

**The Synthesis and Characterization of Novel Group 13
Nanostructured Building Block Heterogeneous
Silicate Catalysts**

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Dedication

To Julia.

Without your unwavering support and
unconditional love the completion of this journey
would not have been possible.

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Abstract

A building block approach and sequential addition methodology was utilized to prepare heterogeneous silicate catalysts containing atomically dispersed group 13 metal (B, Al, Ga) centers. The octa(trimethyltin) silsequioxane, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$, was used as the building block for the synthesis of these materials. Reaction of the building block with a variety of group 13 metal chlorides led to the formation of cross-linked matrices. All prepared materials were characterized by gravimetric analysis, gas absorption, IR, and NMR. In addition, aluminum and boron samples were characterized by ^{27}Al and ^{11}B solid state NMR, and gallium samples were studied using x-ray absorption techniques.

Studies found the nature of the reaction for the aluminum and gallium species to be more complex than expected. This was manifested most prominently in the formation of tetramethyltin, Me_4Sn , an unexpected byproduct that led to unpredictably high connectivity of the metal centers to the silicate matrix. This in turn gave rise to questions regarding the true structural nature of the metal sites.

Characterization of the aluminum systems indicated that multiple types of aluminum sites (4, 5 and 6 coordinate) were present in the matrix. Increased coordination was found to result in part from the in situ formation and reaction of the $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ species. It was determined that the trimethyltin cation in this ionic species was responsible for formation of Me_4Sn through abstraction of a methyl group from unreacted $-\text{OSnMe}_3$ groups remaining on the corners of the silicate building block.

While the gallium analogues showed similar behavior, XANES and EXAFS analyses showed that in nearly every material, gallium had achieved 4-coordinate tetrahedral geometry.

The boron systems behave quite differently than Al and Ga, producing no secondary byproduct, and forming stable 3-coordinate trigonal geometries. Pyridine adsorption studies showed that these trigonal species could at least in part be converted back and forth to pseudo tetrahedral structures.

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1. Introduction & Review of Heterogeneous Catalysis

1.1 Introduction

Though catalysts have likely existed in some form since the first chemical reactions occurred during the formation of the universe, recognition of their existence and understanding of their significance did not arise until much later. Jöns Berzelius is generally credited with defining the concept of catalysis and the term 'catalyst' in 1835 in the course of his investigations and examinations of a number of reactions.^{1,2} In the ensuing 175 years, understanding of catalysts has increased and resulted in the ability to design, synthesize, and incorporate catalytic systems into an astonishing number of important processes, the products of which play important roles in the everyday lives of every person on the planet.

The driving force behind catalyst development and implementation in the last 100 years has been the petrochemical industry, where the annual US market for catalysts now exceeds 4 billion dollars with worldwide sales of more than 10 billion dollars. Beyond this, the value of products synthesized through catalytic processes has been estimated anywhere from 0.5 – 4 trillion dollars worldwide.³ Catalysts are used everywhere in the developed world from the production of transportation fuels, to the creation of high value specialty chemicals, reduction of pollutants, and the production of plastic water bottles and synthetic fibers. It has been estimated that nearly 90% of all chemical manufacturing processes and 20% of all industrial products involve essential catalytic steps.^{3,4}

The need for catalysts that exhibit improved activity, selectivity, and process efficiency in chemical manufacturing has resulted in a sustained push to continually improve and discover new catalytic systems. Research and development into catalyst discovery and application has been an important focus in all facets of research, be it industrial, governmental, or academic. The importance of research in this field is evident as the DOE Basic Energy Sciences division granted more than 42 million dollars for studies involving catalysis in 2009 alone.⁵

This dissertation will detail work carried out over the course of the last six years in the group of Dr. Craig E. Barnes at the University of Tennessee. The primary motivation of the work presented here has been the extension of a developing synthetic methodology for the creation of single site nanostructured heterogeneous catalysts. Work here has focused on the design, synthesis, and characterization of group 13 (B, Al, & Ga) heterogeneous solid acid catalysts. The remainder of this chapter is meant to provide a general background to many of the concepts that are necessary for understanding the goals, methods and applications that have been integral to the design and implementation of the research presented in the following chapters.

1.2 Definition of a catalyst

A catalyst is a chemical species which lowers the activation energy of a chemical reaction without being consumed. This leads to an increase in the rate at which the reaction progresses. This is often illustrated by way of a reaction coordinate diagram (Figure 1.01). While the thermodynamic energies of the initial and final species are unaffected by the catalyst, the kinetic barrier over which the reactants must climb for conversion to products is lowered. The implication here is that it takes less energy for the reaction to occur, or, to put it another way, with the same amount of energy more of the starting material is converted to product. While influencing the rate of the reaction, the catalyst itself is continually regenerated and not consumed. As a result only a small amount of catalyst relative to the amount of substrate is typically needed. The degree to which a catalyst increases the rate is defined in terms of activity, wherein a catalyst that increases the rate more than an equal amount of another catalyst is said to have higher activity. In a reaction where multiple products are observed, there must be multiple reaction pathways possessing similar activation barriers. Ideally, a catalyst may lower one of these activation barriers more than the others, resulting in higher selectivity to a single product. In this context, a catalyst is said to be more selective than a catalyst that might lower several activation barriers equally. A general understanding of the way in which catalysts behave is in hand, but catalytic reactions are widely varied, can require very different catalysts, and progress by different

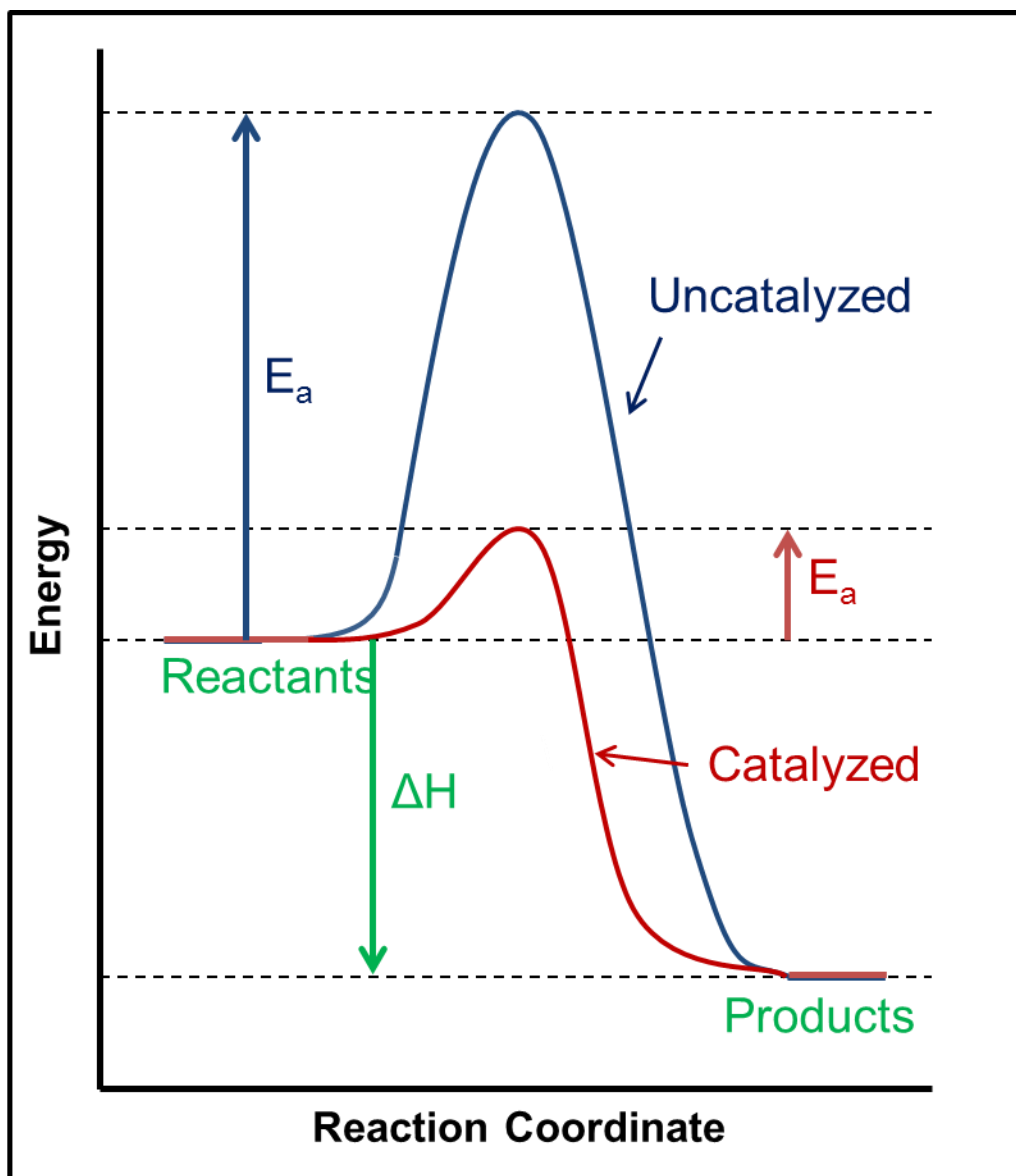


Figure 1.01: Reaction coordinate diagram

mechanisms. It is the detailed knowledge of these mechanistic pathways by which catalysts influence reaction rates that modern research seeks to understand and improve upon.

1.3 Heterogeneous vs. Homogeneous Catalysts

All catalysts can be placed into one of two primary categories: homogeneous or heterogeneous catalysts. Homogeneous catalysts are those that are present in the same phase as the substrate. The most common case is when both the catalyst and substrate are in a solution phase. Heterogeneous catalysts, on the other hand, reside in a different phase than the substrate. Typically heterogeneous catalysts are solids and the substrate is either a liquid or a gas.

There are pros and cons for each of these types of catalysts. A better understanding of structures and catalytic mechanisms generally exist for homogeneous species because the catalysts are typically small molecules that can be prepared, purified and studied by a number of techniques that are unavailable for heterogeneous systems. Furthermore, homogeneous catalysts tend to possess higher per site activity (or turn over frequency) than heterogeneous analogues. Unfortunately, homogeneous catalysts are often very difficult to separate from reaction mixtures once the reaction is complete. Soluble acids that are often used as catalysts can also lead to problems with corrosion resulting in high equipment maintenance and replacement costs in an industrial setting. Homogeneous species also tend to be less stable under harsh reaction conditions.

Heterogeneous catalysts are incredibly important technologically as they are generally more robust, and much easier to recover than homogeneous analogues. In addition, there are a number of high temperature reactions (water gas shift (WGS), Fischer-Tropsch (FT), catalytic cracking) where the rugged stability of heterogeneous catalysts is required. Heterogeneous catalysts are not perfect, as they are often less well understood, harder to characterize, and may possess multiple catalytic sites that lower selectivity and activity relative to their homogeneous analogues. However, the economic advantages presented by recyclability, durability, and a lack of corrosion

issues are the primary reasons why heterogeneous systems are used so prolifically in industrial processes.

1.4 Classes of Heterogeneous Catalysts

1.4.1 – Pure Metals

Pure metal catalysts have been used as catalytic species for a number of important processes. Most of the metals used tend to be transition metals located in groups 8-10 of the periodic table. The noble metals Pt, Pd, and Rh have all been used as noble metal catalysts in catalytic converters where they function primarily as both oxidation and reduction catalysts.^{6,7} In Fischer-Tropsch chemistry, CO and H₂ are catalytically combined to form long chain hydrocarbons. Metallic Co, Fe, and Ru have shown high activity in the FT process, though Co has been primarily used as the active species due to its high activity compared to Fe and its moderate price relative to Ru.⁸⁻¹⁰ Other important processes where metallic catalysts play an important role include hydrogenation,^{11,12} CO oxidation,^{13,14} and epoxidation.¹⁵

In some cases bimetallic and other mixed metal systems have shown unique characteristics that lead to increased activity and stability relative to the monometallic systems listed above. For instance, Pt/Pd alloys supported on zeolites have shown high hydrogenation activity, while displaying a significant increase in resistance to sulfur poisoning over that of the individual metals.¹⁶

1.4.2 – Metal Oxides

Metal oxides encompass an extremely large number of materials, many of which are used in catalysis either directly, or indirectly. Every metal on the periodic table will form at least one oxide. In terms of chemical makeup, metal oxides can vary from simple binary systems (M_xO_y) to ternary oxides (M_xM'_yO_z) to modified zeolites.¹⁷ When metal oxides are discussed in terms of catalytic activity, they might be designated as being either acidic, basic, or redox active. In terms of periodic real estate (Figure 1.02), the basic oxides generally incorporate the alkali and alkaline earth metals, while main group metal oxides are typically acidic and transition metal oxides are red/ox active.¹⁸

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	Se	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Tu	Th	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn						

Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

Figure 1.02: Catalytic nature of metal oxides

Catalytically speaking, metal oxides can be used in one of two ways. The first is as the active catalytic species. Each type of oxide system exhibits unique characteristics that can make it a useful catalyst for a specific reaction. The range of processes that utilize metal oxide catalysts is almost as varied as the number of metal oxides themselves and includes everything from steam reforming,¹⁹ the water-gas shift process,²⁰ alkane isomerization,²¹ and any number of oxidation processes.²² Beyond acting directly as the catalytic species, metal oxides are often used as supports that help to modify the activity of other catalysts. Typically binary oxides such as SiO_2 , Al_2O_3 , and TiO_2 are utilized as supports, and the catalysts deposited on their surfaces can range from metallic nanoparticles to other metal oxides. Surface modification by soluble acids is also a common variation carried out on the metal oxide support structure.²³

For the most part, metal oxide catalysis was developed through an empirical process in which naturally occurring oxides were discovered to be catalytic in certain processes after which adjustments and synthetic alterations were made to optimize activity for a given reaction. In this empirical process, it is very hard to know exactly what the active catalyst “ensemble” is. Here the catalytic “ensemble” is defined as the catalytic center, bound ligands and the links to the support (Figure 1.03). As such, systems that utilize preexisting supports are somewhat limited by the fact that they cannot be synthetically tailored from the ground up to maximize catalytic performance. In many cases, the oxide surfaces possess defect sites that lead to the presence of multiple sites which in turn can reduce selectivity. A problem also exists in the fact that most metal oxides are low surface area species, limiting the number of available active sites and thus overall activity.

1.4.3 – Supported Homogeneous Analogues

A common technique to “heterogenize” catalysts involves attaching highly active homogeneous catalysts to a heterogeneous support in order to make recovery of the catalysts easier and more cost efficient. Key considerations in this strategy include the manner in which the catalyst is bound to the support, the type of support being used,

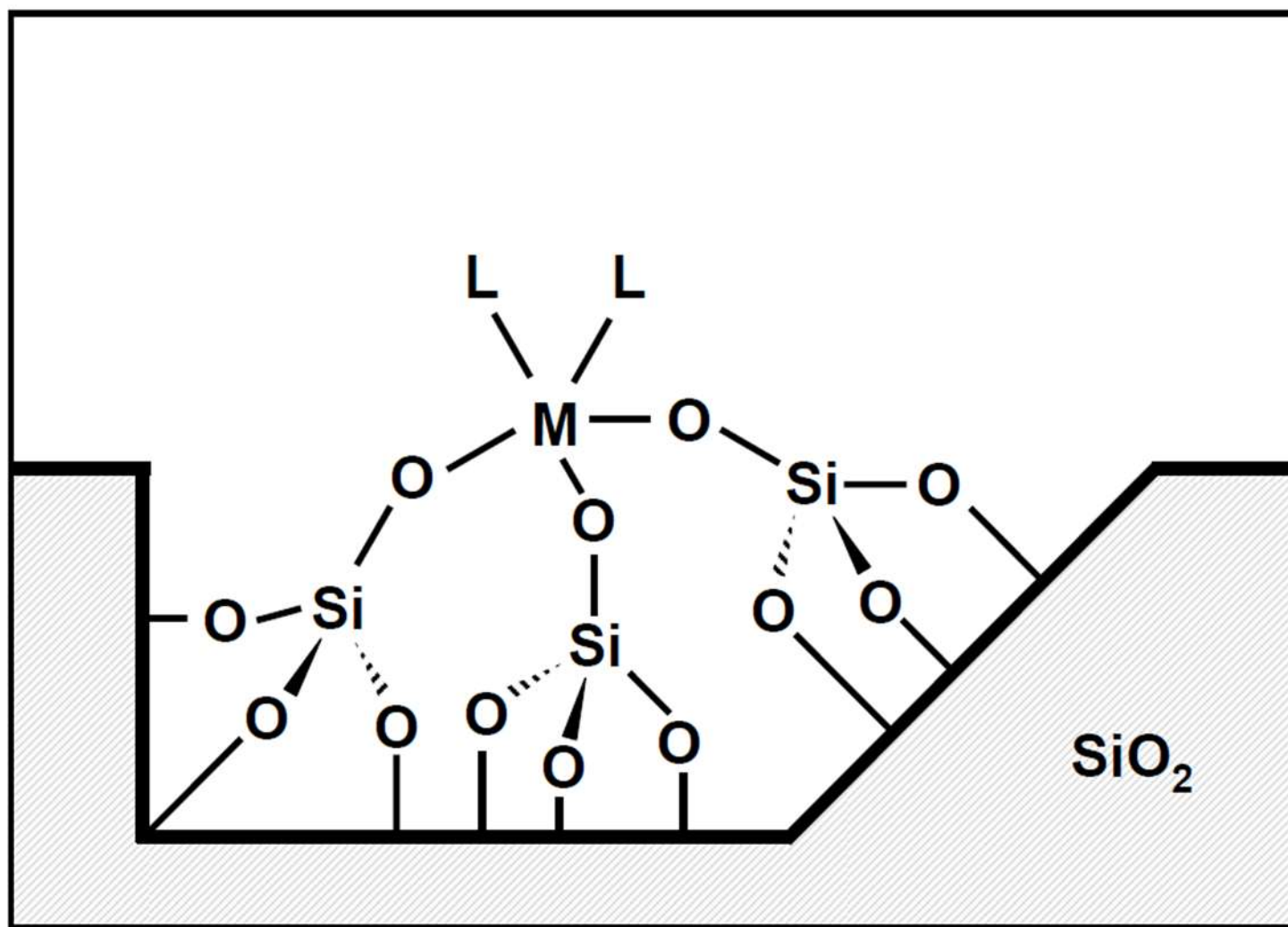


Figure 1.03: Catalyst “Ensemble” depicting SiO_2 support, metal to support links (M-O-Si), and metal ligand (L) interactions

and the nature of the support/catalyst interaction. Often the activity of the catalyst can be significantly altered upon interaction with a support. All types of catalysts including polymerization, red/ox, and solid acid assemblies have been heterogenized through a variety of interactions with a support.

Heterogeneous supports for homogeneous catalysts may include binary metal oxides, complex metal oxides, aluminosilicates, and polymers of which both low and high surface area species with amorphous or well defined structures may be used. Silica, (SiO_2) is by far the most commonly used support, and can vary widely in surface area and morphology.²⁴ The surface of silica is functionalized with silanol (Si-OH) groups which are the most common sites for binding a catalytic species to the surface. Almost all functionalization on silicon oxide relies on these silanol sites. The silanols exist in one of three structural motifs (Figure 1.04). These are isolated, vicinal, and geminal sites.²⁵ In addition, high density silanol “nests” often occur around surface defect sites. Having at least three distinct types of silanol functionalities on the surface can lead to issues when trying to create catalytic sites that are all identical. Because of this, silica supports are often calcined in order to condense neighboring silanols. Even this procedure generally leaves behind a mixture of geminal and isolated silanols, in addition to reducing the number of sites for the catalyst to bind.

It is also important to understand how the homogeneous species will interact with the support. It is possible to construct covalent linkages, but in some cases non covalent interactions such as weak physisorption or coulombic forces between charged species can hold a catalyst to the support.²⁶ For example, impregnation of cationic catalytic precursors into zeolites or aluminosilicates by incipient wetness techniques can lead to charged catalytic centers interacting with the substrate at the anionic Al defect sites. An example of this would be the cesium ions in the zeolite Cs-ZSM-5 (Figure 1.10). A variety of reactions involving a number of complimentary functional groups have been developed that lead to covalent bond formation between catalyst and support.²⁷ These include very common and straight forward reactions of metal chloride and metal alkyl groups with surface hydroxyl groups to create M-O-Si(M) bonds. This is generally referred to as surface grafting where the catalytic species is directly bound to

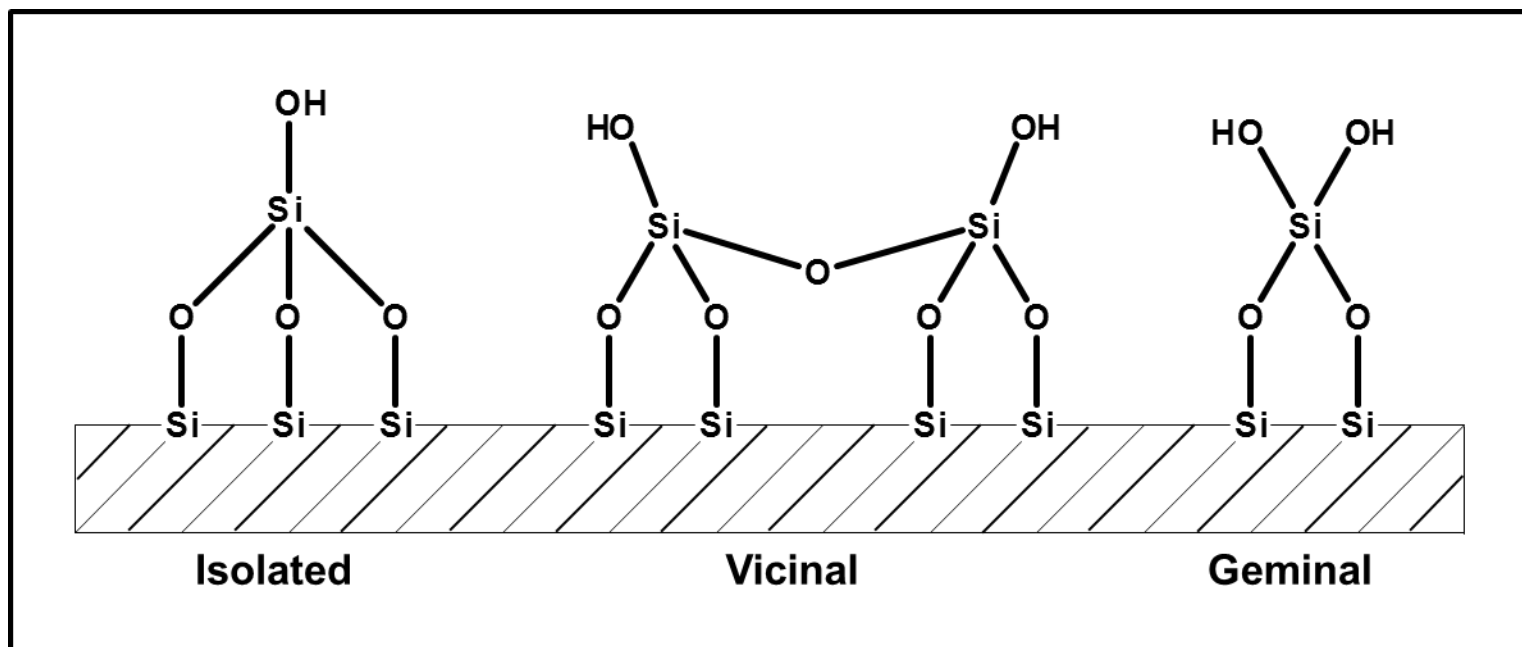


Figure 1.04: Types of surface silanols

the support. In a slightly different approach, catalysts may be “tethered” to the surface. For example, the surface can first be reacted with a chlorosilane, containing Si-H groups, at which point hydrosilation can be used to connect an alkene ligand of the catalyst to the surface. Amines and thiol groups are also commonly used as anchoring points. By utilizing a bifunctional tethering compound, one group can be used to form a connection to the support, while the second serves as ligand to the catalytic center. (Figure 1.05)

It is frequently observed that upon immobilization, a homogeneous catalyst experiences a reduction in activity.^{24,27} This is why understanding the interaction of the support and the catalytic ensemble is so important. To date this has been a largely empirical endeavor, but as synthetic and characterization techniques improve, understanding of structure-activity relationships has helped lead to more directed approaches.²⁸

1.4.4 – Solid Acids

Acid catalysis is extremely important in a large number of industrial processes.²⁹ However, using soluble acids leads to problems with corrosion, toxicity, separation, and recovery. As a result, industry has adopted the use of solid acids in as many cases as possible.

Solid acids are characterized by the presence of either Brønsted and/or Lewis acid sites (*vida infra*). Each of these is in turn defined by the strength, number, and accessibility of those sites. It is common for these catalysts to exhibit either pure Brønsted acidity, or a mixture of Lewis and Brønsted acidity, but it has been more difficult to produce purely Lewis acidic solid acids.^{30,31} The nature of the strength of the acid sites is important in determining which reactions the solid acids are most applicable for. Generally, weaker acid sites are useful in isomerization and reforming reactions, while stronger acid sites are utilized in alkylation and cracking processes (Figure 1.06).³² As of the early 2000s as many as 180 catalytic industrial processes were utilizing a variety of solid acids ranging from aluminosilicates and metal oxides to heteropolyacids, and sulfonated or phosphorylated oxides and polymers.²⁹

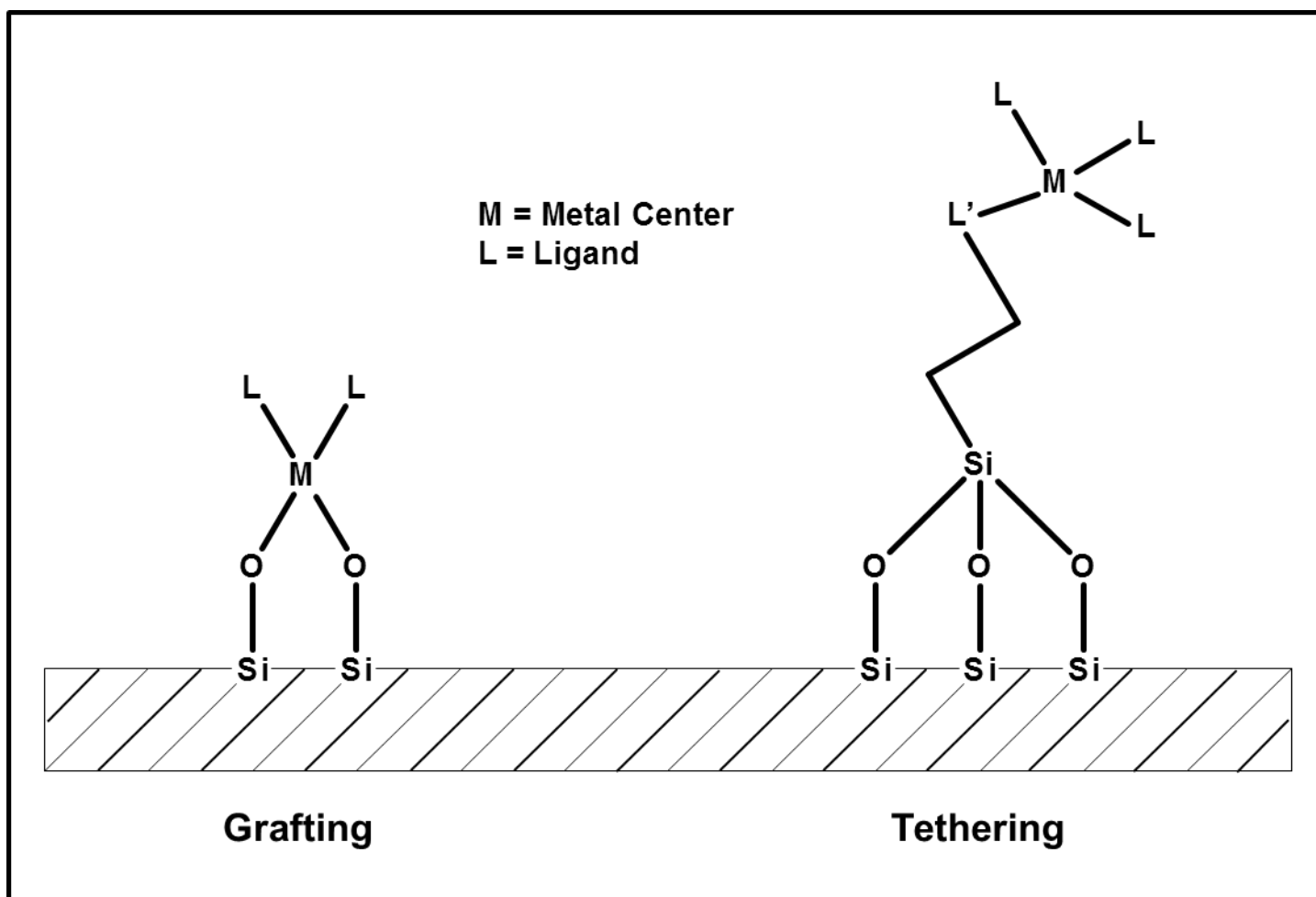


Figure 1.05: Grafting vs. tethering

	formula/example	acid group/ catalytic active species	reaction (ex)	phase	typical T range ($^{\circ}\text{C}$)	deactivation	reactivation
alumina (silicated)	$\text{Al}_2\text{O}_3 \text{ Al}_{2-x}\text{Si}_x\text{O}_{3+x/2}$	AlOH or Al–OH–Al (SiOH) Al^{3+}	olefin skeletal isomerization alcohol dehydration	gas/solid	> 400	coking	burning
silicalite-1	SiO_2	SiOH	Beckmann rearrangement of cyclohexanone-oxime	gas/solid	300	coking tar formation	burning
chlorided alumina	$\text{Al}_2\text{O}_3-x\text{Cl}_{2x}$	Cl_xAlOH Al^{3+}	paraffin isomerization aliphatic alkylation	gas/solid liquid/solid	120–200	chlorine loss coking coking/poisoning	difficult washing
acid-treated montmorillonite clays	$\text{Na}_x[\text{Al}_{2-x}\text{Mg}_x\text{Si}_{4-}\text{O}_{10}(\text{OH})_2] \cdot n\text{H}_2\text{O}$	SiOH Al^{3+}	cracking	gas/solid (liquid/solid)	200–550	coking structural damage	burning
silica–alumina/ aluminated silica	$\text{H}_y\text{Si}_{1-x}\text{Al}_x\text{O}_{2-x/2+2y}$	SiOH	cracking dehydrochlorination alkylation	gas/solid liquid/solid	200–550 200	coking	burning
H-zeolites	$\text{H}_x\text{Si}_{1-x}\text{Al}_x\text{O}_2$	Si–OH–Al	aromatics alkylation paraffin and olefin isomerization cracking aromatics alkylation	gas/solid liquid/solid	200–550 150–250	coking structural collapse poisoning	burning hydrogenation burning
SAPO	$\text{H}_{x-y}\text{Si}_{1-x-y}\text{P}_y\text{Al}_x\text{O}_2$	Si–OH–Al	methanol to olefins	gas/solid	400–450	coking	burning
sulfated zirconia	$\text{H}_2\text{SO}_4\text{-ZrO}_2$	SOH	paraffin isomerization	gas/solid	170–230	coking	difficult
tungstated zirconia	$\text{WO}_3\text{-ZrO}_2$	WOH	paraffin isomerization	gas/solid	200–270	coking	burning
solid phosphoric acid	$\text{H}_3\text{PO}_4/\text{SiO}_2$ (kieselghur)	POH $[\text{H}(\text{H}_2\text{O})_n]^+$	olefin oligomerization and hydration aromatics alkylation	gas/solid	150–300	leaching coking	difficult
heteropolyacid	$\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$	W–OH–W $[\text{H}(\text{H}_2\text{O})_n]^+$	ethyl acetate synthesis	gas/solid liquid/solid	140–250 60		difficult
niobic acid	$\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$	NbOH $[\text{H}(\text{H}_2\text{O})_n]^+$	ethylene hydration fructose dehydration	gas/solid water/solid	200 100	coking	burning
sulfonated polystyrene– polydivinylbenzene resins		– SO_3H $[\text{H}(\text{H}_2\text{O})_n]^+$ $[\text{H}(\text{ROH})]^+$	ether synthesis olefin oligomerization	liquid/solid	40–100	poisoning	washing

Figure 1.06: Solid acid catalysts and their catalytic applications³¹

1.5 Aluminosilicates

1.5.1 – Industrial Applications

Aluminosilicates are a broad class of both naturally occurring and synthetic materials that are often used for catalytic purposes. With few exceptions aluminosilicates are classified as solid acids. Aluminum generally shows very little redox activity in oxide matrices and is almost always found in the +3 oxidation state. Aluminum(I) and (II) compounds are known,^{33,34} but are generally unstable under the normal conditions of catalysis. The +3 oxidation state is so energetically favorable that in most cases spontaneous disproportionation to Al(0) and Al(III) will occur.

Industrially, aluminosilicates are used for a wide variety of important processes. Isomerization of linear alkanes to their more heavily branched analogues is of great importance for generation of high octane fuels. Linear n-heptane has an octane value of zero, while 2-methylhexane and 2,3-dimethylpentane possess respective octane values of 53 and 93.³⁵ The catalyst of choice for these and similar transformations is currently a zeolite or mesoporous aluminosilicate doped with Ni, Pd, or Pt.

Current interest in renewable resources and more environmentally friendly fuel sources, has led to an emphasis on the production of biodiesel.^{36,37} The processes by which biodiesel is synthesized are esterification and transesterification of fats and oils. This involves the conversion of triglycerides or free fatty acids to esters using low molecular weight alcohols often in the presence of an acid catalyst (Figure 1.07).³⁷ Soluble acids can be used, but they require costly neutralization and separation steps.³⁶ Because of this solid acids and specifically aluminosilicates have become important to large scale biodiesel operations.

Aluminosilicates are also of importance in some polymerization reactions. While most types of polymerization reactions do not utilize aluminosilicates as the primary active site for catalysis, many heterogeneous systems have incorporated or tethered active species onto the surfaces of aluminosilicate supports.²⁴ The one polymeric transformation that aluminosilicates have been shown to facilitate directly is the ring opening polymerization of cyclic lactones (Figure 1.08).^{38,39}

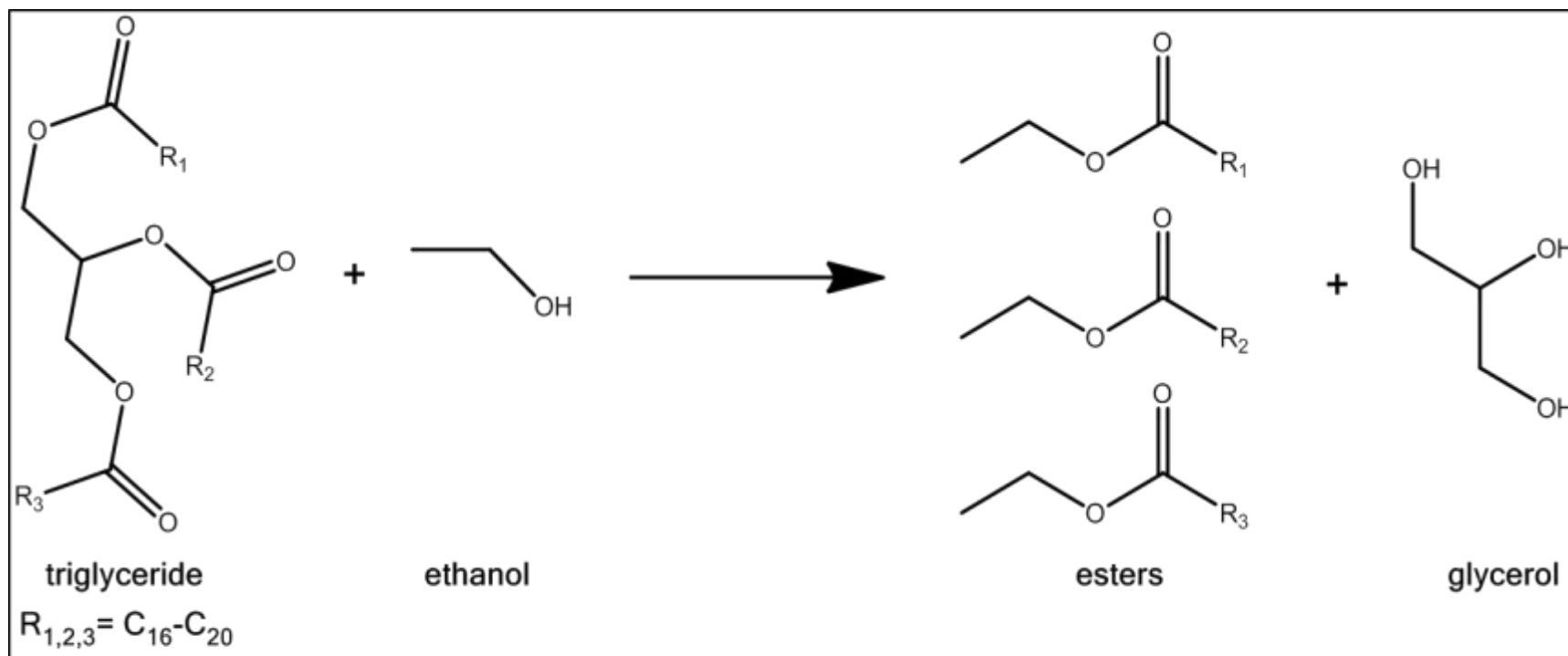


Figure 1.07: Transesterification

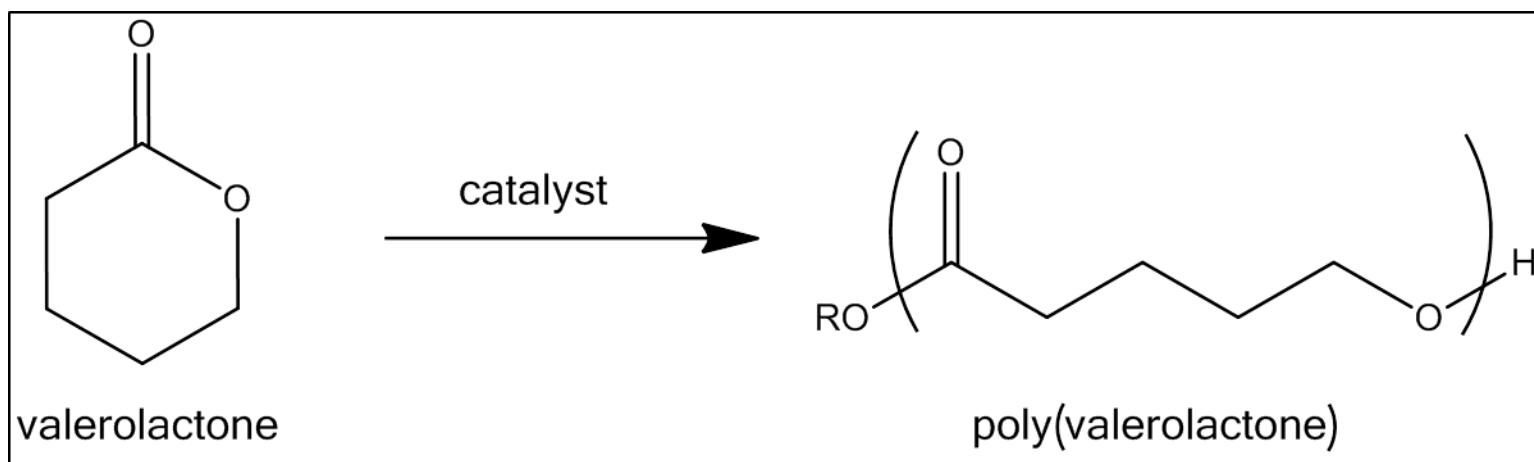


Figure 1.08: Lactone polymerization

The largest use of aluminosilicates in industry involves the fluid catalytic cracking (FCC) and hydrocracking processes (Figure 1.09).⁴⁰ In general, the goal of these processes is to convert heavy hydrocarbon fractions into liquid fuel components. The FCC process typically yields gasoline, while hydrocracking is more often used for the production of kerosene and diesel.

The typical FCC feedstock is the heavy gas oil fraction of crude oil that consists of long chain hydrocarbons with molecular weights between 200-600 amu. The typical FCC catalyst is ultrastable Y (USY) zeolite that is often ion exchanged with lanthanide ions.⁴⁰ The products are generally C₅-C₁₁ hydrocarbons, which in some cases are unsaturated.

Hydrocracking utilizes the heavier fractions of starting materials such as vacuum gas oil (VGO). Due to the nature of the starting feedstock, metal hydrogenation catalysts are often integrated into the hydrocracking catalyst to produce saturated hydrocarbons. While zeolites are very effective cracking catalysts, they are often poor supports for these hydrogenation catalysts. Therefore in many instances, alumina, or silica/alumina are used to retain some acidity while serving as more optimal supports for the hydrogenation cocatalyst.

The brief descriptions of the applications of aluminosilicates provided here illustrate their importance in the refining and chemical production industries. An important question that arises in this context concerns the identity of the active sites that are responsible for their solid acid characteristics.

1.5.2 – Classes of Aluminosilicates

The term aluminosilicate, while hierarchically more descriptive than solid acid, is itself broad to the point that it indicates only the primary elemental components of aluminum, silicon, in addition to the necessary but presumed oxygen. The term does not indicate the method of synthesis, structural design, nor the nature of the catalytic ensemble present in these solids. Because of this, it is beneficial to further delineate the various classes of aluminosilicates in order to examine both their differences and similarities.

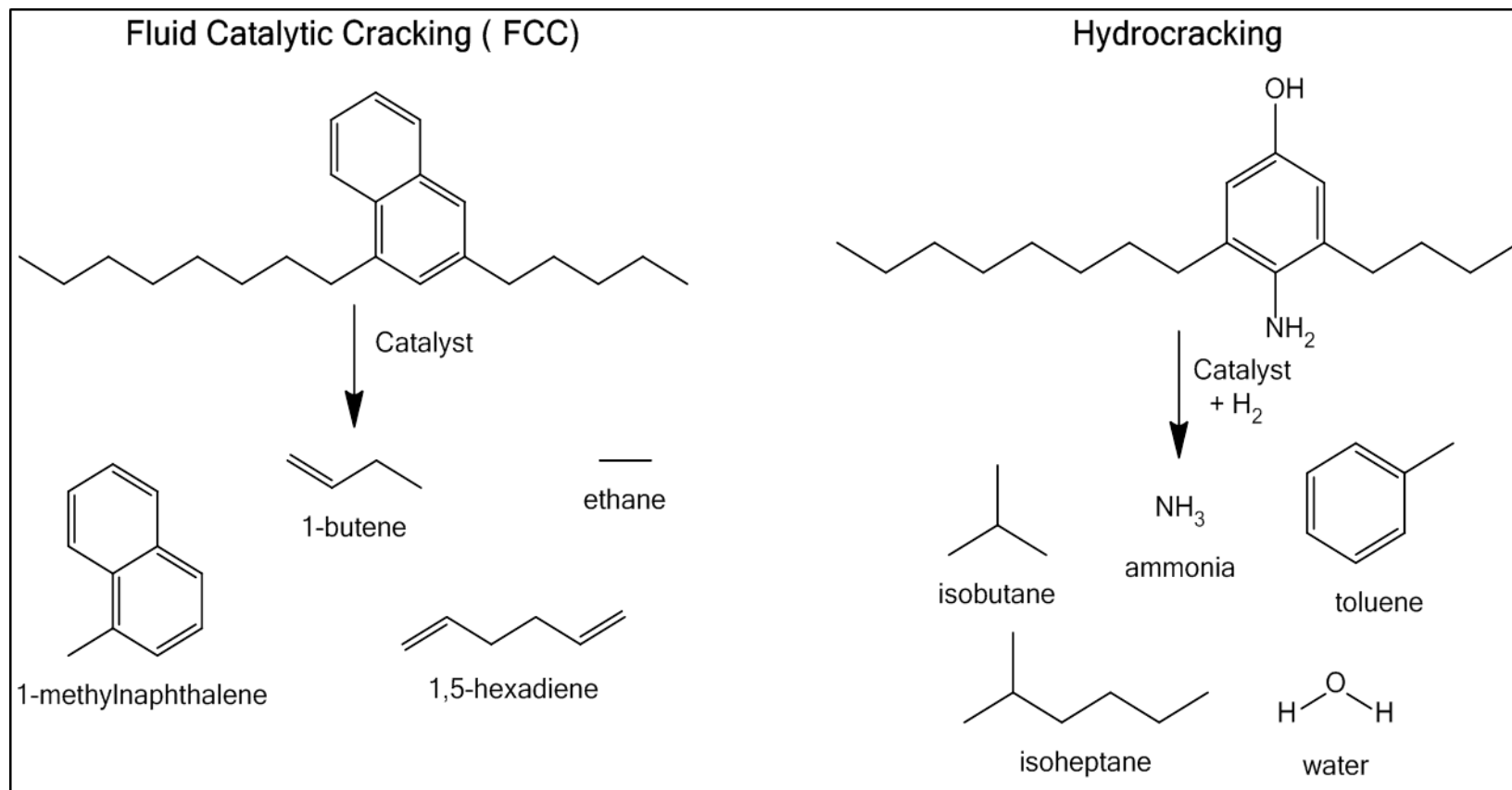


Figure 1.09: Example of fluid catalytic cracking (FCC) and hydrocracking

Many aluminosilicates can be classified simply as silica/alumina ($\text{SiO}_2/\text{Al}_2\text{O}_3$) mixtures. These materials are generally amorphous and typically formed by the co-condensation of silicon and aluminum alkoxides with little control over the structural endpoint of the materials formed. The solid products may contain aluminum metal centers isolated within a silicate matrix with varying degrees of coordination, but the formation of alumina domains is common as the amount of aluminum in the system increases.⁴¹ There is little doubt that multiple types of catalytic sites are present and active. Literature reports indicate that these materials commonly possess both Brønsted and Lewis acidic sites.^{42,43} These systems were some of the first materials synthesized for use in catalytic cracking applications.⁴⁴

While natural zeolites were well known as these early silica/alumina catalysts were developed, they did not become industrially important until synthetic analogues were synthesized in the early 1950s.⁴⁵ Zeolites offer a number of benefits over amorphous silica/aluminas. Foremost among these is the fact that zeolites are ordered crystalline materials (Figure 1.10). As a result, a better understanding of structure and the active site in aluminosilicates developed. One important question answered by in depth crystallographic characterization of zeolites is the most common location of Al atoms within the porous structure.⁴⁶

Zeolites also possess uniform structured porous networks that lead to high surface areas and make them ideal for a variety of catalytic processes that include catalytic cracking, isomerization, and shape selective synthesis of small molecules such as p-xylene.⁴⁷ While the pores can be ideal for the synthesis of certain small molecules, the small pores can also pose problems. Zeolitic materials are generally characterized as microporous with pores <2 nm in diameter. This means that catalytic conversion of large molecules can be difficult owing to their inability to reach the catalytically active sites within the pores.

In response to size exclusion and mass transfer issues that arise with zeolites, a great deal of research has focused on the creation of mesoporous (pores between 2-50 nm) analogues. The first success in this area was the synthesis of MCM-41 by the Mobil Corporation in the early 1990's.⁴⁸ Increased pore sizes were created by utilizing

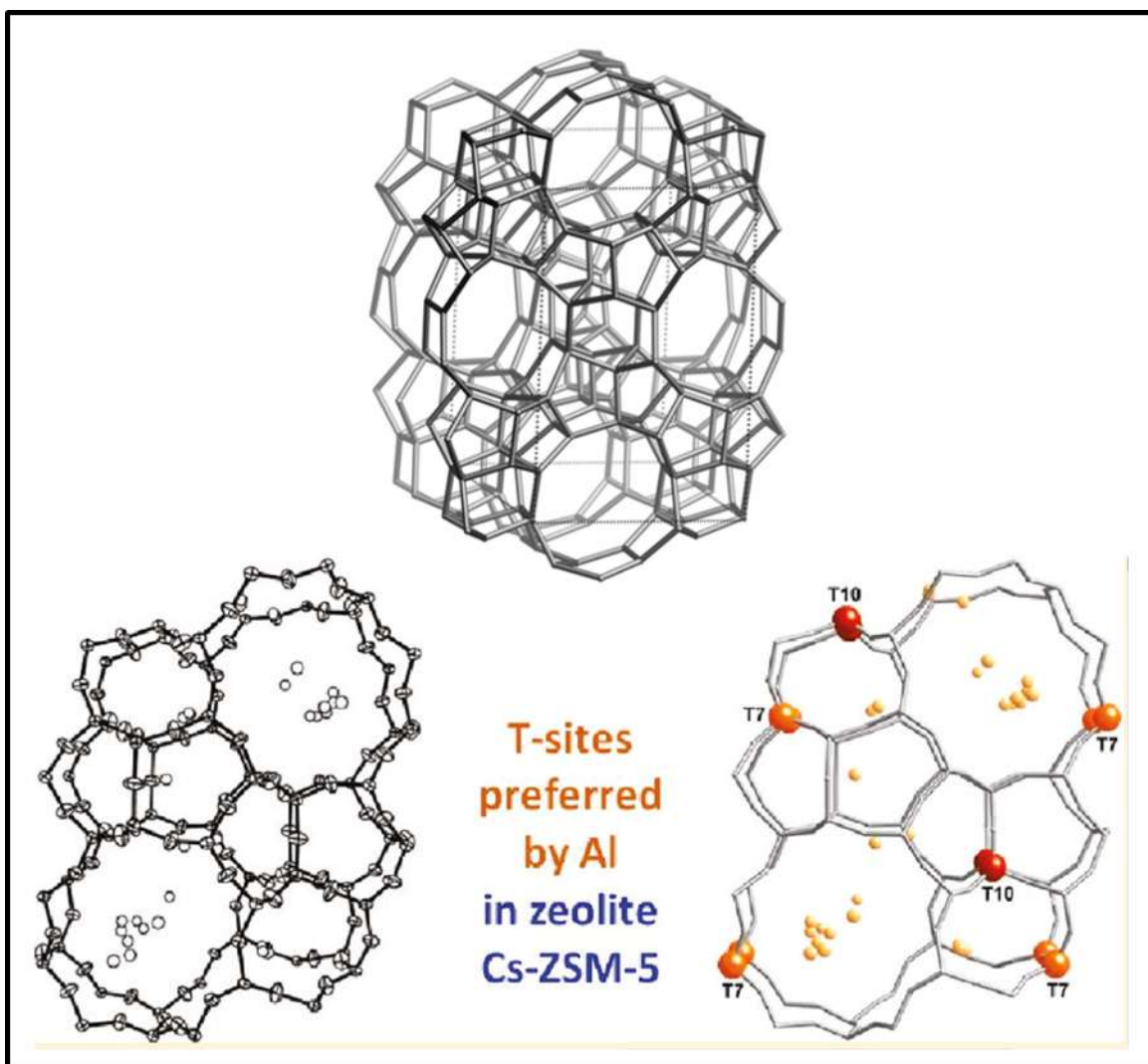


Figure 1.10: Structure and Al location Zeolite Cs-ZSM-5^{46,61}

quaternary ammonium surfactants such as cetyltrimethylammonium hydroxide.⁴⁷ In aqueous solution, the surfactant forms micellar rods that act as templates around which the aluminosilicate matrix forms. Upon completion of the condensation reactions that form the silica matrix, the surfactant must be removed. This generally requires calcination of the material. As a result of this, the organic template is burned and lost, leading to significant increases in the cost of making these materials. Final removal of the template leaves behind an ordered array of mesopores (Figure 1.11). By adjusting the type and size of the template, the pore size of the material can be tuned. Although these mesoporous materials exhibit ordered pore structures, the aluminosilicate walls are amorphous. In the years since the discovery of MCM-41, a large number of mesoporous aluminosilicates have been synthesized utilizing a variety of cationic, anionic, and neutral structure directing agents.⁴⁸

Catalytically, mesoporous aluminosilicates are meant to extend the size range of possible substrates to those for which microporous zeolites are generally ineffective. Unfortunately, it has been demonstrated that under the harsh conditions of the catalytic cracking reactors (700-800°C, steam) hydrothermal deactivation occurs.⁴⁹ This is thought to be a result of the instability of the amorphous walls of the mesoporous aluminosilicate and is found to be more prevalent as Si:Al ratios decrease in the material. In order to facilitate higher stability, lower amounts of Al must be used which in turn reduces the catalytic site density. More recent studies have sought to increase the hydrothermal stability of these materials by developing methods to increase crystallinity in the pore walls.⁴⁹⁻⁵¹

1.5.3 – Nature of the Active Sites in Aluminosilicates

Pure silicates possess a network of SiO_4 corner sharing tetrahedra that gives rise to a net stoichiometric formula of SiO_2 . Within this network the charge on each of the Si^{4+} cations is balanced by two O^{2-} anions. In most aluminosilicates, Al^{3+} centers are substituted for Si^{4+} atoms in framework positions forming a material with a distribution of SiO_4 and AlO_4 tetrahedra. Because the Al centers possess a charge of 3^+ , a net negative charge arises on the AlO_4 group. As the overall net charge of the material

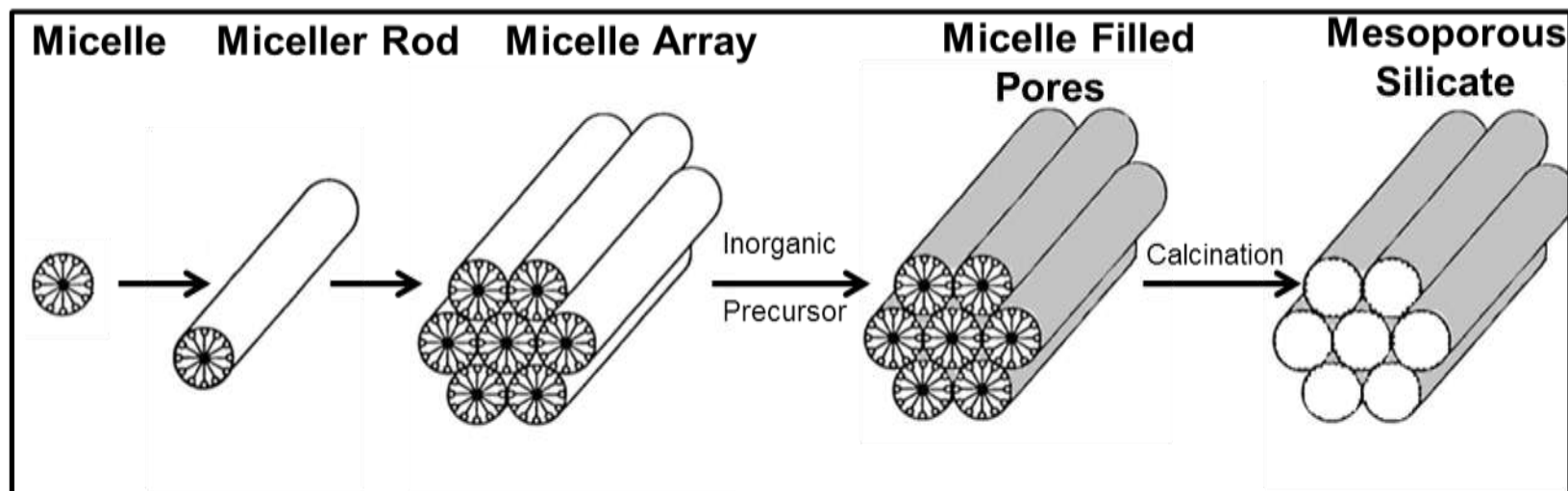


Figure 1.11: Formation of surfactant templated mesoporous silicates

must remain neutral, a cationic species must be present to compensate for the negatively charged Al centers. Based on the method of synthesis, this can be a metal cation, an ammonium or alkyl ammonium cation, or a proton. The acid forms of the aluminosilicate where a proton is the cation tend to be the most useful for catalytic applications. When an acidic proton is the charge balancing species in an aluminosilicate, the proton is generally believed to be somewhat mobile, but is usually drawn on a neighboring oxygen atom (Figure 1.12). The nature of the acidic proton has led to this type of site being labeled a Brønsted acid site.

The aluminum centers themselves can also act as Lewis acidic, electron accepting, centers. There is some uncertainty or lack of general understanding in the literature as to the exact nature of Lewis acidic aluminum centers. Theoretically, Al centers would be expected to act as Lewis acid centers when they possess only three covalently bound ligands. In the context of the octet rule this situation fills the valence electron orbitals with only 6 electrons when having a full 8 electrons would produce a more stable compound. As a result, three-coordinate aluminum species act as strong Lewis acids and bind a variety of Lewis bases (ethers, amines, phosphines, etc.).

In most synthetic strategies (sol-gel, hydrothermal) it is difficult to rationalize the formation of stable three-coordinate aluminum centers, as the aqueous conditions will almost certainly lead to aluminum species with a coordination of four or greater. Yet even in these systems there is strong evidence for Lewis acidic aluminum centers.⁵² One question that does not seem to have been addressed is whether 4-coordinate aluminum centers that possess local Brønsted acidity may also act as Lewis acids, or whether dissociation of the Si-O-Al bond to create a Lewis acidic Al center and a silanol must occur (Figure 1.12).

In general, most aluminosilicates possess a mixture of Brønsted and Lewis acidity as characterized through a number of methods. Purely Brønsted acidic systems have been created (sulfonic acid resins, heteropolyacids)^{53,54}, but to date, few if any purely Lewis acidic aluminosilicates have been synthesized.⁵⁵ The preparation and characterization of purely Lewis acidic heterogeneous aluminosilicates is a challenge, and a primary focus of the work carried out for this dissertation.

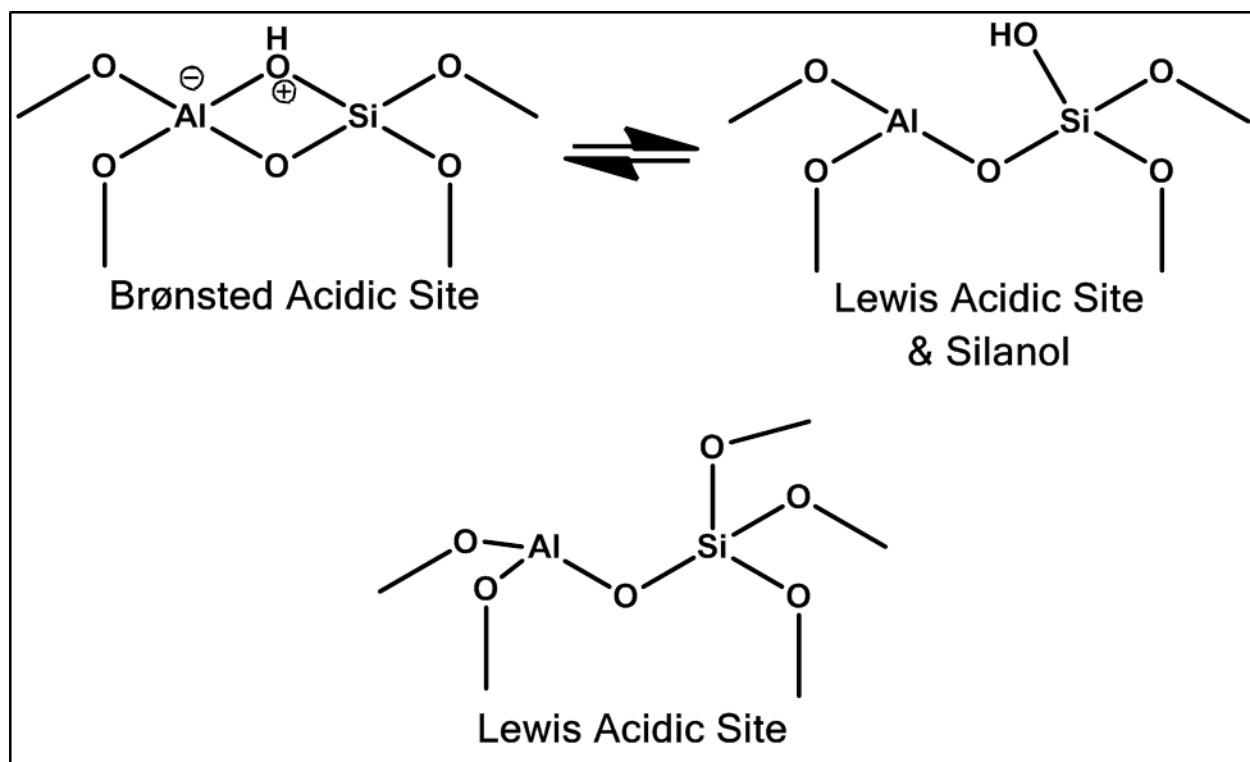


Figure 1.12: Acid sites in aluminosilicates

1.5.4 – Methods for the Synthesis of Aluminosilicates

Synthetic procedures to create aluminosilicates commonly utilize one of three methods: sol-gel synthesis, hydrothermal synthesis, or surface modification.

Sol-gel synthesis of aluminosilicates involves the hydrolysis and co-condensation of aluminum and silicon alkoxides, or silicon alkoxides with aqueous aluminum salts.⁵⁶ Reactions are typically carried out in alcohol solvents such as ethanol or butanol. The degree of condensation can be controlled through the stoichiometric ratio of water to alkoxide in the reaction. Typically the reaction is either base or acid catalyzed and is carried out at temperatures $<100\text{ }^{\circ}\text{C}$.^{57,58} The scheme below (Figure 1.13) shows the mechanistic process by which water leads to hydrolysis of the alkoxide ligand to produce Si-OH bonds which then condense with a second Si(Al)-OR or Si(Al)-OH species to create a Si-O-Si(Al) linkage. Lowenstein's rule states that Si-O-Si and Al-O-Si linkages are more stable than Al-O-Al bonds, and thus are preferentially formed until Al concentrations become large enough to require Al-O-Al bond formation.⁵⁹ As the reaction continues, a gel is formed through repeated crosslinking of the species in solution. The gel is allowed to age before removal of solvent and calcination to produce the final product.

Zeolitic aluminosilicates are synthesized by hydrothermal methods. Hydrothermal synthesis is defined as the crystallization of substances from high temperature aqueous solution under elevated pressures. The necessary materials to carry out the hydrothermal syntheses of aluminosilicate type zeolites include 1) a silicon source, 2) an aluminum source, 3) basic conditions (some synthetic procedures do use acidic conditions), 4) a structure directing agent, and 5) water.^{46,60}

Sources of silica often include aqueous sodium silicate, colloidal silica (e.g. Ludox), fumed silicas (e.g. Cabosil, Aerosil), and tetramethyl- or tetraethylorthosilicate (TMOS & TEOS). Aluminum sources often include aluminum alkoxides, sodium aluminate, or other Al^{3+} salts (e.g. sulfate & nitrate). The base source and template agent are highly interconnected in that the structure directing agents for zeolitic syntheses tend to be hydrated cations. These can either be alkali ions such as K^{+} or Na^{+} or organic alkyl ammonium cation species. Frequently, these ions are introduced in

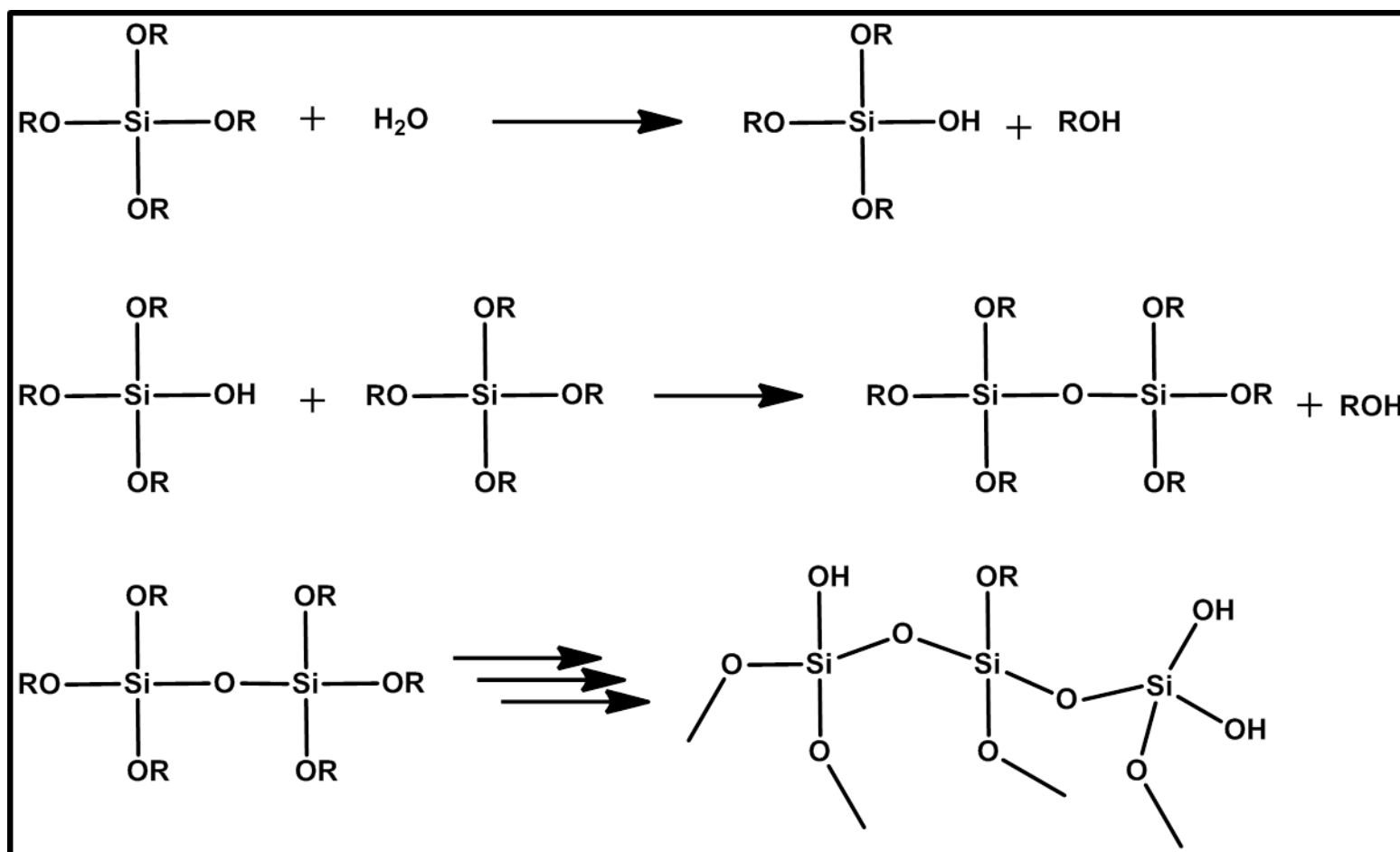


Figure 1.13: Sol-gel condensation mechanism

their hydroxide forms which contribute to the basic conditions necessary for the synthesis. At the same time the cations serve as templating agents and have a significant effect on the pore systems of the synthesized zeolites. As the size of the hydrated cation increases, the pore size within the zeolitic structure generally increases. The large number of adjustable parameters within these systems has led to the identification and synthesis of nearly 200 different zeolite framework structures.⁶¹

Once the desired amounts of source materials are determined, the typical synthetic method begins with the dissolution of the base, silica source, structure directing agent and aluminum source in aqueous solution. The mixture is typically allowed to stir in a Teflon lined stainless steel reaction vessel until a homogeneous mixture is achieved. Often times the mixture will thicken into a gel. At this point, the mixture is heated to between 100-250 °C for anywhere from a few hours to two weeks leading to precipitation of the crystalline zeolite material.⁴⁶ Upon completion of the crystallization process the materials are washed with water and dried.

To create mesoporous aluminosilicates, sol-gel methods are typically followed. The primary difference between these materials and zeolites are larger structure directing agents, often in the form of surfactants that form micelles (Figure 1.11). The larger templating agents lead to larger pores, and consequently larger surface areas. However, the template must often be burned from the pores and cannot be recovered. Also, these materials tend to lack the crystallinity and long range order of the microporous zeolites.⁶²

Surface and post synthesis modification can be applied to materials synthesized by any of the above methods. The general methodology involves adding catalytic species to preexisting support frameworks. This can include direct placement of an active species onto the support surface (Figure 1.05), or the removal and replacement of non-active framework atoms with catalytically active centers. To prepare typical surface grafted catalysts, a catalytic precursor is reacted with the surface hydroxyl groups of some type of oxide support. This can be on the surface of a simple binary phase oxide (SiO_2 , Al_2O_3), or within the pores of high silica zeolites or mesoporous silicates.⁶³ Some of the common catalytic precursors are AlCl_3 ,⁶⁴ $\text{Al}(\text{O}^i\text{Pr}_3)$,⁶⁵ and

$\text{Al}(\text{CH}_3)_3$.⁶⁶ When using surface grafting approaches, it is common practice to first calcine the support in order to create “isolated silanol” groups. This procedure is an attempt to reduce the number of ways a catalytic precursor can bind with the substrate so as to provide the best chance to create a single type of site (Figure 1.14). Calcination leads to condensation of surface hydroxyl sites in close proximity to other hydroxyls. This leaves behind isolated hydroxyl groups, but even after calcination at temperatures up to 800°C, geminal hydroxyl groups are often still present in addition to isolated monohydroxyls.²⁵ In this situation, some species may possess a molecular geometry that allows for binding to the surface in more than one way, thus creating catalytic sites that likely show differing reactivity. A secondary result of high temperature calcination is a drastic reduction in the number of available binding sites, the result of which is low catalytic loading capacities for the surface grafted species

Incorporation of aluminum into the framework of an already synthesized silicate is more challenging. However, there have been studies reporting successful incorporation of Al under basic conditions.^{67,68} This is important due to the highly acidic conditions that some aluminosilicate syntheses require which can at times inhibit the complete framework incorporation of the Al centers.

1.6 Building Block Approach to Aluminosilicate Synthesis

As has been described above, there are a limited number of ways to prepare heterogeneous aluminosilicates, and for the most part these methods do not allow for careful tailoring of the catalytic sites. The catalysts synthesized by these methods are generally limited by the presence of multiple types of sites, a lack of site isolation, or as a consequence of trying to avoid these problems, by low site density. For the past ten years our group has sought to find ways to address these challenges.

The goal of the Barnes group has been to develop a broadly applicable synthetic methodology for the synthesis of silica supported catalysts that are defined by a high density of isolated, identical catalytic centers. This strategy centers around the use of the $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)$ building block, a broad class of catalytic precursors and inert linkers, and a well-defined linking reaction.^{69–71}

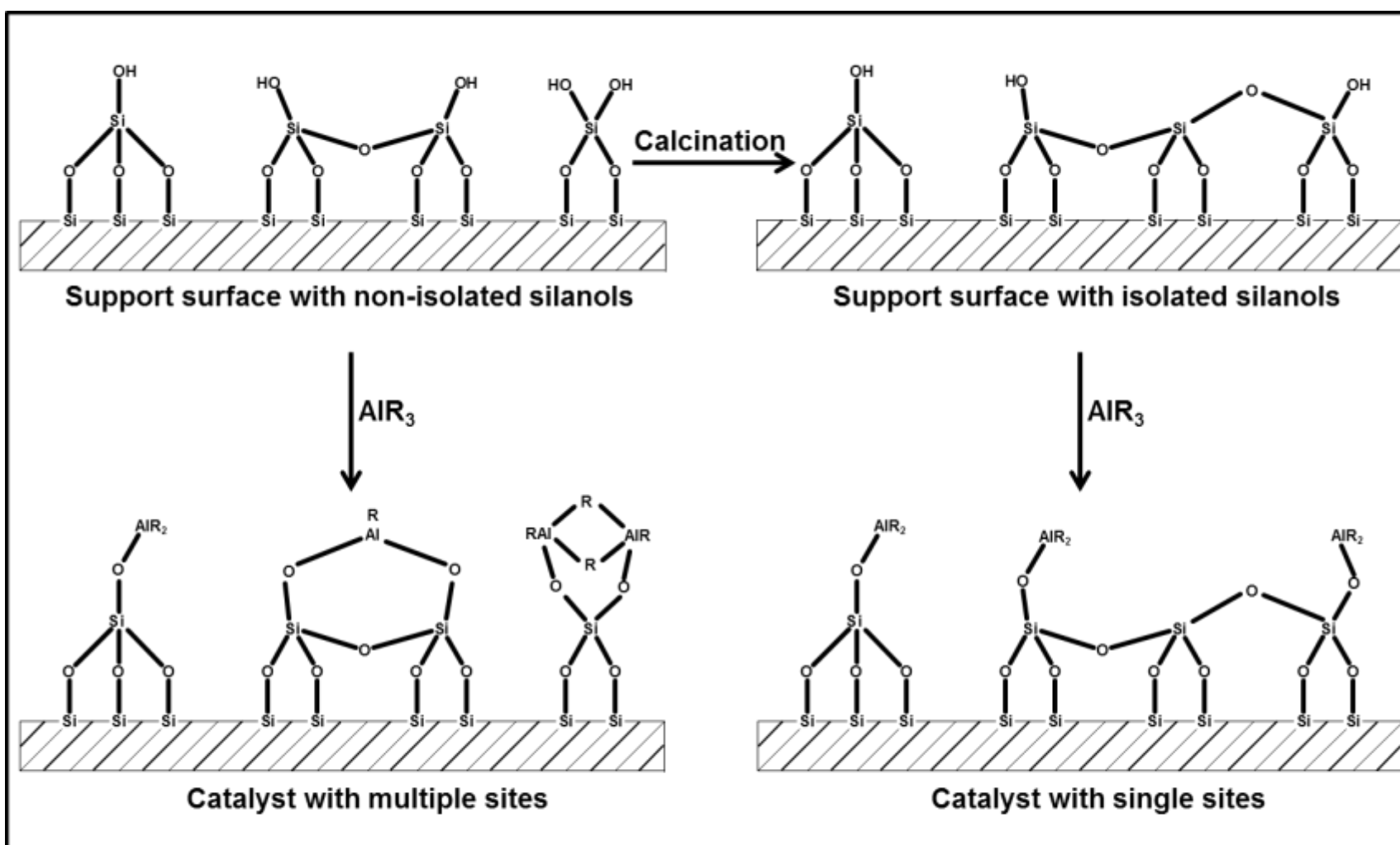


Figure 1.14: Reaction of alkyl aluminum species with isolated and non-isolated surface silanols

The tin functionalized sphaerosilicate, $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)$, (trimethyltin cube, TMT cube, tin cube) serves as the building block and the main component of the silica support in the final matrix. The size and shape of the building block strongly influences the structural nature of the final matrix (Figure 1.15). Its rigid cubic structure and well defined arrangement of functional $-\text{SnMe}_3$ groups help ensure that separation of the catalytic sites is preserved while the building block matrix is formed.

The cross-linking species are typically high valant metal and main group chlorides that may be divided into two groups: those that become the catalytic sites in the matrix, and those that form chemically robust, but inert, cross links between the cubes. A large number of such catalyst precursors exist, allowing for a broad range of catalytic centers to be inserted into these matrices. Investigations within our group have examined the reactivity of AlCl_3 , GaCl_3 , BBr_3 , TiCl_4 , VOCl_3 , VCl_4 , WCl_6 , WOCl_4 , and SnCl_4 as catalytic precursors. The precursors that yield chemically robust links include a number of silyl chlorides (SiCl_4 , HSiCl_3 , Me_2SiCl_2 , Me_3SiCl) that further cross-link the matrix and increase stability.

Properly combining these components enables one to develop a synthetic approach to preparing “nanostructured” materials in which structural influence has been exerted at several length scales. Formation of the catalytic matrix is initiated through the metathesis reaction of the trimethyltin functionalized building block and the precursor metal chlorides (Figure 1.16). M-O-Si bonds are formed cleanly along with the trimethyltin chloride (Me_3SnCl) byproduct. Having A and B functionalities ($-\text{Cl}$ and $-\text{SnMe}_3$) on the matrix precursors is important for the prevention of homocondensation products in the non-aqueous, non-hydrolytic conditions under which the reactions are carried out. As a result, catalytic sites remain isolated and metal oxide domains do not form. Furthermore the size of the building block that separates the catalytic center helps ensure that no two catalytic sites will be closer than 5-7 Å.

Structural control is also derived from the nature of the starting materials. The initial point of control develops at the linking center. As a metal chloride precursor reacts with the tin cube building block, the immediate environment around the metal center (first coordination sphere) is defined by the coordination preferences of that

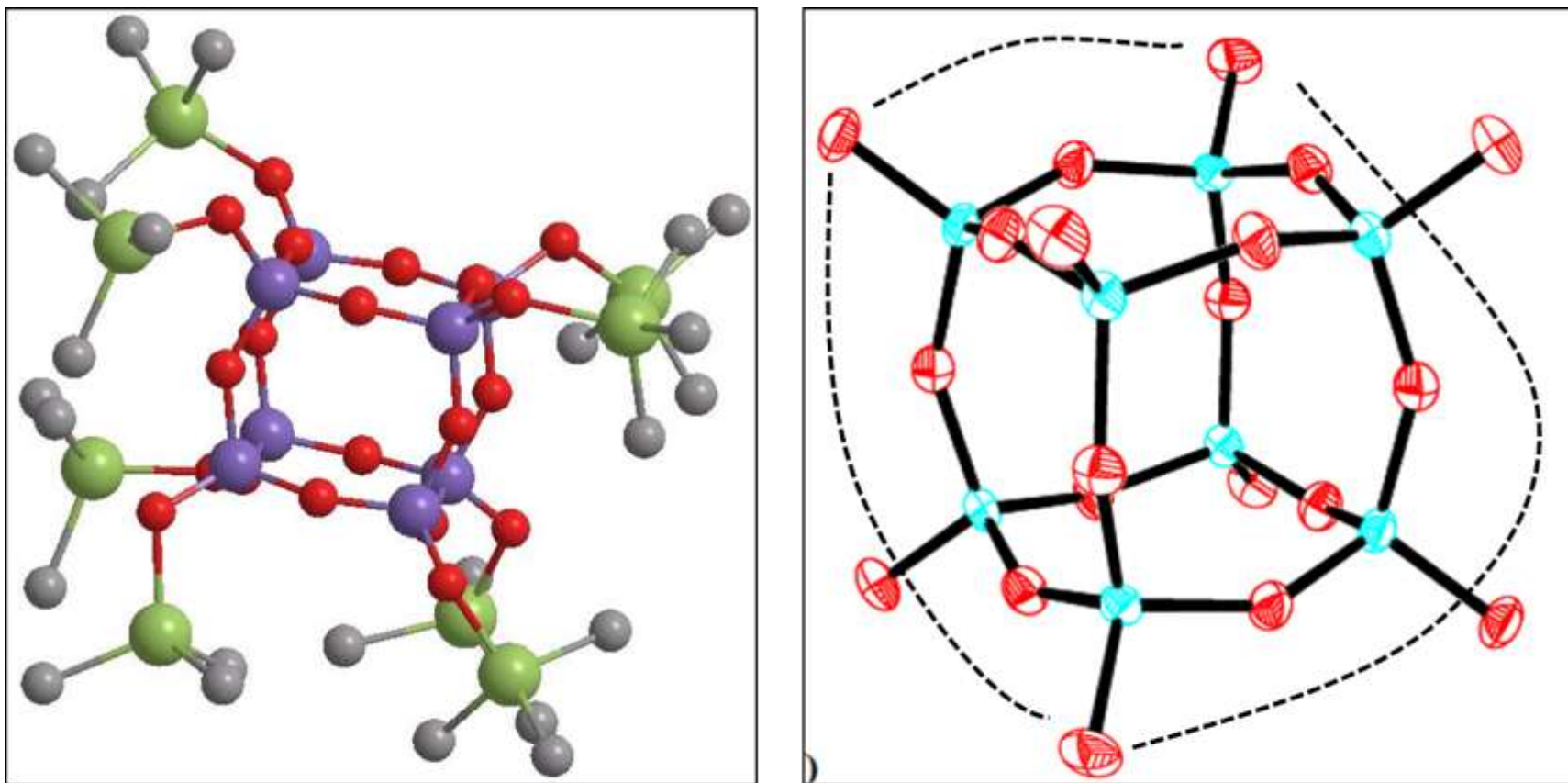


Figure 1.15: $\text{Si}_8\text{O}_{12}(\text{SnMe}_3)_8$ cubic building block & Si_8O_{12} silicate core

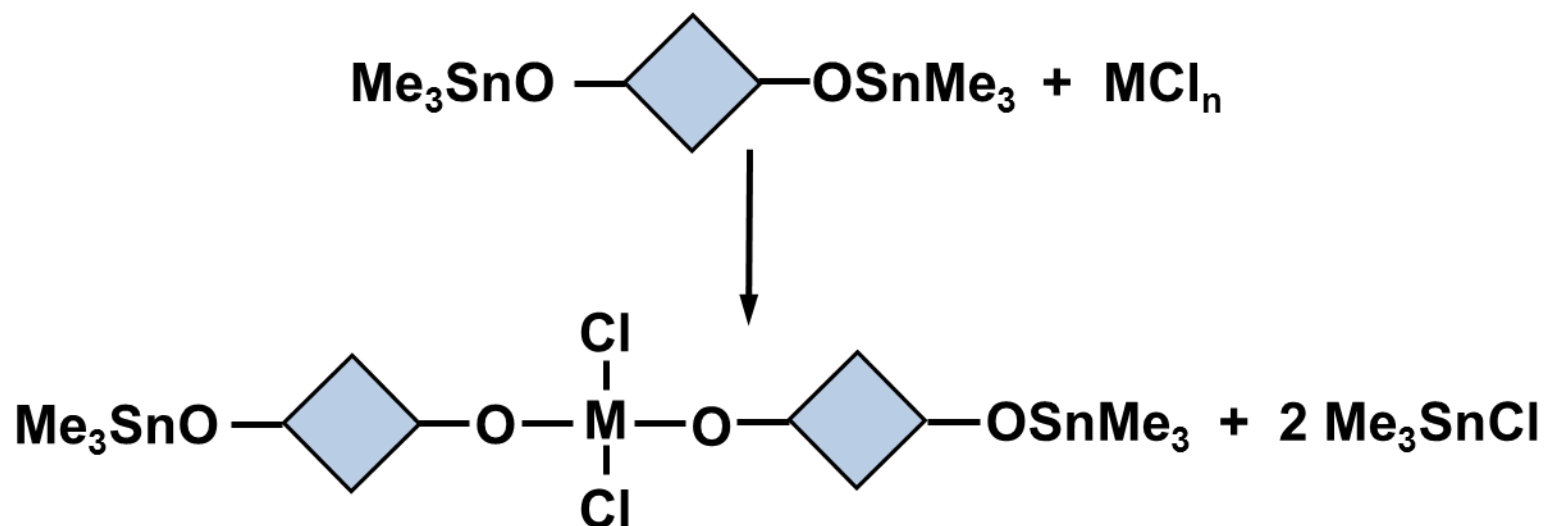
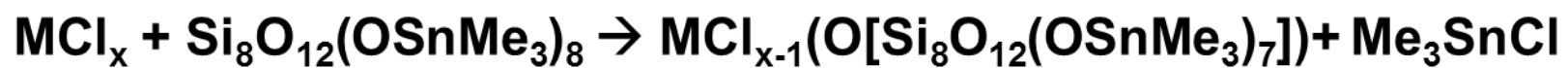


Figure 1.16: Schematic of metathesis reaction between trimethyltin functionalized building block and a metal chloride

metal (coordination number, geometry, M-O bond distances). Theoretically, this leads to centers with higher stability relative to those derived from more traditional preparation methods where removal of an atom in the matrix creates a vacant site which generally will not be geometrically or electronically optimized for the substituted species.

The cross linking reaction between the cube and metal chloride reagents is extremely clean and produces only trimethyltin chloride. This byproduct is volatile and easily removed under vacuum and moderate heating. The simple removal of the byproduct allows for a quick initial determination of the degree to which the cross linking reaction has occurred. To determine this value, gravimetric analysis of the mass change after the removal of Me_3SnCl from the reaction is carried out. From the mass difference, the number of moles of trimethyltin chloride may be calculated. Comparing the number of moles of the trimethyltin chloride lost to the number of moles of chloride added to the system via the metal chloride precursor allows one to determine, on average, how many chlorides have reacted on each metal center and consequently the average connectivity of a linking atom within the matrix.

Depending on the stoichiometric ratio of the building block to cross linker, it is believed that a mixture of small to medium sized oligomers exist after the first cross linking reaction. In order to further rigidify, stabilize, and increase the surface area of the matrix, a second cross linking reaction is performed utilizing a second dose of a silyl chloride. During all phases of cross-linking, some control of the hydrophobicity of the matrix can be accomplished. For instance, cross-linking with SiCl_4 will create a substantially more hydrophilic system than that of a matrix cross-linked with Me_2SiCl_2 (Figure 1.17).

Finally, this methodology can be easily manipulated to change the connectivity of the catalytic site to the matrix. By controlling the reaction stoichiometry, modifying the catalytic precursor, and adjusting the order in which reaction steps are carried out, we have been able to target and produce sites with specific connectivities within the matrix. If a limiting amount of metal chloride is reacted with trimethyltin cube, then all chlorides on the metal center will react to form M-O-Si bonds. This is referred to as an imbedded or framework species (Figure 1.18, top). As the stoichiometric ratio of MCl_x :TMT cube

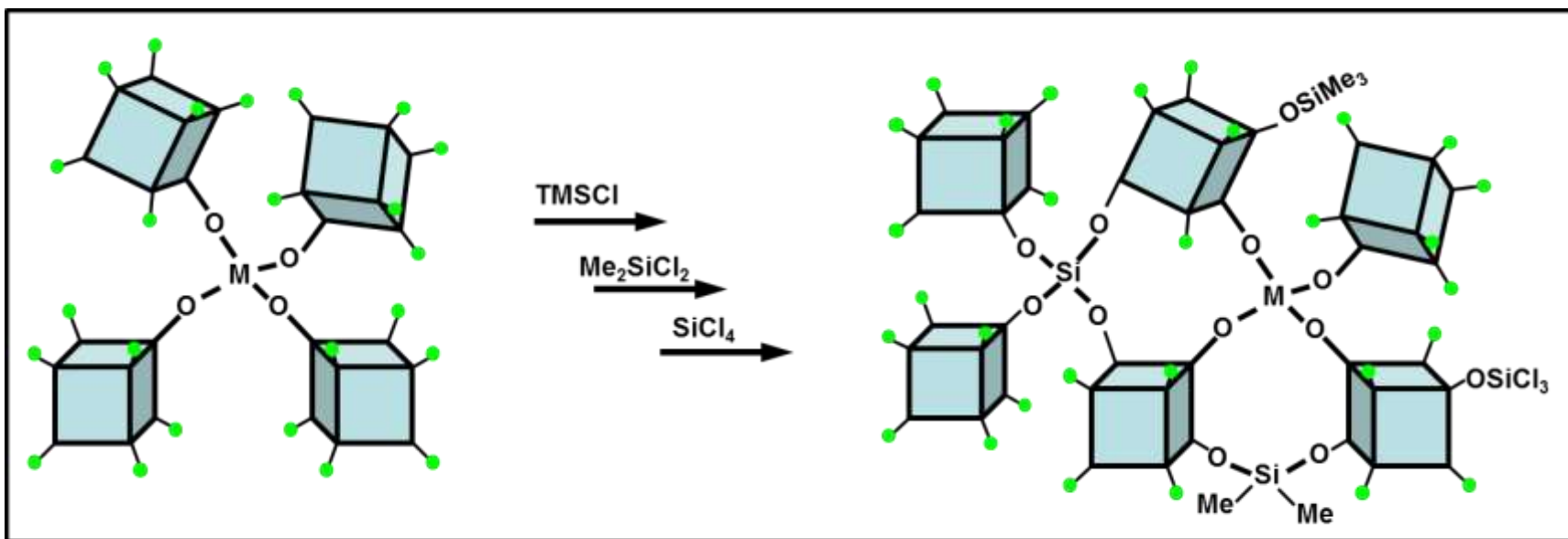


Figure 1.17: Secondary cross-linkers adjust the hydrophobicity of the matrix

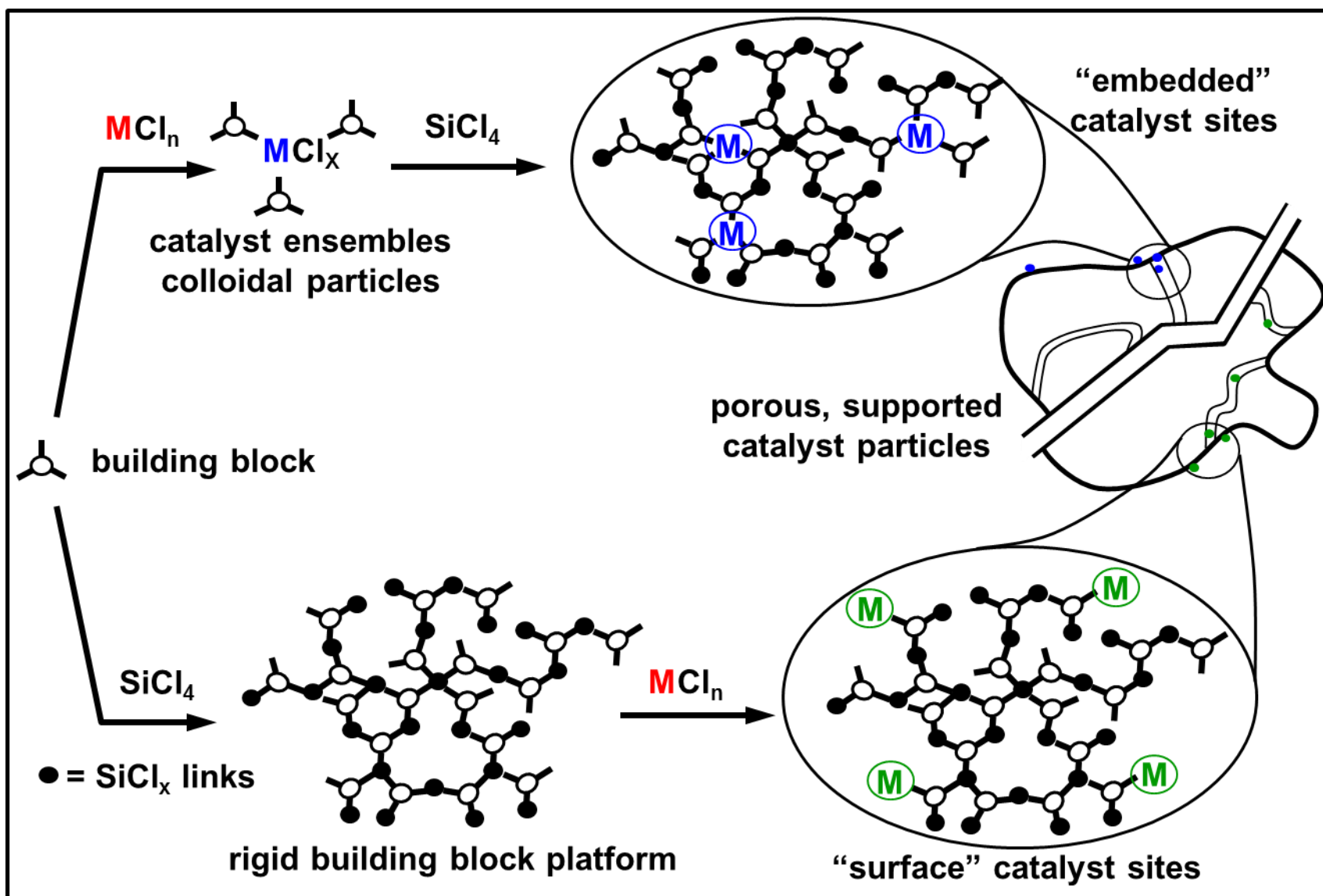


Figure 1.18: Method of sequential additions to produce “imbedded” and “surface” catalysts

increases, the initial stages of reaction and matrix growth will be the same. However, due to the irreversible nature of the linking reaction, at a certain point the matrix will become rigid and the trimethyltin groups and remaining chlorides will become isolated. At this stage the cross linking reaction cannot occur and any unreacted M-Cl bonds will remain. Any metal center with unreacted chlorides cannot be considered fully imbedded and is referred to as “x- connected”, where “x” refers to the average number of chlorides that have reacted with trimethyltin groups to form M-O-Si linkages (Figure 1.19).

