

The Synthesis and Characterization of Nanostructured Titanosilicates for Next Generation Hydrogen Storage

James Humble

5/4/2012

This thesis focuses on the synthesis and characterization of novel nanostructured titanosilicates that contain exposed, isolated low-valent titanium centers on the surface of porous silicate matrices. A system is prepared which contains isolated, reduced titanium centers which have shown the potential to interact with hydrogen via a Kubas type interaction. These reduced materials are investigated using a variety of qualitative and quantitative spectroscopic techniques. After the characterization of the titanium site is completed, hydrogen storage measurements are performed to assess the hydrogen storage capacity of these sites.

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1. Introduction:

This thesis describes work performed in the pursuit of novel electronically and coordinatively unsaturated titanium (III) sites atomically dispersed within a porous silicate matrix which have the potential to be a new system for the storage of hydrogen via a side-on sigma bonding interaction between titanium sites and gaseous hydrogen which is strengthened by pi-back donation from titanium d-electrons. In the course of this investigation these sites have been synthesized and characterized to understand and tailor the potential hydrogen storage ability of the matrix. The impetus for this project was the need for an alternative energy source to provide either a source of electricity for an electric motor or a combustible material for a more traditional combustion engine for use in automotive applications. If successful, the work described here could be used as part of an economy based on hydrogen. Specifically this material would be employed as the hydrogen storage component of a hydrogen fuel cell driven electric propulsion vehicle. The results described here represent many steps toward realizing the goal of a storage device ready for the hydrogen economy.

1.1 Motivation

The problem with fossil fuels derives from their scarcity, non-renewability, limited sources, and environmental concerns related both to their extraction and use.¹ These drawbacks severely limit the feasibility of continuing to use fossil fuels as the primary source of energy for vehicular applications indefinitely. Many governments around the globe have realized the hazards involved in continuing to rely exclusively on coal, oil, and natural gas and have begun both to pledge to reduce their emissions from these sources and to investigate next generation fuels which could eliminate the need for continuing to drive the global economy using a resource which at best has a tenuous future. It is estimated that over the course of the next century² the global temperature average could rise by as much as 4.9 °C. In such a case it is difficult to imagine a scenario which does not involve a drastic change for human life on the planet. If even more drastic climate change is to be avoided it is imperative that the release of carbon dioxide into the atmosphere is curtailed significantly in the immediate future.³

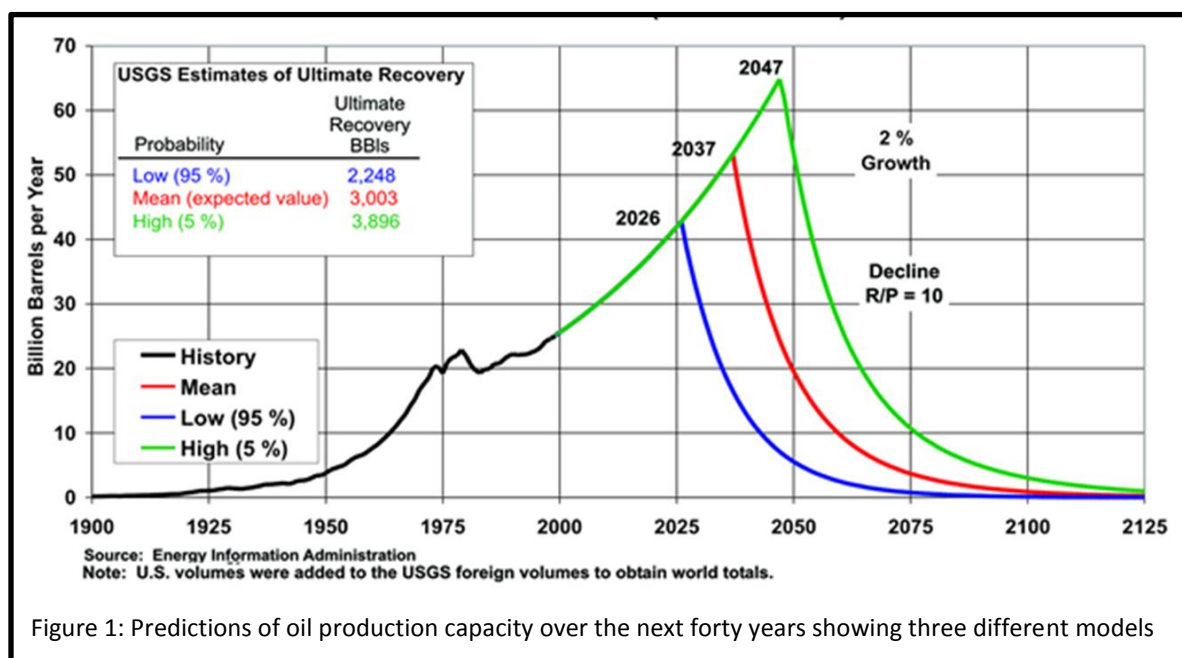


Figure 1: Predictions of oil production capacity over the next forty years showing three different models

The production of fossil fuels also continues to become more difficult and there are fewer and fewer new reserves discovered every day. While there remains a sufficient supply of coal to power the global economy for as much as several hundred years⁴, and recent discoveries of natural gas in the ground beneath the mid-eastern United States (Pennsylvania, Ohio, etc.⁵) make it possible to imagine a stable future for domestic natural gas production, the rate at which the proven reserves of crude oil are being depleted is astounding.⁶ Without some major shift in the rate of discovery of these natural and non-renewable resources or some significant technological advancement making the extraction and purification of currently impractical sources more feasible, it is likely that there will not be sufficient oil to meet the global demand within the next hundred years according to Bloomberg magazine. Figure 1 shows the different potential oil production levels based on three models employing varying degrees of optimism.⁷ While some are more generous than others, each predicts that oil production will begin to decline by 2060. As a result of these developments attention has shifted to alternative sources of electrical power generation within the United States and around the world.

