts in these materials indicate the different Si and Sn environments between hydrous and anhydrous tin cube which are consistent with different Si-O-Sn bond angles and Sn-O bond lengths in the crystal structure.

8.1.2-4 Surface area measurements

The results of surface area measurements indicate the one-dose reaction for preparing embedded vanadyl or vanadium (+4) samples only form oligomeric species with low surface areas. Surface areas increase after using SiCl_4 or Me_2SiCl_2 as second dose reagents. This observation is consistent with the aggregation of small oligomeric species to form porous materials. For the embedded samples, the surface area can be adjusted by adding different stoichiometric amounts of SiCl_4 or Me_2SiCl_2 in the second dose reaction. Longer reaction times and higher reaction temperatures produce materials with higher surface areas. For the surface samples, different silicate platforms have different surface areas. After reacting VOCl_3 or VCl_4 with these silicate platforms, surface areas do not change significantly. This observation is consistent with a model in which one-connected surface vanadyl and vanadium samples are only on the silicate surface and do not change the material's porosity.

8.1.2-5 XANES and EXAFS

XANES data can be used to determine the oxidation state and the geometry of the metal center in a sample that exhibits no longer range order. The differences in the edge features of embedded and surface samples in XANES spectra indicate the chloride ligands coordinated to the vanadium centers have a dramatic effect on the absorption edge. EXAFS spectra of vanadyl and vanadium samples can provide information on interatomic distances as well as average coordination numbers for vanadium in each material. For the

embedded vanadyl sample, a feature corresponding to V-O single bonds was observed in the spectrum with a coordination number close to three. For the embedded vanadium (IV) sample, a similar V-O single bond feature was also observed with a coordination number close to four. No evidence for a V-Cl peak appeared in these spectra. These results indicate all chloride ligands react with trimethyltin groups and form fully embedded three-connected vanadyl and four-connected vanadium compounds.

For surface vanadyl samples, features corresponding to one V=O double bond, one V-O single bond and two V-Cl single bonds were observed in the spectra. For the surface vanadium sample, features corresponding to one V-O single bond and three V-Cl single bonds were observed in the spectra. The results of the EXAFS data analysis are consistent with the SSNMR data and strongly support our original goal of developing a methodology in which materials containing different vanadyl or vanadium centers with different connectivities can be synthesized by design.

8.1.2-6 Single X-ray crystal structures

The single X-ray crystal structure of Me_3SnOOH indicates that one water molecule is bound to the tin center and forms a five-coordinate environment. The water oxygen that coordinates to the tin atom has a longer bond distance than the Sn-peroxide distance.

Obtaining the $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ crystal structure is another important achievement in the work described here. This compound is extremely air

sensitive and easily decomposes if exposed to water. Therefore it is extremely hard to obtain crystals of this molecule. The highly symmetric $(\text{Cl}_3\text{Si})_8\text{Si}_8\text{O}_{20}$ molecule is not like the hydrous or anhydrous tin-cube where the cube Si_8O_{12} core is elongated along an axis through opposite Si_4O_4 faces. The Si-O, Si-Cl bond distances and Si-O-Si, Si-O-Cl bond angles provide useful information for future studies involving neutron and x-ray scattering. This compound also can be used as a second generation building block since the three chloride ligands in each corner are all reactive toward linking reactions with a broad class of reagents.

8.1.3 Application: Catalysis

The preliminary results of catalytic reactions show that both embedded and surface vanadium materials are good solid-acid catalysts. Highly selectivity is the most encouraging results observed so far. The good thermal stability of these catalysts also indicates the robust building blocks provide a good environment to stabilize the catalytic centers. Investigation of the catalytic activities of these materials is ongoing and is currently focused on determining their activation energies.

8.2 Future work

8.2.1 $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ building block

An efficient methodology to separate $\text{H}_8\text{Si}_8\text{O}_{12}$ and $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ provides a potential opportunity to use pure $\text{H}_{10}\text{Si}_{10}\text{O}_{15}$ as a new building block precursor.

Similar synthetic methodologies can be applied to the synthesis of $(\text{Me}_3\text{SnO})_{10}\text{Si}_{10}\text{O}_{15}$. Ten trimethyltin groups in each building block provide more chances to react with more metal halides. The materials made from $(\text{Me}_3\text{SnO})_{10}\text{Si}_{10}\text{O}_{15}$ might have a higher surface area or higher porosity. Using the same procedure to synthesize embedded and surface materials from the $(\text{Me}_3\text{SnO})_{10}\text{Si}_{10}\text{O}_{15}$ building block will be of interest. The relation between surface area and catalytic activity could be studied by comparing properties of Si_8 and Si_{10} derived materials.

8.2.2 Different connectivities between embedded and surface materials

Embedded and surface vanadyl and vanadium materials have been synthesized successfully. However, single site two-connected vanadyl or three-connected vanadium (+4) materials are more difficult to obtain. Changing the reaction time or temperature are two parameters to probe while attempting to achieve this goal. A study of the reaction rates between each chloride ligand and trimethyl tin groups during the synthetic processes will provide insight into the type of connectivity achieved under a given set of conditions. As soon as the other vanadyl or vanadium sites can be synthesized, the study of different catalytic reactions with a series of single-site vanadyl or vanadium samples with varying connectivity will be possible.