As previously described, to make an embedded site, a limiting amount of MCl_x is reacted with tin cube (typically, a Cl : cube ratio of greater than 3 : 1). If the dosing sequence is reversed (Figure 1.18, bottom), isolated, 1-connected surface metal sites can be produced. By initially cross linking with a silyl chloride we can create a cross-linked matrix where any remaining $-OSnMe_3$ groups are spatially isolated. When a second reaction is carried out with a metal chloride reagent, then the isolation of the tin functionalities limits the number of M-O-Si bonds that can be made by each metal center to one. In each of these cases, controlling reaction stoichiometry and the dosing sequence gives rise to silicate matrices that have only one type of metal site. The strategy of manipulating the series of reaction steps has been termed the method of sequential additions (Figure 1.18). If an initial reaction is carried out where the ratio of Cl : cube is greater than 3 : 1, then a mixture of sites will generally result. While the ratio can be manipulated to achieve integer average connectivities, it has been shown that a distribution of species with different connectivities will result.⁶⁹ For instance if $SiCl_4$ were to be reacted in a ratio of 1.75 : 1; $SiCl_4$: TMT cube (7 : 1; Cl : TMT cube), you would achieve an average connectivity of 3. However, ^{29}Si NMR spectra show that the matrix would contain a mixture of 2, 3, and 4-connected species.⁶⁹ This situation can be avoided by utilizing a precursor in which some of the chloride ligands have been replaced with unreactive ligands that serve as blocking groups (Figure 1.20). In the case of titanium, it has been shown that using the titanium chloroalkoxides (e.g. $Ti(O^iPr)Cl_3$ and $Ti(O^iPr)_2Cl_2$) under the right stoichiometric ratios leads to supported

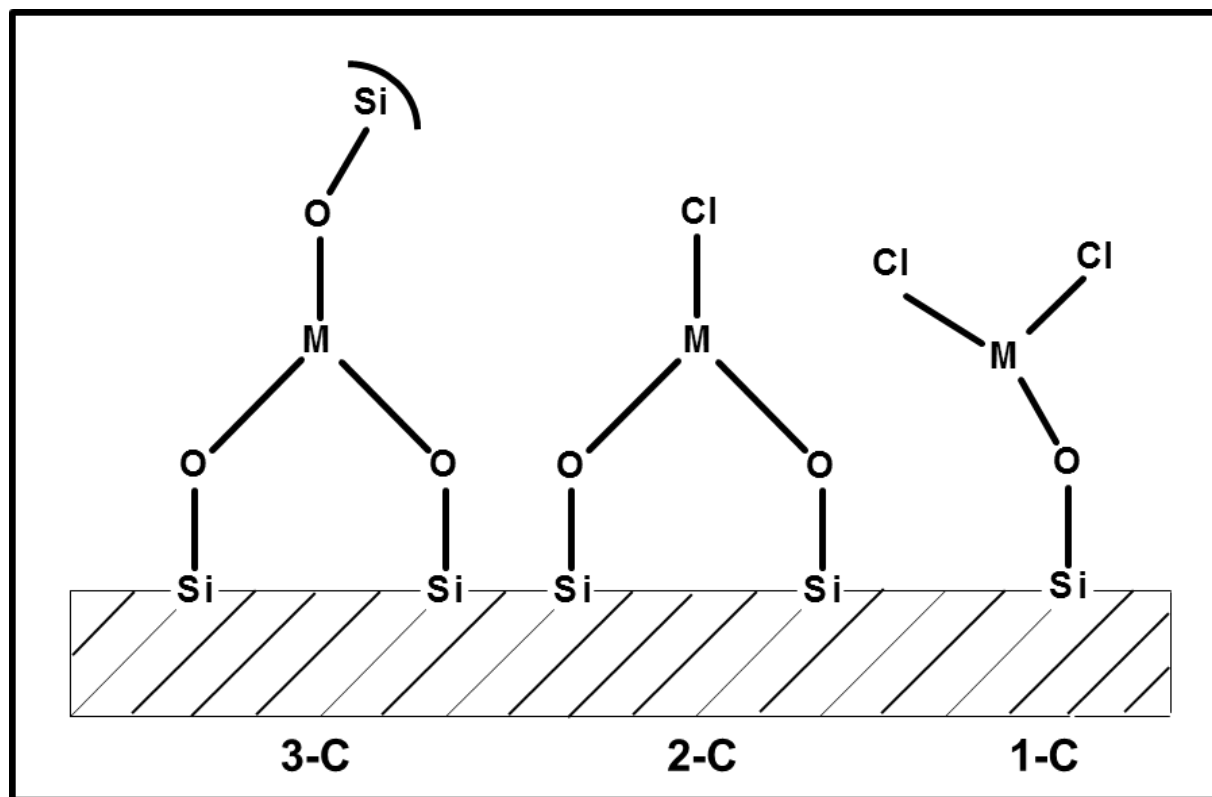


Figure 1.19: 1,2 & 3-connected metal centers

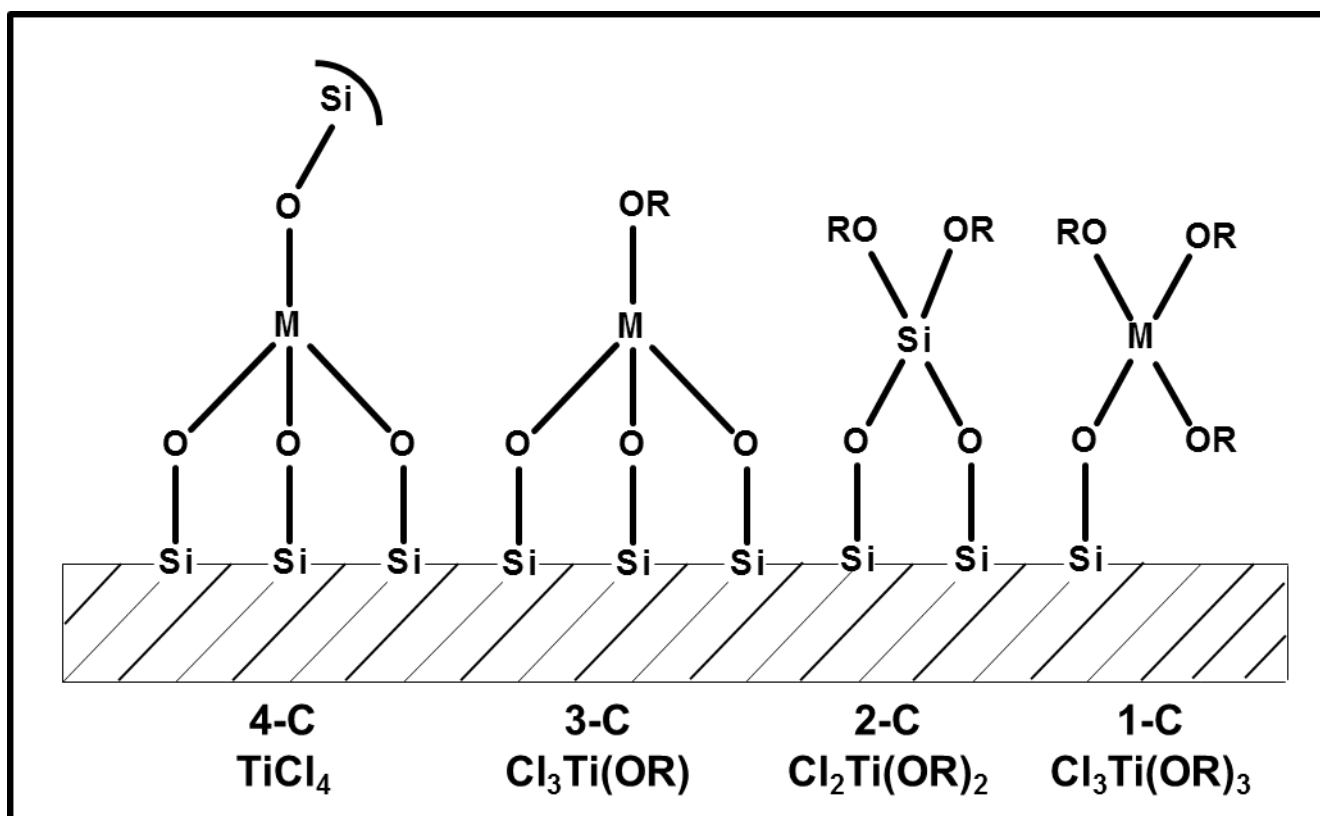


Figure 1.20: Using catalytic precursors with non-reactive blocking groups to ensure single site catalysts with varying connectivity

catalysts possessing integer connectivities with a single type of site. The alkoxide groups are unreactive towards metathesis with the trimethyltin group of the building blocks, and thus the maximum connectivity of the precursor is defined by the number of chloride ligands. The applicability of using this type of blocking group may not be as broad as in the case of pure metal chloride systems due to the instability of some mixed chloroalkoxide species, especially in the case of aluminum.

1.7 Gallium, Boron, & POSS Analogues

A central theme of the work in this thesis is to investigate the reactions of group 13 halides (B, Al, Ga) with trimethyltin cube and to characterize the sites that are formed in the building block matrix. A primary emphasis has been placed on aluminum, but there are a number of reasons that both boron and gallium are also of interest. Borosilicates are a well-known class of materials, and boron itself is unique, in some cases exhibiting different reactivity from that of aluminum and gallium. Because of this, the reactive and structural differences that may result on insertion of boron into the matrix are of great interest. With boron, direct detection of B-O stretching modes by IR can be carried out. Another benefit of looking at boron is the introduction of another NMR active nucleus. The ^{11}B nucleus has a smaller quadrupole moment than aluminum, making it generally less difficult to collect and interpret. Gallium presents another catalytic species that we might expect to be very similar to aluminum. Furthermore, gallium has sufficiently high ionization energy to allow for routine XAS data collection. This introduces another direct characterization technique for looking at the metal centers within the matrix. As gallium analogues of aluminum species are known to exhibit very similar chemical profiles and are active in many of the same catalytic processes,⁷²⁻⁷⁴ this presents an opportunity to extrapolate what is learned about the gallium species back to aluminum, where the only direct characterization technique is SSNMR.

Insoluble amorphous matrices present a number of special challenges with regards to characterizing the sites present. Another approach examined in this work serves to simplify the matrix and reduce some of the challenges faced by the production

of these complex amorphous systems. Utilizing tin functionalized polyhedral oligomeric silsesquioxanes (POSS) (Figure 1.21) in this context serves to prevent the reaction of multiple metal chloride precursors with a single building block. In doing so, extensive crosslinking is avoided. If this can be achieved, theoretically identical sites should develop between the monofunctionalized silicate cubes, creating molecular species instead of an amorphous highly cross linked matrix. If these small oligomers remain soluble, then a number of very powerful characterization techniques become available. Principle among these is solution NMR which is both simpler to interpret and easier to obtain than SSNMR. Additionally, a huge breakthrough could be made if these molecular species could be induced to form crystals suitable for XRD analysis.

1.8 Characterization Methods

1.8.1 – Gravimetric Analysis

The very first notion of the degree to which a linking reaction has progressed was developed through the recognition that a single byproduct is produced when a new M-O-Si bond is formed. Gravimetric analysis is defined by the difference in the mass of the starting materials and the products once the reaction has been stopped. The metathesis reaction between the TMT cube and a metal chloride produces the volatile byproduct Me_3SnCl which can easily be removed from the reaction system by heating under vacuum. Since the weight of the initial reactants is known and the starting materials normally react to form only a non-volatile cross-linked matrix and the volatile Me_3SnCl byproduct, then any mass change that occurs from heating the reacted mixture under vacuum is a result of loss of Me_3SnCl . By quantifying the amount of the byproduct lost and comparing it to the amount of initial metal chloride, the number of chlorides per metal center that have reacted can be calculated. In this way the average connectivity of a catalytic center to the matrix may be determined immediately after the reaction is completed.

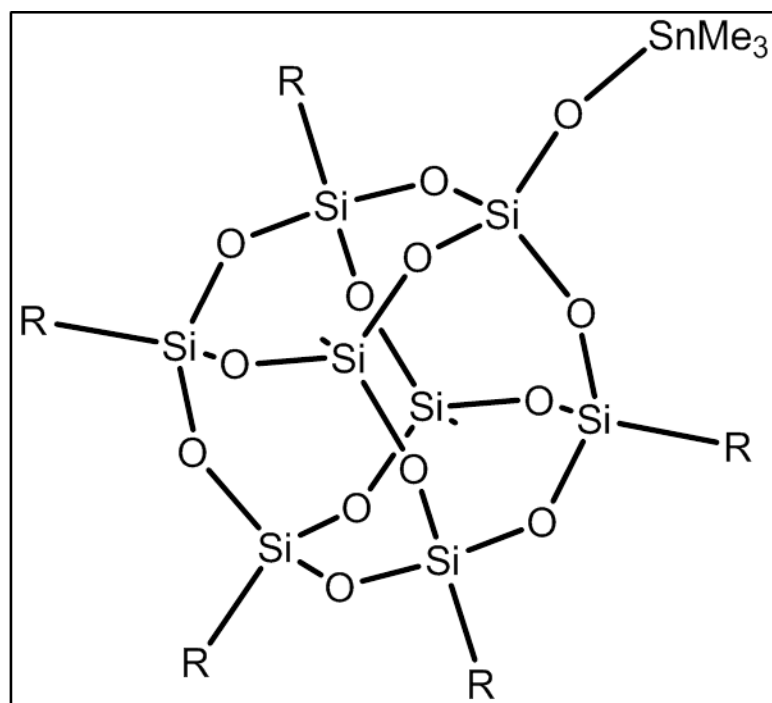


Figure 1.21: Monofunctionalized polyhedraloligomeric-silsesquioxane (POSS) cube analogue ($R=iBu$, $cHex$, Ph)

1.8.2 – Gas Adsorption Measurements

Studies have shown that the surface area and pore sizes of a heterogeneous catalyst can play a large part in determining its activity and selectivity.⁷³ This is largely related to the mass transport characteristics of the system; that is, the ability of the substrate to reach catalytic centers in the pores, react, and the product to leave and reopen the site. Gas adsorption measurements can provide information on the overall surface area of a catalyst in addition to illuminating the nature of the pore structure within the solid system.^{75,76} Typically adsorption measurements are carried out utilizing nitrogen.

1.8.3 – Infrared Spectroscopy (IR)

Infrared (IR) and Raman spectroscopies have been widely used to characterize a variety of materials. In the field of heterogeneous catalysis, IR data can illuminate a number of important features of a given catalyst. IR radiation excites the vibrational modes of individual or small domains of atoms. The absorption wavelengths depend upon the strength of the bonds and nature of the atoms that are chemically bound. This leads to characteristic absorption frequencies for different types of bonding. In the case of metallosilicates, important spectral features include silicon oxygen (Si-O-Si), silicon-oxygen-metal (Si-O-M), hydroxyl (-OH), or alkyl (-CH) groups. Another approach by which vibrational spectroscopy can be used to help characterize catalyst sites is through the analysis of the vibrational signatures of molecules adsorbed on the active sites in the matrix. Such is the case when pyridine adsorption is carried out on solid acid catalysts, and the frequency of the ring carbon-carbon (C=C) vibrations yields structural information regarding the type of acid sites present in the catalyst (Figure 1.22).

1.8.4 – Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

ICP-OES is an analytical technique for determining the concentration of specific atoms in solution.⁷⁷ Because of the insoluble nature of the heterogeneous catalysts synthesized in this work, an initial step to break down and dissolve the catalysts must

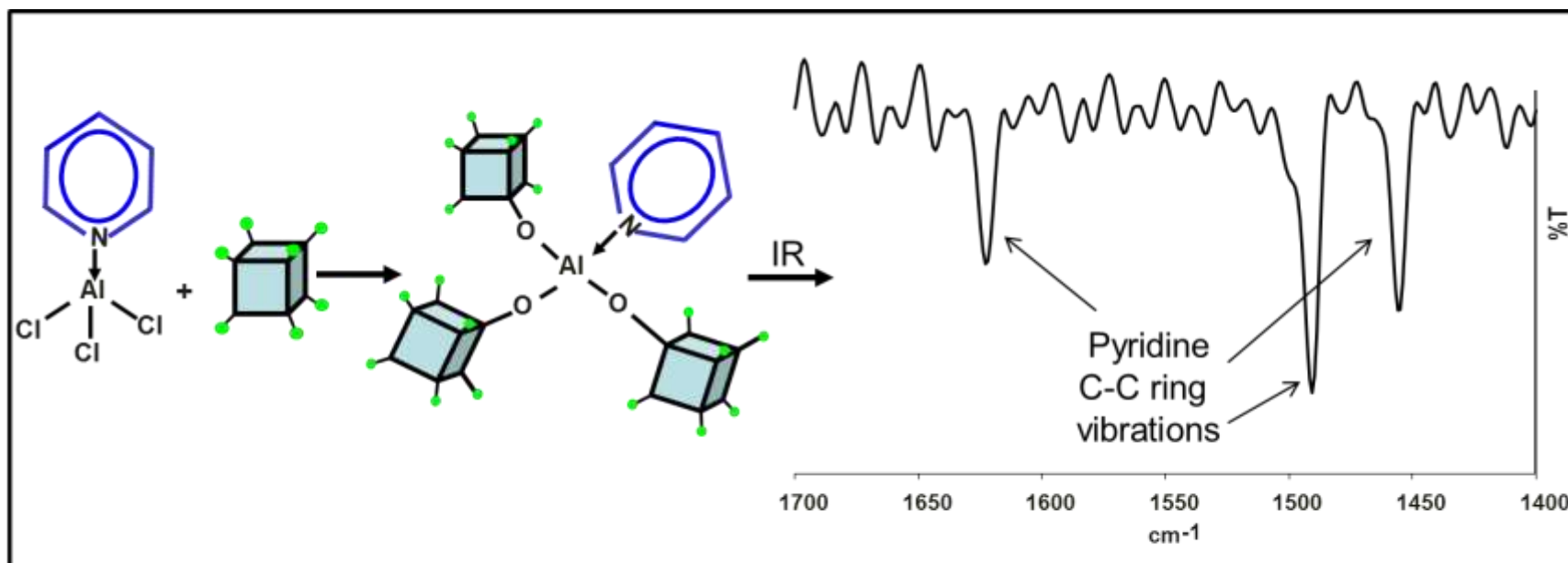


Figure 1.22: IR analysis of pyridine binding to a Lewis acidic center

be carried out before ICP-OES elemental analysis can be done. In the work presented, ICP-OES has been used primarily to determine and confirm the metal content of the catalysts that were synthesized in this work. However, it also serves as a method to check for leaching of metals under catalytic conditions, and in cases where more than one metal may be present in the catalysts (i.e. residual tin centers) it allows for determination of the ratio of the two metals.

1.8.5 – Nuclear Magnetic Resonance Spectroscopy (NMR)

1.8.5.1 – Solution NMR: Solution state NMR is one of the most widely used spectroscopic techniques for structural elucidation in the field of chemistry today.⁷⁴ It is of critical importance in areas where synthetic chemistry is an essential focus. Information garnered from NMR spectra includes chemical shifts, relative signal intensities, and scalar J couplings. The frequency of the chemical shift(s) for a particular atomic center(s) is determined by the local magnetic field as determined by other neighboring atoms. The differences in chemical shift can help to determine and identify the structural nature of an atomic center. When two spin active nuclei are in close proximity, through-bond scalar coupling mechanisms can result in nuclear spin interactions. These interactions lead to well-defined splitting patterns that are determined by the equation $2nI+1$ where, I is the nuclear spin of the neighboring nucleus. These patterns can indicate the number of neighboring spin active nuclei, and provide further structural information. The frequency differences between split signals are inherent characteristics of a specific arrangement of nuclei in a particular molecule. Such splittings are typically measured in hertz and are not dependent on field strength. The signals in a given molecule should always exhibit the same scalar coupling constants. Together these three pieces of data can help determine the chemical structure of a molecule of interest.

1.8.5.2 – Solid State NMR: The most fundamental difference between solution state NMR and solid state NMR lies in the motion of the molecules.⁷⁸ In a solid sample of an amorphous or polycrystalline powder, the molecules do not undergo the fast Brownian motion exhibited by small molecules in solution. Furthermore, individual

crystallites or amorphous domains are positioned in random orientations with respect to each other and the external magnetic field and are unable to change orientation in the time span of the NMR transition. This, of course, is very different than solution state NMR where the molecules are subject to lower barriers to motion and can typically be thought of as randomly tumbling at rates that are much faster than the time scale of the NMR transitions. As a result, all signals from the many orientations of the single molecules in solution average out to yield a single sharp isotropic signal.

For solid state samples this fast averaging does not occur, and the lack of motion manifests itself in the solid state spectrum through a broadening of the spectral lines. This broadening is the result of two types of interactions that are not typically observed in solution state NMR; dipolar coupling, and chemical shift anisotropy (CSA).⁷⁸ Because of these two broadening mechanisms, information regarding the isotropic chemical shift and the J coupling values is often obscured making the spectra obtained significantly more difficult to interpret.

The CSA is manifested in the observation of a low signal-to-noise ratio (S/N) chemical shift envelope (powder pattern) that represents all possible chemical shifts as a result of the distribution of nuclei orientations within the solid sample. The chemical shift of an atom is a result of the external magnetic field interacting with the local magnetic field produced by the electrons surrounding the nucleus of an atom. This external field can add or subtract to the field surrounding the nucleus of an atom resulting in an altered resonance frequency for that nucleus. Since, the distribution of electrons around a nucleus is typically not spherical, (it is better thought of as an ellipsoid) the degree to which the external magnetic field affects the resonance frequency of the nucleus will differ depending on the orientation of the molecule with respect to the external magnetic field.

There is no simple way to combat broadening that results from the chemical shift anisotropy by adjusting the scanning parameters or the pulse sequence. However, an extremely powerful method for dealing with this problem has been developed. This method takes a cue from solution NMR, where the molecules move rapidly and average out the chemical shift anisotropy. While it would be extremely difficult to spin a powder

sample in a manner where the random rapid motion would average out the chemical shift anisotropy, it happens that the axially symmetric isotropic coupling term of the CSA Hamiltonian is proportional to $(3\cos^2\theta-1)$.⁷⁹ When a solid sample is spun at an angle $\theta = 54.74^\circ$ with respect to the external magnetic field (Magic Angle Spinning, MAS), this term is equal to zero and in theory cancels the anisotropic term of the Hamiltonian.⁷⁸ In reality, to completely average the CSA contributions to the line width would require that the sample be spun at frequencies higher than the magnitude of the anisotropic interactions. In many cases, averaging of the chemical shift anisotropy ellipsoid via MAS at slow spinning speeds is not completely successful (Figure 1.23). Instead of observing only the isotropic signal, there is still some non-uniformity and a number of peaks remain within the chemical shift envelope. These peaks are referred to as spinning sidebands. To completely remove all spinning sidebands and leave only the isotropic peak, it is necessary to spin the sample at a frequency that is greater than that of the chemical shift envelope. As spinning rates increase, the spinning sidebands are pushed out of the envelope and disappear. Their intensities are then combined back into the isotropic peak increasing signal to noise, thus improving the spectrum. For some nuclei it is possible to spin faster than the CSA, but for those with very large chemical shift anisotropies (>30-40 KHz) it is not yet possible to mechanically spin the sample fast enough and therefore patterns of spinning sidebands are frequently observed.

The other primary broadening mechanism in SSNMR is that of dipolar coupling which is the result of through space interactions between two magnetically active nuclei. Dipolar coupling results from both homonuclear and heteronuclear interactions. Homonuclear dipolar coupling is of concern for spin active nuclei with high natural abundances, or high magnetogyric ratios.⁷⁸ For elements where the NMR active nuclei are in low abundance it is unlikely that active nuclei would be near enough to each other to cause significant homonuclear dipolar coupling. Also, when the magnetogyric ratio is small, then the homonuclear dipolar coupling constants are smaller. The dipolar interaction also shares the $(3\cos^2\theta-1)$ term, and thus the coupling can be averaged out if the sample is spun at a frequency higher than the coupling constant.

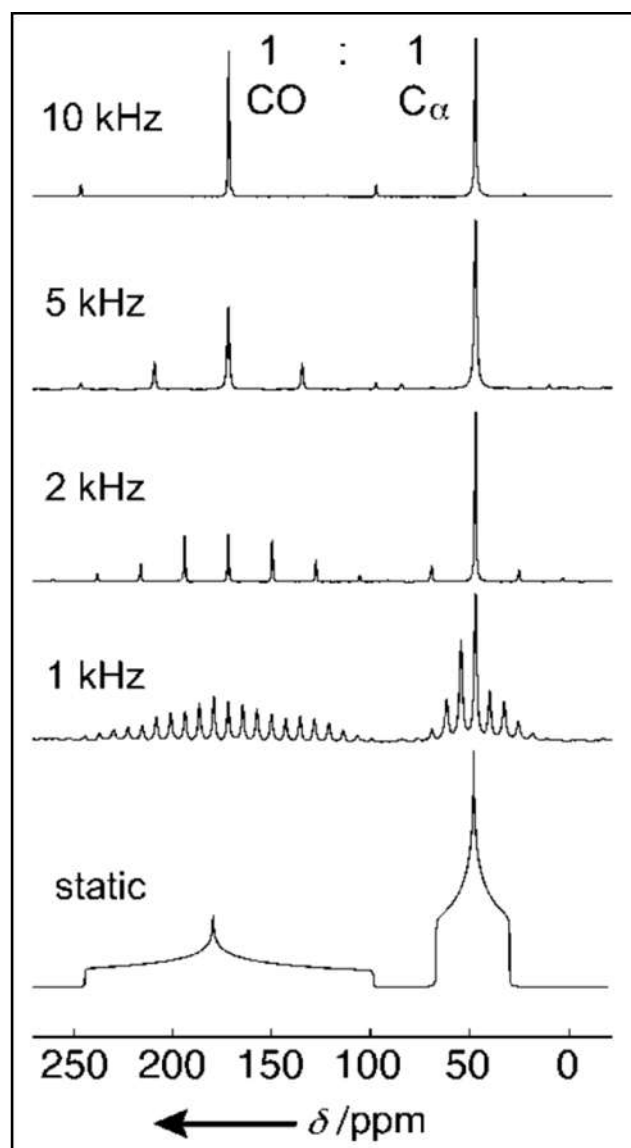


Figure 1.23: ^{13}C SSNMR spectrum of glycine at increasing MAS speeds⁷⁸

When dealing with the SSNMR of hydrogen, which has a high natural abundance and a high magnetogyric ratio, one tends to see only a single broad peak with a typical line width of 50-100 KHz. MAS spinning can help, but as noted above the technology does not currently exist to spin the sample at speeds greater than 50-60 KHz, and thus it is not possible to average out all ^1H - ^1H coupling in these cases.⁸⁰ Heteronuclear dipolar coupling tends to be more important for a variety of samples, and especially those with directly bound protons such as carbon. Coupling constants for ^{13}C - ^1H coupling tend to be in the range of 20-30 KHz and thus MAS is reasonably effective in reducing broadening due to dipolar coupling. In addition to MAS, heteronuclear coupling can be dealt with through high powered dipolar decoupling. This is similar to spin decoupling that occurs in solution state NMR. Using this method, the dipolar coupling of the ^1H nuclei on the ^{13}C spectrum can be averaged to zero by manipulating the ^1H spins. By applying a constant RF pulse at the ^1H resonant frequency, the proton spins will alternate between their α and β spin states on a time scale that is fast relative to measuring the signal of the X nucleus and average the heteronuclear dipolar coupling to zero.⁸⁰ Through the use of high powered decoupling alone, one can reduce the line width of a spectrum and also reveal the degree of the broadening that is a result of the chemical shift anisotropy (Figure 1.24).

When combined, MAS and dipolar decoupling can dramatically improve the quality of a spectrum; however, there is one other significant problem that occurs in SSNMR. Signal intensities in the solid state can be weak due to low natural isotopic abundances, low spin polarization, and long relaxation times. To obtain reasonable signal to noise values, it is often necessary to collect large numbers of scans and with the long relaxation times, this can lead to very long acquisition times. Taking another cue from such solution techniques as INEPT and DEPT that utilize polarization transfer, a solid state technique referred to as cross polarization (CP) has been developed to improve signal intensity, and utilize the shorter relaxation times of protons.⁸⁰ The CP process works because the highly polarized nuclei can, under the proper conditions, be made to transfer magnetization to less polarized nuclei. For a ^1H - ^{13}C system two RF

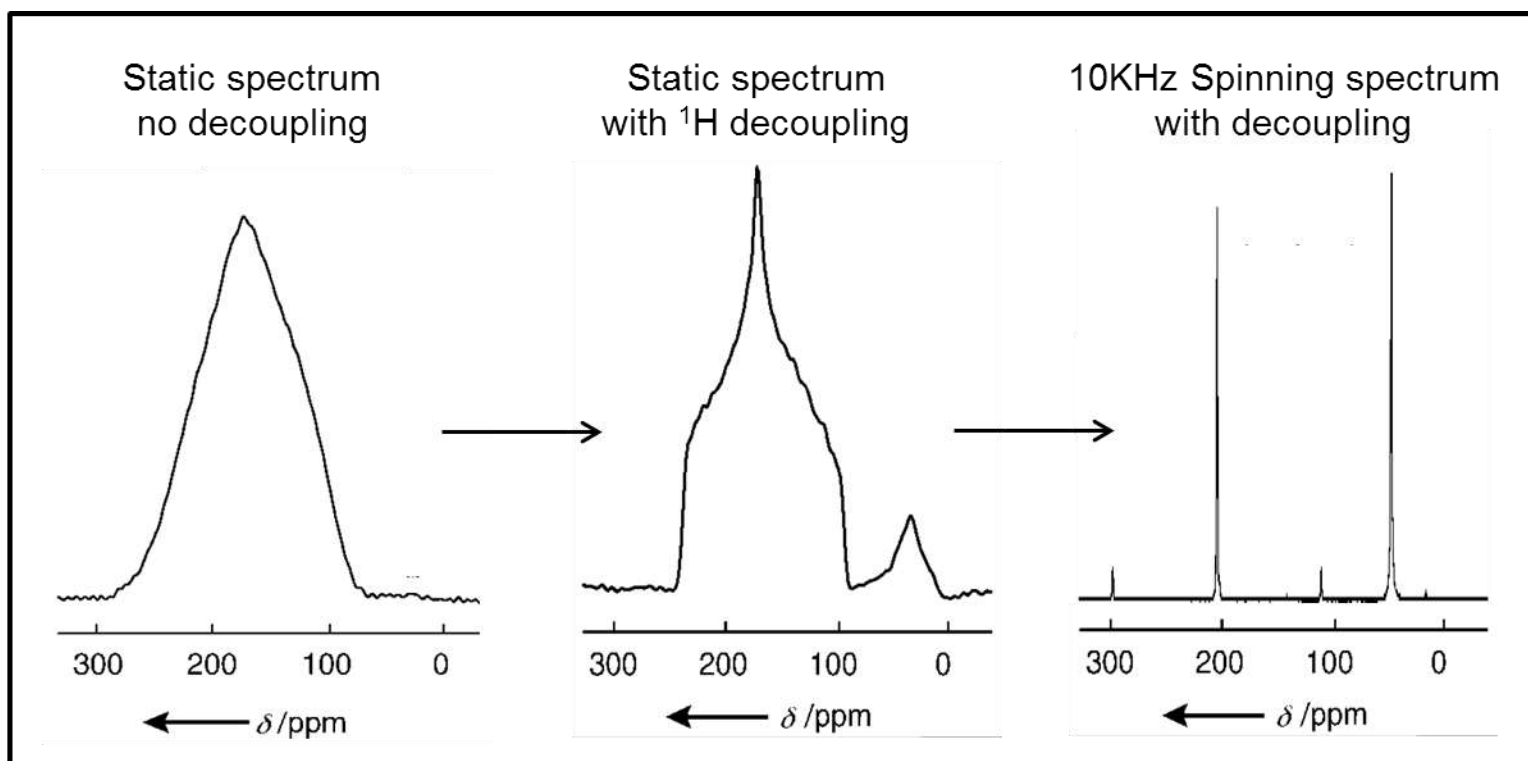


Figure 1.24: The effects of MAS and ^1H decoupling on ^{13}C SSNMR spectra of glycine⁷⁸

fields are applied at the resonance frequencies for each of the nuclei. These two frequencies can be adjusted independently by tuning the field amplitudes so that the rotation rates of the magnetization for each type of nuclei match each other (Figure 1.25). This is referred to as the Hartman-Hahn match.⁷⁹ When this match occurs, the two spin systems can then interact with each other. At this point, a proton spin system can transfer its polarization to the carbon system that does not yield as much signal via direct RF pulses. This process occurs during a period called the mixing time which is dependent on the strength of the dipolar coupling between the nuclei. Once the mixing has been completed, then the proton pulse is turned off, and the signal is detected from the carbon atoms. The improvement in signal can be drastic but the maximum enhancement for a single contact sequence is dependent on the ratio of the magnetogyric ratios of the two atoms. This means that for C-H cross polarization, the maximum enhancement that can be observed for carbon is four fold.⁸⁰ The other great benefit from all of this is that a spectrum requires far less time to collect because the normally long relaxation times required for collecting carbon spectra are significantly reduced.

The previous discussion has focused primarily on the detection of spin $\frac{1}{2}$ nuclei (i.e. ^1H , ^{13}C , ^{15}N , ^{29}Si). However, of the roughly 120 NMR active nuclei, more than two thirds possess spins $>\frac{1}{2}$.^{81,82} Of these, only nine nuclei have integer spins. Therefore, significant effort has been placed on the study of the nearly 80 nuclei possessing non-integer spins $>\frac{1}{2}$. These nuclei have quadrupole moments that arise from a non-spherical electrical charge distribution within the nucleus.

The presence of a quadrupole moment has several significant implications with regard to the number of predicted spectral transitions and signal broadening. If no quadrupolar moment were present for a spin $\frac{3}{2}$ nucleus, then the expected Zeeman splitting would produce four spin states with three allowed transitions ($-\frac{3}{2} \rightarrow -\frac{1}{2}$, $-\frac{1}{2} \rightarrow \frac{1}{2}$, $\frac{1}{2} \rightarrow \frac{3}{2}$). These transition energies would all be the same and thus a single resonance representative of all possible transitions would be expected. When the quadrupolar moment is taken into account, the interaction of the quadrupolar nuclei with

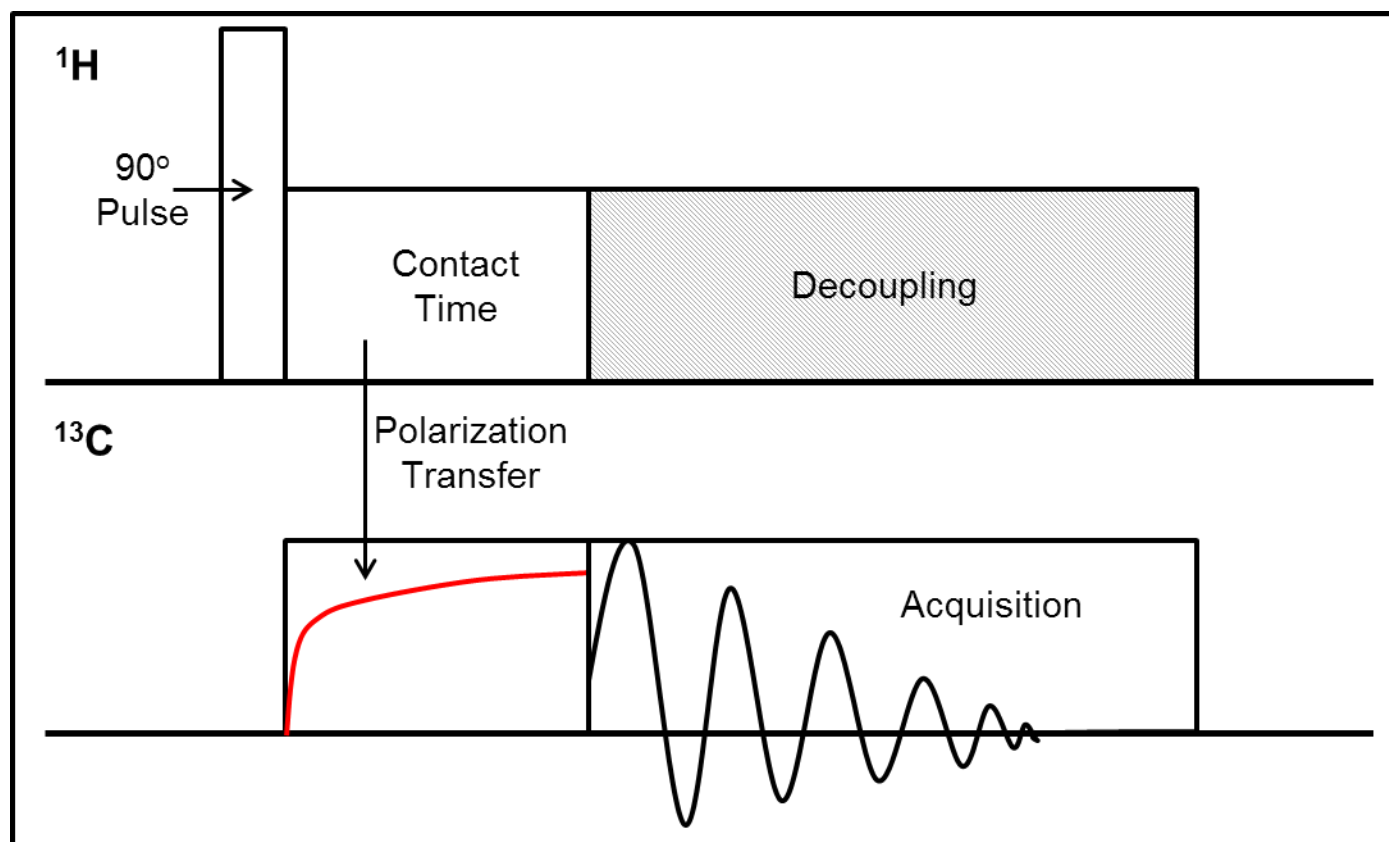


Figure 1.25: Cross Polarization (CP) Pulse Sequence

the external magnetic field results in an electric field gradient that inequivalently perturbs the transition energies between the Zeeman split energy levels. As a result of the different energies of the non-central transitions, multiple resonances may be observed in the spectrum. This leads to lower signal intensity, resolution issues and in the case of integer nuclei, difficulties in identifying the central transition due to considerable frequency shifts from the isotropic shift position. To a first approximation, in the case of non-integer quadrupolar nuclei, the energy of the $-1/2 \rightarrow 1/2$ transition is not affected by these phenomena, so the central transition in the spectrum will always occur at the isotropic chemical shift characteristic of the Zeeman frequency.⁸³

First order quadrupolar interactions can be significantly reduced by MAS, as the interaction is once again dependent on the angular $(3\cos^2\theta-1)$ term. However, when the strength of the quadrupolar perturbation is large, second order broadening effects become significant enough to cause problems that are not as easily dealt with. While the second order quadrupolar interactions also show angular dependency, the angles at which the interactions are cancelled out are different from that of the CSA and first order quadrupolar interactions. Therefore, with most basic NMR setups it is very difficult to remove both first and second order quadrupolar interactions. The primary result of the second order interaction is line broadening.⁸⁴

In the past 15 years the MQMAS (Multiple Quantum Magic Angle Spinning) approach has been developed, allowing for the removal of second order quadrupolar broadening without mechanical manipulation of the rotor between multiple angles.⁸¹ The details of the MQMAS approach are quite technical and beyond the scope of this thesis, however, as a result of such experiments, isotropic data unaffected by quadrupolar interactions can be obtained with high resolution.

1.8.6 – X-ray Absorption Spectroscopy (XAS)

X-ray absorption spectroscopy is an element specific method for the direct detection and characterization of the structural and electronic environment of a chosen elemental component within a sample. It is useful in characterizing a wide variety of naturally occurring and synthetic materials that include both crystalline and amorphous

structures. As a result, it has become a very important technique for the study of metal containing heterogeneous catalysts. Direct detection is important, as for many metals there are very few methods that allow for the characterization of metal centers themselves.

In x-ray absorption an atom absorbs a photon at an energy that is appropriate to eject a core electron to the continuum. The electron hole created by this ejection is then filled by a higher energy bound electron. As a result of the high energy electron falling to a lower energy state, fluorescence radiation is produced (Figure 1.26). The appropriate energy to eject the core electrons happens to be in the x-ray energy range, thus the nomenclature of XAS. To conduct these experiments, tunable, high intensity x-rays are essential and generally requires a synchrotron radiation source.

The two primary techniques that have been utilized are EXAFS (Extended X-ray Absorption Fine Structure), and XANES (X-ray Absorption Near Edge Structure). These two acronyms refer to distinct analyses performed on two different regions of the same x-ray absorption spectrum. The XANES region is generally defined as extending from ~50 eV below the absorption edge to ~50 eV above the absorption edge (Figure 1.26). From this region, information regarding the geometry, oxidation state, and sometimes bound ligands can be extracted.

The EXAFS region runs from ~50 eV above the edge to the point at which EXAFS oscillations superimposed on the absorption background are no longer observable. For isolated metal centers on silica, this is generally in the range of 800-1000 eV above the absorption edge. These oscillations contain information regarding the nearby physical environment of the metal center of interest. The oscillations can be extracted from the absorption background, at which point a Fourier transform can be carried out to produce a radial distribution spectrum that yields information regarding the distance, nature, and number of atoms in close proximity to the nucleus of interest (Figure 1.26).

It can be very difficult to collect XAS data on isolated metal centers for elements with $z < 22$ (Ti), due to the low absorption energies required to eject the core electrons. At energies below ~5 KeV many materials between the sample and the x-ray source absorb strongly. This includes air, ionization detector chambers, and the materials used

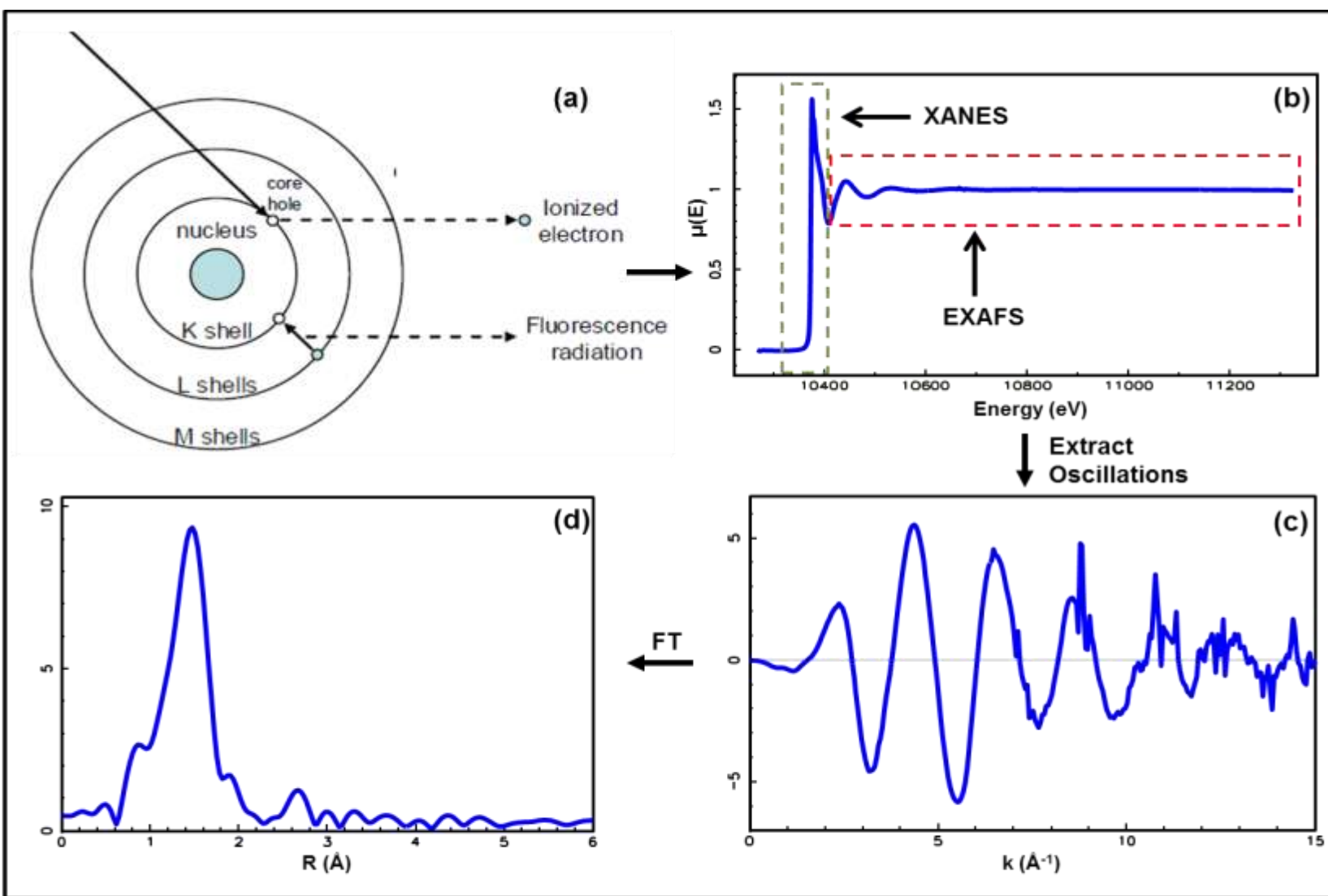


Figure 1.26: Illustration of X-ray absorption & fluorescence (a), with energy spectrum (b), k space plot (c), and radial distribution plot (d)

to seal samples. As a result of strong absorption by non-sample materials, the overall flux of x-rays reaching the sample can be severely reduced, and the signal reaching the detectors too low to measure. Specialized beamlines exist for running x-ray absorption experiments on low energy absorption edges in a vacuum environment. However, these beamlines were not utilized during the course of these studies. Due to this, XAS data was collected only for gallium samples, and not for boron and aluminum.

1.8.7 – Catalytic Test Reactions

Actual catalytic results are obviously seen as the end result of any research focusing on catalyst design. As such, many times catalytic tests are postponed until the catalyst has been fully characterized. In trying to determine structure/activity relationships it is important to have a detailed understanding of the structure of the catalyst. However, some catalysts are very hard to fully characterize, and it may take significant amounts of time to generate a complete understanding of the nature of the catalytic structure. Therefore, waiting until full characterization of a catalyst is complete can sometimes be a mistake, and may not be the best way to proceed. Beyond this, even if a thorough structural profile is developed, once catalytic testing begins, the catalyst may be largely ineffective. At this point all of the time spent developing a structural understanding of the catalyst, while not a complete waste, has almost certainly taken more time and resources than desired for a non-functional catalyst. Catalytic testing earlier in the characterization phase serves as a characterization technique itself. A significant amount of information with regard to catalyst performance and importance can be obtained by running activity tests sooner rather than later.

First among these is catalytic activity. Activity of a catalyst can be viewed as the amount of substrate that is converted to product(s). Generally this is related in a raw percentage that simply relates the total substrate converted. This is not the best way to present the data, as raw conversion values do not indicate the amount of catalyst that was used, and more importantly, the number or density of catalytically active sites that are present in the catalyst. Because of this, an increased conversion percentage might not be indicative of a more active catalyst. To get an accurate indication of the true

catalytic activity, conversion must be related, at the very least, to the weight of catalyst used and if possible to the independently verified number of catalytically active centers present in a specific sample. Determining the number of catalytically active sites in a supported catalyst is not always a simple undertaking, and as a result, catalytic data is often still reported in raw conversion values. When accurate site counts are achieved, then appropriate conversion values are generally reported in either turn-over-number (TON) or turn-over-frequency (TOF). TON is defined as the equivalents of substrate converted per active site (mol converted/site) while TOF is a rate that indicates the time efficiency of conversion (mol converted/[site x sec]) as the rate of conversion is often important.

Equally important to overall activity is selectivity. Selectivity refers to the ability of a catalyst to produce only a small number of products. One of the primary causes of low selectivity is the presence of multiple types of catalytic sites within the catalytic matrix. Ideally a catalyst would produce a single product in much higher amounts than any secondary products. While a particular catalyst may be highly active, if it produces a wide range of products then additional time and resources must be utilized to obtain the desired product in a purified form. The cost of a process significantly increases as more isolation and purification steps are required. These costs may, in the end, lead a company to choose a less active catalyst that has higher selectivity over a very active catalyst that produces a number of products that must be separated.

Catalytic testing is also important for determining the stability of a catalyst. As catalysts are used, deactivation frequently occurs over time. There are various reasons why this happens but the two most common are coking/pore clogging and leaching of the active sites. Coking results from the formation of nonvolatile or insoluble byproducts at the active sites or in the pores of the catalyst making it difficult for the substrate to reach the catalytic sites resulting in reduced activity. Many times coking can be reversed by calcination processes that burn off the unwanted byproducts and clear the blocked active sites. One must be careful however, as the high temperatures and oxidizing conditions typically used for calcination can negatively affect some catalysts.

Leaching refers to the loss of catalytic sites from the catalytic matrix due to unwanted side reactions or stress placed on the system during catalysis wherein solvating interactions are stronger than the bonds that hold the metal center onto the surface of the support. This can be a significant problem that for which there is no simple remedy. As a result of leaching, overall activity can change in nature, and increase, or decrease. If the leached species is an active homogeneous catalyst, then it may appear that catalytic activity initially increases. However, on subsequent catalytic runs where the homogeneous catalyst has been removed or washed away, then some number of catalytic sites will have been lost and the overall activity will decrease. In addition, homogeneous catalysts can behave differently producing a different distribution of products.

1.9 Dissertation Overview

This dissertation details research conducted during the previous six years aimed at demonstrating the applicability of a sequential building block approach to constructing single site heterogeneous silicate catalysts. The work has focused specifically on the incorporation of group 13 metals, (B, Al, Ga) into the building block matrices.

Chapter 2 describes the general synthetic and characterization methods used for preparing these materials, and focuses on the nature of the materials produced by the incorporation of aluminum centers into the catalytic matrices. These investigations show that aluminum behaves differently than any previous metal center that has been used to cross link the Si_8O_{20} silicate cubes in these matrices.

Chapter 3 details the preparation and characterization of gallium systems analogous to those prepared for aluminum. With the use of gallium, x-ray absorption spectroscopy has allowed for detailed structural characterization of a number of the gallium species, providing inferences into what may be happening in analogous aluminum systems.

Chapter 4 is a study of the incorporation of boron into the matrix from which a number of interesting conclusions can be drawn. These systems are distinctly different from their gallium and aluminum counterparts.

A final summary and conclusions in addition to some suggestions for future work are detailed in Chapter 5.

2. Synthesis & Structure of Nanostructured Building-Block Solid Acid Aluminum Catalysts

2.1 Introduction

The wide use and broad applicability of aluminosilicates as catalysts, catalyst supports, and other essential materials has been well documented.⁸⁵ While a detailed understanding of the structural nature of most aluminosilicates has existed for some time, research to create better catalysts is an ongoing endeavor. Aluminosilicates have found the most use as solid acid catalysts, and a general consensus has developed that optimal catalysts will possess a high density of isolated single atom aluminum sites embedded in a mesoporous matrix. While these may seem like straightforward requirements, the ability to create materials that possess all of these characteristics is quite challenging. The general synthetic methodology developed in the Barnes group and utilized here has been designed to create materials that meet all of these guidelines.⁶⁹

The reaction of metal chlorides and the trimethyltin cube building block have been shown to proceed in a straightforward manner for the incorporation of such high valent metals as V, Ti and Zr.^{69,86} Work presented in this chapter examines the behavior of Al under similar reaction conditions, and the results of structural and catalytic characterization of the synthesized materials.

Based upon previous work in our group with other metals,^{69,86,87} there was some initial expectation that utilizing AlCl_3 as the catalytic precursor in a similar manner might lead to unique three-coordinate Lewis acidic Al centers embedded within the catalytic matrix (Figure 2.01). This would produce centers that are quite different from those found in currently known natural or synthesized aluminosilicates.

These systems could also be used as starting points for creating pseudo Brønsted acidic sites utilizing a variety of protic reagents (Figure 2.02). Such catalytic centers would be very similar, though not identical, to the common Brønsted sites that are found in most aluminosilicates. Nearly all aluminosilicates are synthesized under

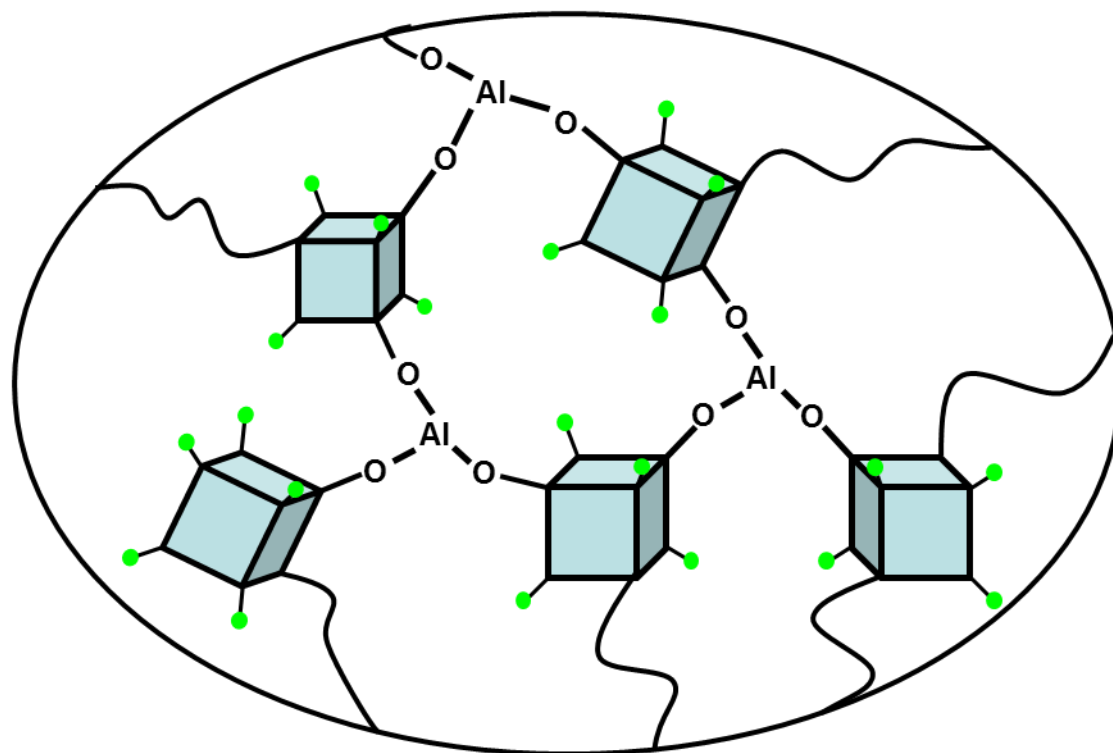


Figure 2.01: Hypothesized “3-Coordinate” Al centers in building-block silicate matrix

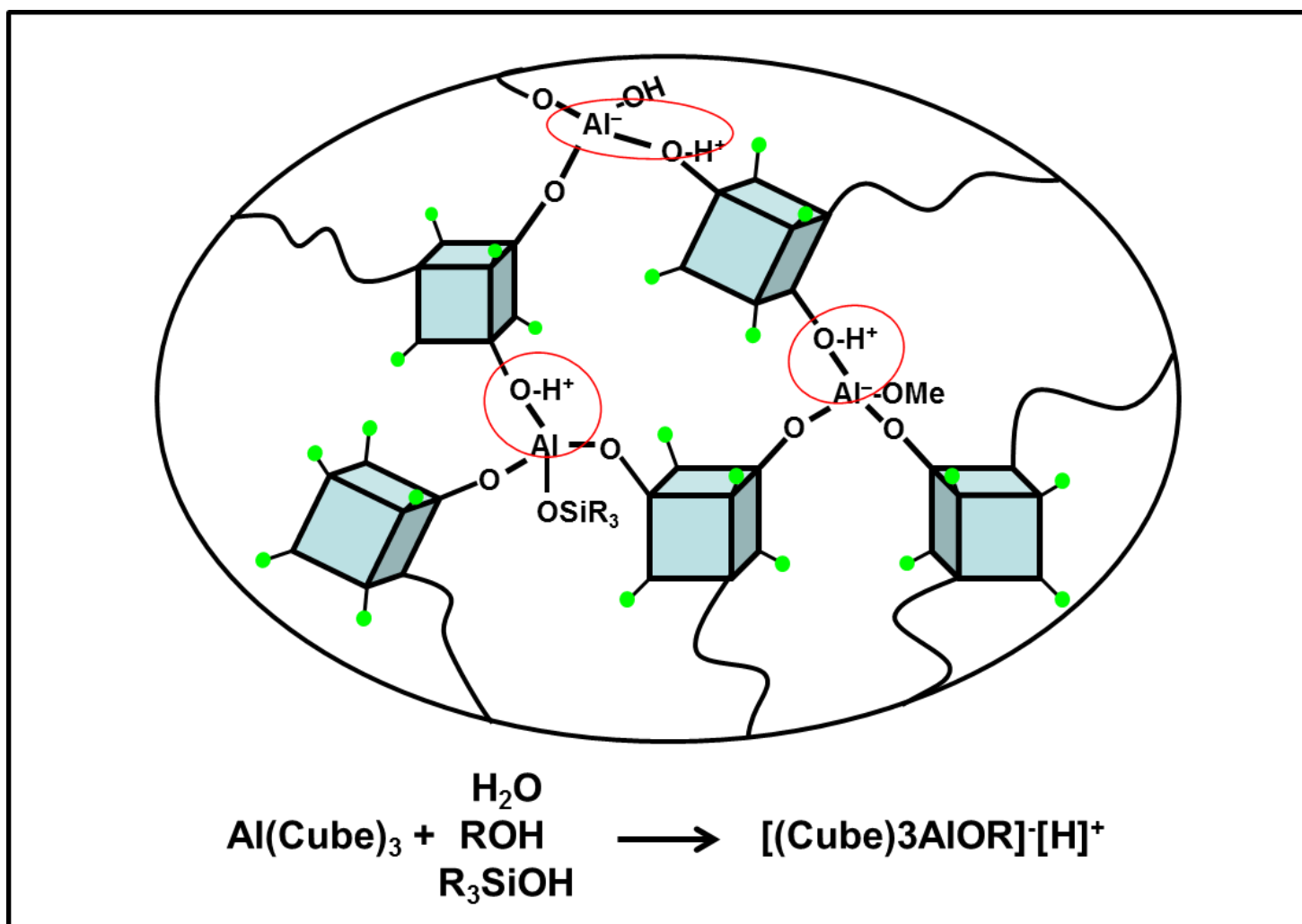


Figure 2.02: Possible psuedo Brønsted acidic Al centers in building-block silicate matrix (3-coordinate sites reacting with H₂O, ROH, and R₃SiOH)

protic conditions where aluminum will almost always end up in a tetrahedral or octahedral environment characteristic of Brønsted acidic sites where the negatively charged AlO_4 center must have a charge balancing cation.

As will be described in the chapter below, the reactions of AlCl_3 with the tin cube were not as simple as first imagined. Initial experiments showed that Al did not behave in a manner similar to the metals that had previously been studied. As a result, what might have been a straightforward investigation has turned out to be a challenging adventure that at times has been frustrating, but at no point less than exciting.

2.2 Experimental

2.2.1 Materials

All reactions were performed using standard Schlenk line techniques. Steps were taken to ensure the exclusion of water and oxygen from all reactants and solvents. In addition, glassware was treated with a chlorotrimethylsilane/triethylamine/methylene chloride solution in order to remove reactive surface hydroxyls. After drying under vacuum, the glassware was then flame dried.

Hexanes, toluene, diethyl ether and THF (Fisher Scientific) were distilled from sodium/potassium alloy (Na/K) and stored under vacuum in Schlenk bulbs containing Na/K. Methylene chloride (Fisher Scientific) was distilled from calcium hydride and stored under vacuum in a Schlenk bulb containing more calcium hydride. Pyridine (Fisher Scientific) was distilled from calcium hydride and stored over 4Å molecular sieves.

The $[(\text{CH}_3)_3\text{SnO}]_8\text{Si}_8\text{O}_{12}$ (trimethyltin cube, TMT cube) building block, was synthesized via two procedures, the first of which has previously been described.⁶⁹ A new and improved procedure is described below. Tetraethylorthosilicate (TEOS, $\text{Si}(\text{OEt})_4$, Acros, 98%) was distilled and stored under nitrogen. Tetramethylammonium hydroxide (Me_4NOH , Acros, 25 wt% in MeOH) was used as received.

Anhydrous aluminum chloride (AlCl_3 , Sigma Aldrich, 99.999%), trimethylaluminum (AlMe_3 , Strem, 98%) and tris(dimethylamino)aluminum ($\text{Al}_2(\text{NMe}_2)_6$, Alfa Aesar, 99%) were stored in a dry nitrogen glove box and used as received. The

aluminum trichloride pyridine adduct ($\text{AlCl}_3 \cdot \text{Py}$)⁸⁸, and the ion paired species $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ ⁸⁹ and $[\text{Me}_3\text{Sn}][\text{CF}_3\text{SO}_3]$ ⁹⁰ were synthesized according to the literature and stored in a dry nitrogen glove box. $[\text{nBu}_4\text{N}][\text{AlCl}_4]$ was prepared by the equimolar reaction of anhydrous ${}^n\text{Bu}_4\text{NCl}$ and AlCl_3 in CH_2Cl_2 in a fashion similar to $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$. Prior to reaction, the ${}^n\text{Bu}_4\text{NCl}$ was heated and stirred at 100 °C *in vacuo* for 8 hours to ensure removal of hydrated water. Relevant spectra of the synthesized precursors can be found in the appendix.

Silicon tetrachloride (SiCl_4 , Acros, 99.8+%), chlorotrimethylsilane (Me_3SiCl , Sigma Aldrich, >97%) and trichlorosilane (HSiCl_3 , Gelest) were distilled, degassed, and stored under vacuum in Schlenk vessels. After checking purity by ${}^1\text{H}$, ${}^{13}\text{C}$, and ${}^{29}\text{Si}$ NMR, $\text{iBuPOSS}(\text{OH})_3$, $\text{cyHPOSS}(\text{OH})_3$, and $\text{PhPOSS}(\text{OH})_3$ ($\text{R}_7\text{Si}_7\text{O}_{12}\text{H}_3$, Hybrid Plastics, >97%) were used as received.

2.2.2 Synthesis

New Synthesis for Dehydrated Trimethyltin Cube, $((\text{CH}_3)_3\text{SnO})_8(\text{Si}_8\text{O}_{12})$

The $((\text{CH}_3)_3\text{SnO})_8(\text{Si}_8\text{O}_{12})$ building block was synthesized by methods similar to those described by Harrison and Hall.⁹¹ The cubic octaanion $(\text{Me}_4\text{N})_8(\text{Si}_8\text{O}_{20})$ was prepared (but not isolated) by dropwise addition of 1.1 eq of ultra-pure H_2O to a stirring mixture of $\text{Si}(\text{OEt})_4$ (tetraethylorthosilicate, TEOS, 1 eq) and 25wt% Me_4NOH in methanol (tetramethylammonium hydroxide, 10 eq) in a plastic bottle at room temperature (RT) over 30 minutes. The bottle was then closed and stirred at RT for 18 hours. The resulting solution was filtered to remove any undissolved material, transferred to an addition funnel and diluted with 20 mL of MeOH.

The above solution was added dropwise over 7-10 hours to a vigorously stirred, cooled solution (0°C) of Me_3SnCl (trimethyltin chloride, 1.2 eq) in ~200mL of Et_2O under a slow nitrogen purge. The cloudy white solution was stirred overnight and allowed to return to room temperature.

The solution was placed into a separatory funnel and the organic phase was separated from the milky white aqueous phase. If clear phase separation did not occur, diethylether (5 mL aliquots) was added until two phases were apparent. The aqueous

phase was extracted three times with ~75mL aliquots of Et₂O. The combined organic phase was dried over anhydrous MgSO₄ (magnesium sulfate, ~15g) for 2 hours. Upon filtration, the solvent was removed under vacuum until a dry white residue formed.

The residue was refluxed in ~400mL of toluene in air until it dissolved. If complete dissolution did not occur, then the hot solution was filtered after which the toluene was removed and the sample dried under vacuum at RT. The white product residue was then redissolved in refluxing hexanes (~300mL) in air, which was reduced to ~30mL for recrystallization. If the hot hexanes solution remained cloudy, then a hot filtration was carried out before solvent volume reduction. The reduced solution was slowly cooled to room temperature at which point colorless needle like crystals began to form. Once the solution reached room temperature the solution was cooled to 5°C overnight.

The mother liquor was decanted from the crystals which were then dried under vacuum. Recrystallized yield for a 20mL (TEOS) scale is generally 15-18g of Si₈O₁₂(OSnMe₃)₈ (~70 - 90% yield). The crystals were ground into a fine powder and dried under vacuum at 100°C overnight to ensure removal of any waters of hydration.

Synthesis of Embedded Aluminum Catalyst from AlCl₃

First Dose Reaction:

The general approach for the synthesis of building block aluminosilicate catalysts follows the methodology previously developed in our group.^{69,86} The physical setup for the synthetic process is displayed in Figure 2.03. A Schlenk flask, reaction “T”, and stirbar were assembled (Figure 2.03d), placed under vacuum, flame dried and weighed. Trimethyltin cube was then placed into the flask. Typical reactions were run on scales of 0.5 - 2 g of tin cube. The Schlenk flask was then heated *in vacuo* for at least 6 hours at 100°C in order to remove any traces of water hydrates bound to the tin cube. When drying under vacuum was complete, the Schlenk flask was reweighed (under vacuum) in order to determine the actual mass of trimethyltin cube. The flask was taken into a dry nitrogen atmosphere glovebox where an appropriate amount of AlCl₃ was added (for fully embedded samples <1 molar eq.) Upon removal from the glove box, vacuum was

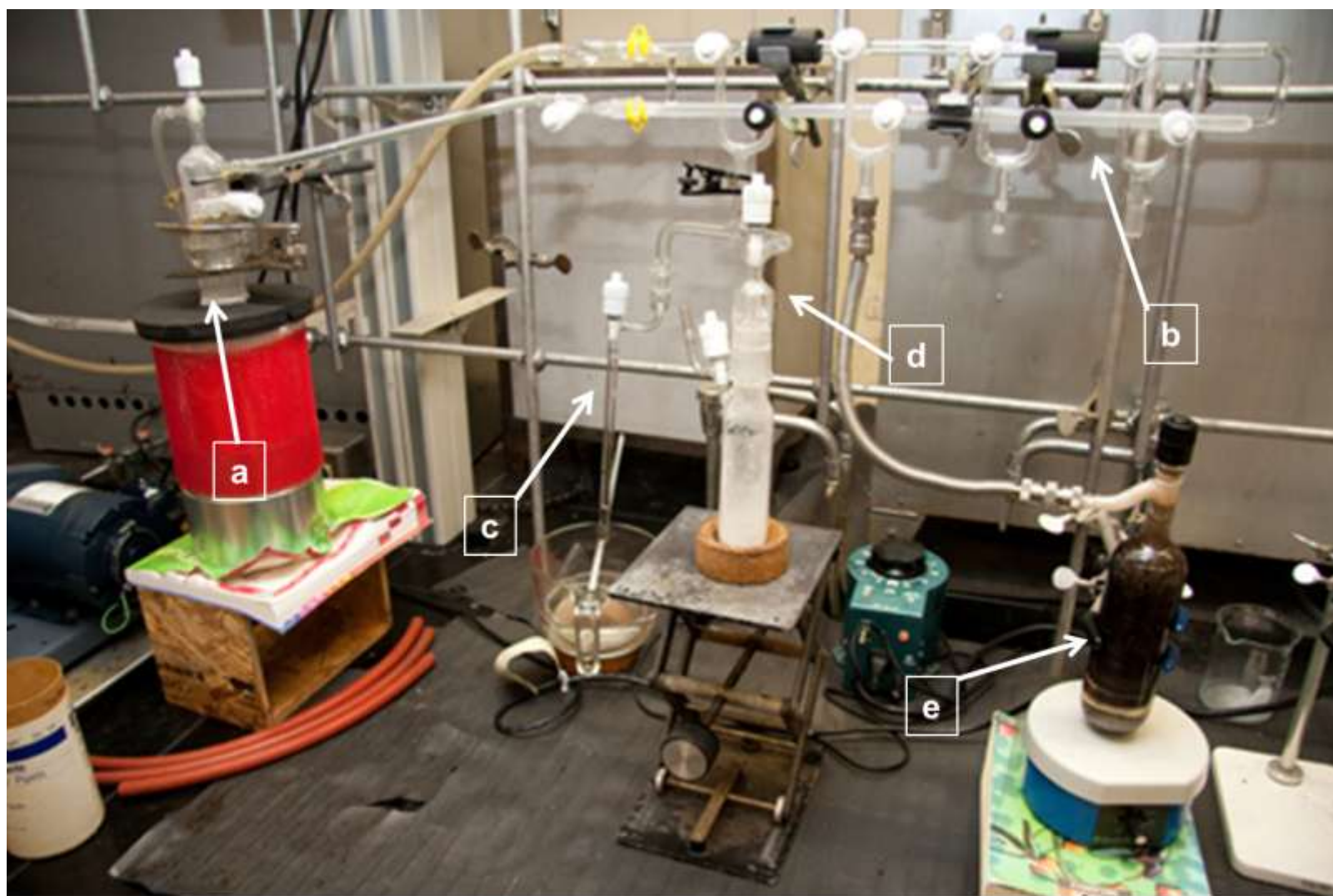


Figure 2.03: Synthetic setup, showing a) cold trap, b) Schlenk line, c) reagent capillary, d) Schlenk flask & transfer “T”, e) solvent bulb

reestablished in the Schlenk vessel which was reweighed to determine the actual mass of AlCl_3 added. At this point, approximately 20mL of toluene (per 1 gram of trimethyltin cube) was vapor transferred into the flask at 77K (Figure 2.03e). The flask was warmed to room temperature and then placed in a hot oil bath at 80-100°C for 24-48 hours. After ~4-12 hours, evidence of reaction consisted of the formation of a gel or increased viscosity in the reaction solution. While there is no clear point at which the reaction is complete, it is generally believed that most reaction is complete after 24-48 hours. Upon completion of the reaction, the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100°C for at least 8 hours or until two consecutive weightings indicated no further mass change due to removal of volatile byproducts. The final mass of the Schlenk flask under vacuum was measured.

Gravimetric analysis in conjunction with solution NMR analysis of the collected volatile byproducts of the reaction were conducted to determine the number of reacted chlorides (in the form of Me_3SnCl) per aluminum (i.e. the average connectivity achieved at the aluminum center). Also, from this calculation an estimate of the number of remaining $-\text{SnMe}_3$ groups in the matrix could be determined. This value is necessary for calculations in second and third dose reactions.

Second Dose Reaction:

The general purpose of carrying out a second dose reaction is to further rigidify the catalytic matrix and increase surface area. In addition, a large amount of the excess trimethyltin groups can be removed from the final material. Typically a second dose reaction is carried out immediately upon completion of the first dose reaction without any manipulation of the product after drying. In some cases analyses of samples between doses is necessary or different secondary reactions are carried out on portions of the same large scale first dose product. It has been determined however, that gravimetric analysis is most reliable in the second dose reactions when no intermediate manipulation is carried out. The secondary reactions do raise some concerns with respect to the possibility of rechlorination of the existing M-O-Si bonds established during the first dose reactions. Some of the silyl chlorides used here are very strong

chlorinating agents (i.e. SiCl_4), and the reaction conditions can be somewhat forcing. This concern is specifically addressed in Chapter 3 where XAS analysis of gallium centers after second dose reactions were carried out.

Based on gravimetric analysis from the first dose reaction, a silyl chloride containing multiple chlorides (2-4) was used to further crosslink the matrix. An added goal behind the addition of a secondary dose of a silyl chloride is the production of a high surface area material. From previous studies,⁸⁷ it has been determined that the highest surface area materials arise when a total of 5-6 corners (from first two reactions) of the cube building block have been reacted. A typical procedure is as follows.

To the Schlenk flask, ~20mL of toluene, per gram of sample, was vapor transferred at 77K. A calculated amount of the silyl chloride (typically 0.5-3.5 molar eq. to initial trimethyltin cube) was then vapor transferred into the flask at 77K from a capillary of known diameter (Figure 2.03c). The capillary is weighed before and after removal of the silyl chloride in order to determine the exact mass of reactant added to the system. The Schlenk flask was warmed to room temperature and placed in a hot oil bath at 80-100 °C for 24-48 hours. Upon completion of the reaction the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100°C for at least 8 hours until no further mass change due to removal of volatile byproducts was observed. The final mass of the Schlenk flask under vacuum was measured and gravimetric analysis used to determine the extent to which the silyl chlorides had reacted and to calculate the number of remaining $-\text{SnMe}_3$ groups in the matrix.

Third Dose Reaction:

Once again without intermediate manipulation, the third dose reaction was carried out on the product of the first two doses. Trimethylchlorosilane (TMSCl) has typically been used in the third (and usually final) dose in order to remove any unreacted $-\text{SnMe}_3$ groups. ~20mL of toluene*, per gram of sample, was vapor transferred to the Schlenk flask at 77K. A calculated excess (2.5-5 eq. based on remaining $-\text{SnMe}_3$ groups) was then vapor transferred into the flask from a capillary of known diameter. The Schlenk flask was warmed to room temperature and then placed

in a hot oil bath at 80-100 °C for 24-48 hours. Upon completion of the reaction, the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100 °C until no further mass change due to removal of volatile byproducts was observed. The final mass of the Schlenk flask under vacuum was measured and gravimetric analysis used to determine the extent to which the $-\text{SnMe}_3$ groups were removed. The final product was isolated and stored in a dry, nitrogen glove box.

*Note: In some cases the TMSCl reaction was carried out neat, without toluene as a solvent.

Synthesis of Surface Aluminum Catalysts from Aluminum Trichloride (AlCl_3)

First Dose Reaction:

By reversing the first and second dose reaction steps from the previous sections, surface aluminosilicates were synthesized. A Schlenk flask, reaction “T”, and stirbar were assembled, placed under vacuum, flame dried and weighed. Trimethyltin cube was then placed into the flask. The Schlenk flask was then heated *in vacuo* for at least 6 hours at 100 °C in order to remove any traces of bound water. When finished with the drying step, the Schlenk flask was reweighed (under vacuum) in order to determine the actual mass of trimethyltin cube. To the Schlenk flask, ~20mL of toluene, per 1 gram of cube, was vapor transferred at 77K. Silicon tetrachloride (typically 2-2.5 molar eq.) was then vapor transferred into the flask from a capillary of known diameter. The capillary is weighed before and after removal of the silyl chloride in order to determine the exact mass of reactant added to the system. The Schlenk flask was warmed to room temperature and then placed in a hot oil bath at 80-100 °C for 24-48 hours. Upon completion of the reaction the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100 °C until no further mass change due to removal of volatile byproducts was observed.

Second Dose Reaction:

Based on gravimetric analysis from the first dose reaction, the number of remaining $-\text{SnMe}_3$ sites is calculated. The flask was taken into a dry, nitrogen

atmosphere glovebox where an appropriate amount of AlCl_3 was added (<1 molar eq. based on remaining $-\text{SnMe}_3$ groups). Upon removal from the glove box, vacuum was reestablished in the Schlenk vessel which was then reweighed to determine the actual mass of AlCl_3 added. To the Schlenk, ~20mL of toluene, per gram of sample, was vapor transferred at 77K. The Schlenk flask was warmed to room temperature and then placed in a hot oil bath at 80-100 °C for 24-48 hours. Upon completion of the reaction the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100 °C until no further mass change due to removal of volatile byproducts was observed. The final mass of the Schlenk flask under vacuum was measured and gravimetric analysis used to determine the extent to which the aluminum chloride had reacted.

Synthesis of Embedded Aluminum Catalysts from $\text{AlCl}_3 \cdot (\text{C}_5\text{H}_5\text{N})$

Procedures for creating both embedded and surface catalysts from the monopyridine adduct of aluminum trichloride, $\text{AlCl}_3 \cdot (\text{C}_5\text{H}_5\text{N})$, ($\text{AlCl}_3 \cdot \text{Py}$) are identical to those utilizing AlCl_3 as the precursor. The pyridine adduct of AlCl_3 was prepared in the following manner.

A Schlenk flask, reaction “T”, and stirbar were assembled, placed under vacuum, flame dried and weighed. The flask was taken into a glovebox where the desired amount of AlCl_3 was added (1 eq). Upon removal from the glove box, vacuum was reestablished in the Schlenk vessel which was reweighed to determine the actual mass of AlCl_3 added. At this point, approximately 30 mL of benzene, per gram of AlCl_3 , was vapor transferred into the flask at 77K. After solvent transfer, while still at 77K, baseline vacuum was reestablished in the Schlenk flask and pyridine (1 eq) was vapor transferred from a capillary of known diameter through the reaction “T” into the reaction Schlenk. Care must be taken to use only one equivalent of pyridine to avoid the disproportionation reactions that occur when excesses are used. The vessel was sealed and allowed to return to room temperature at which point all reactants dissolved and a clear colorless solution resulted. The solution was stirred at RT for 6 hours after which the solvent was removed under vacuum, and the product dried at RT overnight.

The resulting product is a white microcrystalline powder. ^1H NMR (C_6D_6) δ = 6.27 (d, *o*- $\text{C}_5\text{H}_5\text{N}$), 6.67 (t, *p*- $\text{C}_5\text{H}_5\text{N}$), 8.21 (d, *m*- $\text{C}_5\text{H}_5\text{N}$); $^{13}\text{C}\{^1\text{H}\}$ (C_6D_6) δ = 125.75 (*o*- $\text{C}_5\text{H}_5\text{N}$), 142.72 (*p*- $\text{C}_5\text{H}_5\text{N}$), 145.99 (*m*- $\text{C}_5\text{H}_5\text{N}$); ^{27}Al δ = 103.1 (solution & solid state). The aluminum chemical shift matches that reported in the literature.⁸⁸

Synthesis of Catalysts from $\text{Al}(\text{CH}_3)_3$, $[\text{Al}_2(\text{N}(\text{CH}_3)_2)_6]$, $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ & $[\text{nBu}_4\text{N}][\text{AlCl}_4]$

Procedures for creating both embedded and surface catalysts from trimethylaluminum, $\text{Al}(\text{CH}_3)_3$, tris(dimethyl-amidoaluminum) $\text{Al}_2(\text{N}(\text{CH}_3)_2)_6$, trimethyltin tetrachloroaluminate, $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$, and n-butylammonium tetrachloroaluminate $[\text{nBu}_4\text{N}][\text{AlCl}_4]$ are identical to those where AlCl_3 was used as the precursor. In the case of the liquid AlMe_3 , the Al precursor was introduced to the reaction by vapor transfer methods identical to those described above.

Synthesis of Trimethyltin Funtionalized Polyhedral Oligomeric Silsessquioxanes (POSS)

The terminology used to refer to the polyhedral oligomeric silsequioxanes is as follows. The incompletely condensed starting materials, $\text{R}_7\text{Si}_7\text{O}_{11}\text{H}_3$, are referred to as $\text{RPOSS}(\text{OH})_3$ while the fully condensed species $\text{R}_7\text{Si}_8\text{O}_{12}\text{H}$ and $\text{R}_7\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)$ are referred to as $\text{RPOSS}(\text{H})$ and $\text{RPOSS}(\text{OSnMe}_3)$ respectively (Figure 2.04). The synthetic procedures for the hepta-isobutyl- OSnMe_3 (iBuPOSS) and hepta-cyclohexyl- OSnMe_3 (cyHPOSS) POSS are nearly identical; however, the synthesis of the hepta-phenyl- OSnMe_3 (PhPOSS) POSS requires a slight adjustment of procedure.

Typical reaction scales utilized 5-10 g of POSS starting material. The POSS trisilanol ($\text{RPOSS}(\text{OH})_3$, 1 eq.) was weighed out and placed in a three neck round bottom flask with a stirbar. A nitrogen purge was set up in the first neck, an addition funnel was placed in the central neck, and the third neck was capped. Freshly distilled solvent (~20 mL of solvent per gram of POSS, Et_2O for iBuPOSS, THF for cyHPOSS & PhPOSS) was then added followed by triethylamine (Et_3N , 3 eq).

Trichlorosilane (HSiCl_3 , 1 eq) and an appropriate amount of solvent were vapor transferred into a separate Schlenk flask and transferred to the addition funnel under a nitrogen purge. The trichlorosilane solution was added dropwise over 1 hour to the

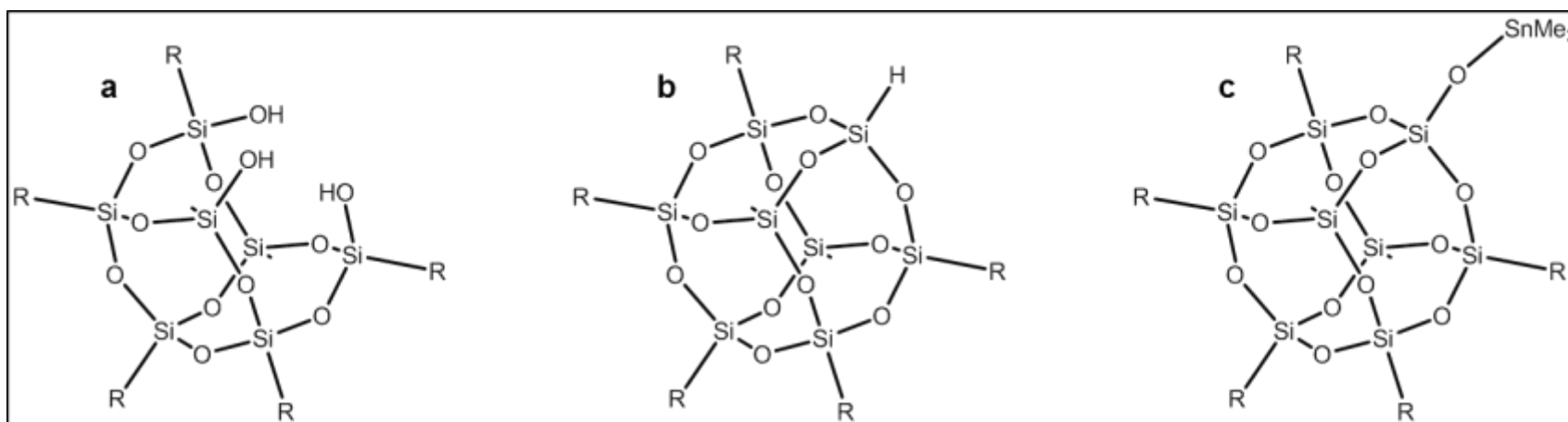


Figure 2.04: Polyhedraloligomeric silsesquioxanes (POSS) a) incompletely condensed trisilanol [RPOSS(OH)₃], b) fully condensed monosilane RPOSS(H), c) fully condensed trimethyltin functionalized [RPOSS(OSnMe₃)]; (R=iBu, cHex, Ph)

POSS/Et₃N solution at room temperature. Immediate precipitation of the white Et₃N·HCl byproduct occurred. After the addition was complete, the mixture was stirred overnight under a slow nitrogen purge.

In the case of the PhPOSS analog, the Et₃N must be added after the HSiCl₃, as the PhPOSS is not stable in the presence of Et₃N for extended time periods. This also means that the HSiCl₃ must be added more quickly as the POSS species is also unlikely to be stable in the presence of high HCl concentrations over long periods.

The reaction mixture was then filtered and the solvent removed under vacuum. The resulting product (R₇Si₈O₁₂H, RPOSS(H)) was checked for purity by NMR but not purified further prior to stannylation.

The RPOSS(H) was redissolved in freshly distilled THF and titrated with a solution of bistrimethyltin ether [(Me₃Sn)₂O] in Et₂O⁹² until ¹H NMR indicated that no silane (Si-H) groups remained. The solvent was removed under vacuum and the product [RPOSS(OSnMe₃)] recrystallized from a methylene chloride / acetone mixture. Spectra for these species can be found in Appendix 1.

Synthesis of POSS Molecular Analogues of Embedded Heterogeneous Al Catalysts

A Schlenk flask, reaction “T”, and stirbar were assembled, placed under vacuum, flame dried and weighed. Trimethyltin POSS [RPOSS(OSnMe₃), 3 eq.] was placed into the flask. The Schlenk vessel was then heated *in vacuo* for at least 6 hours at 100 °C in order to remove any traces of bound water. When finished with the drying step, the Schlenk was reweighed (under vacuum) in order to determine the actual mass of POSS. The flask was taken into a dry nitrogen atmosphere glovebox where an appropriate amount of the catalytic precursor (eg. AlCl₃ or AlCl₃·Py) was added (1 eq.) Upon removal from the glove box, vacuum was reestablished in the Schlenk vessel which was reweighed to determine the actual mass of precursor added. At this point, approximately 20 mL of toluene, per gram of POSS, was vapor transferred into the flask at 77K. The flask was warmed to room temperature and then placed in a hot oil bath at 80-100 °C for 12-24 hours.

Upon completion of the reaction the volatiles were removed *in vacuo* and collected in a secondary cold trap. The reaction product was heated under vacuum at 100°C for at least 8 hours or until two consecutive weightings indicated no further mass change due to removal of volatile byproducts. The final mass of the Schlenk under vacuum was measured.

2.2.3 Characterization

Gravimetric Analysis

The reaction flask was weighed empty, after the addition of each reactant, and after drying the reaction products. All measurements were carried out with the reaction flask under vacuum. The mass difference between the initial reactants and the final product was used to calculate the amount of Me_3SnCl lost, and thus the degree of cross-linking. It is important to note that the scale of the reaction must be large enough that the change in mass as a result of loss of Me_3SnCl is large enough to measure on a laboratory balance. Generally the variability in consecutive weighing on such scales is on the order of 3-5 mg, and as a result reactions with a predicted weight change of less than 50 mg are not recommended. Typical reaction scales (1-2 g of TMT cube, 0.5-1:1 Al:Cube) using aluminum precursors yield mass changes of 300-500 mg.

Nitrogen Adsorption

Surface area analyses were performed using the BET (Brunauer-Emmett-Teller) method⁷⁵ where data was collected on a Quanta Chrome Corp. Nova 1000 High Speed Surface Area and Pore Size Analyzer using nitrogen as the adsorption gas. The adsorption portion of the isotherm was used to calculate surface area. Pore size distributions for samples were calculated using the BJH (Barret-Joyner-Halenda) formula.⁷⁶

Infrared Spectroscopy (IR)

Unless otherwise specified, infrared spectra were obtained using a Thermo Scientific Nicolet IR 100 spectrometer with Encompass software. The instrument was located inside a dry, nitrogen atmosphere glove box. Pellets were prepared for IR analysis by mixing an appropriate amount of sample (~3-8 wt%) with potassium bromide

(KBr) and pressing into self-supporting pellets. An appropriate KBr blank was run as a background spectrum, and all IR spectra represent the sum of 32 scans from 400-4000 cm^{-1} .

Pyridine adsorption studies were carried out by exposing a small amount of aluminosilicate powder to an excess of pyridine vapor at room temperature. The mixture was allowed to stand at room temperature for 1 hour, followed by evacuation at 100 °C to remove any physisorbed pyridine. The samples were then prepared as above.

Extinction coefficients for solid acids with Lewis acidic bound pyridine bands have been published, but show significant variability.⁹³ As a result the values were reexamined here. Initial tests were carried out using the molecular precursor $\text{AlCl}_3\cdot\text{Py}$ diluted in KBr at varying concentrations (2-300 $\mu\text{mol/g}$). The KBr/ $\text{AlCl}_3\cdot\text{Py}$ dilutions were mixed in a “Wig-L-Bug” apparatus to ensure homogeneity. Self-supporting pellets were pressed from 40 mg of each sample and absorption spectra were collected. The actual weight (or thickness) of the pellets do not have to be exactly the same as long as the weight of the pellet is measured and the number of μmol of pyridine contained in the pellet can be calculated. The Lewis acidic pyridine bands at 1455 and 1625 cm^{-1} were integrated using the Thermo Fisher Encompass software. A plot of integrated absorbance vs μmol of pyridine in each pellet was created (Figure 2.05). It was found that above ~ 5.5 μmol of Py, signal saturation occurred and the linearity of the plot was lost. Therefore, a linear fit was applied to the plot for all samples below this concentration. Based on Equation 2.1, the integrated molar extinction coefficient

$$IMEC = \text{slope} * (\pi r^2) \quad (\text{eq. 2.1})$$

(IMEC)⁹⁴ in $\text{cm}/\mu\text{mol}$ is then determined by multiplying the slope of the linear fit by the area of the pellet. While values for the 1625 cm^{-1} band are not reported, the value of 2.13 $\text{cm}/\mu\text{mol}$ determined here for the 1455 cm^{-1} band agrees well with at least one published report.⁹⁴

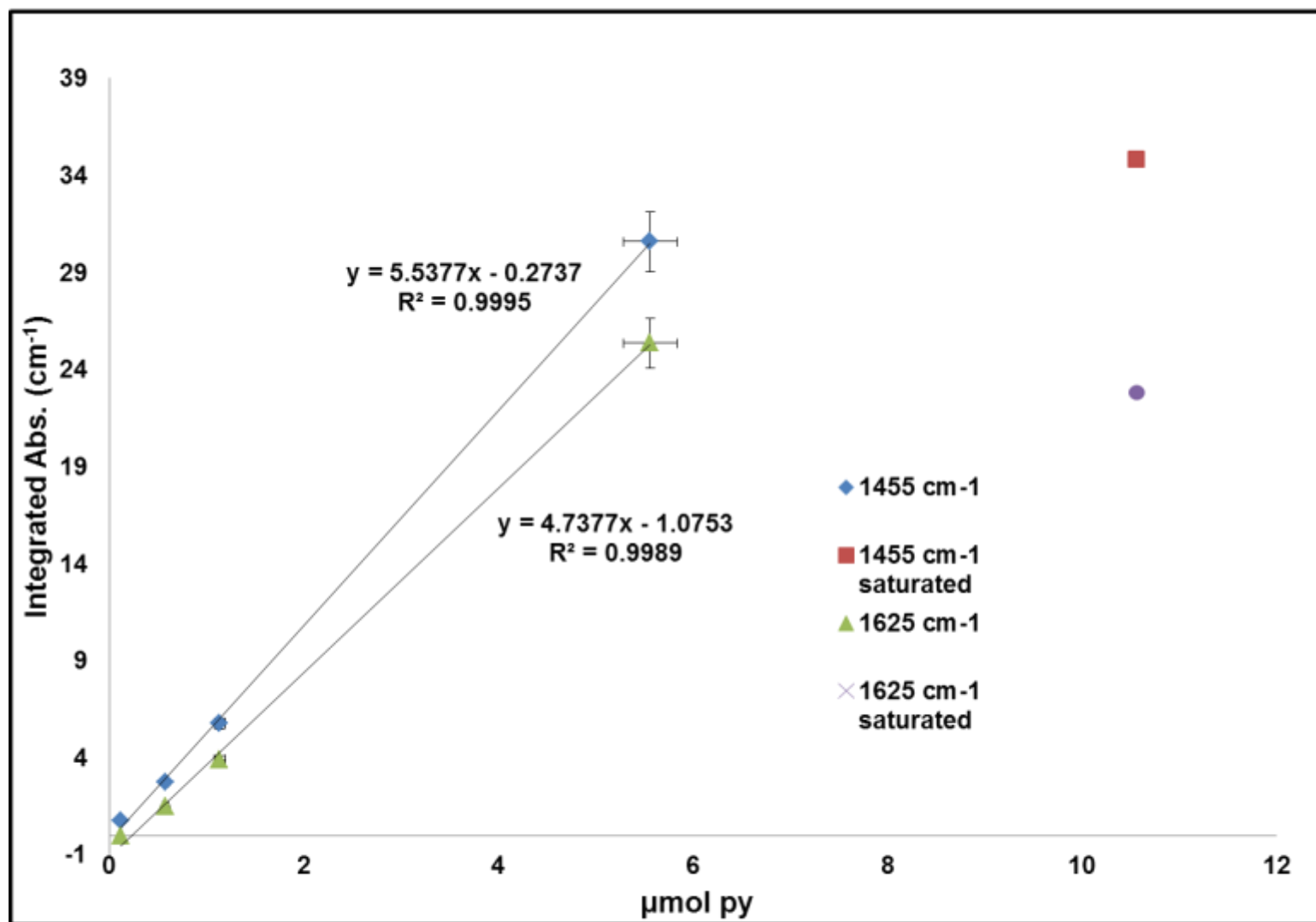


Figure 2.05: Determination of integrated molar extinction coefficients for Lewis acidic bound pyridine bands at 1455 and 1625 cm⁻¹

Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES)

ICP-OES measurements were carried out on a Perkin Elmer Optima 2100 DV spectrometer equipped with a Scott spray chamber.⁹⁵ The basic procedure in determining metal content of a sample consists of three steps. 1) Samples were weighed out (~25-50 mg) into 60 mL Nalgene bottles. Typically, final concentrations of 10-50 ppm of the active metal were sought for ease of detection. In order to digest both the silicate and remaining organic groups, a combination of 50% hydrofluoric acid (~1.5 mL) and concentrated nitric acid (~1.5 mL) were added. The lids were placed on the bottles and the samples allowed to digest for 2 hours at room temperature. The solutions were then diluted to 50 g total mass using ultrapure deionized water. 2) Calibration standards were made using Fluka TraceCert® 1000 mg/Kg ICP standards. Standards typically were created to cover the concentration range from 1-100 ppm. 3) Calibration and sample data were collected and compared in order to calculate the concentration of the metal centers in the catalytic matrix.

Nuclear Magnetic Resonance Spectroscopy (NMR)

Solution NMR spectra were collected at 9.4 Tesla on a Bruker Avance wide-bore NMR spectrometer utilizing a broadband inverse probe. ¹H, ¹¹B, ¹³C, ²⁷Al, ²⁹Si, and ¹¹⁹Sn spectra were acquired at 400.00 MHz, 128.32 MHz, 100.60 MHz, 104.32 MHz, 79.48 MHz, and 149.16 MHz, respectively. Chemical shifts were referenced internally or externally to ¹H NMR δ [C₆D₆, CDCl₃, Me₄Si]: 7.15, 7.26, 0.00 ppm; ¹¹B NMR δ [B(OH)₃]: 19.2 ppm; ¹³C NMR δ [C₆D₆, CDCl₃, Me₄Si]: 128.0, 77.0, 0.0 ppm; ²⁷Al NMR δ [Al(H₂O)₆]: 0.0 ppm; ²⁹Si δ [Me₄Si]: 0.0 ppm; ¹¹⁹Sn δ (SnMe₄): 0.0 ppm.

Solid state NMR data were collected at 9.4 Tesla on a wide-bore Varian Inova NMR spectrometer using a broadband probe. ¹¹B, ¹³C, ²⁷Al, ²⁹Si, and ¹¹⁹Sn spectra were acquired at 128.32 MHz, 100.60 MHz, 104.32 MHz, 79.48 MHz, and 149.16 MHz respectively. Magic angle spinning rates were typically in the range of 4-10 KHz. Samples were loaded in 5 mm pencil rotors and in the case of air sensitive samples sealed with silicon grease and paraffin wax. Chemical shifts were referenced externally to ¹¹B NMR δ [B(OH)₃]: 19.2 ppm; ¹³C NMR δ [adamantane]: 38.68 ppm; ²⁷Al NMR δ [Al(H₂O)₆]: 0 ppm; ²⁹Si δ [(Me₃SiO)₈Si₈O₂₀]: 11.72 ppm; ¹¹⁹Sn δ (SnMe₄): 0 ppm.

Gas Chromatography / Mass Spectrometry (GC/MS)

GC/MS data was collected on a HP 6890 gas chromatograph with attached HP 6890 series mass selective detector. The GC was equipped with a 30m x 0.25mm x 0.25 μ m HP-5MS column with a (5%-Phenyl)-methylpolysiloxane stationary phase. Instrument control and data manipulation were carried out through the HP Enhanced Chemstation suite (G1701BA, Version B.01.00). Typically, ~2 μ L of sample were injected in split mode (20 : 1, instrument default setting) with a temperature program as follows; 40 °C (2 min. hold) $\rightarrow$ 250 °C (20° C/min, 1 min hold) for a total run time of 13.5 minutes.

2.3 Results and Discussion

The characterization of the aluminum sites formed in these building block matrices turned out to be significantly more difficult than any of the cases that have been studied previously (e.g. Ti, V, Zr, Si, Sn). The primary reason for this was the unexpected production of tetramethyltin in addition to trimethyltin chloride, the typical byproduct formed in the metathesis reaction creating the M-O-Si links. The observation of SnMe₄ suggests that a methyl group in the matrix has been cannibalized but the challenges that we were confronted with included determining the source of the methyl group, elucidating the mechanism that leads to tetramethyltin formation, and identifying the nature of the species left behind in the matrix.

The following section of this thesis represents a multiline approach to consciously piece together the puzzle that confronted us. We first attempted to define the stoichiometric ratios of the two volatile byproducts in various different reactions. This was followed by a multinuclear (Al, Si, C, Sn) NMR study of the aluminum centers and the surrounding atomic environment. Finally a series of alternative chemical approaches to constructing the aluminum sites in these matrices were investigated resulting in several important insights into the pathways leading to tetramethyl tin and indirectly to the identity of the aluminum sites.

2.3.1 One Dose Embedded Aluminum Catalysts Starting From AlCl₃

For reactions of the tin cube with other metal centers (Ti, V, Zr, Si), the metathesis reaction forming M-O-Si bonds and the byproduct Me₃SnCl has been well established (Equation 2.2).^{69,86} Based on this, it was initially believed that the reaction of AlCl₃ with the tin cube might lead to the creation of unique isolated 3-coordinate



Lewis acidic Al centers (Figure 2.1). In order to produce such embedded aluminum sites, wherein the catalytic center possesses the maximum number of links to the matrix and has no remaining bound chlorides, it has been established that the Cl : TMT cube ratio must remain < 3 : 1.⁸⁶ In the case of aluminum, this means that the maximum ratio to achieve an embedded catalytic center is 1 : 1, AlCl₃ : TMT cube.