The idea of using some renewable and significantly cleaner source of energy is an enticing one, there remain many challenges to the implementation of such technologies. First, according to the American Society of Civil Engineers (ASCE) the energy infrastructure in the United States has not seen a major overhaul in at least the past thirty years.⁸ As a result the electric grid is not able to deal effectively with electricity generators which cannot be operated at a steady level (i.e. any source other than coal,

oil, natural gas, nuclear, geothermal, and hydroelectric power plants). This means that next generation technologies such as wind, solar, and tidal installations cannot be the primary source of electricity for any given area, as they cannot generate electricity on demand. Many efforts focus on remedying the concerns surrounding alternative power generation sources, but there is another critical area of the energy picture which is also in serious need of improvement. Automobiles have not had significant changes to their operating conditions in a very long time, as the internal combustion engine has been used as the primary means of powering cars for almost the entire last century. Only within the last twenty years have any serious competitors begun to enter the market. Even the fuel used to power these vehicles has not seen any major modifications during the last century beyond the slight modification of the additives employed to improve combustion characteristics. Crude oil continues to be fractionated into its various components with gasoline (consisting mainly of octane) and diesel (made up of slightly heavier fractions of hydrocarbons) being the most widely used.

Despite this glacial pace of change within the petroleum industry, government funded efforts have helped to incentivize the implementation of a commercial scale conversion of commodity crops such as corn and soybeans into ethanol. This ethanol has been added to the gasoline mixture used in cars and commonly comprises up to 10% of the total volume of commercial gasoline. The problem with this continues to be the efficiency of conversion between the initial organic material and the final combustible product. Some estimates even postulate that the amount of energy required to synthesize a gallon of fuel grade ethanol is greater than the energy contained within a gallon of tradition gasoline⁹. If this is true then the use of corn to make ethanol for combustion is at the very least a dubious prospect. Additionally, corn is also used as a food source not only for livestock and other animals, but also for humans themselves; this increases the opportunity cost of using valuable and limited arable land to produce second rate fuel products. Other sources of biofuels are significantly better from an environmental standpoint but frequently have other drawbacks. Biodiesel for example is a very promising way to use otherwise wasted materials such as old cooking oil and other degraded organic oils, however the volume of these supplies will always be limited. Meanwhile cellulosic ethanol remains a promising target because the cellulose used to produce it is easily obtained as waste from many industrial processes and cellulose containing plants can be grown with relative ease in areas which cannot support agriculture.¹⁰ The problem with cellulosic ethanol is that it is very difficult to produce efficiently and no truly effective commercially viable catalyst has yet been developed.¹¹

Given the problems surrounding alternative combustion sources for traditional engines, some alternative to any form of traditional combustion engine appears to have the best chance of success in the future. Of the various alternative fuels and propulsion systems the best hopes continue to lie in two regimes: electric batteries and fuel cells. These two systems operate at very high efficiency and have the potential to serve as viable alternatives to the traditional hydrocarbon combustion engine. Of these two the electric battery is the most mature with several production vehicles incorporating this technology as the primary means of propulsion. There remain, however, major drawbacks to vehicles which use electric motors and batteries. First, the range of an electric vehicle continues to be limited by the number of amps of electricity which can be stored within the battery arrays. To date no production vehicle from a major automotive corporation has been able to show an effective range significantly greater than 100 miles and they generally need around eight hours to fully recharge. Batteries also require large amounts of lithium and other reactive metals which have raised concerns about their safety. Finally, the electricity used to charge electric vehicles today can come from sources which actually generate more carbon dioxide than would be generated by simply powering the same vehicle using a combustion engine.¹² While it is possible that in the future industrial power generation will be a much cleaner prospect than it is today, currently the gains afforded by switching to an electric-battery vehicle appear to be small.

The other contender for the alternative propulsion vehicle is the fuel cell. Fuel cells have many advantages not present with batteries. First, fuel cells provide electricity through a chemical reaction (i.e. the conversion of hydrogen and oxygen to water) which has the potential to be exploited with great efficiency. The key to gaining the most from this reaction is to have a very effective catalyst to facilitate this conversion, and significant progress has been made in this area². The second advantage of the fuel cell is that the only by-product of this reaction is pure water. This water could then be used to help alleviate the strain on municipalities to provide clean water to their citizens. Also, just as water is the only by-product, so too may it be possible to generate the hydrogen necessary for this process through the solar electrolysis of water (with seawater being a particularly tempting prospect). Finally, the range on these vehicles could be on the order of traditional combustion engines making them a viable target for the consumer marketplace. With so many advantages it would seem that fuel cells would be the obvious choice, but there remain many crucial problems standing in the way of an economy based on hydrogen.

The major issues surrounding fuel cells are three-fold. First, current fuel cells require the use of expensive catalysts (often employing platinum) to efficiently produce electricity through the combination of hydrogen and atmospheric oxygen.¹³ These catalysts also can be quite fragile and prone to poisoning after only a few cycles unless extraordinarily pure hydrogen gas is used. For any commercial application to be viable there must be advances in the fuel cell technology such that vehicles can have reasonable lifespans without needing to replace the expensive catalytic cells. Also, using hydrogen generated through the reformation of methane gas still produces significant amounts of carbon dioxide and carbon monoxide.¹⁴ Until it is possible to generate hydrogen gas using the solar electrolysis of water there is little chance of achieving a truly environmentally friendly hydrogen fuel cell.