8.2.3 Improvement of EXAFS data collection at NSLS

Obtaining good quality EXAFS data relies on careful sample preparation. Besides this, we notice that different beam lines (X19A verse X18B) at NSLS provide data of different quality. At X18B (unfocused beam), more concentrated samples (weight percentage > than 3~4%) are required when a PIPS detector is used. For X19A (focused beam), low concentration samples (weight percentage < 3%) provide better spectra when the Ge detector is used. These observations provide useful information and will help us to prepare samples with proper concentrations for the beam time used.

The relation between edge jump and weight percentage is another interesting project that is worth more investigation. If the weight percentage can be determined from the edge jump of the XANES spectra accurately, it will provide more information to compare with the results from gravimetric analysis.

8.2.4 ^{17}O building block application

Our investigations of ^{17}O labeled building blocks are still ongoing in collaboration with Dr. Edward Hagaman and Dr. Jian Jiao at ORNL. The three-connected embedded vanadyl sample was prepared and analyzed but the low concentrated vanadyl weight percentage (3.5%) in this sample made it hard to observe clear spectra to identify the $\text{V-}^{17}\text{O-Si}$ environment. High weight percentage surface vanadyl samples or all capping vanadyl molecular species with labeled ^{17}O building block will be prepared in the future. If ^{17}O SSNMR spectra do present good results to distinguish different $\text{V-}^{17}\text{O-Si}$ environments,

the reactions of other metal chlorides such as TiCl_4 or WCl_6 will be investigated and ^{17}O SSNMR data collected.

8.2.5 Next generation catalysts

Single site catalysts should provide higher selectivities in the reactions that they catalyze. But the activity of different types of vanadyl and vanadium samples has not been determined yet. Several different protocols to test the catalysts, such as changing the flow rate and temperature profiles, are still ongoing. A more accurate response factor for each catalytic reaction from the GC should also be investigated. Determining the reaction rate by using different flow rates as a function of temperature will provide the information to derive the activation energy. Determining the activation energies and the turnover numbers can be used to decide which types of vanadyl or vanadium samples exhibit higher activity.

Different catalytic reactions such as oxidation, epoxidation, and olefination reactions can be tested with different types of the vanadium samples in the gas phase catalytic micro-reactor. In the future, liquid phase reactions such as transesterification and esterification can also be investigated. A variety of investigations of these new generation catalysts will be very important. We believe single site and site- isolated, robust catalysts in the Si_8O_{20} -based building block are representative of “next generation” catalysts of the future.

References

1. Gregory, S., John Roebuck: 18th century entrepreneur. *Chemical Engineer (Rugby, United Kingdom)* **1987**, 443, 28-31.
2. Blair, J.; Gibb, J. G., Efficiency of platinum gauzes in the manufacture of nitric acid. A method for determining the frequency of pickling. *Platinum Metals Review* **1967**, 11, (3), 100-3.
3. Corma, A., From Microporous to Mesoporous Molecular Sieve Materials and Their Use in Catalysis. *Chemical Reviews (Washington, D. C.)* **1997**, 97, (6), 2373-419.
4. Feher, F. J.; Weller, K. J., Phosphorus(III)-containing silicates via a new aprotic building-block approach to multicomponent silicates. *Chem. Mater.* **1994**, 6, (1), 7-9.
5. Newville, M., IFEFFIT: interactive XAFS analysis and FEFF fitting. *Journal of Synchrotron Radiation* **2001**, 8, (2), 322-24.
6. Ravel, B.; Newville, M., ATHENA, ARTEMIS, HEPHAESTUS: data analysis for X-ray absorption spectroscopy using IFEFFIT. *J Synchrotron Radiat FIELD Full Journal Title:Journal of synchrotron radiation* **2005**, 12, (Pt 4), 537-41.
7. Feher, F. J.; Soulivong, D.; Eklund, A. G., Controlled cleavage of R₈Si₈O₁₂ frameworks: a revolutionary new method for manufacturing precursors to hybrid inorganic-organic materials. *Chem. Commun.* **1998**, (3), 399-400.
8. Feher, F. J.; Wyndham, K. D., Amine and ester-substituted silsesquioxanes: synthesis, characterization and use as a core for starburst dendrimers. *Chem. Commun.* **1998**, (3), 323-24.

9. Murfee, H. J.; Thoms, T. P.; Greaves, J.; Hong, B., New metallodendrimers containing an octakis(diphenylphosphino)-functionalized silsesquioxane core and ruthenium(II)-based chromophores. *Inorg. Chem.* **2000**, 39, (23), 5209-17.
10. Provatas, A.; Luft, M.; Mu, J. C.; White, A. H.; Matison, J. G., Silsesquioxanes: Part I: A key intermediate in the building of molecular composite materials. *J. Organomet. Chem.* **1998**, 565, (1-2), 159-64.
11. Agaskar, P. A., New synthetic route to the hydridospherosiloxanes Oh-H₈Si₈O₁₂ and D_{5h}-H₁₀Si₁₀O₁₅. *Inorg. Chem.* **1991**, 30, (13), 2707-8.
12. Buergy, H.; Calzaferri, G., Separation of the oligomeric silsesquioxanes (HSiO_{3/2})₈₋₁₈ by size-exclusion chromatography. *J. Chromatogr.* **1990**, 507, 481-6.
13. Marcolli, C.; Laine, P.; Buehler, R.; Calzaferri, G.; Tomkinson, J., Vibrations of H₈Si₈O₁₂, D₈Si₈O₁₂, and H₁₀Si₁₀O₁₅ as determined by INS, IR, and Raman Experiments. *J. Phys. Chem. B* **1997**, 101, (7), 1171-79.
14. Feher, F. J.; Weller, K. J., Synthesis and characterization of labile spherosilicates: [(Me₃SnO)₈Si₈O₁₂] and [(Me₄SbO)₈Si₈O₁₂]. *Inorg. Chem.* **1991**, 30, (5), 880-2.
15. Luijten, J. G. A.; van der Kerk, G. J. M., Organotin compounds. XIX. Preparation of some organotin compounds. with heterocyclic nitrogen tin bonds. *Recueil des Travaux Chimiques des Pays-Bas* **1963**, 82, (11), 1181-8.
16. Armitage, D. A.; Robinson, R. N.; Abel, E. W., Bis(trimethyltin) oxide (hexamethyldistannoxane). *Inorg. Synth.* **1977**, 17, 181-3.