Reactions were carried out in toluene at 80-100 °C for 6–48 hours. Upon transfer of solvent and warming, the aluminum chloride did not dissolve initially. In the first 30 minutes of reaction, the solution would go through a period where the solution would turn bright yellow, after which it would return to colorless. Generally, phase separation (gelation) was noticeable after 4–6 hours. Upon completion of the reactions, the volatiles were removed and analyzed by NMR and GC/MS. Expectations were that only Me₃SnCl should be observed as had been the case for all similar reactions conducted with other metal chlorides. However, a second component, identified as Me₄Sn, was also found to be present in significant quantities (Figure 2.06). In an unknown manner the reaction was following a different reaction pathway (Equation 2.3).



Subsequent tests showed that Me₄Sn was produced quite quickly during the reaction (<30 min). It was apparent at this point that AlCl₃ was not reacting in a fashion similar to other metal chlorides.

Gravimetric analysis also yielded evidence to confirm the unusual nature of the reaction. Normal gravimetric analysis is quite simple (Equation 2.4). The weight change as a result of the loss of Me₃SnCl is determined, and the moles of byproduct are

calculated and divided by the number of moles of metal chloride precursor. This calculation gives a value that indicates the number of tin centers reacted per metal

$$\frac{\left(\frac{\text{Mass of Reactants} - \text{Mass of Products}}{199.27 \text{ (mw of Me}_3\text{SnCl)}} \right)}{\text{mol AlCl}_3} = \text{Equiv. Sn Lost} \quad (\text{eq. 2.4})$$

center. In the case of an embedded Al center we would expect this value to be very close to 3.0, corresponding to the reaction of all three chlorides present on AlCl₃. However, with the addition of a second byproduct, accurate molar and mass ratios of the two had to be determined in order to calculate the actual amount of Sn removed from the system. The molar ratio of byproducts was determined by integration of the methyl tin signals in the ¹H NMR spectrum of the volatiles. It was discovered that in a standard embedded Al reaction, the total amount of Sn lost per Al center was greater than 3.0.

For example, analysis of the volatiles of the reaction to produce sample Al080, a 1-dose reaction with an initial reaction ratio of 0.9 : 1, Al : Sn, showed the tin species present were 54 mol% tetramethyltin and 46 mol% trimethyltin chloride. These ratios coupled with a gravimetric loss of 0.518 g equated to a total loss of 2.76 mmol of Sn, or 3.9 equivalents of Sn per Al center. It should also be noted that due to the production of Me₄Sn, some degree of chloride still remains in the system which is atypical of reactions with other metal chlorides. In this case, only 1.9 eq of tin were in the form of Me₃SnCl, while 2.0 equivalents were in the form of Me₄Sn. This means that there is still 1 eq of chloride remaining in the matrix. The mechanistic and structural implications of these findings will be discussed in depth below.

While this reaction has been repeated a number of times, the gravimetric results have been inconsistent. The ratio of tetramethyltin to trimethyltin chloride byproducts is not always the same, and the total equivalents of Sn lost is also variable. Table 2.1 compares a number of 1-dose reactions utilizing the AlCl₃ precursor.

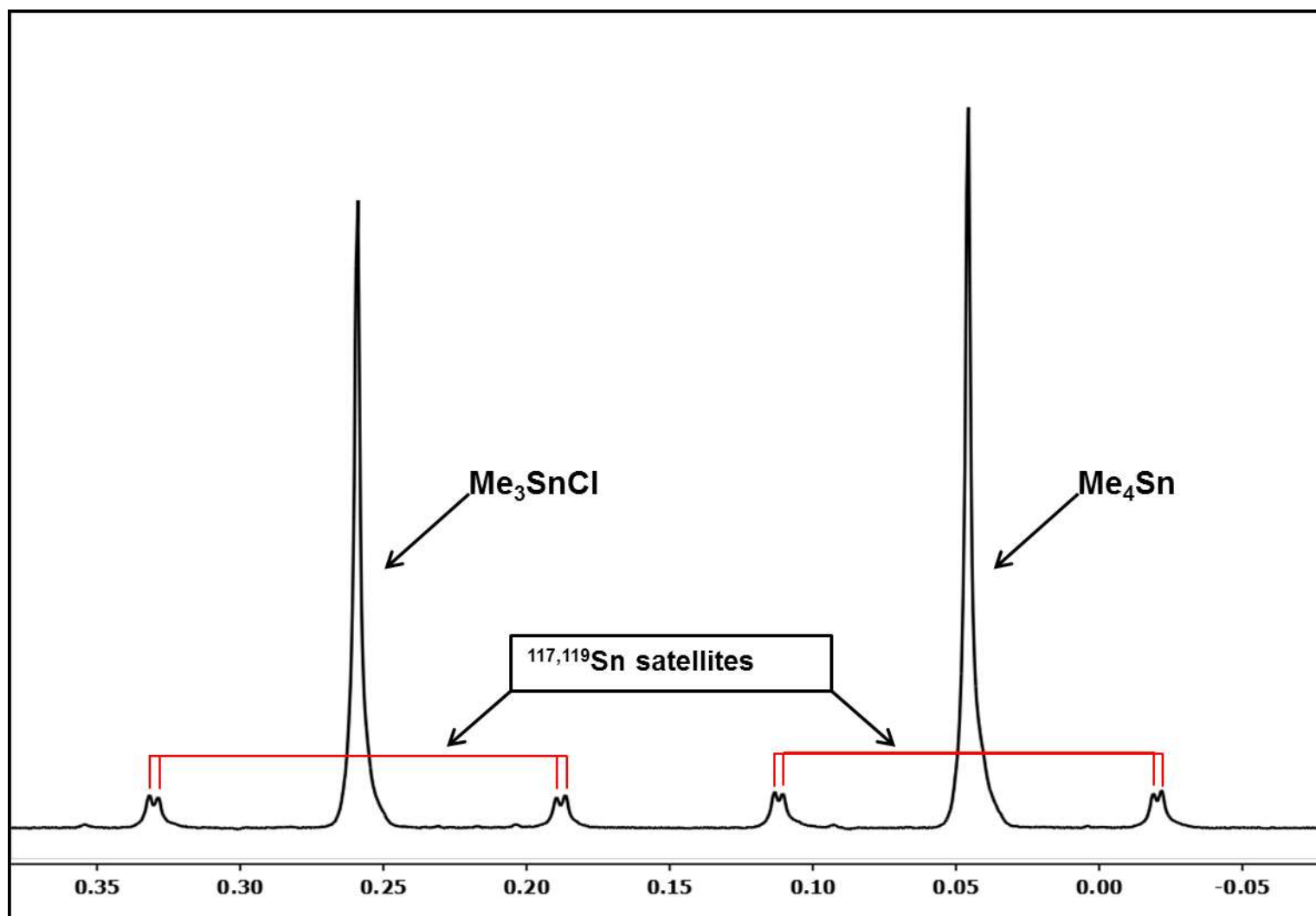


Figure 2.06: ^1H NMR spectrum of reaction volatiles from embedded 1-dose reaction of AlCl_3 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

Table 2.1 – Reaction conditions & gravimetric data for reactions of AlCl_3 with TMT Cube

Sample #	Precursor	M:Cube	eq TMTCl	eq TMT	Total eq Sn	Temp	Rxn Time (hrs)
AI065	AlCl_3	0.915	2.02	2.15	4.17	80	40
AI066	AlCl_3	1	1.61	2.15	3.76	90	47
AI067	AlCl_3	1.02	2.25	1.74	3.99	90	116
AI068	AlCl_3	1.04	2.7	0.39	3.09	90	190
AI075	AlCl_3	0.83	2.6	0.48	3.08	90	72
AI076	AlCl_3	0.93	1.54	2.51	4.05	90	48
AI077	AlCl_3	1.09	2.02	1.65	3.67	90	48

ICP-OES analysis was used to validate the amount of Al in the matrix and to determine the ratio of Al to remaining Sn groups. While this ratio is not of great importance in the single dose case, other than verifying the gravimetric results, it becomes more important when trying to remove all of the non-reacted tin groups in second and third dose reactions. For a single dose reaction of AlCl_3 and the trimethyltin cube at a ratio of 1 : 1 (8 : 1; Sn : Al) where 4 equivalents of tin are lost as Me_3SnCl and Me_4Sn , then the theoretical ratio of Sn : Al remaining in the system should be 4 : 1. For a sample reaction (AI080) with an initial Al : cube ratio of 0.9 : 1, (8.9 : 1; Sn : Al) which by gravimetric analysis lost 3.87 equivalents of Sn, the theoretical final ratio of Sn : Al should be 5.0 : 1. ICP results showed the actual ratio to be 5.27 : 1 which matches well with the predicted results (within ~5%) based on gravimetric analysis. Similar results were obtained with other samples described in these investigations.

Previous studies have shown that the reaction of other metal chlorides with the TMT cube at low stoichiometric ratios, produces materials with embedded catalytic centers of very low surface areas ($<10 \text{ m}^2/\text{g}$).⁸⁷ However, it was found that single dose embedded Al matrices possess moderate surface areas on the order of $150\text{-}250 \text{ m}^2/\text{g}$. Figure 2.07 shows a typical N_2 absorption/desorption isotherm for a single dose Al reaction. The shape of the isotherm is classified as Type 1 with an H4 hysteresis.⁹⁶ These designations are both indicative of a highly microporous solid with small external surfaces and narrow slit like pores. The reason that the hysteresis loop does not close can be due to irreversible uptake of N_2 into the pores as a result of swelling, or due to an irreversible chemical interaction with the adsorbate.⁹⁶ Utilizing a t-plot analysis, (Figure 2.08) the nature of the porosity within the matrix can be defined as primarily microporous (75-90%) with the remaining surface area a result of meso- and

macropores. The BJH pore size distribution clearly shows that the majority of the pores are less than 2 nm in diameter (Figure 2.07).

While IR analysis of the matrix does not yield direct evidence regarding the nature of the Al centers (no clearly distinguishable Al-O-Si vibrational bands, or bands indicative of Al coordination), it can be quite useful in a couple of other respects. The first is in regards to the presence of –OH within the system. These materials are synthesized under strictly aprotic conditions, and therefore should possess no –OH. With the IR spectrometer located within a dry N₂ glovebox, analysis of the samples can also be carried out relatively simply without exposure to air or water.

The IR spectrum (Figure 2.09a) of these samples show expected Si-O-Si modes in the 850 – 1250 cm⁻¹ range, methyl C-H bands below 3000 cm⁻¹, and in the 1500-1200 cm⁻¹ region. The assignments of the features in the 1700-1950 cm⁻¹ range and at 2360 cm⁻¹ are not well understood, but are present in the cubic building block starting material. It is important that the pristine unexposed 1-dose Al sample does not show any absorption in the –OH region of the spectrum. Exposure to even trace amounts of water is easily seen by IR, demonstrating the high sensitivity of these materials (Figure 2.09b,c). Exposure to air for longer periods (>6 hrs) results in a strong, broad feature, between 3000-3700 cm⁻¹, attributed to the absorption of large amounts of moisture.

Finally, a well-developed literature exists regarding the characteristic binding of probe molecules to solid acids and their characterization by spectroscopic methods including IR.⁹⁷⁻¹⁰⁰ The probe molecule pyridine is of most interest with regards to aluminosilicates and the focus of the IR studies presented here. Pyridine is a strong base (pKa [H₅C₅NH⁺] = 8.75) and can interact with silanols, Brønsted and Lewis acid sites that are normally present in aluminosilicate matrices. As a result of binding to any of these types of sites, the pyridine C-C ring vibration modes are perturbed resulting in vibrational signatures unique to each type of site (Figure 2.10).¹⁰¹

Based on the nonaqueous synthetic method, the presence of silanol and Brønsted sites were not expected to be present in the matrix. As a result, when the

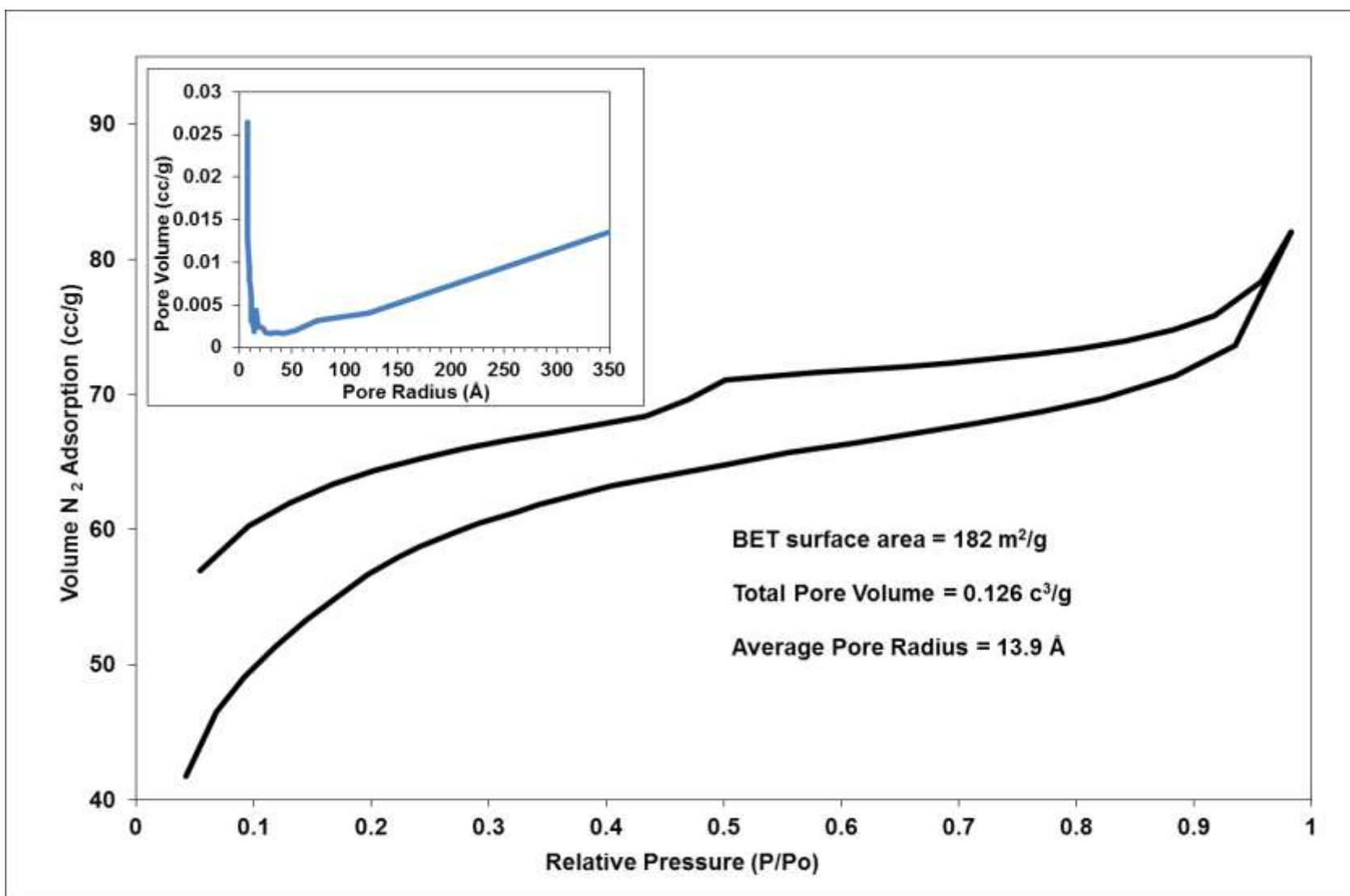


Figure 2.07: Typical N_2 adsorption isotherm for embedded 1-dose Al matrix, with BJH pore size distribution (inset).

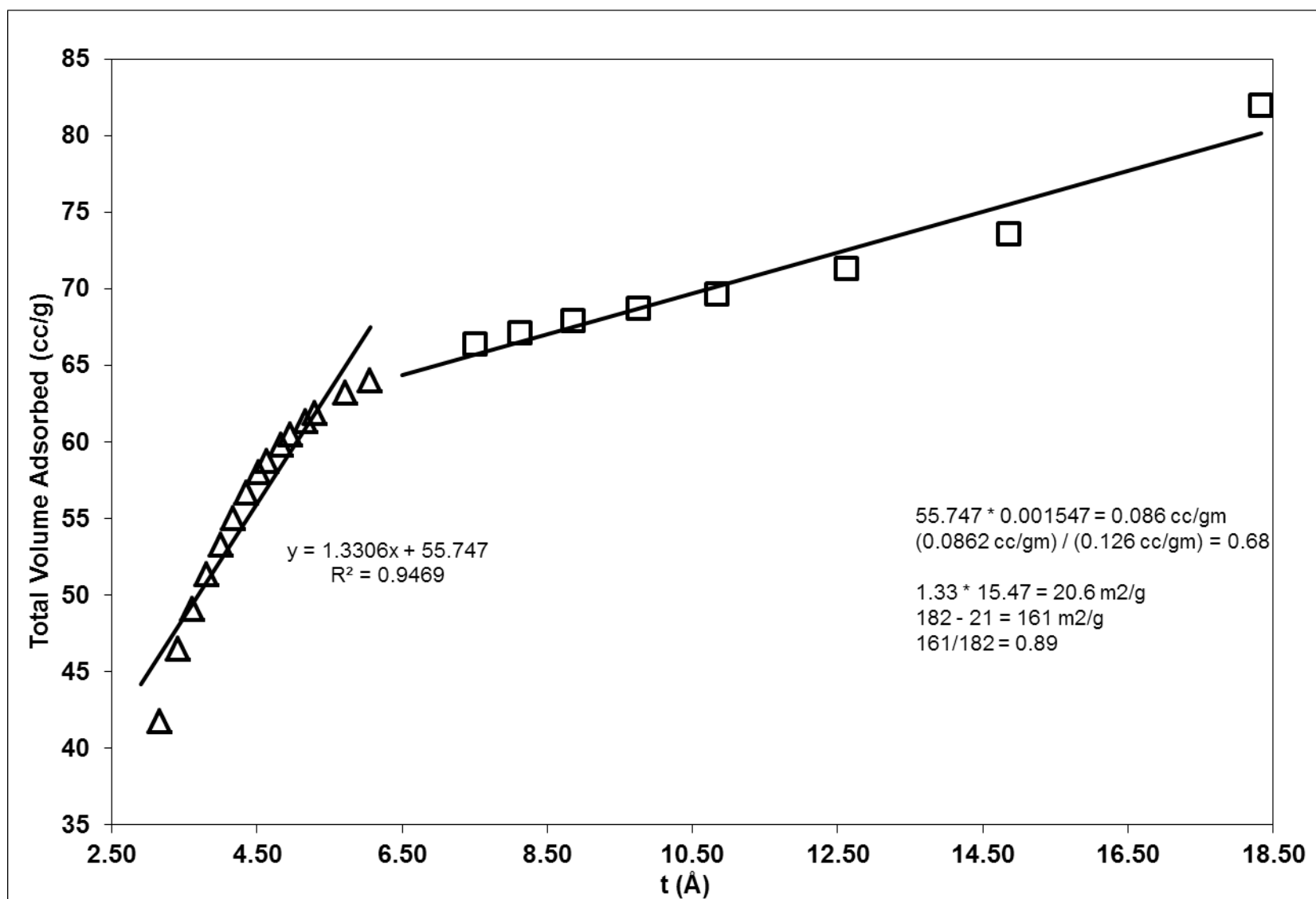


Figure 2.08: Typical t-plot indicating high microporosity for embedded 1-dose Al matrix

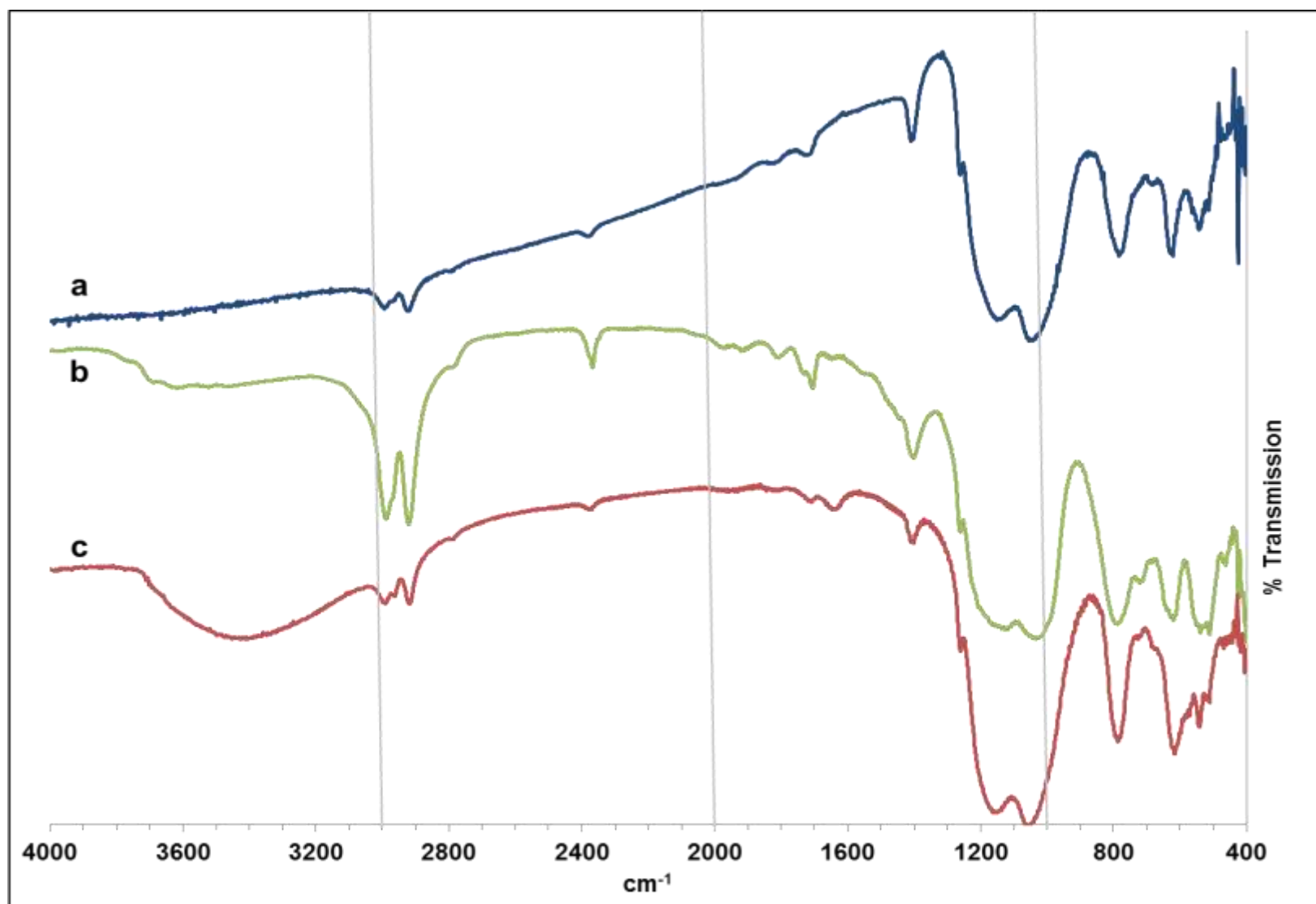


Figure 2.09: IR spectrum of embedded 1-dose Al matrix, (a) unexposed, (b) 5 min. exposure to moisture, (c) 24 hrs exposure to moisture

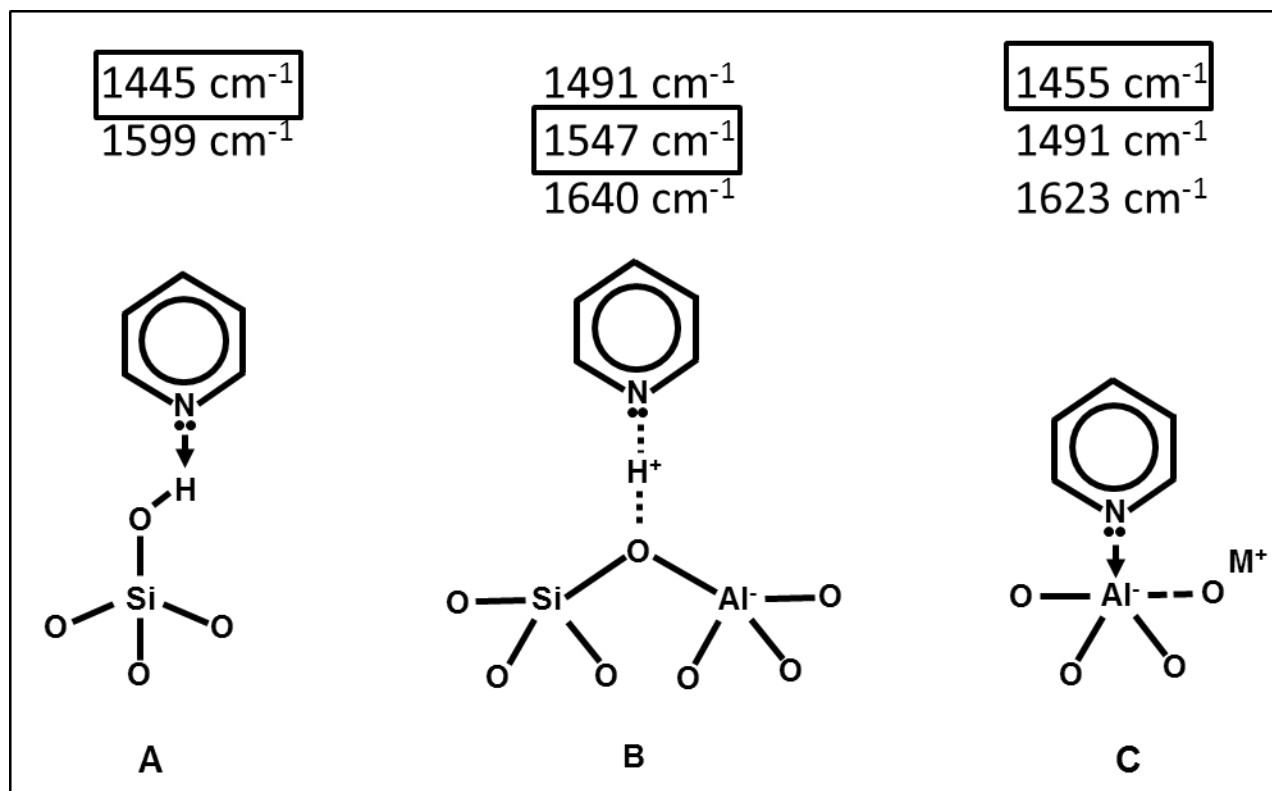


Figure 2.10: Modes & frequencies of pyridine binding on Aluminosilicates (a) silanol, (b) Brønsted acid, (c) Lewis acid

pristine cross-linked aluminum matrix (Figure 2.7a) is exposed to pyridine, the C-C stretching frequencies (1455 & 1623 cm^{-1}) associated with pyridine bound to Lewis acidic sites are prominent (Figure 2.11). There is a small contribution from Brønsted acid bound pyridine as seen by the bands at 1545 and 1640 cm^{-1} . This seems to be a result of some exposure to moisture during the pyridine treatment, as examination of the -OH region of the IR shows a small but noticeable, broad -OH band ($3400\text{-}3700\text{ cm}^{-1}$, Figure 2.12). It has also been confirmed that pyridine does not bind to silicon platforms (synthesized in a similar fashion) that do not contain Al centers. The degree of Brønsted acidity is further increased by exposing the pristine sample to moisture and then exposing the sample to pyridine. The IR data for pyridine binding to the Al sites in the building block matrices clearly indicates that the majority of the sites are Lewis acidic in nature.

Solid state NMR (SSNMR) spectroscopy presents one of the very few ways of directly observing the aluminum centers themselves. As previously discussed, nuclei with large quadrupolar moments can present a number of challenges for both data collection and analysis. These challenges are magnified as the symmetry around the nuclei of interest is lowered. In the case of aluminum, due to large quadrupolar broadening effects, it would be highly unlikely that an observable signal could be seen for any 3-coordinate aluminum even if such a species was present.¹⁰² Studies where successful detection of signals arising from 3-coordinate aluminum centers in the solid state are essentially nonexistent, and in the few cases of molecular three coordinate aluminum species in solution, the ^{27}Al spectra show extremely large line widths,^{103,104} or are often not reported at all.^{105–107} For example, the ^{27}Al feature associated with trimesitylaluminum, $[\text{Al}(\text{C}_9\text{H}_{11})_3]$, has a linewidth of $\sim 10,000\text{ Hz}$ at half height.¹⁰³

In aluminum SSNMR, general chemical shift regions have been related to various geometries around the Al center. The regions of greatest interest for these materials are shown in figure 2.13.¹⁰⁸ Figure 2.14 shows the 1d ^{27}Al SSNMR spectrum

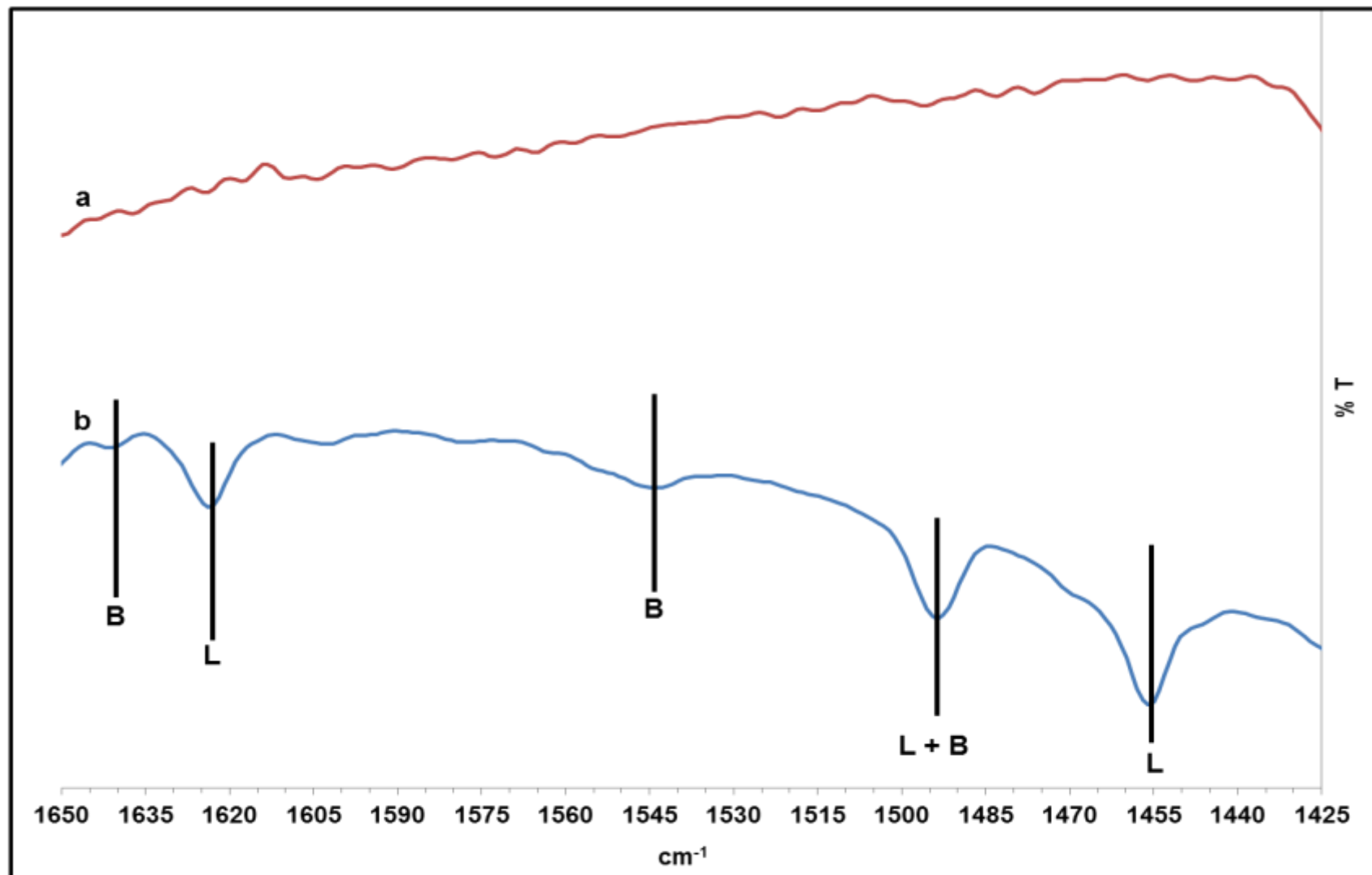


Figure 2.11: IR spectrum (Pyridine Region) of 1-dose aluminum sample before pyridine adsorption (a) and after (b) (B=Brønsted, L=Lewis)

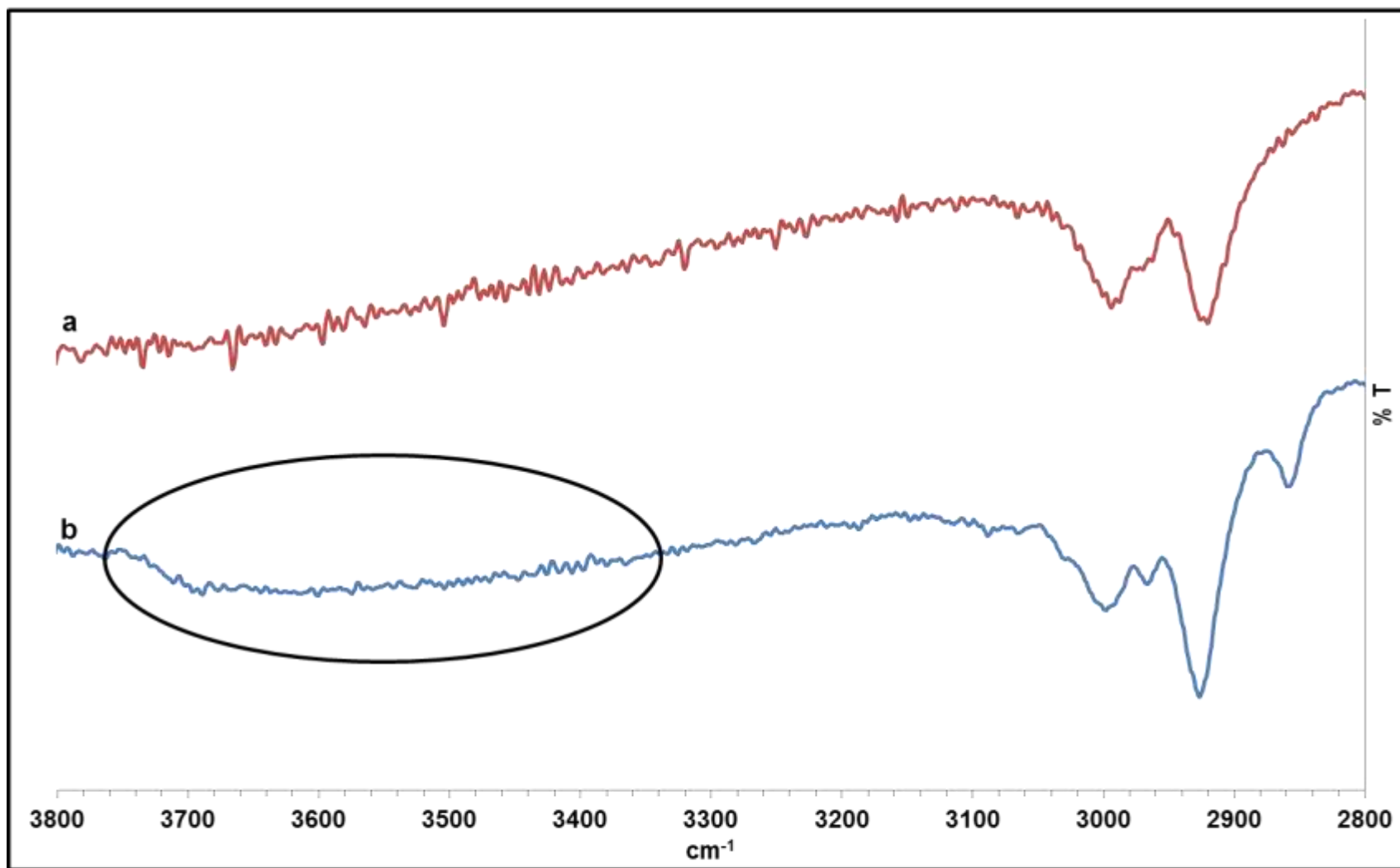


Figure 2.12: IR spectrum (-OH Region) of 1-dose aluminum sample before pyridine adsorption (a) and after (b)

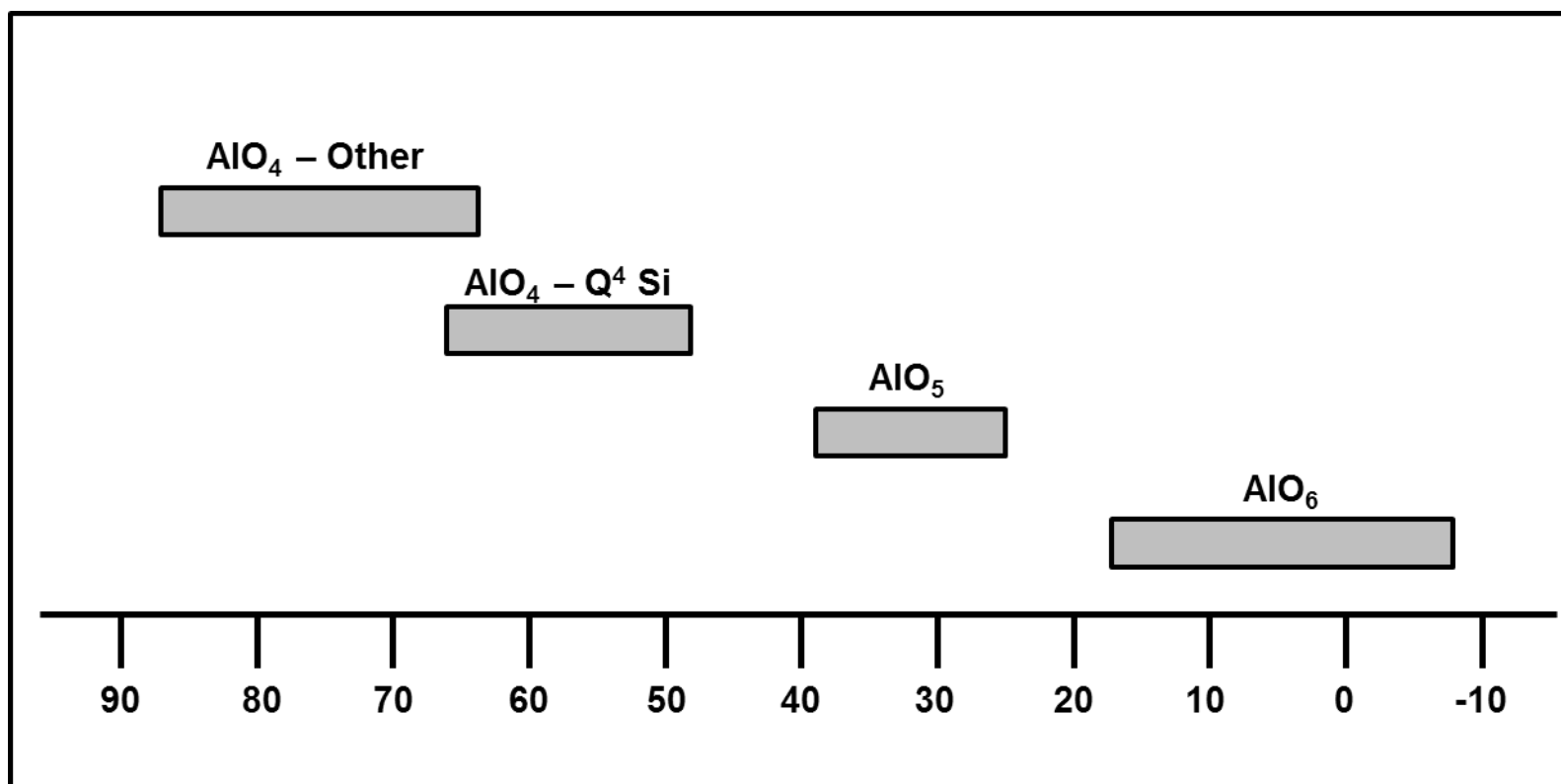


Figure 2.13: Isotropic chemical shift ranges for various Al coordination environments (0 ppm = $\text{Al}(\text{H}_2\text{O})_6$)

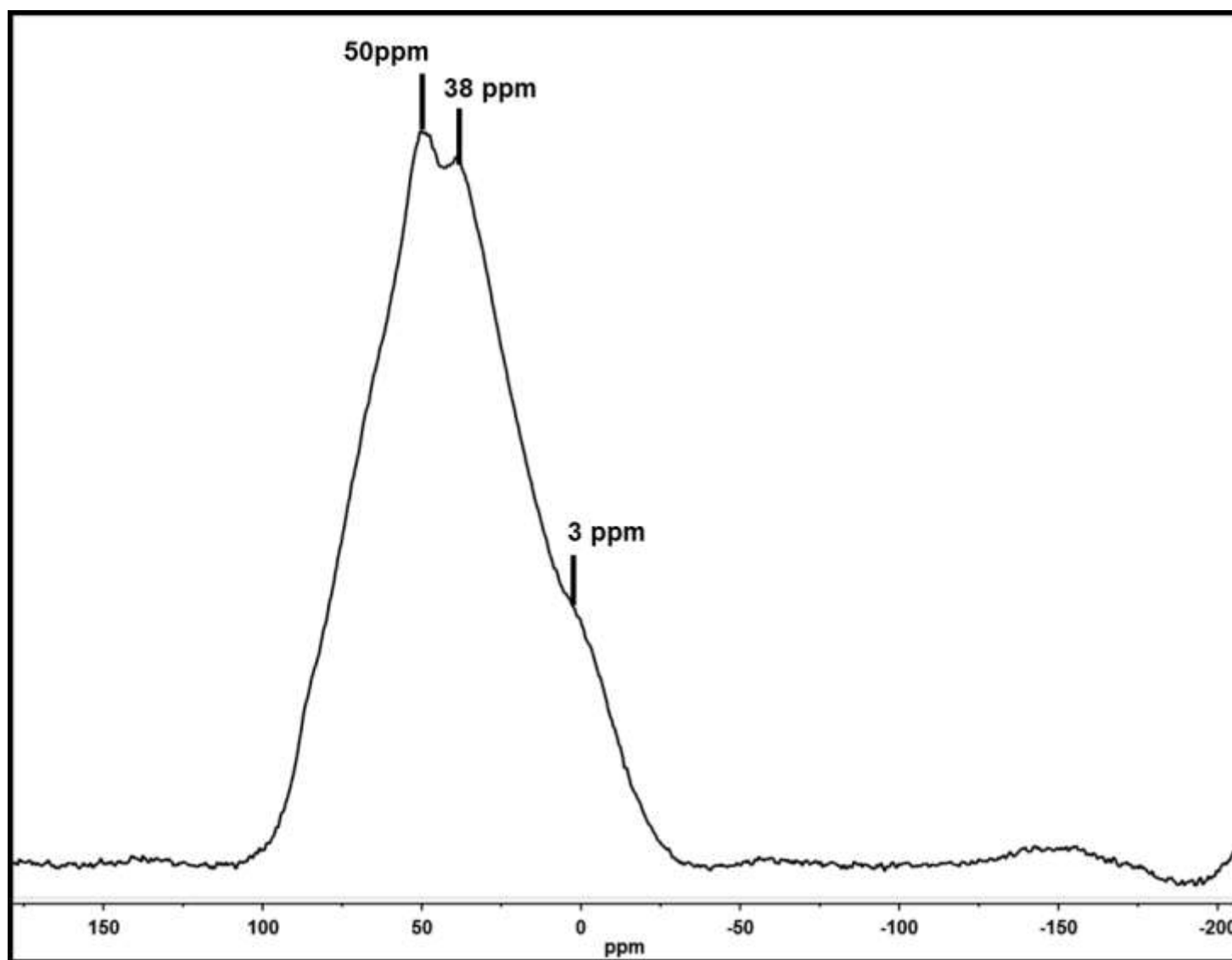


Figure 2.14: ^{27}Al MAS spectrum of “pristine” embedded 1-dose Al sample

of a pristine embedded 1-dose aluminum sample. This spectrum shows a broad feature most probably indicating the presence of multiple types of aluminum centers. There appear to be three distinct features at $\delta = 50, 38, \text{ and } 3 \text{ ppm}$. These are tentatively assigned to 4, 5 and 6 coordinate Al centers respectively. However, it is somewhat difficult to determine if the upfield shoulder is truly 6-coordinate aluminum, or a quadrupolar lineshape effect.

The ability of these Al catalysts to absorb moisture has been discussed, and can also be observed in the ^{27}Al NMR. After the spectrum in Figure 2.14 was collected, the sample was removed from the NMR rotor, exposed to air, repacked, and a second spectrum was collected. Even with only brief exposure to air, the natures of the Al sites in the catalyst are significantly changed with respect to the previous spectrum. Most noticeable is an increased resolution between the three features. With very low exposures, the features associated with 5-coordinate aluminum become more prominent, and the 6-coordinate feature also begins to grow in (Figure 2.15). As exposure to moisture is increased, the 4- and 6-coordinate species begin to dominate the spectrum though a significant 5-coordinate component remains. Though the chemical shifts remain very similar to those seen in the pristine sample, it is difficult to imagine that the species represented by the three features in the exposed sample are the same as those seen in the pristine sample. While the hydration process is not well understood, it is likely that the initial sites present in the pristine sample have been transformed into a completely new set of aluminum species. It would be expected that the coordinately unsaturated centers (4 and 5-coordinate) would absorb moisture resulting in an increased coordination of 5 or 6. However, there could be some degree of steric hindrance that prevents all of the centers from achieving a coordination of 6. Experiments were run trying to examine the reversibility of water binding, but the hydration process was found to be generally irreversible as heating the aluminum sample did not change the ^{27}Al SSNMR spectrum.

Analysis of the ^{29}Si SSNMR spectra for the one dose samples is more straightforward. A broad feature with a significant shoulder indicative of at least two signals

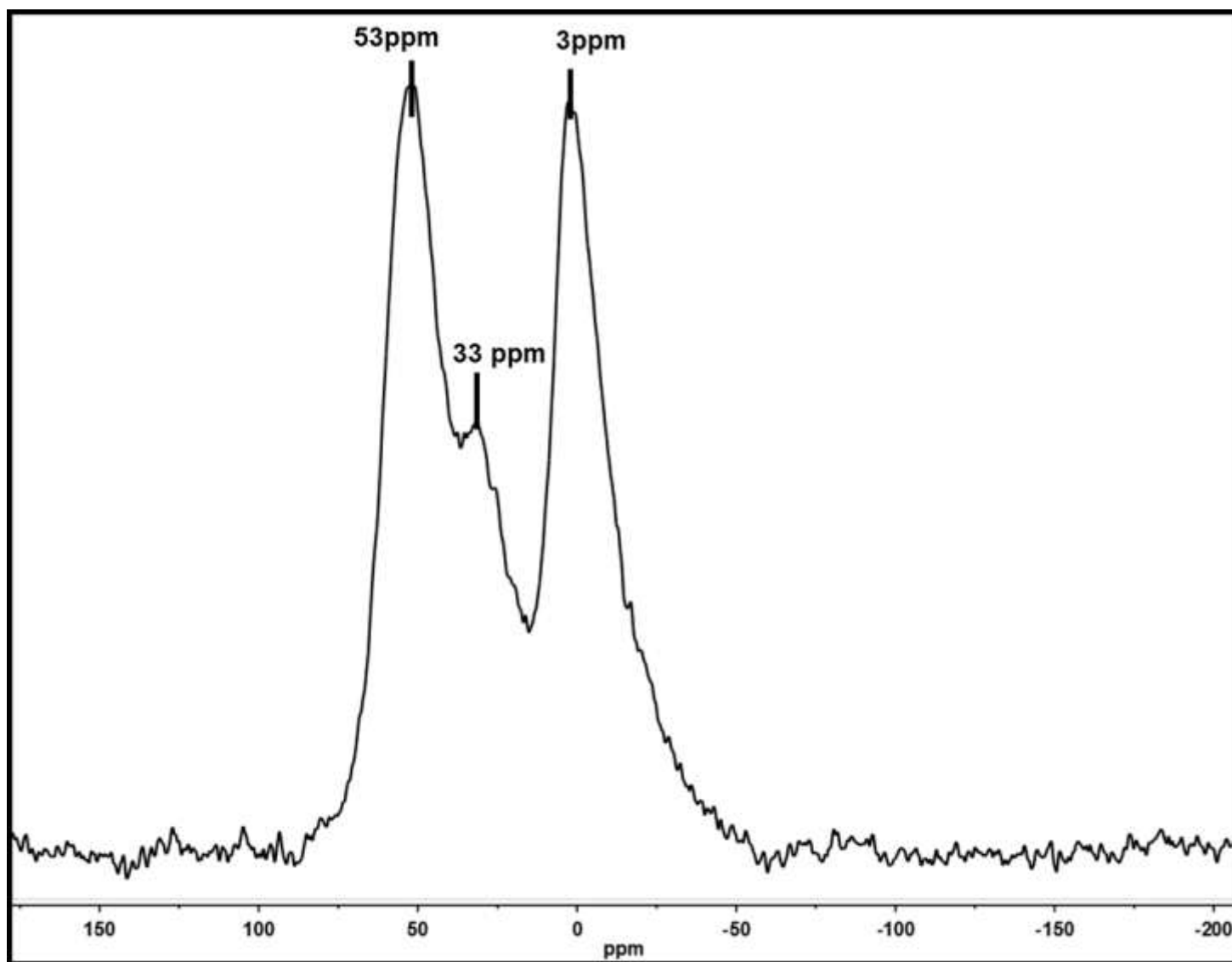


Figure 2.15: ^{27}Al MAS spectrum of “exposed” embedded 1-dose Al sample

(Figure 2.16) is observed. Deconvolution of the feature assuming the presence of only two types of silicon gives rise to an excellent fit of the data. The first silicon signal at $\delta = -102.3$ ppm ($w_{1/2} = 350$ Hz) is assigned to silicon atoms on the unreacted corners of the cubic building block ($\equiv\text{Si-O-SnMe}_3$) while the second feature at $\delta = -106.3$ ppm ($w_{1/2} = 670$ Hz) can be assigned to silicon centers ($\equiv\text{Si-O-Al}$) that result from the reaction of the cubic building block with the AlCl_3 precursor. The larger linewidth for the ($\equiv\text{Si-O-Al}$) species likely arises from having a distribution of silicon atoms in slightly different geometric orientations leading to a distribution in chemical shifts and thus a broader feature. It is also important to note the lack of other silicon signals in the spectrum which would indicate that AlCl_3 is breaking open or attacking the cubic cage in any way (i.e. chlorination of the silicon that would lead to signals between $-50 - -90$ ppm).⁶⁹

If the reaction of AlCl_3 and TMT cube were to proceed as expected, then the ^{13}C SSNMR would show only a single feature at ~ -3 ppm representing the remaining unreacted $-\text{OSnMe}_3$ groups on the cube. This is illustrated in Figure 2.17 by the ^{13}C CPMAS spectrum of a 1-dose platform synthesized by the reaction of SiCl_4 with the TMT cube (no aluminum present). In this spectrum only the feature at -2.3 ppm assigned to unreacted $-\text{OSnMe}_3$ groups is observed. In the ^{13}C CPMAS spectrum (Figure 2.18) for the 1-dose AlCl_3 sample, a downfield shoulder on the expected signal is indicative of the presence of a second type of carbon. Deconvolution of the broad feature results in a very good fit for two resonances. The upfield peak at -4 ppm is assigned to the remaining $-\text{OSnMe}_3$ species left in the matrix, while the downfield feature at 2.1 ppm represents a second unknown type of carbon nucleus within the system. There is also a small third feature at ~ 30 ppm that is a result of wax used to seal the NMR rotor.

We tentatively assign the unknown carbon signal to carbon atoms of methyl groups on tin atoms that are cationic and associated with negatively charged aluminum atoms in the sample. The exact identity of these groups has been one of the most difficult questions to answer in these investigations. When the reaction begins, only trimethyltin groups are present, all of which are essentially identical. After removal of all trimethyltin chloride and tetramethyl tin, there must be a species in the matrix that was

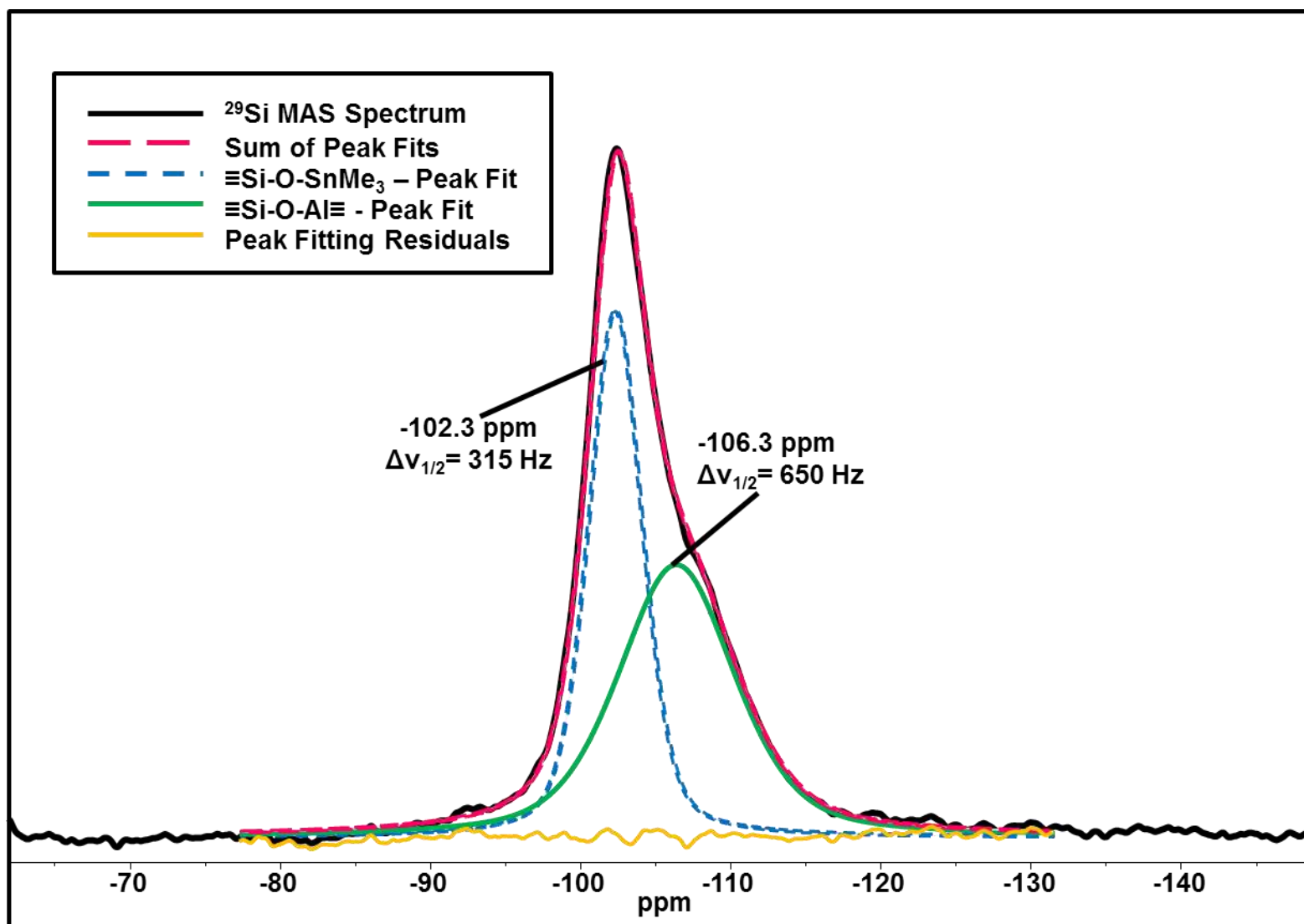


Figure 2.16: ^{29}Si MAS spectrum of embedded 1-dose Al sample with deconvolution of peaks

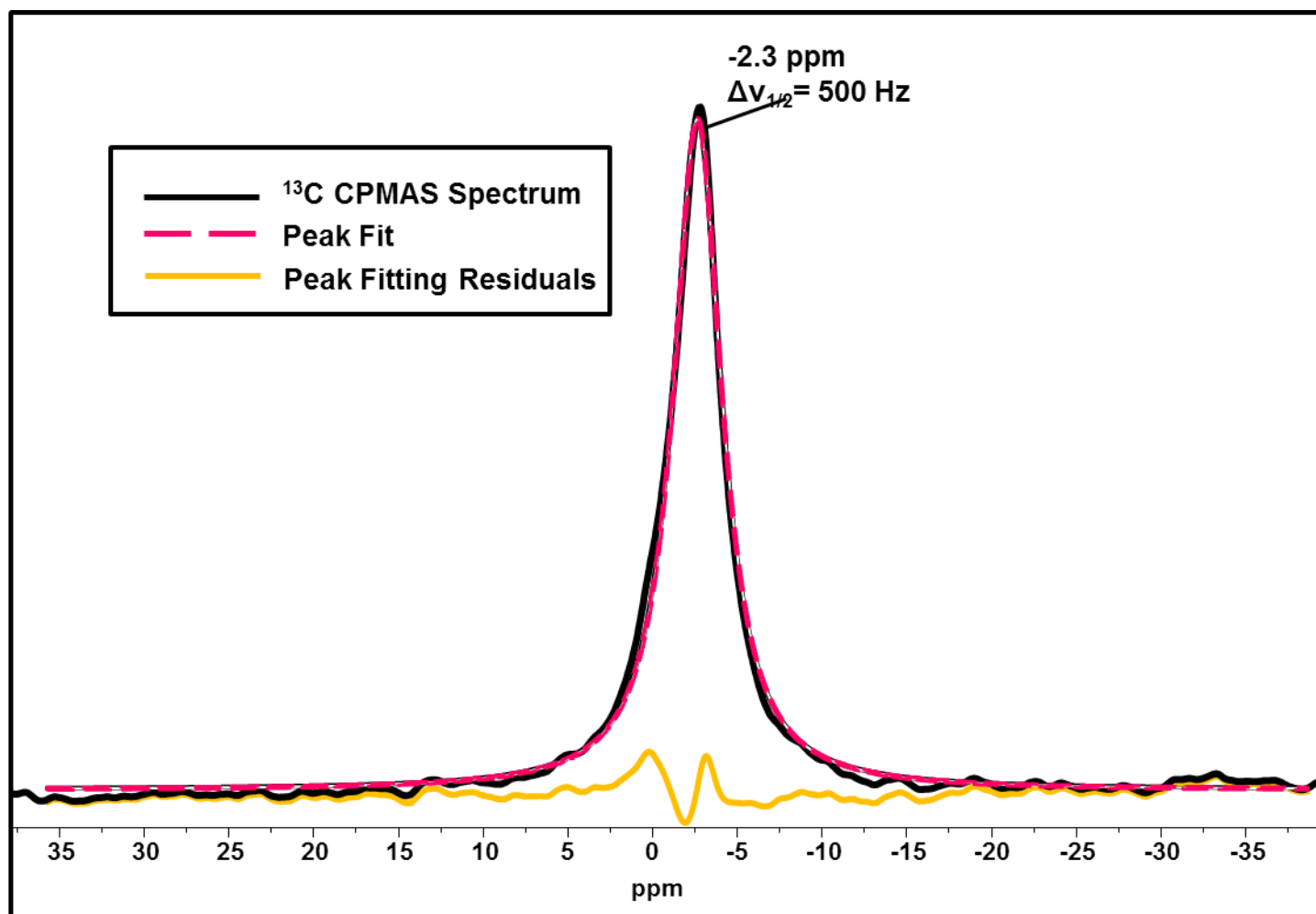


Figure 2.17: ^{13}C CPMAS spectrum of 1-dose platform showing unreacted $-\text{OSnMe}_3$ groups

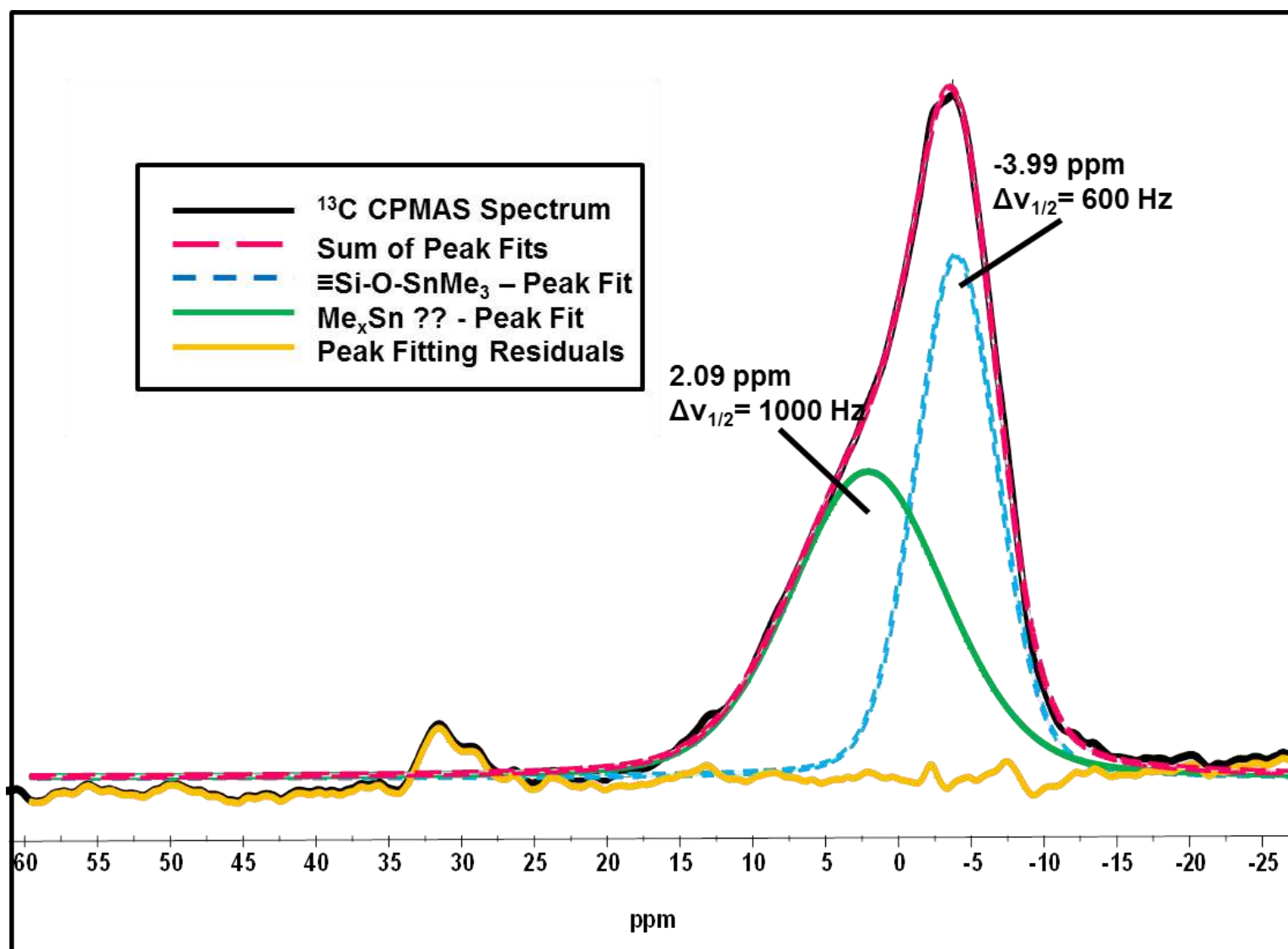


Figure 2.18: ^{13}C CPMAS spectrum of embedded 1-dose Al sample

formerly a trimethyl tin group but has had a methyl group abstracted in some fashion. The downfield shift of the new signal observed in figure 2.18 implies that the tin group that the carbon is bound to is now more deshielded. A group that is consistent with the deshielded nature of the cation in question and accounts for the formation of tetramethyltin is a cation $-\text{OSnMe}_2^+$ group in close proximity to an anionic, 4-coordinate aluminum center as illustrated in Figure 2.19. Determination of the mechanism by which such a secondary reaction might occur will be discussed in more detail later in this chapter.

The fact that there are multiple ^{13}C signals leads to the expectation that a similar number of ^{119}Sn signals will be observed, as all carbons in the system are bound to tin centers. The ^{119}Sn SSNMR resonance of the remaining tin groups present in the, non-aluminum containing, silicon platform analogue is known to come at ~ 130 ppm (Figure 2.20), similar to some of the reported literature chemical shifts for covalently bound Si-O-SnMe₃ species.^{109–111} However, the silicon platform possesses tin species that are dissimilar to the ionic $-\text{SnMe}_3$ groups proposed in the literature and that are believed to exist in our samples. One would not expect the cationic and neutral tin centers to have such similar chemical shifts, giving more credence to the idea of an ionic $-\text{SnMe}_2^+$ group having a chemical shift significantly downfield of ~ 130 ppm.

The aluminosilicates synthesized in this work show a large ^{119}Sn signal at $\delta = 130$ ppm that represents the remaining unreacted corner methyl tin groups (Figure 2.21). Furthermore, if the aluminum centers are assumed to be negatively charged, 4-coordinate centers, then it would be necessary for a second, cationic, tin center to be present for charge balance. Evidence for the presence of a second species has not been observed in the ^{119}Sn spectrum of these samples. As tin has an extremely wide chemical shift range (6500 ppm),¹¹² care was taken to survey a wide swath of this range, but no second signal was observed.

The literature for ^{119}Sn SSNMR of alkyl tin groups on silica or zeolitic materials is relatively small, and consists of several reports presenting varying chemical shifts for a number of species.^{109–111} For proposed $-\text{OSnMe}_3$ groups grafted on zeolites, chemical shift values range from 130–260 ppm. Typically these systems are created by reaction

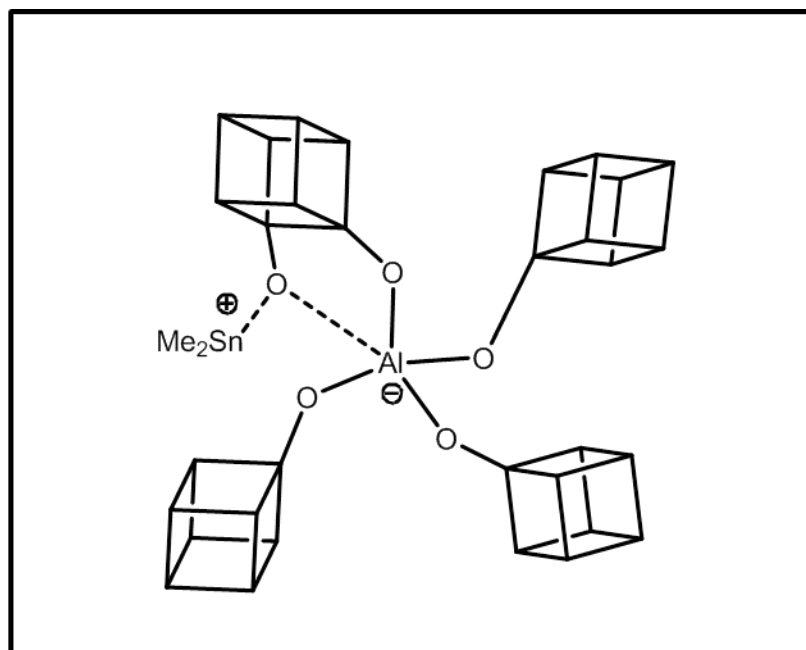


Figure 2.19: Proposed $-\text{OSnMe}_2^+$ sites in proximity to tetrahedral anionic AlO_4^- centers

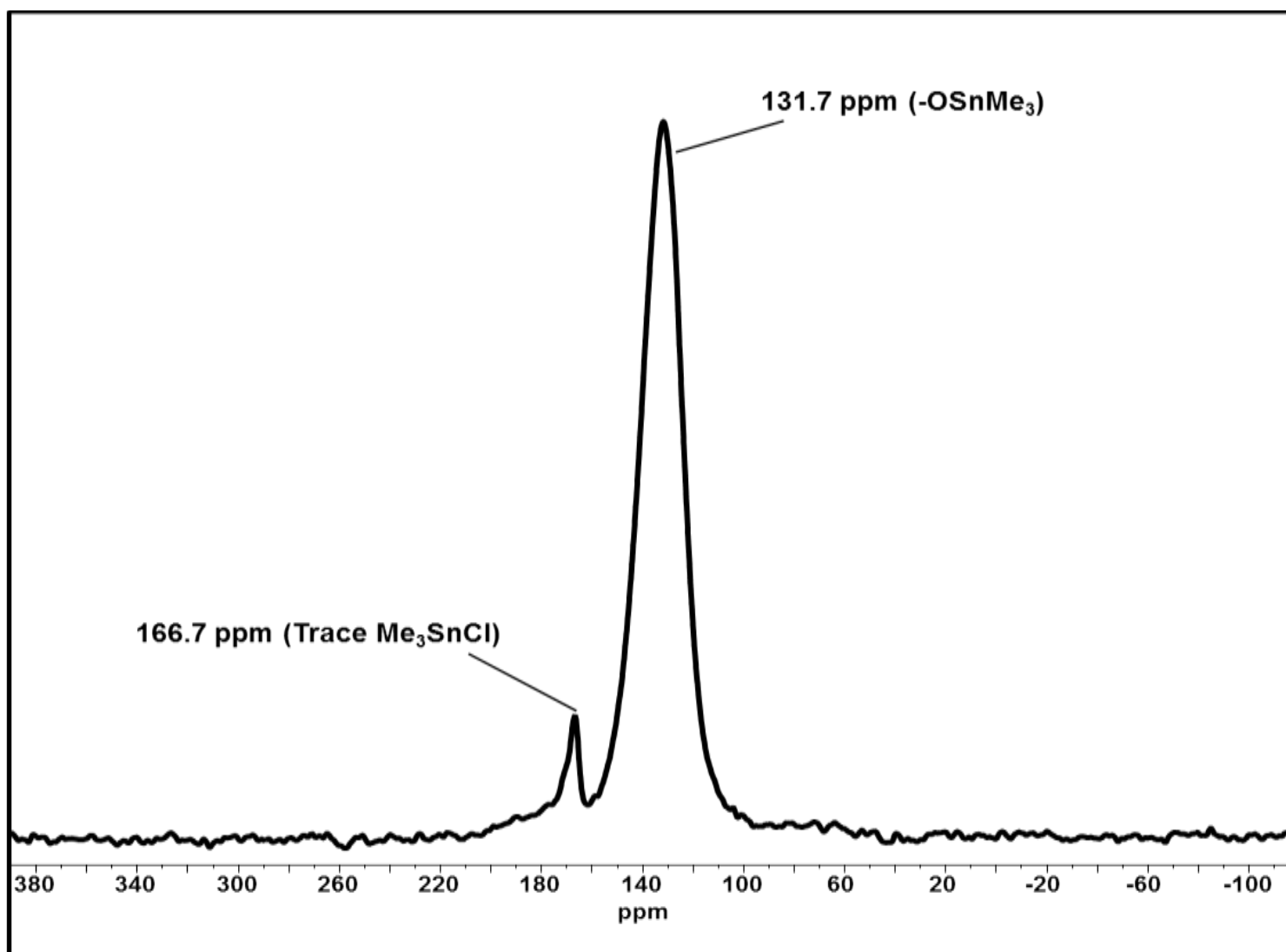


Figure 2.20: ^{119}Sn MAS spectrum of 1-dose platform showing unreacted $-\text{OSnMe}_3$ groups

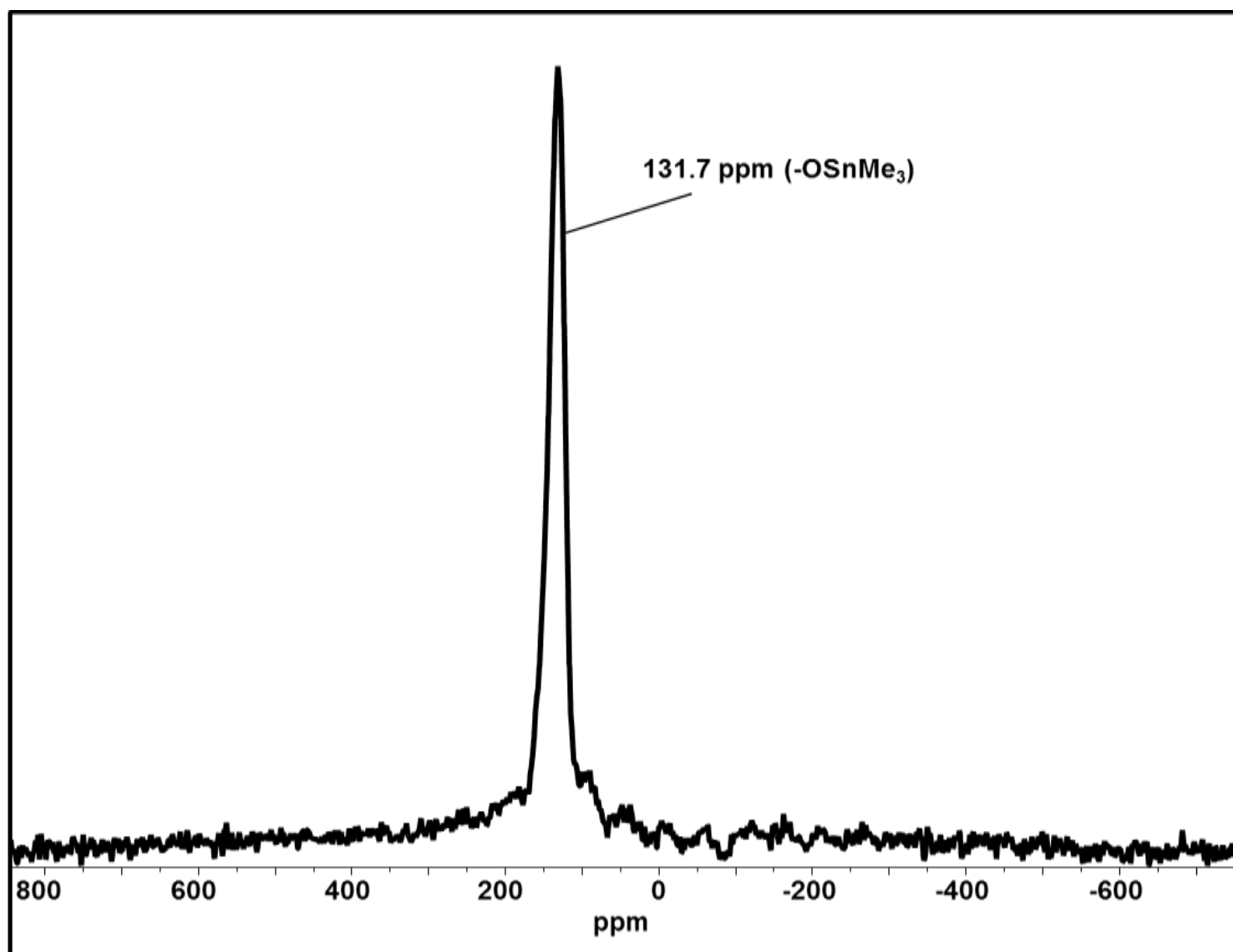


Figure 2.21: ^{119}Sn MAS spectrum of embedded 1-dose Al sample

with one of two functionalities present in zeolites (Figure 2.22). The first involves the reaction of Me_4Sn with surface silanol groups. In this reaction, a group similar to that found in the TMT cube or a silicon platform is formed (Figure 2.22a). This should give a nearly identical ^{119}Sn resonance to what has previously been observed. Alternately, if the tin species reacts with Brønsted acid sites, then the cationic trimethyltin group that is formed will act to replace the acidic proton, and may be said to be bound to a bridging oxygen (Figure 2.22b). These proposed sites are similar to the second type of tin center proposed to exist in the 1-dose embedded Al matrix. An important question to examine in this context is the nature and strength of the Sn-O bond. The literature suggests that these sites possess a relatively high partial positive charge which should lead to significant deshielding of the tin center and therefore a significant downfield shift for the isotropic peak.

2.3.2 One Dose Embedded Aluminum Catalysts Starting From $\text{AlCl}_3\cdot\text{Py}$

Reactions utilizing the monopyridine adduct of aluminum trichloride ($\text{AlCl}_3\cdot\text{Py}$) were carried out for several reasons. Foremost amongst these is its well characterized structure⁸⁸ both as a solid and in solution, and its solubility in toluene. The pyridine adduct is a pseudo tetrahedral and exists as discrete molecules in both the solid state and in solution. This is quite different from AlCl_3 which exhibits a polymeric structure with bridging chlorides in the solid state. This polymeric bonding leads to low solubility, and a questionable notion of the structure in solution. The attributes of the pyridine adduct make it a distinctly more desirable starting point than AlCl_3 . Furthermore, the initial binding of pyridine to form the 1:1 adduct puts an important spectroscopic IR probe in place prior to the reaction with the trimethyltin cube. Perhaps the one drawback to starting with pyridine bound to aluminum is the inability to remove the bound pyridine from the site that develops in the final product. This is due to the strength of the $\text{N}\rightarrow\text{Al}$ interaction in the final matrix.

Preparation of the one dose heterogeneous matrix was carried out in an identical fashion to those prepared starting from AlCl_3 . Reaction of $\text{AlCl}_3\cdot\text{Py}$ and TMT Cube (1 : 1) was conducted at 90 °C for 48 hrs in toluene. The volatiles were removed

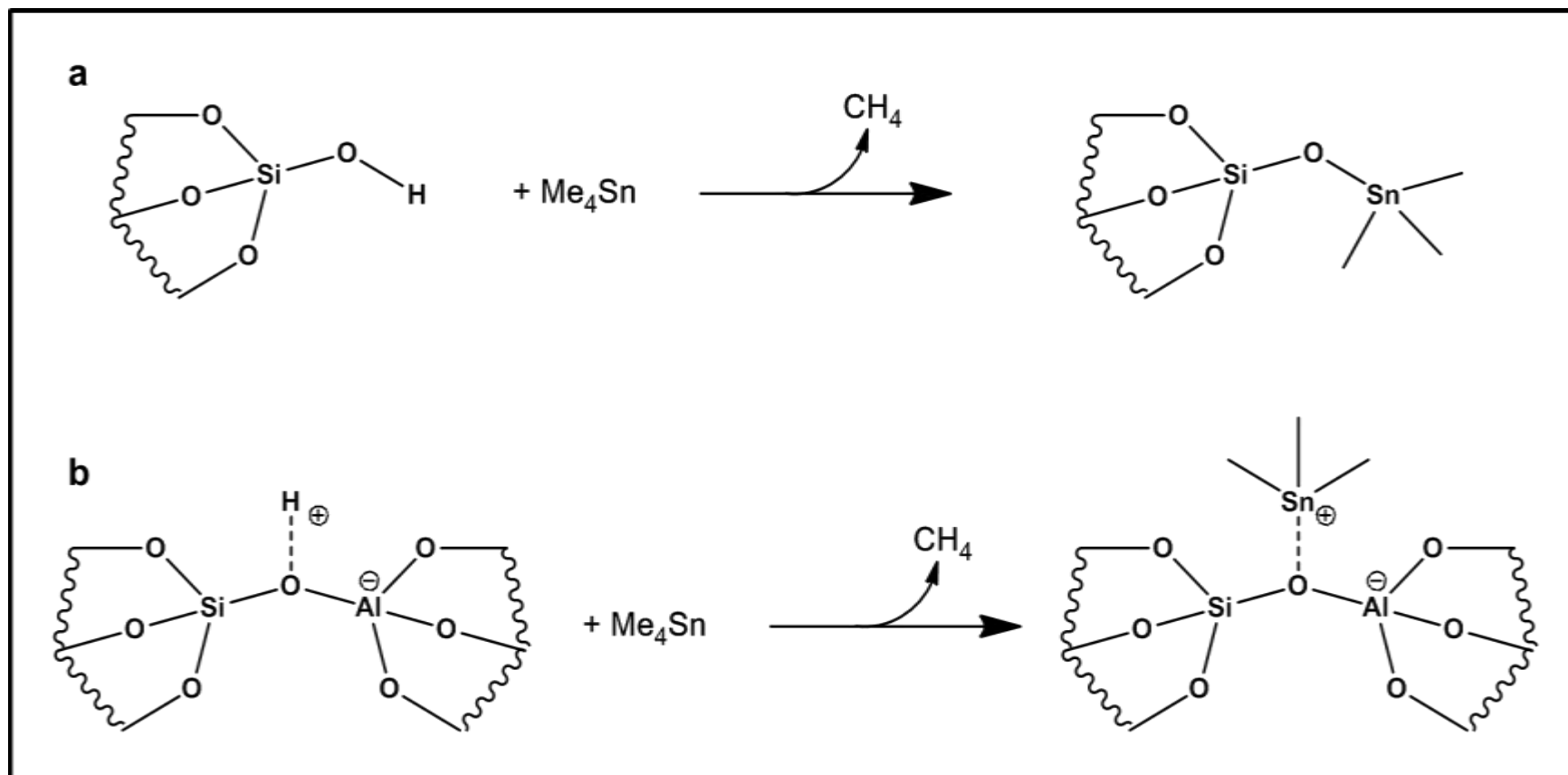
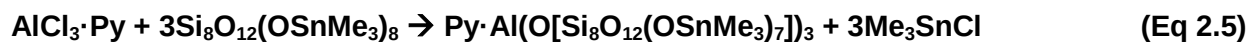


Figure 2.22: Proposed literature Me_3Sn sites in zeolites treated with Me_4Sn (a) reaction with silanol groups, (b) reaction with Brønsted acid sites

and analyzed by NMR and GC/MS. It was found that in this reaction, the only byproduct produced was Me₃SnCl (Equation 2.5). No evidence for the formation of Me₄Sn was



observed, in stark contrast to the analogous reactions with AlCl₃. Additionally, no pyridine was observed in the volatiles after heating at 100 °C for several hours.

Gravimetric analysis showed that at ratios of <1 : 1, AlCl₃·Py : TMT Cube, 2.9 equivalents of Me₃SnCl were lost per AlCl₃·Py precursor molecule. This follows with what has typically been seen for similar reactions with other metal chlorides but is different from that seen in the case of the AlCl₃ precursor.

Surface area measurements on the product from this reaction tend to be significantly less (<10 m²/g) than that seen when starting from AlCl₃. The values are similar to what has been seen when carrying out other one dose reactions with metal chlorides of Ti, V, and W.

Qualitatively, the IR spectrum (Figure 2.23) for this sample shows clear evidence for pyridine binding to Lewis acidic centers, and only trace amounts of Brønsted binding. With no evidence of pyridine in the reaction volatiles, the presence of pyridine bound to the Al centers in the precursor molecule, and the moderate conditions under which the sample was treated, this was an expected result. The nature of the pyridine binding interaction is very similar to that seen previously when pyridine was absorbed on a one dose embedded Al center synthesized from the AlCl₃ precursor. This is interesting as it is unlikely that the sites present in the two materials are the same. Theoretically, the pyridine bound to an AlO₄·Py center and an AlO₃·Py should be different, but that does not seem to be the case. The strength of the N→Al interaction should be different enough that the position of the pyridine C=C bond deformation stretches that are typically analyzed should shift. In the case of pyridine bound to B for instance (Chapter 4) there are shifts in the stretch position. Perhaps in this case, the difference in the strength of the interaction is just not different enough to measure.

²⁷Al SSNMR analysis of samples where AlCl₃·Py was used as the precursor yields a spectrum (Figure 2.24) that is dominated by a single peak (δ = 51 ppm)

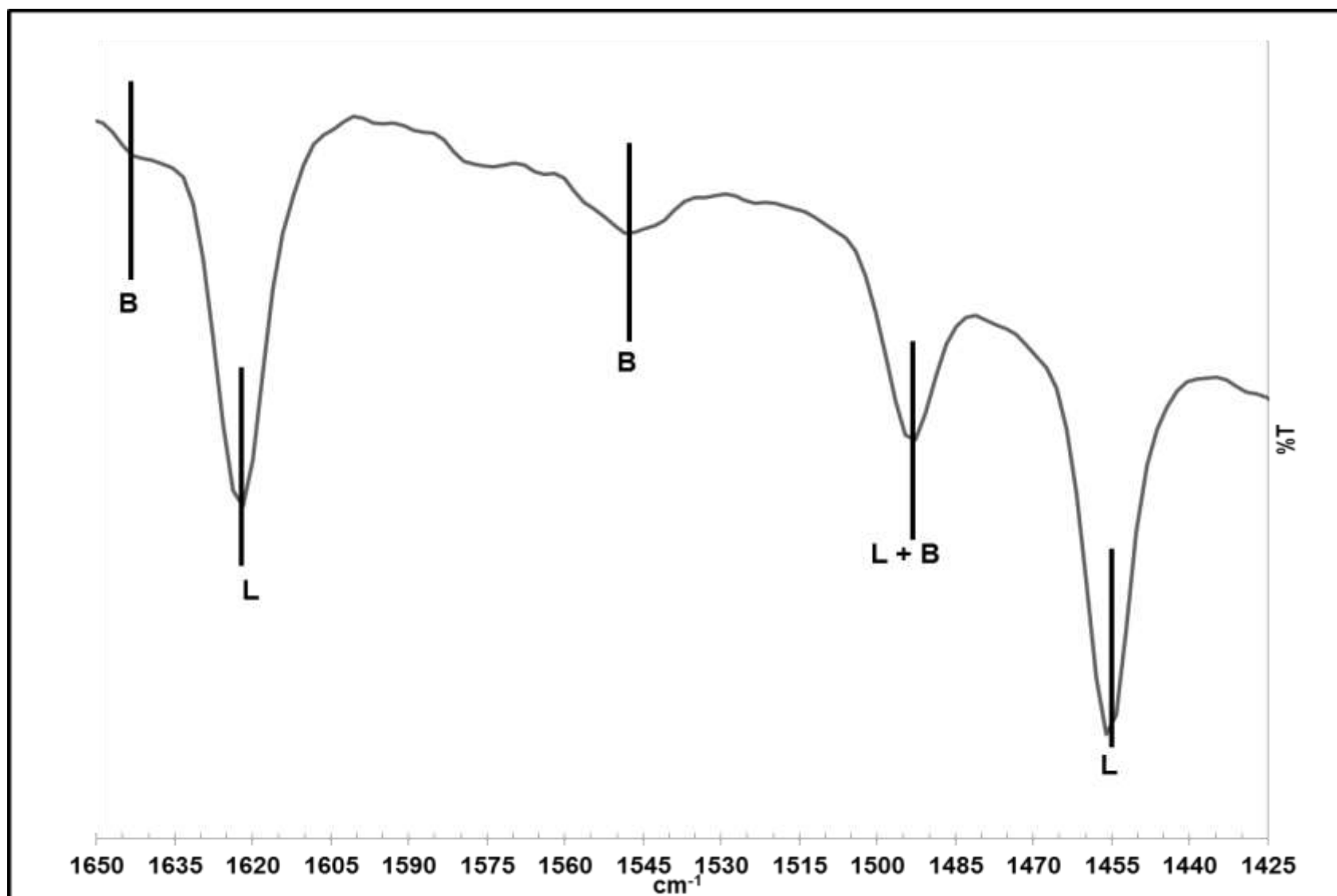


Figure 2.23: IR spectrum of embedded 1-dose Al matrix using $\text{AlCl}_3 \cdot \text{Py}$ precursor

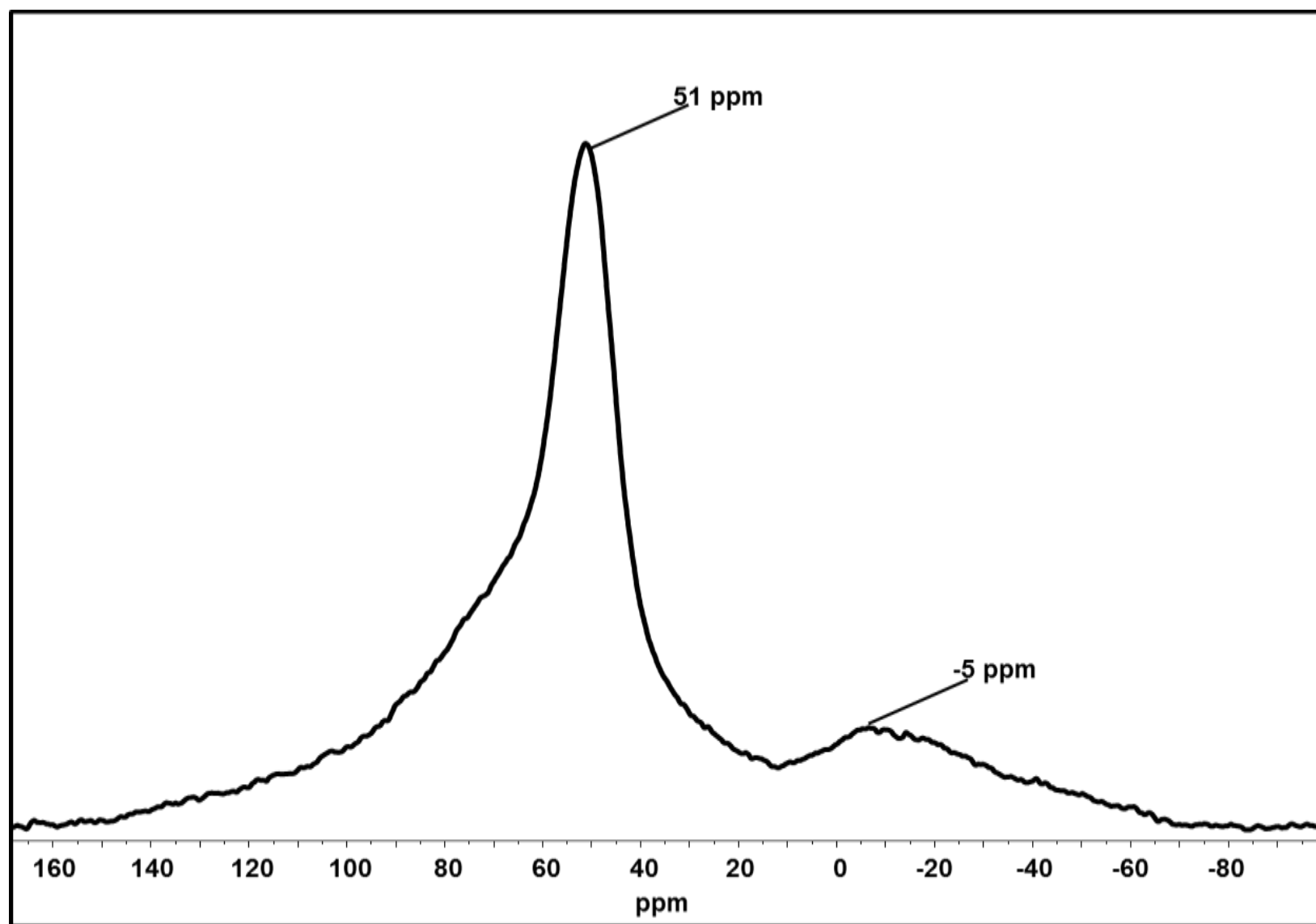


Figure 2.24: ^{27}Al MAS NMR spectrum of embedded 1-dose Al-Py sample

identified as aluminum centers in a tetrahedral (4-coordinate) geometry. There is a small broad resonance centered at $\delta = -5$ ppm that is attributed to 6-coordinate aluminum centers possibly from traces of adsorbed water. The apparent stability of the pseudo-tetrahedral aluminum center ($\text{O}_3\text{Al-N}$) within the silicate matrix was further confirmed by exposing the sample to air for increasing amounts of time. ^{27}Al spectra were taken at different times during exposure (Figure 2.25), and while an initial growth of the 6-coordinate species is evident, a point is reached where the signal stops increasing. In this overlay plot, the tetrahedral component has been normalized to show the relative increase in 6-coordinate aluminum centers.

Solid state ^{29}Si NMR (Figure 2.26) for this sample resulted in a spectrum appearing nearly identical to those of the materials produced from the AlCl_3 precursor. The ^{13}C NMR however (Figure 2.27), showed a single broad feature at $\delta = -2$ ppm associated with the remaining trimethyltin groups and a series of broad signals from $\delta = 120$ -150 ppm confirming the presence of bound pyridine. The spectrum indicates that there is no second methyl species, in agreement with a lack of tetramethyltin formation.

2.3.3 One Dose Embedded Aluminum Catalyst From $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$

Eisch et al. have described the reaction of Me_3SnCl and AlCl_3 to produce the polymeric ion paired species $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$.⁸⁹ This was an important piece of information in the present context because it is possible that this reaction, or something similar, was occurring in the early stages of the reaction of AlCl_3 with the TMT cube (Figure 2.28). As the reaction proceeds, Me_3SnCl is produced before all of the AlCl_3 has dissolved in solution providing the necessary components for such a side reaction to progress. The $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ complex is also a deep yellow/green color in solution. This corresponds well with the formation of a yellow solution within the first 30 minutes of the reaction of AlCl_3 with TMT cube. This is also important as this species could provide some insight into how tetramethyltin formation is occurring. In order to test this hypothesis that we were producing the ion paired species *in situ*, we first prepared and isolated $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ and then utilized it as the Al precursor source in reactions with the trimethyltin cube.