For any hydrogen economy to be feasible three different technologies must all reach maturity. First, there must be a clear and readily accessible source of pure hydrogen gas. Once this hurdle has been overcome the second problem is how to store the hydrogen in an onboard vehicular system. Finally, it must be possible to effectively use this hydrogen to provide energy to drive this system. If any one of these components is shown to be impractical then the entire system will not be practicable. Currently, hydrogen storage remains the greatest challenge to a market based on the sale and use of consumer vehicles powered by hydrogen fuel cells.

1.2 Production of Hydrogen Gas

Hydrogen gas production is the first of the three pillars supporting the hydrogen based market. Currently there are two major industrial sources of hydrogen gas: the reformation of methane and the electrolysis of water. In addition to these two major sources, the decomposition of metal hydrides forms a much smaller, yet still significant portion of the entire hydrogen production system¹⁵. Currently no one system is able to meet the hydrogen generation targets which would be required in a market based on vehicles using hydrogen technologies. To enable the implementation of this next generation market, advances in these hydrogen generation systems must be achieved.

First there is the reformation of methane. This process involves a complex catalytic process through which methane (CH_4) is converted into carbon dioxide (CO_2) and methane (CH_4). The reactions



involved in this process are shown above in equations one and two. While this process has recently become much more attractive due to the increased reserves of natural gas discovered across the Ohio valley, it is still a rather energy intensive procedure which requires the use of hydrocarbons and generates carbon dioxide. The advantage to using either fractioned hydrocarbons or coal is that there are vast reserves of both currently available. The abundance of these materials makes their use economically attractive, but these reserves are limited and will eventually run out. Additionally, the energy intensive nature of extracting hydrogen from these sources means that there is likely to be little, if any, environmental advantage to using these materials as hydrogen sources. One potential exception to this is methane. As methane is much simpler to produce than any other hydrocarbon (no refining is required), it provides a more promising source of energy than more traditional auto fuels such as octane and other fractioned hydrocarbons. The largest downside to using methane as a source of hydrogen gas is that the reformation of methane has as its products four hydrogen molecules and one carbon dioxide molecule. Therefore reforming methane still results in the production of at least one carbon dioxide molecule for every four hydrogen molecules generated with the actual emissions being significantly higher due to heat loss and energy input. While producing carbon dioxide in one central location may make it easier to sequester as it is produced, this process will still add many tons of carbon dioxide to the carbon cycle which had previously been indefinitely stabilized below ground. Finally, the methane itself can be combusted much more cleanly than most hydrocarbons, so it may be best employed as a temporary bridge between long chain hydrocarbon combustion and the next generation of electric vehicles.

The second, and at first glance much more environmentally sound, source of hydrogen available is that contained in every water molecule on the planet. By applying sufficient energy to a water molecule it is possible to reduce the hydrogen and oxidize the oxygen forming molecular oxygen and



hydrogen gases as shown in equation 3. This system has two potentially huge advantages. First, there is no carbon dioxide directly generated in the electrolytic process itself, as the equation above shows. Second, this splitting completes the fuel cell cycle by regenerating the hydrogen which is converted to water by the fuel cell itself. As an added benefit it may be possible to perform this electrolysis on sources of water which are otherwise unusable for human purposes (such as seawater or sewage). Despite the promise of electrolytically generated hydrogen, there remain many barriers preventing it from being employed on a large scale. To reduce the need for fossil fuels the energy required to split

water into its component elements must come from a source other than traditional coal or gas power plants. The cleanest option available is solar energy. While solar energy has a very promising future, presently the amount of energy generated through solar cells is miniscule compared to the amount which would be needed to make a serious dent in the energy demands of the United States, not to mention the rest of the globe.¹⁶ One of the more futuristic solutions recently proposed is the use of space-based solar stations which would suffer from few of the efficiency diminishing concerns of ground based stations. This energy could be collected in space and then transferred to the ground through a microwave array based on the surface.¹⁷ There are already plans in the works for the first of these stations, although some point out that the amount of fuel required to boost such an installation into orbit could diminish its “green” characteristics rather dramatically. Regardless, space-based solar gathering stations will likely form a major component of the next generation of power plants.

The other major drawback to electrolysis is the very high purity of hydrogen gas required for use in hydrogen fuel cells today. To produce such extraordinarily pure samples of hydrogen factories will need either very good separation columns or very clean water to begin with. Very pure water must pass through several energy intensive steps which would again diminish the effectiveness of the system. Although this may seem like a bleak prospect it should be remembered that the water produced by the fuel cell itself will be very clean, so it may be possible to recycle this water (perhaps even automatically) thus reducing the amount of water which will have to be purified on a regular basis. The benefits of electrolysis hold great promise that this will eventually be the major source of hydrogen for all applications, however the current limitations of this technology mean that it will still require much more investigation before large industrial scale implementation.

1.3 Storage of Hydrogen Gas

Once there is a readily available, economically feasible, and sufficiently pure source of hydrogen gas, the second issue which must be addressed is how to store enough hydrogen gas in a vehicular system without adding too much weight or volume to the vehicle itself. This target is one of the most difficult hurdles preventing the development of a hydrogen economy. The department of energy has set some targets which would permit the commercial development of a system for hydrogen storage in vehicles similar to those of today.¹⁸ For the first generation of hydrogen vehicles the areas of interest are three fold: weight, volume, and fill rate. To closely simulate the end-user experience of an internal combustion engine it is important that sufficient hydrogen can be stored on a vehicle to enable a similar range as that experienced with engines today (~300-400 miles). The department of energy has

estimated that 5 Kg of accessible hydrogen would be sufficient to give a vehicle a 300 mile range. They have additionally established that this amount of hydrogen will need to be stored with a total gravimetric density of at least 5.5% and a volume density of 40 g H₂/L to be feasible in a vehicular application. Lastly it must be possible to recharge the hydrogen storage medium in a reasonable amount of time to make the experience of the consumer minimally intrusive, and the time deemed acceptable is roughly three minutes and twenty seconds (or about 1.5 kg H₂/min). Currently, no system is capable of meeting these requirements under ambient conditions, although significant progress has been observed over the past five years. This means that more work is needed to develop a system which has a strong likelihood of success.