17. Dannley, R. L.; Aue, W. A., The synthesis and properties of tin hydroperoxides. *J. Org. Chem.* **1965**, 30, (11), 3845-8.
18. Brown, J. M.; Chapman, A. C.; Harper, R.; Mowthorpe, D. J.; Davies, A. G.; Smith, P. J., Characterization of triorganotin hydroxides and of bis(triorganotin) oxides by infrared and Moessbauer spectroscopy. *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999)* **1972**, (3), 338-41.
19. Lefferts, J. L.; Molloy, K. C.; Hossain, M. B.; Van der Helm, D.; Zuckerman, J. J., The crystal and molecular structure of trimethyltin(IV) chloride, a chlorine-bridged, linear polymer. *J. Organomet. Chem.* **1982**, 240, (4), 349-61.
20. Tudela, D.; Gutierrez-Puebla, E.; Monge, A., Crystal structure of triphenyltin fluoride. *Journal of the Chemical Society, Dalton Transactions: Inorganic Chemistry (1972-1999)* **1992**, (6), 1069-71.
21. Kasai, N.; Yasuda, K.; Okawara, R., The crystal structure of trimethyltin hydroxide. *J. Organomet. Chem.* **1965**, 3, (2), 172-3.
22. Blaschette, A.; Wieland, E.; Jones, P. G.; Hippel, I., Polysulfonylamines. XXXVIII. Preparation and solid state structure of bis(trimethyltin)dimesylamide hydroxide $[\text{Me}_3\text{Sn}\{\text{m}-(\text{MeSO}_2)_2\text{N}\}\text{Me}_3\text{Sn}(\text{m-OH})]_n$. *J. Organomet. Chem.* **1993**, 445, (1-2), 55-9.
23. Glidewell, C.; Liles, D. C., The crystal and molecular structures of hydroxotriphenyltin(IV) and hydroxotriphenyllead(IV). *Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry* **1978**, B34, (1), 129-34.

24. Deacon, G. B.; Lawrenz, E.; Nelson, K. T.; Tiekink, E. R. T., Crystal structure of polymeric triethyltin hydroxide. *Main Group Met. Chem.* **1993**, 16, (5), 265-9.
25. Glidewell, C.; Liles, D. C., The crystal and molecular structure of oxobis[triphenylgermanium(IV)]. *Acta Crystallographica, Section B: Structural Crystallography and Crystal Chemistry* **1978**, B34, (1), 119-24.
26. Hess, C.; Drake, I. J.; Hoefelmeyer, J. D.; Tilley, T. D.; Bell, A. T., Partial Oxidation of Methanol Over Highly Dispersed Vanadia Supported on Silica SBA-15. *Catalysis Letters* **2005**, 105, (1-2), 1-8.
27. Liu, Y.-M.; Feng, W.-L.; Li, T.-C.; He, H.-Y.; Dai, W.-L.; Huang, W.; Cao, Y.; Fan, K.-N., Structure and catalytic properties of vanadium oxide supported on mesocellulose silica foams (MCF) for the oxidative dehydrogenation of propane to propylene. *Journal of Catalysis* **2006**, 239, (1), 125-36.
28. Lopez Nieto, J. M.; Concepcion, P.; Dejoz, A.; Knozinger, H.; Melo, F.; Vazquez, M. I., Selective oxidation of n-butane and butenes over vanadium-containing catalysts. *Journal of Catalysis* **2000**, 189, (1), 147-57.
29. Lopez Nieto, J. M.; Concepcion, P.; Dejoz, A.; Melo, F.; Knozinger, H.; Vazquez, M. I., Oxidative dehydrogenation of n-butane and 1-butene on undoped and K-doped VOx/Al₂O₃ catalysts. *Catalysis Today* **2000**, 61, (1-4), 361-67.
30. Nguyen, L. D.; Lorient, S.; Launay, H.; Pigamo, A.; Dubois, J. L.; Millet, J. M. M., Study of new catalysts based on vanadium oxide supported on mesoporous silica for the partial oxidation of methane to formaldehyde: Catalytic properties and reaction mechanism. *Journal of Catalysis* **2006**, 237, (1), 38-48.