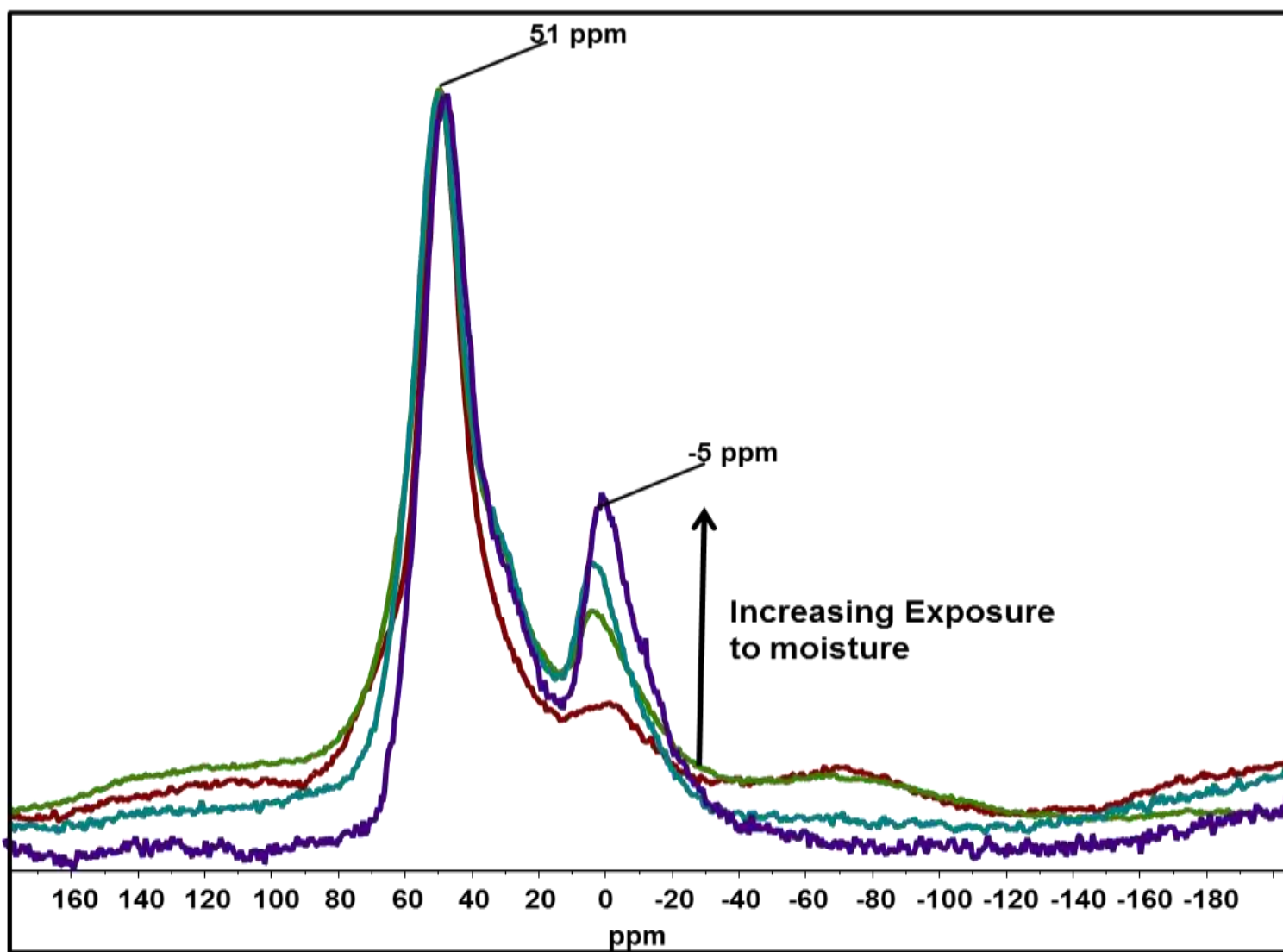


Figure 2.25: ^{27}Al MAS NMR spectrum of embedded 1-dose Al-Py sample exposed to moisture

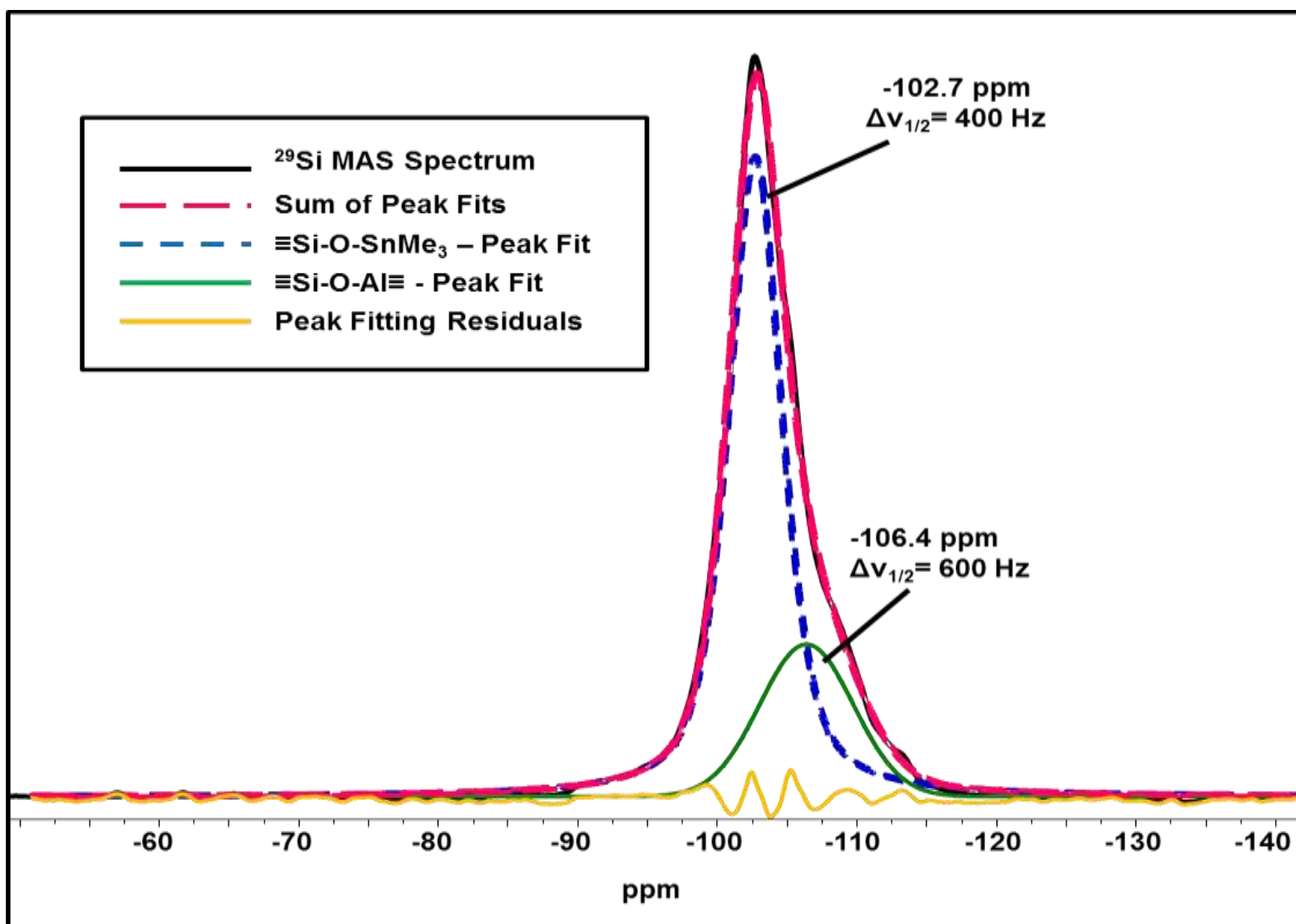


Figure 2.26: ^{29}Si CPMAS NMR spectrum of embedded 1-dose Al-Py sample with deconvolution of peaks

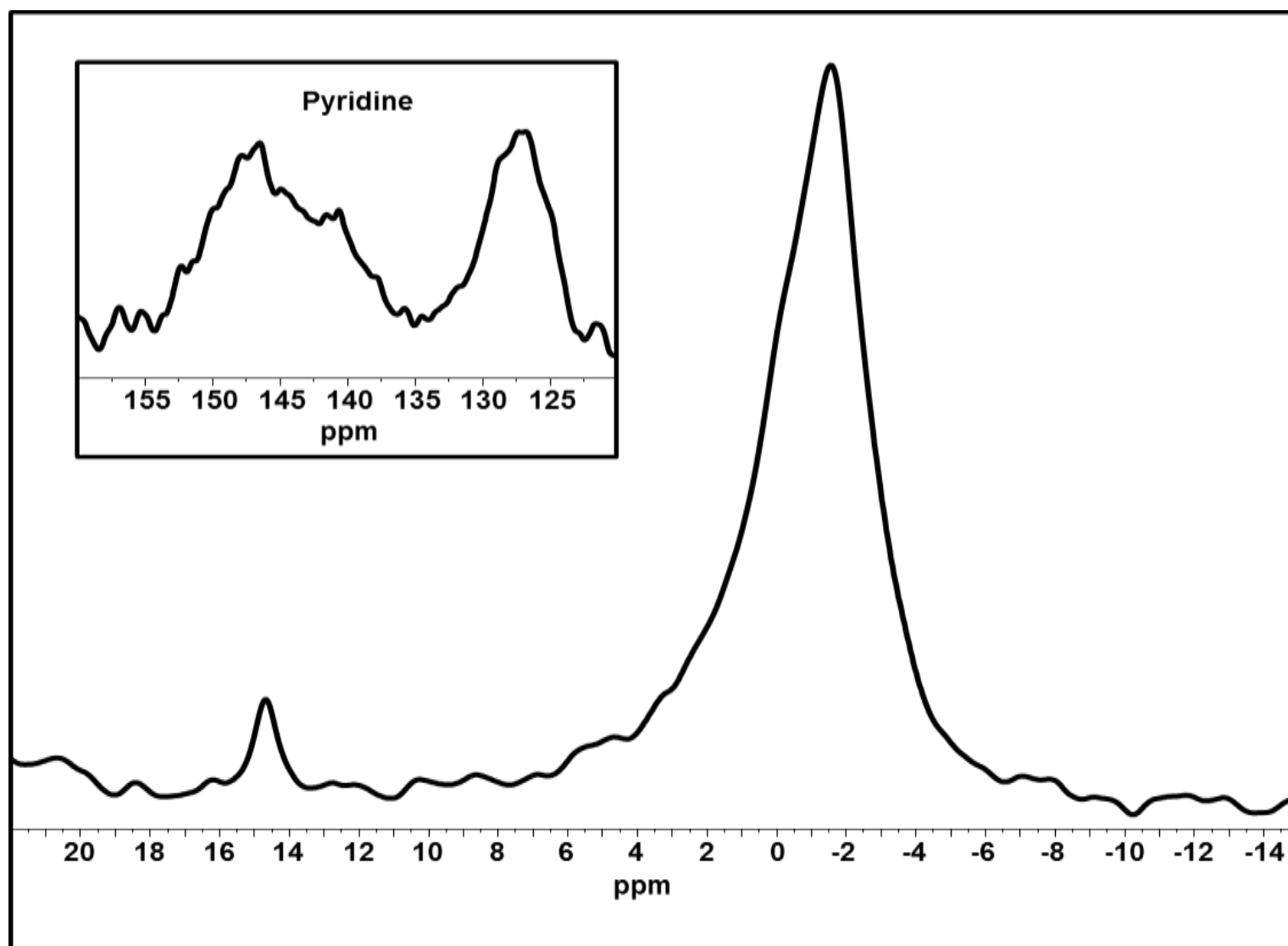


Figure 2.27: ^{13}C CPMAS NMR spectrum of embedded 1-dose Al-Py sample

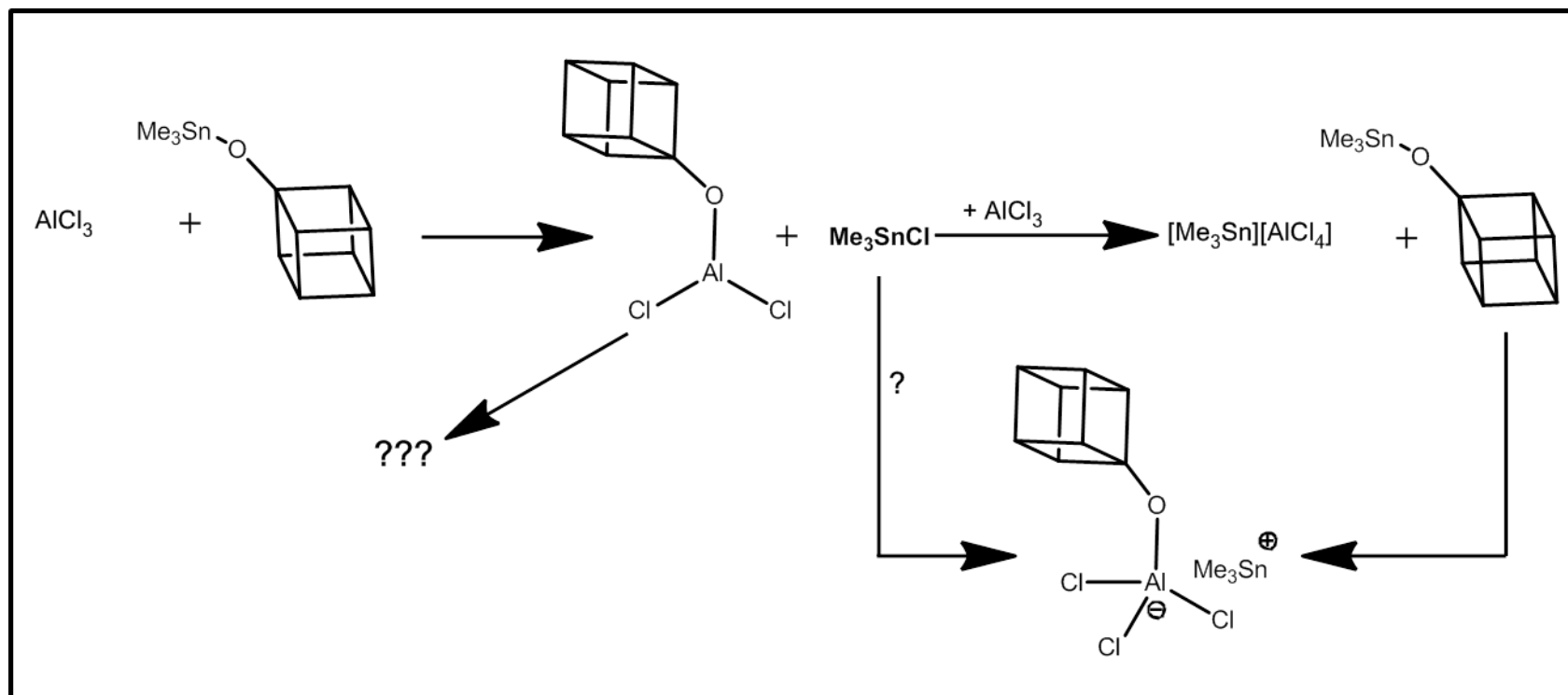


Figure 2.28: Possible reaction pathway to form tetrahedral Al centers and the trimethyltin cation

Reaction of $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ and TMT cube (0.5 : 1) was conducted under similar conditions as used for similar reactions (90 °C; 24 hrs; toluene). The volatiles were removed and analyzed by NMR and GC/MS. It was found that this reaction produced both trimethyltin chloride and tetramethyltin (Equation 2.6). Gravimetric results also



showed that more than three, and in this case more than five equivalents of tin were lost as volatile byproducts. Again, the number of equivalents of tin lost was variable.

The ^{27}Al SSNMR again appears to show three primary features (Figure 2.29), with a lineshape more similar to that of the species synthesized from AlCl_3 than that created from $\text{AlCl}_3\cdot\text{Py}$. The farthest downfield shoulder at $\delta = 51$ ppm is significantly reduced, while the strongest feature appears to be at $\delta = 24.5$ ppm in the 5-coordinate Al range. In addition there is a significant amount of octahedral aluminum present based on the feature at $\delta = -4$ ppm. The spectrum is different enough from both of the systems described above and does not allow us to easily connect the Al sites from the $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ product to those derived from AlCl_3 or $\text{AlCl}_3\cdot\text{Py}$.

The ^{13}C spectrum again shows a similar downfield shoulder (Figure 2.30) to that seen in the reaction of the tin cube with the AlCl_3 precursor. This downfield shoulder is thought to correspond to the methyl groups on the charged $-\text{OSnMe}_2^+$ species. The ^{29}Si spectrum (Figure 2.31) for this sample shows three resonances. The first at -102.7 ppm is once again assigned to unreacted $\text{Si}-\text{OSnMe}_3$ groups, while that at -106.4 is assigned to silicon centers bound to aluminum ($\text{O}_3\text{Si}-\text{OAl}$). The new feature at -112.4 has not been seen before, and is tentatively assigned to the silicon centers bound to the proposed $-\text{OSnMe}_2^+$ groups (vide infra).

The presence of a new signal in the ^{29}Si NMR in addition to the second signal seen in the ^{13}C spectrum, gave reason to believe that a second feature might finally be observed in the ^{119}Sn spectrum (Figure 2.32). However, as in all previous spectra, no second signal was observed.

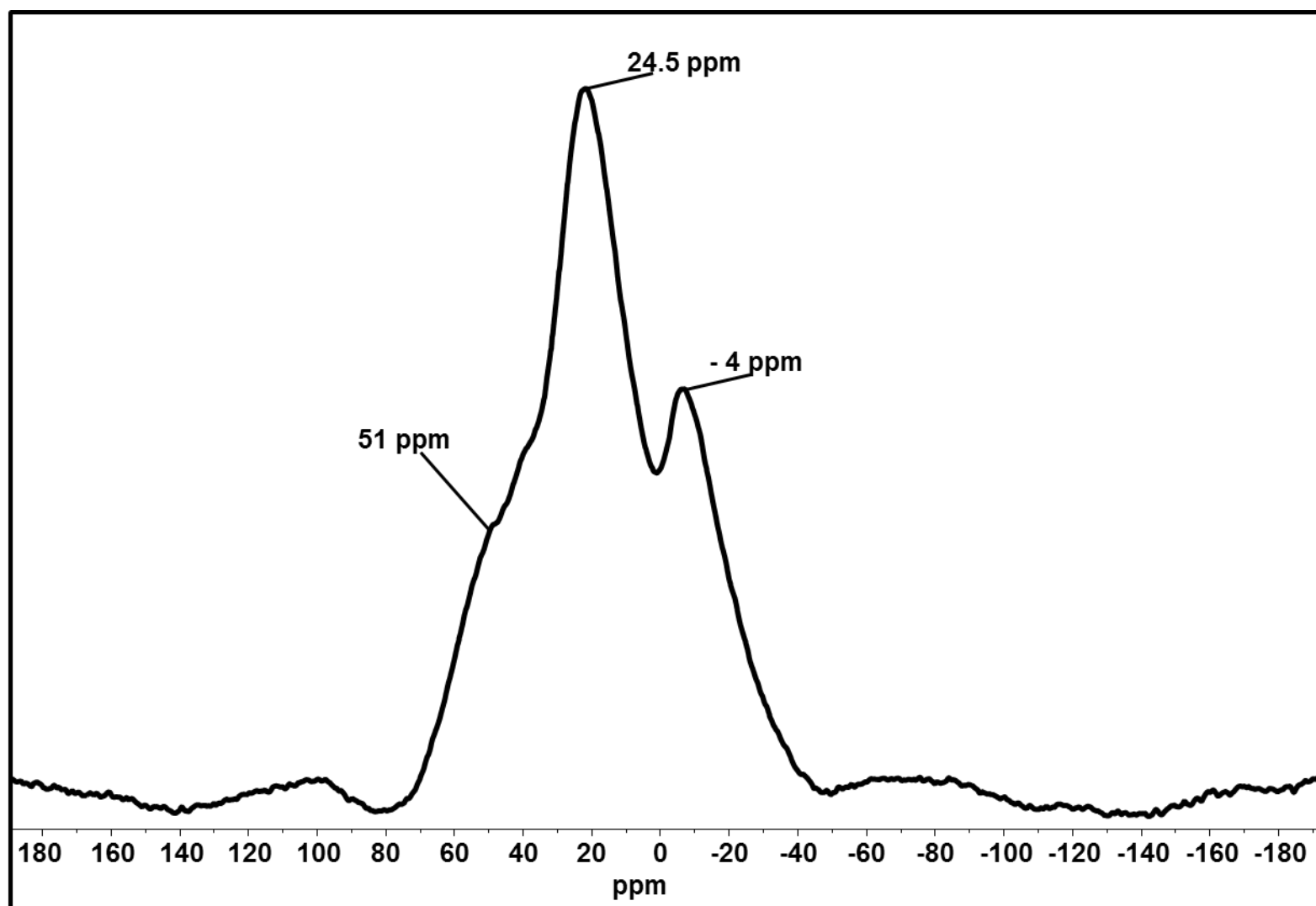


Figure 2.29: ^{27}Al MAS NMR spectrum of 1-dose $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ sample

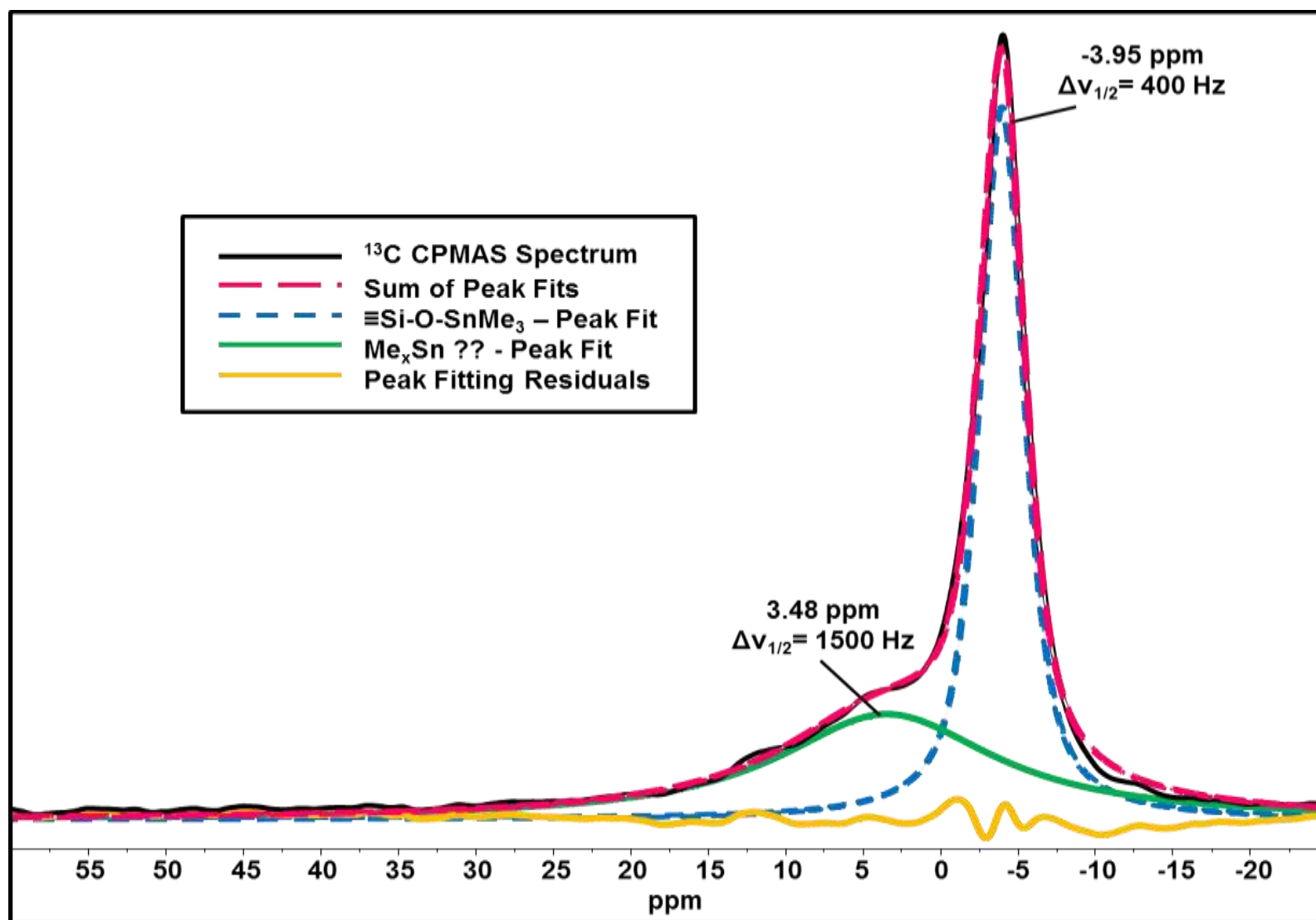


Figure 2.30: ^{13}C CPMAS NMR spectrum of 1-dose $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ sample with deconvolution of peaks

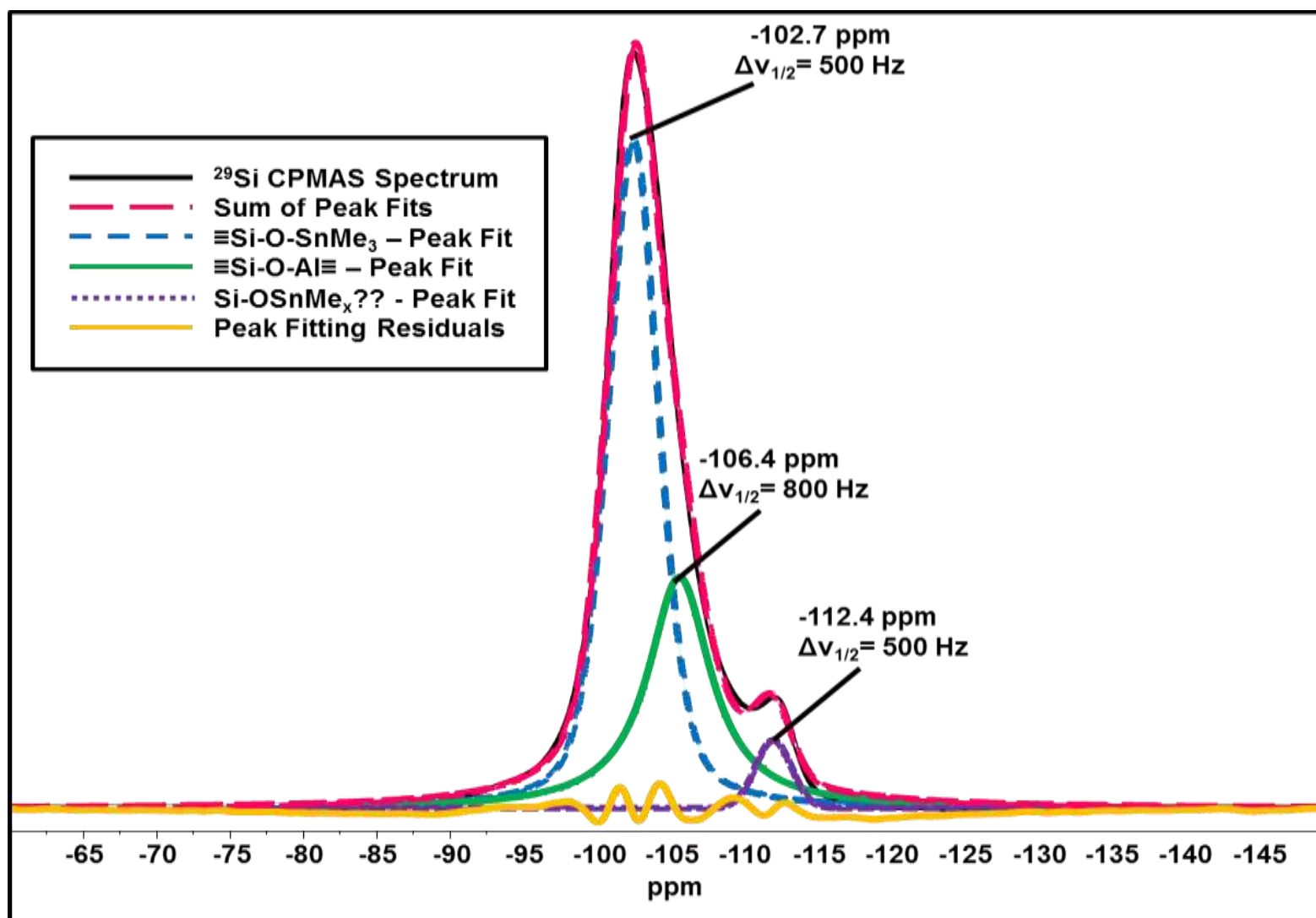


Figure 2.31: ^{29}Si CPMAS NMR spectrum of 1-dose $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ sample with deconvolution of peaks

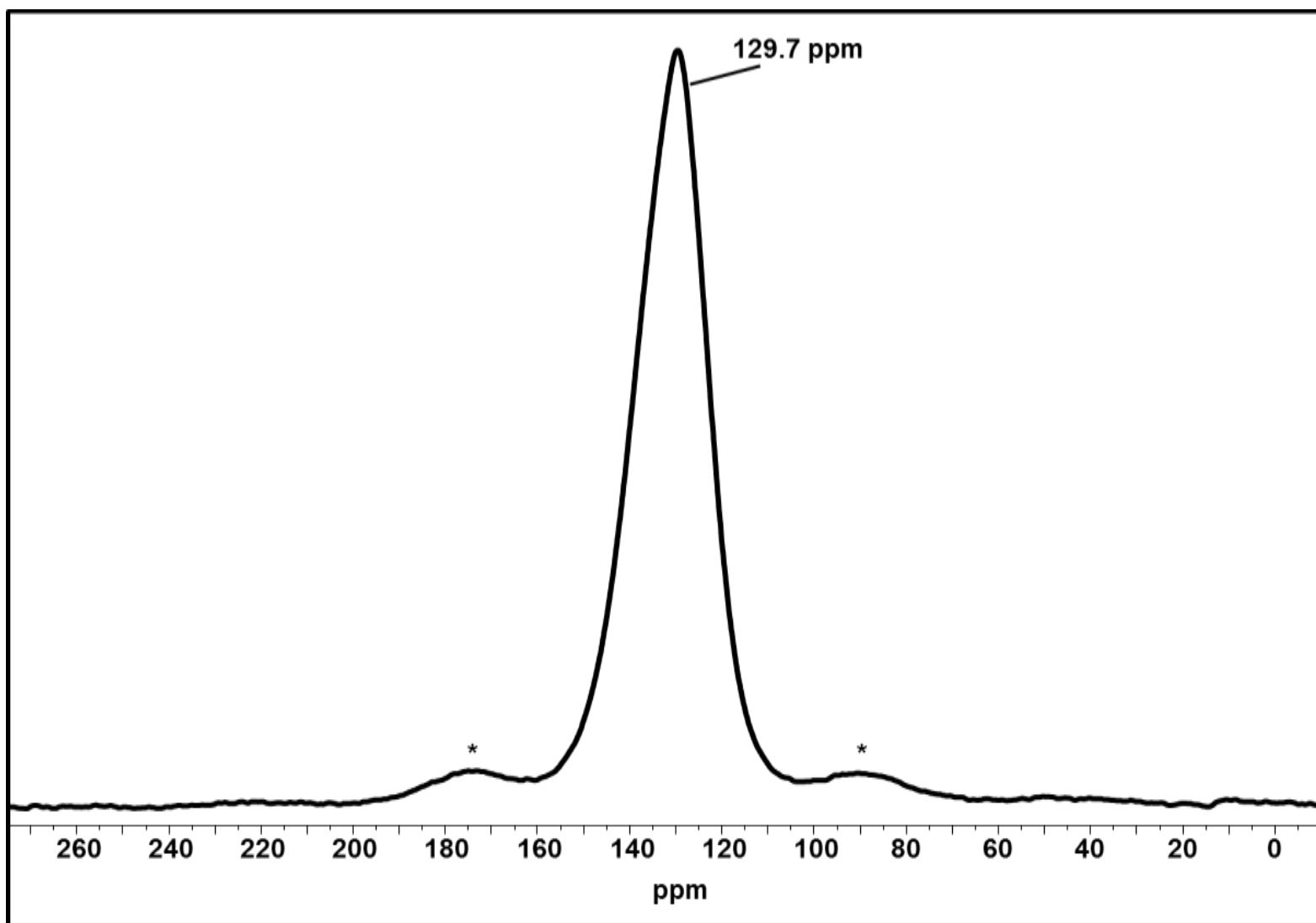


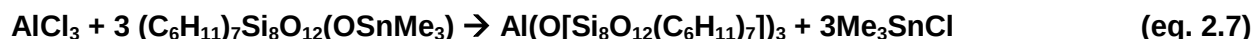
Figure 2.32: ^{119}Sn MAS (6 KHz) NMR spectrum of 1-dose $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ sample
(* = spinning side bands)

2.3.4 POSS Molecular Analogues of One Dose Embedded Aluminum Catalysts

In order to better understand the nature of the reactions occurring between the trimethyltin cube and aluminum chloride, it was determined that trying to synthesize polyhedral oligomeric silsesquioxane (POSS) molecular analogues could be helpful for a number of reasons. As previously stated, the POSS species of interest are of the general formula $R_7Si_8O_{12}(OSnMe_3)$ (Figure 2.04c). By creating soluble analogues, solution NMR would become a viable characterization technique. In addition, the possibility of isolating single crystals of the reaction products arises.

Cubic POSS precursors with three different R groups (ⁱBu, Ph, cyH) were prepared and initially tested for reaction with aluminum trichloride. These reactions were carried out in toluene with a slight excess of POSS ($\geq 3 : 1$, POSS : $AlCl_3$). In all cases, the reaction produced **only** trimethyltin chloride. However, with all three species, reactions did not proceed to completion. Gravimetric analysis showed that in no instance were the full three equivalents of trimethyltin chloride produced. The degree of reaction did appear to vary with the R group on the POSS molecule with total reaction connectivity decreasing in the order of cyH > ⁱBu > Ph.

A typical reaction of aluminum trichloride with cyclohexyl POSS (Equation 2.7)



produced anywhere from 2-2.5 equivalents of Me_3SnCl . The reaction products did remain completely soluble in toluene, and analysis was carried out using solution NMR.

¹H NMR shows clear evidence for the production of trimethyltin chloride (Figure 2.33), and the ²⁹Si NMR shows evidence for the production of Al-O-Si bonds at $\delta = -105.8$ ppm (Figure 2.34). These spectra were collected on a sample in a Young valve NMR tube, at such a small reaction size that exact stoichiometric ratios were difficult to achieve. As a result, there is still a significant amount of the unreacted POSS material seen at $\delta = 0.31$ ppm in the ¹H spectrum and -102.5 ppm in the ²⁹Si spectrum. The ¹H and ²⁹Si spectra also clearly show the distribution of cyclohexyl protons, and the Q³ silicon centers they are bound to. Analysis of the reaction product by ²⁷Al solution NMR interestingly failed to produce a discernible feature that could be associated with the

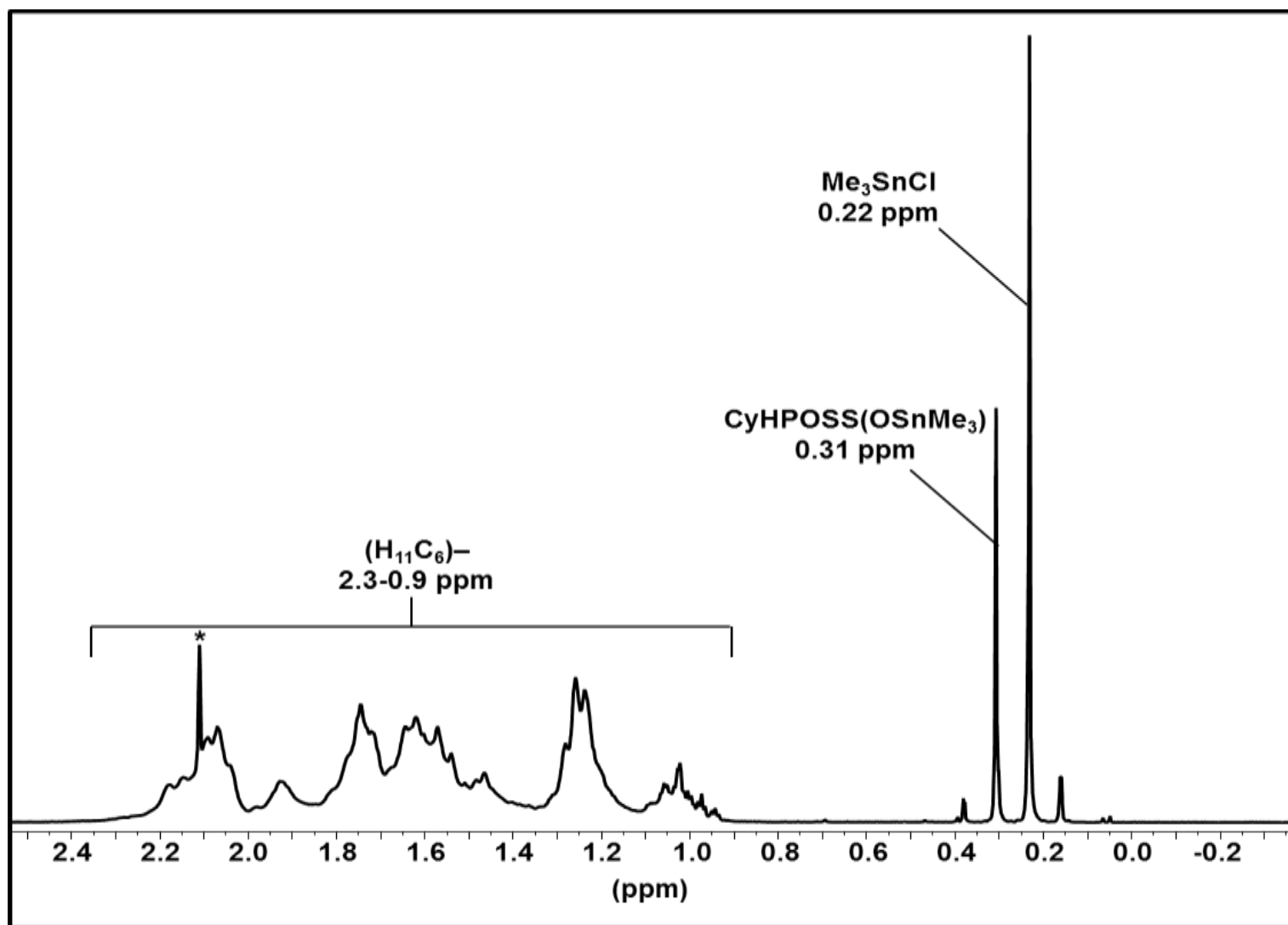


Figure 2.33: ^1H NMR (C_6D_6) spectrum of $\text{AlCl}_3 + \text{CyHPOSS}(\text{TMT})$ reaction product. (* = Toluene)

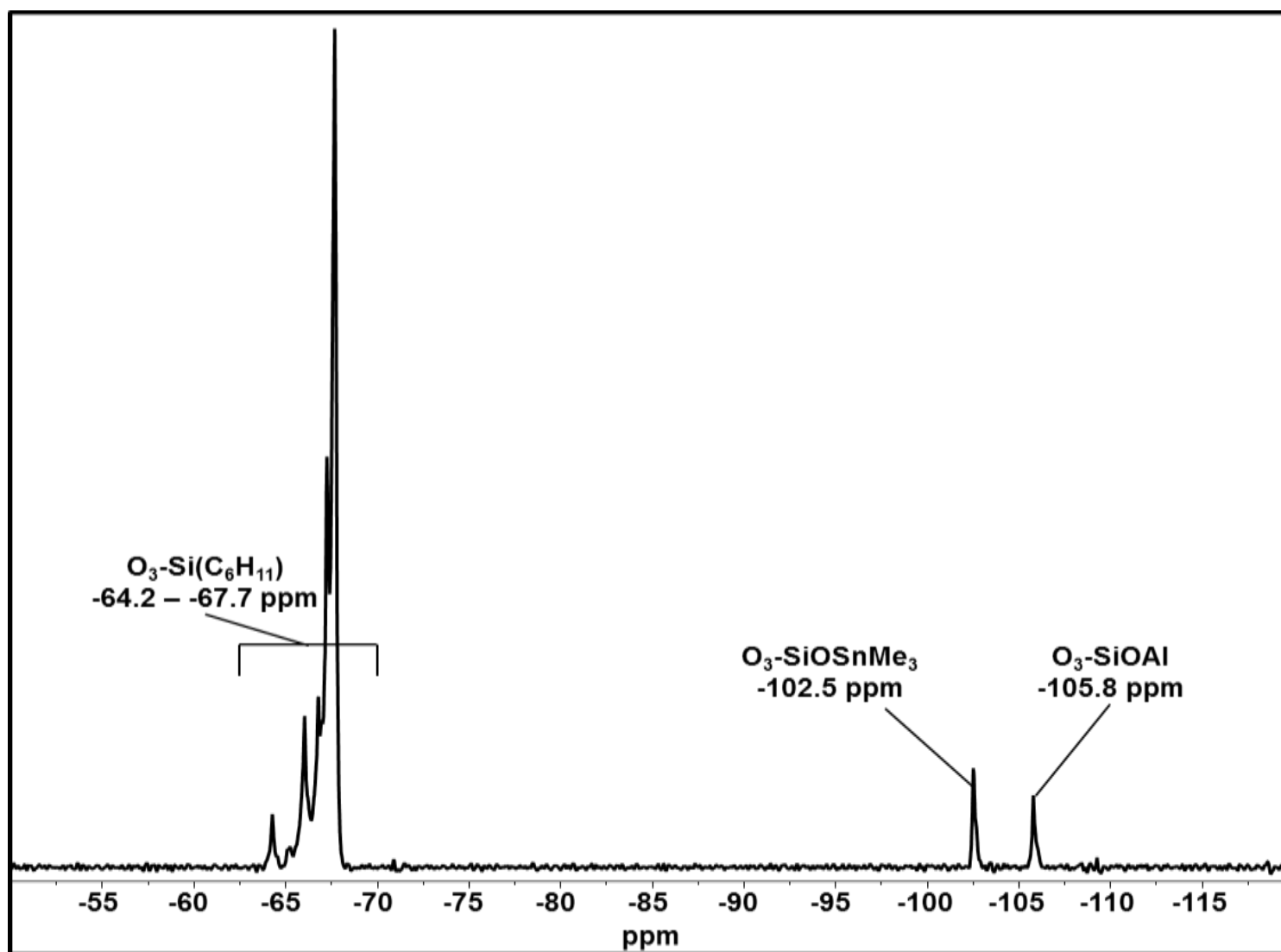


Figure 2.34: ^{29}Si NMR (C_6D_6) spectrum of $\text{AlCl}_3 + \text{CyHPOSS}(\text{TMT})$ reaction product

proposed tetrahedral aluminum center. The reason for this is most likely due to fast quadrupolar relaxation times as a result of low symmetry. The low symmetry of the system likely results in a large quadrupolar coupling constant that allows for very efficient relaxation leading to significant lifetime broadening of the signal.

The same reaction was carried out with $\text{AlCl}_3 \cdot \text{Py}$ (Equation 2.8) and yielded similar results in terms of total connectivity (2-2.5). Again, no tetramethyltin was observed. The ^1H and ^{29}Si solution NMR once again shows signs of reaction with the



production of the Me_3SnCl byproduct (Figure 2.35) and the formation of Al-O-Si bonds (Figure 2.36). Similar to the experiment starting from AlCl_3 , no signal was discernible in the ^{27}Al NMR spectrum.

The IR spectrum (Figure 2.37) of the product clearly showed two spectroscopic bands associated with Lewis acid bound pyridine ($1495, 1620 \text{ cm}^{-1}$) though the band generally seen at 1445 cm^{-1} is obscured by features inherent to the $\text{cyHPOSS}(\text{OSnMe}_3)$ species ($1462, 1448 \text{ cm}^{-1}$). Despite this, the presence of two of the three characteristic Lewis acid bands is enough to indicate that the nature of the aluminum center had not changed upon reaction.

These results indicate that the POSS systems behave differently than the trimethyltin cube with regards to reaction with AlCl_3 as there is no production of tetramethyltin. The primary reasons could have to do with steric or electronic differences between the two cubic building blocks. The cyclohexyl groups are bulkier than the trimethyltin groups, and the RSiO_3 corner silicons possess more electron density than the $(\text{Me}_3\text{SnO})\text{SiO}_3$ corners on the tin cube. Despite this, the possibility also exists that having a second adjacent $-\text{OSnMe}_3$ on the same cube plays a role in the formation of tetramethyltin.

2.3.5 One Dose Reactions with $[\text{Me}_3\text{Sn}][\text{SO}_3\text{CF}_3]$ and $[\text{nBu}_4\text{N}][\text{AlCl}_4]$

The results of the reactions above indicate that the formation of tetramethyltin in the reaction of AlCl_3 and TMT cube is a result of the formation of and subsequent reaction of the $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$. It made sense then to separate the constituent ions of

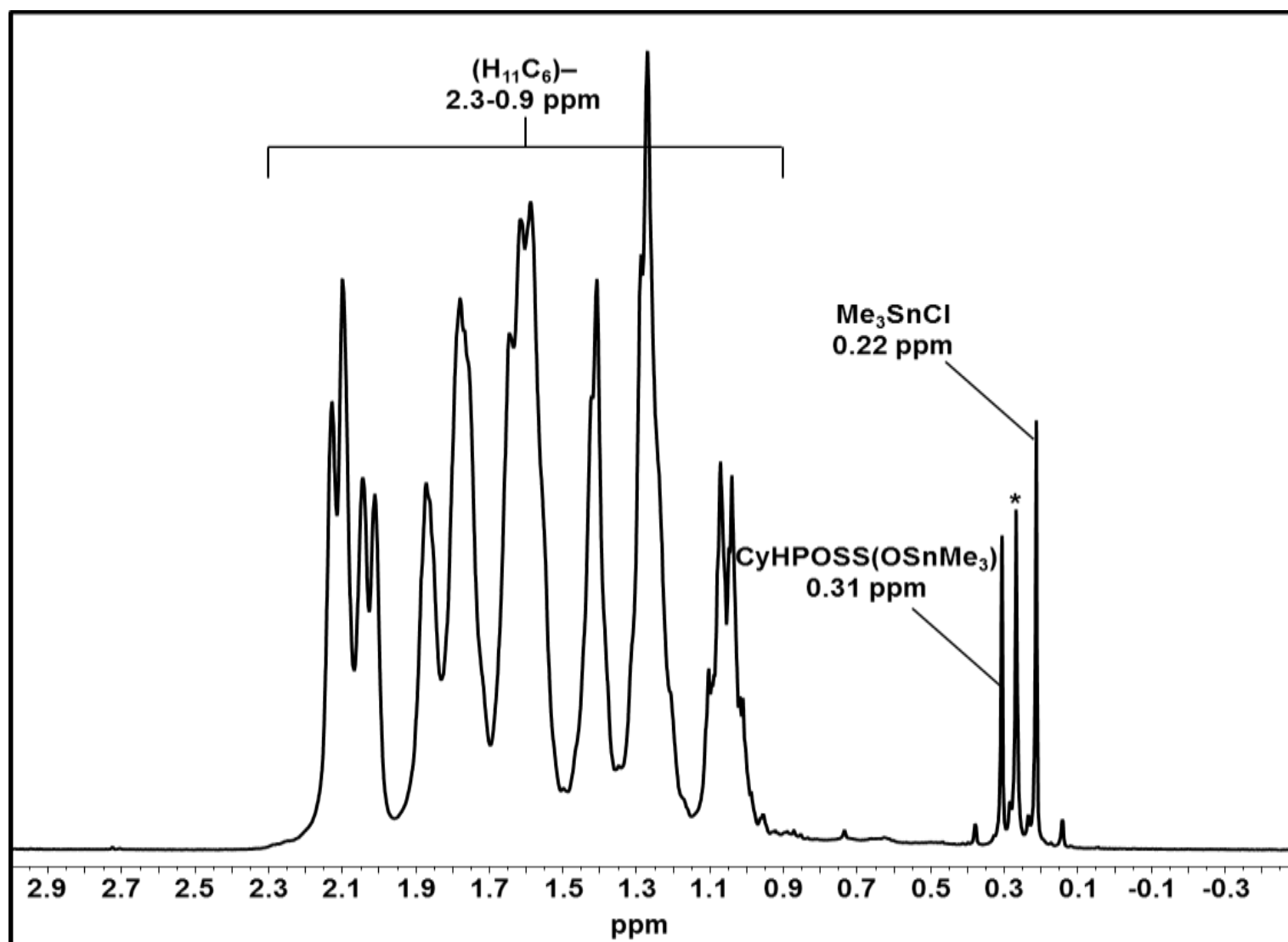


Figure 2.35: ^1H NMR (C_6D_6) spectrum of $\text{AlCl}_3\cdot\text{Py}$ + $\text{CyHPOSS}(\text{TMT})$ reaction product (* = silicon grease)

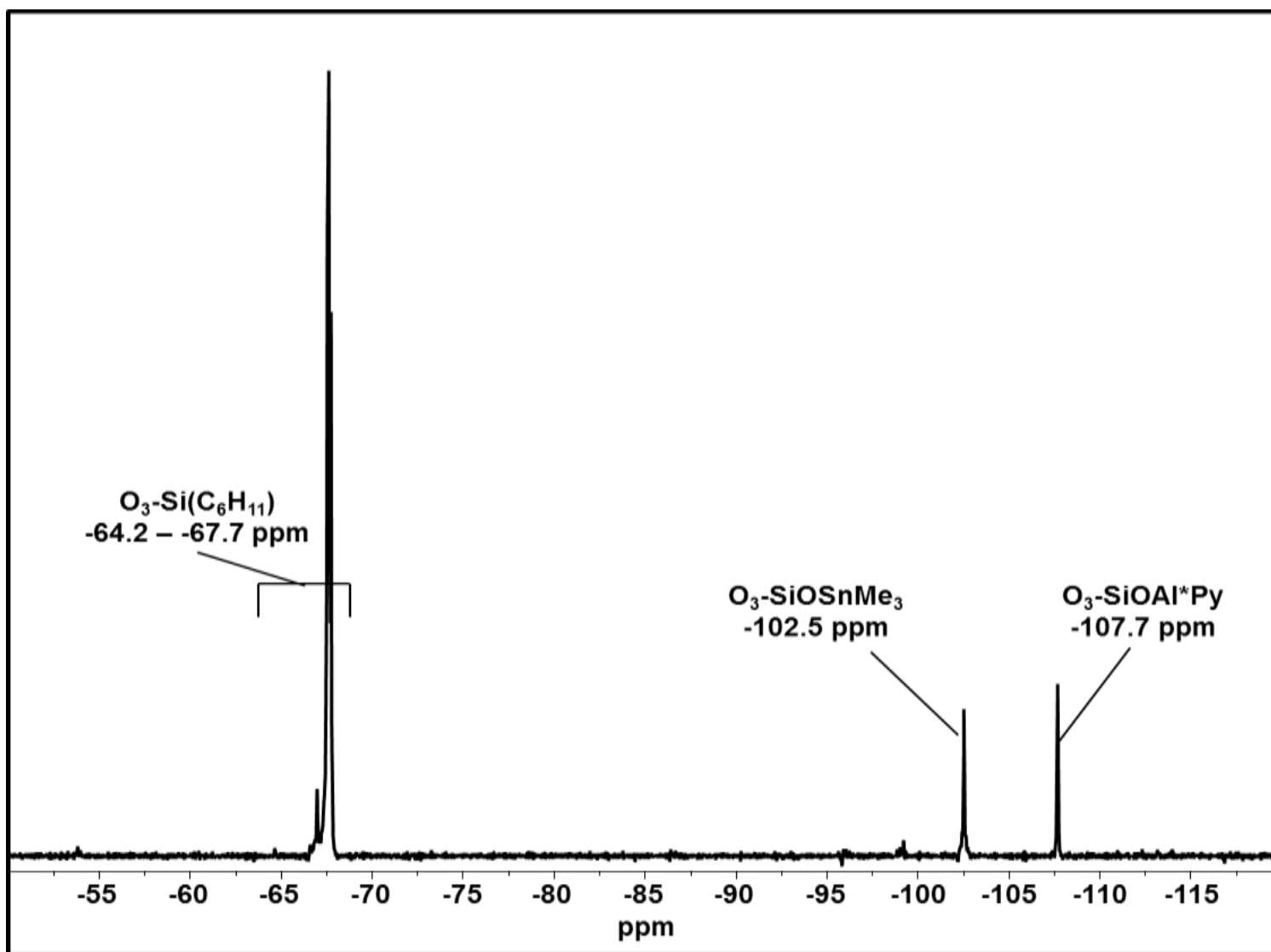


Figure 2.36: ^{29}Si MAS NMR spectrum of $\text{AlCl}_3\cdot\text{Py}$ + CyHPOSS(TMT) reaction product

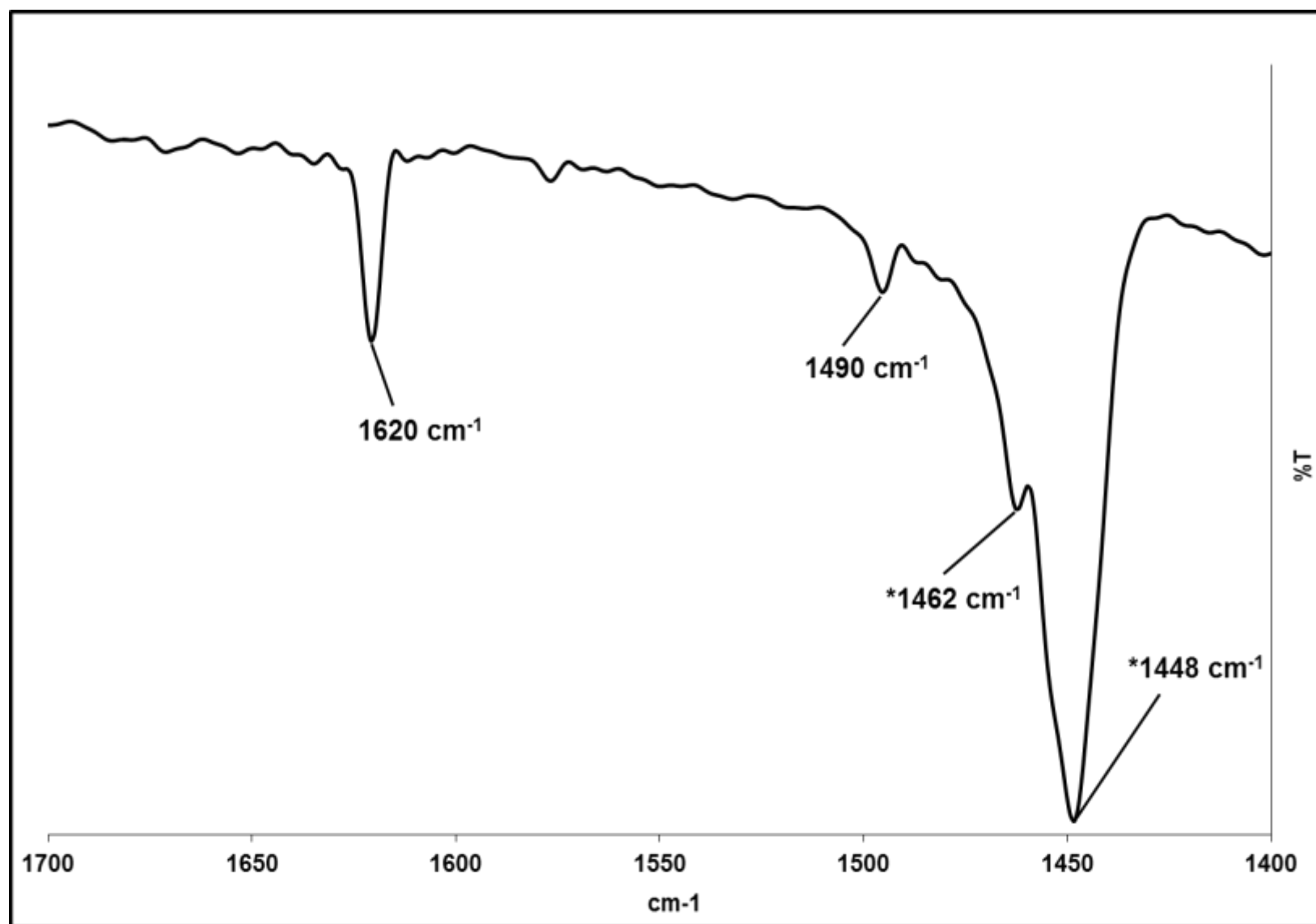


Figure 2.37: IR spectrum of $\text{AlCl}_3 \cdot \text{Py}$ + CyHPOSS(TMT) reaction product (*= cyHPOSS bands)

this ion paired species to look at their individual reactivity. To do this, trimethyltin triflate ($[\text{Me}_3\text{Sn}][\text{SO}_3\text{CF}_3]$; $[\text{Me}_3\text{Sn}][\text{Tf}]$) and n-butyl ammonium tetrachloroaluminate ($[\text{nBu}_4\text{N}][\text{AlCl}_4]$) were synthesized and reacted with trimethyltin building block. In this way, a determination could be made of whether the Me_3Sn^+ cation or the AlCl_4^- anion was causing the formation of tetramethyltin. Reactions were carried out between each of the two precursors and both trimethyltin cube and cyHPOSS(TMT).

The reaction of trimethyltin triflate with trimethyltin cube clearly showed evidence for the formation of tetramethyltin (Equation 2.9). The reaction was carried out in



methylene chloride due to the more favorable solubility properties of the $[\text{Me}_3\text{Sn}][\text{Tf}]$ species. The reactants were combined at a ratio of 1.5 : 1; $[\text{Me}_3\text{Sn}][\text{Tf}]$: cube. During the reaction there was no phase separation. Removal of the volatiles and gravimetric analysis of the reaction showed that 1 eq of Me_4Sn was produced (per mole equivalent of the triflate salt). As equation 2.9 shows, in order for the tetramethyltin to form, a methyl group must be removed from a corner $-\text{OSnMe}_3$ species on the cube leaving behind a $-\text{OSnMe}_2^+$ charged center.

SSNMR of the product after removal of all volatiles was very interesting. Figure 2.38 shows the ^{13}C MAS spectrum, and there two clear features in the methyl region that are not completely resolved. Deconvolution and peak fitting yields chemical shifts at $\delta = 3.48$ and -1.95 ppm. The latter resonance is assigned to the unreacted trimethyltin groups on the building block cube, while peak at 3.48 ppm is assigned to the $[-\text{SiOSnMe}_2][\text{Tf}]$ center that results from the formation of tetramethyltin. The location of this feature is in agreement with the second methyl feature observed in a number of the previously discussed samples. The sharpness of the peak is likely due to the more molecular nature of the species here where no cross linking of building blocks has occurred. The ^{29}Si CPMAS NMR spectrum (Figure 2.39) is in agreement with the ^{13}C spectrum showing two features representative of the unreacted trimethyltin groups, and the new feature assigned as $[-\text{SiOSnMe}_2][\text{Tf}]$. This second feature comes at $\delta = -111$ ppm in a very similar location to the third silicon feature seen in the reaction of TMT

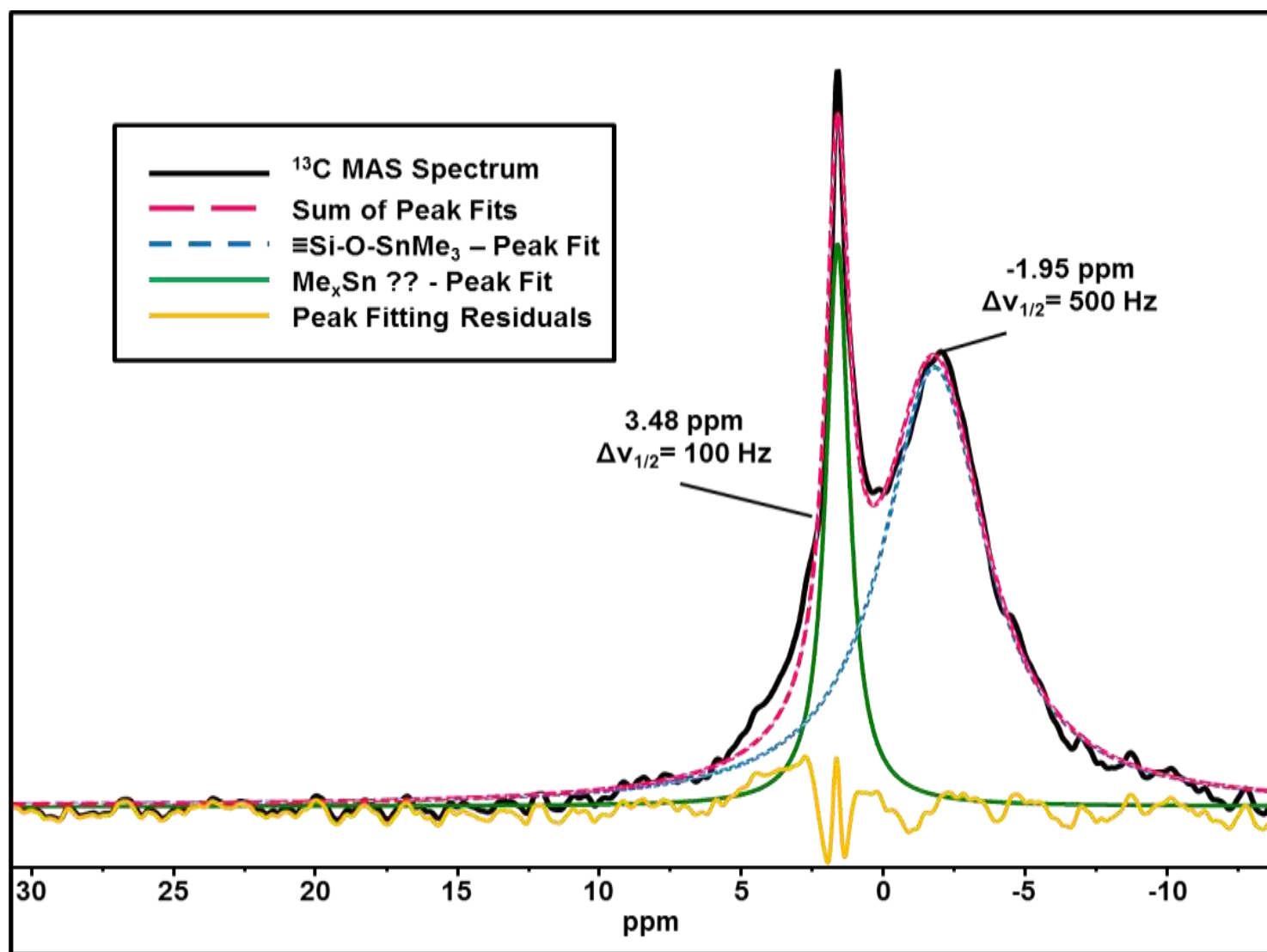


Figure 2.38: ^{13}C MAS SSNMR showing product from $[\text{Me}_3\text{Sn}][\text{Tf}]$ reaction with tin cube

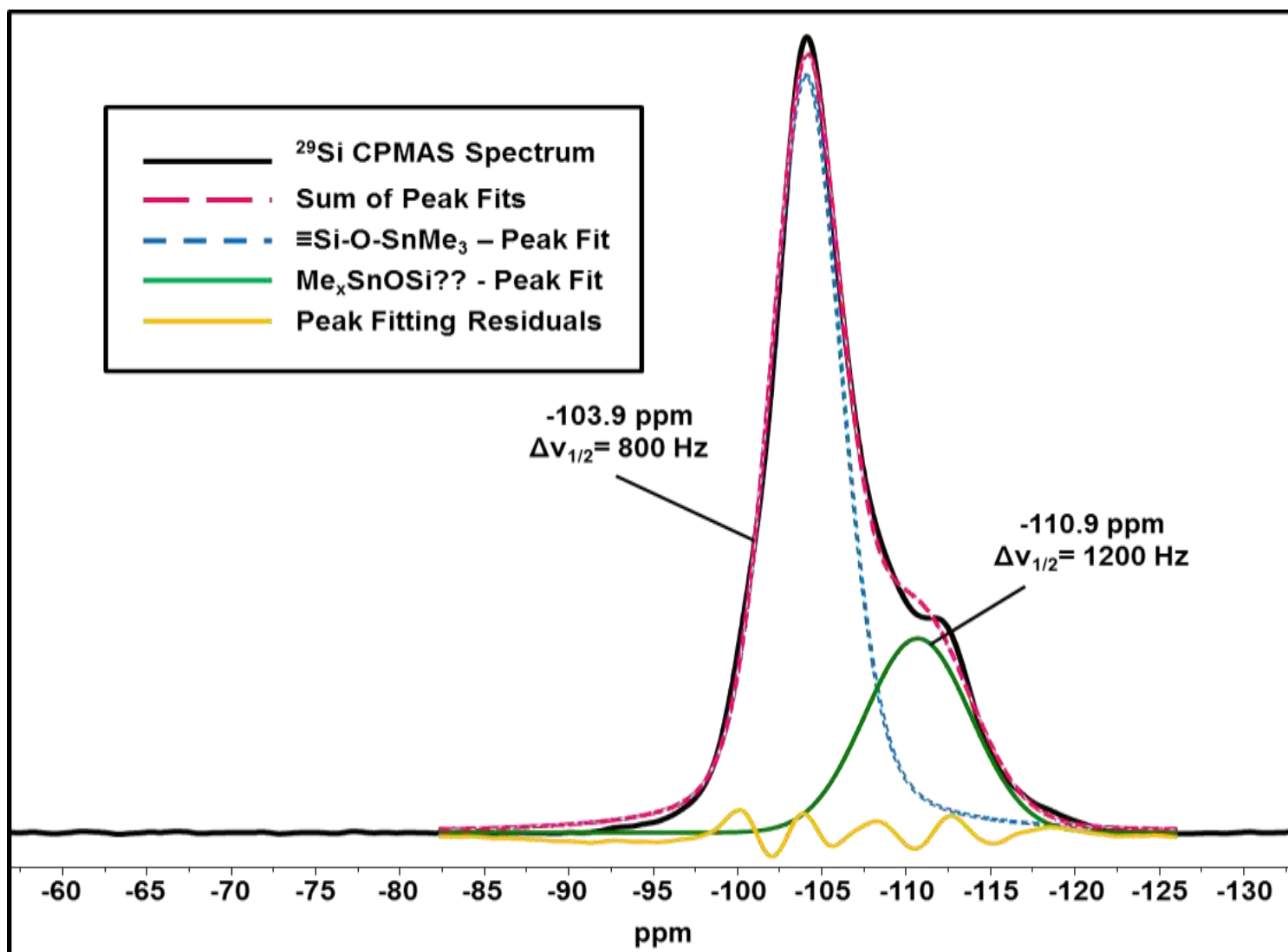


Figure 2.39: ^{29}Si CPMAS SSNMR showing product from $[\text{Me}_3\text{Sn}][\text{Tf}]$ reaction with Tin cube

cube with $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ (Figure 2.31). Even in this sample, with strong evidence for a second tin species, a second signal was not observed within a 3000 ppm window for the ^{119}Sn NMR (Figure 2.40).

Having seen no formation of tetramethyltin in the reaction of AlCl_3 with $\text{CyHPOSS}(\text{TMT})$, there was some question as to whether the formation of tetramethyltin could be expected from the reaction of the trimethyltin triflate species and $\text{CyHPOSS}(\text{TMT})$. The reaction was carried out in methylene chloride in a Young NMR tube, and it was quickly apparent that, just as in the case of the trimethyltin cube, tetramethyltin was formed. This result seems to contradict the previous reaction of the POSS with AlCl_3 . These opposing outcomes might be justified by surface reaction effects of the building blocks with the insoluble AlCl_3 starting material. It is likely that the initial reactions of the building blocks occur at the surface of the insoluble AlCl_3 material. In the case of the tin cube, this brings a number of other reactive Me_3Sn - groups into close proximity of the surface. When the side reaction of the Me_3SnCl byproduct with the aluminum chloride surface forms the $[\text{Me}_3\text{Sn}]^+$ species then these other tin groups are close enough to quickly react. In the case of the POSS analogues, there is only one reactive tin species on each cube, and a number of sterically hindering R groups to prevent other reactive tin groups from getting close to the same spot on the surface. This would prevent the $[\text{Me}_3\text{Sn}]^+$ cations from easy access to reactive trimethyltin centers.

In a similar fashion, the butylammonium tetrachloroaluminate precursor was reacted with the tin cube in both toluene and methylene chloride solutions. Analysis of the volatile byproducts showed only the presence of Me_3SnCl , with no evidence of Me_4Sn . As a result, the reaction is proposed to proceed according to Equation 2.10.



Gravimetric analysis showed that the reaction did not proceed to completion achieving connectivity on the order of 3.0-3.5 for the aluminum centers.

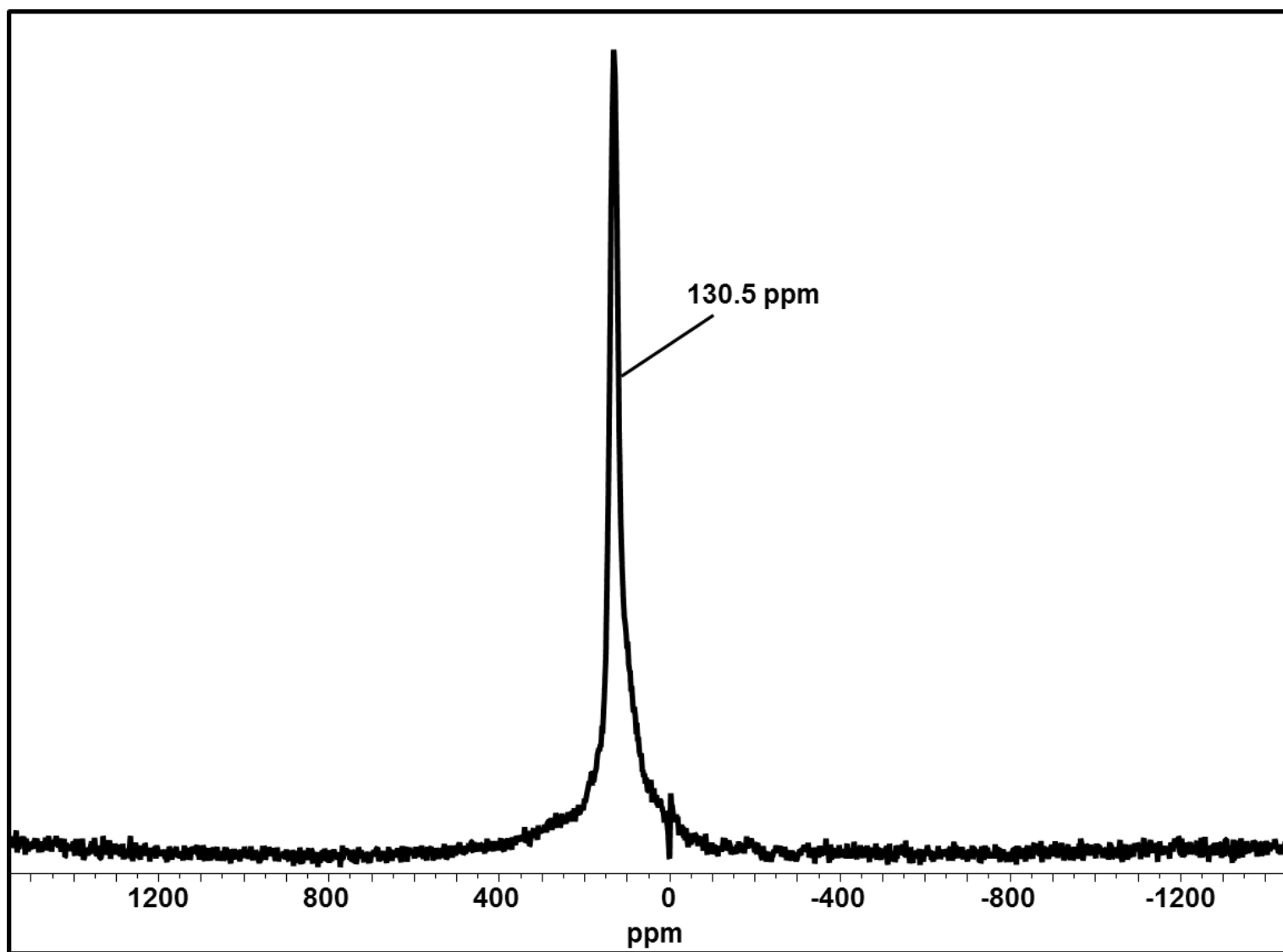


Figure 2.40: ^{119}Sn SSNMR showing product from $[\text{Me}_3\text{Sn}][\text{Tf}]$ rxn with Tin cube

This reaction coupled with the previous reaction clearly shows that the source of the tetramethyltin is methyl scavenging of the trimethyltin cation, $[\text{Me}_3\text{Sn}]^+$. While the reaction of the n-butylammonium tetrachloroaluminate did not proceed to completion to ensure a single type of site in the matrix, such precursors may be an important way forward. It is difficult to tell in this case if the lack of complete reaction is a result of the steric bulkiness of the $[\text{nBu}_4\text{N}]^+$ cation, or electronics that result in reduced activity of the aluminum center once most of the chlorides have reacted.

2.3.6 Solvent Effects on the Reaction of AlCl_3 and $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$

Most of the reactions discussed to this point were carried out in either toluene or methylene chloride. In both cases, the general outcome was the production of significant amounts of both trimethyltin chloride and tetramethyltin. Experiments were also conducted in THF and diethyl ether solutions. In each case, there was a drastic reduction in the amount of tetramethyltin produced. Whereas reactions in CH_2Cl_2 or toluene could produce $\text{Me}_4\text{Sn} : \text{Me}_3\text{SnCl}$ of greater than 1 : 1, the diethyl ether and THF reactions yielded ratios of ~1 : 9.

Early in the investigations when knowledge of the formation of tetramethyltin first came to light, a survey of other solvents was conducted. These other solvents included diethyl ether and THF. These early tests showed the formation tetramethyltin as well, though the amounts were not quantified at the time. There were also concerns that these coordinating solvents would cause aluminum to disproportionate into species of the formula $[\text{L}_2\text{AlCl}_2][\text{AlCl}_4]$ (L = solvent). According to the literature this is known to occur with THF though there is a some debate, as both the $\text{AlCl}_3 \cdot (\text{THF})_2$ ¹¹³ and $[\text{AlCl}_2 \cdot (\text{THF})_4][\text{AlCl}_4]$ species have been identified.¹¹⁴ What might be taken from this is evidence for the existence of multiple species present in solution. In such a case, the whole idea of creating single site catalysts would be immediately jeopardized. However, in ether solution, there has been no conclusive evidence for formation of such compounds, though solutions of AlCl_3 in ether do show measureable conductance that is indicative of the formation of ionic species.¹¹⁵

1-dose reactions of AlCl_3 with the trimethyltin cube were repeated in both THF and diethyl ether, and then analyzed by IR and SSNMR. In the reaction carried out in

ether, the starting materials dissolved, and the system was heated at 35°C. After ~ 1 hour, phase separation of a flocculent fine white precipitate was observed. The reaction was allowed to continue for 24 hrs before the removal of volatiles. Gravimetric analysis showed the loss of 2.4 equivalents of tin in the aforementioned ratio of 9 :1 Me₃SnCl : Me₄Sn. The lower connectivity is likely due to the relatively fast phase separation making it more difficult for the partially crosslinked aluminum centers to fully react. The IR spectrum of the product (Figure 2.41) shows a fairly clean –OH region. The ²⁷Al spectrum (Figure 2.42) of the sample is relatively clean, showing a dominant tetrahedral feature at δ = 50ppm, with a small amount of octrahedral aluminum around δ = -2 ppm. The IR and ¹³C SSNMR (Figure 2.43) spectra show little evidence for diethyl ether bound to the Al centers. However, a final test where the dried product (100°C, overnight) was resuspended in benzene-*d*₆ and exposed to pyridine showed strong evidence for the presence of ether. Figure 2.44 shows an overlay of the ¹H spectrum of the suspended solid. Before pyridine addition, there is a small trace of ether, but addition of pyridine appears to displace significantly more ether from the aluminum centers. This is clear evidence of ether bound to the aluminum centers during and after synthesis.

The same reaction was carried out in THF at 60 °C for 24 hrs. This reaction differed from the reaction carried out in ether in that no phase separation was observed over the course of the reaction. Upon removal of the volatile components, gravimetric analysis showed the loss of 3.2 equivalents of tin again at a 9 :1 Me₃SnCl : Me₄Sn ratio. IR and NMR spectra (Figures 2.45-46) were very similar to those seen in the product of the ether reaction. The ²⁷Al NMR spectrum shows a dominant tetrahedral signal at 50 ppm with a small signal at -1ppm indicative of octahedral Al. While the IR still did not show evidence of THF bound to the aluminum centers, the ¹³C SSNMR spectrum (Figure 2.47) did show weak signals that could be attributed to THF. Resuspension and exposure to pyridine again showed displacement of the coordinating solvent (THF) in the same manner as ether in the previous sample (Figure 2.48). Once again this indicates that THF was likely bound to the Aluminum centers. If it were assumed that one THF molecule was bound to each aluminum center, then it is possible that an

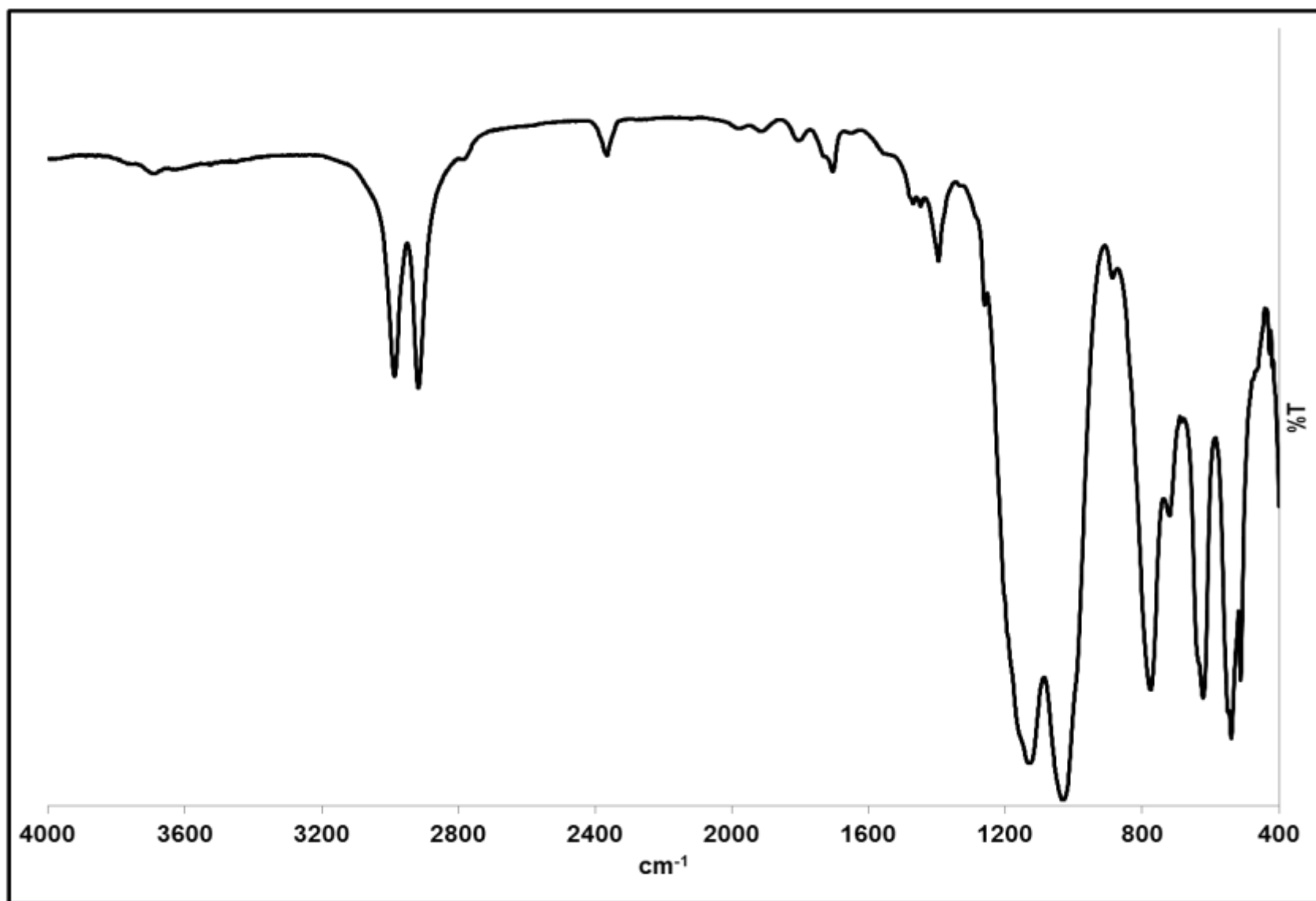


Figure 2.41: IR spectrum of 1-dose Al matrix using AlCl_3 in Et_2O

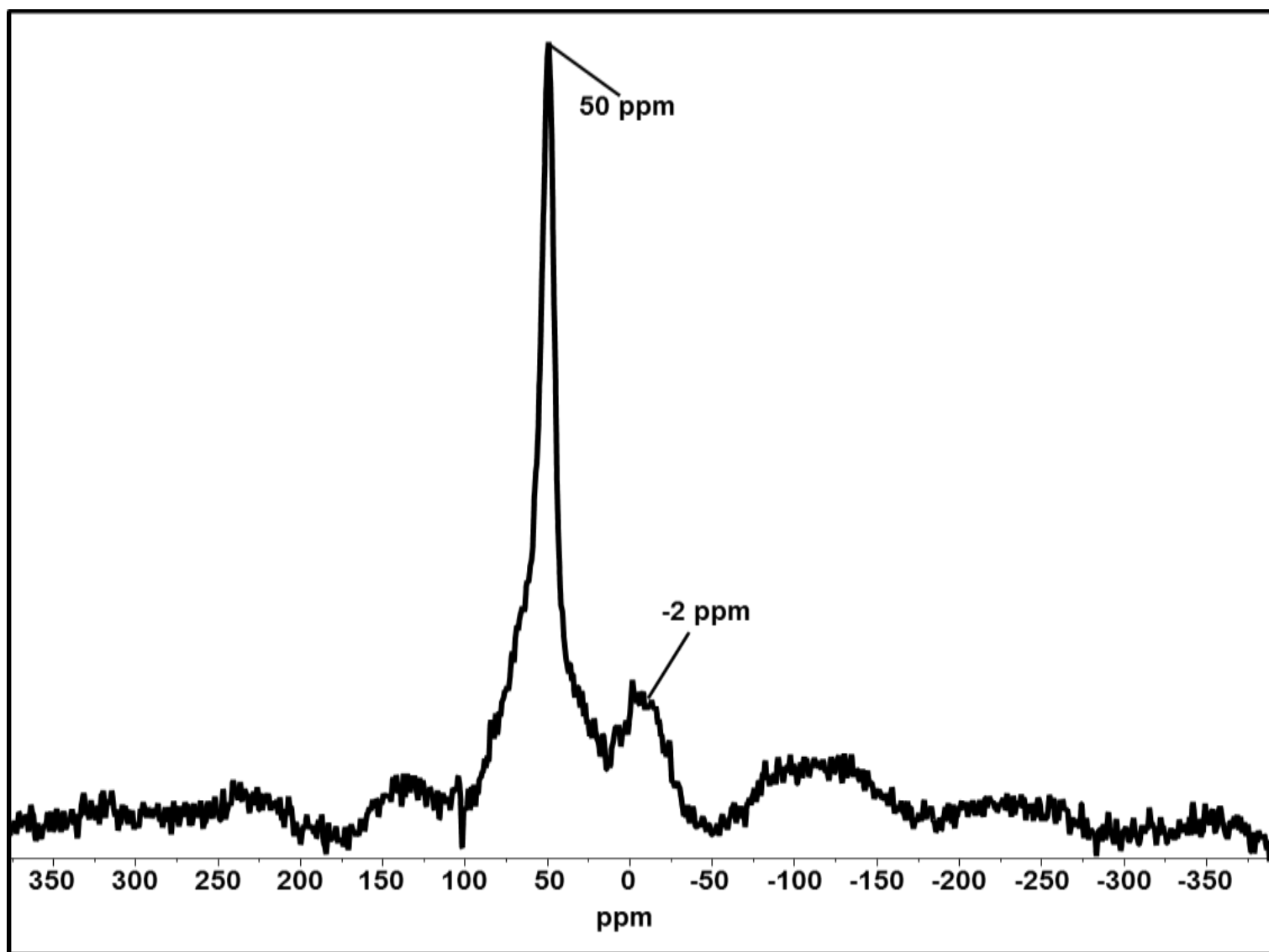


Figure 2.42: ^{27}Al SSNMR spectrum of 1-dose Al sample from AlCl_3 in Et_2O

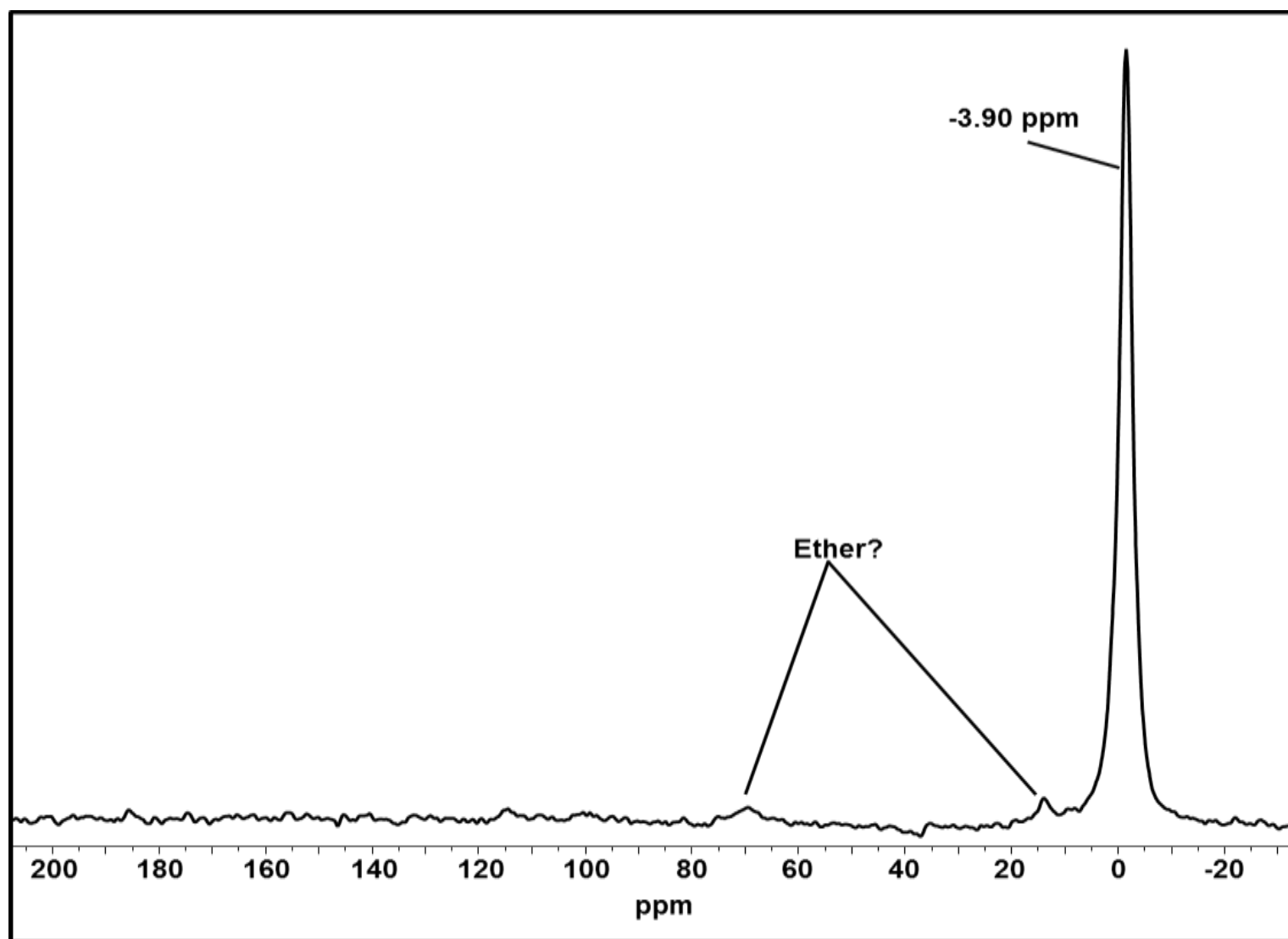


Figure 2.43: ^{13}C CPMAS SSNMR spectrum of 1-dose Al sample from AlCl_3 in Et_2O

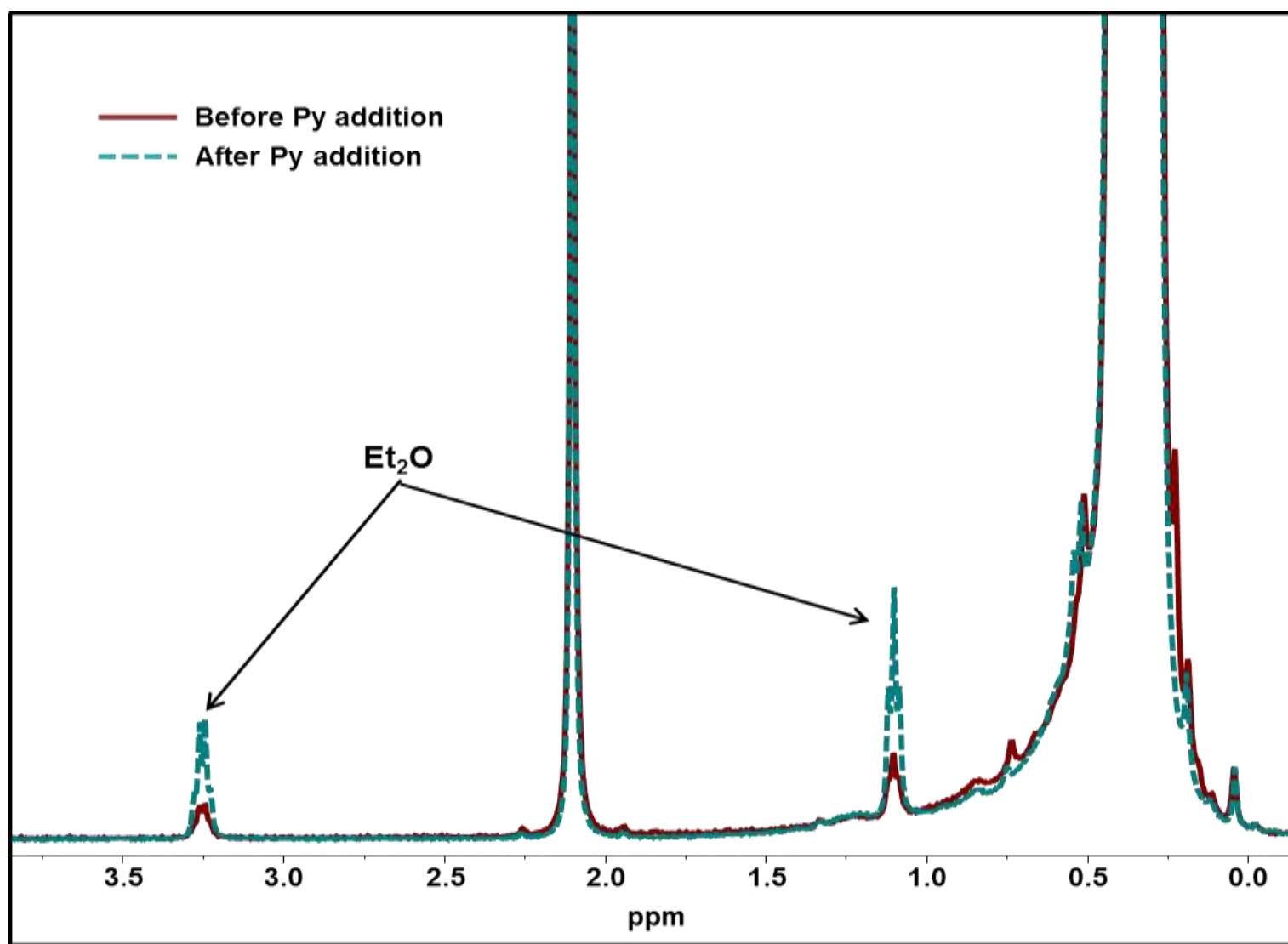


Figure 2.44: Overlay of ^1H NMR spectra of 1-dose Al sample from AlCl_3 in Et_2O dried and suspended in C_6D_6 , before and after pyridine addition

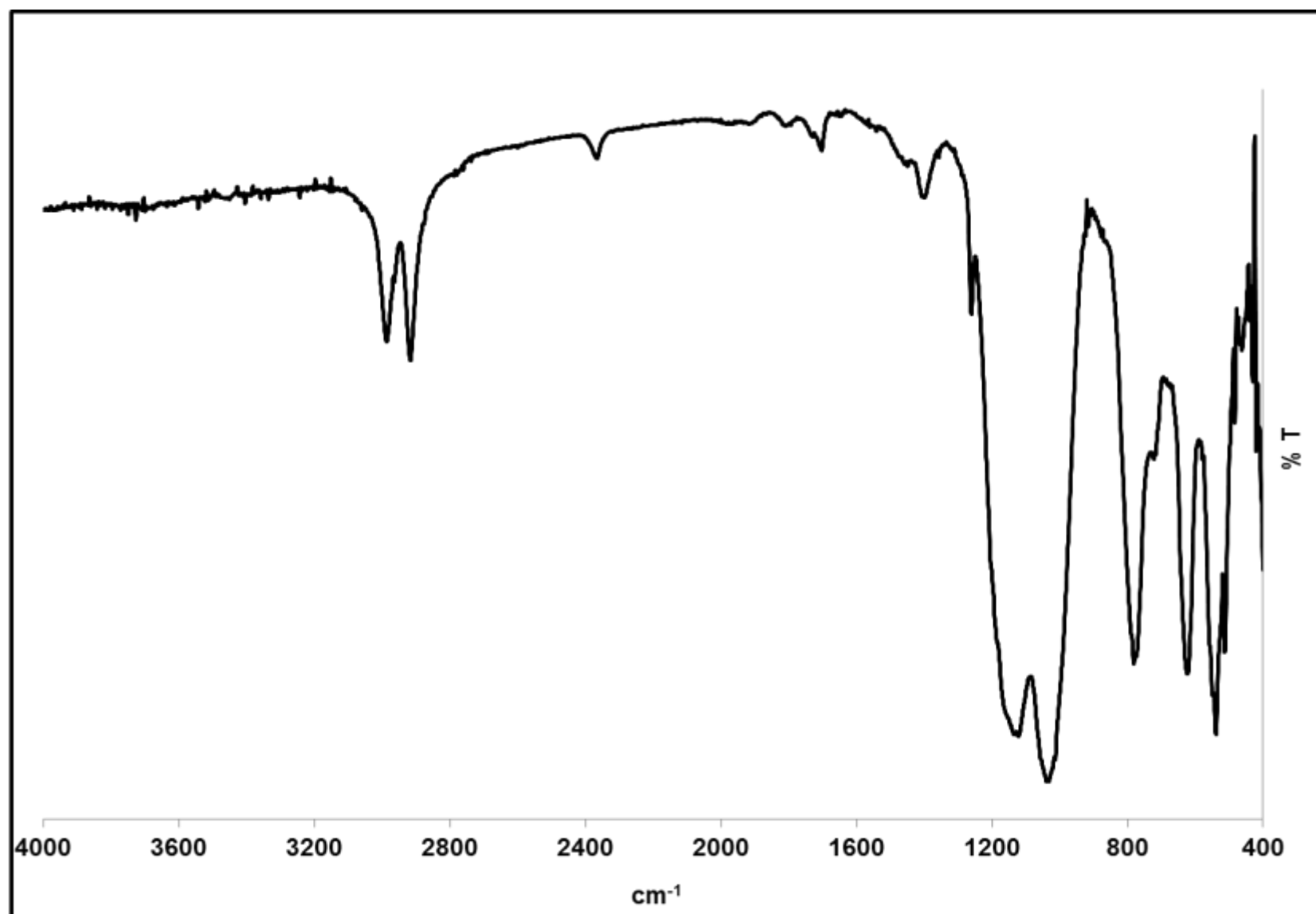


Figure 2.45: IR spectrum 1-dose Al matrix using AlCl_3 in THF

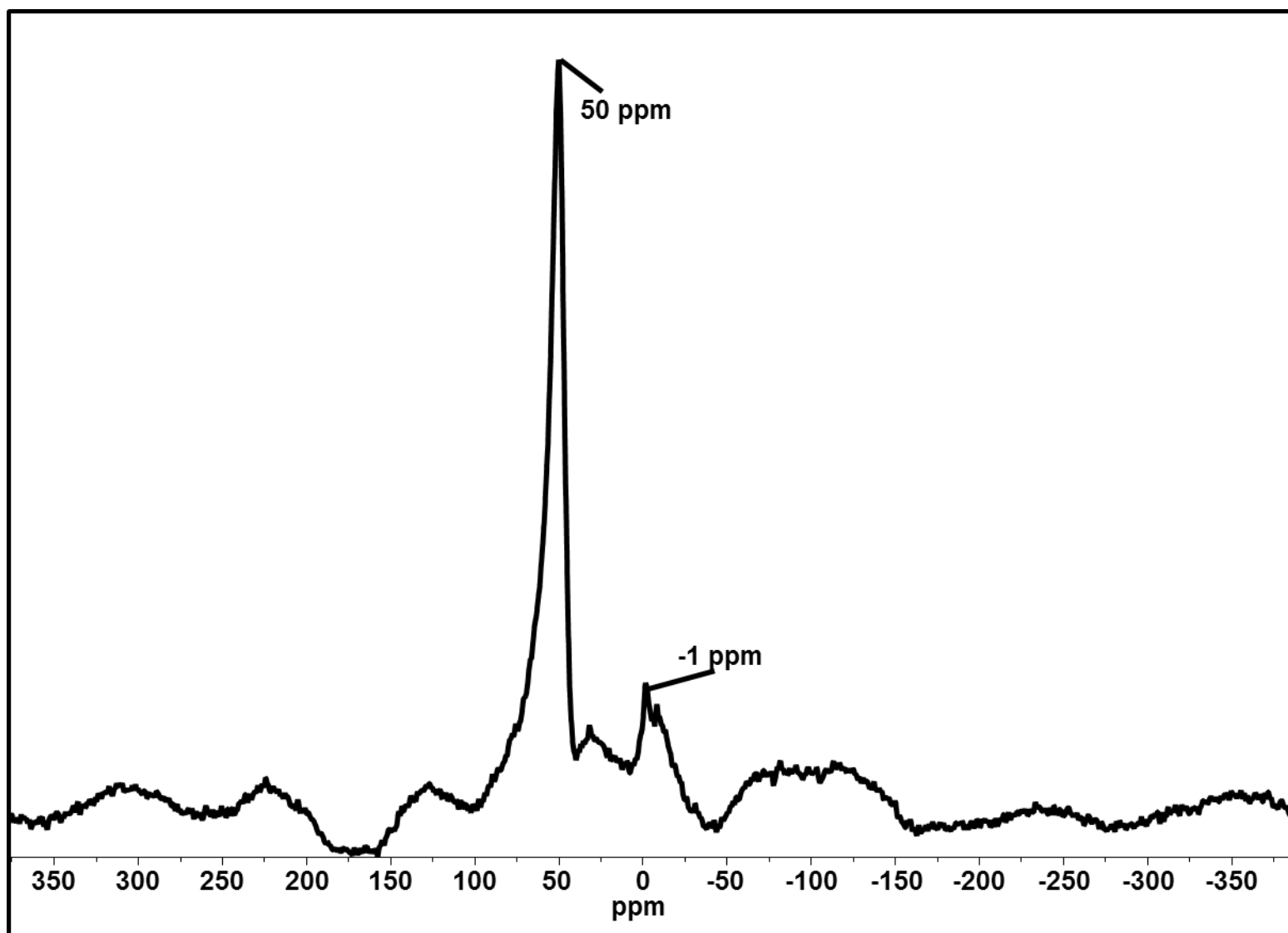


Figure 2.46: ^{27}Al SSNMR spectrum of 1-dose Al sample from AlCl_3 in THF

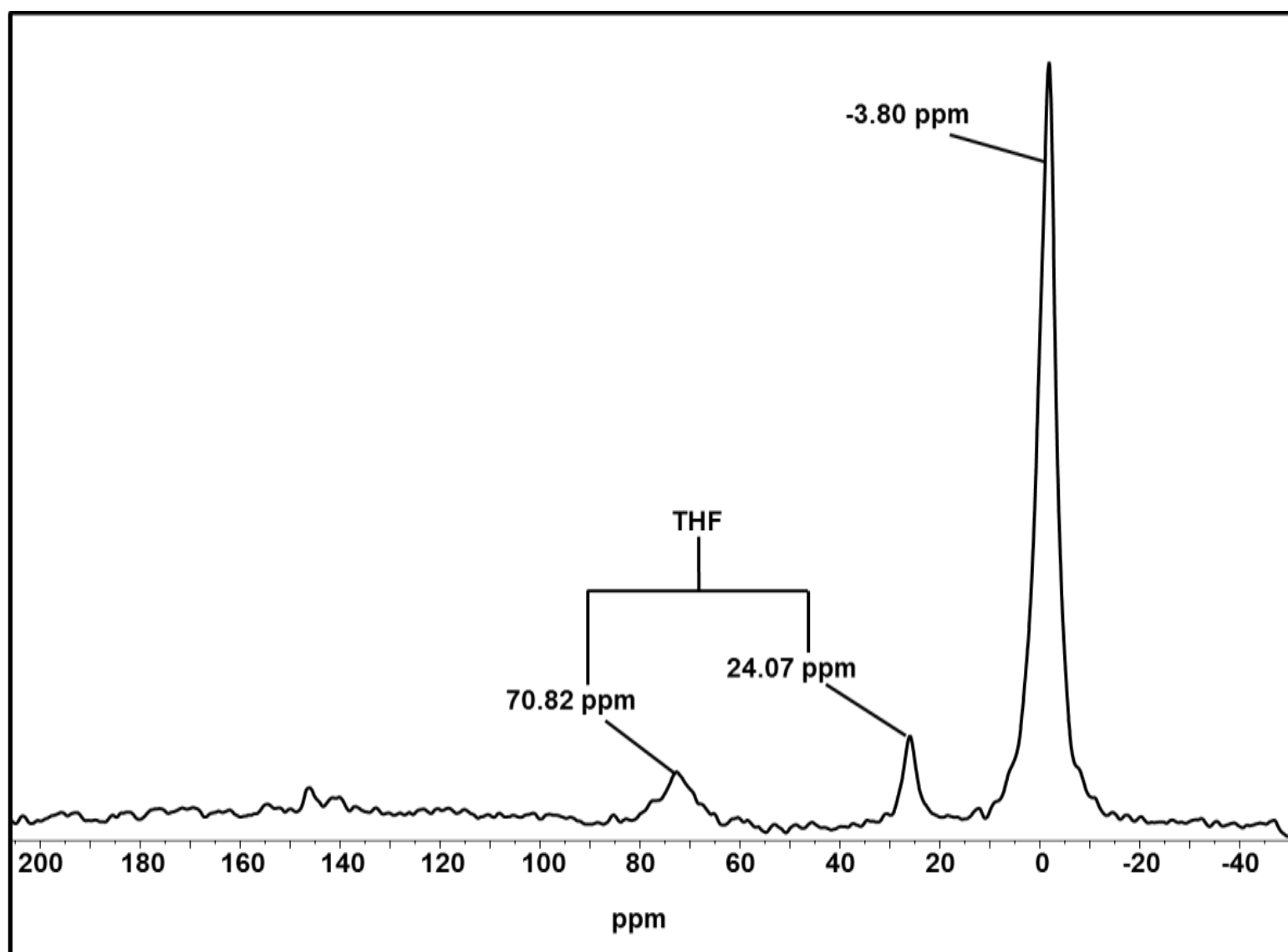


Figure 2.47: ^{13}C CPMAS SSNMR spectrum of 1-dose Al sample from AlCl_3 in THF

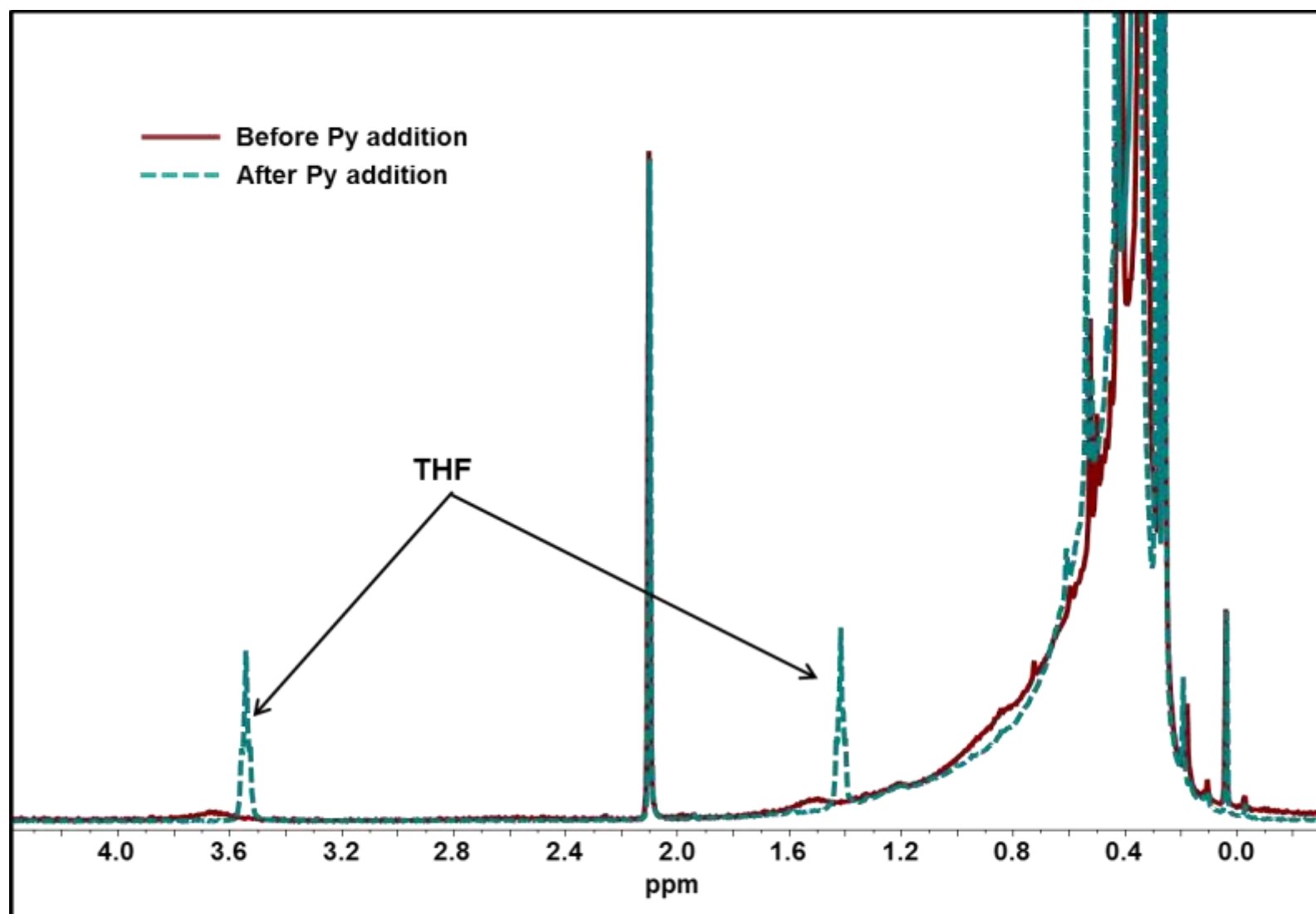


Figure 2.48: Overlay of ^1H NMR spectra of 1-dose Al sample from AlCl_3 in THF dried and suspended in C_6D_6 , before and after pyridine addition

additional ~33 mg of mass (resulting from volatile tin byproducts) may have been lost. This would increase the total equivalents of tin lost to 3.5.