Several different technologies have been studied for the on-board storage of hydrogen. These include compressed hydrogen gas, cryocompressed hydrogen gas, metal hydrides (LAH, MgH₂, etc.), mixed-metal hydrides (NaMn(BH₄)₄, etc.)¹⁹, non-metallic hydride sources (NH₃, BH₃, etc.)²⁰, traditional sorbents (porous carbon, carbon foams, etc.)²¹, and so-called “next generation” sorbents (Metal Organic Frameworks “MOFs” and aerogels).²² None of these has yet been shown to be effective under conditions that would be necessary for commercial implementation of this system. Many of these systems, such as NH₃BH₃ have very high gravimetric densities of hydrogen (here ~16 wt% H), but cannot be easily regenerated and require high temperatures to drive off the covalently bound hydrogen. Other materials, such as carbon foams or MOFs, do not bind hydrogen strongly enough and must be cooled to temperatures at or below the boiling point of nitrogen to have any affinity for hydrogen. Between these two areas lies an area where the affinity of a material for hydrogen would be strong enough, so that it could be stored under ambient or near ambient temperature and pressure, but where the bonds formed would still be weak enough that the hydrogen could be driven off either passively or through only mild heating. This “sweet spot” corresponds to a binding energy for molecular hydrogen of about 30 kJ/mol. A material which meets the storage targets of the DOE will likely show binding energies near to this value, and be able to be cycled many hundreds or thousands of times to succeed.

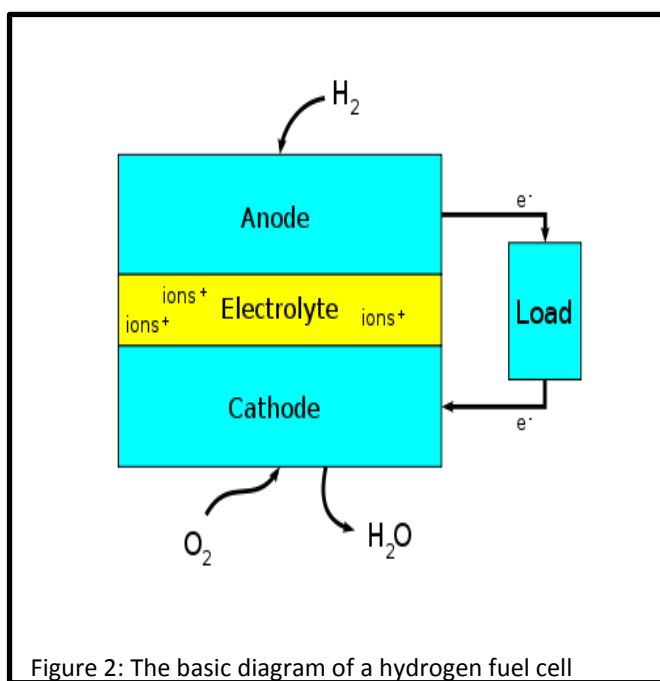
1.4 Implementation of Fuel Cell Systems into vehicular applications

Once it is possible to efficiently store adequate amounts of hydrogen in vehicular systems the final barrier to industrial scale implementation of hydrogen fuel-cells must be overcome. To reap an environmental benefit from the use of hydrogen as a fuel source it is crucial that all of the steps necessary to develop the hydrogen fuel cell do not result in more carbon dioxide actually being produced as a waste product from the energy required to manufacture and implement the technology.

This “life-cycle analysis” must include every component of the production and use of vehicles employing hydrogen as a fuel source. The key component which will largely determine whether or not a benefit can be gained through the use of these materials is the fuel cell system itself. Electric motors are a mature technology capable of efficiently converting electricity into motion, but the transition from chemical energy to free electrons available for use in an electrical circuit is another matter entirely. The combination of hydrogen and oxygen to produce water is an exothermic process, as shown in equation



4. For every mole of water synthesized, up to 486.6 kJ of energy are released. Fuel cells harness this



energy by spatially isolating the two half-reactions involved in this process and harnessing the electrical current generated across this gap, as shown in figure 2²³. If a catalyst does not have a very effective means for converting that energy to electricity then some of that energy will be lost as heat²⁴. Therefore to maximize the efficiency of these vehicles it is crucial that very good fuel cell catalysts are employed to dramatically reduce the amount of energy wasted as evolved heat. Currently the greatest achieved efficiency in a known fuel cell catalyst is around 90 % only considering the cell itself for a system capable of operating under near ambient conditions. However no system which has reached full scale commercialization has achieved efficiency greater than ~60%²⁵. Work has also been done to make use of some of the lost heat as a way to increase the efficiency of the systems.²⁶ As fuel cells are built which waste less energy the hydrogen economy will continue to grow more practicable. There is one system which currently holds the most promise: Polymer electrolyte membrane cells.

Polymer electrolyte membrane (PEM) fuel cells have shown the ability to achieve 60% efficiency when applied to transportation applications. They also operate under relatively mild conditions (i.e. $\sim 80^{\circ}\text{C}$). Finally, unlike other catalyst systems which may require the use of pure oxygen at the cathode (alkaline fuel cells, for example), PEM fuel cells can operate using simple air. These three factors combine to make a strong argument for the use of these systems, which has led to their large-scale commercial implementation.²⁷ The major drawback to this type of fuel cell is the catalyst. Platinum is employed in these cells, so they can be very expensive. Also, as the abundance of platinum is extremely low (5 ppb in earth's crust), there would not be enough platinum metal to provide for all of the planet's needs. Additionally, any carbon monoxide present in the hydrogen gas flow will poison the system and make it useless over time. For all of these reasons other catalytic systems must be employed to permit the wide-scale implementation of this technology.