31. Nieto, J. M. L., Microporous and mesoporous materials with isolated vanadium species as selective catalysts in the gas phase oxidation reactions. *Topics in Catalysis* **2001**, 15, (2-4), 189-94.
32. Panizza, M.; Resini, C.; Busca, G.; Fernandez Lopez, E.; Sanchez Escribano, V., A study of the oxidative dehydrogenation of cyclohexane over oxide catalysts. *Catalysis Letters* **2003**, 89, (3-4), 199-205.
33. Pyatnitskii, Y. I.; Raevskaya, L. N.; Bostan, A. I.; Borisenko, M. V., Comparative Effectiveness of Oxygen and Nitrous Oxide in the Partial Oxidation of Methane on V₂O₅/SiO₂. *Theoretical and Experimental Chemistry (Translation of Teoreticheskaya i Eksperimental'naya Khimiya)* **2004**, 40, (3), 172-76.
34. Zhang, Q.; Wang, Y.; Ohishi, Y.; Shishido, T.; Takehira, K., V-MCM-41 for selective oxidation of propane to propene and acrolein. *Chemistry Letters* **2001**, (3), 194-95.
35. Clark, J. C., The Development of Building Block Methodologies to Produce Nanostructured Heterogeneous Catalysts by Design. *Thesis (University of Tennessee, Knoxville)* **2005**.
36. Kruk, M.; Jaroniec, M., Gas adsorption characterization of ordered organic-inorganic nanocomposite materials. *Chemistry of Materials* **2001**, 13, (10), 3169-83.
37. Kodre, A.; Arcon, I.; Gomilsek, J. P., X-ray absorption spectroscopy and related techniques. *Acta Chim. Slov.* **2004**, 51, (1), 1-10.

38. Meitzner, G.; Gardea-Torresdey, J.; Parsons, J.; Scott, S. L.; Deguns, E. W., The effect of cryogenic sample cooling on X-ray absorption spectra. *Microchem. J.* **2005**, 81, (1), 61-68.
39. Meitzner, G. D.; Fischer, D. A., Distortions of fluorescence yield x-ray absorption spectra due to sample thickness. *Microchem. J.* **2002**, 71, (2-3), 281-86.
40. Rulkens, R.; Male, J. L.; Terry, K. W.; Olthof, B.; Khodakov, A.; Bell, A. T.; Iglesia, E.; Tilley, T. D., Vanadyl tert-Butoxy Orthosilicate, OV[OSi(OtBu)₃]₃: A Model for Isolated Vanadyl Sites on Silica and a Precursor to Vanadia-Silica Xerogels. *Chem. Mater.* **1999**, 11, (10), 2966-73.
41. Furdala, K. L.; Tilley, T. D., New Vanadium Tris(tert-butoxy)siloxy Complexes and Their Thermolytic Conversions to Vanadia-Silica Materials. *Chem. Mater.* **2002**, 14, (3), 1376-84.
42. Sutton, S. R.; Karner, J.; Papike, J.; Delaney, J. S.; Shearer, C.; Newville, M.; Eng, P.; Rivers, M.; Dyar, M. D., Vanadium K edge XANES of synthetic and natural basaltic glasses and application to microscale oxygen barometry. *Geochim. Cosmochim. Acta* **2005**, 69, (9), 2333-48.
43. Wong, J.; Lytle, F. W.; Messmer, R. P.; Maylotte, D. H., K-edge absorption spectra of selected vanadium compounds. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1984**, 30, (10), 5596-610.
44. Bair, R. A.; Goddard, W. A., III, Ab initio studies of the x-ray absorption edge in copper complexes. I. Atomic copper(2+) and copper(II) dichloride. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1980**, 22, (6), 2767-76.

45. Booth, C. H.; Bridges, F., Improved self-absorption correction for fluorescence measurements of extended X-ray absorption fine-structure. *Phys. Scr., T* **2005**, T115, (12th X-Ray Absorption Fine Structure International Conference (XAFS12), 2003), 202-04.
46. Pfalzer, P.; Urbach, J. P.; Klemm, M.; Horn, S.; denBoer, M. L.; Frenkel, A. I.; Kirkland, J. P., Elimination of self-absorption in fluorescence hard-x-ray absorption spectra. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, 60, (13), 9335-39.
47. Roy, M.; Gurman, S. J., Amplitude reduction in EXAFS. *Journal of Synchrotron Radiation* **1999**, 6, (3), 228-30.
48. Oldroyd, R. D.; Sankar, G.; Meurig Thomas, J.; Hunnius, M.; Maier, W. F., Creation, characterization and performance of vanadyl active sites in microporous and mesoporous silica-based catalysts for the selective oxidation of hydrocarbons. *J. Chem. Soc., Faraday Trans.* **1998**, 94, (20), 3177-82.
49. Rost, M.; Goerls, H.; Imhof, W.; Seidel, W.; Thiele, K., Synthesis and structures of vanadium(III) and vanadium(IV) silanolates. *Z. Anorg. Allg. Chem.* **1998**, 624, (12), 1994-2000.
50. Deguns, E. W.; Taha, Z.; Meitzner, G. D.; Scott, S. L., An X-ray Absorption Study of Two VOCl₃-Modified Silicas: Evidence for Chloride-Silica Interactions. *J. Phys. Chem. B* **2005**, 109, (11), 5005-11.
51. George, S. M., Introduction: Heterogeneous Catalysis. *Chemical Reviews (Washington, D. C.)* **1995**, 95, (3), 475-6.