The presence of a strong tetrahedral aluminum feature with a relatively narrow linewidth and symmetric lineshape in both of these cases is strong evidence of the existence of a highly symmetrical, single type of Al center within the matrix. This is also evidence against the formation of a distribution of Al precursor species in solution. The evidence for the clean formation of these species (Figure 2.49) demonstrates that running these reactions in coordinating solvents may be the way to proceed in the future.

2.3.6 Two and Three Dose Embedded Aluminum Catalysts

The primary reasons for carrying out second and third dose reactions on the Al samples are to further cross-link (rigidify) the matrix, adjust hydrophobicity, and to remove excess unreacted tin groups (Figure 1.17). These are all modifications that are important for eventual use in catalytic applications. It is important to have a well cross-linked matrix that will make the final catalyst more robust under catalytic conditions. The hydrophobicity of the matrix can be tailored depending on what type of substrate or solvent a particular catalytic reaction requires. Finally, it is important to remove as much of the remaining tin as possible as there is a possibility that some catalytic reactions may be influenced by the presence of a second metal center in the matrix.

A variety of chlorosilanes (SiCl_4 , HSiCl_3 , Me_2SiCl_2 , Me_3SiCl) can be used for secondary reactions. Deciding how much which silane to use is dependent on the hydrophobicity desired in the final matrix, the degree of connectivity needed, and whether or not it is harmful to leave Si-Cl bonds (that can hydrolyze to form HCl) behind. While hydrophobicity of the matrix has been linked to catalyst effectiveness in some heterogeneous reactions, the effects of modifying the hydrophobic nature of the catalysts synthesized here have not been well studied at this point.¹¹⁶ This puts more emphasis on the final two factors. If a first dose reaction has produced a low surface area material then it may be desirable to add a secondary linker with more chlorides to provide the ability to cross-link to a higher degree. The correct stoichiometric amount must be used, of course, to obtain the desired connectivity. When high ratios of

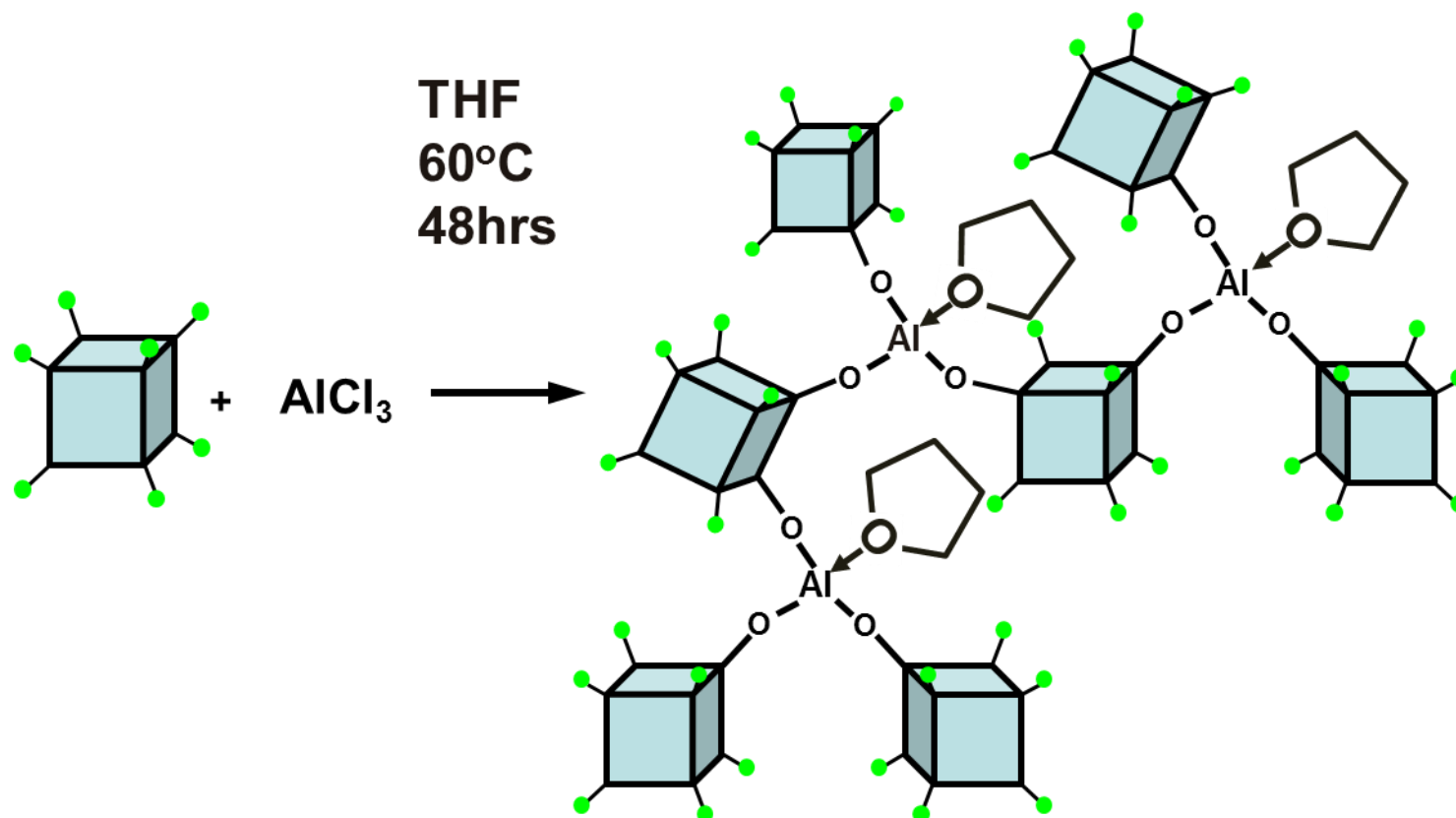


Figure 2.49: Proposed reaction to produce 4-coordinate Al centers in the coordinating solvent THF

a polychloro silane are used then the average connectivity of the silane to the matrix will be lower resulting in a large number of Si-Cl bonds remaining. This can be a problem for samples that may be sensitive to leaching by HCl as will be discussed later. Me_3SiCl is typically used last in order to remove as much of the remaining tin from the system as possible.

Due to the unusual nature of the initial reactions of AlCl_3 with the tin cube and the extensive investigation of its nature, the effects and products of second and third dose reactions were not studied in depth. Some general trends were clear however. Analysis of the volatiles in the second and third dose reactions showed only the expected Me_3SnCl byproduct. As long as no intermediate handling of the 1-dose sample was carried out, then gravimetric analysis in the second and third dose reactions could generally be trusted.

IR of these samples showed few changes other than changes in the C-H stretches and vibrations due to replacement of $\text{Me}_3\text{Sn-}$ groups with silane groups. As previously mentioned, the moisture sensitivity of the catalyst does increase in the case where a large number of Si-Cl bonds remain in the matrix making it difficult to handle the sample without the formation and observation of $-\text{OH}$ in the system. The other primary concern involves the possible rechlorination of Al in the secondary doses. This is a very difficult concern to address due to the lack of techniques for direct characterization of Al centers. As a result, such concerns have been explored in depth in Chapter 3, where XAS data can be used to detect the chloride bound to gallium.

2.4 Conclusions

Taken together, the many synthetic and characterization avenues that have been described above fail to present as complete a picture as we would have wished of the aluminum sites that develop in the matrix when AlCl_3 is reacted with $\text{Si}_8\text{O}_{12}(\text{OSnMe}_3)_8$. However, it is instructive to review the many pieces of evidence that have been collected and described thus far. In doing so, a generally consistent picture of the different chemical reactions at play during AlCl_3 and the tin cube can be developed.

1. Reaction of AlCl_3 with the tin cube in non-coordinating solvents is complicated, resulting in the production of multiple byproducts. The insolubility of AlCl_3 , and the known reactivity of AlCl_3 with Me_3SnCl to form $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ are believed to influence the final products of the reaction and account for the variability in final product composition (i.e. connectivity) that has been observed.
 - a. The nature of the structure of aluminum trichloride in different media is of practical interest here. In solid form AlCl_3 is octahedral,¹¹⁷ while it exists as the tetrahedral dimer Al_2Cl_6 in the liquid and gas phases. It is unclear what form AlCl_3 exists as in the toluene solutions utilized in most of the reactions described here. It is known that anhydrous AlCl_3 has a very low solubility in toluene, however, it has been shown that trace amounts of water and the resultant HCl produced can increase the solubility of AlCl_3 by conversion to carbonium aluminate ($[\text{CH}_3\text{C}_6\text{H}_6][\text{AlCl}_4]$) salts. This is often seen in Friedel-Crafts type reactions.¹¹⁸ Our procedures for drying and transferring solvent to the reactions conducted here should be adequate to ensure the exclusion of water, but the effect of possible trace contamination is not completely known at this time.
 - b. Assuming that water has been completely excluded, the low solubility of AlCl_3 in toluene implies that this reaction should progress very slowly, but as previously stated, using standard conditions, significant reaction is seen to occur within 0.5-1hr. A possible reason for this is the production of $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ from the reaction of the trimethyltin chloride (Me_3SnCl) byproduct in toluene with the solid toluene/ AlCl_3 slurry.⁸⁹ In the solid state this species forms a polymeric chain of tetrahedral AlCl_4 centers bridged by planar Me_3Sn cations but in solution appears to be fully dissociated.
2. Based on the data in hand, we postulate that AlCl_3 initially reacts with tin cube (possibly on the surface of AlCl_3 solid) to form an initial link between aluminum and the cube forming at least one (Al-O-Si) linkage and producing one or more

equivalents of Me_3SnCl (Figure 2.49). From this point on, at least two parallel reactions appear to be operative.

- a. The linking reaction between tin cube and the 1-connected “ OAlCl_2 ” center can lead to a 3-connected Al center. It is, however, unlikely that a 3-coordinate aluminum is the ultimate product in this sequence of steps as it is known to be a very high energy species. With this in mind, it is not completely known what the identity of the Al site(s) are from this leg of the reaction manifold. Interpretation of Al SSNMR is complicated by quadrupolar effects but appears to indicate that multiple Al species are present in the final matrix.
- b. Once Me_3SnCl is present in the reaction mixture, it also reacts with AlCl_3 to form $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$. Based on experiments with $[\text{nBu}_4\text{N}][\text{AlCl}_4]$ and $[\text{Me}_3\text{Sn}][\text{Tf}]$, the reactivity of the constituent trimethyltin cation, and aluminate anion are thought to now progress somewhat independently.
- c. The aluminate species $[\text{AlCl}_4]^-$ is believed to react by the expected metathesis reaction to produce Me_3SnCl and Al-O-Si linkages to the matrix until all its chlorides have reacted. Of central importance in the context of this reaction is the question of whether $[\text{AlCl}_4]^-$ ions can react with Me_3Sn groups on the cube to form tetramethyl tin. Based on the data in hand, the answer to this question is no, the reactions of $[\text{AlCl}_4]^-$ do not account for the formation of Me_4Sn . $[\text{AlCl}_4]^-$ anions could ultimately lead to an interesting 4-connected Al site in the matrix but experiments starting with the butylammonium aluminate precursor invariably gives an Al-cube connectivity of less than four and therefore a distribution of Al sites exists in the matrix.
- d. One of the most interesting results of this research has come from investigating the reactions of the trimethyltin cation. Starting from two different salts containing the trimethyltin cation ($[\text{AlCl}_4]^-$, triflate), our investigations have shown that it reacts quickly with oxotrimethyl tin groups ($-\text{OSnMe}_3$) extracting a methyl group to form one equivalent of Me_4Sn . Based on these results, we believe that the formation and subsequent reaction of the

- trimethyl tin cation is the *primary* source of tetramethyl tin formation in these reactions. The reason that we cannot say it is the *only* source of Me_4Sn is the variability in Me_4Sn formation in the reactions of AlCl_3 and the tin cube. Quantitative evaluations of the amount of Me_4Sn produced are generally higher than can be accounted for by the formation of one equivalent of the aluminate and trimethyl tin cation per original AlCl_3 center.
- e. The nature of the coproduct that results as a consequence of methyl extraction also remains uncertain. The main reason for this is the difficulties that were encountered in either isolating this species (tentatively identified as a dimethyloxotin $[\text{-OSnMe}_2]^+$ or obtaining clear unequivocal spectroscopic data that would signal its presence or explicitly identify its components. In our investigations, ^{13}C and ^{29}Si resonances have been tentatively assigned to such a species, however no such species has been identified in the ^{119}Sn SSNMR spectra collected thus far. Attempts to prepare molecular analogues have also been stymied by unexpected side reactions, multiple products and our inability to isolate pure or crystalline samples for diffraction analysis.
 - f. Based on the evidence gathered here, we propose the reaction pathway presented in Figure 2.49, as the most likely routes by which tetrahedral aluminum centers are produced via the reaction of trimethyltin cube and aluminum trichloride.
3. Given the complexity that was uncovered with the reactions of AlCl_3 in non-coordinating solvents, a number of alternate routes were explored with varying degrees of success.
- a. The reactions of several of the reactants described above with POSS analogues to the cube which contain only one trimethyl tin group were explored. In all cases but one, *no* tetramethyl tin was observed to form in these reactions, only Me_3SnCl . Unfortunately full connectivities were not observed in these reactions preventing the isolation of pure products. The

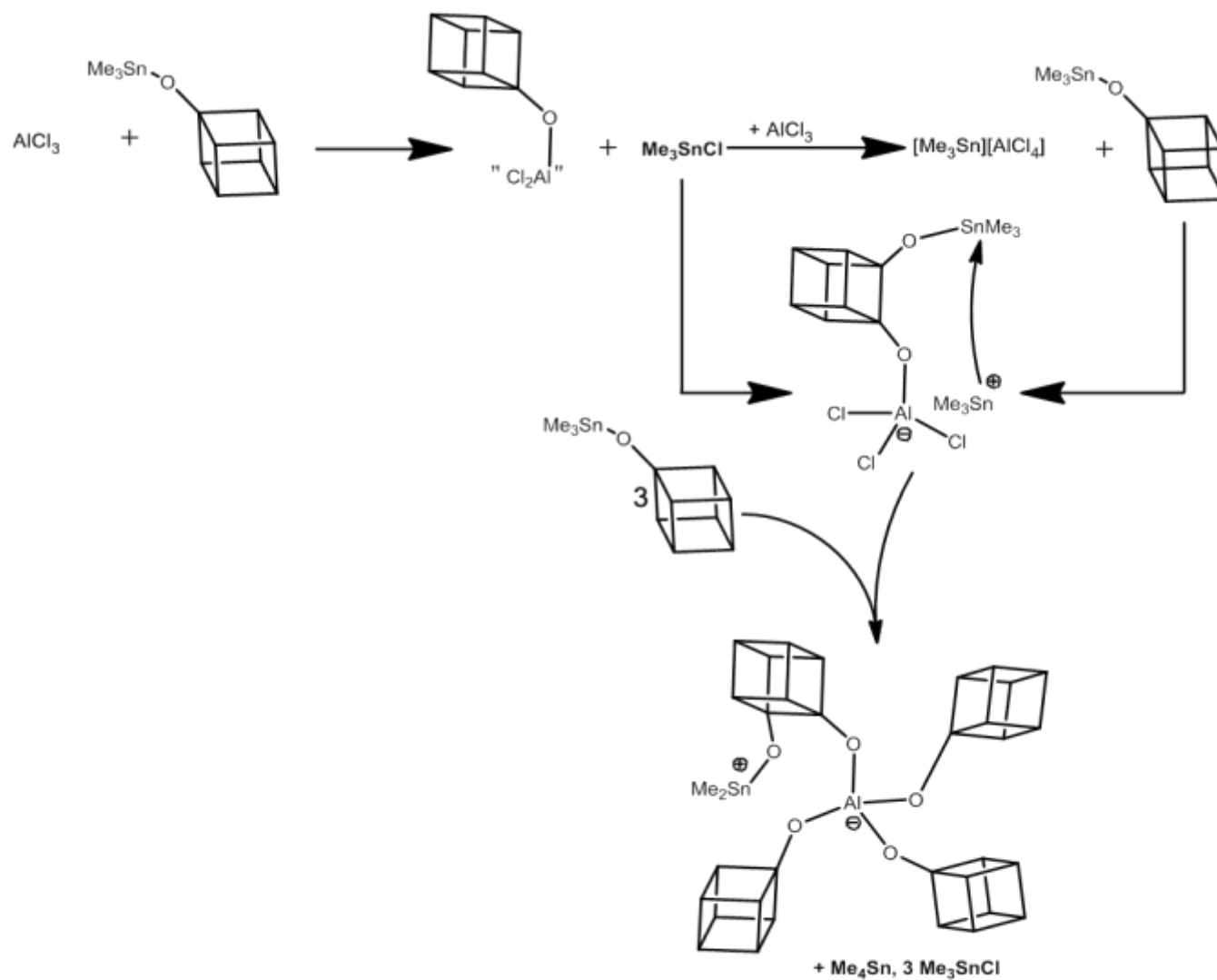


Figure 2.50: Proposed Reaction Mechanism to produce 4-coordinate Al centers Me_3SnCl , and Me_4Sn

one instance in which tetramethyltin was observed involved the reaction of $[\text{Me}_3\text{Sn}][\text{Tf}]$ with POSS in which tetramethyltin was the exclusive product.

- b. A promising avenue of investigation in this research involves first exposing AlCl_3 to a Lewis base such as pyridine. In the case of pyridine, the adduct is stable and can be isolated. Reaction of the pyridine adduct with the tin cube gave rise to near limiting connectivities (3-connected) and good Al spectra consistent with a predominant 4-coordinate aluminum site in the matrix, presumably the desired pseudo tetrahedral $\text{Py}\cdot\text{Al}(\text{O-Si})_3$ site. No tetramethyltin was observed in these reactions. Unfortunately, in the context of exploring the chemistry of the aluminum sites in these matrices pyridine is bound so strongly that interesting ligand exchange reactions to create Brønsted sites are not possible without heating the matrix to $\geq 500^\circ\text{C}$.
- c. Similar reaction of AlCl_3 and the tin cube using coordinating solvents such as ether or THF also appear to simplify the reaction significantly. Very little tetramethyltin (<10% of the volatile tin) was observed in the byproducts and a connectivity between 3 and 4 was obtained in the case of THF. Our expectation in these reactions is that THF and ether will complex to AlCl_3 to form weak 4-coordinate complexes and prevent reaction with the trimethyltin chloride byproduct, and the subsequent production of tetramethyl tin. Once aluminum is incorporated into the cube matrix, evidence suggests that these solvent ligands continue to occupy the fourth coordination position. Simple ligand exchange experiments where solid products were exposed to pyridine clearly showed the displacement of these ligands, presumably from coordination to aluminum. Finally, the solid state ^{27}Al NMR spectra show some of the cleanest, most well defined signals for 4-coordinate Al sites observed to date with little evidence of 5- or 6-coordinate aluminum sites.

3. Synthesis & Structure of Nanostructured Building-Block Solid Acid Gallium Catalysts

3.1 Introduction

Gallium lies below aluminum in group 13 of the periodic table, and possesses similar chemical reactivity.^{117,119} Gallium analogues for a great number of aluminum species also exist. In addition, the applications of these analogues are often similar. This is especially the case in heterogeneous catalysis where gallium oxide and gallosilicates have been shown to be quite active for a number of the same catalytic processes as aluminosilicates.^{120–123}

As questions about the nature of the reaction between aluminum chloride and the trimethyltin cube building block were multiplying, it seemed like an obvious step to examine whether the same issues occur when gallium trichloride is substituted. Furthermore, the use of gallium also allows for the collection of X-ray Absorption Spectroscopy (XAS) data for the direct characterization of the metal centers within the catalytic matrix. Whereas the ionization energy of aluminum (k edge; 1.56 KeV) is too low for routine collection of EXAFS and XANES data, the ionization energy (k edge; 10.37 KeV) for gallium is sufficiently high to allow for the gathering of high quality data.

The goal of the work with gallium was to verify that gallium trichloride behaved in a similar fashion to aluminum trichloride, and consequently to determine the structure of the cross-linking gallium centers in our building block matrices by modeling the EXAFS data. Quantitative structure determination was successful in many cases. In samples where satisfactory modeling of the data was not possible, qualitative analyses still managed to reveal important information.

3.2 Experimental

3.2.1 Materials & Synthesis

All reactions were performed using the materials, methods and techniques outlined in Chapter 2 of this dissertation. Synthetic procedures for the production of

these gallosilicate catalysts are identical to those previously discussed, with the simple replacement of the aluminum species with their gallium analogues. These gallium precursors include anhydrous gallium chloride (GaCl_3 , Strem, 99.999%), and tris(dimethylamino)gallium ($\text{Ga}_2(\text{NMe}_2)_6$, Strem, 98%). The gallium trichloride pyridine adduct ($\text{GaCl}_3 \cdot \text{Py}$) and the ionic butyl ammonium gallium tetrachloride species $[\text{nBu}_4\text{N}][\text{GaCl}_4]$ were prepared using procedures similar to their aluminum analogues. Attempts to synthesize and isolate the ion paired species $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$ were unsuccessful, and will be discussed below.

3.2.2 Characterization

Details of the methods used for characterization of these samples by gravimetric analysis, nitrogen adsorption, IR, NMR, ICP-OES, and GC/MS can be found in Chapter 2 of this dissertation, while specifics of XAS data collection protocols are discussed here.

Gallium XAS samples were prepared in copper, aluminum or polycarbonate sample cells with polyimide (Kapton) windows sealed with two-sided transparent tape. XAS data for gallium (10367 eV) were collected at the National Synchrotron Light Source (NSLS) on beamlines X19A (focused beam, 2.1-17 keV) and X18B (unfocused beam, 4.7-40 keV). Transmission and fluorescence data were collected simultaneously by orienting the sample holder at 45° to the incident x-ray beam. Ionization chambers served as the detectors for transmission data while a solid-state “passivated implanted planar silicon” (PIPS) detector collected fluorescence data. Both beamlines utilized dual Si(111) crystals for a monochromator. The incident beam was detuned 25-30% to suppress harmonics. Spectra were collected over four energy regions relative to the Ga edge as follows: (-150)-(-15) eV, 5 eV steps, 1s integration; (-15)-75 eV, 0.5 eV steps, 2s integration; 75 eV-12k, 0.05 k steps, 3s integration; and 12-16k, 0.05k steps, 4s integration. Calibration of the monochromator was carried out using a Ga_2O_3 filter where the top of the white line was defined as 10375eV.¹²⁴ In general, no significant energy corrections to the monochromator readings were observed. Two to four scans were collected for each sample. Data analysis was performed with the IFEFFIT data

analysis software suite.¹²⁵ Athena¹²⁶ was used for data reduction and the generation of merged files after aligning multiple sample scans. Artemis¹²⁶ was used for data modeling. The theoretical phase and amplitude functions were generated from FEFF6L or FEFF8.¹²⁷

3.3 Results & Discussion

3.3.1 One Dose Embedded Gallium Catalysts From GaCl₃

Based upon the reaction of AlCl₃ with the tin cube, it was expected that the analogous reaction using GaCl₃ would behave similarly, and that the secondary byproduct Me₄Sn would be produced in addition to the primary metathesis product Me₃SnCl (Equation 3.1).



Reactions were carried out in toluene at 80-100 °C for 6 – 48 hours. Upon transfer of solvent and warming, the gallium chloride was almost completely solubilized, in stark contrast to AlCl₃. This is likely due to the fact that GaCl₃ is a dimer in the solid state rather than the 6-coordinate layered lattice structure of AlCl₃. In addition, there is evidence in the literature¹²⁸ that GaCl₃ forms weak complexes with arene hydrocarbon solvents such as benzene and mesitylene, and similar species may in fact be forming in toluene, increasing GaCl₃ solubility.

During the course of the reaction, the solution becomes cloudy and a small amount of gel formation on the side of the flask is observed. No visible color change was detected as in the case of the aluminum system. Upon completion of the reaction, the volatiles were removed and analyzed by NMR and GC/MS. As expected, both trimethyltin chloride and tetramethyltin were detected.

Just as in the case of the aluminum reactions, the relative ratio Me₄Sn : Me₃SnCl was variable. However, the relative amount of Me₄Sn produced was always smaller than seen in reactions with AlCl₃, never totaling more than 30 mole percent of the volatile tin fraction. These ratios coupled with gravimetric analysis of the mass change after reaction showed overall losses of 2.9 – 3.6 equivalents of tin.

It was determined that single dose embedded Ga matrices possess surface areas on the order of $<200 \text{ m}^2/\text{g}$. Figure 3.01 shows an N_2 absorption/desorption isotherm for a high surface area single dose Ga material. The shape of the isotherm is classified as Type 1 with an H4 hysteresis.⁹⁶ These designations are both indicative of a highly microporous solid with small external surfaces and narrow slit like pores. Unlike the case with the aluminum species, the hysteresis loop does close indicating reversible uptake of N_2 into the pores.⁹⁶ The BJH pore size distribution once again, clearly shows that the majority of the pores are less than 2 nm in diameter (Figure 3.01, inset).

The IR spectrum (Figure 3.02) of these samples show expected Si-O-Si modes in the $850 - 1250 \text{ cm}^{-1}$ range, methyl C-H bands below 3000 cm^{-1} , and in the $1500-1200 \text{ cm}^{-1}$ region. Similar to the aluminum analogues, the assignments of the features in the $1700-1950 \text{ cm}^{-1}$ range and at 2360 cm^{-1} are not well understood, but are present in the cubic building block starting material. It is important that the pristine 1-dose gallium samples do not show any absorption in the $-\text{OH}$ region of the spectrum, and that is the case here. When the pristine cross-linked gallium matrix is exposed to pyridine, the C-C stretching frequencies (1454 & 1617 cm^{-1}) associated with pyridine bound to Lewis acidic sites are prominent (Figure 3.03). There is little to no evidence for Brønsted acid bound pyridine in this IR spectrum (1545 & 1640 cm^{-1} , pyridinium bands).

While ^{71}Ga SSNMR is possible, we were not able to collect spectra of sufficient quality with our instrument, ^{13}C and ^{29}Si spectra were collected. The ^{13}C CPMAS SSNMR is of little help in elucidating the structure or composition of the gallium centers in the matrix (Figure 3.04). There is no obvious shoulder or second feature that could represent a second type of methyl group that might be assigned to the presence of an $-\text{OSnMe}_2^+$ species. In the spectrum shown, there are only the primary $-\text{OSnMe}_3$ signal at $\delta = -2 \text{ ppm}$, and a very small second peak that is a result of silicon grease contamination in the sample (polydimethylsiloxane, $\delta = 1.4 \text{ ppm}$). The ^{29}Si spectrum (Figure 3.05) however shows the presence of second feature that is associated with the

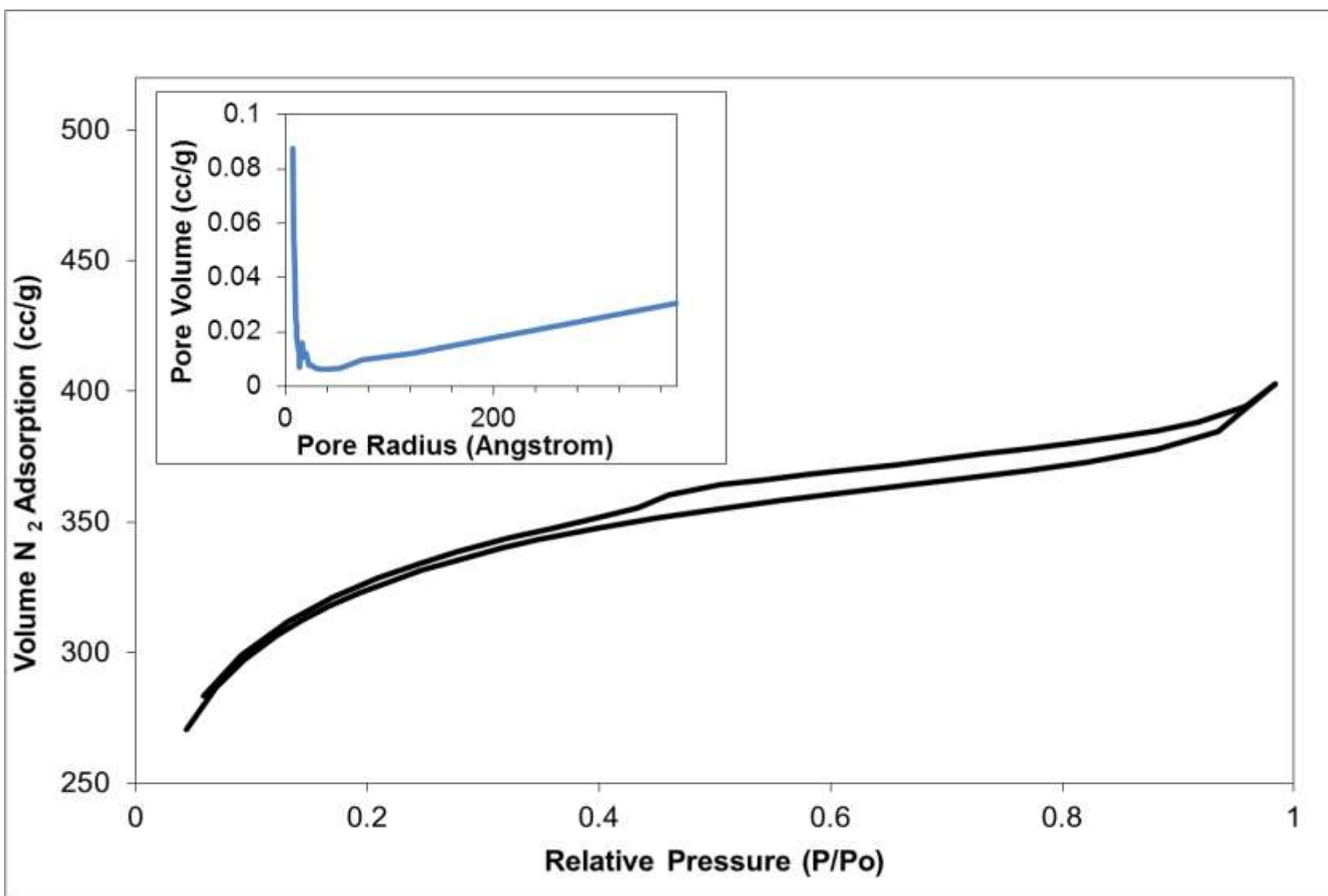


Figure 3.01: BET isotherm of embedded Ga sample and BJH pore size distribution (inset)

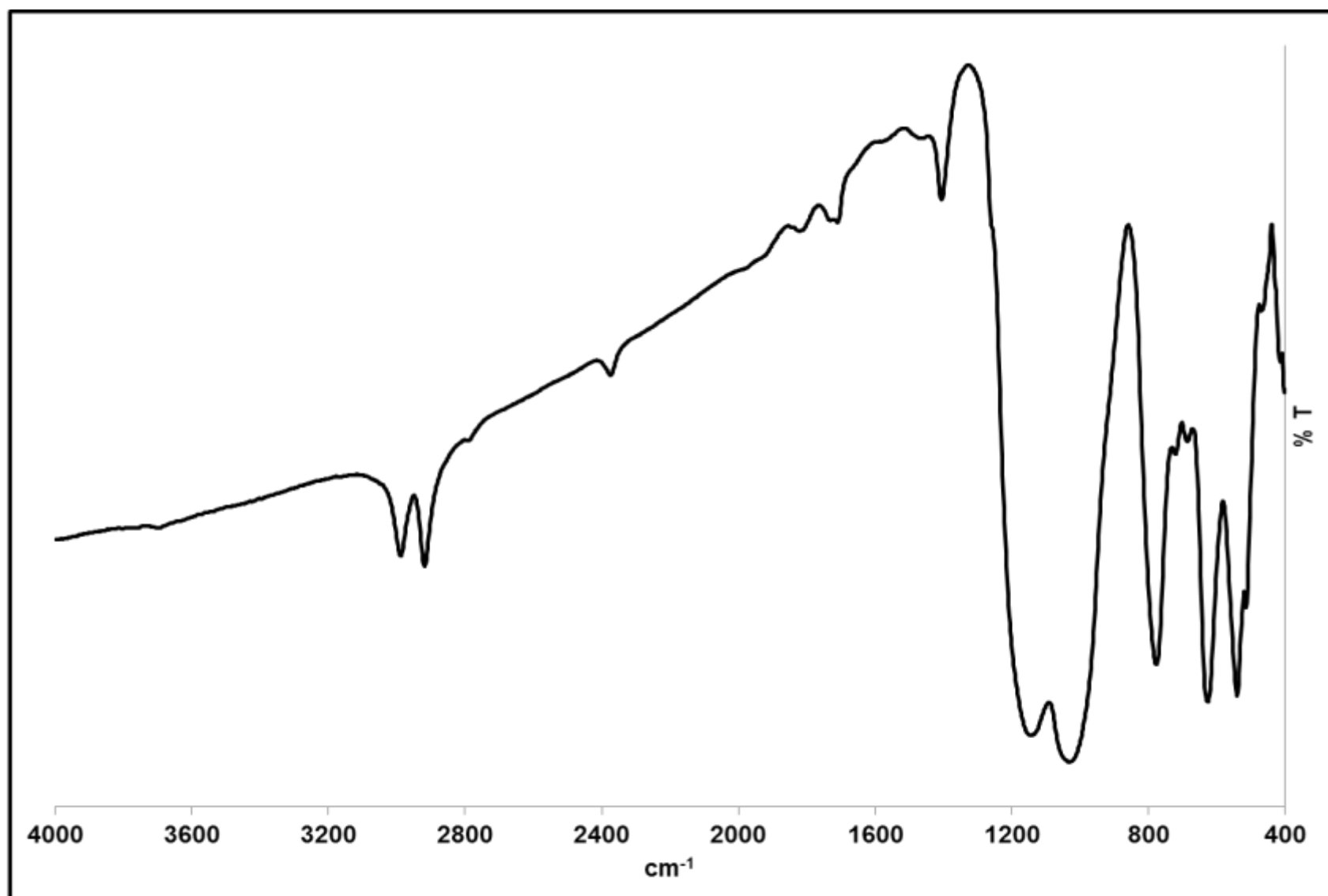


Figure 3.02: IR spectrum for Embedded Ga sample (from GaCl₃)

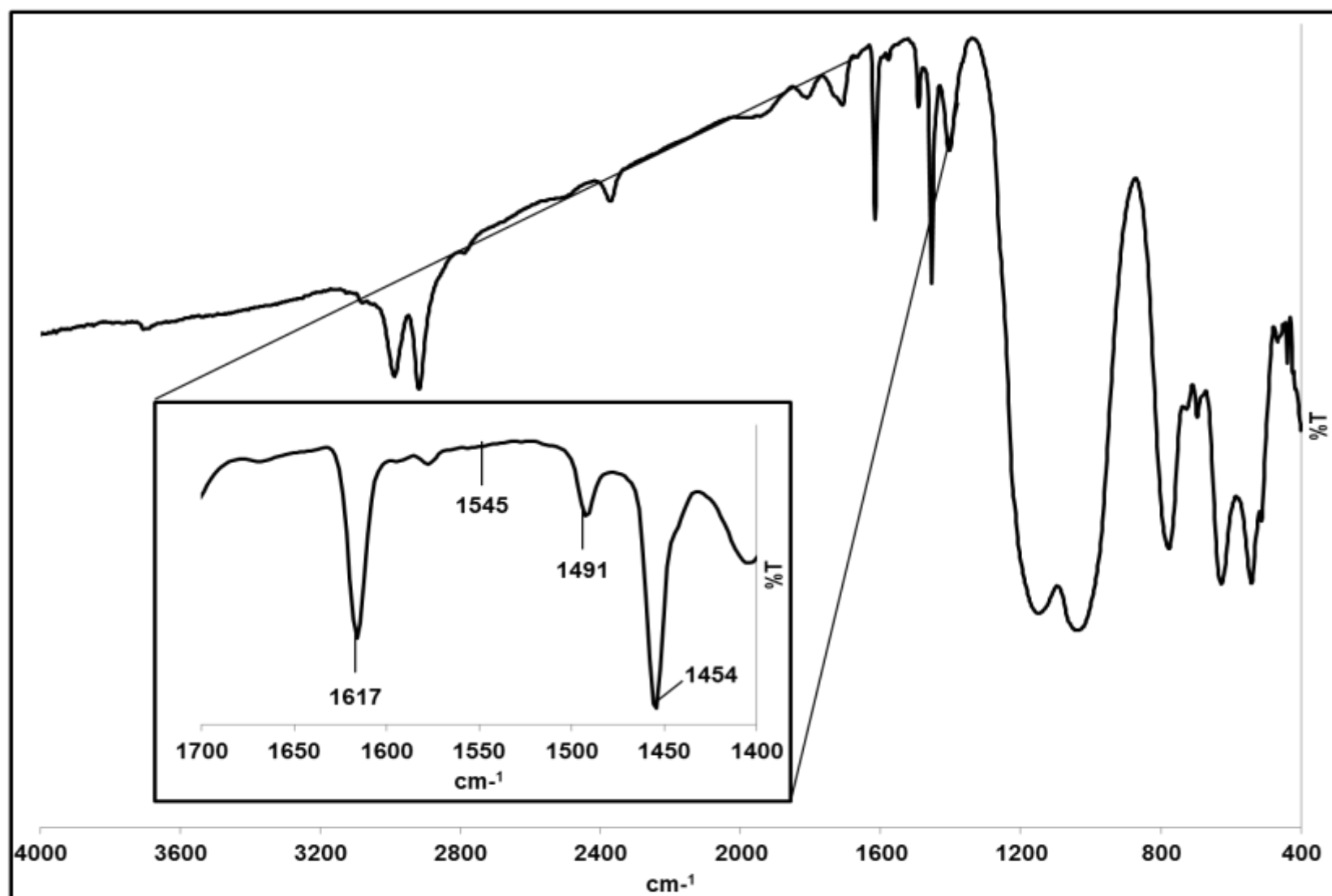


Figure 3.03 IR spectrum of embedded Ga sample (from GaCl₃) with absorbed pyridine and bound pyridine C=C stretching region (inset).

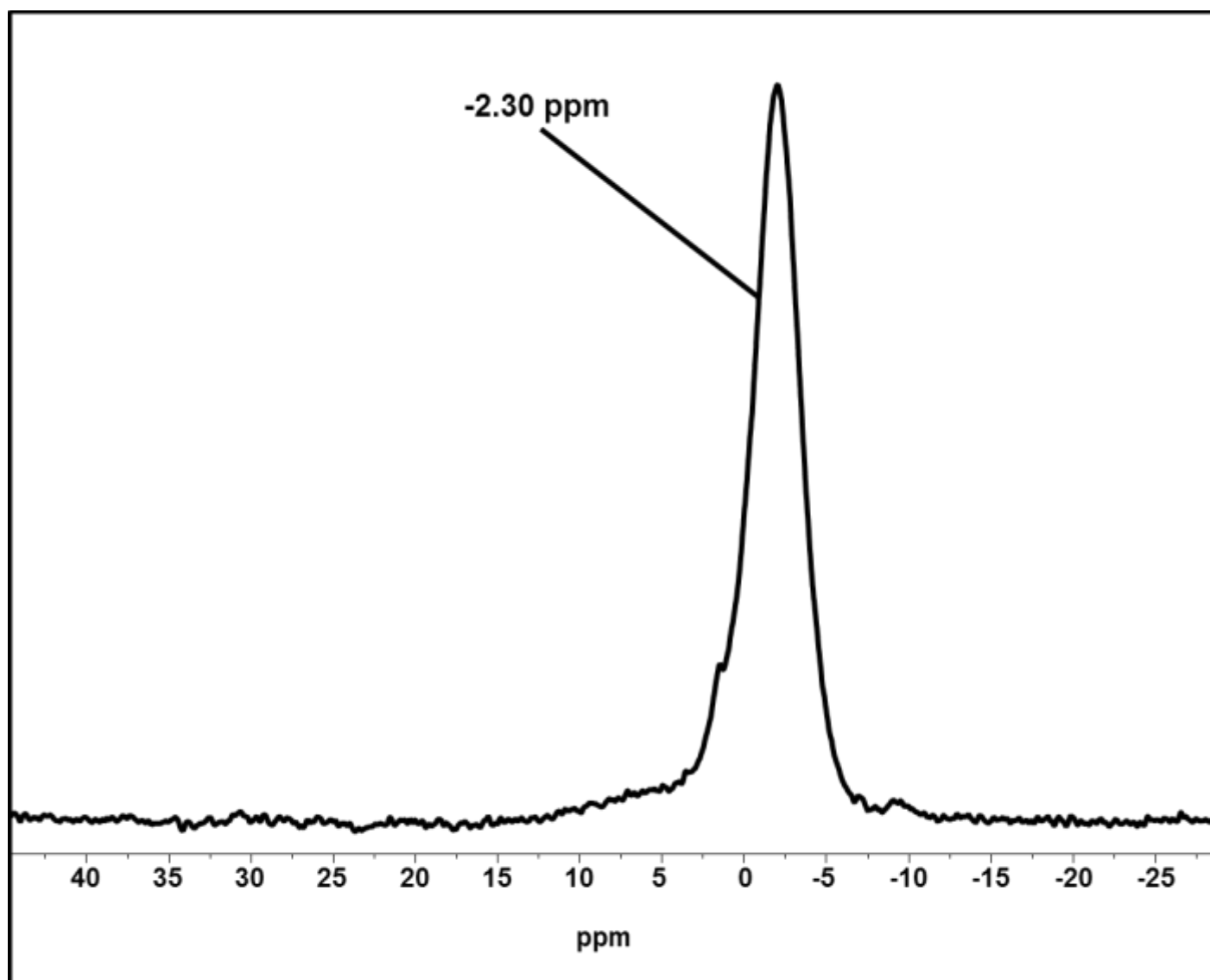


Figure 3.04: ^{13}C MAS SSNMR of Embedded Ga Catalyst

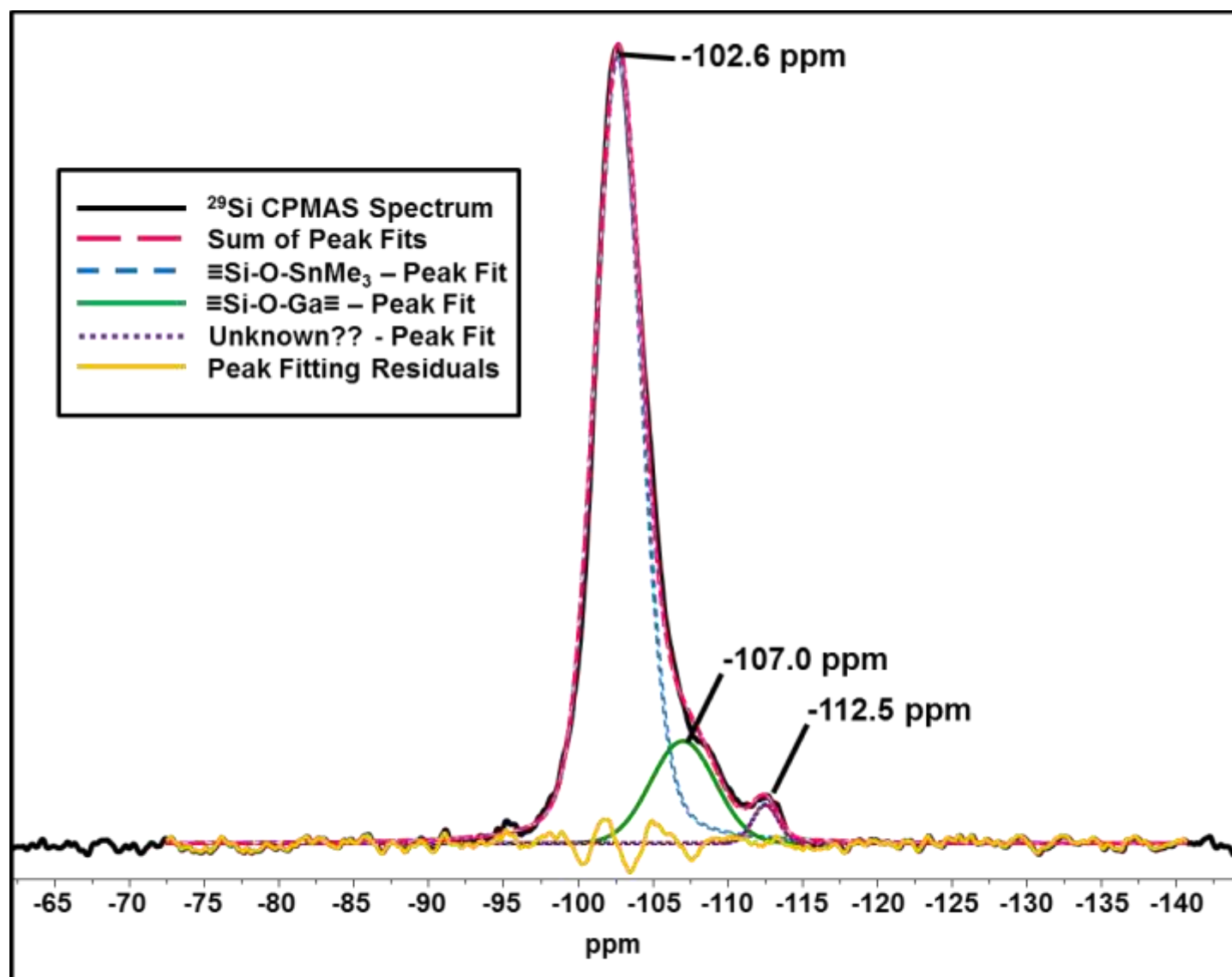


Figure 3.05: ^{29}Si CPMAS SSNMR of embedded Ga catalyst

silicon bound to gallium through oxygen ($\equiv\text{SiO}-\text{Ga}=\$, $\delta = -106.7$ ppm) in addition to the remaining $\equiv\text{SiO}-\text{SnMe}_3$ groups ($\delta = -102.6$ ppm). The value for the silicon near the gallium agrees well with the literature.¹²⁹ There does appear to be a very small feature at $\delta = -112.6$ ppm, that is very similar to the feature seen in aluminum analogues that we have tentatively assigned to silicon centers bound to the $-\text{OSnMe}_2^+$ species.

X-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) methods were used to examine the nature of the gallium sites in the catalytic matrix. The XANES spectrum for a 1-dose $\text{GaCl}_3 + \text{TMT}$ cube sample (Figure 3.06) shows two primary features near the ionization edge. These features occur at 10375 and 10379 eV respectively. The ionization edge at 10373 eV (determined by the maximum in the first derivative of the spectrum; Figure 3.07) and the primary peak at 10375 eV are also consistent with gallium in the +3 oxidation state.¹³⁰ It has been suggested that the feature at 10379 eV is actually indicative of the presence of octahedral Ga centers.¹²⁴ However, this two band pattern has also been seen before in amorphous gallosilicates containing only tetrahedral coordinated gallium centers.¹³¹

The edge structure is significantly different from the gallium trichloride starting material (Figure 3.08) serving as further evidence that reaction has occurred. The feature at 10375 eV is much stronger, though there is still a small feature evident at 10379 eV. The presence of the second feature in a species that is known to be tetrahedral (though slightly distorted due to its dimeric nature), suggests that this feature may not necessarily indicate the presence of octahedral gallium centers as has been stated in the literature.

While XANES analysis is largely a qualitative exercise, EXAFS data can be quantitatively modeled and fit in addition to such qualitative examinations. The fine structure oscillations are extracted from the energy spectrum by fitting a background function to the absorption edge. The result of this extraction is the creation of a k space spectrum (Figure 3.09). From this k space data, an appropriate k range is selected, and then processed by Fourier transform (FT) to produce a radial distribution, or R space plot. Selection of the data range in k space is of importance as a larger k range typically yields higher resolution, however, by including ill-defined and noisy regions of the k

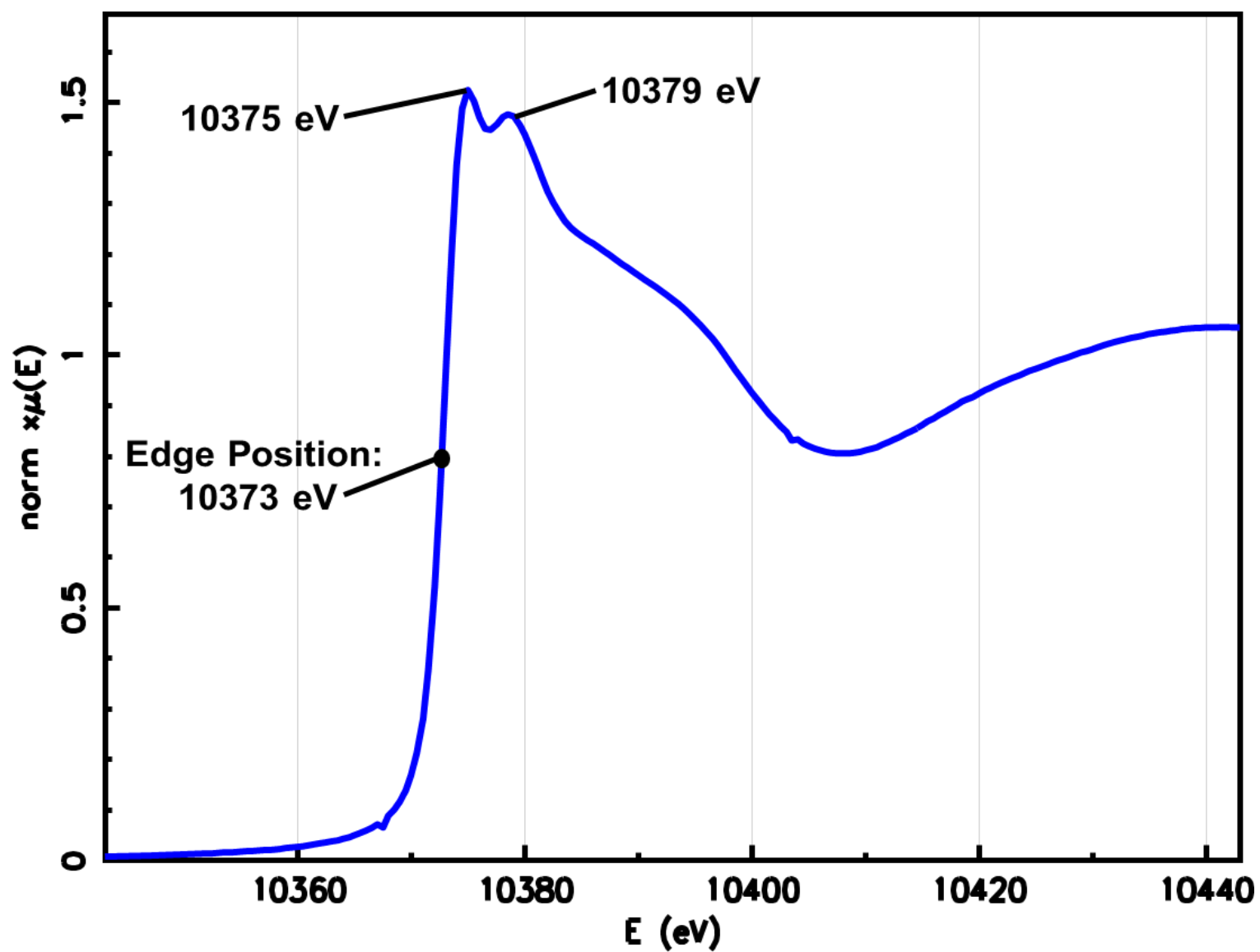


Figure 3.06: XANES spectrum for embedded Ga catalysts (from GaCl_3)

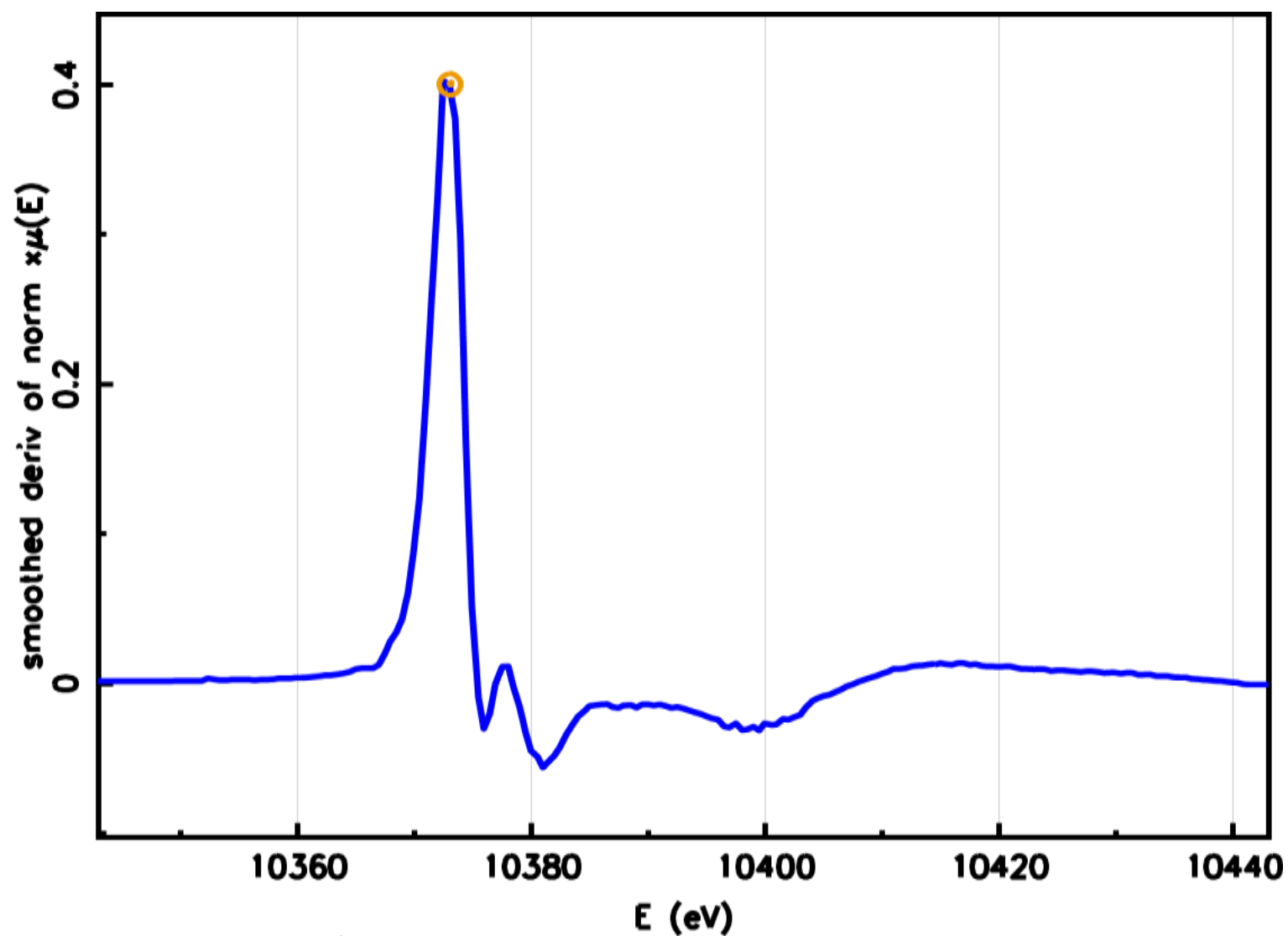


Figure 3.07: 1st derivative of embedded Ga XANES spectrum showing selection of edge position

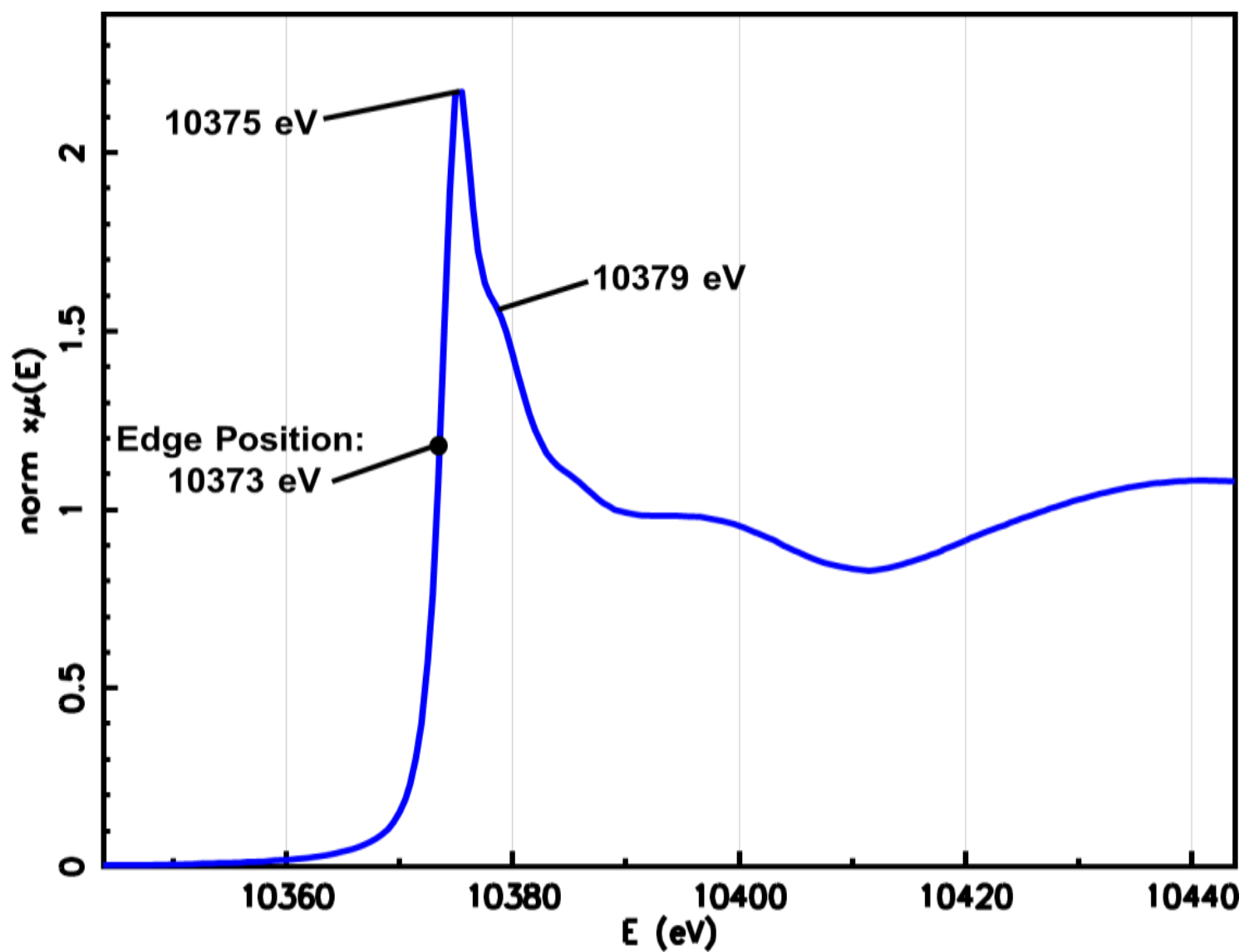


Figure 3.08: XANES spectrum of GaCl₃ precursor

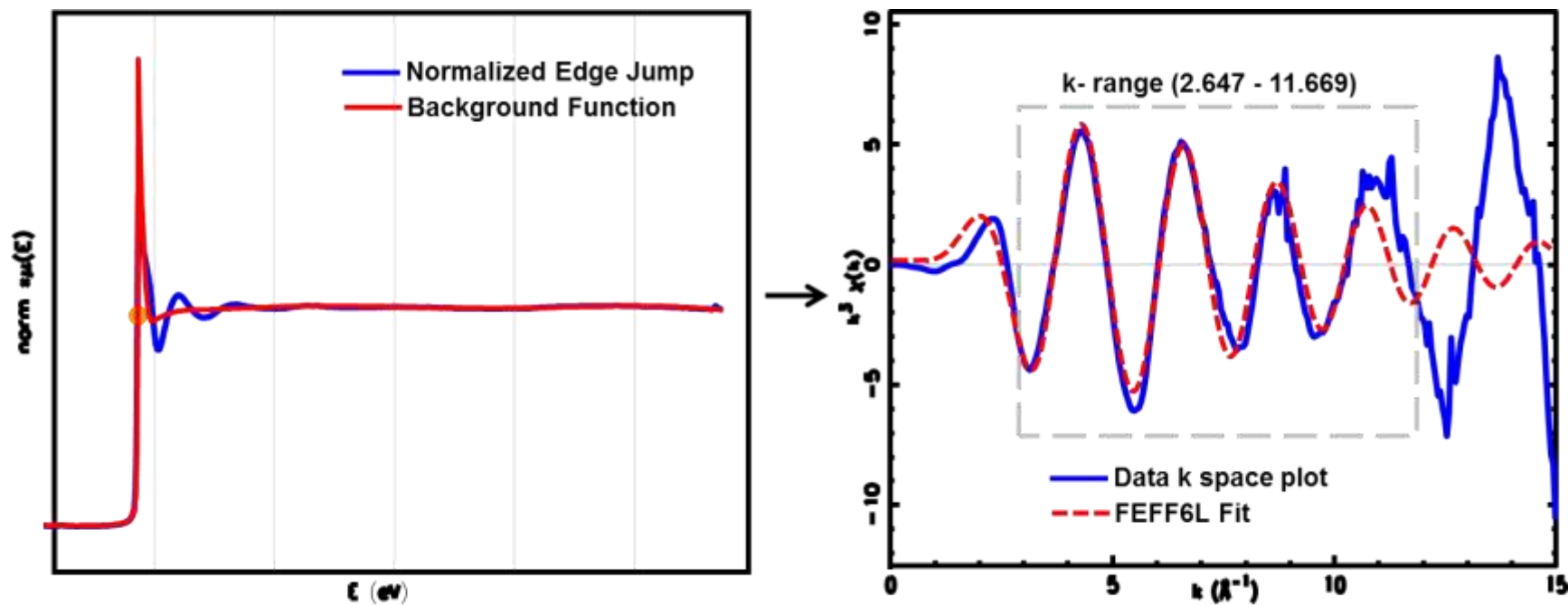


Figure 3.09: Extraction of EXAFS oscillations from embedded Ga sample (from GaCl_3) to produce k space plot, selection of k-range (box), and model fit to k-range data

space plot it is easy to propagate the noise into the R space spectrum. Once the k range has been determined, a Fourier transform of the data is conducted to produce the R space plot. This spectrum allows for the identification of atoms nearby the absorbing center based on bond lengths. For amorphous materials, features are rarely seen beyond 3 Å due to high disorder in the material. As a result, identification of nearby atoms is generally limited to the first, and in ideal cases second coordination shells. The complete process will be explained in detail for the first sample below.

For a typical embedded gallium catalyst, extraction of the oscillations superimposed on the smooth ionization edge yields the k space plot seen in Figure 3.09. The dashed box in the figure shows the range of data which was Fourier transformed to produce the R space spectrum (Figure 3.10). The selection of a proper k range is generally dependent on the quality of the data, but is usually selected to be as large as possible. In this case the k range is relatively small, and this is manifested in the R space plot by broad features. Increasing the k range did not change the R space spectrum significantly, but did make it much more difficult to model and fit the spectrum.

Qualitatively, the R space spectrum (Figure 3.10) shows three features of possible interest at 0.95, 1.41, and 2.70 Å. It should be noted that the bond lengths obtained from the R space spectrum are shorter than true bond lengths in the sample. This is due to a phase shift in the EXAFS oscillations that is unique for each type of scattering atom, and is generally left uncorrected in R space plots. True bond lengths are obtained through structure modeling as is discussed below. Typical phase shifts are on the order of 0.3-0.4 Å.

The feature at 0.95 Å (uncorrected) is referred to as a low R artifact, as it occurs at an unrealistically small distance for a Ga-X bond. Even if the phase adjustment were made, the distance would be too small to represent one of the possible scatters in these materials. The feature at 1.41 Å (uncorrected) is indicative of O bound to the Ga center. This is in the expected distance range as typical Ga-O bonds are ~1.8 Å. The small peak at ~2.7 Å could be representative the second shell Si atoms that would be ~3 Å from the Ga center. This third feature is quite small however, and did not significantly

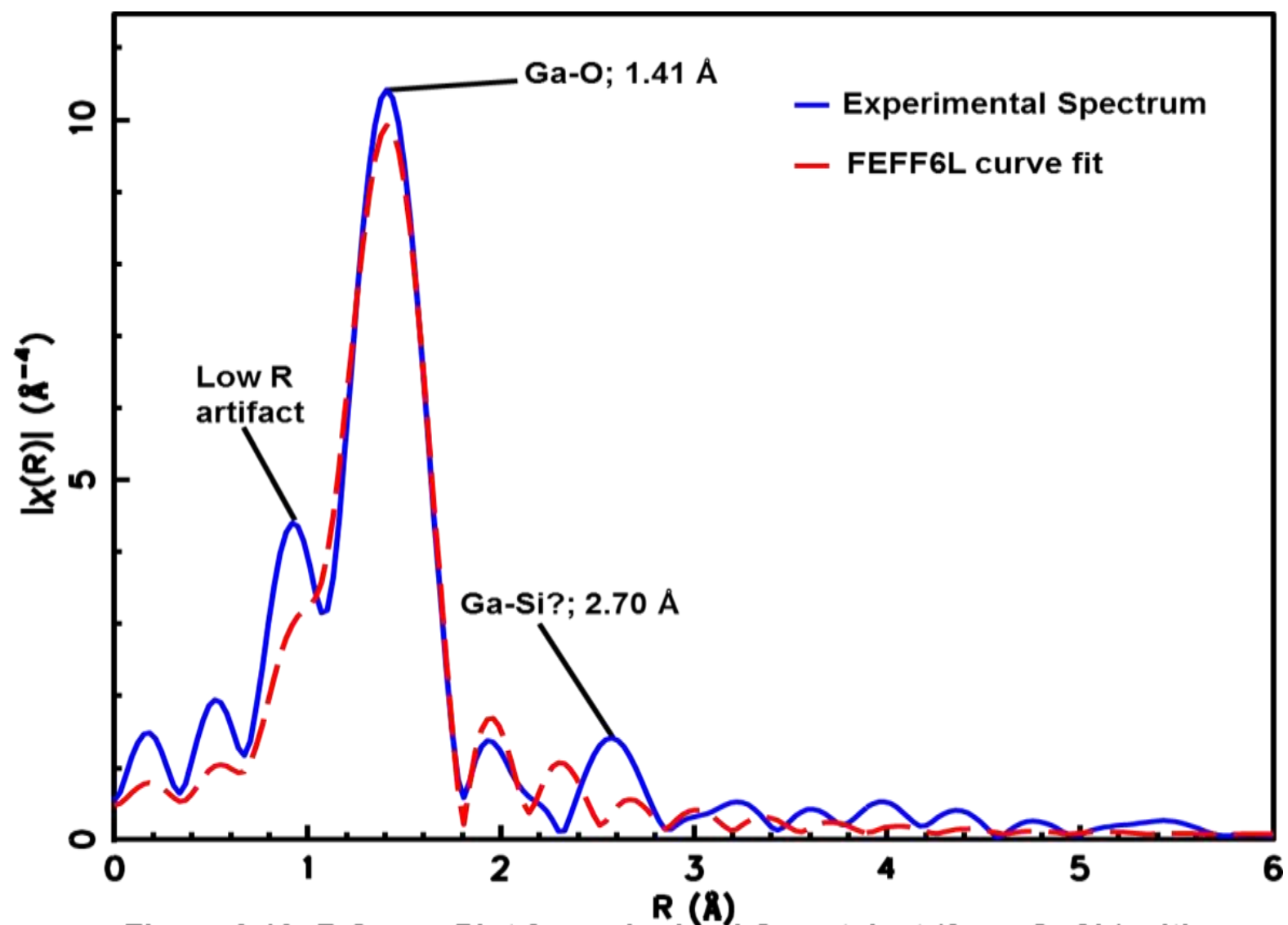


Figure 3.10: R Space Plot for embedded Ga catalyst (from GaCl_3) with modeling fit

impact the fit described below. For the fits described here, only scattering atoms within the first shell were considered. Interestingly, there doesn't appear to be evidence for the presence of a Ga-Cl feature although gravimetric analysis for this particular sample (2.25 eq Me₃SnCl; 0.95 eq Me₄Sn) indicated that there is still chloride left in the matrix, and the most likely place for those chlorides to be would be on the Ga centers. Ga-Cl bonds are typically on the order of 2.15 Å, and ought to be present around 1.8 Å in the R space plot. In this case, there is not even a hint of a shoulder indicating that all chlorides have been removed from the Ga centers.

Modeling of the EXAFS data is based upon the EXAFS equation (Equation 3.2) which is quite complex and has a great number of variables.

$$X_i(k) = \frac{(N_i S_0^2) F_{\text{eff}_i(k)}}{k R_i^2} \sin[2k R_i + \phi(k)] e^{-2\sigma_i^2 k^2} e^{\frac{-2R_i}{\Lambda(k)}} \quad (\text{eq. 3.2})$$

where

$$R_i = R_{0i} + \Delta R_i \quad (\text{eq. 3.3})$$

and

$$k^2 = \frac{2m_e(E - E_0 + \Delta E_0)}{\hbar} \quad (\text{eq. 3.4})$$

Here, R_i is the refined distance between the absorbing atom and the backscattering atom, R_{0i} is the distance between the absorbing atom and the backscattering atom in the theoretical model, ΔR_i is the resulting calculated difference between R_{0i} and R_i , and ΔE_0 is the resulting calculated adjustment of the initial E_0 assignment.

The variables of most importance and those that are generally manipulated to produce a fit to the experimental spectrum are S_0^2 , N , ΔR , ΔE_0 , and σ^2 . Table 3.1 describes these terms and their generally acceptable limits for defining a good fit.

Based on the unlikely existence of a three coordinate Ga center, especially coming from a tetrahedral starting material, the first model chosen for fitting was a gallium center with 4 oxygen atoms in a tetrahedral geometry (Figure 3.11). An initial bond distance of 1.78 Å was utilized. From this model, using Artemis and feff6L

Table 3.1: Description of EXAFS model fitting parameters

Symbol	Parameter	Description
N	Coordination Number	This term represents the number of backscatter atoms of present at a given path length. In the EXAFS equation it modifies the amplitude reduction factor. Values are sample dependent.
S_0^2	Amplitude Reduction Factor	This term modifies the amplitude of the EXAFS signal and does not have a k dependence. Typical values = 0.7 - 1.0
σ^2	Debye-Waller Factor	The σ^2 term attempts to model dynamic (thermal) disorder as well as static disorder (structural heterogeneity) within a single shell of backscatters. Typical values = 0.003 - 0.020 Å ² .
R(ΔR)	Bond Distance (Change in Bond Distance)	R is the calculated bond distance. ΔR represents a change in the interatomic distance relative to the initial path length R_i . Typical values < 0.5 Å.
ΔE_0	Change in Edge Position	This term relates to a change in the photoelectron energy. This value is used to align the energy scale of the theoretical spectrum to match the measured spectrum. Typical values < 10 eV.

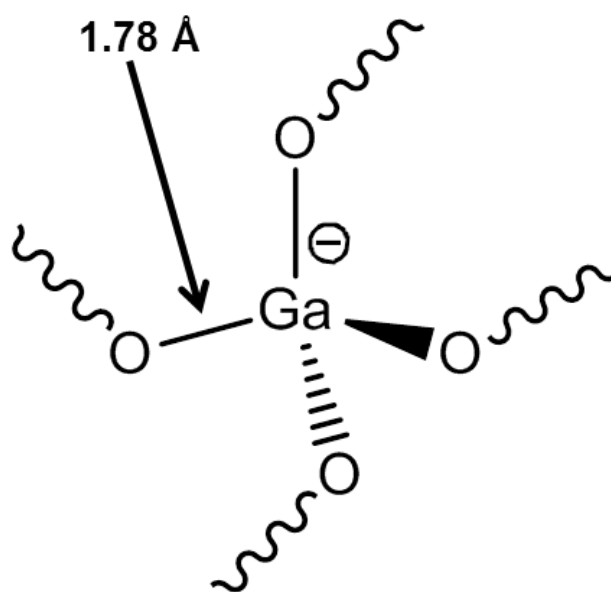


**Figure 3.11: Embedded Ga model
for EXAFS fit**

software packages, the modeling parameters (S_0^2 , N , ΔR , ΔE_0 , and σ^2) were defined for each scattering path and refined iteratively until the parameters converged to stable and acceptable values and the quality of the fit as defined by the statistical parameters R-factor, χ^2 , and reduced χ^2 . In the case of the sample presented here (Figure 3.10), this model was found to fit the experimental data very well both visually, and statistically. The statistical fit parameters can be seen in Table 3.2. The values for coordination number and the Ga-O bond lengths are very close values expected for the chosen model.

The EXAFS and XANES analysis along with NMR evidence for Si-O-Ga bond formation strongly indicate the presence of isolated, 4-coordinate, tetrahedral Ga centers in the matrix bound to four building block corners (Figure 3.11). While there may have been concerns about gallium remaining as a dimer upon insertion into the matrix, the EXAFS data show no evidence of a Ga...Ga feature. An example of a strong Ga...Ga feature is demonstrated in the tris(dimethylamido)gallium starting material (Figure 3.12).

Table 3.2: EXAFS model optimized fitting parameters for embedded Ga catalyst (from GaCl₃) *Values in parentheses indicate uncertainties in the final digit as calculated by a least squares fitting procedure

Parameter	Fit Values
N	4.1(2)
S_0^2	0.89(7)
σ^2	0.005(1)
R[ΔR_0]	1.85 [.07(1)]
E_0	2.30(2.28)
R factor	0.027

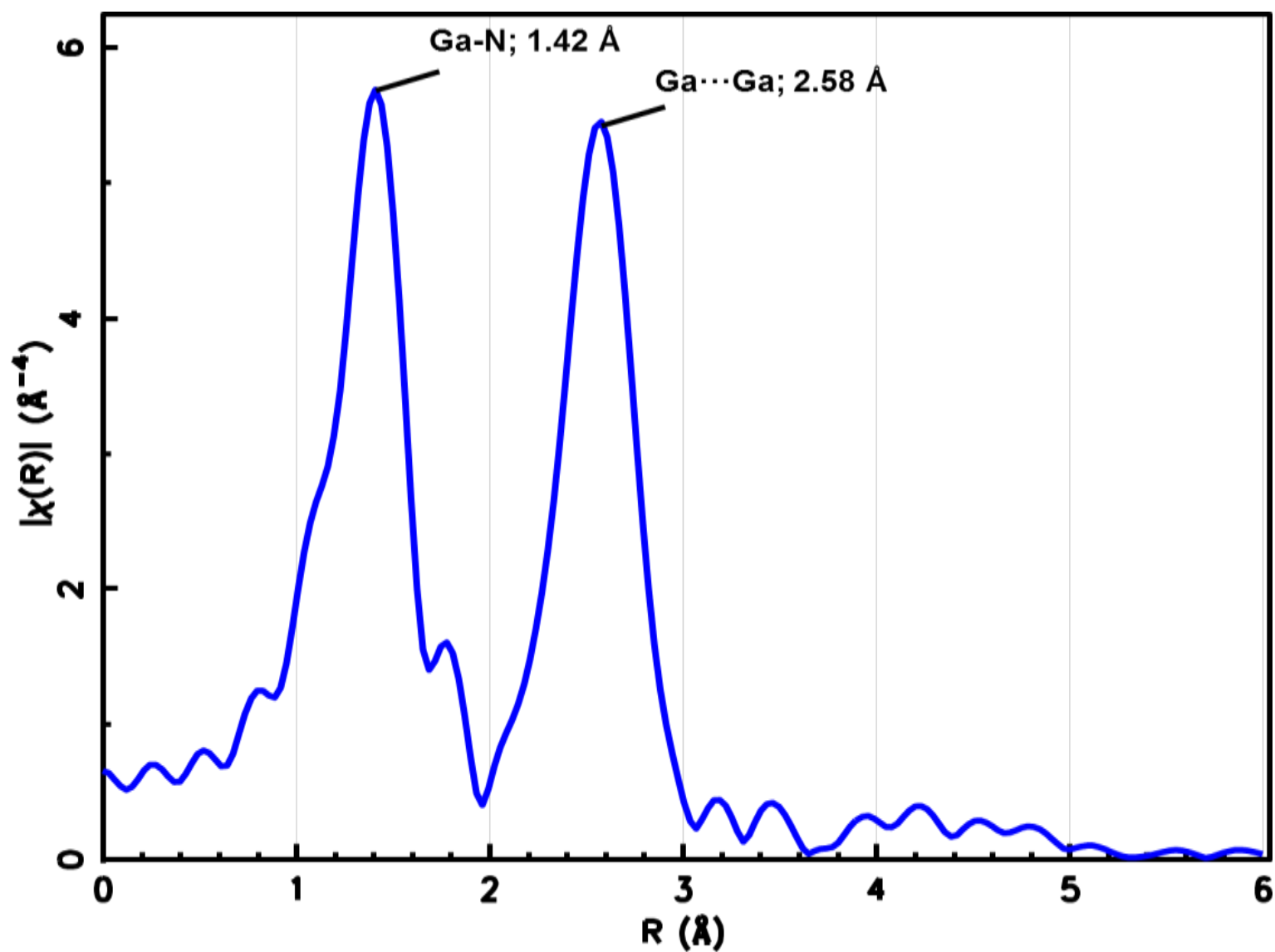


Figure 3.12: R space plot of $[(\text{NMe}_2)_3\text{Ga}]_2$ dimer showing Ga...Ga feature

3.3.2 One Dose Embedded Gallium Catalysts Starting From GaCl₃·Py

Reaction of GaCl₃·Py with the tin cube was expected to proceed in a very similar fashion to that of the analogous reaction using AlCl₃·Py. As was the case previously, none of the secondary byproduct Me₄Sn should be produced and the reaction should proceed as follows (Equation 3.4). Reactions were carried out in toluene at 80-100 °C



for 6 – 48 hours. Upon transfer of solvent and warming, the gallium trichloride pyridine adduct was completely solubilized. After reaction and removal of the volatile byproducts, gravimetric analysis showed that 2.7 equivalents of tin were lost. Analysis of the volatiles for this sample was not carried out, however, based on what has previously been seen with Al, it can be inferred that little to no tetramethyltin was formed during the course of the reaction.

The IR spectrum (Figure 3.13) of these samples show expected Si-O-Si modes in the 850 – 1250 cm⁻¹ range, methyl C-H bands below 3000 cm⁻¹. This is similar to both the aluminum analogue and the embedded GaCl₃ sample. This spectrum has a very clean –OH region, and when the pyridine bands from 1400-1700 cm⁻¹ are analyzed, it is once again apparent that evidence for only Lewis acidic binding of pyridine is observed. The C-C stretching frequencies (1456 & 1619 cm⁻¹) associated with pyridine bound to Lewis acidic sites are prominent. The sample has no Brønsted acid bound pyridine based on a lack of bands at 1545 and 1640 cm⁻¹.