If a new catalyst can be found which is less expensive, more abundant, and less prone to poisoning then it is likely that PEM fuel cells will be the technology of choice for making use of the stored hydrogen in vehicular applications. However, it is also possible that some, as yet, unknown system will emerge which will operate in an entirely different and improved way. Regardless, fuel-cell technologies are advanced enough so that if the generation and storage of hydrogen become mature and efficient technologies then there will be a fuel cell which can make use of it. Also, it is important to remember that in comparison to any internal combustion engine, which will generally have efficiency in the 14-26% range²⁸, most fuel cells are a major improvement.

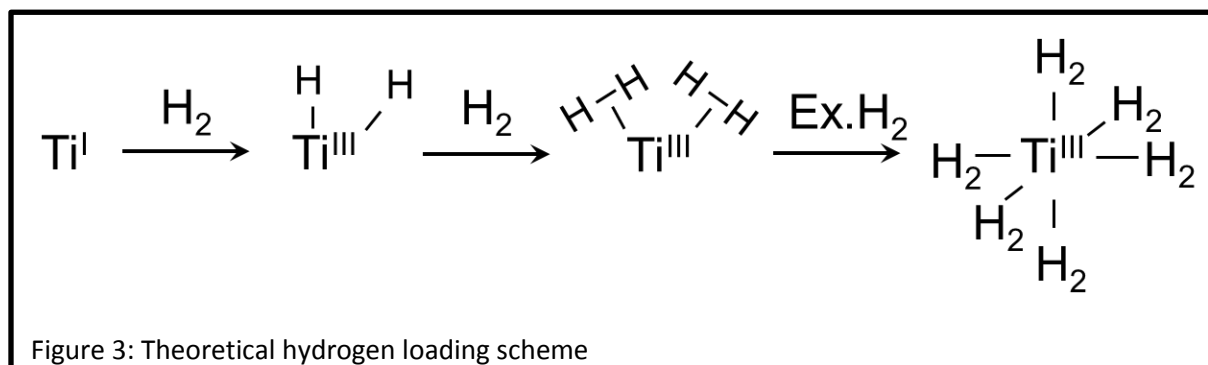
In summary, each of the requisite components of the hydrogen economy: hydrogen generation, storage, and utilization through fuel cell technologies, continues to face significant challenges before any potential entry into the commercial marketplace can occur. Despite these problems, the potential gains promised if these efforts come to fruition are so great that to abandon the progress made thus far and continue to ignore the known problems associated with a petroleum based economy, would be foolhardy at best and disastrous at worst. It is therefore imperative that attention for these issues does not flag over the coming years.

The work presented in this thesis attempts to address the second leg comprising the hydrogen fuel cell problem, the storage of hydrogen for vehicular application. As mentioned above, there is no storage system which can meet the requirements which have been established for a storage system. While some systems can meet one or more of the individual components (with either gravimetric

density being the easiest to meet) none of these systems can operate under conditions which would be favorable for use in vehicular applications.

The ideal system would have a strong enough affinity for hydrogen that it would adsorb a significant amount with only a slight overpressure (<100 bar), but would then easily release the hydrogen readily upon demand. Such a material would constitute a passive system for delivering the hydrogen gas to the fuel cell system, which would simply be driven by a pressure gradient produced as the hydrogen was consumed. Such a system would be able to operate without the need for any advanced pumping or regulatory connections and would require minimal maintenance. Furthermore, it would be possible to operate filling stations very similar to those currently in use across the country which would employ the same system for storing the hydrogen on a much larger scale.

One material which has been shown through several theoretical²⁹ and experimental³⁰ studies to bind hydrogen in a region near to this “sweet spot” is a matrix of isolated, exposed titanium sites. Theoretical models indicate that it may be possible to bind up to six hydrogen molecules to an exposed titanium center.³¹ The first hydrogen to bind in this model is associated so closely that it splits as appears as two hydride species, but once two or more hydrogen molecules become associated with the titanium center each appears indistinguishable from the others (Fig. 3). Once the system is activated it is



impossible to remove all six hydrogen molecules in a reversible manner as the final molecule will dissociate into two hydrides which are much more difficult to cleave from the titanium. Although the theoretical study involved an idealized system with spatially isolated titanium atoms simply surrounded by hydrogen, the promise of this model was sufficient to inspire this project to investigate synthetic routes to mimic this theoretical system. In fact, the theoretical model gives a total hydrogen gravimetric density above 20%, with 16.8% being easily accessed. To attempt to synthesize a material which could imitate the results presented by the theoreticians', two conditions must be met. First, each titanium center must be isolated from the others, this is crucial to prevent the agglomeration of the metal which

would significantly diminish its ability to store hydrogen owing to changes in its electrical properties. Second, the titanium centers must be low-valent to have sufficient electron density to interact with the associated hydrogen molecules via Kubas type hydrogen interactions.³² Finally, to function as a usable hydrogen storage material it is crucial that there are sufficient titanium sites such that the total gravimetric density of hydrogen remains in a regime suitable to industrial applications.

A few pieces of experimental evidence have been gathered by Antonelli among others showing the potential of these types of systems to bind hydrogen reversibly using a variety of metals.^{30,31,33} Problems remain for many of these materials, however. Specifically it is difficult for anyone to achieve sufficient loadings of isolated metal sites to have a reasonable likelihood of meeting any of the department of energy standards. The problem is that most metal doped materials cannot contain loadings of metal which exceed some small value without having major issues regarding coagulation.³⁴ Previous work in the Barnes group has shown that by using molecular precursors which react irreversibly with a variety of high-valent metal chlorides it is possible to achieve very high loadings of metals which, owing to the steric demands of the precursor molecules, remain site-isolated. These high valent metal centers must then be reduced to make them able to bind dihydrogen. This work will detail the synthesis and characterization of isolated surface titanium species dispersed in a silicate matrix with the goal of achieving enhanced hydrogen adsorption under mild conditions.