52. Fajdala, K. L.; Tilley, T. D., Design and synthesis of heterogeneous catalysts: the thermolytic molecular precursor approach. *J. Catal.* **2003**, 216, (1-2), 265-75.
53. Haw, J. F., Zeolite acid strength and reaction mechanisms in catalysis. *Phys. Chem. Chem. Phys.* **2002**, 4, (22), 5431-41.
54. Coperet, C., Single site Heterogeneous Catalysts for Selective Organic Transformations. *Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001* **2001**, ORGN-598.
55. Coperet, C.; Chabanas, M.; Petroff Saint-Arroman, R.; Baudouin, A.; Basset, J.-M., Toward single site heterogeneous catalysts via surface organometallic chemistry. *Abstracts of Papers, 221st ACS National Meeting, San Diego, CA, United States, April 1-5, 2001* **2001**, INOR-007.
56. Hlatky, G. G., Heterogeneous Single-Site Catalysts for Olefin Polymerization. *Chemical Reviews (Washington, D. C.)* **2000**, 100, (4), 1347-76.
57. Zhao, Z.; Yamada, Y.; Ueda, A.; Sakurai, H.; Kobayashi, T., The roles of redox and acid-base properties of silica-supported vanadia catalysts in the selective oxidation of ethane. *Catal. Today* **2004**, 93-95, 163-71.
58. Evans, O. R.; Bell, A. T.; Tilley, T. D., Oxidative dehydrogenation of propane over vanadia-based catalysts supported on high-surface-area mesoporous MgAl_2O_4 . *J. Catal.* **2004**, 226, (2), 292-300.
59. Kresnawahjuesa, O.; Gorte, R. J.; de Oliveira, D.; Lau, L. Y., A Simple, Inexpensive, and Reliable Method for Measuring Bronsted-Acid Site Densities in Solid Acids. *Catal. Lett.* **2002**, 82, (3-4), 155-60.

60. Gorte, R. J., What do we know about the acidity of solid acids? *Catal. Lett.* **1999**, 62, (1), 1-13.
61. Gorte, R. J.; Biaglow, A. I., Methods for the characterization of acid sites in FCC catalysts. *Prepr. - Am. Chem. Soc., Div. Pet. Chem.* **1996**, 41, (2), 381-4.
62. Gorte, R. J., Recent advances in the understanding of zeolite acidity. *Trends in Physical Chemistry* **1991**, 2, 115-24.
63. Soled, S.; McVicker, G. B., Acidity of silica-substituted zirconia. *Catal. Today* **1992**, 14, (2), 189-94.
64. Corma, A.; Ortega, F. J., Influence of adsorption parameters on catalytic cracking and catalyst decay. *J. Catal.* **2005**, 233, (2), 257-65.
65. Ashbrook, S. E.; Smith, M. E., Solid state ^{17}O NMR - an introduction to the background principles and applications to inorganic materials. *Chem. Soc. Rev.* **2006**, 35, (8), 718-35.
66. Prochnow, D.; Grimmer, A.-R.; Freude, D., Solid-state NMR studies of ^{17}O -enriched pyrophosphates. *Solid State Nucl. Magn. Reson.* **2006**, 30, (2), 69-74.
67. Prasad, S.; Clark, T. M.; Sharma, R.; Kwak, H.-T.; Grandinetti, P. J.; Zimmermann, H., A combined ^{17}O RAPT and MQ-MAS NMR study of L-leucine. *Solid State Nucl. Magn. Reson.* **2006**, 29, (1-3), 119-24.
68. Hodgkinson, P.; Hampson, M. R., Quantitative analysis of ^{17}O exchange and T_1 relaxation data: Application to zirconium tungstate. *Solid State Nucl. Magn. Reson.* **2006**, 30, (2), 98-105.

69. Peng, L.; Liu, Y.; Kim, N.; Readman, J. E.; Grey, C. P., Detection of Bronsted acid sites in zeolite HY with high-field ^{17}O -MAS-NMR techniques. *Nat. Mater.* **2005**, 4, (3), 216-19.
70. Iuga, D.; Morais, C.; Gan, Z.; Neuville, D. R.; Cormier, L.; Massiot, D., NMR Heteronuclear Correlation between Quadrupolar Nuclei in Solids. *J. Am. Chem. Soc.* **2005**, 127, (33), 11540-41.
71. Julian, B.; Gervais, C.; Rager, M.-N.; Maquet, J.; Cordoncillo, E.; Escribano, P.; Babonneau, F.; Sanchez, C., Solid-State ^{17}O NMR Characterization of PDMS-M_xO_y (M = Ge(IV), Ti(IV), Zr(IV), Nb(V), and Ta(V)) Organic-Inorganic Nanocomposites. *Chem. Mater.* **2004**, 16, (3), 521-29.
72. Hampson, M. R.; Hodgkinson, P.; Evans, J. S. O.; Harris, R. K.; King, I. J.; Allen, S.; Fayon, F., The nature of oxygen exchange in ZrW₂O₈ revealed by two-dimensional solid-state ^{17}O NMR. *Chem. Commun. (Cambridge, U. K.)* **2004**, (4), 392-93.
73. Kwak, H.-T.; Prasad, S.; Clark, T.; Grandinetti, P. J., Enhancing sensitivity of quadrupolar nuclei in solid-state NMR with multiple rotor assisted population transfers. *Solid State Nucl. Magn. Reson.* **2003**, 24, (2 & 3), 71-77.
74. Clark, T. M.; Grandinetti, P. J., Dependence of bridging oxygen ^{17}O quadrupolar coupling parameters on Si-O distance and Si-O-Si angle. *J. Phys.: Condens. Matter* **2003**, 15, (31), S2387-S95.
75. Freude, D.; Loeser, T.; Michel, D.; Pingel, U.; Prochnow, D., ^{17}O NMR studies of low silicate zeolites. *Solid State Nucl. Magn. Reson.* **2001**, 20, (1/2), 46-60.