The ¹³C CPMAS SSNMR is of more interest in this case as there is some evidence for the presence of pyridine in the sample (Figure 3.14). The ¹³C spectrum of pyridine should have three signals. There are two visible here, and the third is likely being covered up by the large feature that results from the Teflon endcap in the NMR rotor. Just as in the non-pyridine adduct, the main methyl feature at δ = -2.3 ppm does not appear to have any significant shoulder or secondary feature. The silicon spectrum (Figure 3.15) once again shows the presence of a second feature that is associated with the silicon centers near gallium (Si-O-Ga, δ = -106.7 ppm) in addition to the remaining

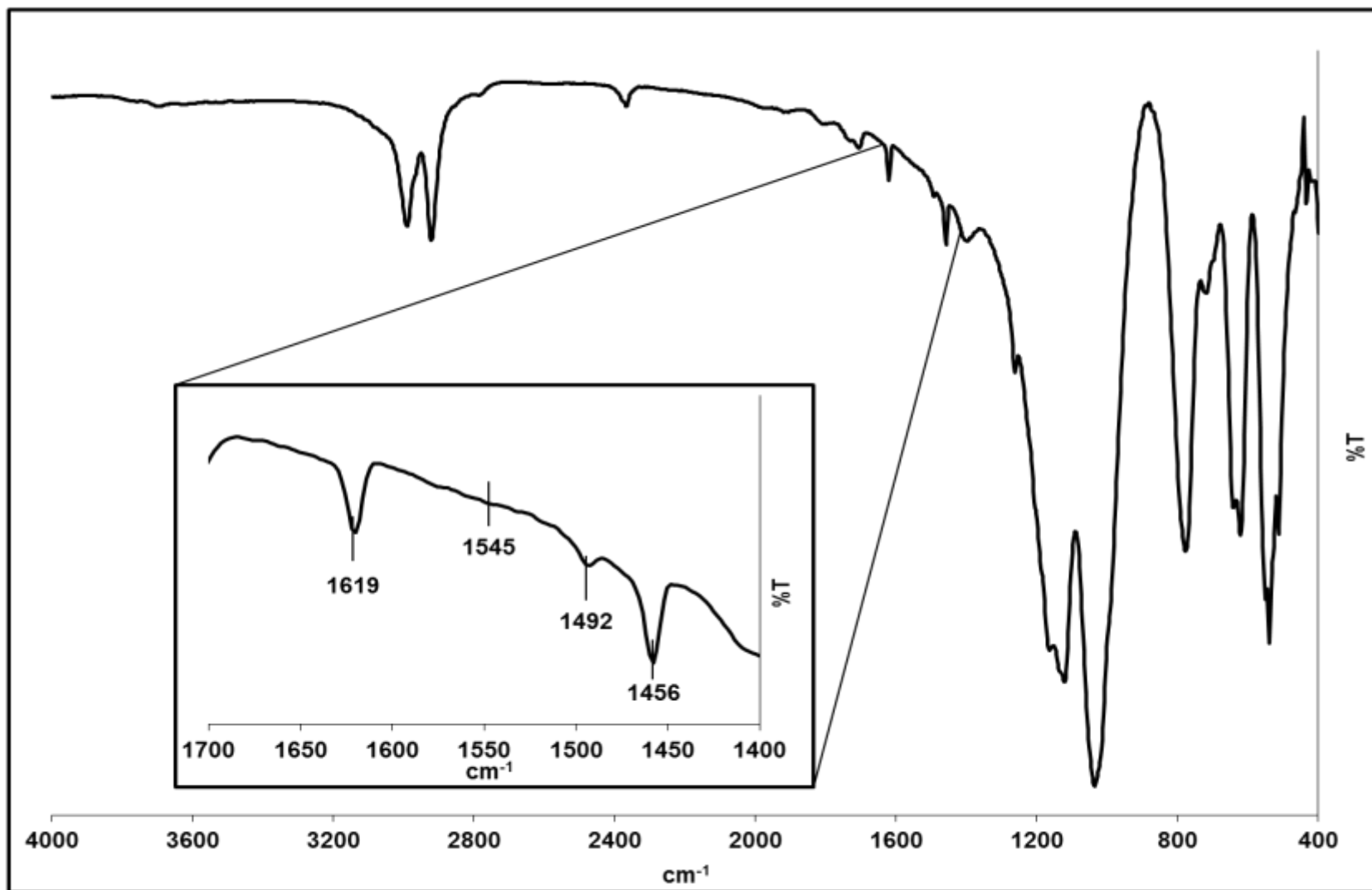


Figure 3.13: IR spectrum of embedded Ga-Py sample (from $\text{GaCl}_3\cdot\text{Py}$) with absorbed pyridine and bound pyridine C=C stretching region (inset)

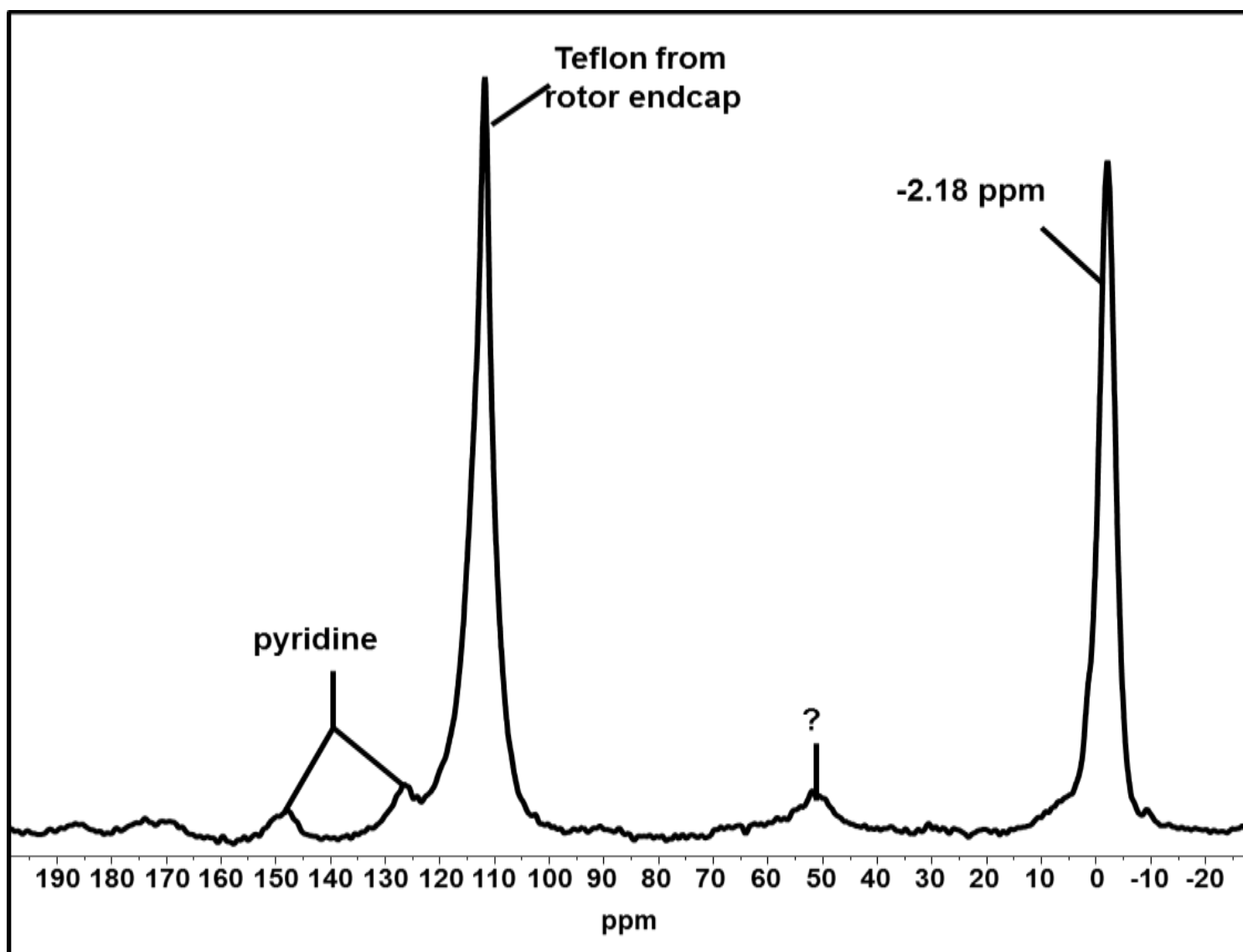


Figure 3.14: ^{13}C MAS SSNMR of Embedded Ga·Py (from $\text{GaCl}_3\cdot\text{Py}$) catalyst

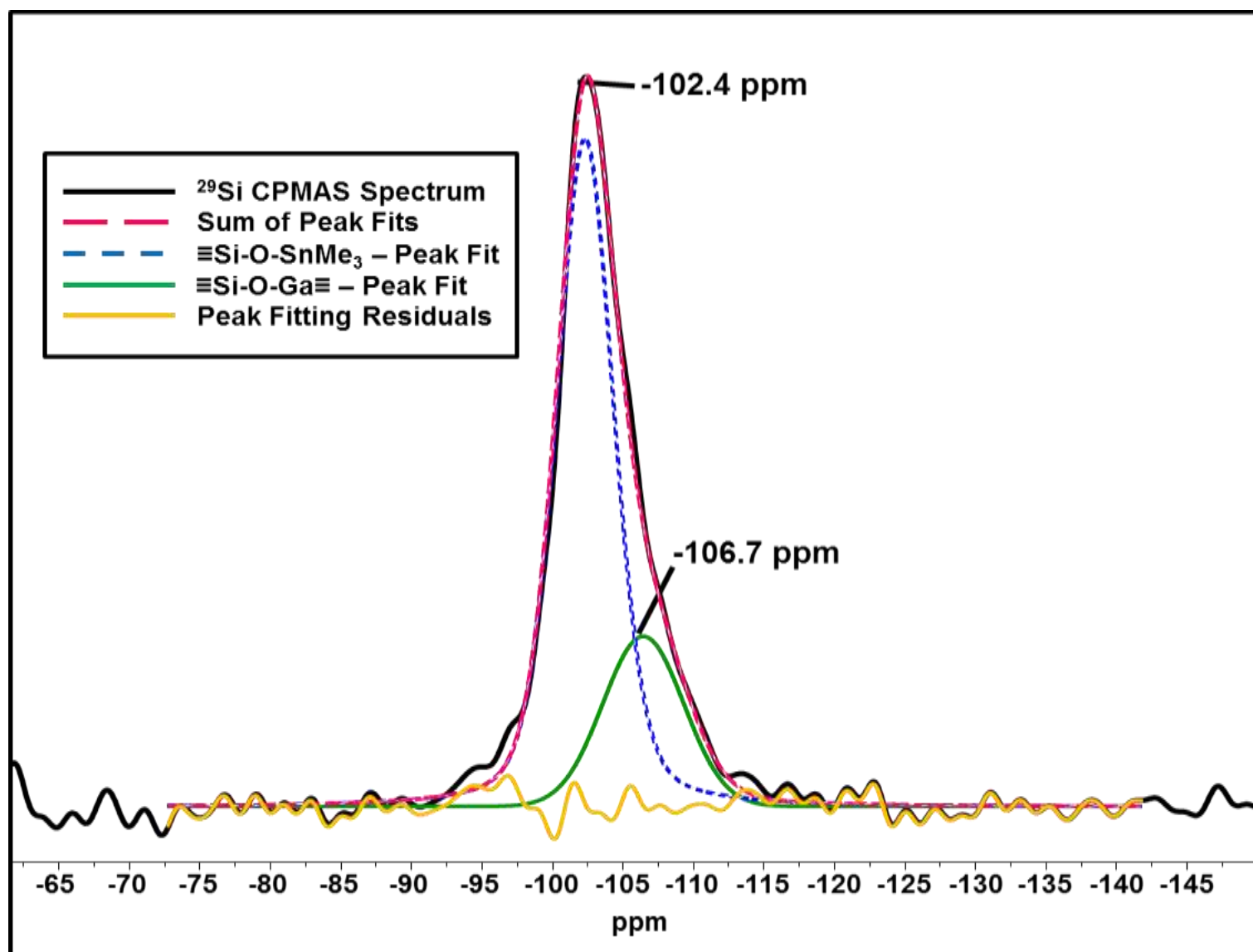


Figure 3.15: ^{29}Si CPMAS SSNMR of embedded $\text{Ga}\cdot\text{Py}$ (from $\text{GaCl}_3\cdot\text{Py}$) catalyst

SiO-SnMe₃ groups ($\delta = -102.6$ ppm). The small upfield feature present in the previous sample is not observed in this case.

The XANES spectrum for a 1-dose embedded GaCl₃·Py sample (Figure 3.16) shows only one primary feature near the ionization edge. The ionization edge comes at 10373 eV with the white line edge feature occurring at 10375 eV. As in the GaCl₃ embedded sample, these are indications of a tetrahedral Ga(III) center. The general shape of the edge is significantly different from that seen in the sample prepared from GaCl₃, and in fact is quite similar in the initial edge structure of the pure GaCl₃·Py precursor (10360-10390 eV; Figure 3.17). Only as the EXAFS oscillations begin (beyond 10390 eV; $k=2.5$) do differences between the two become very apparent.

Figures 3.18 and 3.19 show the k and R -space plots for the embedded pyridine adduct sample. A larger k range was usable for this sample, and the resultant R space plot shows improved resolution relative to the sample above. Excluding the low R artifact, there appear to be two features of possible interest with regards to the first coordination sphere. These occur at 1.40, 1.81, and 2.54 Å (uncorrected) respectively. The peak at 1.4 Å is clearly the Ga-O feature that once phase shifting is applied will be in the expected range of 1.8 Å. Initially, the feature at 1.81 Å was believed to be associated with the interaction of pyridine with the Ga center, however, a final bond distance after phase adjustment would be on the order of 2.2 Å which is too long based on comparisons with similar GaCl₃ adducts with nitrogen bases. While the crystal structure for GaCl₃·Py has not been reported, it is difficult to believe that the Ga-N bond would be longer than the 2.05 Å distance seen in the more sterically hindered GaCl₃·(2,6-Ar₂C₆H₃N) analogue (Ar = 2,4,6-Pr₃C₆H₂).¹³²

Since the actual distance of the Ga-N bond in this system is not well known, the distance was estimated to be 1.95 Å (Figure 3.20) in the initial model for fitting the experimental spectrum. After fitting the EXAFS data using theoretical phase and amplitude factors generated by FEFF6L based on this initial model, the individual backscattering path profiles could be examined. Figure 3.21 clearly shows that the EXAFS feature for the Ga-N bond does not match the peak position or profile for the feature observed at 1.81 Å. The Ga-N feature is weaker, and is in fact not well resolved

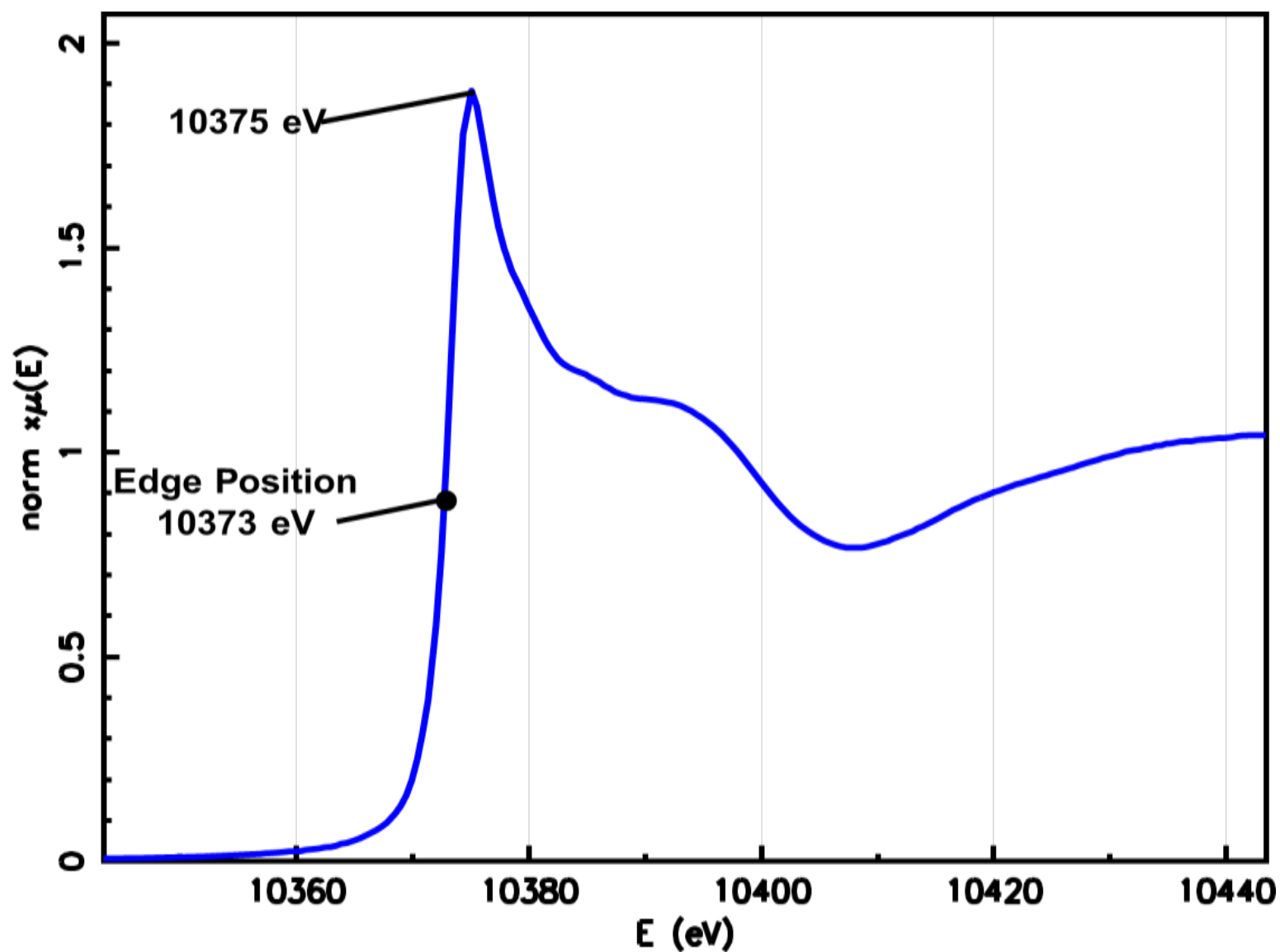


Figure 3.16: XANES spectrum for embedded Ga·Py catalyst (from GaCl₃·Py)

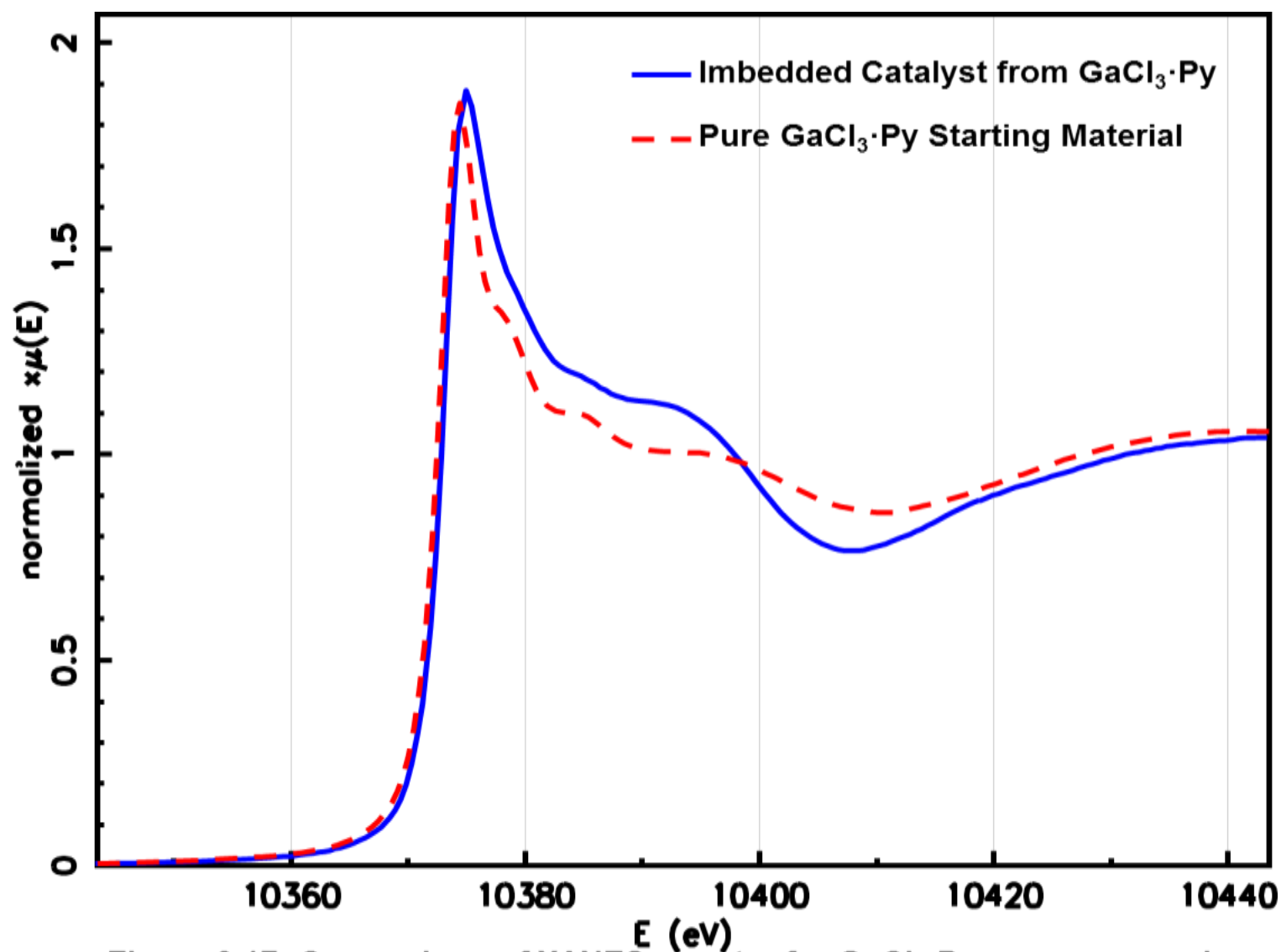


Figure 3.17: Comparison of XANES spectra for $\text{GaCl}_3 \cdot \text{Py}$ precursor, and $\text{Ga} \cdot \text{Py}$ embedded catalyst

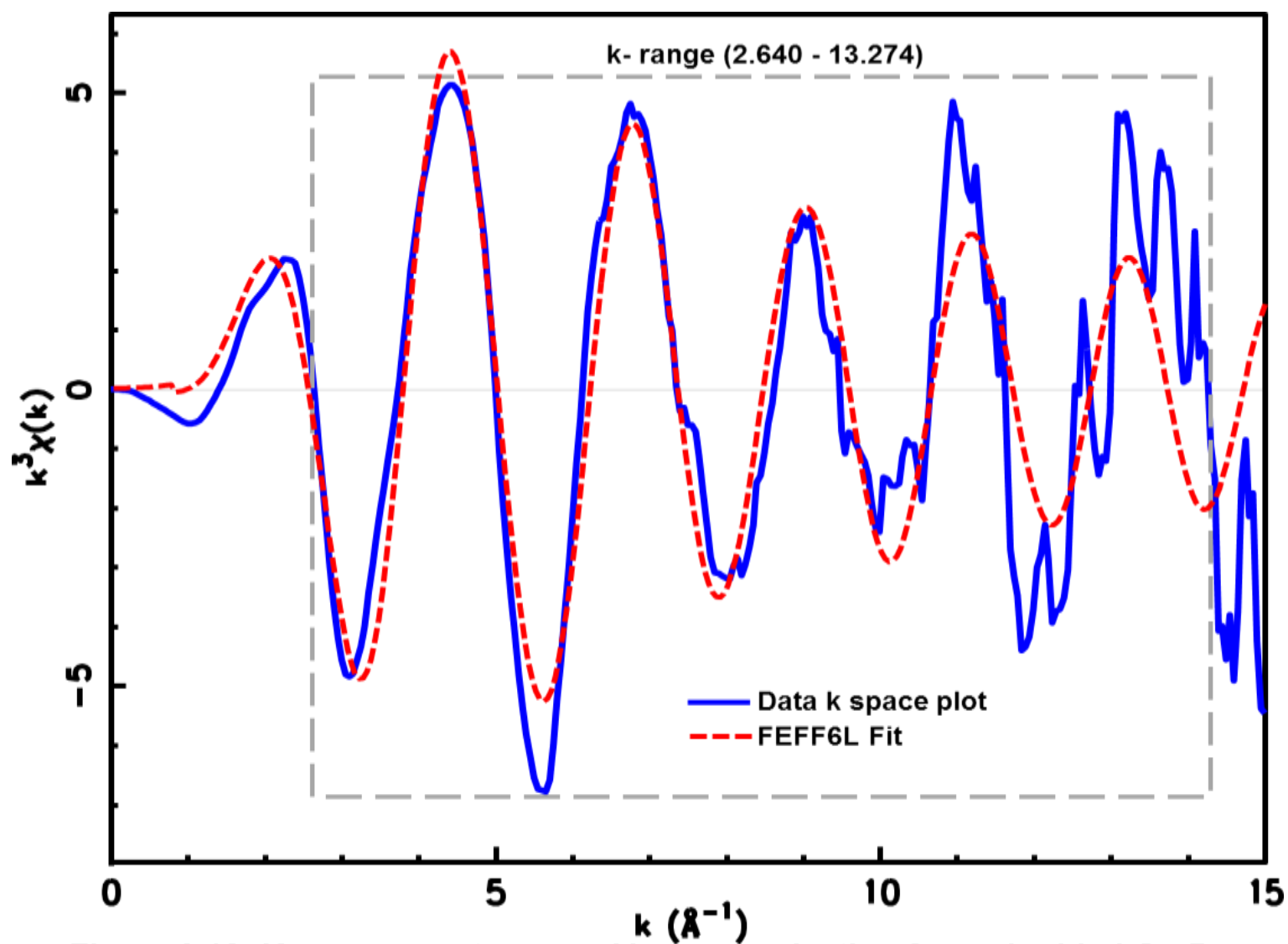


Figure 3.18: K space spectrum, and k-range selection for embedded Ga·Py catalyst (from $\text{GaCl}_3\cdot\text{Py}$), and modeling fit

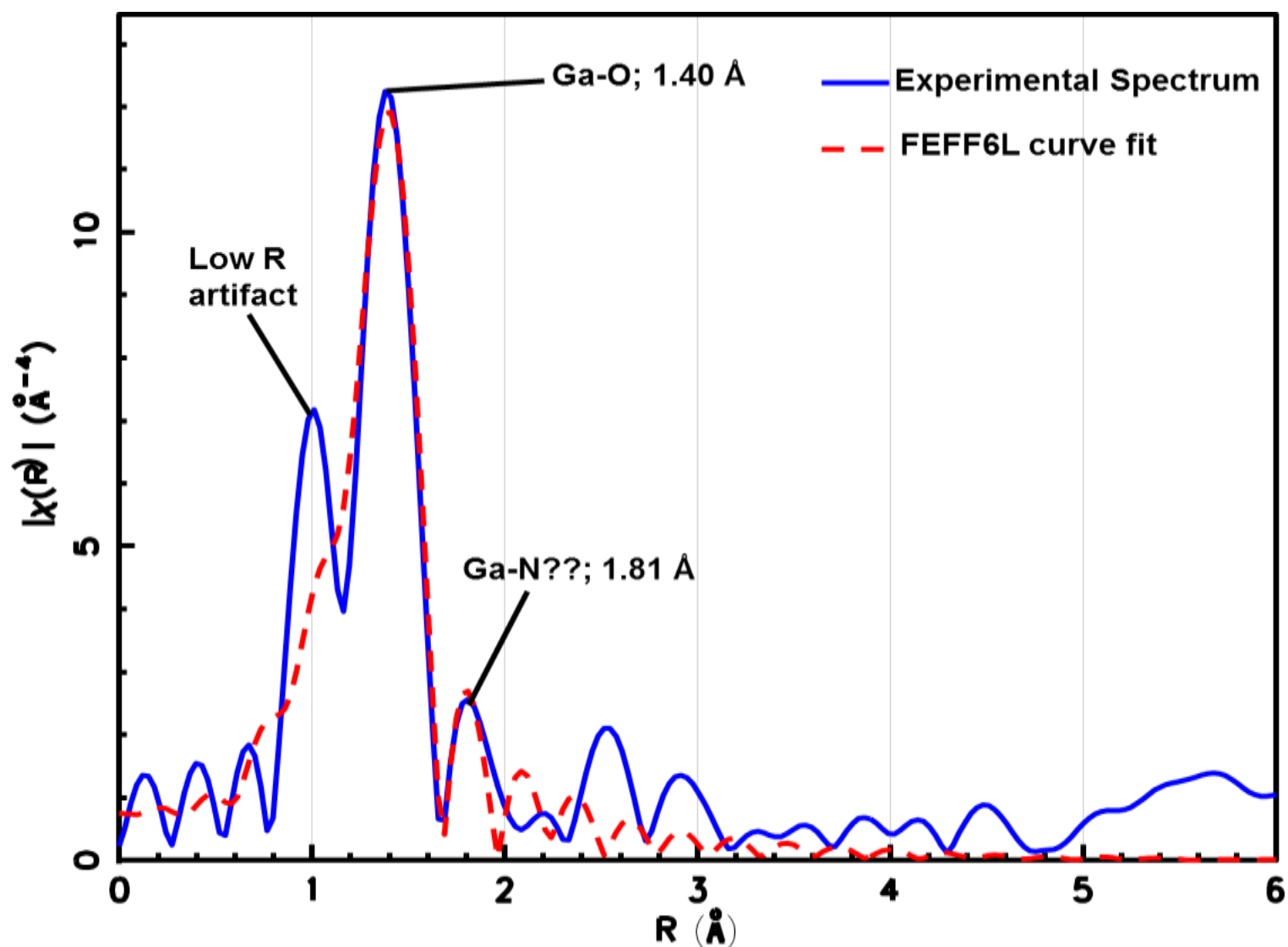


Figure 3.19: R space plot embedded Ga-Py catalyst (from $GaCl_3 \cdot Py$) with modeling fit

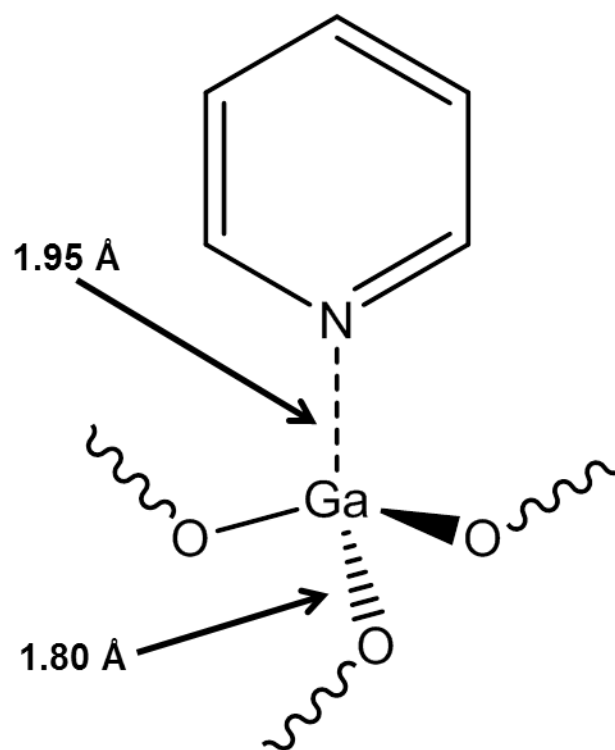


Figure 3.20: Embedded Ga·Py model for EXAFS fit

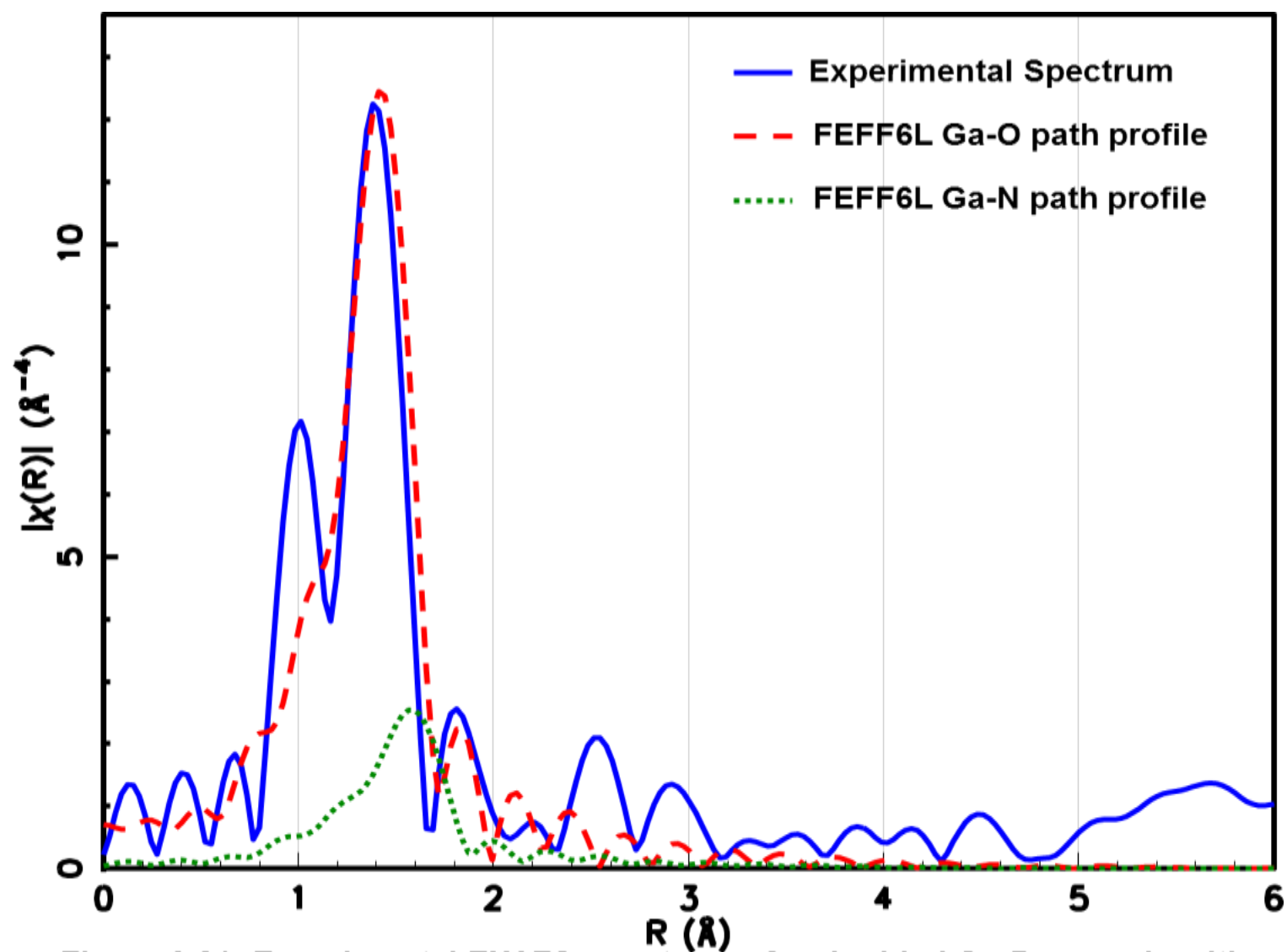


Figure 3.21: Experimental EXAFS spectrum of embedded Ga·Py sample with FEFF6L model path profiles

Table 3.3: EXAFS model fitting parameters for embedded Ga·Py species (from GaCl₃·Py)

Parameter	Fit Values O	Fit Values N
N	3.0(2)	1.1(5)
S_0^2	0.99(24)	
σ^2	0.003(1)	0.004(3)
R[ΔR]	1.80 [0.003(10)]	1.95 [0.04(6)]
E ₀	2.4(2.0)	
R factor	0.078	

from the primary Ga-O peak. Upon creating the model, the fit parameters were optimized as described above to yield the over fit seen in Figure 3.19. Once again, a very high quality fit to the experimental data was found. The final bond lengths for the Ga-O and Ga-N bonds were found to be 1.80 and 1.95 Å, respectively. The values for coordination numbers were also quite reasonable. A summary of the fit parameters is found in Table 3.3.

3.3.3 One Dose Embedded Gallium Catalysts Starting From [Me₃Sn][GaCl₄]

As previously mentioned, attempts to synthesize and isolate the gallium analogue of [Me₃Sn][AlCl₄] were unsuccessful. The aluminum species is synthesized by simple addition of a toluene solution of Me₃SnCl, to a slurry of AlCl₃ in toluene. When the reaction is complete, the solvent is removed under vacuum. When the same procedure is followed for the gallium species, a dark viscous impure liquid with multiple –Me₃Sn signals in the proton NMR is obtained. There was however some evidence in

the solution ^{71}Ga NMR for the formation of the GaCl_4 anion. As a result, the $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$ (Equation 3.5) precursor was prepared and reacted with the tin cube *in*



situ. A 1 : 1 mixture of Me_3SnCl and GaCl_3 was prepared in toluene, followed by the addition of tin cube. The reaction was carried out in toluene at 80 °C for 48 hours. Gravimetric analysis of the reaction product indicated the loss of 3.7 eq of tin. Analysis of the volatiles for this sample was not carried out, but it is assumed that significant amounts of tetramethyltin were produced in addition to Me_3SnCl .

XAS methods were the only type of characterization carried out on this sample. The XANES spectrum for the 1-dose embedded $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$ catalyst (Figure 3.22) shows a broadened feature at the top of the ionization edge. The ionization edge comes at 10373 eV with the white line edge feature occurring at 10376 eV. Once again, these indicate a tetrahedral Ga(III) center. The general shape of the edge is somewhat intermediate between the GaCl_3 , and $\text{GaCl}_3\cdot\text{Py}$ systems, though the broadness of the white line is more similar to the former (Figure 3.23). Though this sample does not contain the resolved double peak pattern seen for the embedded site derived from GaCl_3 , the broadness of the feature in this sample is more similar to that sample than to the embedded $\text{GaCl}_3\cdot\text{Py}$ catalyst.

Selection of the k range can be seen in Figure 3.24. The R space plot (Figure 3.25) once again has a low R artifact at 1.00 Å. Based on the analysis of the previous sample the small feature at 1.95 Å is assumed to be a Fourier ripple associated with the Ga-O backscattering path, while the peak at 1.41 Å, is assigned to O bound to the Ga center. This appears to be the only peak present in this sample. From this observation, it is evident that all chloride ligands on the gallium centers were lost in the reaction with the trimethyltin groups of the cubic building block. Because of the strong similarities between the catalyst synthesized from GaCl_3 and this sample, the same model was used with only a single shell of oxygen atoms at bond distance of 1.8 Å (Figure 3.11). The fit parameters were optimized as described above. Once again, a high quality fit to the experimental data was found (Figure 3.25). The final bond length for Ga-O was

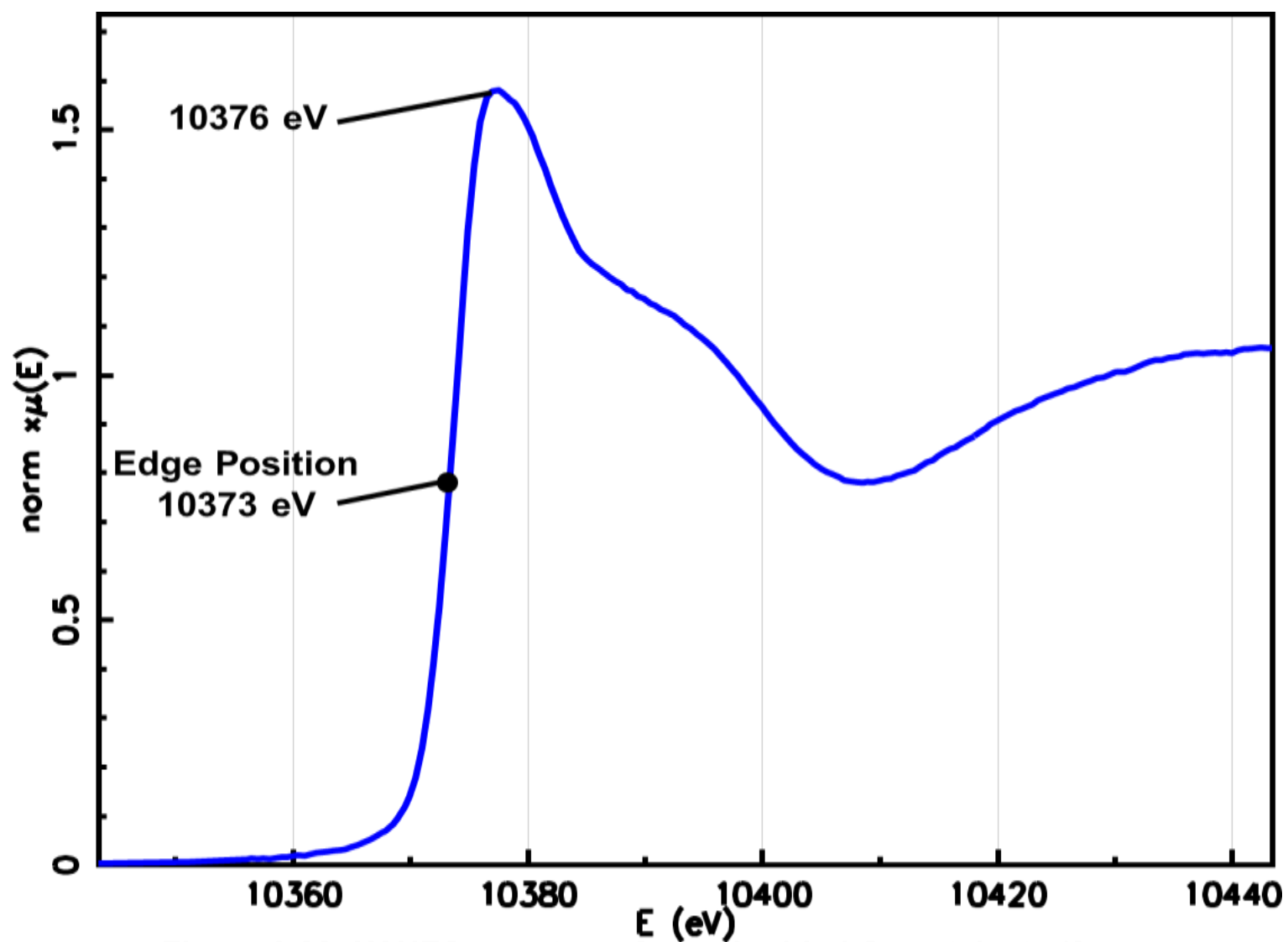


Figure 3.22: XANES spectrum for embedded Ga catalysts (from $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$)

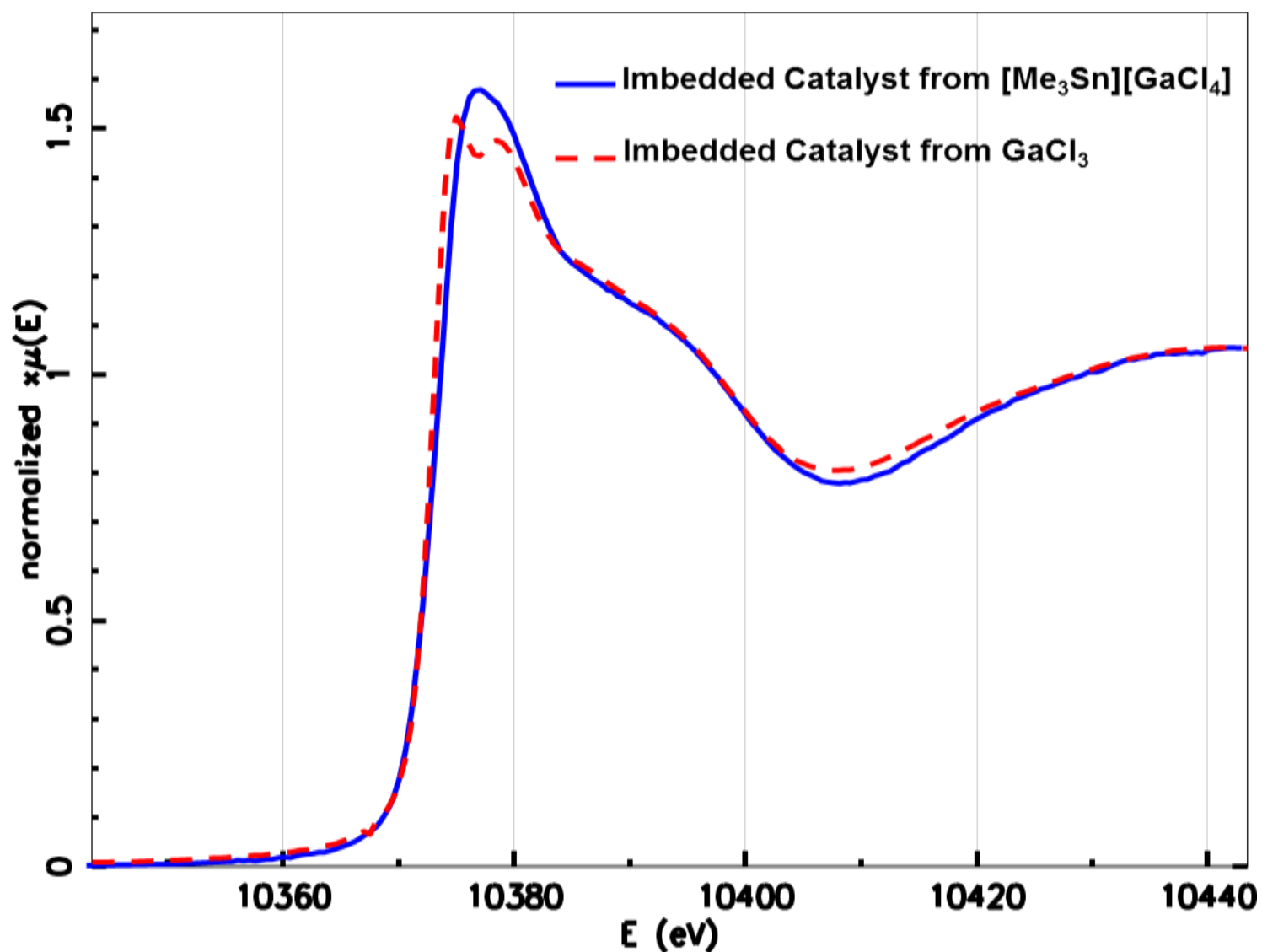


Figure 3.23: Comparison of XANES spectra for embedded Ga catalysts from GaCl_3 and $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$

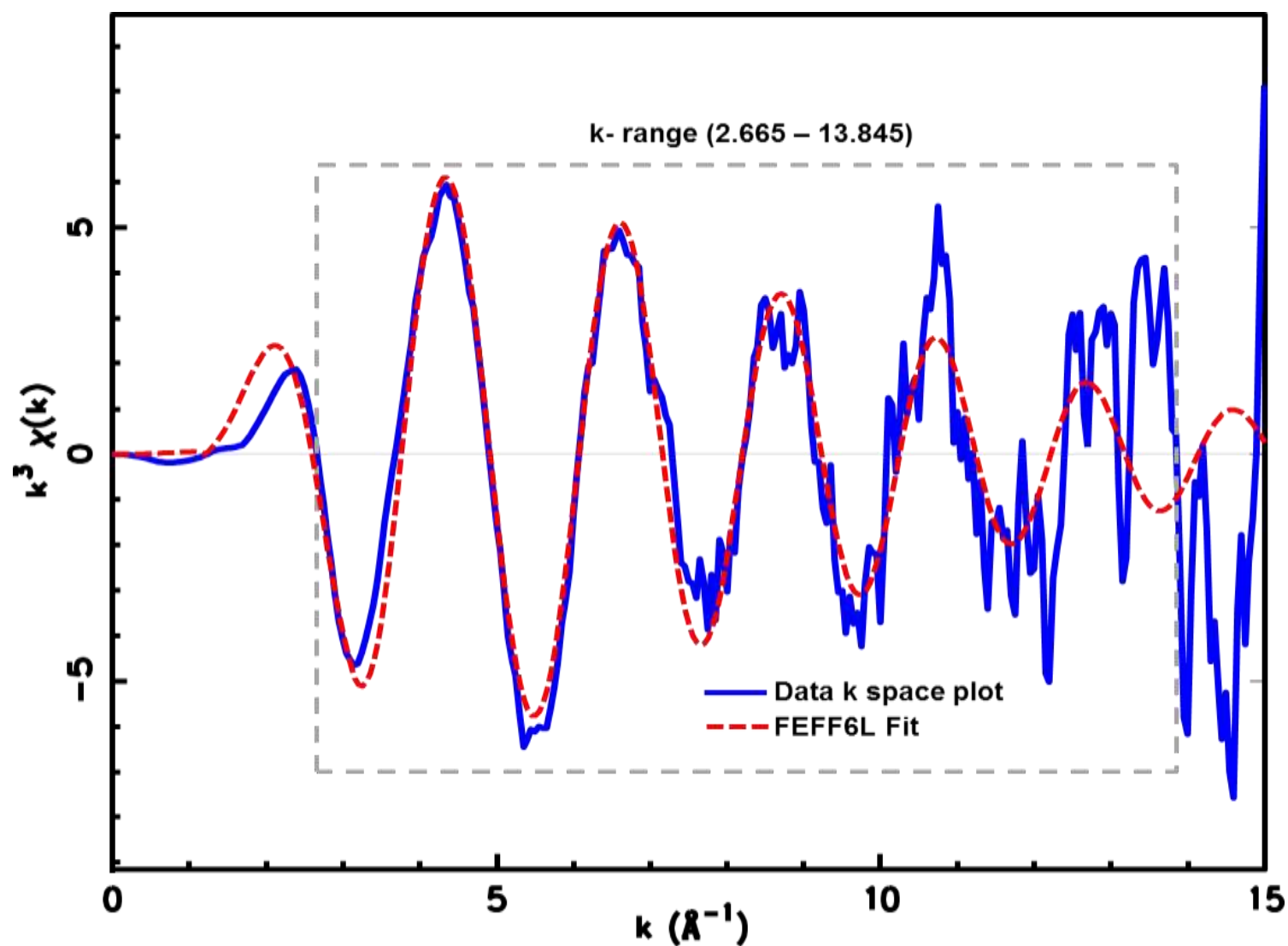


Figure 3.24: K space spectrum, and k-range selection for embedded Ga catalyst (from $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$), and modeling fit

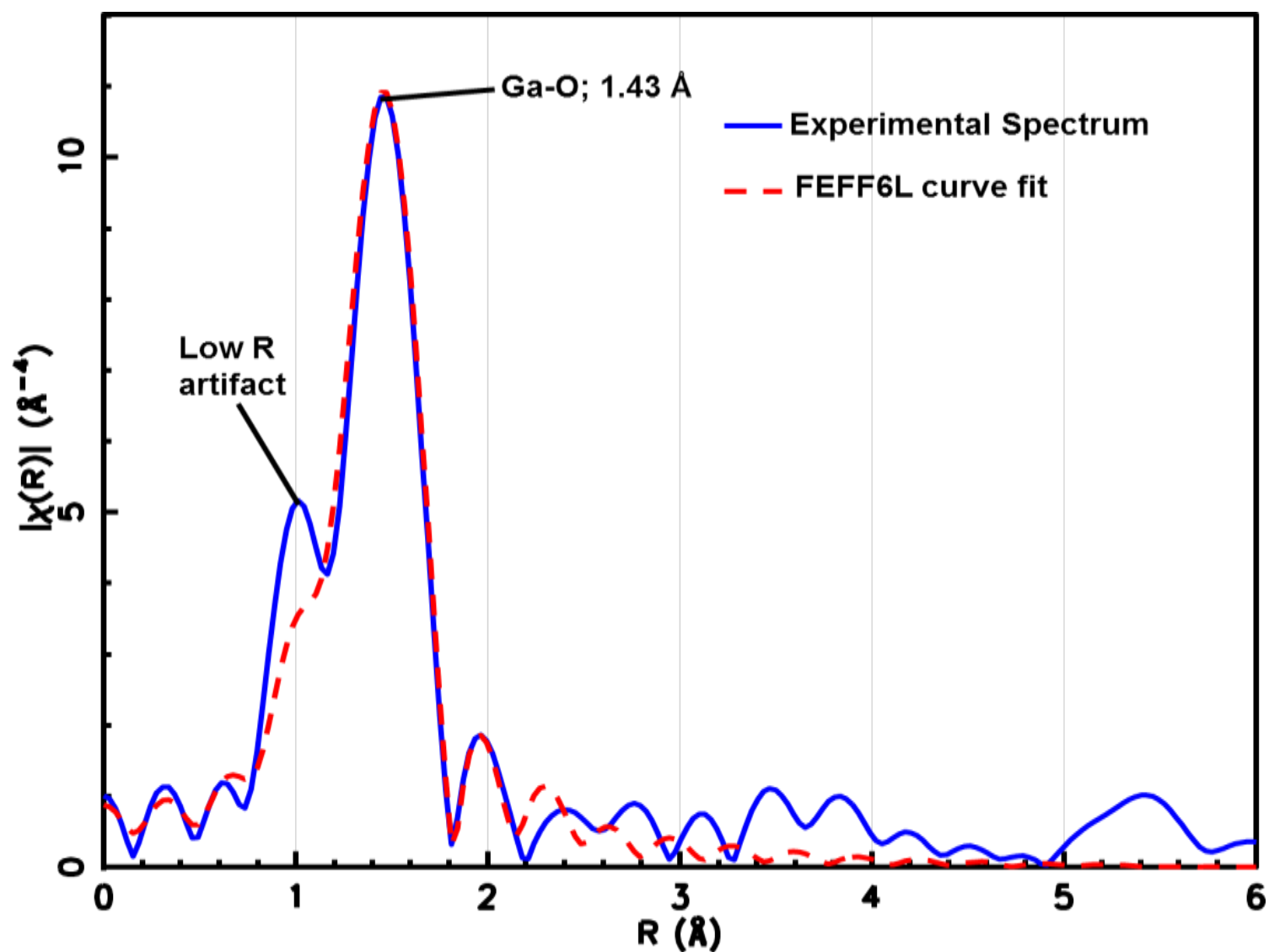


Figure 3.25: R space plot for embedded Ga catalyst with modeling fit (from $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$)

Table 3.4: EXAFS model fitting parameters for embedded Ga catalyst (from [Me₃Sn][GaCl₄])

Parameter	Fit Values
N	4.0(2)
S ₀ ²	0.93(5)
σ ²	0.005(1)
R[ΔR ₀]	1.86 [.07(1)]
E ₀	5.43(1.39)
R factor	0.035

found to be 1.86 Å, nearly identical to that of the GaCl₃ sample. The value for coordination numbers was found to be 4, just as expected. All of the fit parameters can be seen in Table 3.4.

3.3.4 The Nature of the Gallium Centers in Embedded Catalysts

While the characterization techniques with regard to the aluminum centers described in Chapter 1 left some ambiguity with respect to the nature of the final catalytic site, the XAS techniques available for characterizing the gallium analogues has been much more revealing and conclusive. The gallium centers embedded in the three Si₈ building block matrices described above have all been found to exist as Ga(III) centers in tetrahedral coordination environments (Figure 3.26). It appears that in all of these cases, the centers reacted completely to form tetrahedra with no remaining unreacted chloride ligands remaining.

It is very illuminating to note that the species obtained by starting with the two precursors GaCl₃ and [Me₃Sn][GaCl₄] are nearly identical. This gives strong support to

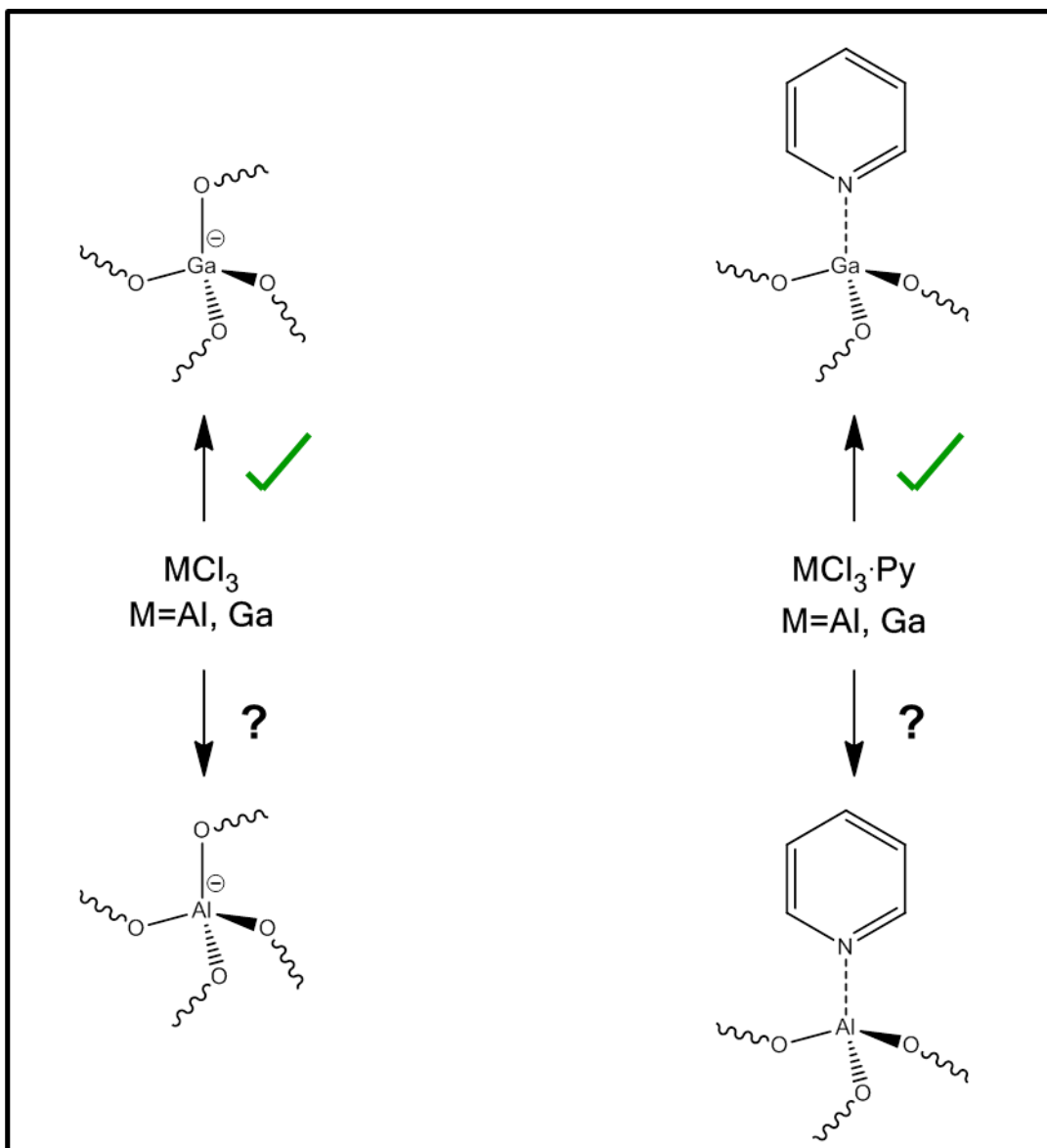


Figure 3.26: Imbedded gallium centers & possible Al analogues

the belief that the GaCl_3 starting material undergoes reaction *in situ* to form the $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$ ion pair in the course of reacting with the trimethyl tin building block.

This of course also has implications with regards to the nature of the catalytic sites in the aluminum analogues (Figure 3.26). If Al and Ga react similarly, then the XAS data collected for the gallium species implicates that AlO_4 sites are the preferred geometry and final species present in those analogues.

3.3.5 Two and Three dose embedded Gallium catalysts

As indicated in Chapter 1 for the newly synthesized aluminosilicate catalysts, there are two primary reasons for carrying out second or third dose reactions. The second dose reactions are typically used to increase crosslinking in the matrix to make for a more robust catalyst matrix with higher surface area. The third dose is used to remove as much of the remaining trimethyltin groups as possible.

Deciding how much chlorosilane to add to achieve a high surface area material has been studied in our group previously,⁸⁷ but the effect of such reactions on the metal centers is an important issue that cannot be overlooked or ignored in the context of their intended use as catalysts. There has always been some concern with regards to rechlorination of the metal centers, in effect beginning to remove the embedded centers from the matrix (i.e. leaching) in the second and third dose reactions. Furthermore, creating a matrix where a large number of (M,Si)-Cl bonds exist opens the door for hydrolysis to form HCl. The question of the nature of these reactions, and their subsequent effects on the the metal sites was explored by collection XAS data on embedded Ga catalysts that had been treated with secondary doses of SiCl_4 and Me_3SiCl .

Figure 3.27 shows the R space plots of three gallium catalysts. The first is the 1-dose embedded gallium catalyst synthesized from GaCl_3 that was modeled to be a tetrahedral GaO_4 center. The second and third samples contain embedded gallium sites that have been treated with a 2nd dose of Me_3SiCl , or SiCl_4 . Inspection of the plot indicates that the second dose treatment with Me_3SiCl does not have a significant impact on the nature of the gallium centers. The Ga-O feature remains the only peak,

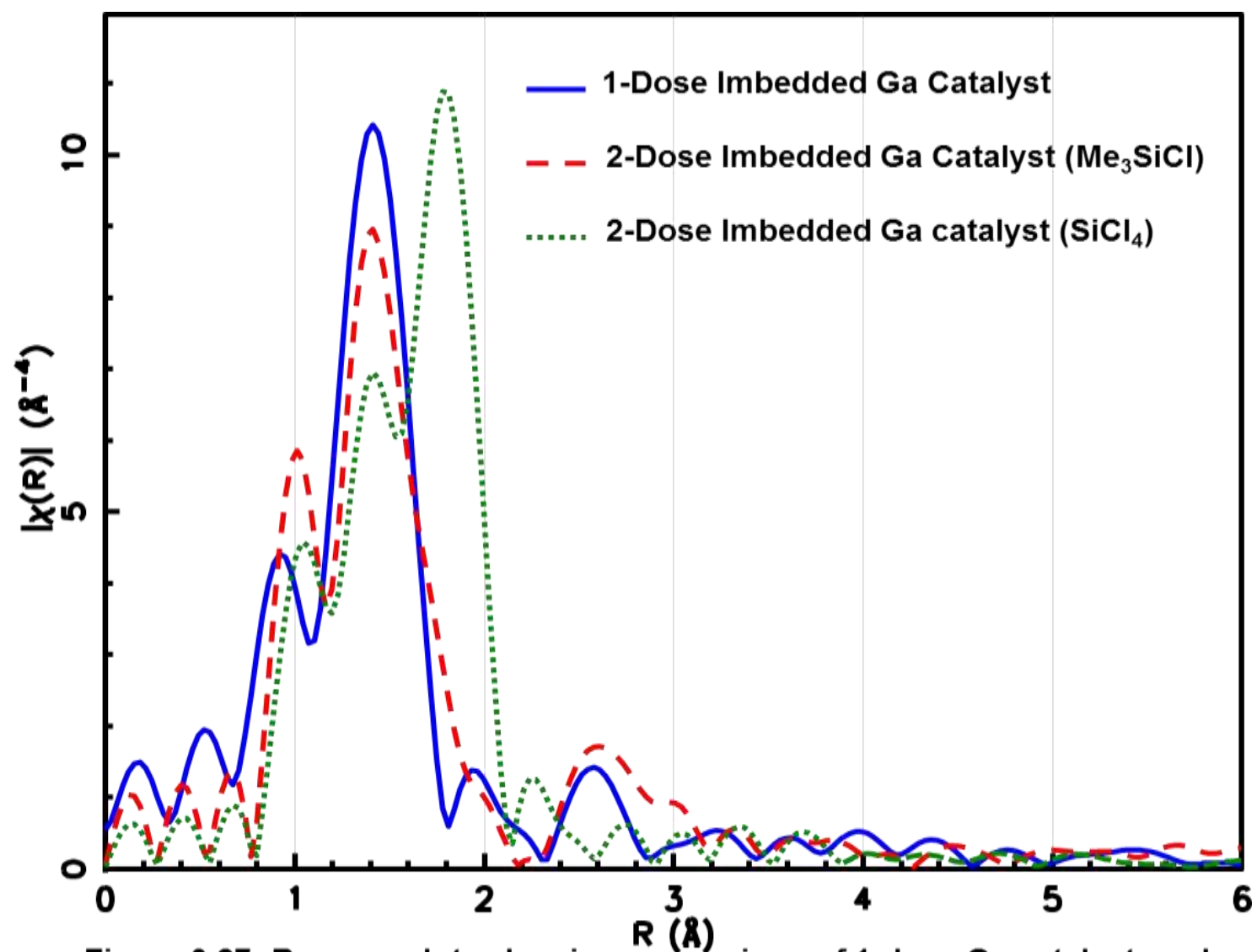


Figure 3.27: R space plots showing comparison of 1-dose Ga catalyst, and 2-dose catalysts with second doses of SiCl_4 or Me_3SiCl

though it is somewhat broadened. On the other hand, the reaction of the 1-dose catalyst with SiCl_4 appears to result in significant changes to the gallium center. In this case a strong Ga-Cl peak is now present in the R space plot consistent with rechlorination of the gallium centers. In a sense, what were once embedded 4-connected gallium centers now exist as a distribution of sites with lower connectivity to the matrix (i.e. 3, 2, or 1).

This same trend is evident in the case of the materials synthesized from $\text{GaCl}_3 \cdot \text{Py}$ (Figure 3.28). For this sample the Me_3SiCl second dose reaction once again appears to have almost no effect on the gallium centers, but the reaction with SiCl_4 still produces a large number of Ga-Cl bonds in effect starting to leach the gallium centers from the matrix. Attempts to quantify the degree to which chlorination of the gallium centers has progressed were made by trying to model the data and obtain average coordination values for Ga-O vs Ga-Cl. These attempts were unsuccessful as reasonable fits to the data with satisfactory statistics could not be obtained.

In trying to understand why this might be occurring, it is informative to look at the full picture of the reaction that is occurring. If a Ga-Cl bond is being formed, then there must also be a $\text{Cl}_3\text{Si-O}$ bond forming (Figure 3.29). Going back and looking at the initial metathesis reaction (Equation 3.1) the primary driving force is believed to be the formation of the M-O bond. However, for gallium, the Ga-O bond is actually weaker than that of a Ga-Cl bond.¹³³ In addition, the Sn-O bond is stronger than that of the Sn-Cl bond. These are the bonds being broken and formed in the initial metathesis reactions, and these values seem to imply that the thermodynamic stability of the starting materials (GaCl_3 & $-\text{OSnMe}_3$) is higher than that of the products (GaO_4 & Me_3SnCl). The values used to determine this are average values for a wide variety of A-B bond types,¹³³ and cannot be applied in an exact manner to these samples, however, at the very least they raise some concern regarding the stability of the gallium centers towards rechlorination. The bond energy values for the gallium rechlorination reaction that might occur when a second dose of silyl chloride is introduced indicate a thermodynamically favorable process based on the increase in stability that arises from creation new Si-O and Ga-Cl bonds.

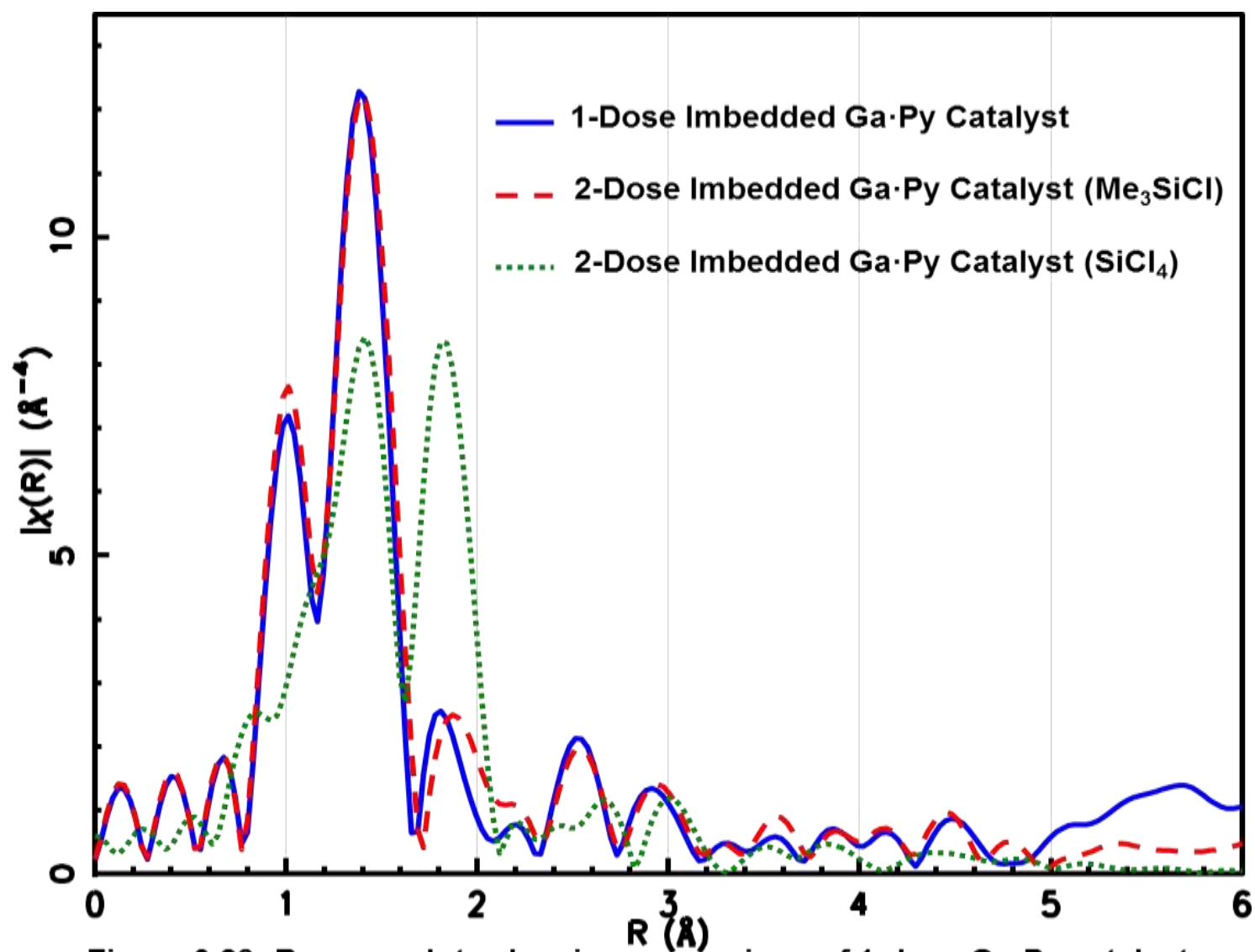
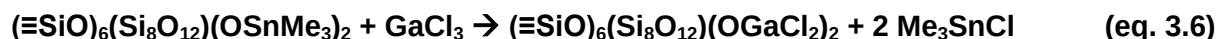


Figure 3.28: R space plots showing comparison of 1-dose Ga-Py catalyst, and 2-dose catalysts with second dose of SiCl_4 or Me_3SiCl

3.3.6 Two Dose Surface Gallium Catalysts Starting from GaCl₃

For preparation of the surface gallium species, it was first necessary to prepare a rigid cross-linked matrix (platform) wherein all remaining tin groups have become spatially isolated from one another. This ensures that in subsequent reaction of the platform with a metal chloride that only one chloride on each metal center can react, in theory producing a 1-connected three coordinate surface species (Equation 3.6). The reaction to create the platform substrate utilized a 3.0 : 1 ratio of SiCl₄ : TMT cube and achieved a connectivity of 1.8. This left ~2.5 isolated unreacted trimethyltin groups on each cube.



Once the trimethyltin chloride byproduct was removed and the platform dried, toluene was added in addition to a limiting 0.8 equivalents of GaCl₃. The solution was then stirred at 80-100°C for 16-48 hours, followed by removal of the volatiles and drying. Analysis of the volatile byproducts of the second dose reaction with GaCl₃ showed only the byproduct Me₃SnCl. Gravimetric analysis yielded an average connectivity of 1.3.

Based on the susceptibility of the embedded gallium species to leaching, the general stability of this sample was in doubt. This sample was prepared solely as a conformation of the sequential addition proof of concept, and with the exception of gravimetric analysis, the only other characterization carried out was XAS spectroscopy.

The XANES spectrum (Figure 3.30) in this instance appears similar to that of the pure GaCl₃, and does not present the double feature seen for the fully embedded material from the same precursor. As has been seen in all of the gallium samples, the edge position is 10373 eV. An appropriate k range was chosen (Figure 3.31) and transformed to create the subsequent R space plot (Figure 3.32). The low R artifact is less prominent here, and the Ga-O and Ga-Cl features are not clearly resolved. Because it is highly unlikely that the Ga centers are in a trigonal geometry, a tetrahedral model for this spectrum (Figure 3.33) was chosen to have a Ga-O bond length of 1.8 Å, and a Ga-Cl bond length of 2.1 Å. As the gravimetric analysis implies some mixture of

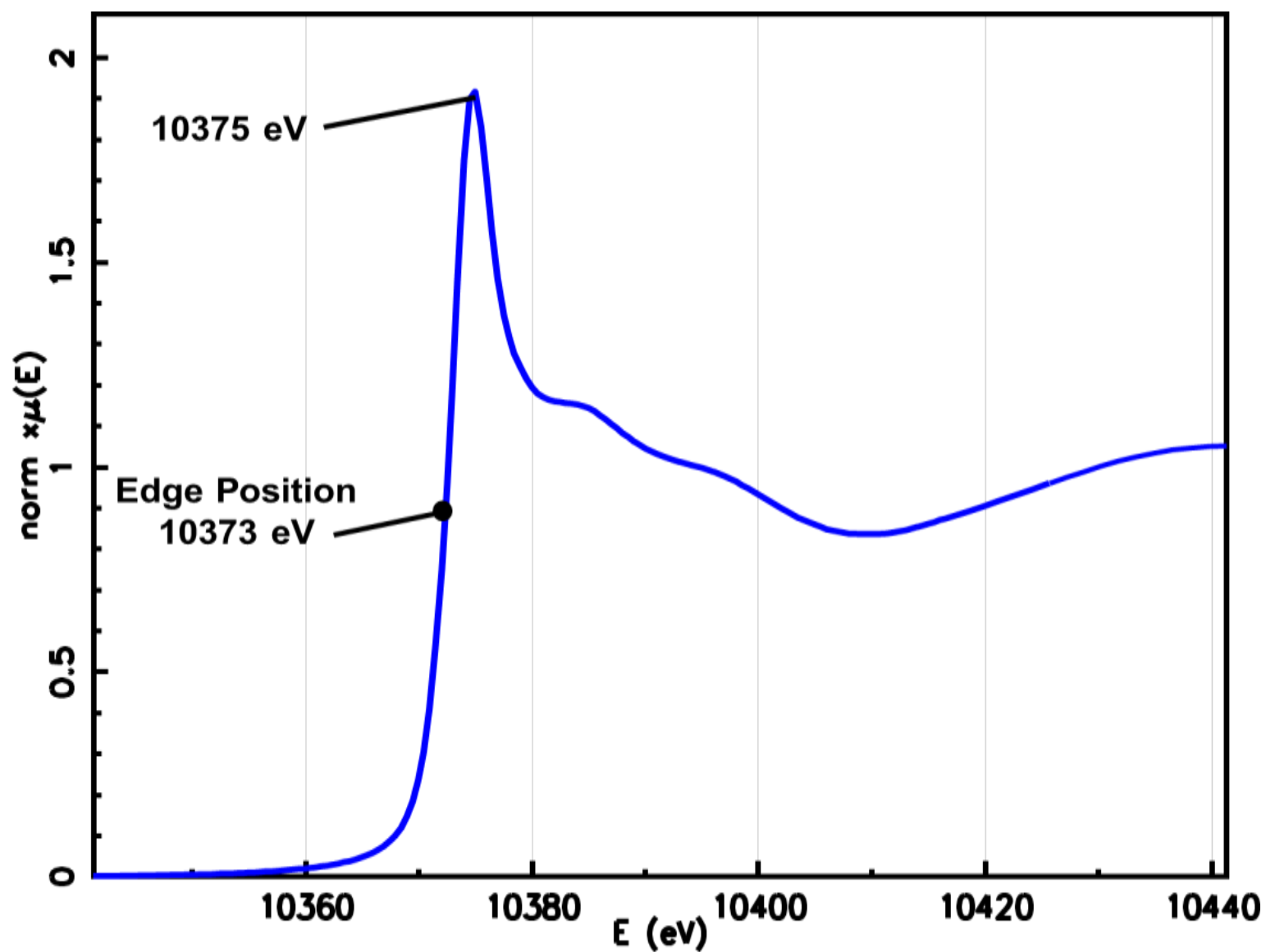


Figure 3.30: XANES spectrum for surface Ga catalyst (From GaCl_3)

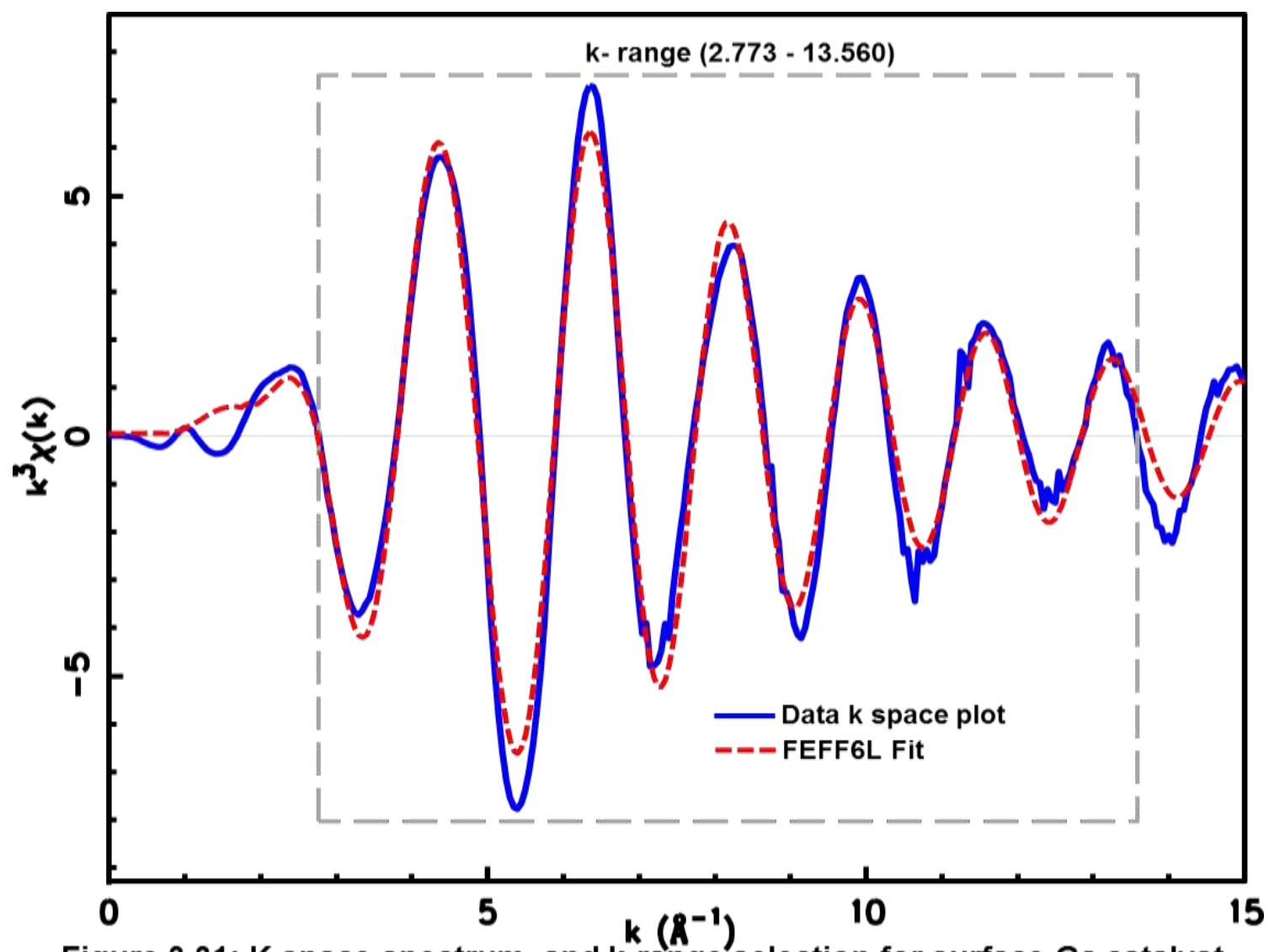


Figure 3.31: K space spectrum, and k-range selection for surface Ga catalyst (From GaCl_3), with modeling fit

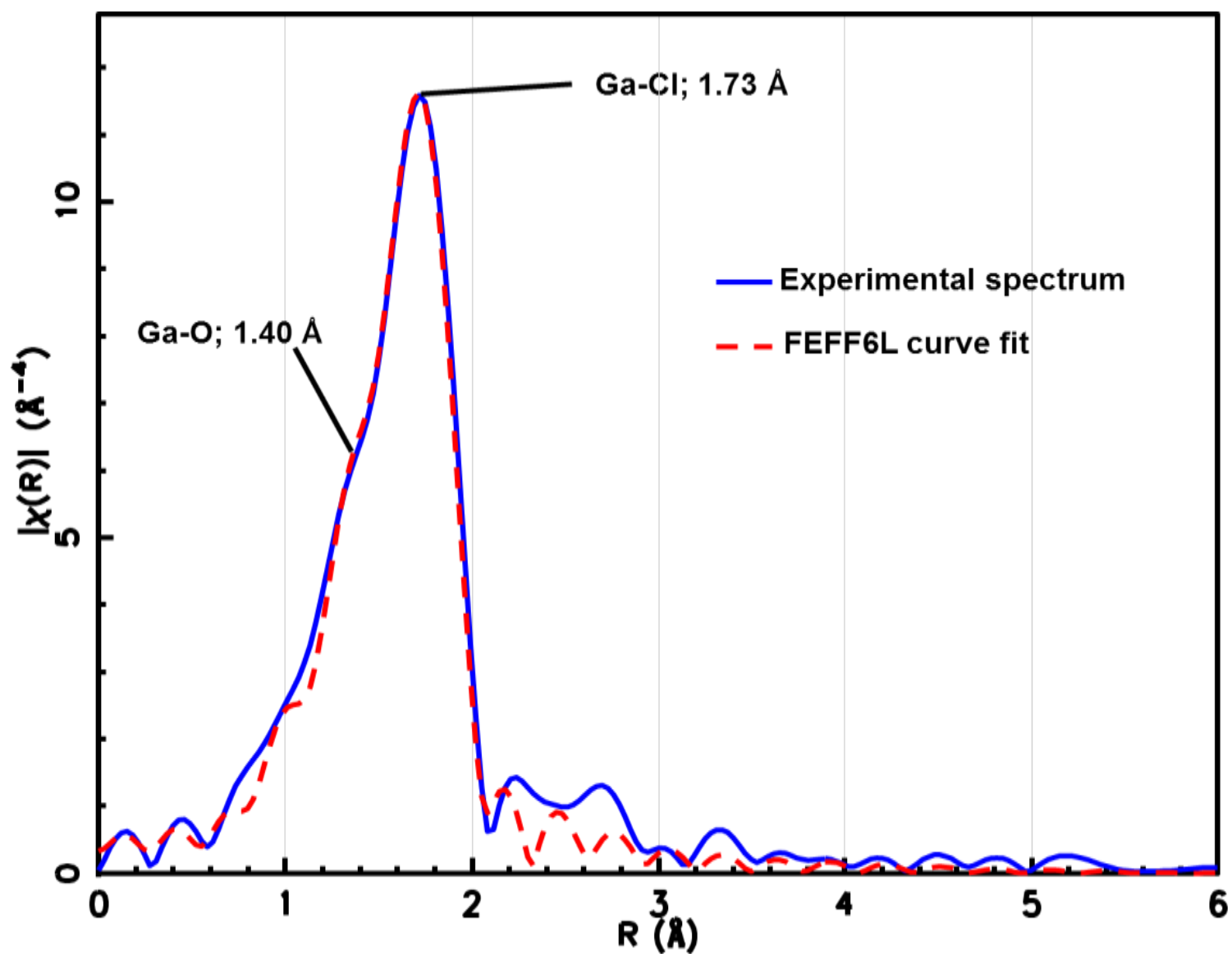


Figure 3.32: R space plot for surface Ga catalyst (From GaCl_3) with modeling fit

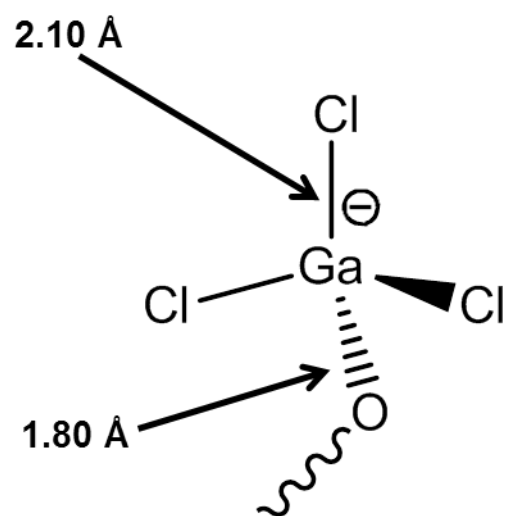


Figure 3.33: Surface Ga model for EXAFS fit

Table 3.5: EXAFS model fitting parameters for surface Ga catalyst (From GaCl₃)

Parameter	Fit Values O	Fit Values N
N	1.3(3)	2.9(2)
S ₀ ²	0.84(5)	
σ ²	0.005(2)	0.005(1)
R[ΔR ₀]	1.85 [.05(2)]	2.13 [0.03(1)]
E ₀	1.9(7)	
R factor	0.018	

1- and 2-connected gallium centers, it was expected that the coordination numbers from this model would have non-integer values. Iterative optimization of the fit parameters did in fact lead to coordination values that fit well with the gravimetric analysis with the Ga-O coordination number equaling 1.3. The remaining fit parameters can be seen in Table 3.5.

The total coordination in the fit model is ~4 indicating that the Ga centers are tetrahedral. Since no tetramethyltin was observed, this raises a question as to what the charge balancing cation would be in this case. A non-charged tetrahedral species with bridging chlorides could theoretically exist (Figure 3.34a). If this were the case, then a Ga···Ga feature would be present in the EXAFS data for this sample, and it is not. What is more likely the case is that a tetrahedral [-OGaCl₃][Me₃Sn] center does in fact form. However, the lack of remaining -OSnMe₃ groups in close proximity to the Ga

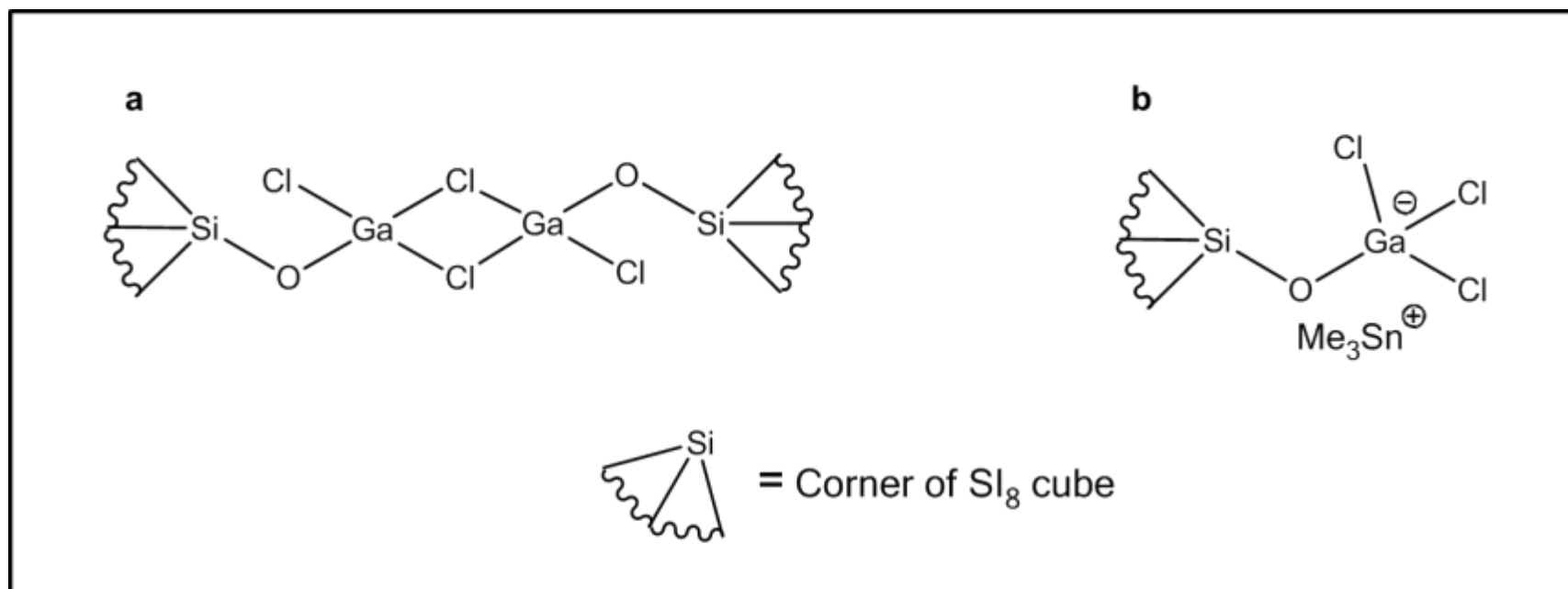
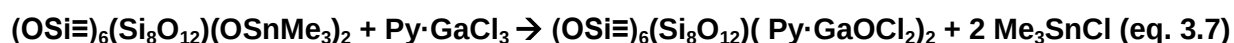


Figure 3.34: Possible surface sites prepared from GaCl_3 a) Neutral dimeric 4-coordinate, b) ionic 4-coordinate

center means that there are no methyl groups remaining for the Me_3Sn^+ cation to scavenge. In this way, the Me_3Sn^+ cation is trapped in the system (Figure 3.34b), making this sample ideal for further attempts to identify the cation species.

3.3.7 Two Dose Surface Gallium Catalysts Starting From $\text{GaCl}_3 \cdot \text{Py}$

The reaction to create the platform substrate utilized a 3.0 : 1 ratio of SiCl_4 : TMT cube and achieved a connectivity of 1.8. This left ~2.5 isolated unreacted trimethyltin groups on each cube. Once the trimethyltin chloride byproduct has been removed, and



the platform dried, toluene was added in addition to a limiting 0.8 equivalents of $\text{GaCl}_3 \cdot \text{Py}$. The solution was then stirred at 80-100 °C for 16-48 hours, followed by removal of the volatiles and drying. Analysis of the volatile byproducts of the second dose reaction with GaCl_3 showed only the byproduct Me_3SnCl . Gravimetric analysis yielded an average connectivity of 1.1.

The XANES spectrum (Figure 3.35) in this instance again shows a single feature superimposed on the ionization edge at 10375 eV, and the edge position occurs at 10373 eV as seen in all of the gallium samples. An appropriate k range was chosen (Figure 3.36) and transformed to create the subsequent R space plot (Figure 3.37). Qualitatively, the R space plot looks to be better resolved than the previous sample, with an Ga-O feature at 1.4 Å, and a Ga-Cl feature at 1.8 Å. Interestingly, the Ga-Cl feature is nearly a tenth of an angstrom longer than that of the non-adduct surface species (Figure 3.38). This is consistent with the Ga center having more electron density, with one of the covalent Ga-Cl bonds replaced by the lone pair donation of the pyridine. For modeling of the spectrum, a tetrahedral model (Figure 3.39) was chosen to have a Ga-O bond length of 1.8 Å, a Ga-Cl bond length of 2.1 Å, and a Ga-N length of 1.95 Å.

While the data for this sample appear to be of very high quality, a satisfactory fit could not be obtained. While it is relatively simple to model two different atoms in the first coordination sphere of the absorbing atom, introducing a third seems to introduce a number of variables into the system that make achieving a high quality fit difficult.