Titanium was selected as the initial metal to be investigated because it is predicted to have a very stable and reasonable affinity for hydrogen (between 36 and 41 kJ/mol for $[\text{TiL}_n]^+$)³³ which is actually slightly above the binding energies (10-20 kJ/mol) theoretically required for operation under ambient conditions at reasonably low pressures (3-100 atm) and reasonable temperatures (-20 – 85°C).²⁵ Considering the predicted strong interaction between hydrogen and this low-valent titanium species it was decided that it would be a good system to study initially.

1.5 Constructing the matrix

The Barnes group has worked for the past several years to develop a methodology which is optimally designed to give very well-defined, single-site, metal centers dispersed within porous amorphous silicate matrices. This requires the use of a “building block” (BB) which forms the skeleton of the system. Each BB molecule contains a cubic core with the molecular formula Si_8O_{12} (although other sized cores are also possible³⁵). This silsesquioxane core is then functionalized on each corner to activate the building block towards the linking reactions necessary for constructing the desired system. Materials

of this type are grouped under the title of sphaerosilicates or POSS for short, and come in a wide variety of configurations. Some are even available commercially (<http://www.hybridplastics.com/>).

Although it is possible to functionalize building blocks in a variety of ways,³⁵ thus far the system most applicable to the synthetic methodology required for the group's needs involves the use of trialkyl tin groups ($-\text{SnR}_3$). In particular the trimethyltin moiety has been found to be advantageous for several

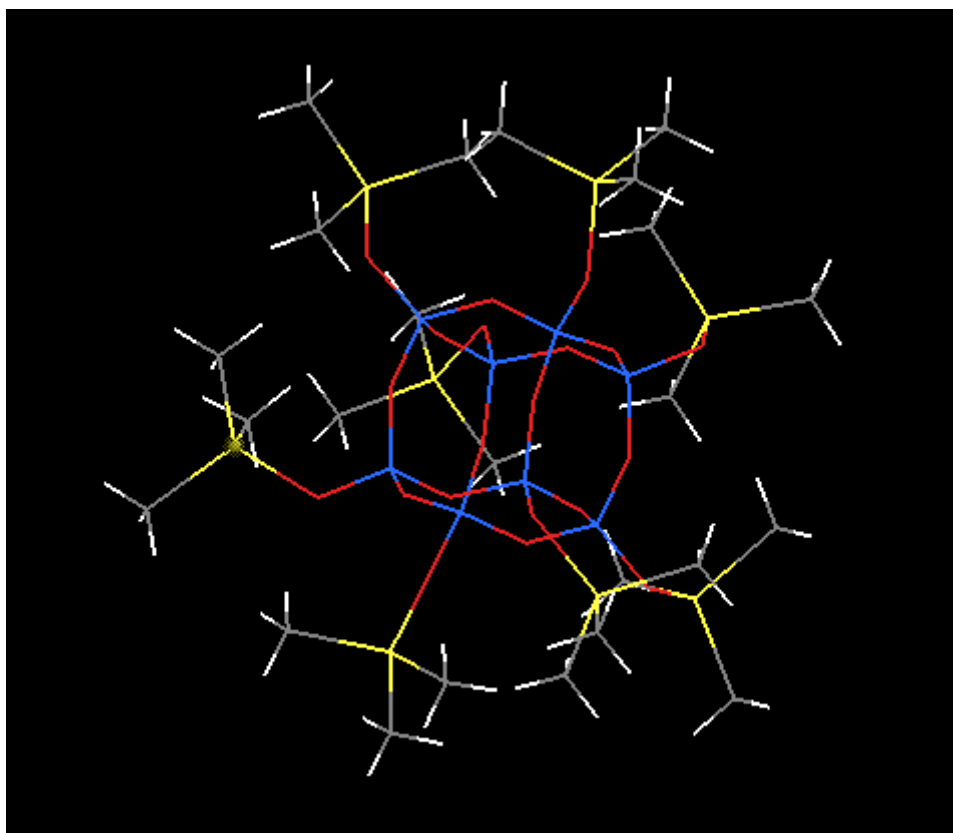
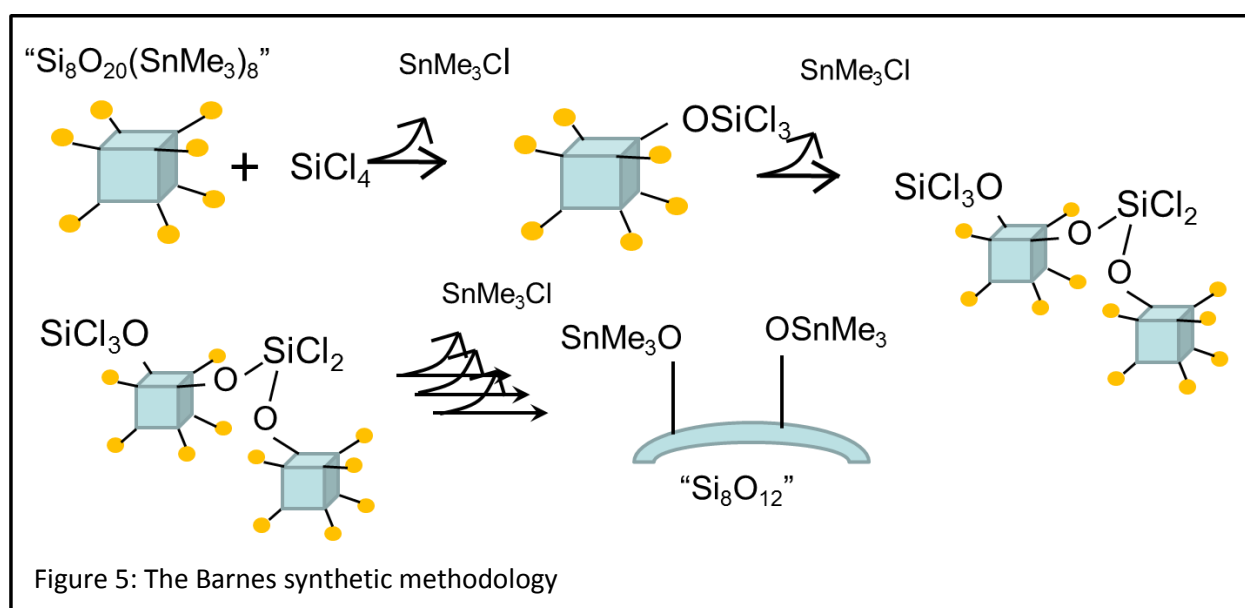