76. Xu, Z.; Maekawa, H.; Oglesby, J. V.; Stebbins, J. F., Oxygen Speciation in Hydrated Silicate Glasses: An Oxygen-17 NMR Study. *J. Am. Chem. Soc.* **1998**, 120, (38), 9894-901.
77. Clark, J. C.; Saengkerdsub, S.; Eldridge, G. T.; Campana, C.; Barnes, C. E., Synthesis and structure of functional spherosilicate building block molecules for materials synthesis. *J. Organomet. Chem.* **2006**, 691, (15), 3213-22.
78. Auner, N.; Ziemer, B.; Herrschaft, B.; Ziche, W.; John, P.; Weis, J., Structural studies of novel siloxysilsesquioxanes. *Eur. J. Inorg. Chem.* **1999**, (7), 1087-94.

Appendices

Appendix A

X-ray Tables for Me₃SnOOH·H₂O

Table A-1. Crystal data and structure refinement for Me₃SnOOH·H₂O

Identification code	Me ₃ SnOOH·H ₂ O	
Empirical formula	C ₃ H ₁₂ O ₃ Sn	
Formula weight	214.84	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2 ₁ /n	
Unit cell dimensions	a = 6.6488(16) Å	α = 90°
	b = 10.682(3) Å	β = 94.152(4)°
	c = 10.590(3) Å	γ = 90°
Volume	750.2(3) Å ³	
Z	8	
Density (calculated)	2.936 Mg/m ³	
Absorption coefficient	6.563 mm ⁻¹	
F(000)	624	
Crystal size	0.25 x 0.10 x 0.05 mm ³	
Theta range for data collection	2.71 to 23.36°.	
Index ranges	-7 ≤ h ≤ 7, -11 ≤ k ≤ 11, -11 ≤ l ≤ 11	
Reflections collected	5564	
Independent reflections	1086 [R(int) = 0.0330]	
Completeness to theta = 23.36	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	1086 / 0 / 79	
Goodness-of-fit on F ²	1.116	
Final R indices [I > 2σ(I)]	R ₁ = 0.0172, wR ₂ = 0.0458	
R indices (all data)	R ₁ = 0.0193, wR ₂ = 0.0471	
Largest diff. peak and hole	0.377 and -0.373 eÅ ⁻³	

Table A-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_3\text{SnOOH} \cdot \text{H}_2\text{O}$. U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Sn(1)	1137(1)	2866(1)	2844(1)	22(1)
O(1)	1297(3)	4544(2)	3996(2)	23(1)
O(3)	885(5)	1233(3)	1339(3)	46(1)
C(3)	4310(5)	2680(4)	2842(4)	36(1)
C(2)	-452(6)	3938(3)	1414(3)	40(1)
C(1)	-456(6)	1744(4)	4085(4)	41(1)
O(2)	1972(4)	4179(2)	5315(2)	30(1)

Table A-3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $\text{Me}_3\text{SnOOH} \cdot \text{H}_2\text{O}$.

Sn(1)-C(2)	2.118(3)
Sn(1)-C(1)	2.119(4)
Sn(1)-C(3)	2.119(4)
Sn(1)-O(1)	2.167(2)
Sn(1)-O(3)	2.361(3)
O(1)-O(2)	1.487(3)
C(2)-Sn(1)-C(1)	120.23(16)
C(2)-Sn(1)-C(3)	119.67(16)
C(1)-Sn(1)-C(3)	119.34(16)
C(2)-Sn(1)-O(1)	87.54(11)
C(1)-Sn(1)-O(1)	97.16(13)
C(3)-Sn(1)-O(1)	94.00(12)
C(2)-Sn(1)-O(3)	84.81(13)
C(1)-Sn(1)-O(3)	89.24(14)

(Table A-3. continued) Bond lengths [Å] and angles [°] for Me₃SnOOH·H₂O.

C(3)-Sn(1)-O(3)	87.25(13)
O(1)-Sn(1)-O(3)	171.81(9)
O(2)-O(1)-Sn(1)	108.13(15)
Symmetry transformations used to generate equivalent atoms: none	

Table A-4. Anisotropic displacement parameters (Å² × 10³) for Me₃SnOOH·H₂O.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²
Sn(1)	21(1)	21(1)	23(1)	-1(1)	-1(1)	2(1)
O(1)	29(1)	24(1)	17(1)	1(1)	1(1)	0(1)
O(3)	32(2)	43(2)	61(2)	-29(1)	-15(1)	11(1)
C(3)	25(2)	44(2)	38(2)	-9(2)	1(2)	5(2)
C(2)	51(2)	38(2)	30(2)	1(2)	-8(2)	13(2)
C(1)	38(2)	38(2)	45(2)	11(2)	-3(2)	-13(2)
O(2)	28(1)	37(1)	24(1)	-2(1)	-2(1)	8(1)

Table A-5. Hydrogen coordinates (× 10⁴) and isotropic displacement parameters (Å² × 10³) for Me₃SnOOH·H₂O.

	x	y	z	U(eq)
H(3A)	4863	3402	2414	53
H(3B)	4635	1911	2394	53
H(3C)	4900	2640	3716	53
H(2A)	-1438	3404	939	61
H(2B)	501	4277	838	61
H(2C)	-1154	4628	1805	61

(Table A-5. continued) Hydrogen coordinates ($\times 10^4$) and isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $\text{Me}_3\text{SnOOH} \cdot \text{H}_2\text{O}$.