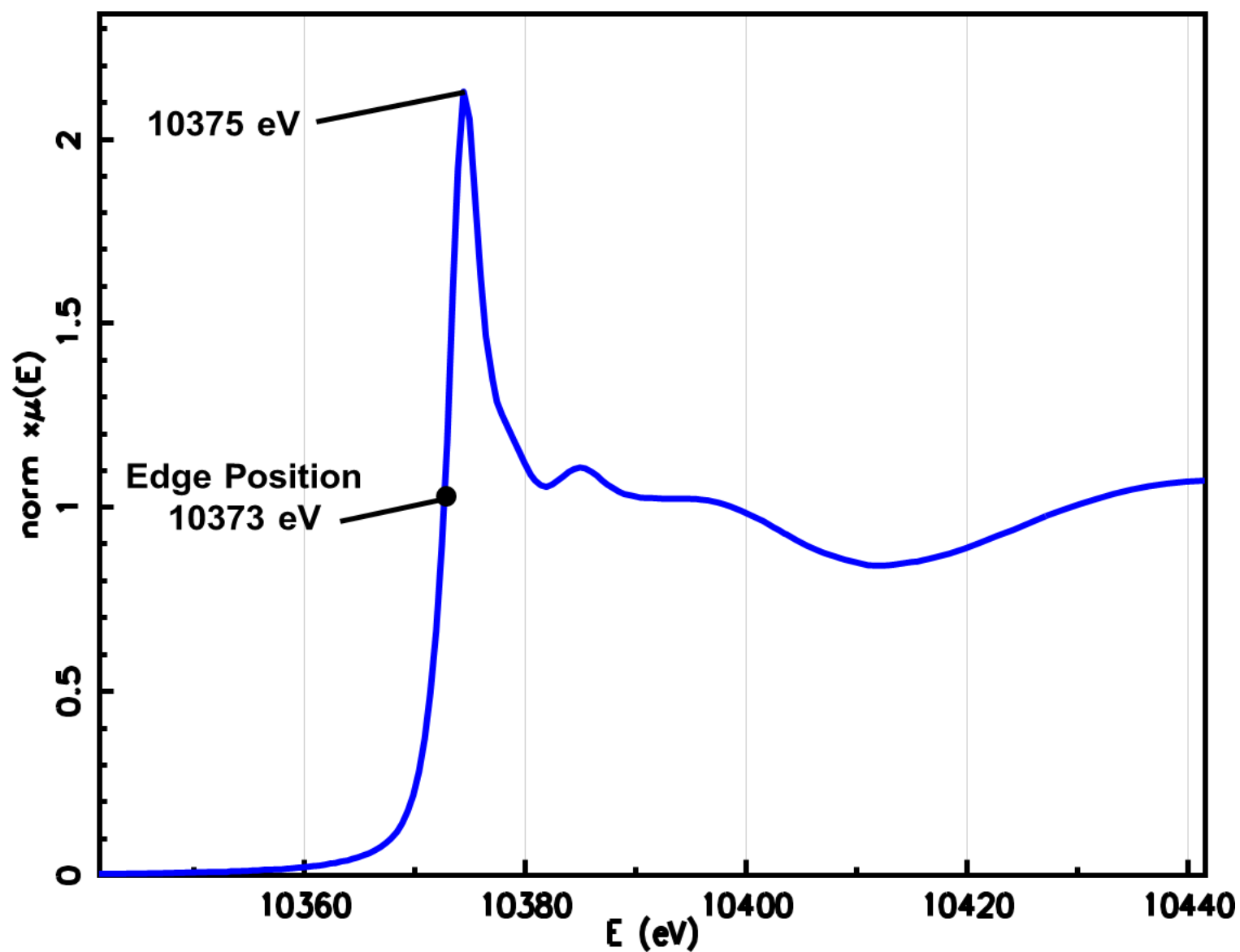


Figure 3.35: XANES spectrum for surface Ga catalyst (from $\text{GaCl}_3 \cdot \text{Py}$)

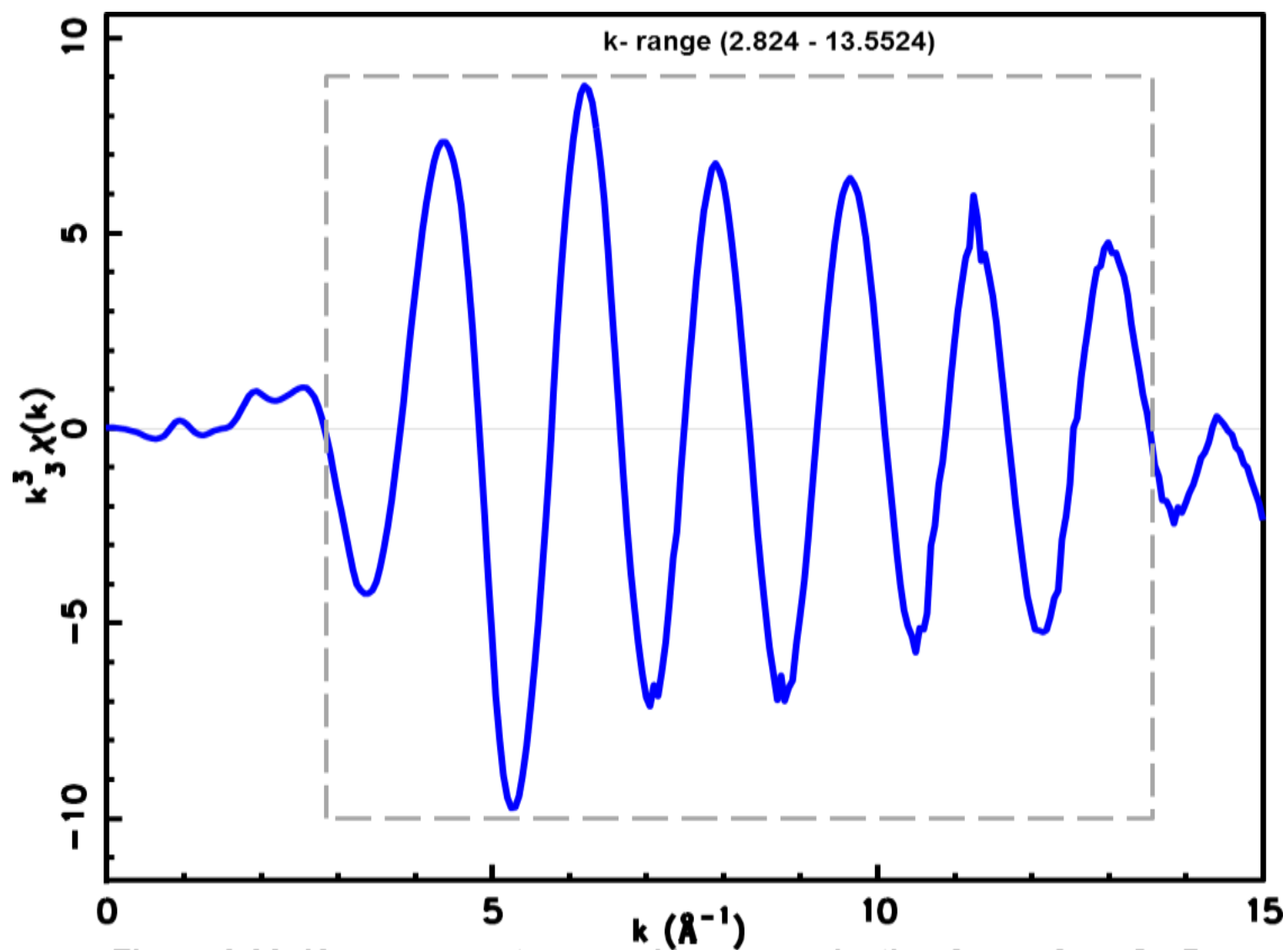


Figure 3.36: K space spectrum, and k-range selection for surface Ga·Py catalyst (from $\text{GaCl}_3 \cdot \text{Py}$)

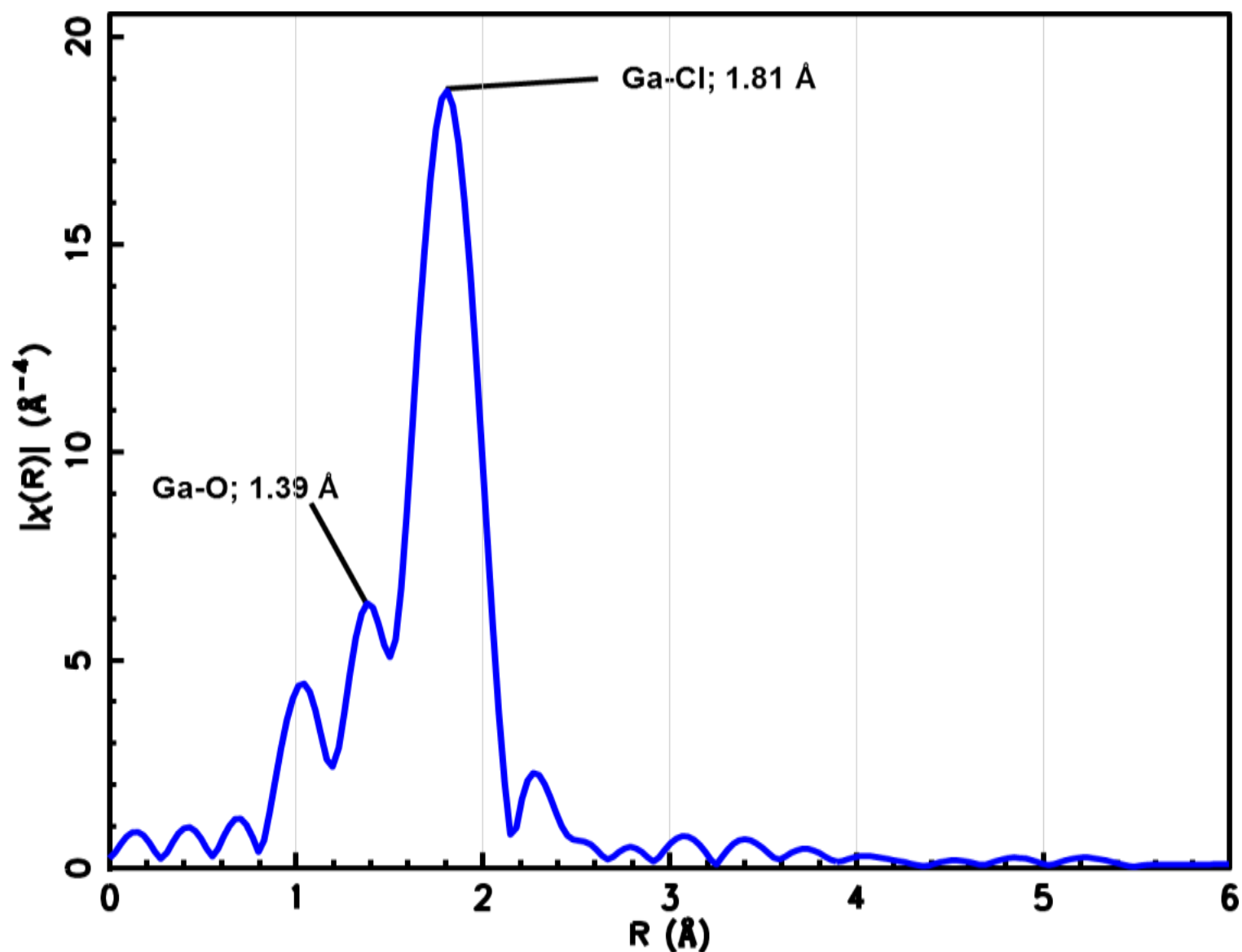


Figure 3.37: R space plot for surface Ga·Py Catalyst (from GaCl₃·Py)

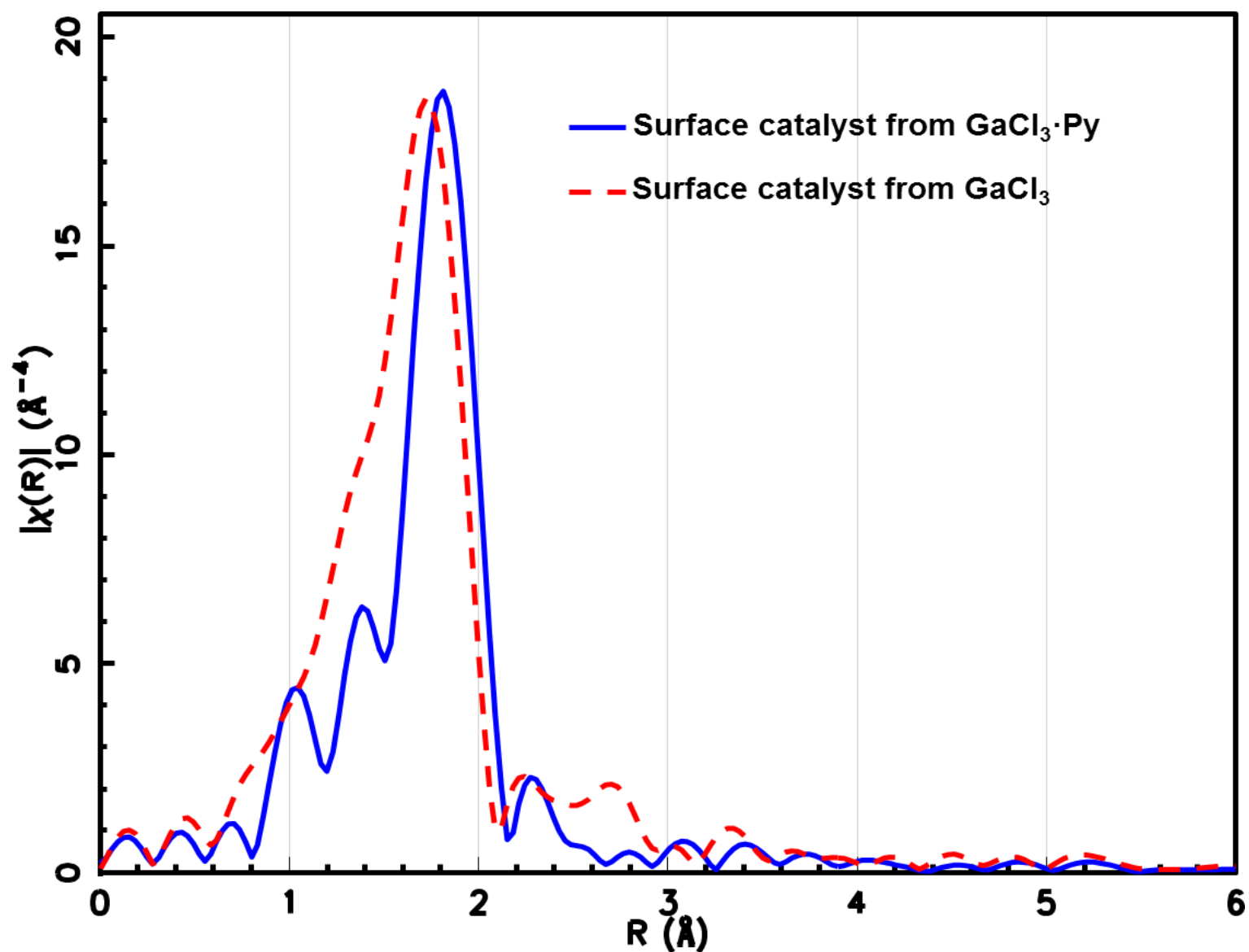


Figure 3.38: Comparison of R space plots for surface Ga and Ga·Py catalysts

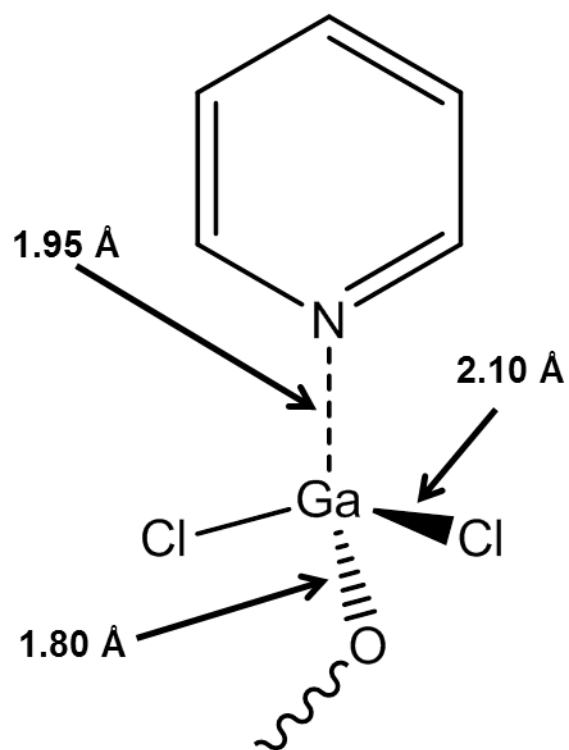


Figure 3.39: Surface Ga-Py model for EXAFS fit

Theoretically, there is enough data present to solve for the increased number of variables,¹³⁴ but to this point an acceptable fit has not been obtained. Many variations on the structural model were explored, but none resulted in a significantly improved fit.

3.3.8 The Nature of Surface Gallium Centers in Surface Catalyst

The gallium species immobilized on the surface of a high surface area platform from the precursor GaCl_3 exist as Ga(III) centers in tetrahedral geometry. This has been shown through the use of XANES and EXAFS characterization methods. While the byproduct tetramethyltin was not seen in the grafting reaction, it is likely that the Me_3Sn^+ species is present in the matrix as a counter ion to the surface $-\text{OGaCl}_3^-$ anionic species. Due to the lack of remaining tin centers (i.e. other $-\text{OSnMe}_3$ groups) in close proximity to the grafted catalytic centers (and associated Me_3Sn^+ ions), there are no appropriate sources of the methyl groups needed to form Me_4Sn .

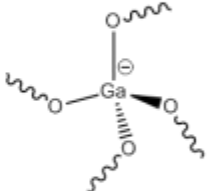
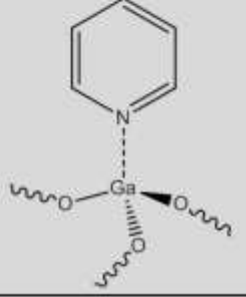
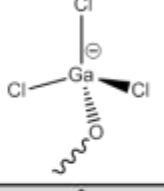
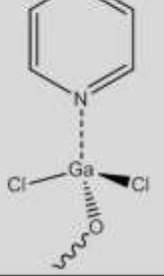
While a satisfactory EXAFS model and fit could not be created for the surface $-\text{OGaCl}_2\cdot\text{Py}$ species, the XANES analysis still indicates a tetrahedral, Ga(III) species. Qualitative analysis also shows clear evidence of Ga-O and Ga-Cl bonds, and the Ga-N feature may be obscured under these features. The lengthened Ga-Cl feature with respect to surface gallium centers without pyridine is consistent with the presence of a datively bound pyridine ligand.

3.4 Conclusions

The synthesis of materials containing well-defined isolated gallium(III) centers has been accomplished from the reaction of trimethyltin cube with the precursors GaCl_3 and $\text{GaCl}_3\cdot\text{Py}$. A targeted building block approach was used to introduce the gallium centers into a silicate matrix to create both fully embedded and surface species (Table 3.6).

Gallium centers were embedded into the matrix, achieving complete replacement of the chloride ligands with Ga-O bonds creating isolated GaO_4 sites in amorphous silicate matrices. This was carried out by reacting limiting amounts of the GaCl_3 ,

Table 3.6: Synthesized Ga species

Precursor(s)	Substrate	Confirmed by EXAFS Modeling	Structure
GaCl_3 $[\text{Me}_3\text{Sn}][\text{GaCl}_4]$	TMT Cube	Yes Yes	
$\text{GaCl}_3 \cdot \text{Py}$	TMT Cube	Yes	
GaCl_3	SiCl_4 crosslinked platform	Yes	
$\text{GaCl}_3 \cdot \text{Py}$	SiCl_4 crosslinked platform	No	

GaCl₃·Py, or [Me₃Sn][GaCl₄] precursors with the trimethyltin cube. Characterization of the embedded centers showed strong similarities to the aluminosilicates discussed in Chapter 2 of this thesis. Significant amounts of tetramethyltin were observed in addition to the formation of the expected trimethyltin chloride byproduct. This indicated the likely formation of tetrahedral GaCl₄, and was confirmed by the reaction of the *in situ* prepared precursor [Me₃Sn][GaCl₄] with the trimethyltin cube. Further characterization by gravimetric, IR, and SSNMR was carried out. In addition EXAFS modeling confirmed the tetrahedral nature of these species yielding high quality fits with acceptable fitting parameters (Table 3.7).

Surface gallium species with a single Ga-O bond connecting the metal center to the matrix were created by first forming a high surface area cross linked building block matrix wherein the remaining reactive sites are isolated. Subsequent reaction with the gallium precursors led to isolated surface sites. Similar steps were taken to analyze the surface species, and evidence was obtained indicating that the surface species were also tetrahedral in nature. Structural EXAFS models (Table 3.6 & 3.7) confirmed the tetrahedral nature of the surface species derived from GaCl₃, and while a similar model for the GaCl₃·Py species was not obtained, XANES analysis points towards the expected tetrahedral structure.

Table 3.7: Gallium EXAFS fit parameters

Sample	CN _O	CN _X (¹ =N, ² =Cl)	R _O	R _X (¹ =N, ² =Cl)	σ ² _O	σ ² _X (¹ =N, ² =Cl)
GaO ₄ – 1	4.1(2)	-	1.85(1)	-	0.005(1)	-
GaO ₄ – 2	4.0(2)	-	1.86(1)	-	0.005(10)	-
GaO ₃ ·Py	3.0(2)	1.1(5) ¹	1.80(1)	1.95(1) ¹	0.003(1)	0.004(3) ¹
GaOCl ₃	1.3(3)	2.9(2) ²	1.85(1)	2.13(1) ²	0.005(2)	0.005(1) ²
GaOCl ₂ ·Py	-	-	-	-	-	-

4. Synthesis & Structure of Nanostructured Building-Block Solid Acid Boron Catalysts

4.1 Introduction

While borosilicates have not traditionally been used as catalysts without modification, they are a well characterized and understood class of materials.^{135–138} Their lack of use as catalysts generally derives from the weak acidic nature of the sites present,^{139,140} though there are a few cases where weak Lewis acidity is useful for catalytic applications.¹⁴¹ Borosilicates find their primary use in glasses and tend to be employed for their physical and optical properties. Because of their widespread use for a variety of applications, an in depth understanding of the structural nature of borosilicates exists. Due to the well understood nature of these systems, it was believed that an investigation of materials synthesized through the reaction of BBr_3 and the $(\text{Me}_3\text{SnO})_8\text{Si}_8\text{O}_{12}$ building block could provide useful insights with respect to the more complex group 13 analogues.

While boron halides and the resultant borosilicates synthesized here share a number of similarities with their aluminum counterparts, there are a several important differences. Most pronounced among these is the stability of boron in planar three-coordinate geometries. While borosilicates synthesized in protic environments are likely to contain domains of B_2O_3 and $\text{B}(\text{OH})_3$, calcination of these materials often leads to the presence of trigonal BO_3 units.^{137,142}

The goal of the work presented in this chapter is to examine the structure of boron centers embedded into a building block silicate matrix. Based on the synthesis of these materials under aprotic conditions it is expected that unlike the aluminum and gallium analogues, boron will form stable three coordinate species without calcination. Effects of pyridine adsorption and desorption on the structure are investigated in addition to studies of the molecular POSS analogue.

4.2 Experimental

4.2.1 Materials & Synthesis

All reactions were performed using the materials, methods and techniques outlined in Chapter 2 of this dissertation. Synthetic procedures for the production of these borosilicate catalysts are identical to those previously discussed, with the simple replacement of the aluminum species with their boron analogues. The boron precursors include anhydrous boron trichloride (BCl_3 , 1M in hexanes, Acros), and boron tribromide (BBr_3 , Acros, 99.9%). The boron tribromide pyridine adduct ($\text{BBr}_3\cdot\text{Py}$) was prepared in a similar fashion to the aluminum analogues. As BCl_3 is a gas at room temperature, it could only be obtained in solution. Thus, after an initial test with such a solution, BBr_3 was utilized as it could be obtained in a pure form. This of course means that the primary byproduct in the reaction with the tin cube should be Me_3SnBr . Hexanes solutions of BCl_3 were syringed into a solution of tin cube, while the liquid BBr_3 was vapor transferred into the reaction via methods similar to SiCl_4 as outlined in Chapter 2.

4.2.2 Characterization

Details of the methods used for characterization of these samples by gravimetric analysis, nitrogen adsorption, IR, NMR, and GC/MS can be found in Chapter 2 of this dissertation. 16.4T SSNMR was carried out with the help of Dr. Ed Hagaman at ORNL.

4.3 Results & Discussion

4.3.1 One Dose Embedded Boron Catalysts Starting From BBr_3

Reaction of BBr_3 and TMT cube (1 : 1) was conducted under conditions similar to those used for both the aluminum and gallium analogues (80 °C; 24 hrs; toluene). Upon warming the reaction mixture to room temperature, phase separation was noticeable almost immediately. While the BBr_3 precursor is bright orange in color, the reaction solution quickly became colorless. Complete reaction may have occurred within a relatively short time period, but the reaction mixture was heated and stirred for a full 24 hours. After heating, the volatiles were removed and analyzed by NMR and GC/MS.

The only byproduct produced present was Me₃SnBr. There was no evidence for the formation of Me₄Sn; hence the reaction likely precedes as shown (Equation 4.1),



producing trigonal boron centers as seen in Figure 4.01. Gravimetric analysis indicated the loss of 2.9 equivalents of Me₃SnBr signifying that the boron centers were fully embedded within the matrix.

The surface area of the embedded boron matrix was found to be 7.5 m²/g. This is in line with surface areas for other one dose metal chloride reactions with the TMT cube (with the exception of Al).⁸⁷ Figure 4.02 shows a typical N₂ absorption/desorption isotherm for a single dose B reaction. The shape of the isotherm is classified as reversible Type 2 with no hysteresis.⁹⁶ This designation is indicative of a non-porous or macroporous solid which is further evidenced by looking at the BJH pore size distribution (Figure 4.02, inset). This type of isotherm is different from what has been seen in similar samples prepared from other metal chlorides as the sample lacks both micro and mesopores.

The IR spectrum of the embedded boron sample (Figure 4.03) shows a very clean –OH region, as well as the expected Si-O-Si modes in the 850 – 1250 cm⁻¹ range, methyl C-H bands below 3000 cm⁻¹. The nature of the weak features in the 1700-1950 cm⁻¹ range and at 2360 cm⁻¹ are not well understood, but are present in the cubic building block starting material. The most important feature seen in the IR spectrum is the broad but relatively intense band at 1405 cm⁻¹. This feature is assigned as the B-O asymmetric stretching vibration of boron in a three-coordinate environment. The position of the vibration varies from ~1265–1400 cm⁻¹, where higher frequencies indicate the substitution of the next nearest neighbor atom from B³⁺ to Si⁴⁺.^{143,144} The high frequency location of this vibration in the experimental spectrum agrees well with this observation. In the synthesized borosilicate samples, it is expected that only B-O-Si bonds will exist, and no B-O-B bonds will form. The vibrations at 710 and 670 cm⁻¹ while less intense, are also associated the formation of B-O-Si linkages. Typically, a

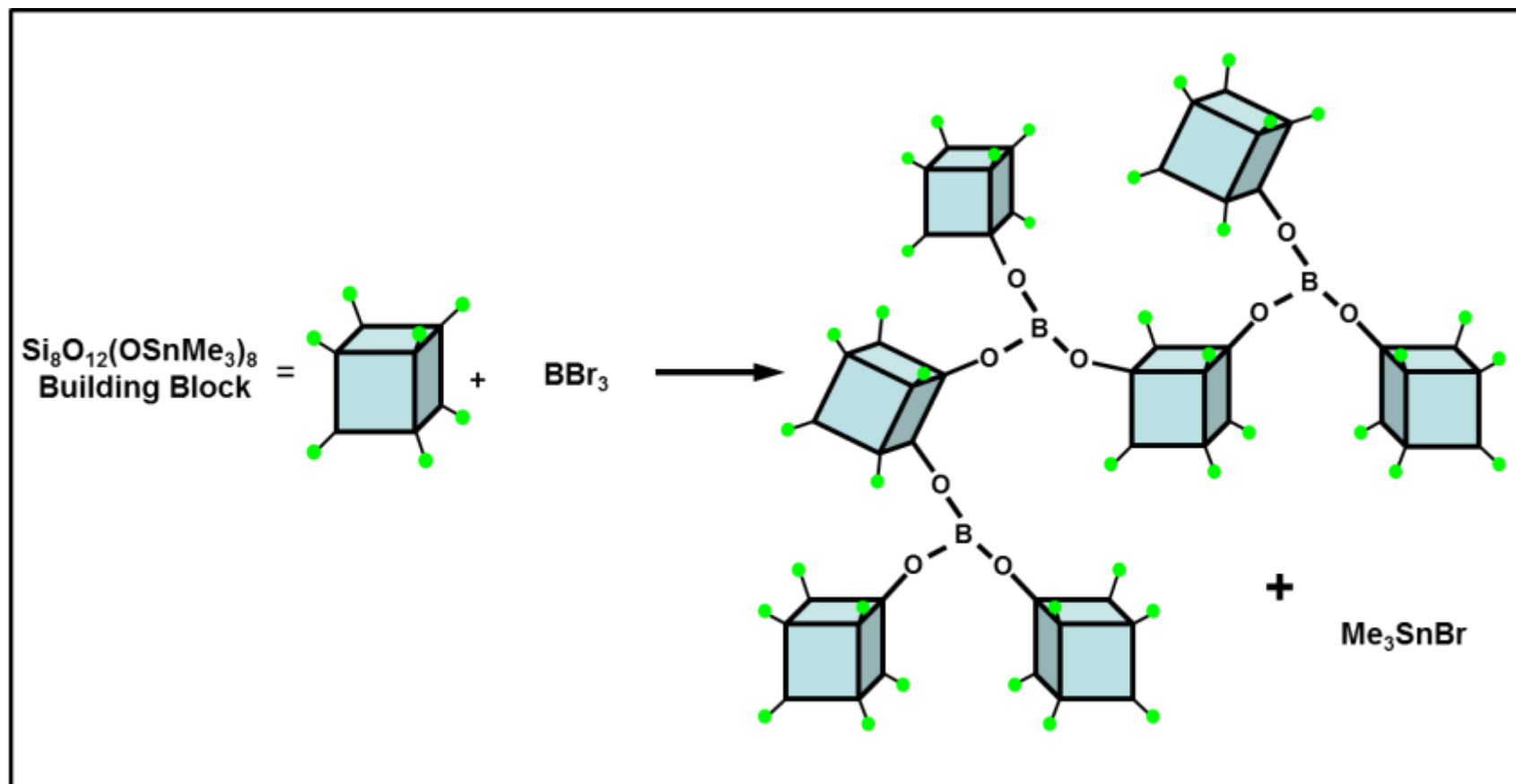


Figure 4.01 Synthesis and predicted structure of 1-dose embedded boron catalyst

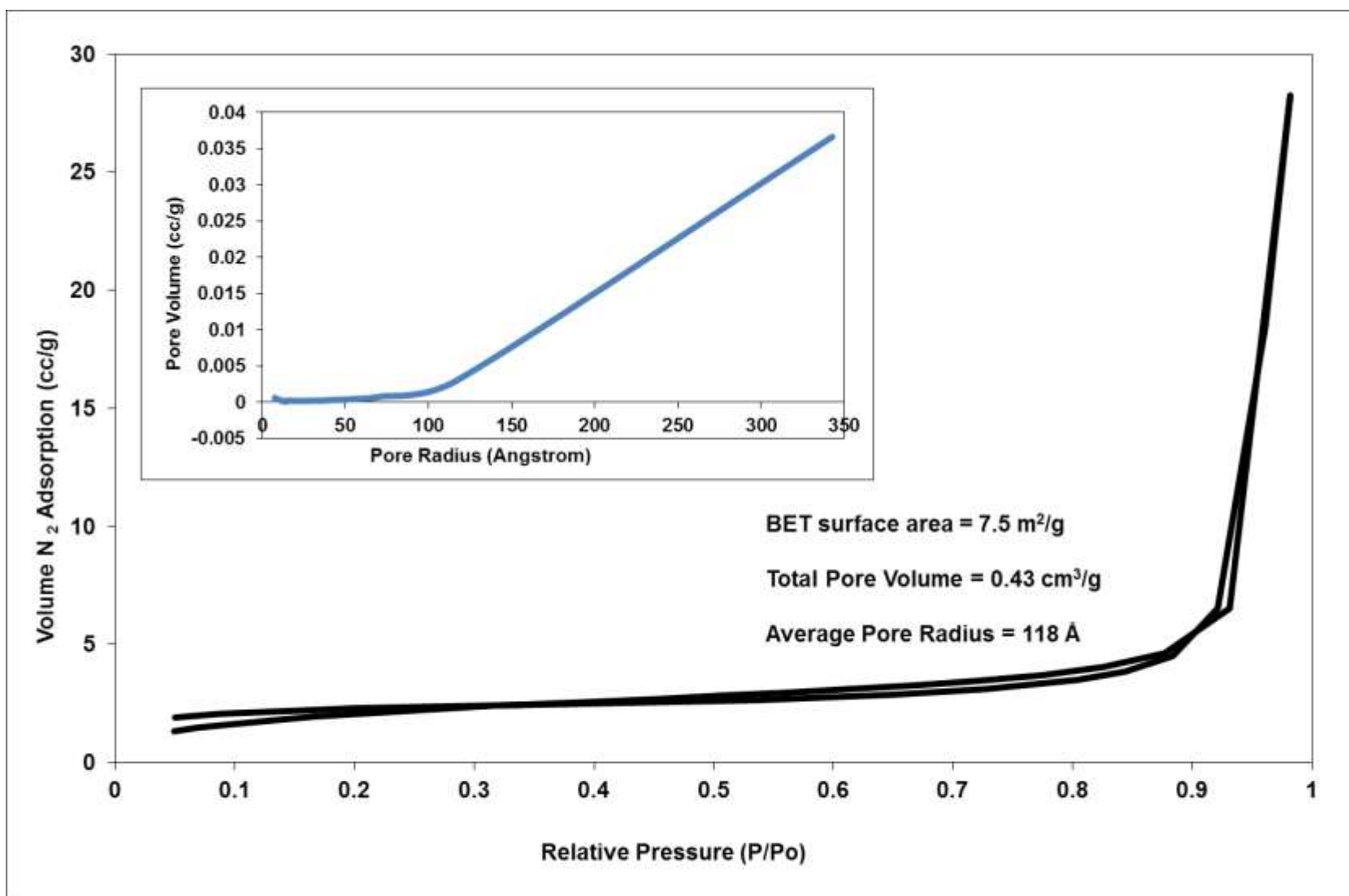


Figure 4.02: N_2 adsorption isotherm for embedded B sample with BJH pore size distribution (inset).

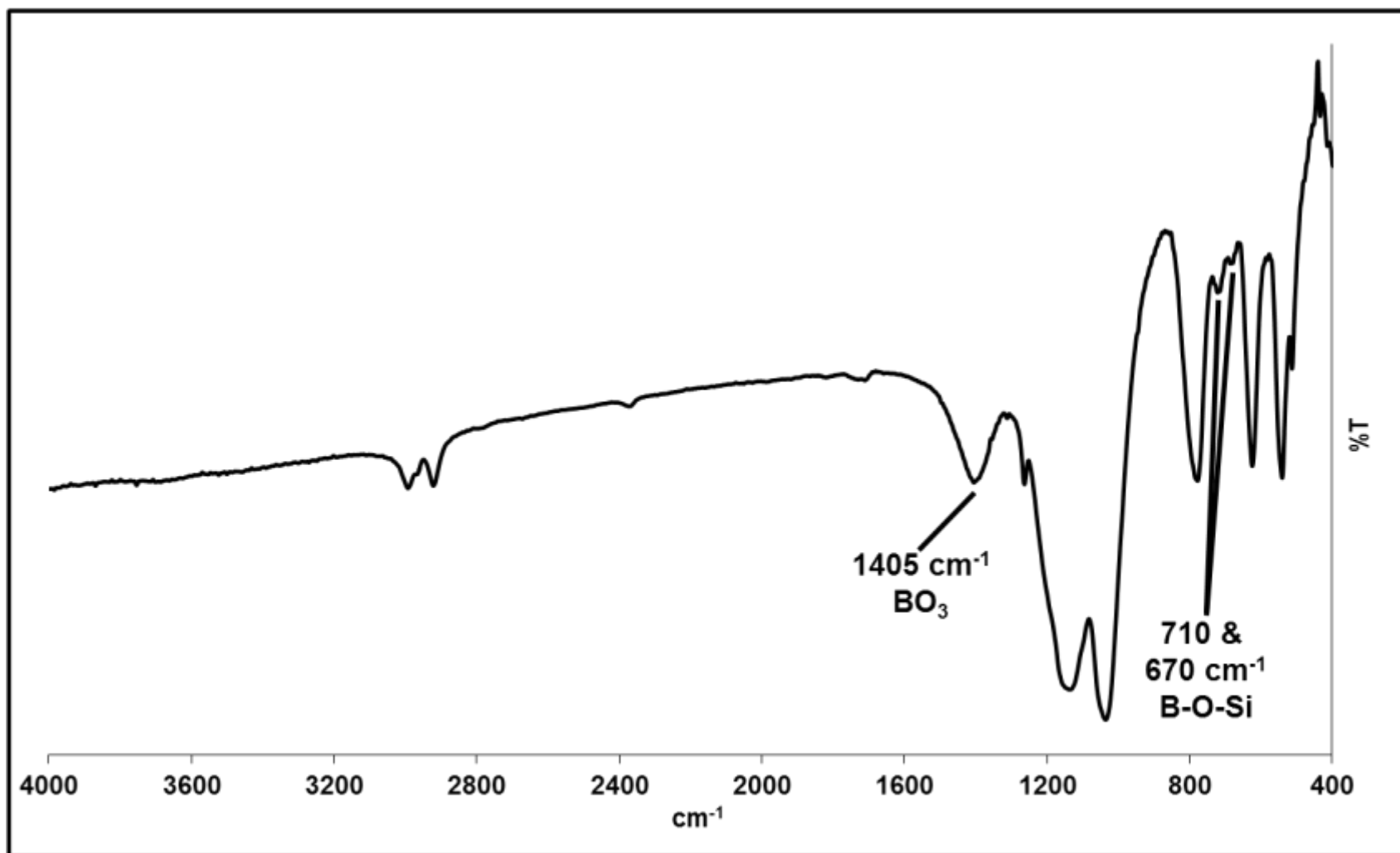


Figure 4.03: IR spectrum of embedded B centers from BBr_3

band at 920-950 cm^{-1} is also observable, but this appears to be covered by a more prominent Si-O-Sn feature on the low energy side of the Si-O-Si vibrations.¹⁴⁵

The manner in which both water and pyridine bind to these trigonal Boron centers was also explored using IR. Allowing the sample to remain exposed to moisture in the air for a period of 16 hours led to an IR spectrum (Figure 4.04) where the only visible change was the appearance of a broad band centered around 3400 cm^{-1} associated with hydrogen bonded -OH in the matrix. This is most likely due to weak bonding of H_2O to the boron centers. No disruption of the trigonal BO_3 band at 1405 cm^{-1} was observed as has been seen in other binding studies.¹⁴³ Upon heating the sample to remove any weakly bound water, the broad -OH feature goes away, indicating that the weak binding of water is reversible.

Adsorption of pyridine followed by evacuation at room temperature gives a more distinct indication of binding to the boron centers (Figure 4.05). IR bands indicative of Lewis acidic binding of pyridine are visible at 1461, 1493, and 1627 cm^{-1} . Heating the sample to 100 $^\circ\text{C}$ under vacuum results in the removal of a majority of the pyridine. This relatively low temperature of desorption again shows the reduced acid strength that is generally associated with the weaker Lewis acidity of borosilicates in comparison to aluminum and gallium analogues. Interestingly, when pyridine is bound, the broad feature at 1405 cm^{-1} undergoes a small shift to lower frequency which would indicate a slight weakening and elongation of the B-O bonds consistent with the addition of a fourth ligand donating electron density to the boron center. When the pyridine is mostly removed by heating, the feature shifts back towards its original position.

Unfortunately, for the samples prepared here, IR is not a good technique for identifying the presence of BO_4 tetrahedral units. This is due to the presence of strong Si-O-Si features that obscure the range in which the BO_4 identifying features are located (926 & 1130 cm^{-1}). ^{11}B SSNMR was found to be more useful in this regard.

The ^{13}C CPMAS spectrum of the 1-dose embedded boron sample (Figure 4.06) showed only the resonance associated with unreacted trimethyltin groups. This spectrum is nearly identical to that of a silicon platform with no boron present. This is consistent with other analyses that indicate that there should not be a second type of

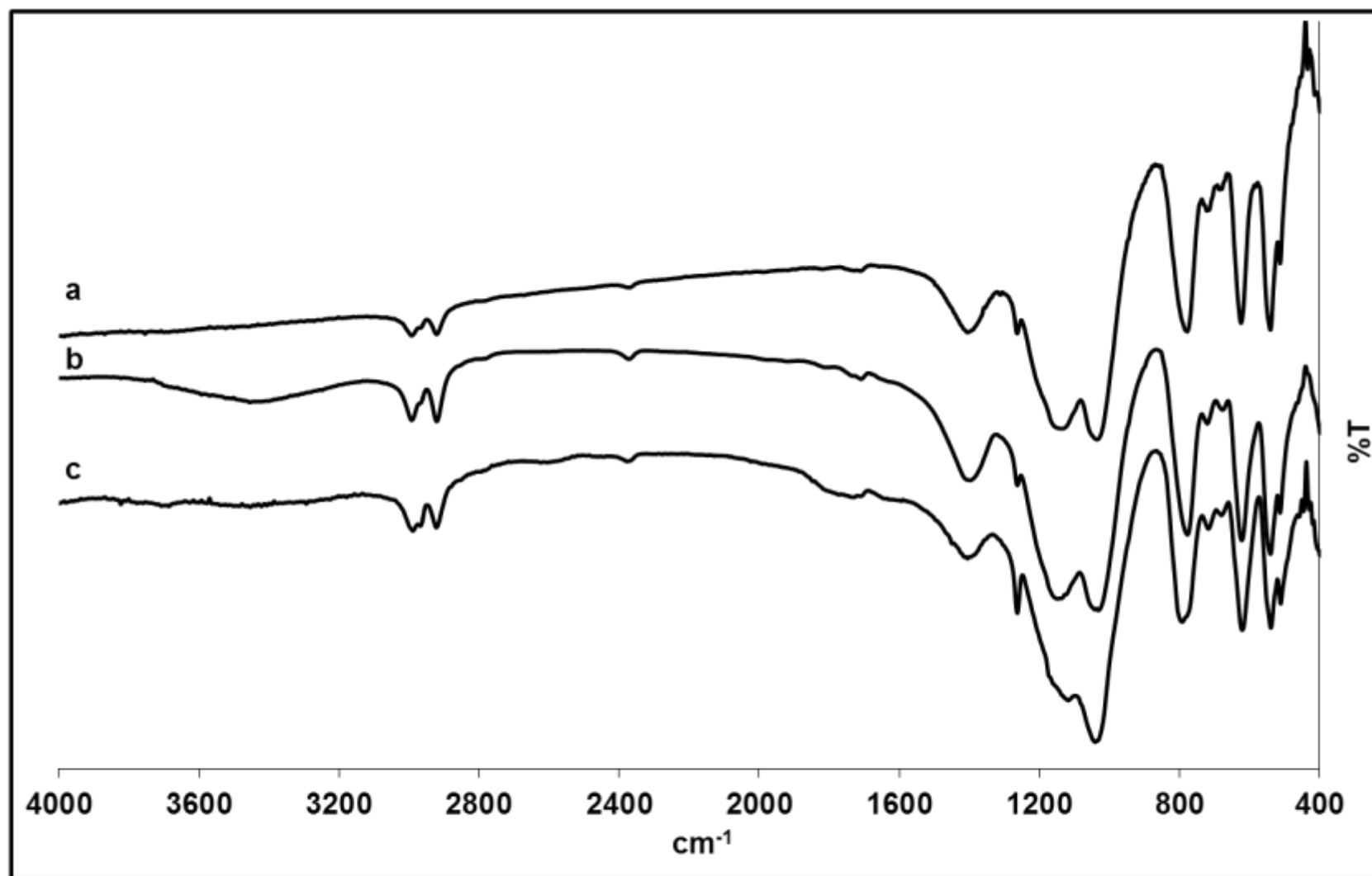


Figure 4.04: IR spectrum of (a) embedded B matrix, (b) exposed to air for 16 hours, (c) dried at 100 °C

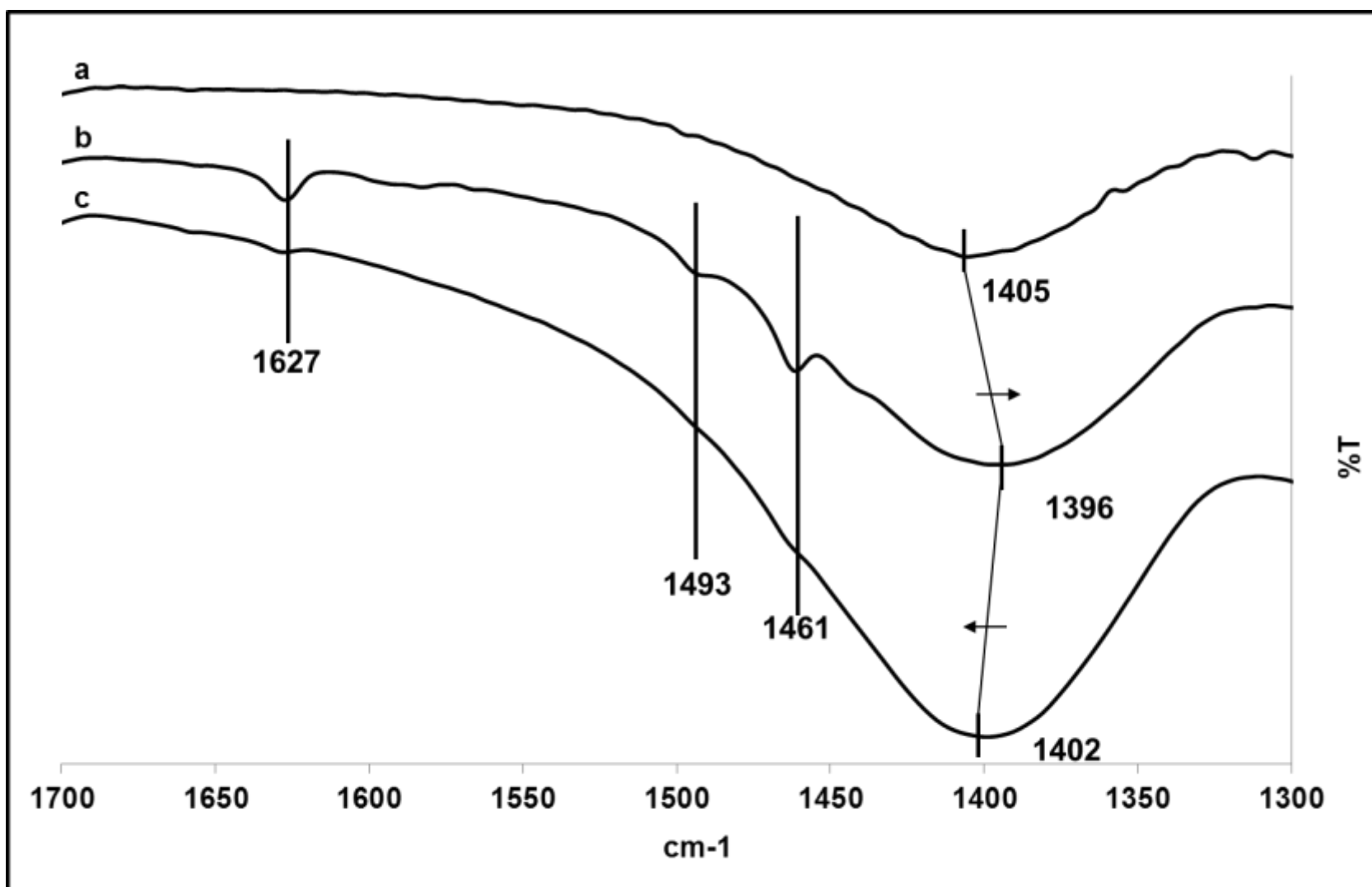


Figure 4.05: IR spectrum of (a) embedded B matrix, (b) exposed to pyridine, (c) dried at 100 °C

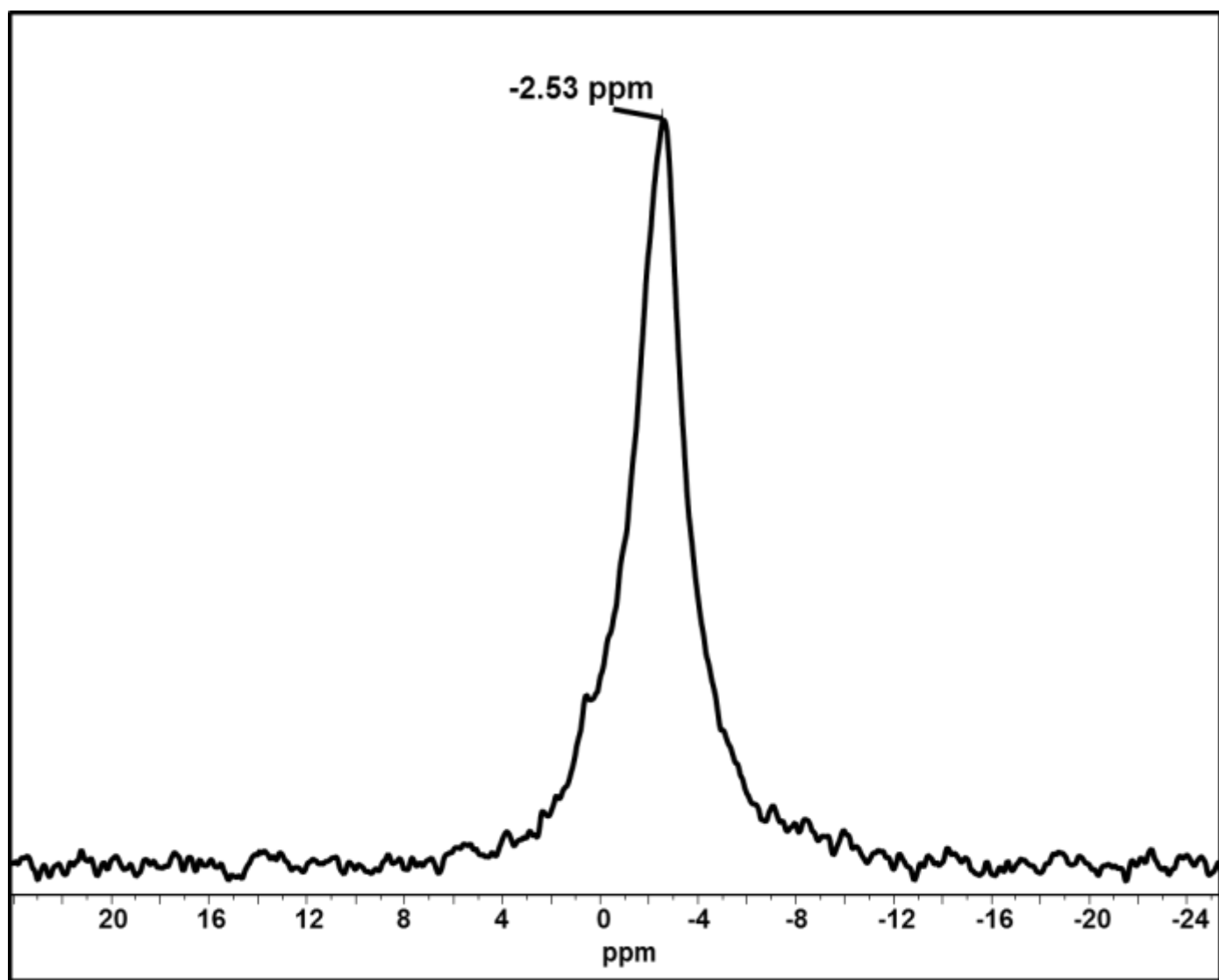


Figure 4.06: ^{13}C CPMAS spectrum of embedded 1-dose B sample from BBr_3

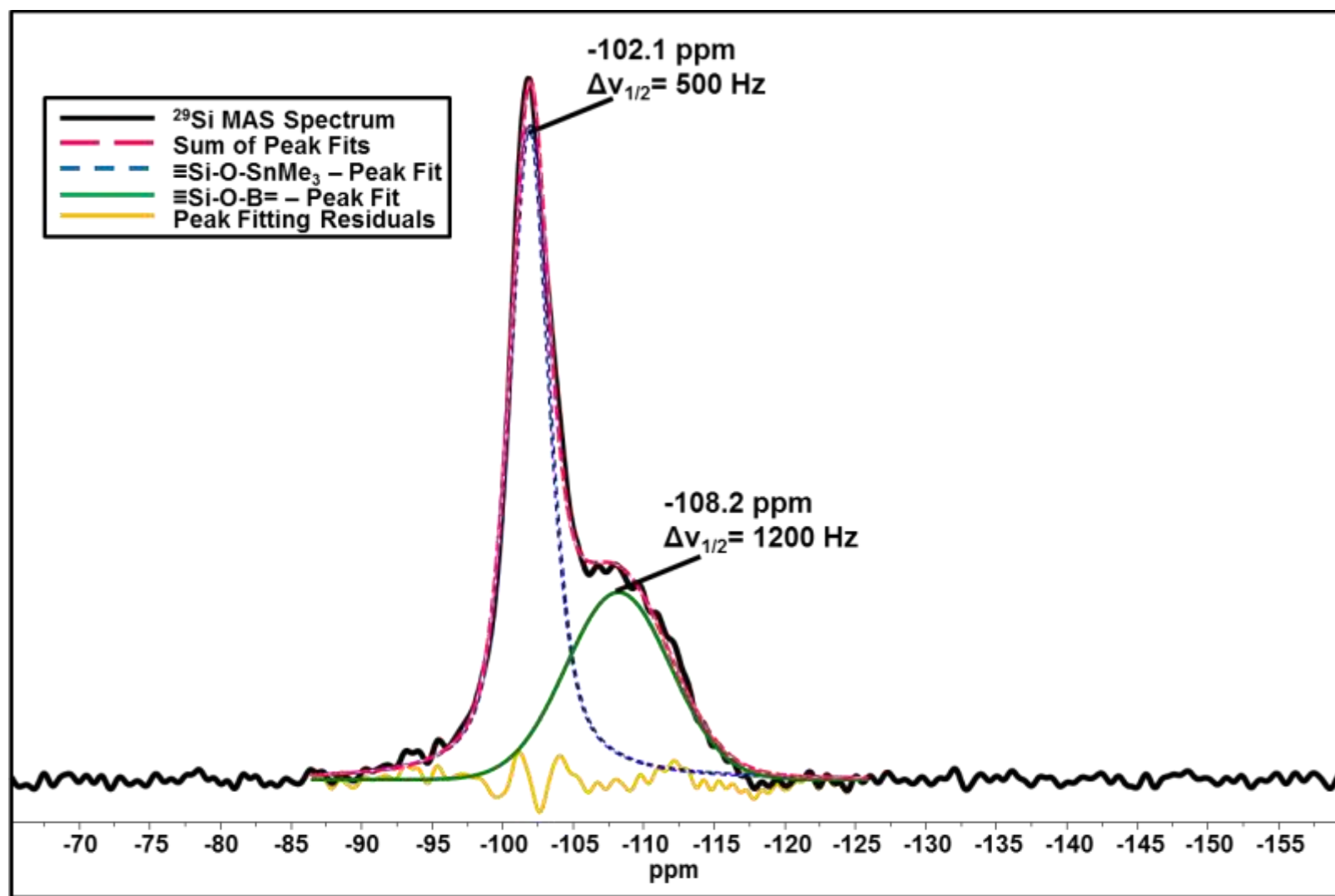


Figure 4.07: ^{29}Si MAS spectrum of embedded from BBr_3 1-dose B sample with deconvolution of peaks

carbon in the matrix. Two non-resolved features were observed in the ^{29}Si MAS NMR spectrum (Figure 4.07). Peak fitting reveals the two resonances are located at -102, and -108 ppm. These are assigned to the $\equiv\text{Si-OSnMe}_3$, and $\equiv\text{Si-O-B}$ silicon centers respectively.

^{11}B MAS NMR spectra were collected at both 9.4 and 16.4T (ORNL).¹⁴⁶ Figure 4.08 shows the spectrum collected at 9.4T, which shows a broad resonance that possesses a fairly classic quadrupolar lineshape with two singularities at 16 and -6 ppm. This type of lineshape is common for trigonal boron centers in borosilicates.^{137,147,148} The feature at 10.5 ppm is not part of the same quadrupolar lineshape, and may indicate a second type of trigonal boron. The low frequency shoulder at -2ppm is also part of the quadrupolar lineshape. ^{11}B , has a relatively narrow chemical shift range, and at lower field strengths, the BO_3 , and BO_4 signals can overlap. This was confirmed when ^{11}B spectra were recollected at 16.4T. In figure 4.09, two small tetrahedral boron components become fully resolved. Assuming similar relaxation times for all species, the tetrahedral components represent roughly 7% of the boron centers. The lineshape of the trigonal boron signal at this higher field indicates the presence of a distribution of closely related boron species. This is implied as there is no longer a single, clearly defined quadrupolar lineshape. On the other hand, the tetrahedral boron species show no quadrupolar lineshape because the spinning frequency is larger than the quadrupolar coupling constant.

When pyridine was adsorbed onto the borosilicate matrix, a clear change is observed in the ^{11}B spectrum (Figure 4.10 & 4.11). In the 9.4T spectrum, a sharp intense feature is now observed on the high field side of the trigonal boron resonance. This feature is assigned to the original boron centers which now have pyridine bound to them. The chemical shift for the resonance (7.2 ppm) is somewhat high for a tetrahedral species, but could be indicative of the inability of the boron center to achieve a fully tetrahedral geometry once locked into the matrix. Better resolution in the 16.4T spectrum shows that the intensities of the two tetrahedral features ($\delta = -1.03$ and 1.68 ppm) seen previously have increased significantly. The fact that two tetrahedral centers are present at all is quite interesting, and no good explanation for this is currently in

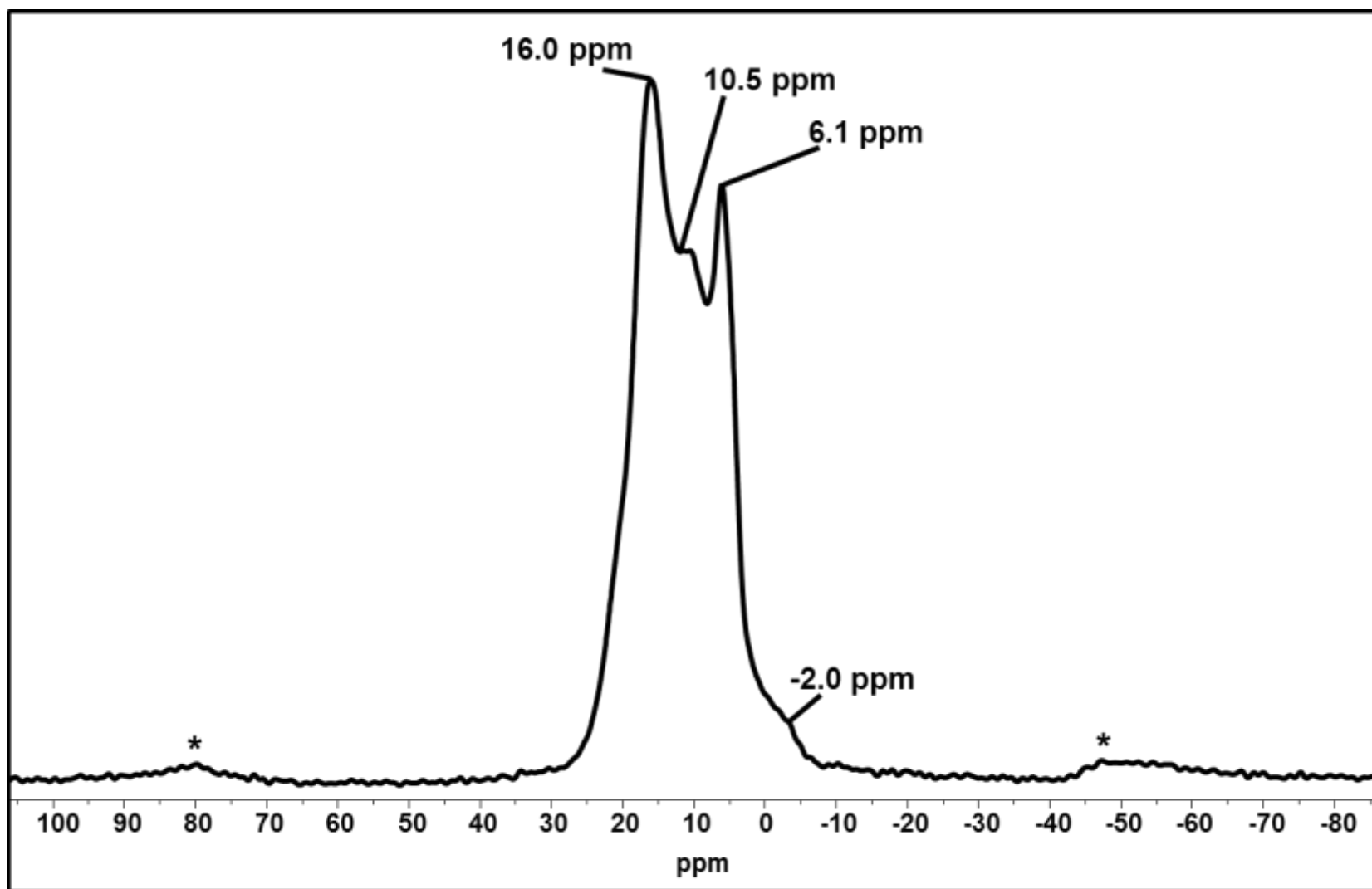


Figure 4.08: ^{11}B MAS (9.4T, 8 KHz) NMR spectrum of 1-dose embedded B sample from BBr_3
(* = spinning side bands)

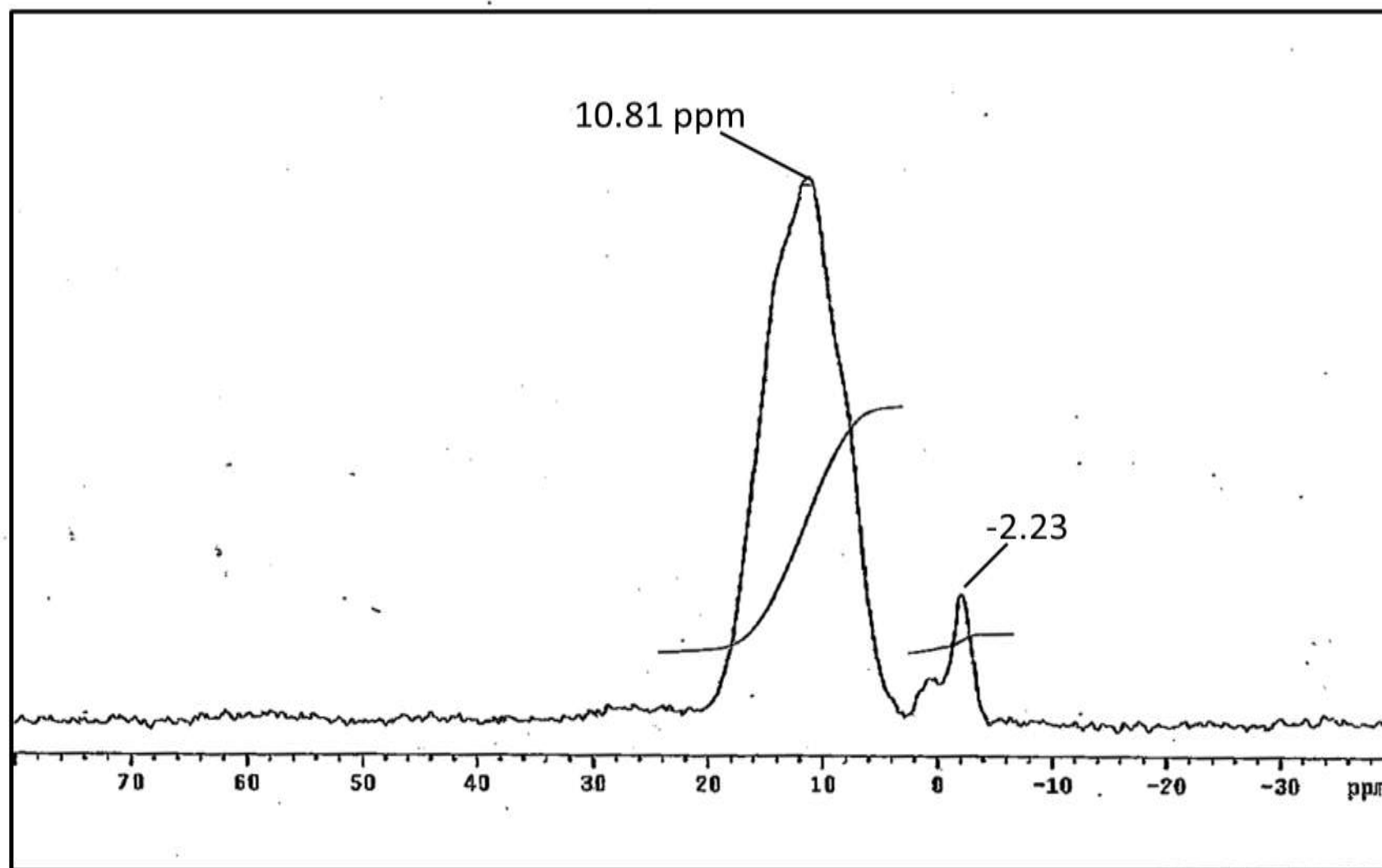


Figure 4.09: ^{11}B MAS (16.4T, 10 KHz) NMR spectrum of 1-dose embedded B sample from BBr_3

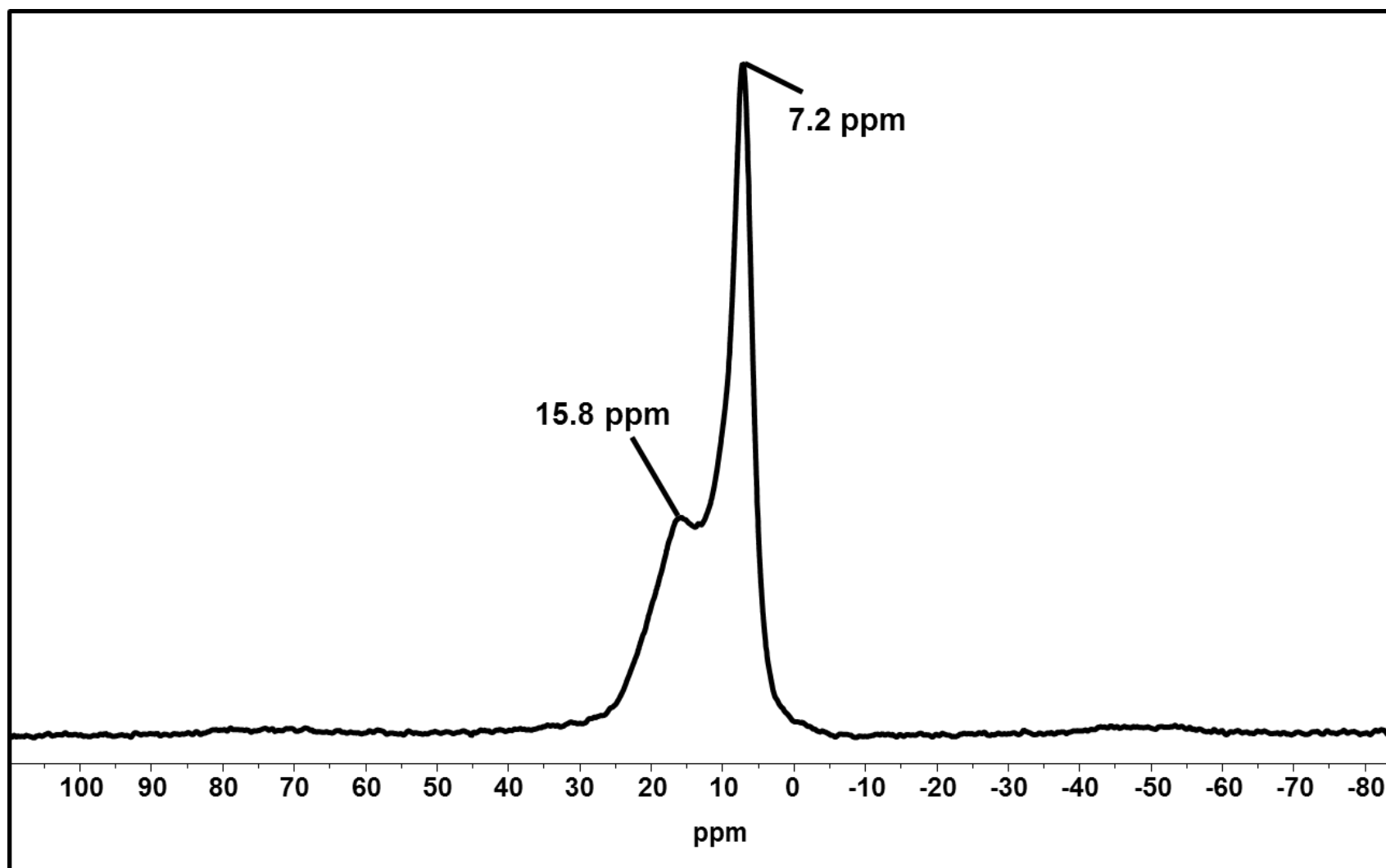


Figure 4.10: ^{11}B MAS (9.4T, 8 KHz) NMR spectrum of 1-dose embedded B sample from BBr_3 dosed with pyridine

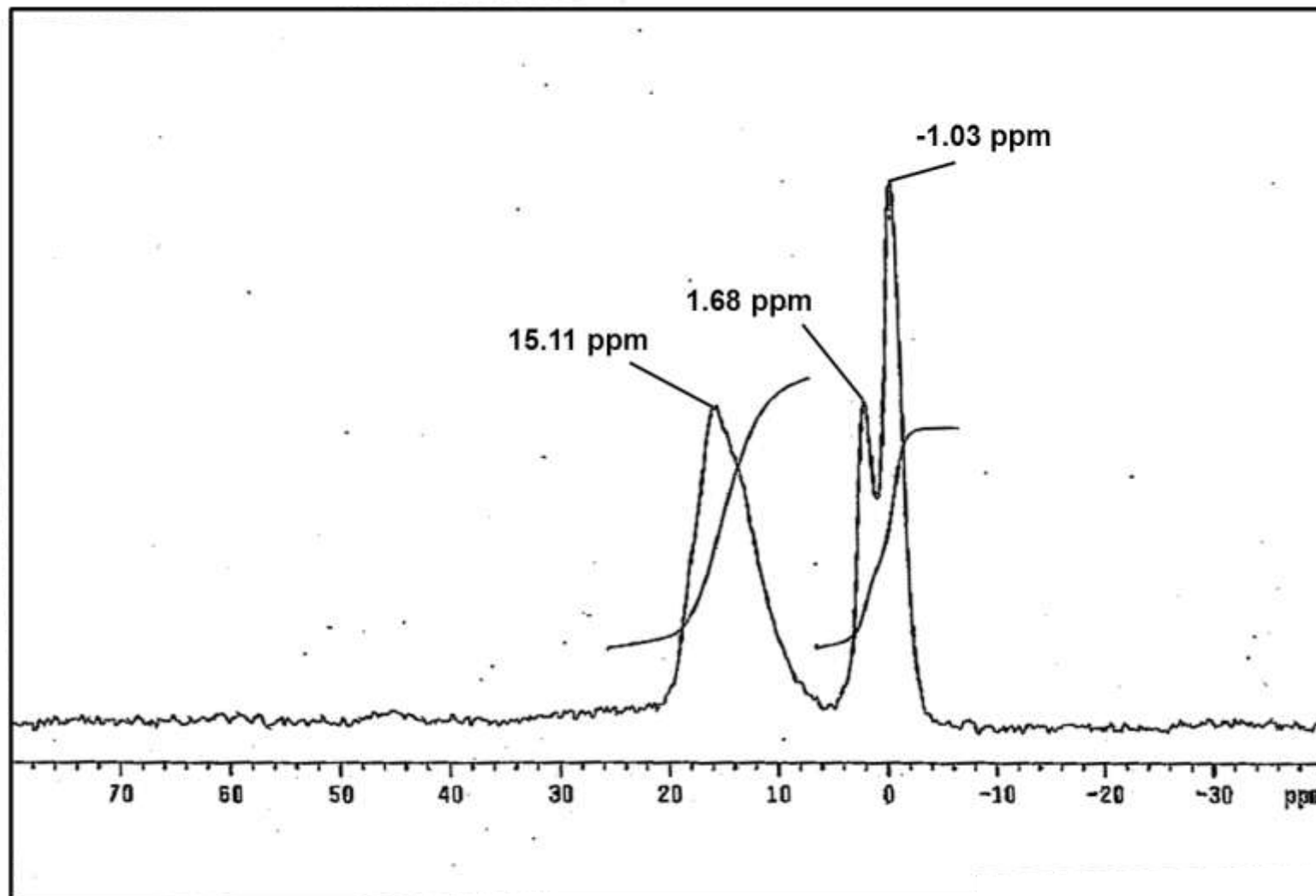


Figure 4.11: ^{11}B MAS (16.4T, 10 KHz) NMR spectrum of 1-dose embedded B sample from BBr_3 dosed with pyridine

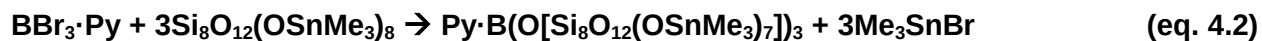
hand. Unlike in the low field spectrum, the chemical shift position of these tetrahedral species fall within the shift range expected for such species. The approximate ratio of these tetrahedral centers does appear to be the same as that seen in the unexposed sample. Once pyridine has bound, tetrahedral boron centers now represent nearly 50% of all boron in the sample. The general shape of the remaining trigonal boron feature ($\delta = 15.11$ ppm) has not changed indicating that a distribution of similar trigonal boron sites still remain in the matrix.

Previously, IR analysis showed that heating (100 °C) of the matrix containing pyridine bound to boron, caused a majority of the pyridine to be removed. This was also examined using ^{11}B SSNMR. Spectra for the initial boron complex (Figure 4.08), and the boron matrix with bound pyridine (Figure 4.10) have been discussed. Figure (4.12) shows an overlay of these two spectra in addition to a spectrum of the boron centers with bound pyridine after heating at 100 °C overnight under vacuum. It is quite evident that upon heating, the upfield signal assigned to the tetrahedral $\text{BO}_3\cdot\text{Py}$ centers, is significantly reduced, and the general quadrupolar lineshape of the initial boron centers begins to return. The spectrum does not fully return to that of the original matrix, but this may be a consequence of failing to heat the sample to a high enough temperature, or for a long enough time. However, it does confirm that the strength of the boron Lewis acid centers are much lower than that of either the aluminum or gallium centers where little to no pyridine is lost under similar conditions.

4.3.2 One Dose Embedded Boron Catalysts Starting from $\text{BBr}_3\cdot\text{Py}$

Having created trigonal BO_3 centers, converted them to a pseudo tetrahedral species through exposure to pyridine, and shown the reversibility of the process, it was of interest to examine whether there would be any differences by starting with the $\text{BBr}_3\cdot\text{Py}$ tetrahedral precursor.

In order to do this, the $\text{BBr}_3\cdot\text{Py}$ species was synthesized by the combination of BBr_3 and pyridine in a 1:1 stoichiometric ratio in CH_2Cl_2 . Once isolated, the $\text{BBr}_3\cdot\text{Py}$ adduct was reacted with tin cube in toluene at 80 °C for 48 hrs (Equation 4.2). Upon



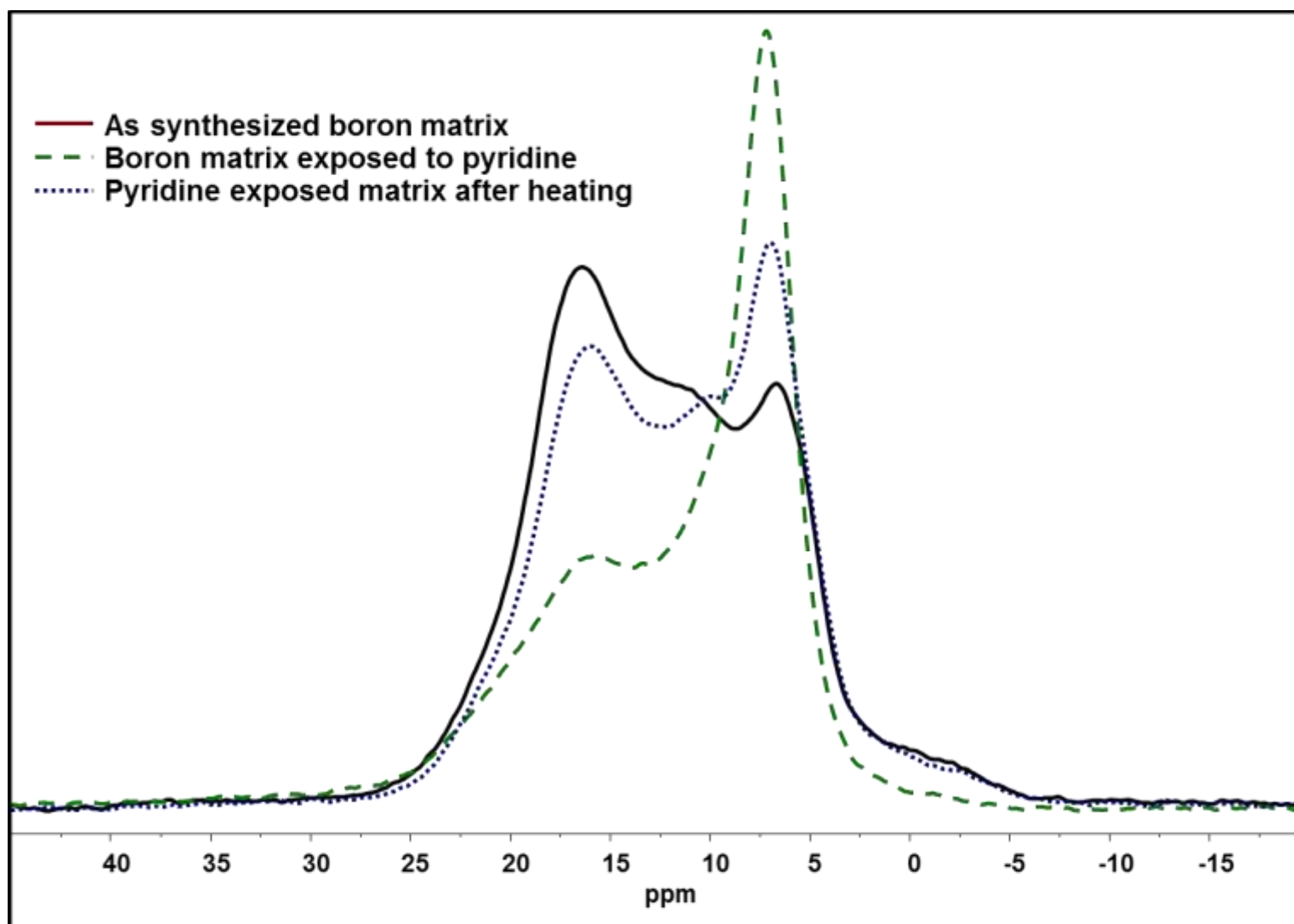


Figure 4.12: Comparison of ^{11}B MAS NMR spectrum of 1-dose embedded B sample exposed to pyridine and heated under vacuum

completion, the volatiles were removed and the sample dried at 40 °C overnight. This is a lower temperature than normal, and was chosen so as not to remove pyridine bound to the boron centers. The volatiles were analyzed by NMR and the only byproduct present was found to be Me₃SnBr. There was no evidence for the formation of Me₄Sn, and there were only trace amounts of pyridine present. Gravimetric analysis showed a connectivity of only 1.7, but this low value may be due to the fact that the sample was not heated to 80 °C to ensure removal of all trimethyltin bromide.

The IR spectrum (Figure 4.13a) of the sample clearly shows the trigonal BO₃ feature at 1386 cm⁻¹ which is nearly 20 cm⁻¹ lower than that seen in the initial spectrum of the non-pyridine adduct previously discussed (Figure 4.05). This could be a result of having the pyridine already bound to B center during synthesis. This is also evidenced by the fact that as pyridine is removed, the BO₃ vibration shifts to higher frequency (Figure 4.13b). The IR also clearly shows the expected pyridine bands characteristic of Lewis acidic binding.

The ¹¹B solid state NMR is very interesting (Figure 4.14). There is a very prominent tetrahedral boron species at $\delta = 1.2$ ppm with no observable quadrupolar lineshape. In addition, there is a set of signals possessing significant quadrupolar lineshape centered at $\delta = 11$ ppm. These latter signals are very similar to the trigonal boron centers that have been previously observed. The tetrahedral signal is shifted significantly from that seen upon addition of pyridine to the already embedded trigonal BO₃ centers constructed in the reaction of BBr₃ with TMT cube. The signal also possesses a narrower linewidth. The similarities and differences of this species to the one previously prepared by secondary addition of pyridine become clear when the two boron spectra are overlaid (Figure 4.15). The presence a trigonal boron signal in this spectrum implies that even gentle heating the sample to 40 °C in order to remove the volatile trimethyltin bromide byproduct may also have resulted in the removal of pyridine from some boron centers.

The shifted BO₃ vibration in the IR, and the change in the tetrahedral boron signal in the ¹¹B SSNMR imply that the boron centers in the matrix differ depending on

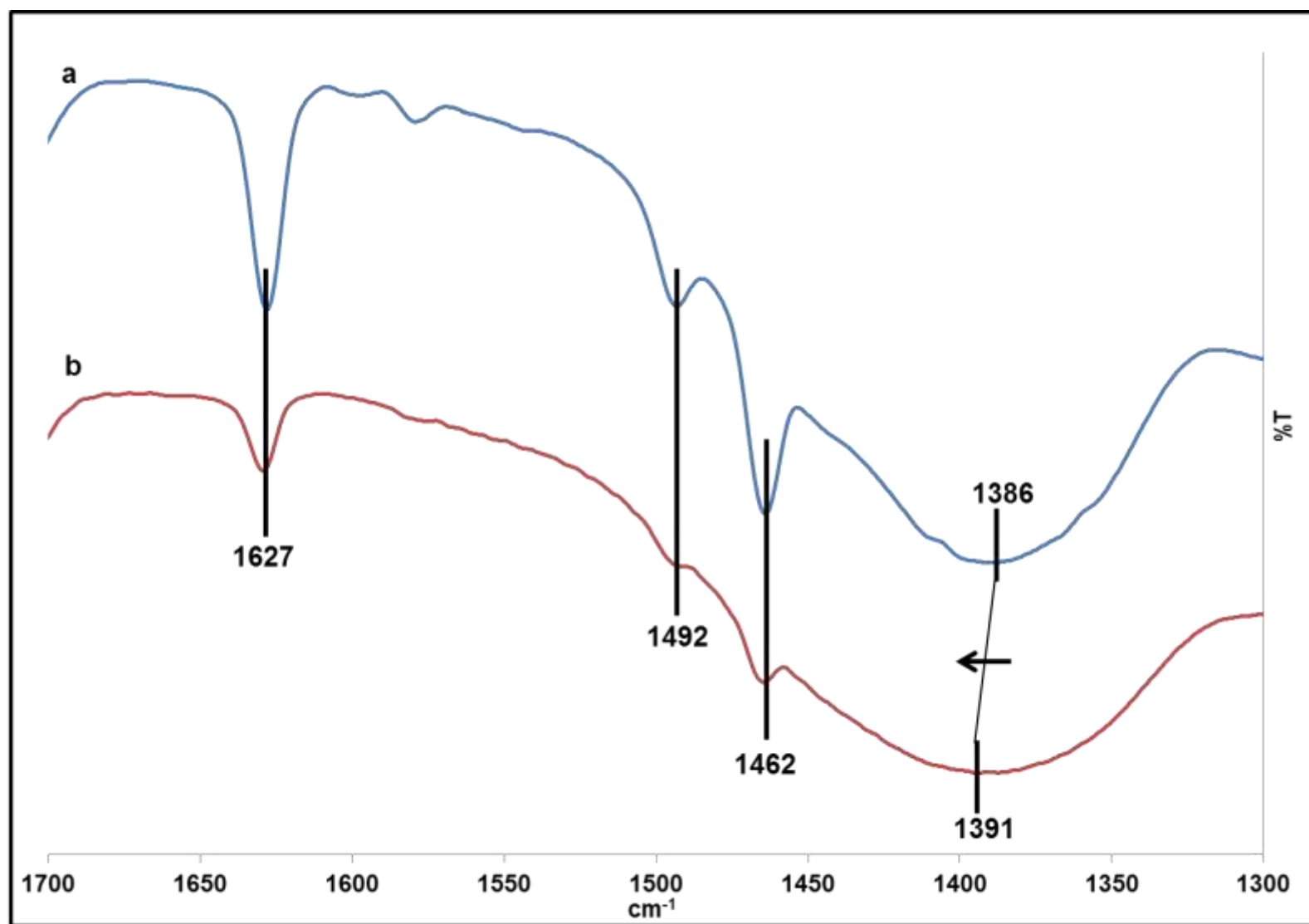


Figure 4.13: IR spectrum of (a) embedded B·Py matrix, (b) after heating under vacuum

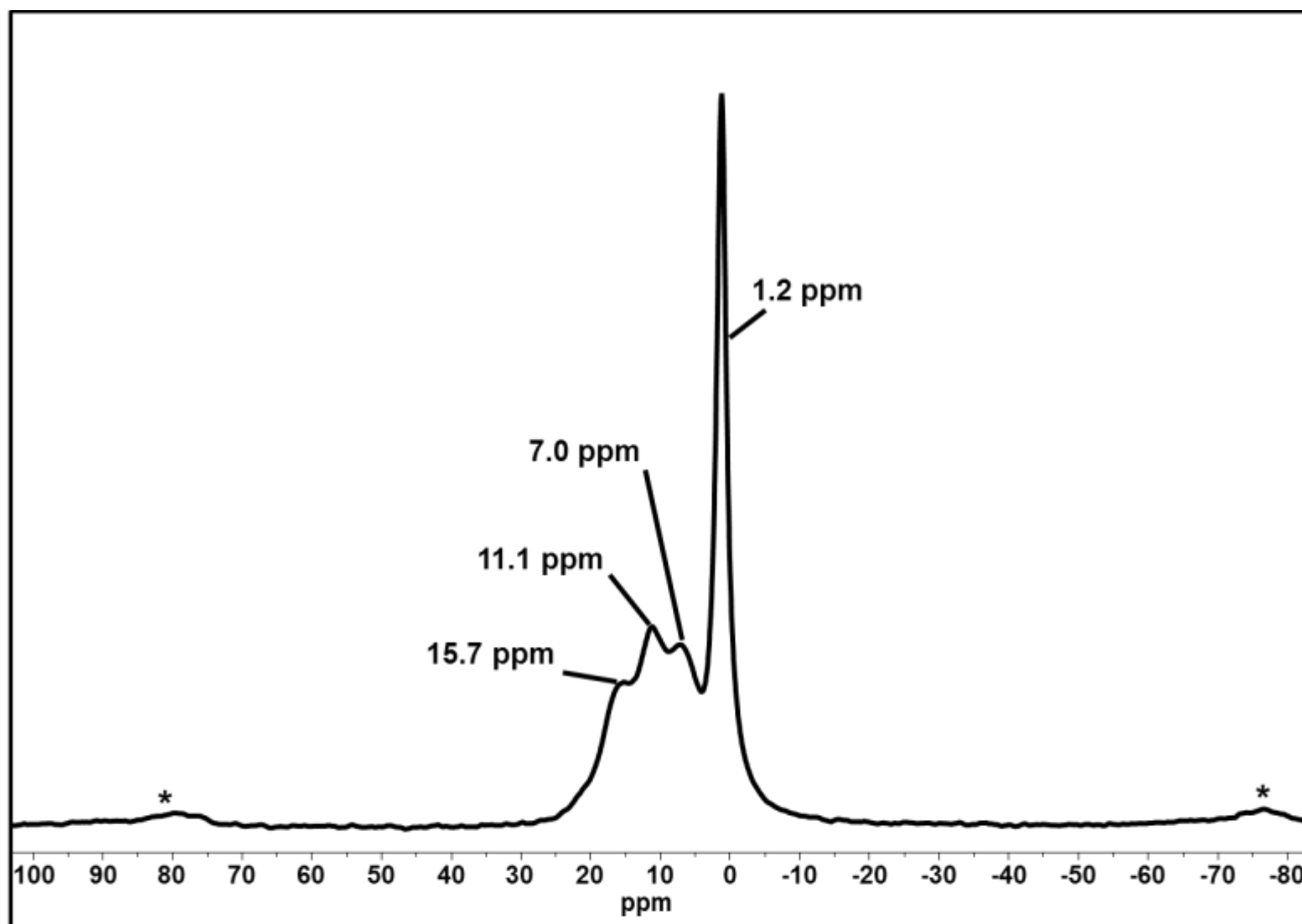


Figure 4.14: ^{11}B MAS (9.4T, 10 KHz) NMR spectrum of 1-dose embedded B·Py sample
(* = spinning side bands)

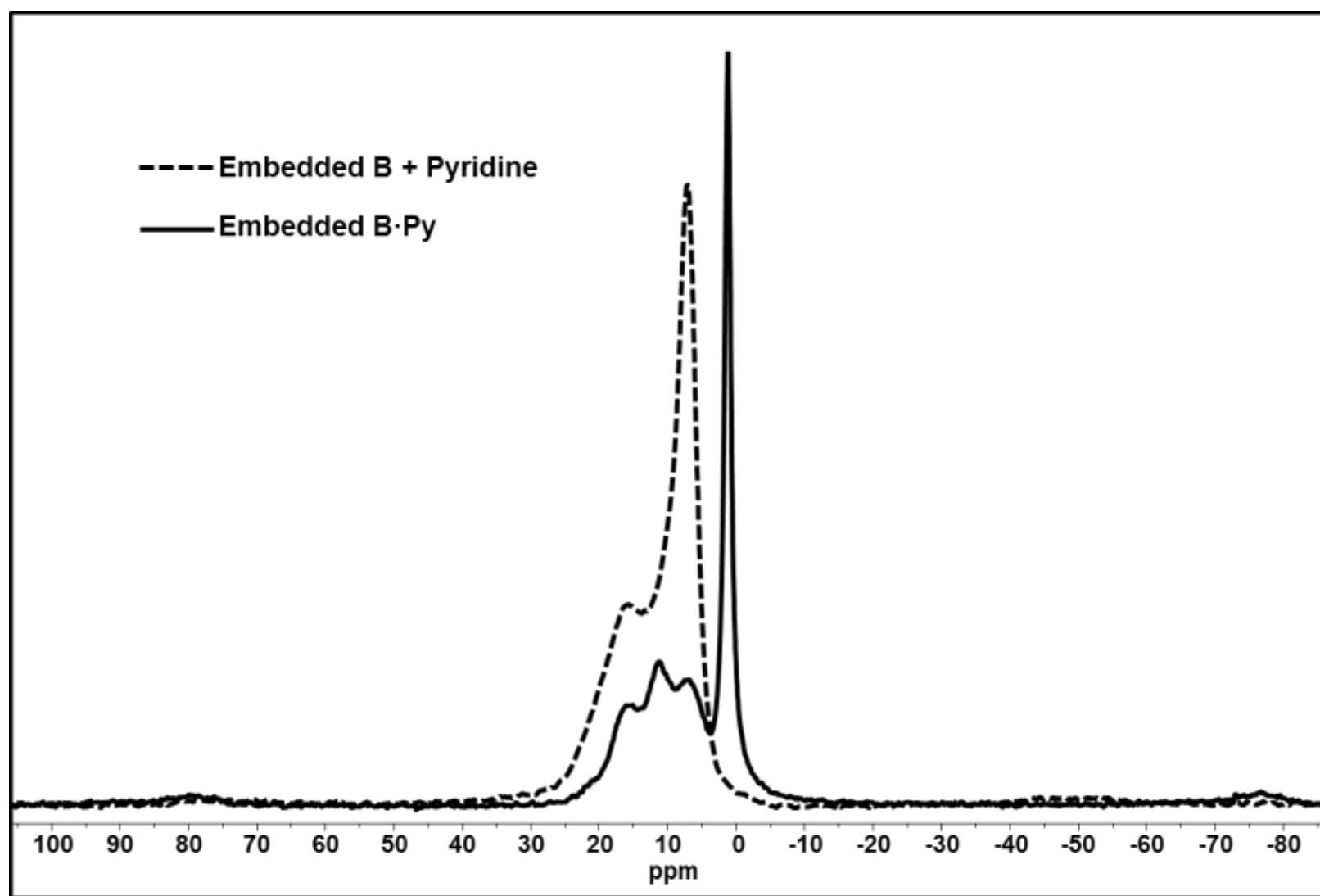


Figure 4.15: Comparison of ^{11}B MAS NMR spectrum of 1-dose embedded B sample exposed to pyridine, and 1-dose embedded B·Py sample.

when the pyridine is added. That is, boron centers that are imbedded into the matrix and then treated with pyridine are not the same as boron centers with pyridine bound before being embedded into the matrix. It is not unreasonable to believe that when pyridine is adsorbed post synthesis that the trigonal boron centers may not change to a fully tetrahedral species due to the rigidity of the cross linked matrix. On the other hand, when starting from the tetrahedral $\text{BBr}_3\cdot\text{Py}$ precursor, once the boron center is imbedded, it is already in a tetrahedral geometry.

4.3.3 POSS Molecular Analogues of One Dose Embedded Boron Catalysts

The more tractable nature of the reaction of BBr_3 with trimethyltin cube made synthesizing molecular analogues extremely enticing. The reaction was carried out by



reacting 3.6 equivalents (20% excess) of iBuPOSS(TMT) with 1 equivalent of BBr_3 in toluene. The reaction was carried out at 80 °C for 48 hours with no evidence of phase separation. The volatiles were removed and the product dried under vacuum. Analysis of the volatiles showed only trimethyltin bromide, and gravimetric analysis indicated a loss of 3.0 equivalents of tin (Equation 4.1).

IR and both solution and solid state NMR were used to characterize the molecular species. The IR spectrum (Figure 4.16) is significantly more complicated than those observed for the amorphous borosilicates described above. This is primarily due to the R groups found on the iBuPOSS. Despite the complexity, a few important details can be gleaned from the spectrum. First and foremost, there is no evidence for $-\text{OH}$ in the spectrum. Also, looking in the fingerprint region (Figure 4.17) clues for the formation of B-O-Si bond formation can be observed. The clearest sign of B-O-Si bond formation would be the presence of the broad BO_3 feature in the 1300-1400 cm^{-1} range. In this case, there are a number of sharp features from the iBuPOSS in that region (Figure 4.17b), however, in the post reaction spectrum (Figure 4.17a), there appears to be a broad underlying feature upon which the sharp iBuPOSS vibrations are superimposed. More clearly however, the feature at 925 cm^{-1} that is present only in the

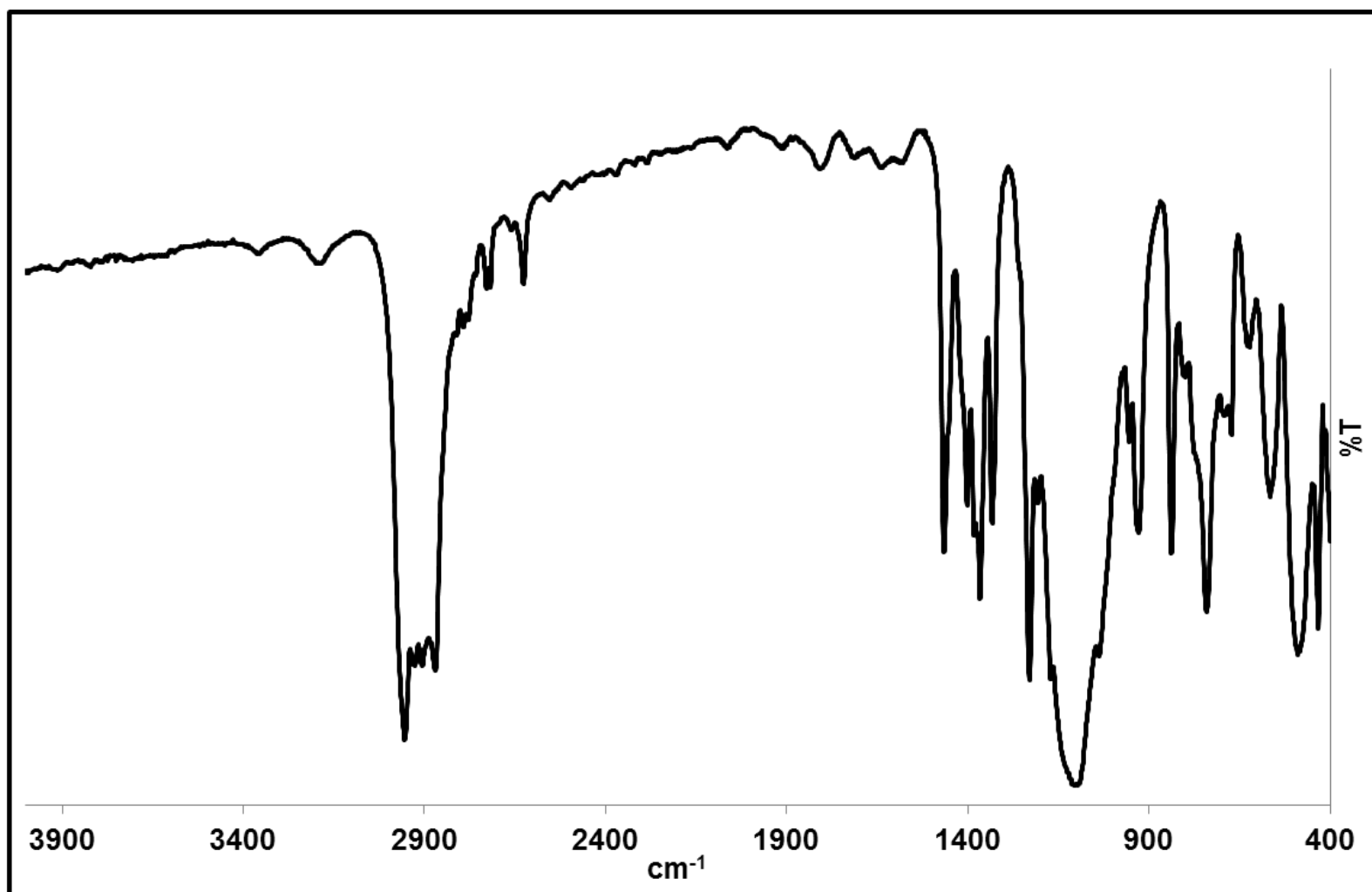


Figure 4.16: IR spectrum of B(iBuPOSS)₃ molecular species

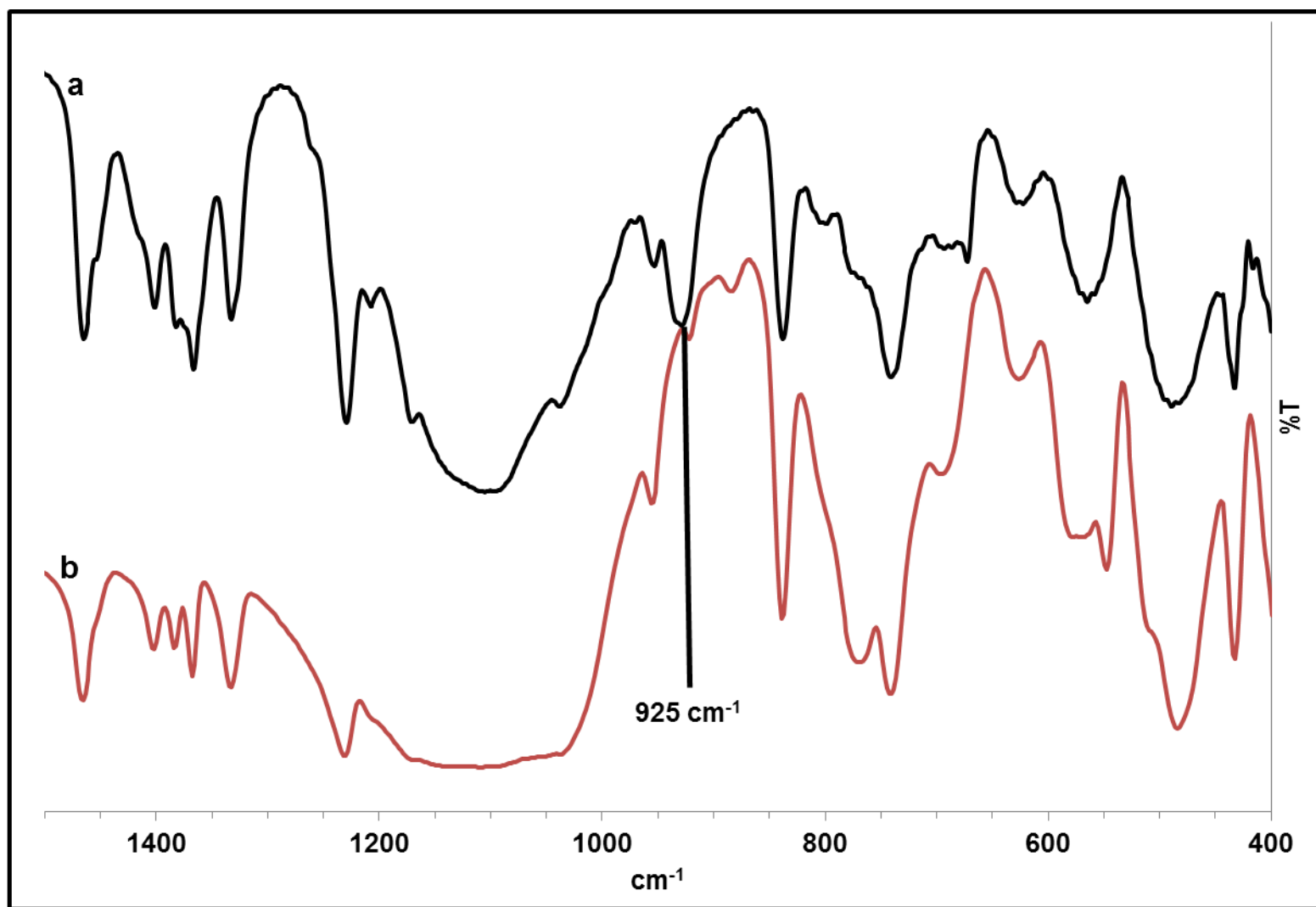


Figure 4.17: Comparison of IR spectra of a) the $\text{B}(\text{iBuPOSS})_3$ molecular species, and b) the $\text{iBuPOSS}(\text{TMT})$ precursor

product spectrum is a clear indication of B-O-Si bond formation.¹⁴³ There are other subtle changes that indicate some reaction has occurred such as the reduction in the width of the very broad feature centered at 1100 cm^{-1} , specifically on the low frequency side. This is attributed to the loss of most of the Si-O-Sn bonds during reaction. Features in the iBuPOSS precursor at 545, 690, and 760 cm^{-1} are also significantly altered or missing in the spectrum of the product.