Figure 4: Wire model of the "tin cube" sphaerosilicate. Here blue atoms represent silicon, red are for oxygen, yellow are for tin, grey represents carbon, and white is for hydrogen.

reasons. First, in reactions with metal chlorides there is a clean and irreversible reaction which has as a product the volatile compound trimethyltin chloride. Additionally, this material can be quantitatively removed by heating under vacuum and if necessary could be reused to synthesize more silsesquioxane units for further reactions. The final structure of the building block therefore has the formula $((\text{SnMe}_3\text{O})_8\text{Si}_8\text{O}_{12})$ and is shown in figure 4. This structure will be referred to as the "tin cube".

This "tin cube" forms the foundation of most materials synthesized in the Barnes group and plays an integral role in the synthesis of single-site, heterogeneous systems which have most commonly

been used to model catalysts.³⁶ Using this foundation it is possible to construct a variety of metal-silicate systems varying in size from glassy oligomeric materials, which have little to no surface area, all the way up to rigid, high surface area, amorphous powders. Each of these can be made simply by using an inert silicon cross-linking reagent in the appropriate stoichiometric ratio with the tin cube. Silicon tetrachloride (SiCl_4) and its bispyridine adduct ($\text{SiCl}_4 \cdot 2\text{py}$) are the most frequently used examples. For most applications the bispyridine adduct is used, as it tends to give more surface area. It is hypothesized that this effect is a result of the basic nature of the pyridine groups bound to the silicon. These pyridines are capable of scavenging any trace acid formed in the reaction mixture, which can otherwise disrupt the cross-linking process and lead to low surface area gels. Previous work within the group by Katherine Sharp and Michael Peretich established the stoichiometric ratios of tin cube and SiCl_4 or $\text{SiCl}_4 \cdot 2\text{py}$ necessary to tailor the amount of porosity present in a given reaction. This methodology gives unprecedented control over the structure and pore morphologies of samples prepared in this way, and which makes it possible to synthesize materials which contain a much larger number of the specific targeted metal sites either in the framework of the BB pore structure or on its surfaces. An illustration of the synthetic progression used to make these porous “platforms” is shown in figure 5.



Research in the Barnes group has traditionally focused on heterogeneous catalysis, using atomically dispersed, well-defined metal sites in an attempt to probe the fundamental processes which underlie the many industrial catalysts in use today. While this research can provide answers to many important questions surrounding heterogeneous catalysts today, it may not be immediately evident why such systems could be applicable to the hydrogen storage conundrum. Interestingly most of the catalytic

centers synthesized in the group would probably not be ideal hydrogen storage centers and visa-versa. The problem is that to function as a supported catalyst the metal sites must not leach from the matrix. Typical catalyst reaction conditions include elevated temperatures and moist or oxygen rich environments. In this context, generally at least two links to the matrix are thought to be required to ensure a stable catalytic center. Hydrogen adsorption conditions, on the other hand, permit the use of systems which are much less robust. Here metal sites are generally only exposed to pure hydrogen gas under mild temperatures and pressures. These conditions minimize the risk of metal leaching during hydrogen cycling and mean that it may be possible to use fragile titanium sites which only have one connection to the silicate framework.

Once a platform has been titanated, as shown in figure 6, it must still be activated to enable it to effectively bind hydrogen. Fully oxidized metals have no valence electron density on the metal to