H(1A)	-1030	2278	4720	61
H(1B)	469	1137	4510	61
H(1C)	-1544	1297	3601	61
H(5)	-220(70)	1060(40)	1020(40)	63(15)
H(4)	1180(50)	4530(30)	5620(30)	29(11)
H(6)	1650(70)	730(50)	1200(40)	62(16)

Appendix B

X-ray Tables for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$

Table B-1. Crystal data and structure refinement for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$

Identification code	$(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$	
Empirical formula	Cl ₂₄ O ₂₀ Si ₁₆	
Formula weight	1620.24	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Rhombohedral	
Space group	R-3	
Unit cell dimensions	a = 16.6337(9) Å	$\alpha = 90^\circ$
	b = 16.6337(9) Å	$\beta = 90^\circ$
	c = 16.6438(9) Å	$\gamma = 120^\circ$
Volume	3988.1(4) Å ³	
Z	3	
Density (calculated)	2.024 Mg/m ³	
Absorption coefficient	1.646 mm ⁻¹	
F(000)	2376624	
Crystal size	0.10 x 0.05 x 0.05 mm	
Theta range for data collection	1.87 to 27.47°.	
Index ranges	-14 ≤ h ≤ 21, -15 ≤ k ≤ 21, -21 ≤ l ≤ 21	
Reflections collected	7370	
Independent reflections	2041 [R(int) = 0.0567]	
Completeness to theta = 23.36	100.0 %	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2041 / 0 / 128	
Goodness-of-fit on F ²	1.045	
Final R indices [I > 2σ(I)]	R1 = 0.0646, wR2 = 0.1807	
R indices (all data)	R1 = 0.1039, wR2 = 0.2227	
Largest diff. peak and hole	0.547 and -0.334 eÅ ⁻³	

Table B-2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$. U (eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
Si(1)	3333	6667	10104(1)	49(1)
Si(2)	3416(1)	5240(1)	11145(1)	51(1)
Si(3)	3333	6667	8274(1)	80(1)
Si(4)	3355(2)	3662(1)	10228(1)	86(1)
O(1)	3393(2)	5815(2)	10414(2)	59(1)
O(2)	2515(2)	4903(2)	11652(2)	62(1)
O(3)	3333	6667	9173(3)	77(2)
O(4)	3469(3)	4388(3)	10834(2)	69(1)
Cl(1)	4390(9)	6839(8)	7752(6)	175(4)
Cl(2)	3308(16)	4094(9)	9119(3)	202(7)
Cl(3)	4320(9)	3411(11)	10351(14)	235(7)
Cl(4)	2161(10)	2561(9)	10377(7)	180(5)
Cl(1')	4608(10)	6898(16)	8069(13)	238(8)
Cl(2')	3933(11)	4260(12)	9272(8)	202(6)
Cl(3')	3970(18)	3009(15)	10545(17)	252(12)
Cl(4')	2118(9)	2773(15)	10173(15)	210(9)

Table B-3. Bond lengths [$\text{\AA}$] and angles [$^\circ$] for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$.

Si(1)-O(3)	1.549(5)
Si(1)-O(1)#1	1.556(3)
Si(1)-O(1)#2	1.556(4)
Si(1)-O(1)	1.556(3)
Si(2)-O(4)	1.553(4)

(Table B-3. continued) Bond lengths [Å] and angles [°] for (Cl₃SiO)₈Si₈O₁₂.

Si(2)-O(2)#3	1.558(4)
Si(2)-O(2)	1.560(4)
Si(2)-O(1)	1.561(3)
Si(3)-O(3)	1.496(5)
Si(3)-Cl(1)#2	1.851(10)
Si(3)-Cl(1)#1	1.851(10)
Si(3)-Cl(1)	1.851(10)
Si(3)-Cl(1')#2	1.986(11)
Si(3)-Cl(1')#1	1.986(11)
Si(3)-Cl(1')	1.986(11)
Si(4)-O(4)	1.510(4)
Si(4)-Cl(4')	1.839(12)
Si(4)-Cl(3)	1.861(12)
Si(4)-Cl(2')	1.868(13)
Si(4)-Cl(3')	1.902(17)
Si(4)-Cl(4)	1.929(12)
Si(4)-Cl(2)	1.996(7)
O(2)-Si(2)#4	1.558(4)
O(3)-Si(1)-O(1)#1	109.39(13)
O(3)-Si(1)-O(1)#2	109.39(13)
O(1)#1-Si(1)-O(1)#2	109.55(13)
O(3)-Si(1)-O(1)	109.39(13)
O(1)#1-Si(1)-O(1)	109.55(13)
O(1)#2-Si(1)-O(1)	109.55(13)
O(4)-Si(2)-O(2)#3	109.3(2)
O(4)-Si(2)-O(2)	109.6(2)
O(2)#3-Si(2)-O(2)	109.30(14)
O(4)-Si(2)-O(1)	109.3(2)

(Table B-3. continued) Bond lengths [Å] and angles [°] for (Cl₃SiO)₈Si₈O₁₂.