Formation of B-O-Si bonds is further confirmed by ^{29}Si NMR both in solution (Figure 4.18), and in the solid state (Figure 4.19). In the solution spectrum, the resonances at -66, and -67 ppm result from the $-\text{O}_3\text{Si-R}$ silicon species, while the feature at -103.6 ppm is the excess unreacted $-\text{O}_3\text{Si-O-SnMe}_3$ silicon. The peak at -107.3 ppm is assigned to the $-\text{O}_3\text{Si-O-B}$ species. The presence of unreacted iBuPOSS(TMT) is expected based on the excess used in the reaction, and the position of the $-\text{O}_3\text{Si-O-B}$ peak is in good agreement with that seen in the case of B centers embedded in the amorphous building block matrix (Figure 4.07).

Attempts to collect solution ^{11}B NMR for this POSS analogue were surprisingly unsuccessful, and no boron signal was observed. The logical explanation for this is that the quadrupolar coupling constant resulting from the low symmetry of the trigonal boron center is large enough to broaden the signal to such a degree that it is essentially invisible. This is similar to experiments with aluminum POSS analogues, where no observable aluminum signal was obtained. ^{11}B SSNMR (Figure 4.20) proved to be more fruitful, and a signal displaying a classic quadrupolar lineshape was observed indicating the presence of trigonally coordinated boron. The chemical shift of the signal envelope is shifted upfield from those seen in the embedded amorphous building block matrices containing boron. This might be explained by the nature of the POSS ligand where seven of the eight silicon centers are Q^3 instead of Q^4 in the case of the tin cube. The presence of the single R ligand on each of the silicon corners makes the entire POSS ligand more electron rich, and thus less electronegative.

Having successfully synthesized the trigonal $\text{B}(\text{iBuPOSS})_3$ molecular species, the next goal was to prepare high quality single crystals for structural analysis by x-ray diffraction. Crystals were successfully grown from a toluene/methylene chloride mixed

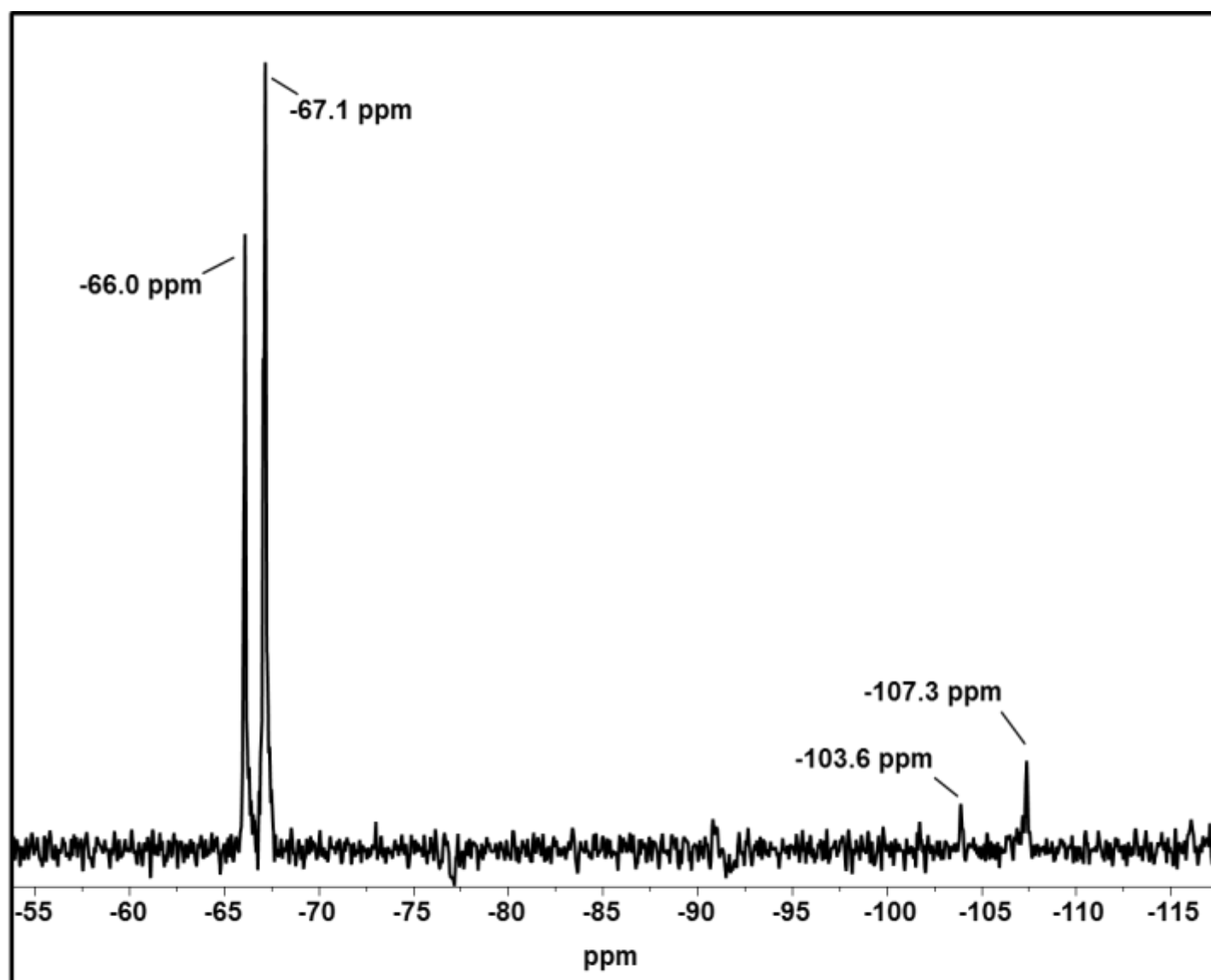


Figure 4.18: Solution ^{29}Si NMR spectrum of $\text{B}(\text{iBuPOSS})_3$

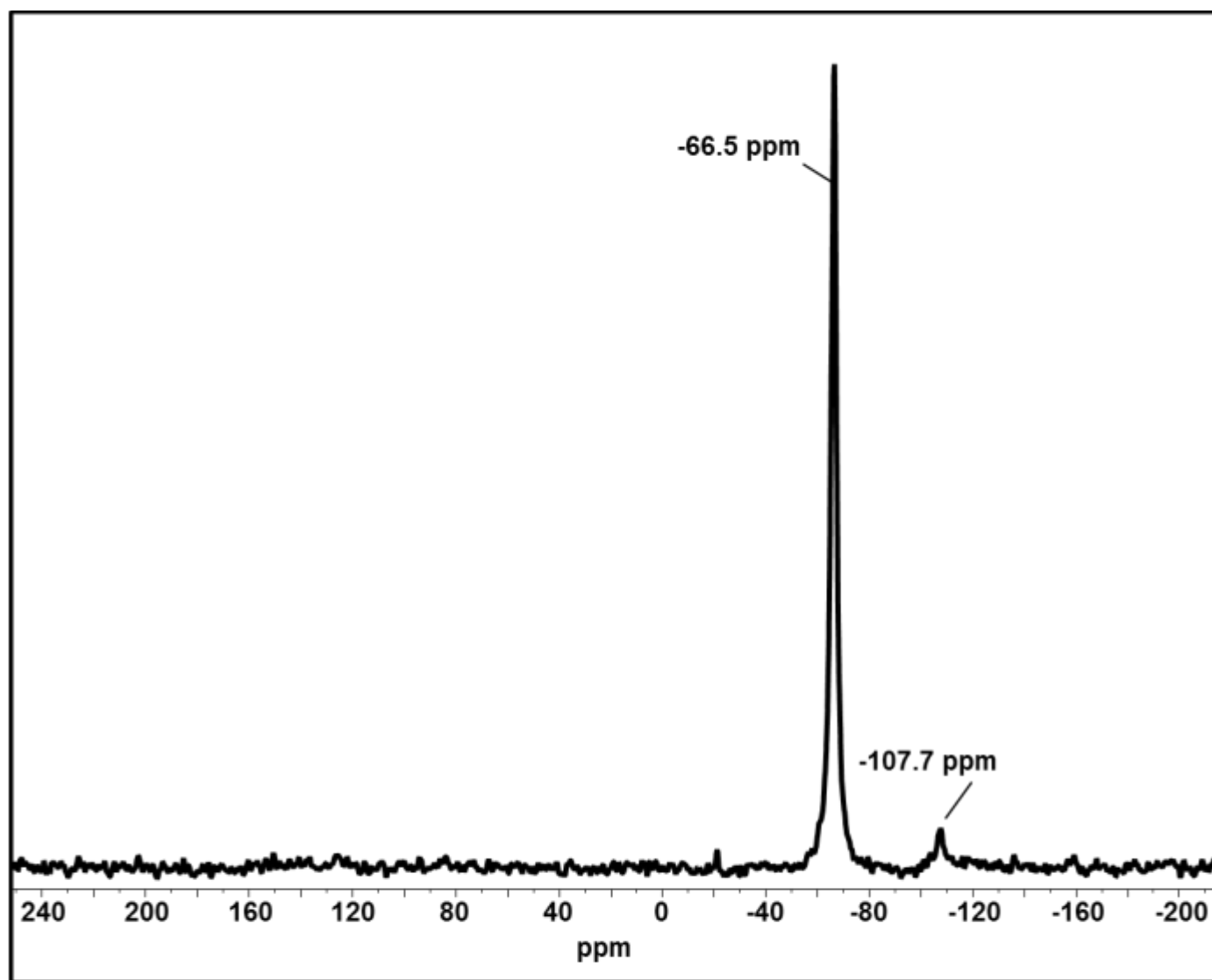


Figure 4.19: Solid State ^{29}Si MAS spectrum of $\text{B}(\text{iBuPOSS})_3$

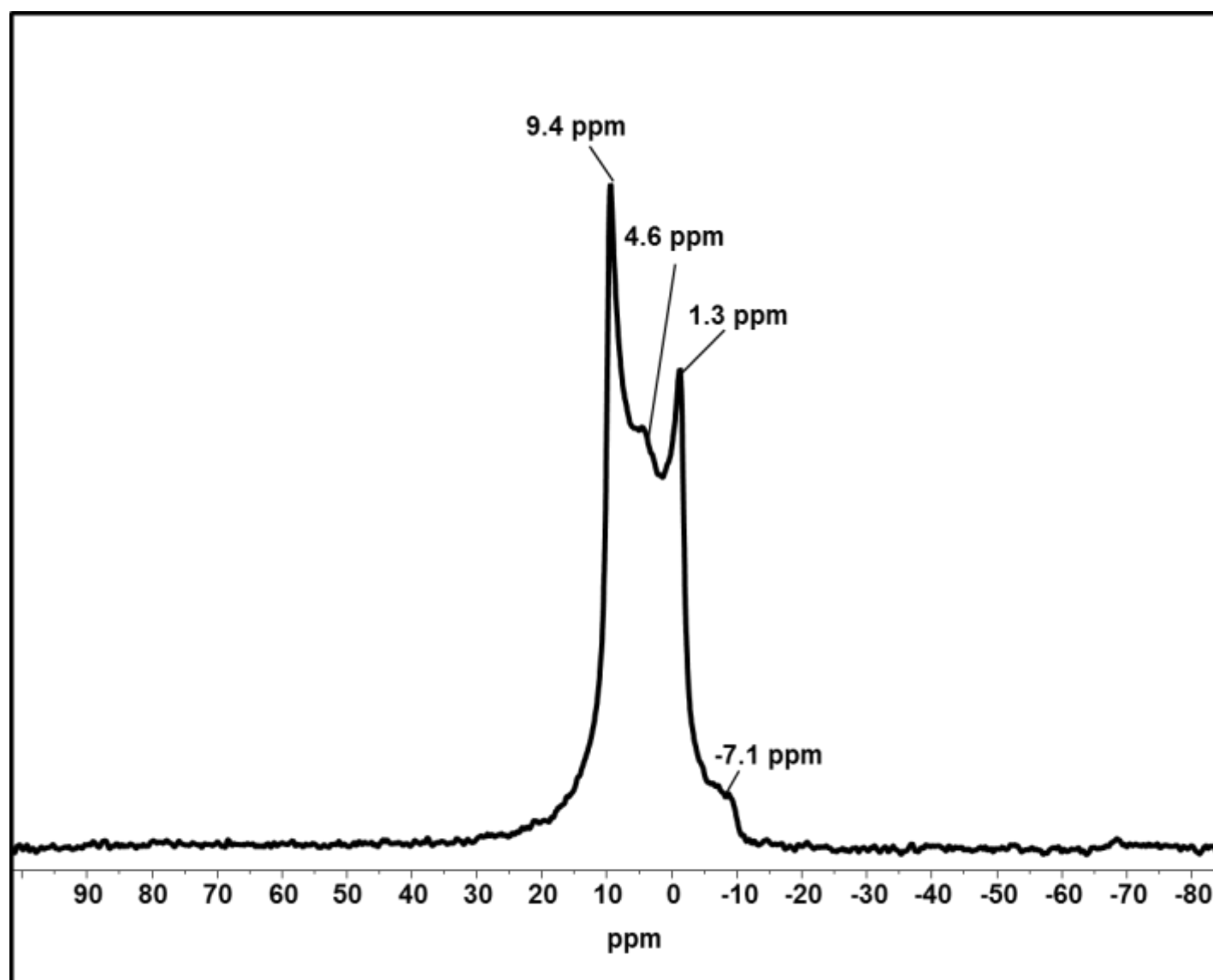


Figure 4.20: ^{11}B MAS (9.4T, 8 KHz) NMR spectrum of $\text{B}(\text{iBuPOSS})_3$

solvent system, but they were not of high enough quality to obtain an acceptable crystal structure.

4.4 Conclusions

Embedded boron catalysts have been prepared via the reaction of trimethyltin cube with BBr_3 and $\text{BB}_3\cdot\text{Py}$. The incorporation of these precursors has led to the formation of trigonal and tetrahedral boron centers in amorphous building block matrices. Pyridine binding to the boron centers is much weaker than in the aluminum and gallium analogues. As a result, the conversion of trigonal centers to tetrahedral centers and vice versa is possible through adsorption of pyridine, and subsequent heating of the pyridine bound species under vacuum. These materials have been characterized using BET, IR, NMR, and gravimetric analyses. In addition, synthesis of the molecular analogues $\text{B}(\text{iBuPOSS})_3$ was successful. However, suitable crystals for obtaining a high quality crystal structure have not yet been obtained. It is clear from these studies that boron is significantly different than both aluminum and gallium, manifested most prominently in the stability of planar three-coordinate species. This is a very interesting system that could be studied further in its own right in the future.

5. Conclusions and Future Work

5.1 Conclusions

Preparing heterogeneous catalysts that possess a single type of highly dispersed active site represents a major challenge in catalysis science. The need for these catalysts to exhibit improved activity, selectivity, and process efficiency in chemical manufacturing has resulted in a sustained effort to improve and discover new catalytic systems. Essential for the design of improved catalysts is a deep understanding of structure activity relationships, and central to this concept is the study of the catalytic activity of catalysts where the structural nature of the active site is well characterized. For this to occur, it is necessary for a catalytic matrix to possess the fewest possible number of distinct catalytic sites (ideally one). The synthetic methodology utilized in the work presented in this dissertation illustrates a promising way to integrate a variety of unique catalytic precursors and ensembles into high surface area matrices in a manner that ensures structural similarity between the final sites. This work has sought to examine the applicability of the building block synthetic methodology to the creation of heterogeneous group 13 (B, Al, Ga) single site catalysts, and to characterize the nature of the synthesized materials.

When this research project began, the primary focus was to apply the principles of the building block synthetic methodology to aluminum. Successful application of the method at that point had been carried out with Ti, V, and Si centers. Incorporating aluminum centers into the building block matrix was a logical next step due to the ubiquitous use of aluminosilicates in a wide variety of catalytic applications.

Investigations found that in this system, aluminum does react to produce a cross linked matrix of Si_8O_{20} cubes. However, early in the study of these materials it became clear that the reaction proceeded in a different fashion than had previously been observed. One of the strong selling points of the tin functionalized Si_8O_{20} building block is the well behaved nature of the metathesis reaction with metal chlorides to form M-O-Si bonds, and a single volatile product, trimethyltin chloride. This was not the case in the reaction of aluminum trichloride with the trimethyltin cube, as a second byproduct,

identified as tetramethyltin, was being produced in significant quantities. Direct characterization of the resultant aluminum centers by ^{27}Al solid state NMR yielded spectra that were more complicated than expected, and indicated the presence of multiple types of aluminum centers.

In order to better understand the nature of aluminum sites in these catalytic matrices, two thrusts of investigation were pursued. The first of these was to examine a number of variations on the reaction by modifying the aluminum precursor ($\text{AlCl}_3\cdot\text{Py}$, $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$, $[\text{nBu}_4\text{N}][\text{AlCl}_4]$) and the building block (POSS). In the second thrust, analogous group 13 species (B, Ga) were examined to determine their similarities and differences to Al.

It was determined that the pathway for production of the secondary byproduct, Me_4Sn , could be shut down by starting with either the $\text{AlCl}_3\cdot\text{Py}$, or $[\text{nBu}_4\text{N}][\text{AlCl}_4]$ precursors. When the precursor $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ was used, significant amounts of tetramethyltin were observed in the reaction volatiles, in a fashion very similar to what was seen when starting from AlCl_3 . These results, in conjunction with literature precedence for the preparation of $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ from AlCl_3 and Me_3SnCl , indicate that $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$ was likely being formed in situ from during the crosslinking reaction starting from the AlCl_3 precursor. Furthermore, based on the fact that reaction of trimethyltin cube with $[\text{nBu}_4\text{N}][\text{AlCl}_4]$ did not produce tetramethyltin, then the culprit could only be the trimethyltin cation $[\text{Me}_3\text{Sn}]^+$. This was confirmed by preparing and reacting $[\text{Me}_3\text{Sn}][\text{Tf}]$ with the tin cube where tetramethyltin was the only volatile reaction product observed.

The nature of the aluminum sites created in these reactions was difficult to determine, and left a number of questions. Direct characterization of the aluminum sites by solid state ^{27}Al nmr, showed multiple signals indicative of multiple sites in the matrix. These materials were found to be extremely moisture sensitive, leading to significant alteration of the aluminum sites initially present. To the best of the knowledge gained through the experiments detailed in this dissertation, it is our belief that the embedded aluminum centers are primarily tetrahedral upon completion of the cross linking

reaction, but extremely sensitive to absorption of moisture which can result in increased coordination.

Carrying out the crosslinking reaction with analogous gallium trichloride, similar reaction properties were seen, and both Me_3SnCl , and Me_4Sn were produced as byproducts. Characterization of these materials by x-ray absorption spectroscopy, and specifically, modeling of the EXAFS data resulted in the conclusion that embedded gallium centers had taken the form of tetrahedral GaO_4 centers. These data are the strongest evidence we have for the true nature of the metal sites in these catalytic matrices, and is in agreement with what we believe about the structure of the aluminum analogues.

Similar reactions carried out with BBr_3 showed behavior that was different from its aluminum and gallium analogues. This was not unexpected as boron is known to form stable trigonal BO_3 units. Using IR, and ^{11}B SSNMR we were able to show that the initial boron sites embedded in the matrix were in fact trigonal, but more interestingly, that they could be modified, at least in part, to tetrahedral geometries, through exposure to pyridine. Furthermore the pyridine could be removed by heating under vacuum to return the boron centers to their original trigonal geometry.

5.2 Future Work

While progress has been made, this research has opened the door for future work with these materials. There are a number of experimental directions that could provide fruitful results that could further the understanding and applicability of these group 13 silicate catalysts.

5.2.1 Synthesis in Coordinating Solvents & Modification of Adduct Species

The reaction of trimethyltin cube with aluminum or gallium trichloride appears to proceed in a much cleaner fashion in diethyl ether and THF solution. We have shown that this is likely a result of bound solvent adducts preventing the formation of the $[\text{Me}_3\text{Sn}]^+$ species in the reaction of AlCl_3 and the Me_3SnCl byproduct. In addition the bound solvent could be displaced by exposure to a stronger donor (i.e. pyridine). This

presents an opportunity to adjust and modify the nature of the fourth coordination site on the aluminum and gallium centers. For example if a 4-coordinate $L \cdot AlO_3$ center were to be exposed to an alcohol, then it is conceivable that the Lewis acidic aluminum center could be converted to a pseudo Brønsted acid site (Figure 5.01). This would open up a whole new way of creating such acid sites starting from a well-defined isolated aluminum center in a silicate matrix.

Similarly, it has been difficult to remove donor molecules from the aluminum center due to the low stability of a three coordinate species (excepting B). However, attempting to use sterically hindered species such as 2,6-dimethylpyridine similar could lead to a more weakly bound adduct with the possibility of removal.

5.2.2 Utilizing Chloro-Aluminates and Gallates

Experience has shown that $[AlCl_4]^-$ and $[GaCl_4]^-$ species react cleanly with the tin cube as long as the accompanying cation is not $[Me_3Sn]^+$. In the few trials using the $[nBu_4N][MCl_4]$ species, only trimethyltin chloride has been observed. However, fully embedded centers have yet to be observed. It is unknown if this is a steric effect from the large cation, or an electronic effect resulting from the more stable tetrahedral species. There is plenty of work to do here in terms of exploring this question by changing the nature of the cation to something smaller such as the tetramethyl ammonium analogue. One could even explore using the ammonium cation, with the additional intriguing question as to whether heating such a species after embedding it into the matrix would result in the loss of ammonia, and formation of true Brønsted acid site.

5.2.3 Molecular Models

Through all of this research, a concerted effort has been made to try to prepare molecular models that could be crystallized and structurally characterized by crystallographic methods. While such a material has not yet been successfully prepared, the ability to grow some crystals, while not of the highest quality, keeps the belief alive that the right materials under the right conditions exist and are still waiting to be found. While the POSS materials are the most obvious target, recent test reactions

looking at $\text{Me}_3\text{SiOSnMe}_3$ as an analogue of the cube have been interesting, and need to be examined further.

5.2.4 Boron Systems

While the aluminum and gallium cross linked matrices offer more promise for development of active catalysts, the boron system has proven to be far more tractable. As a result, it presents a number of opportunities for continued study with likely positive results. It was shown that pyridine could be absorbed and desorbed from the BO_3 centers to a certain degree. It would be interesting to see if complete conversion of the boron centers to tetrahedral adduct species could be carried out successfully, and then whether the adduct could be completely removed.

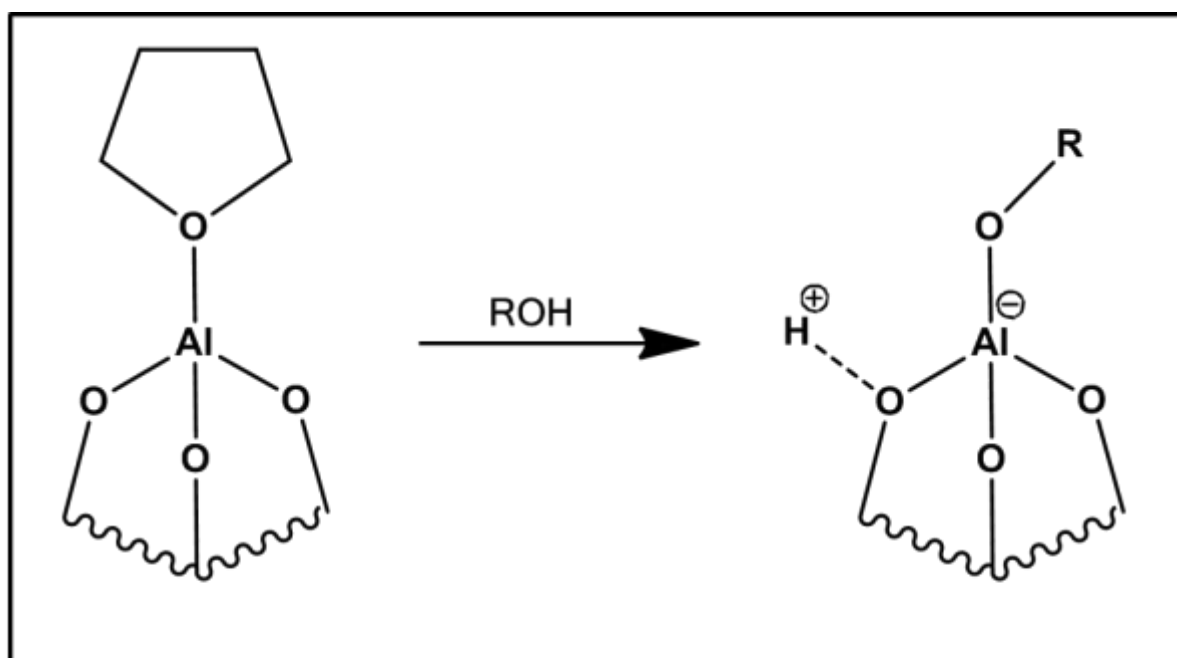


Figure 5.01: Conversion of Lewis acid bound THF adduct to pseudo Brønsted acid site

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Appendix

Spectra of Synthesized Precursors:

1. $\text{AlCl}_3 \cdot \text{Py}$

- a. ^1H
- b. ^{13}C
- c. ^{27}Al

2. $[\text{Me}_3\text{Sn}][\text{AlCl}_4]$

- a. ^1H
- b. ^{13}C
- c. ^{27}Al

3. $[\text{nBu}_4\text{N}][\text{AlCl}_4]$

- a. ^1H
- b. ^{13}C
- c. ^{27}Al

4. $[\text{Me}_3\text{Sn}][\text{OSO}_2\text{CF}_3]$

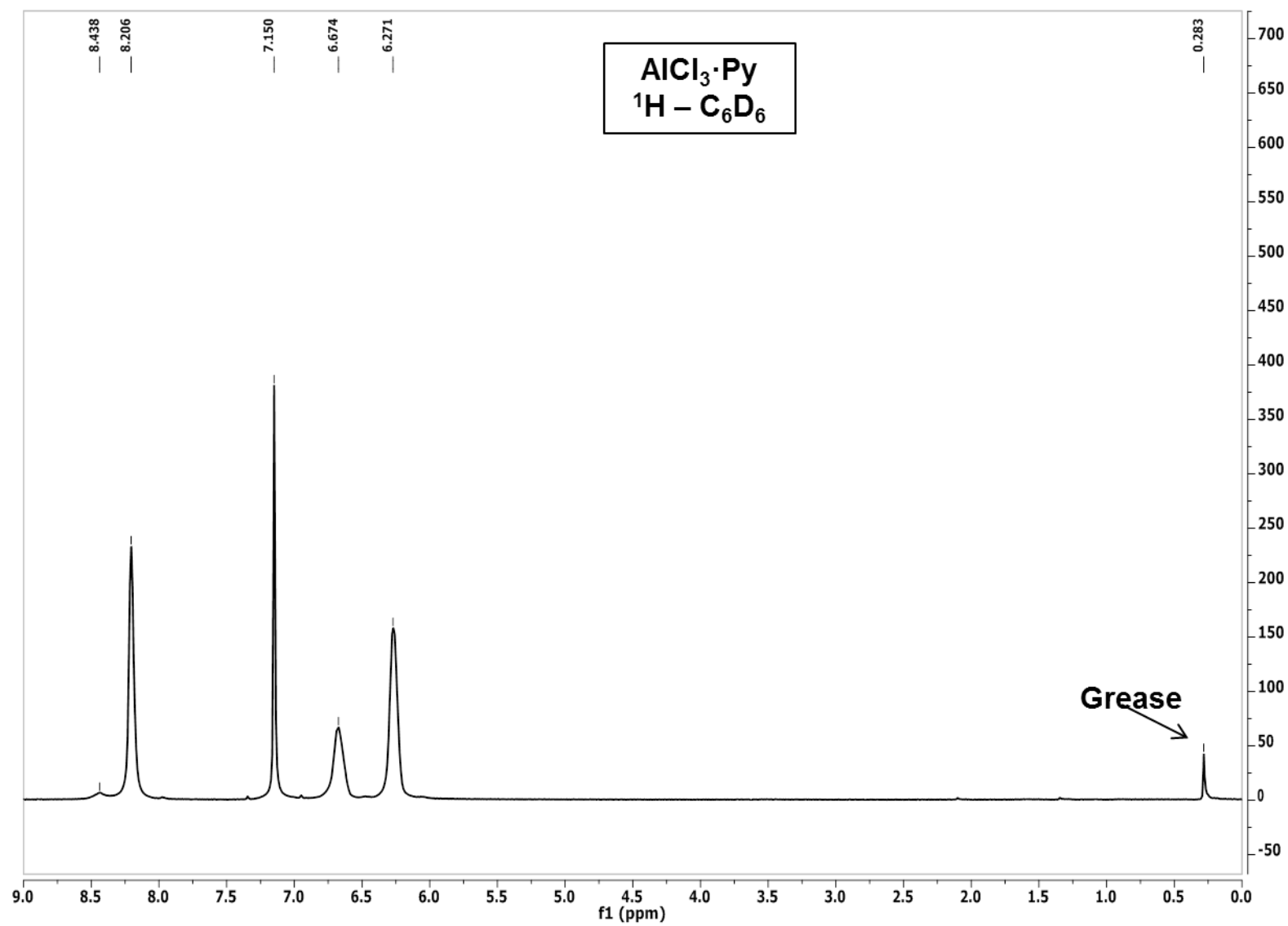
- a. ^1H
- b. ^{13}C
- c. ^{119}Sn

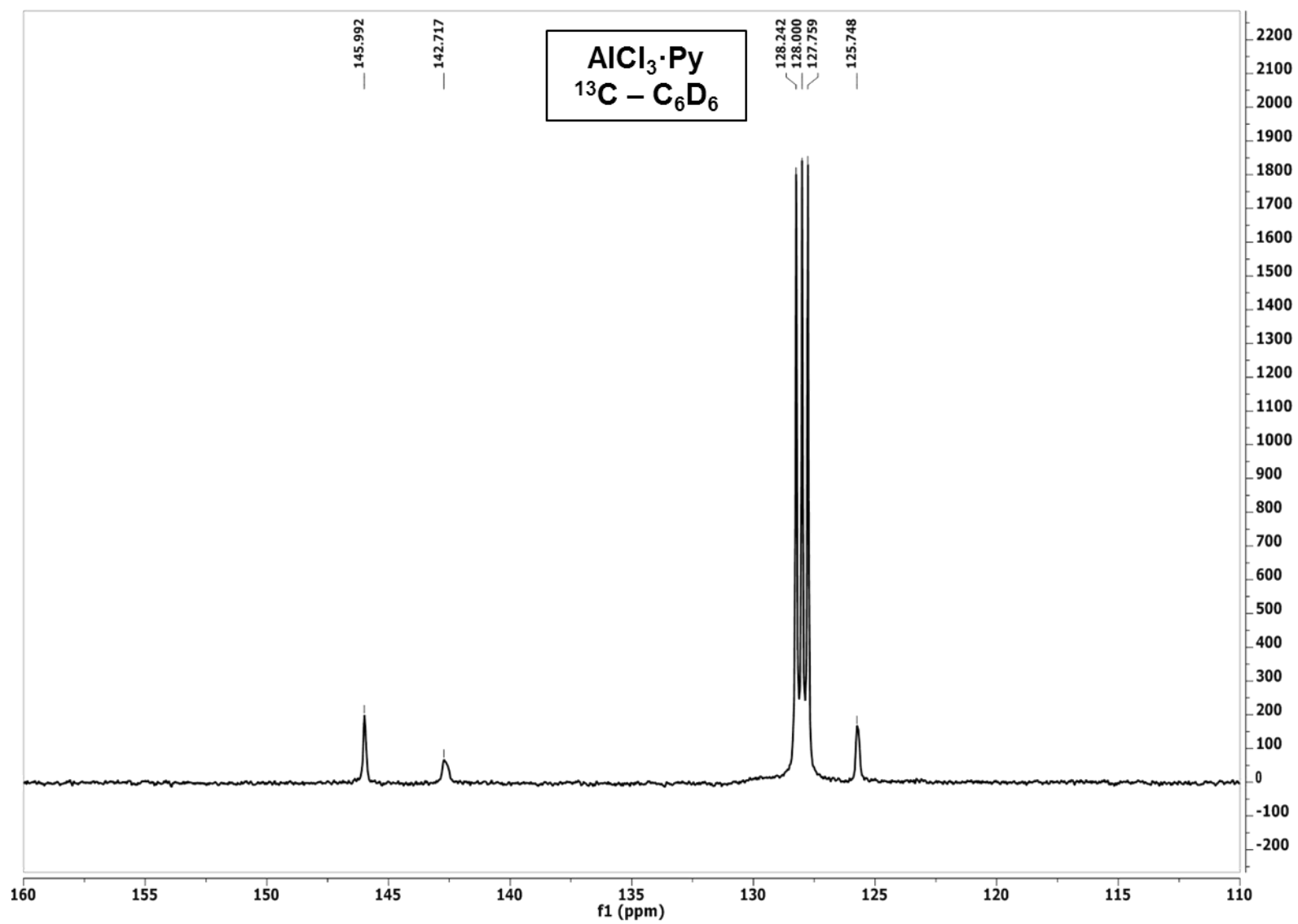
5. $[\text{nBu}_4\text{N}][\text{GaCl}_4]$

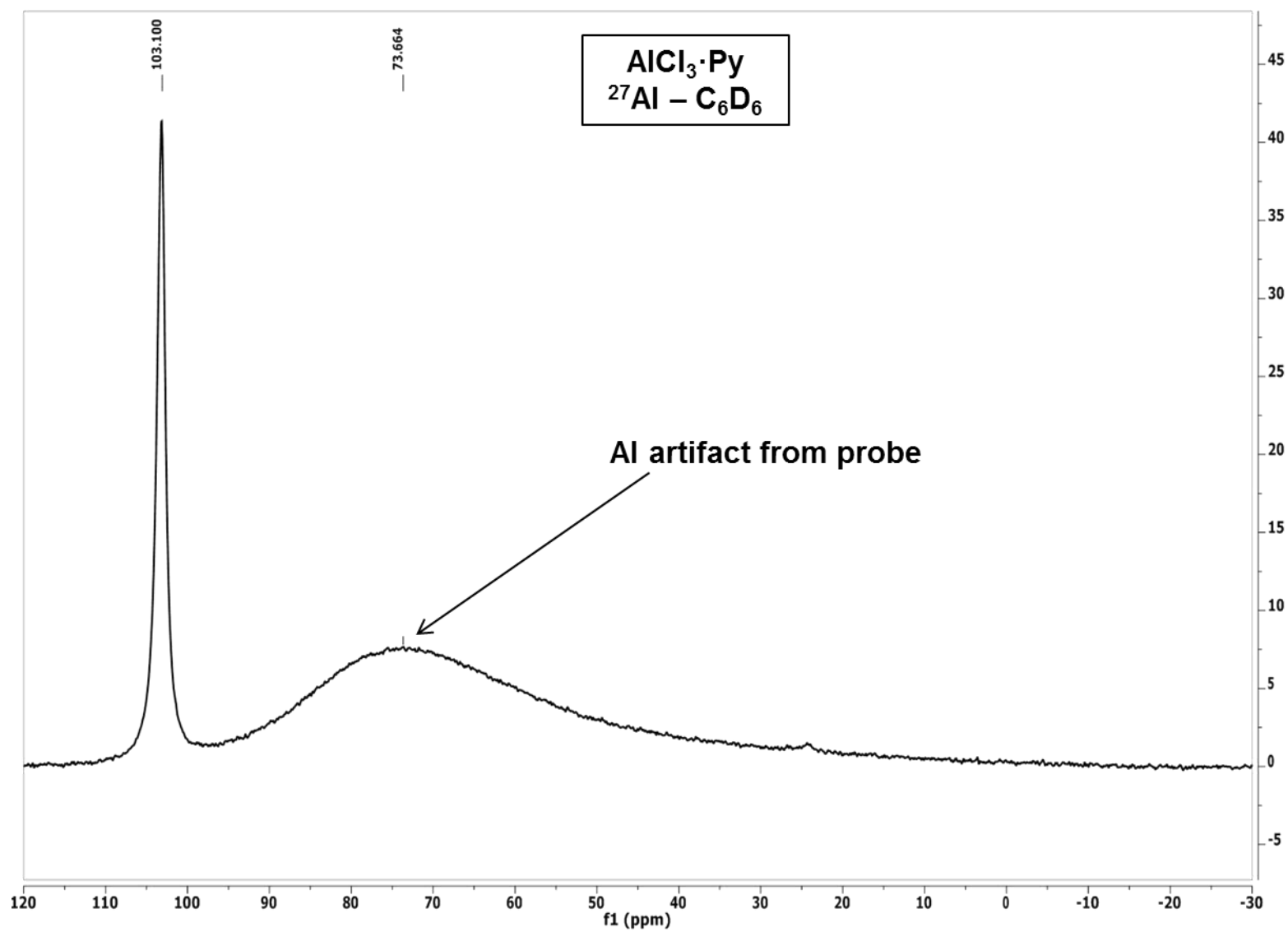
- a. ^1H
- b. ^{13}C
- c. ^{71}Ga

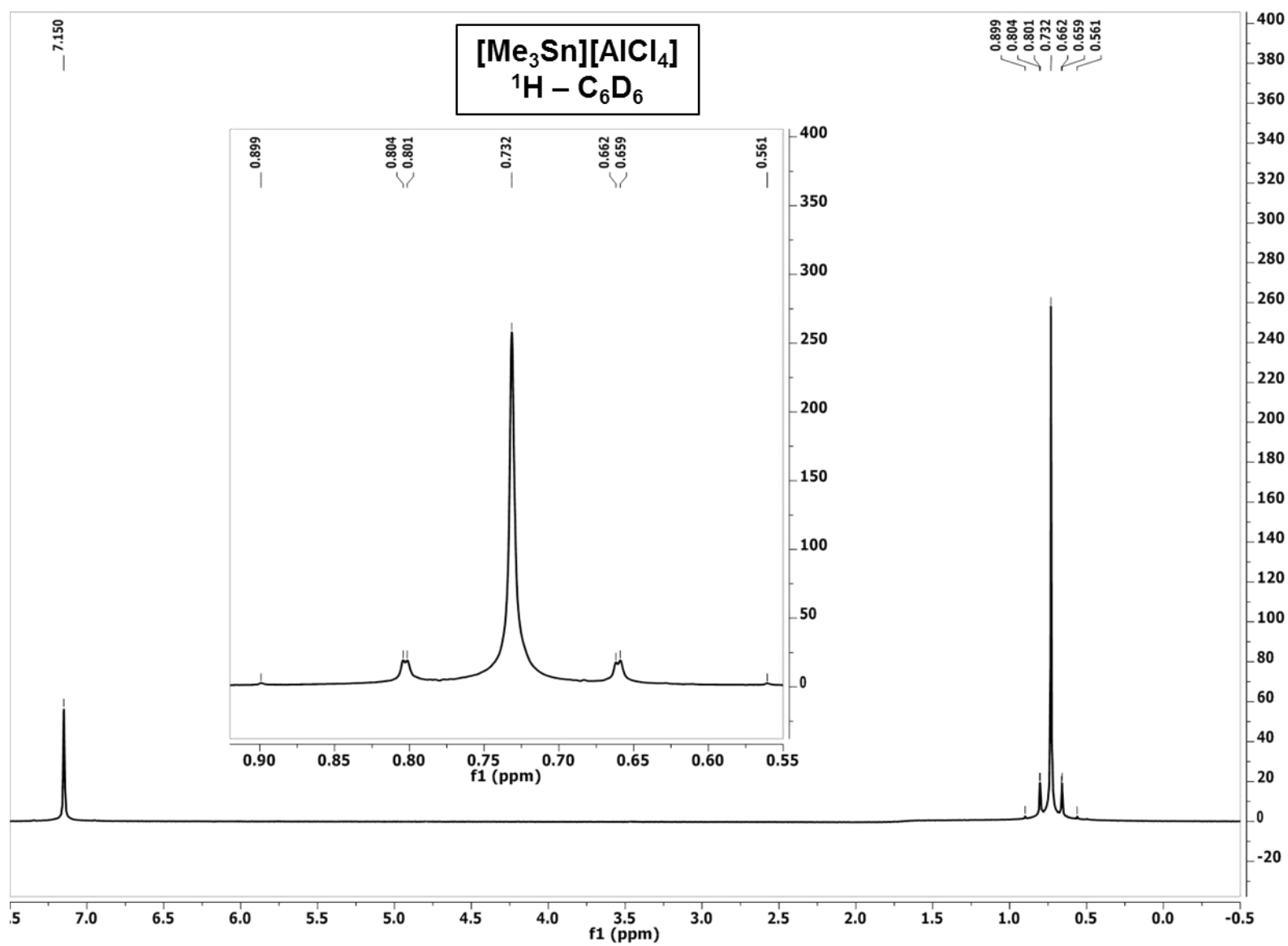
6. $\text{BBr}_3 \cdot \text{Py}$

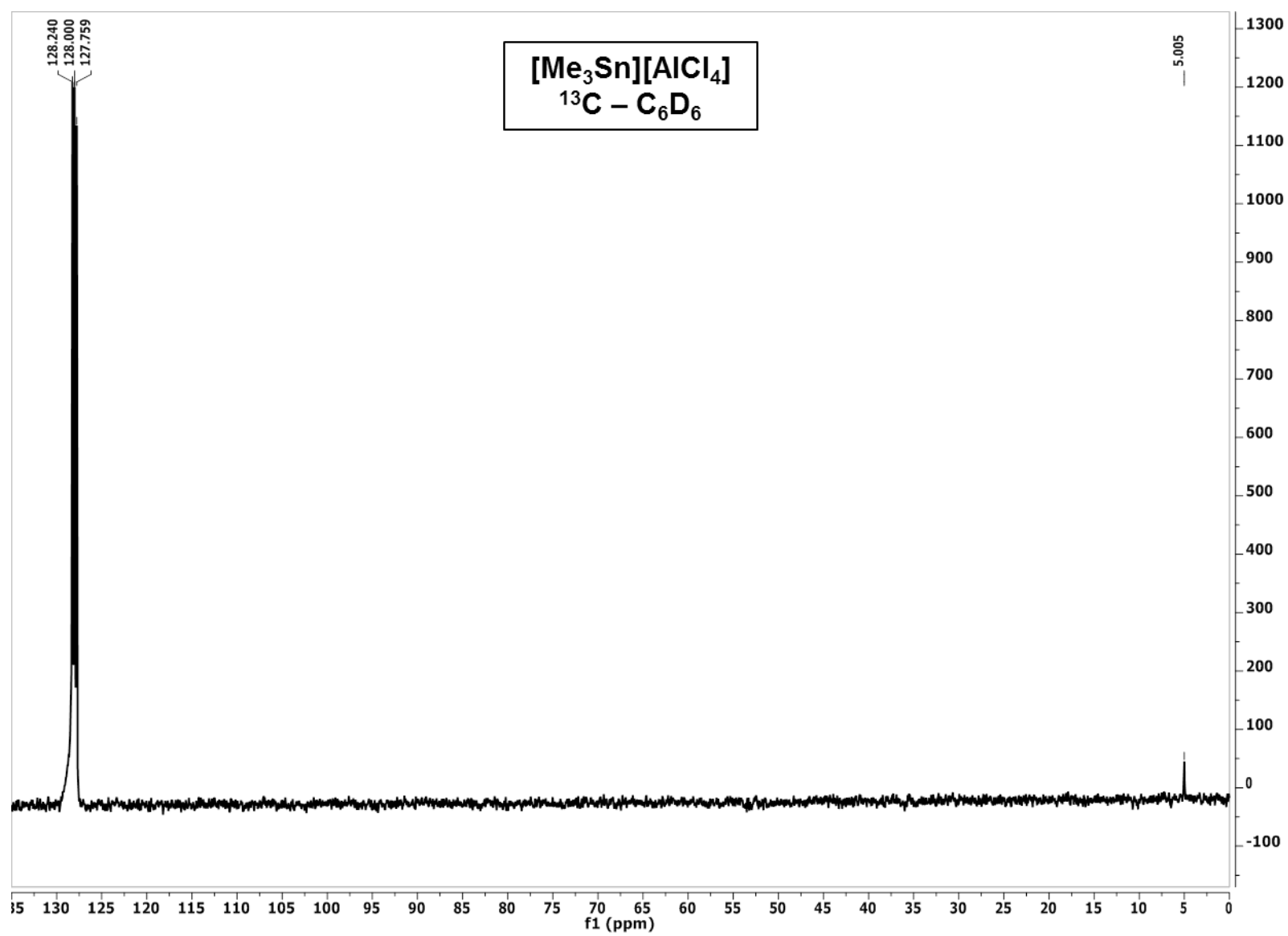
- a. ^1H
- b. ^{13}C
- c. ^{11}B

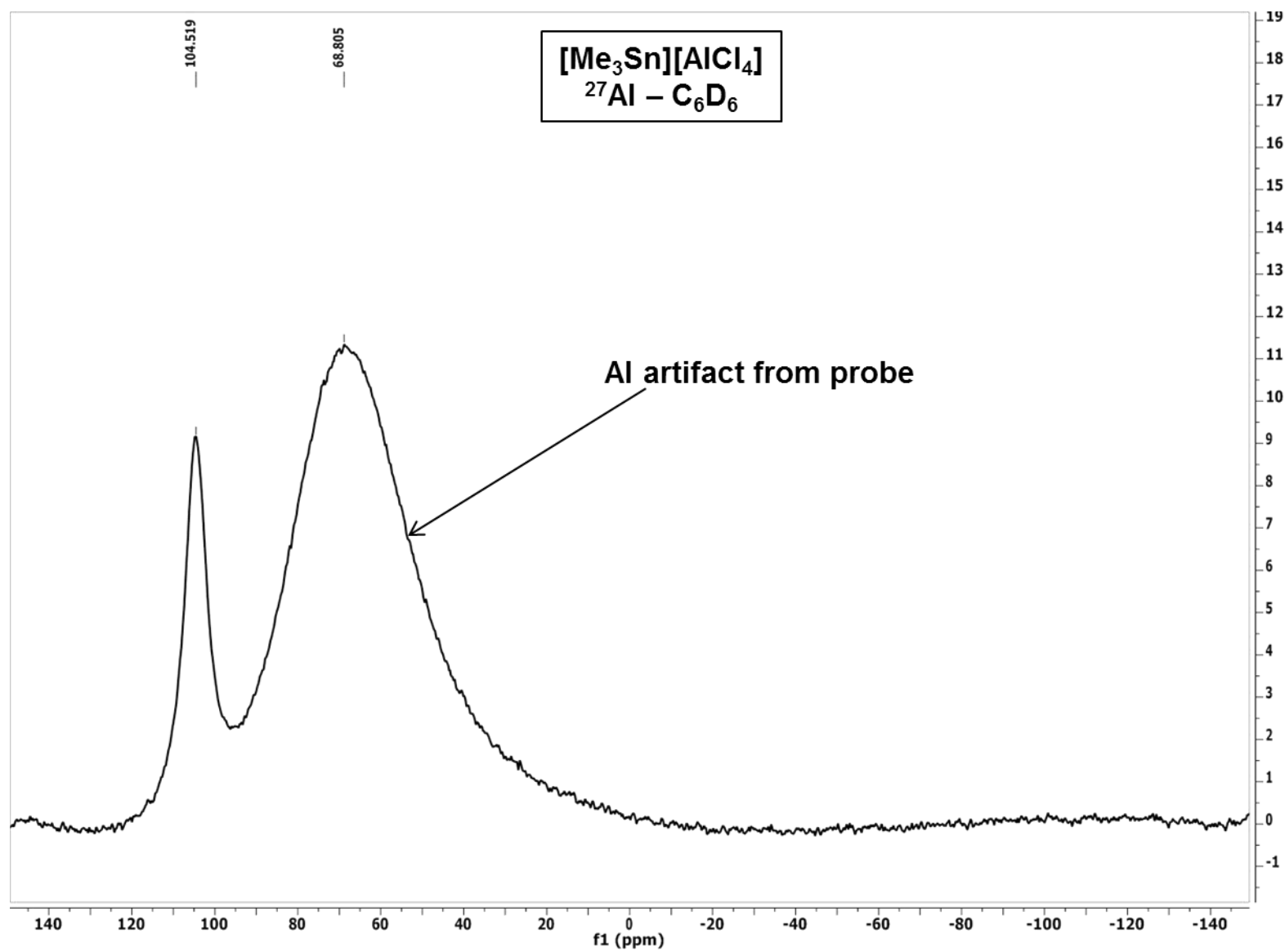


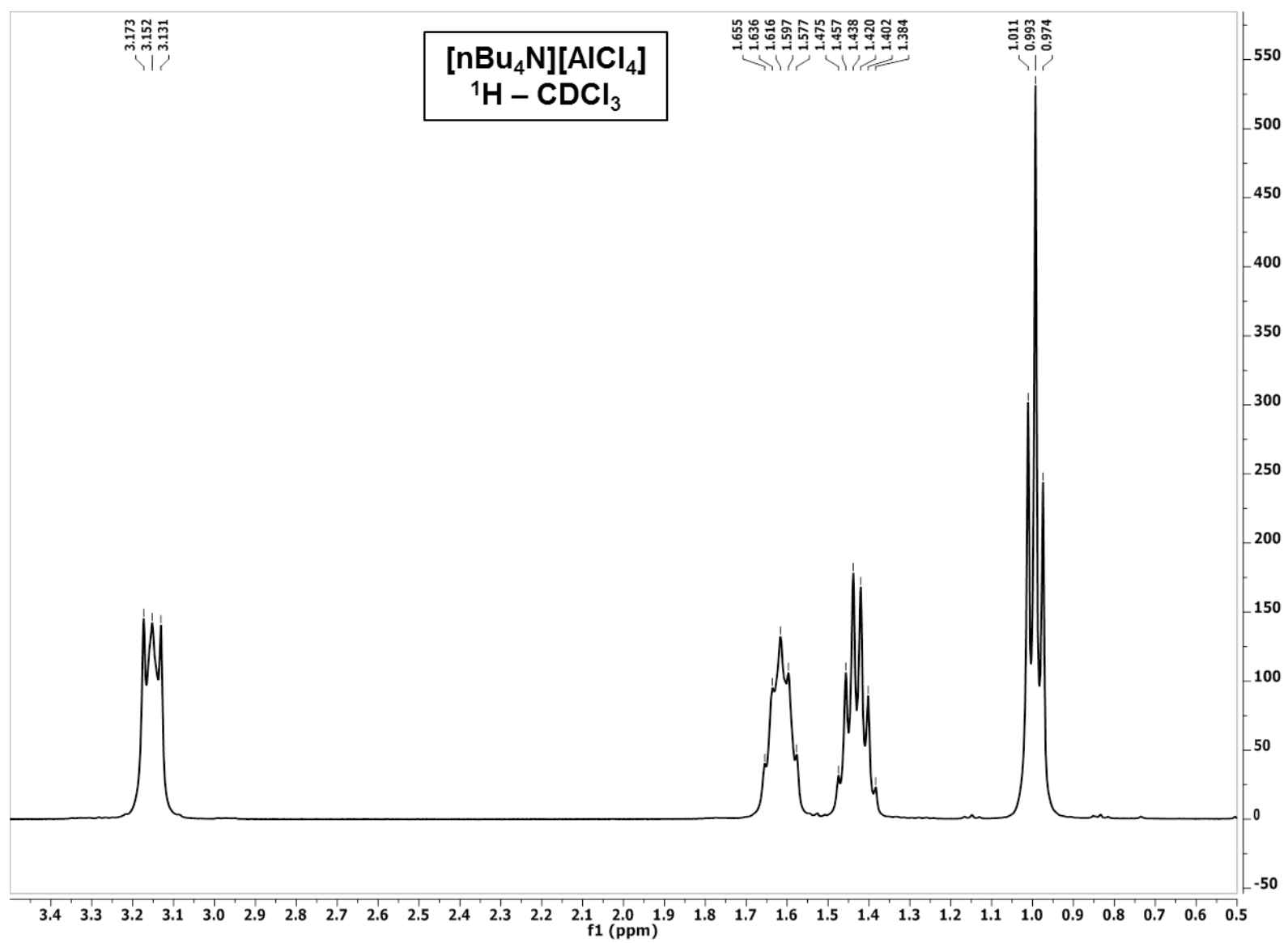


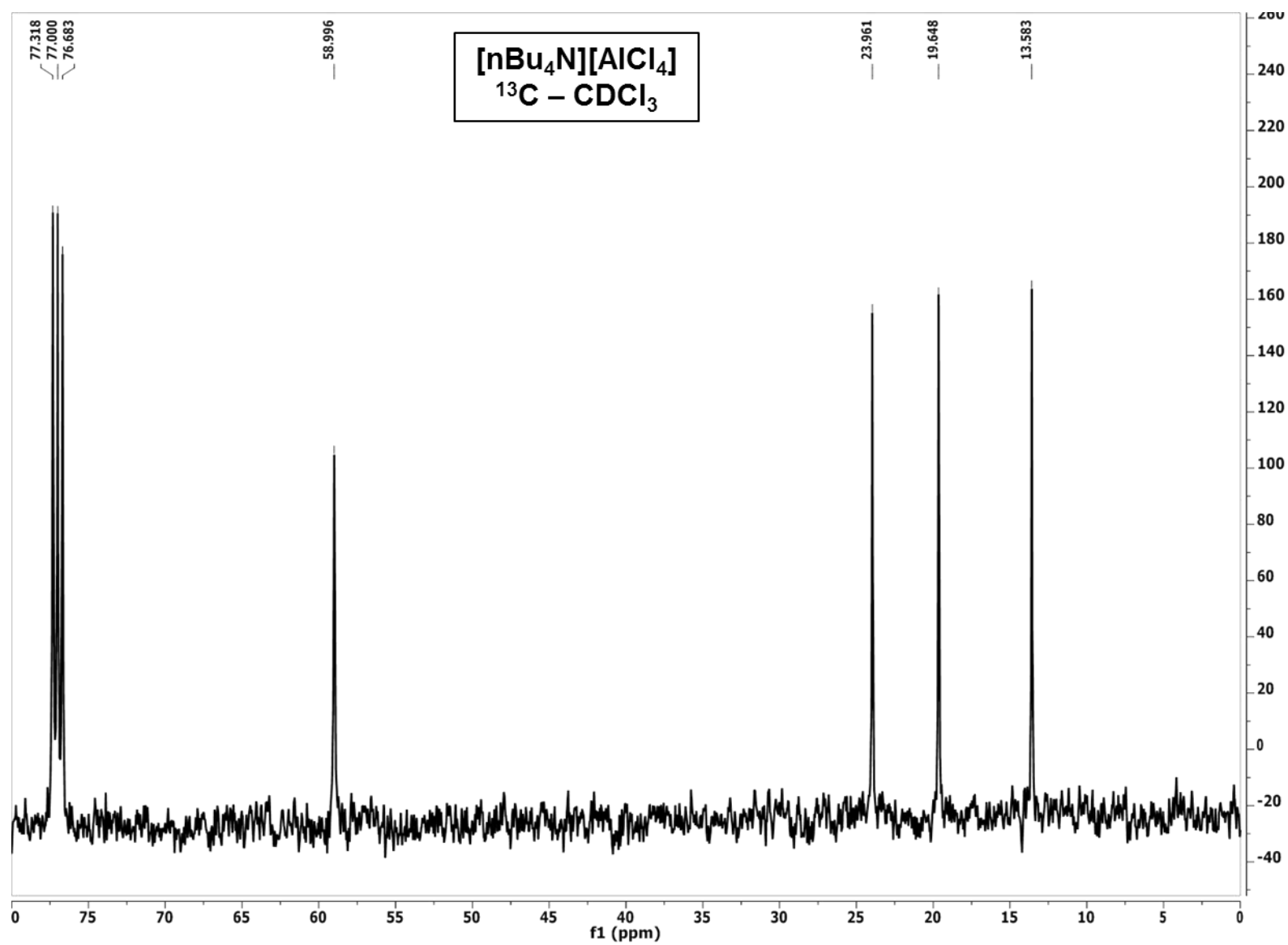


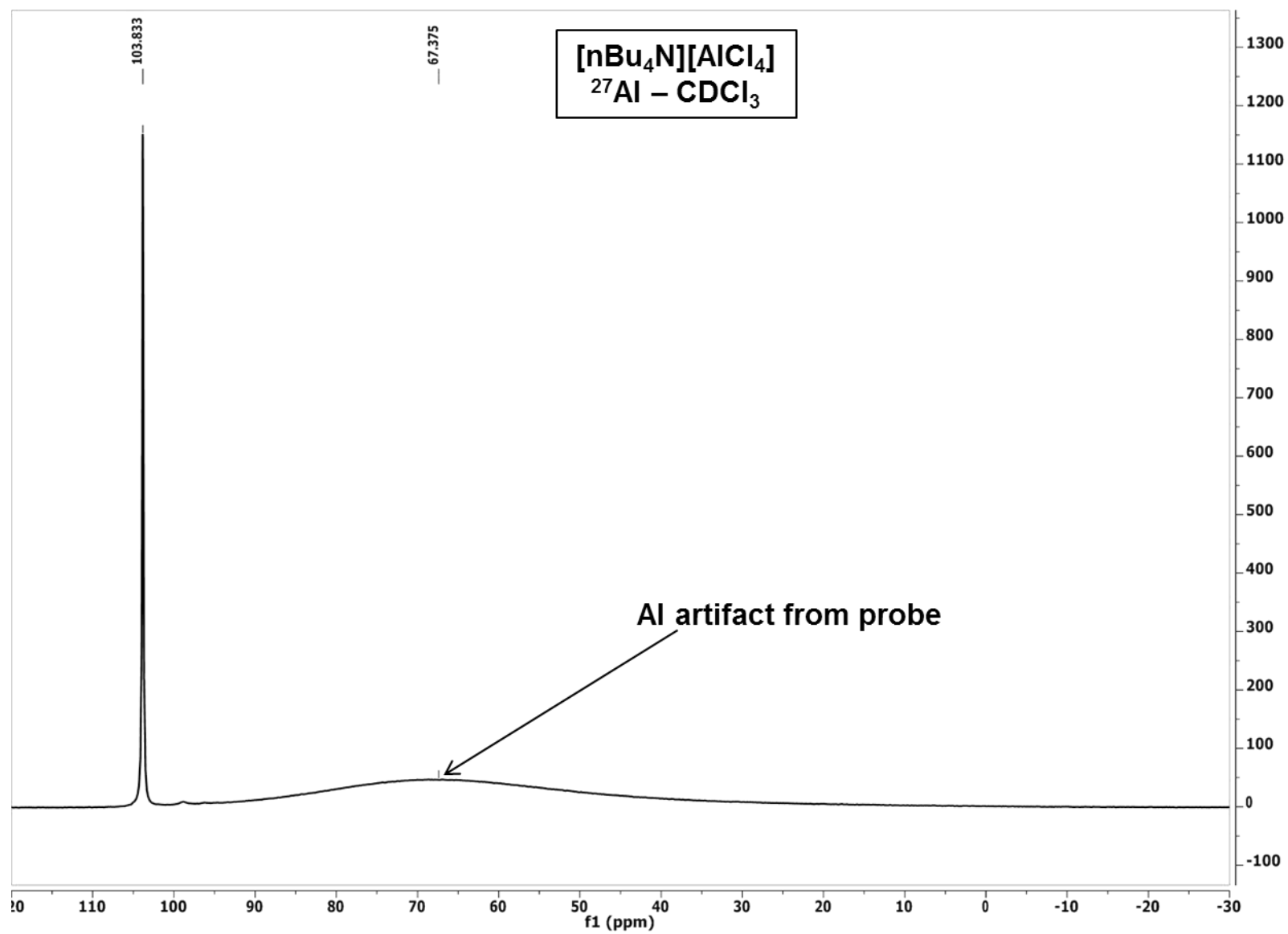


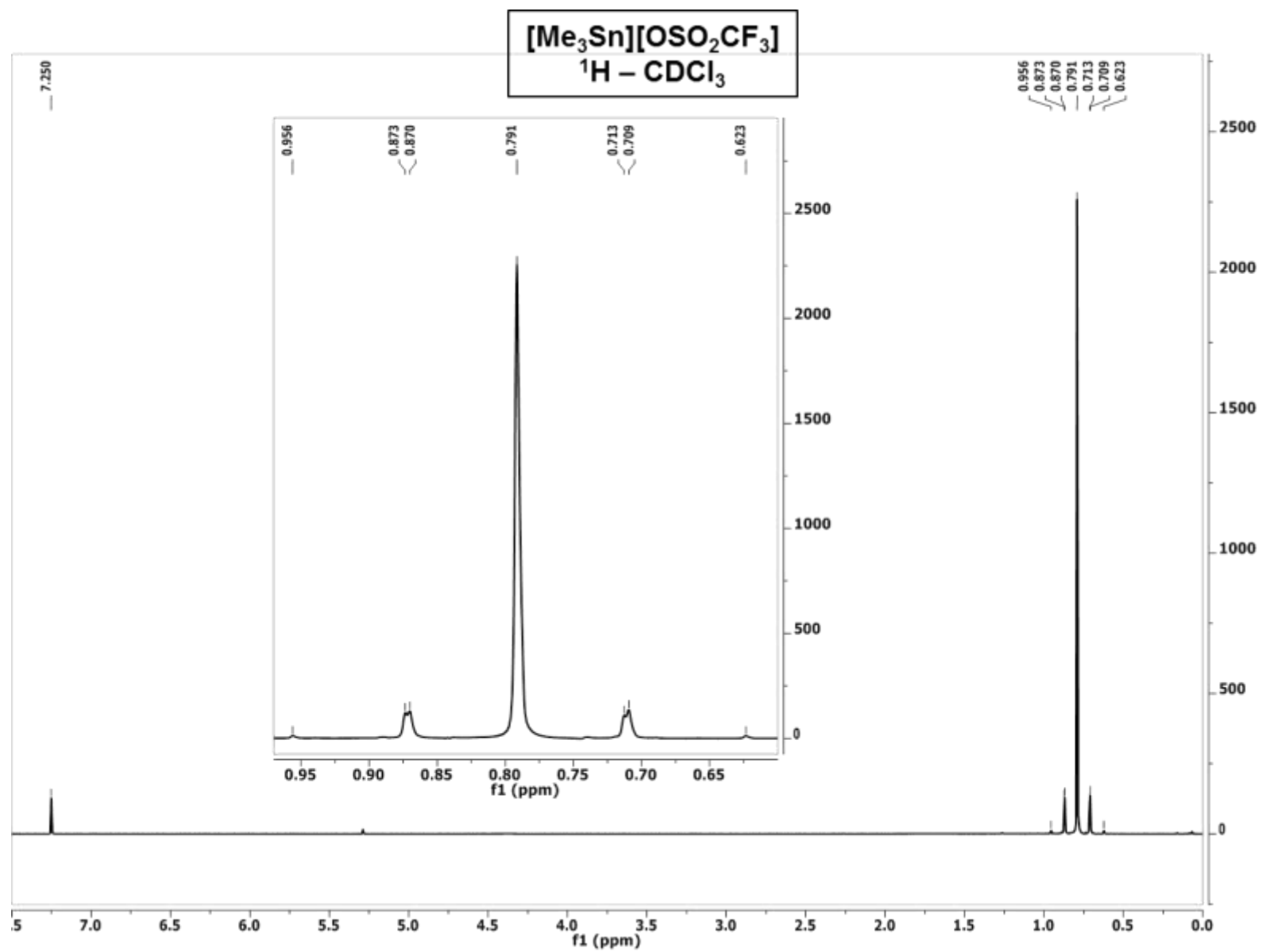


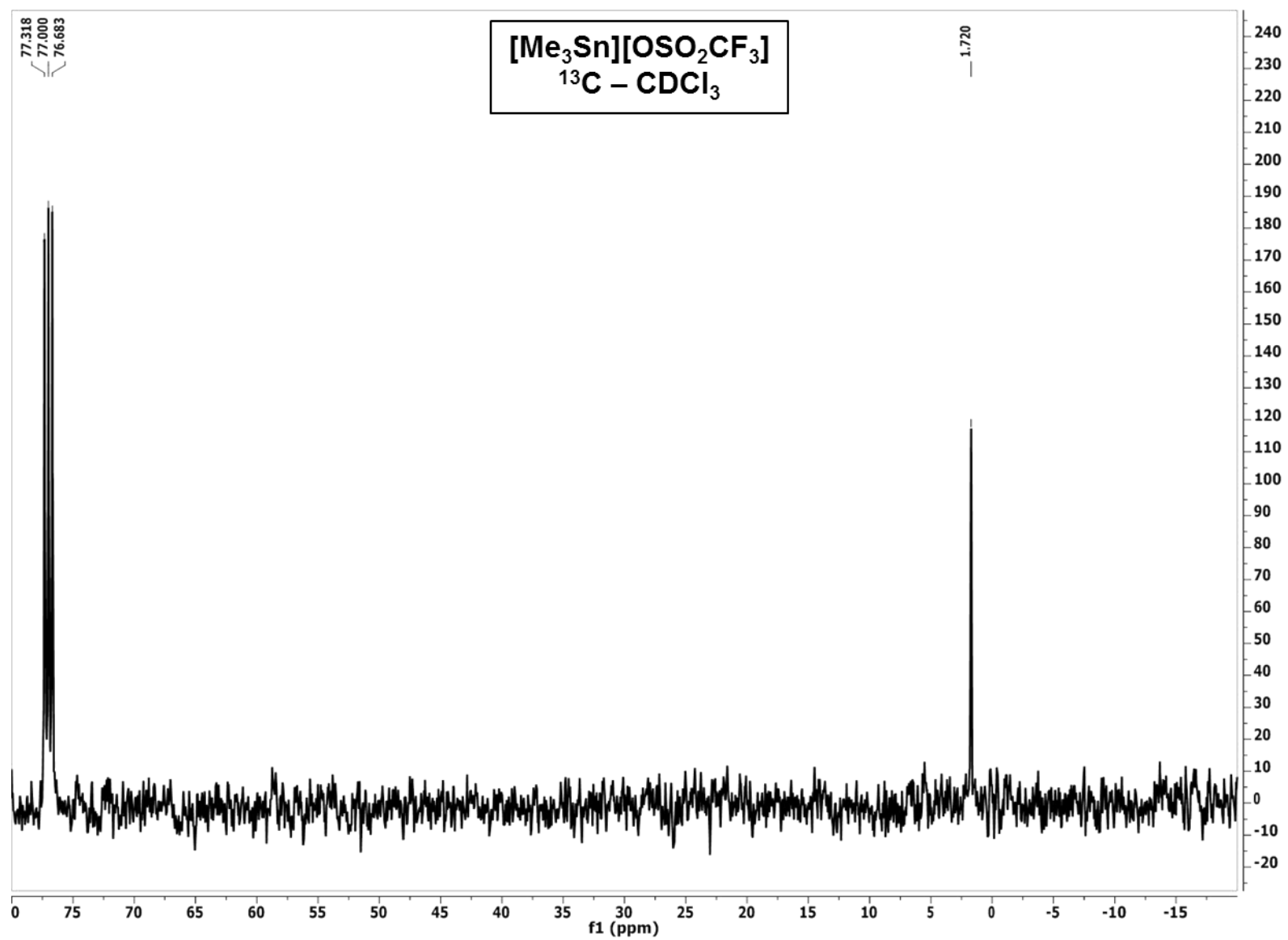


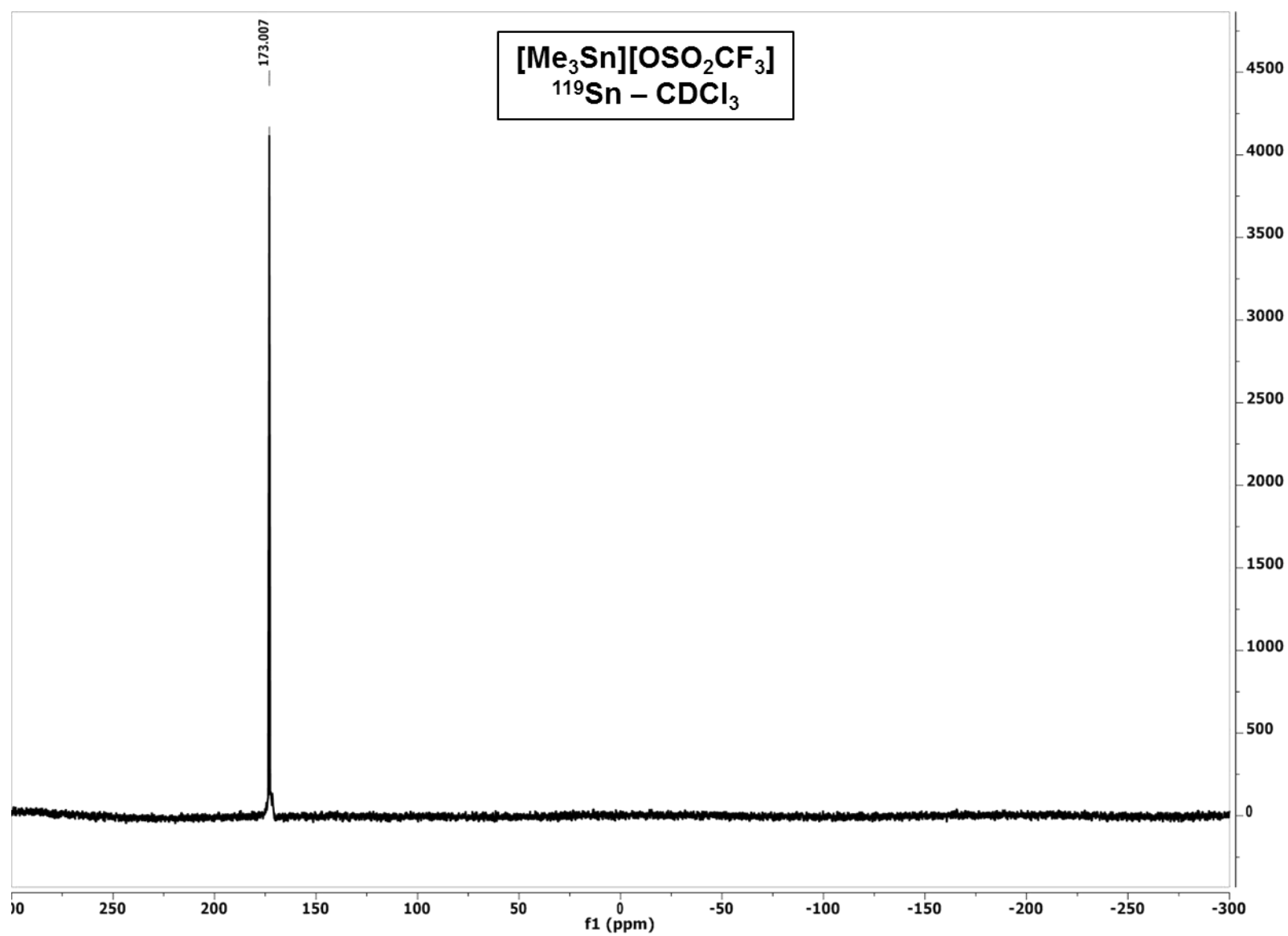


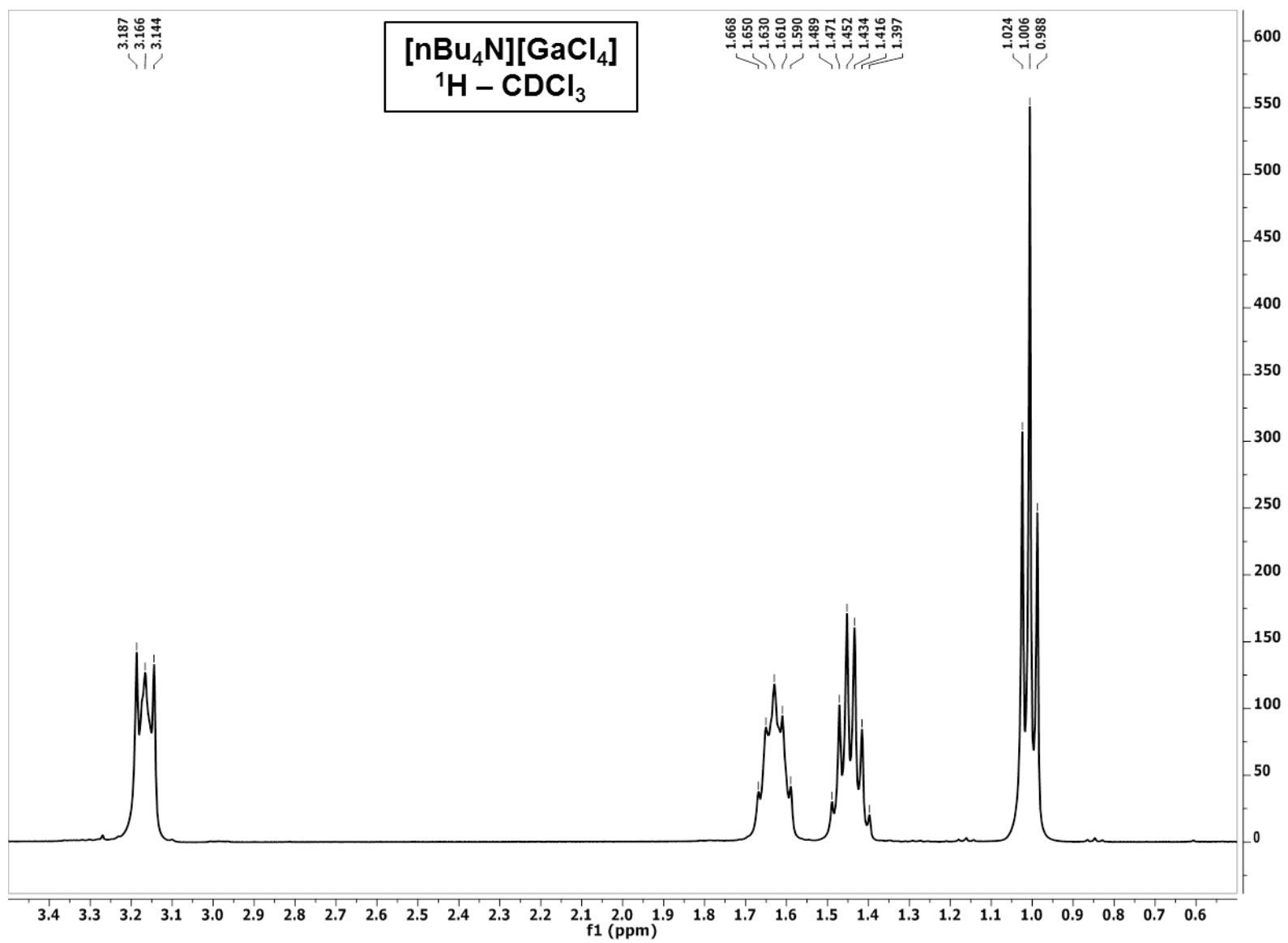


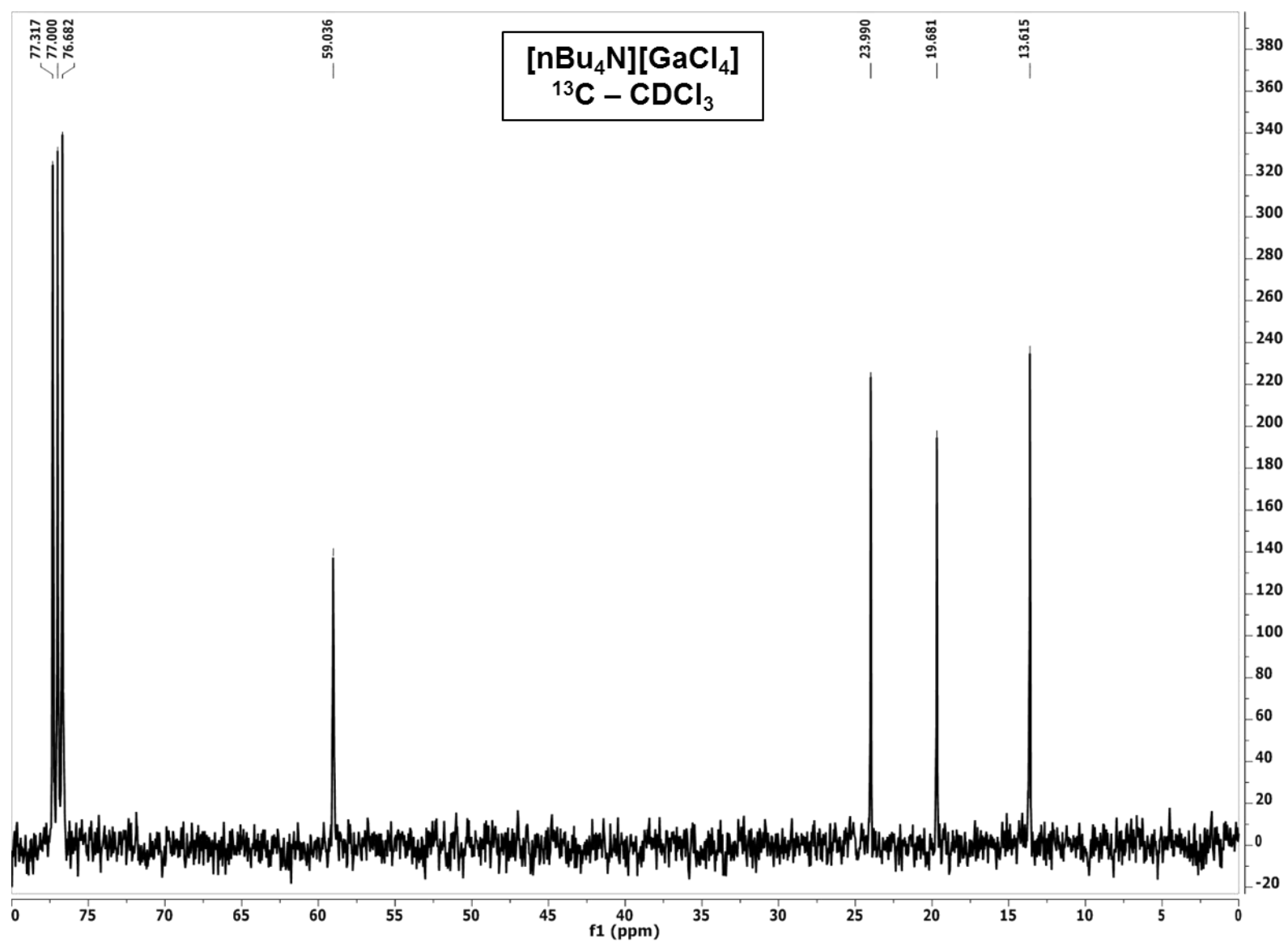


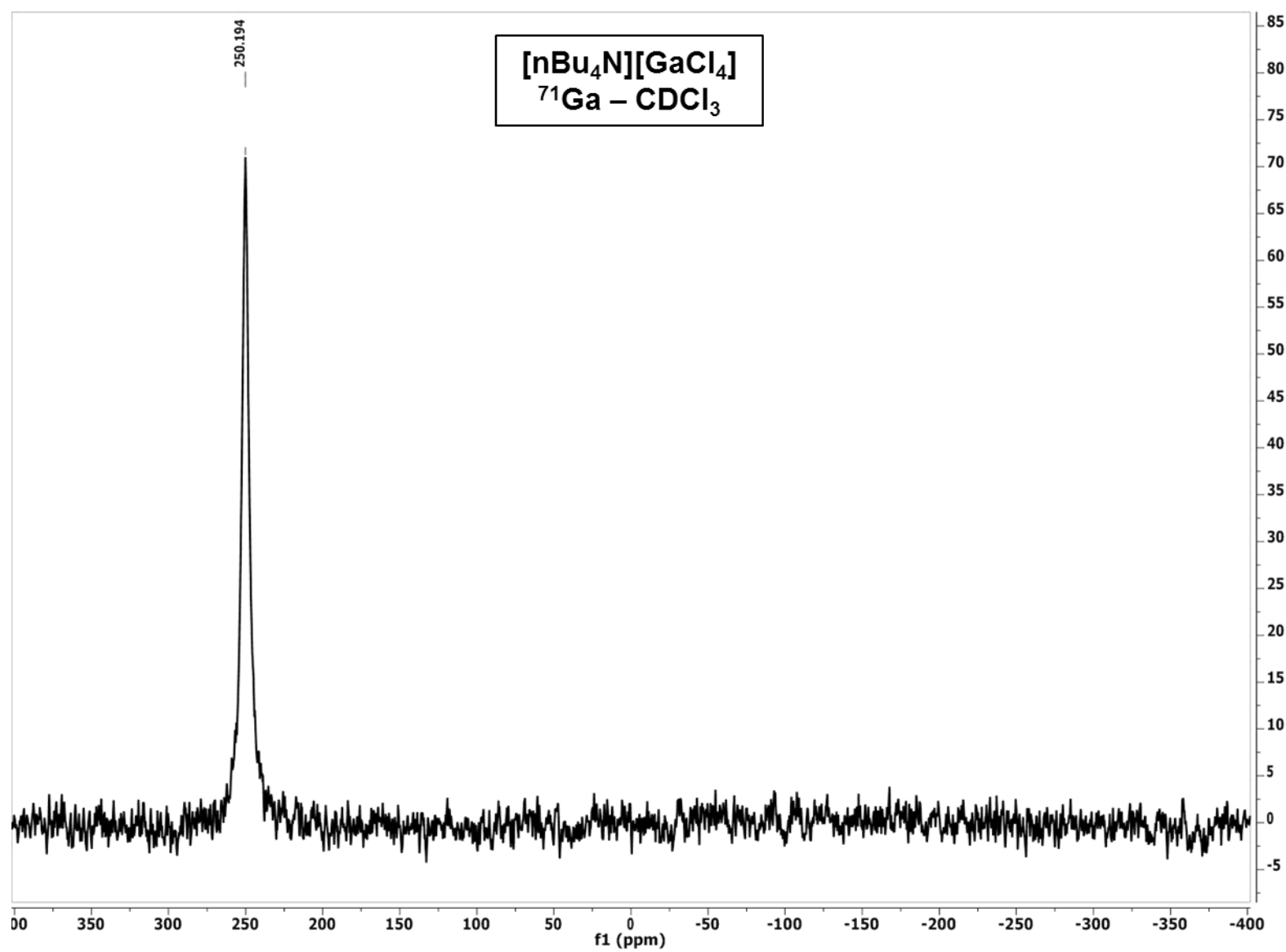


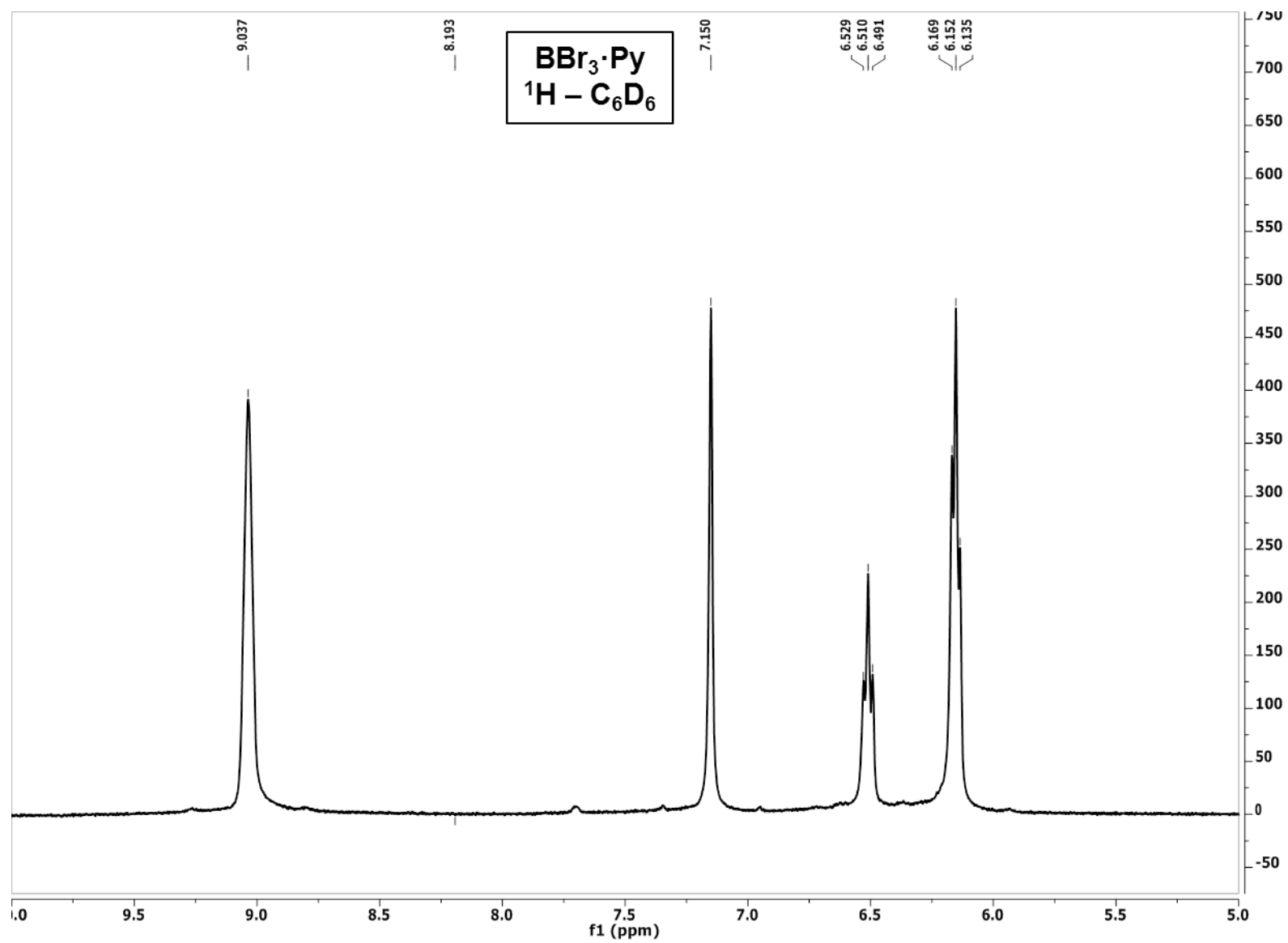


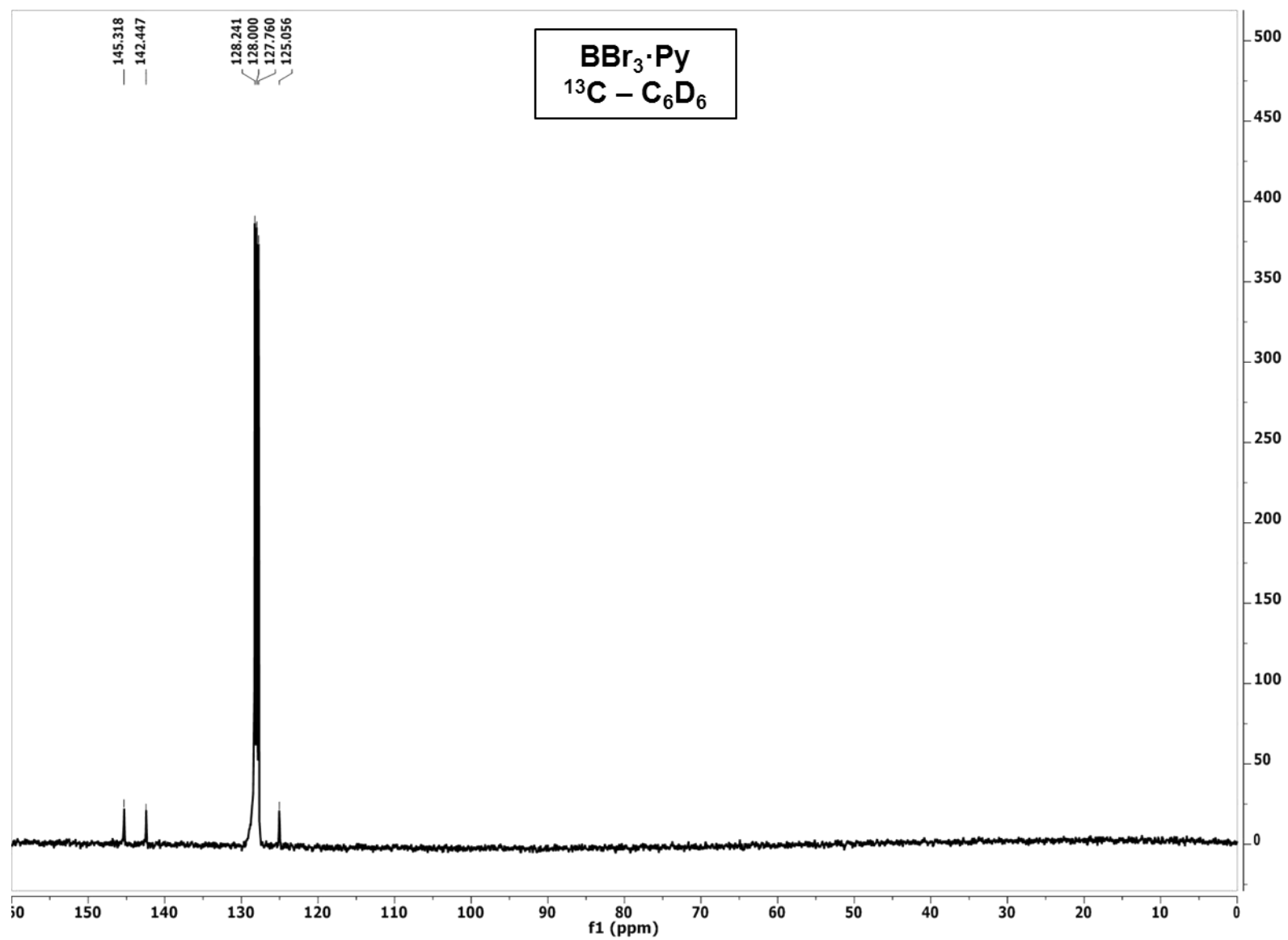


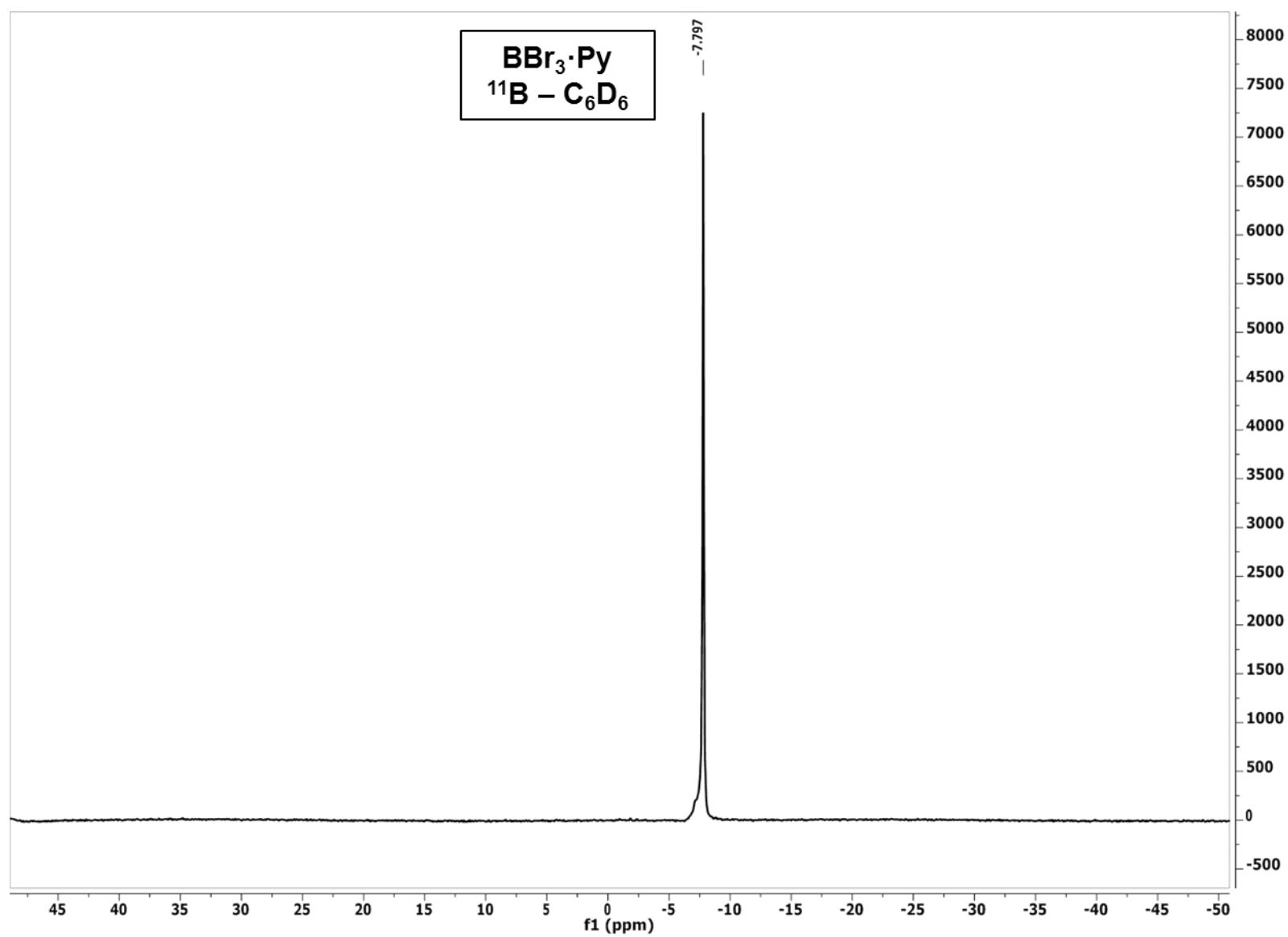












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Vita

Joshua Garth Abbott was born on August 10th, 1984 in Abingdon, VA. He grew up in LaGrange, KY and graduated with honors from Oldham County High School in 2002. He enrolled at Centre College in Danville, KY receiving his B.S. in Chemistry in 2006. During his undergraduate studies, he conducted research on new detection methods for the herbicide atrazine with Dr. Preston Miles. In 2005, he was also selected to participate in a summer REU program at the University of Montana in Missoula, MT where, under the guidance of Dr. Chris Palmer, he worked on the development of methods for the detection of VOC's extracted from airborne particulates. While attending Centre College he met his future wife and fellow chemist Julia Covington Abbott.

In the summer of 2006 Joshua enrolled in the chemistry department at the University of Tennessee in Knoxville, where he began his pursuit of a doctoral degree. He chose to study inorganic chemistry under the direction of Dr. Craig E. Barnes, whose research involved the synthesis and characterization of novel building block catalysts. While conducting his graduate studies, Joshua served as a teaching assistant, research assistant, and student operator for three departmental NMR instruments. During his time at UT he was awarded the first year achievement award, and presented his work at national chemistry and chemical engineering conferences. He completed the requirements for a Doctor of Philosophy degree in Chemistry in August of 2012.