O(2)#3-Si(2)-O(1)	110.2(2)
O(2)-Si(2)-O(1)	109.2(2)
O(3)-Si(3)-Cl(1)#2	118.0(4)
O(3)-Si(3)-Cl(1)#1	118.0(4)
Cl(1)#2-Si(3)-Cl(1)#1	99.8(5)
O(3)-Si(3)-Cl(1)	118.0(4)
Cl(1)#2-Si(3)-Cl(1)	99.8(5)
Cl(1)#1-Si(3)-Cl(1)	99.8(5)
O(3)-Si(3)-Cl(1')#2	99.9(6)
Cl(1)#2-Si(3)-Cl(1')#2	18.1(6)
Cl(1)#1-Si(3)-Cl(1')#2	109.9(9)
Cl(1)-Si(3)-Cl(1')#2	111.6(10)
O(3)-Si(3)-Cl(1')#1	99.9(6)
Cl(1)#2-Si(3)-Cl(1')#1	111.6(10)
Cl(1)#1-Si(3)-Cl(1')#1	18.1(6)
Cl(1)-Si(3)-Cl(1')#1	109.9(9)
Cl(1')#2-Si(3)-Cl(1')#1	117.1(4)
O(3)-Si(3)-Cl(1')	99.9(6)
Cl(1)#2-Si(3)-Cl(1')	109.9(9)
Cl(1)#1-Si(3)-Cl(1')	111.6(9)
Cl(1)-Si(3)-Cl(1')	18.1(6)
Cl(1')#2-Si(3)-Cl(1')	117.1(4)
Cl(1')#1-Si(3)-Cl(1')	117.1(4)
O(4)-Si(4)-Cl(4')	108.6(7)
O(4)-Si(4)-Cl(3)	109.1(6)
Cl(4')-Si(4)-Cl(3)	124.6(9)
O(4)-Si(4)-Cl(2')	108.5(5)
Cl(4')-Si(4)-Cl(2')	117.2(8)
Cl(3)-Si(4)-Cl(2')	86.6(8)

(Table B-3. continued) Bond lengths [Å] and angles [°] for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$.

O(4)-Si(4)-Cl(3')	112.5(7)
Cl(4')-Si(4)-Cl(3')	105.1(10)
Cl(3)-Si(4)-Cl(3')	21.6(11)
Cl(2')-Si(4)-Cl(3')	105.0(9)
O(4)-Si(4)-Cl(4)	109.4(5)
Cl(4')-Si(4)-Cl(4)	15.6(11)
Cl(3)-Si(4)-Cl(4)	111.5(7)
Cl(2')-Si(4)-Cl(4)	128.8(6)
Cl(3')-Si(4)-Cl(4)	90.9(9)
O(4)-Si(4)-Cl(2)	110.0(3)
Cl(4')-Si(4)-Cl(2)	90.8(8)
Cl(3)-Si(4)-Cl(2)	112.0(8)
Cl(2')-Si(4)-Cl(2)	28.7(4)
Cl(3')-Si(4)-Cl(2)	126.2(8)
Cl(4)-Si(4)-Cl(2)	104.7(7)
Si(1)-O(1)-Si(2)	148.2(2)
Si(2)#4-O(2)-Si(2)	148.3(3)
Si(3)-O(3)-Si(1)	180.000(1)
Si(4)-O(4)-Si(2)	155.6(3)

Symmetry transformations used to generate equivalent atoms:

#1 $-x+y, -x+1, z$ #2 $-y+1, x-y+1, z$ #3 $x-y+2/3, x+1/3, -z+7/3$

#4 $y-1/3, -x+y+1/3, -z+7/3$

Table B-4. Anisotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for $(\text{Cl}_3\text{SiO})_8\text{Si}_8\text{O}_{12}$.

The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + \dots + 2 h k a^* b^* U^{12}]$

	U11	U22	U33	U23	U13	U12
Si(1)	61(1)	61(1)	24(1)	0	0	31(1)
Si(2)	64(1)	53(1)	40(1)	-5(1)	1(1)	32(1)
Si(3)	106(2)	106(2)	29(1)	0	0	53(1)
Si(4)	107(2)	80(1)	80(1)	-23(1)	6(1)	55(1)
O(1)	76(2)	65(2)	42(2)	-1(1)	2(1)	39(2)
O(2)	69(2)	61(2)	55(2)	-1(2)	8(2)	31(2)
O(3)	103(3)	103(3)	27(2)	0	0	51(2)
O(4)	92(3)	64(2)	60(2)	-9(2)	1(2)	46(2)
Cl(1)	211(9)	203(7)	106(5)	17(4)	87(5)	101(6)
Cl(2)	400(20)	233(9)	49(2)	0(3)	10(5)	211(12)
Cl(3)	152(7)	223(14)	403(16)	-41(12)	29(8)	148(9)
Cl(4)	205(11)	92(4)	139(5)	-24(4)	-22(5)	-3(4)
Cl(1')	130(7)	450(20)	173(13)	15(12)	58(8)	170(10)
Cl(2')	206(11)	329(14)	73(5)	-20(6)	44(5)	134(10)
Cl(3')	320(20)	199(15)	360(20)	-129(16)	-120(19)	226(17)
Cl(4')	92(6)	152(13)	320(20)	-84(12)	-56(9)	10(6)

Vita

Ming-Yung Lee was born in Taipei, Taiwan on November 30, 1973. He received his B.S Degree in chemistry from the National Taiwan University in 1997. Under the supervision of Prof. Ru-Shi Liu, his undergraduate research was on the synthesis, characterization, and complexation with piezo materials to PZT (Lead Zirconate Titanate). After college, he completed two years military service in Taiwan and then started his master degree in the Department of Chemistry at the National Taiwan University in fall 1999. Working under the supervision of Prof. Shie-Ming Peng, he conducted research on syntheses and structure of metal complexes with oligo- α -pyridylamine ligands. After he received his M.S degree in summer 2001, he worked one year as a teaching assistant in the same university. In the fall of 2002, he then moved to the U.S. to obtain his Ph.D. degree in Chemistry at the University of Tennessee, Knoxville (UTK), where he worked under the supervision of Prof. Peter Zhang (2002-2003) and Prof. Craig Barnes (2003-2007). In March 2007, he completed the requirements for a Doctor of Philosophy Degree in chemistry.