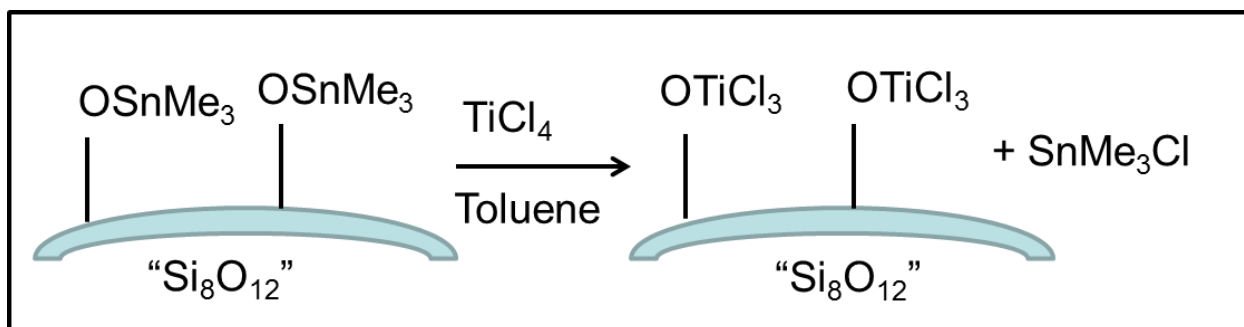


Figure 6: Titanation of a silicon platform

donate into the hydrogen σ^* antibonding orbital as part of a sigma bond interaction. Titanium oxide containing samples are most commonly found fully oxidized as Ti(IV) and need to be reduced to have the potential to interact favorably with hydrogen. There are many different methods which can be employed to effect this reduction. Both traditional and non-traditional hydride reducing agents provide options for this chemical change. Among the traditional reducing agents are lithium aluminum hydride and sodium borohydride, while silane reagents (H_3SiR) can provide a milder alternative to these harsh traditional reductants. The cleanest alternative to these more chemically active reagents is hydrogen gas itself, but this requires having systems which are activated toward reduction in this manner. Chlorinated titanium systems generally require temperatures on the order of 500-600 °C to effect a reduction using hydrogen gas.³⁷ This is quite high and would possibly permit many other reactions to occur simultaneously. It is possible to significantly diminish the temperature required by using organo-titanium systems such as neopentyl titanium which can be reduced in a hydrogen atmosphere at roughly 150 °C.³⁸ These systems are even more challenging to prepare and so to make use of the

simplest processes initially, it was decided that the traditional reductants and silane reagents would be employed first.

1.6 Characterization Techniques

Solid, amorphous systems can be notoriously difficult to characterize because the two most commonly used techniques for analyzing crystalline materials with metal centers, x-ray crystallography and solution state NMR techniques, are not available. Despite these challenges there are several methodologies which can be used to probe the properties of prepared samples. Frequently, the first tool in the chemist's arsenal is sight, and qualitative changes in these samples, including color shifts and gas evolution, can be very enlightening. Beyond direct visual observation, gravimetric analysis, Fourier Transform Infrared spectroscopy (FTIR), BET surface area analysis, BJH pore size distributions, Electron Paramagnetic Resonance Spectroscopy (EPR), X-Ray Adsorption Near Edge Spectrometry (XANES), Extended X-Ray Adsorption Fine Structure (EXAFS), X-Ray Photoelectron Spectrometry (XPS), ICP-AES, Diffuse Reflectance Infrared Fourier Transform Spectrometry (DRIFTS), and Raman Spectrometry may each contribute pieces of information which help determine the properties of a sample. By combining the data obtained from a selection of these techniques it is possible to infer a significant amount of information concerning both the local environment surrounding an "active site" within the matrix, and the characteristics of the macrostructure in which it is located. Knowledge of both of these components is integral to obtain a material capable of effectively storing hydrogen.

The first set of data which any scientist obtains is what he or she directly observes throughout the course of a reaction. Qualitative changes in the sample can yield important information about its properties. In our systems, molecular materials are reacted to yield amorphous glasses and it is possible to estimate whether or not a sample will have porosity based simply upon the appearance of the material which results after the initial cross-linking reaction. Samples which appear "glassy" generally have little to no surface area, while those which appear to be flocculent powders generally are quite porous. It is also generally possible to obtain qualitative information about the oxidation state of the titanium in the system simply by observing the reduction reaction. A fully oxidized titanium center has no d-electrons and therefore does not absorb in the visible region of the spectrum. A reduced titanium center (be it Ti(III)-Ti(0)) does have d-electron density, and therefore can absorb in the visible region giving reduced samples a dark coloration (Figure 7). These two basic sets of observations help to distinguish reduced from unreduced samples.

Next it is possible using our synthetic methodology to develop a good understanding of the composition of a sample simply by careful measurements of the mass changes which take place during the course of a series of reactions. During the first step in synthesizing a platform, the average number of connections established between the silicon located in the $\text{SiCl}_4 \cdot 2\text{py}$ and various cube structures within the matrix can be determined by measuring the mass lost as trimethyltin chloride in the course of

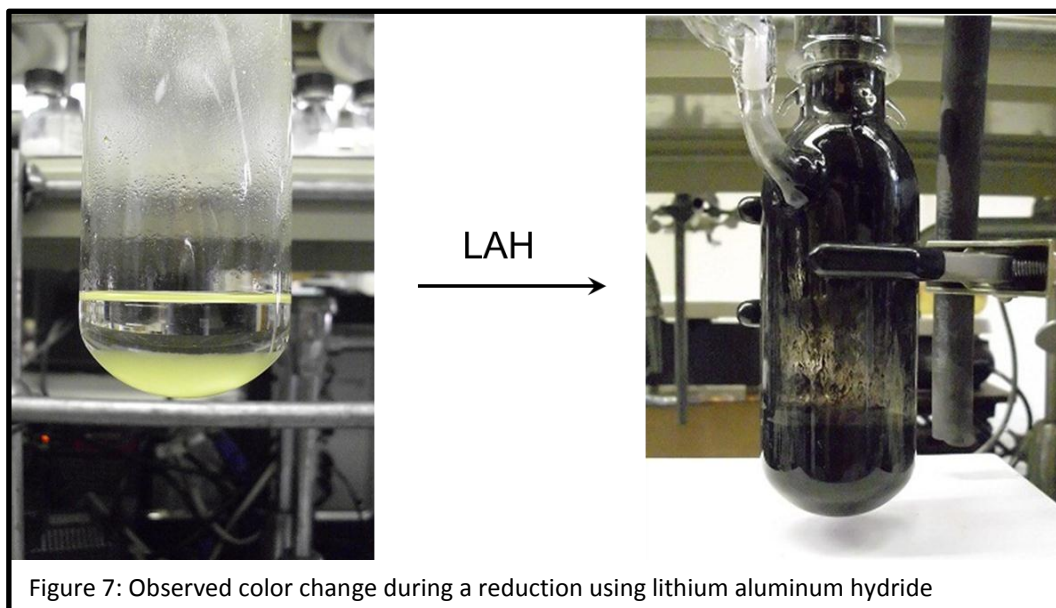


Figure 7: Observed color change during a reduction using lithium aluminum hydride

this initial reaction. This “connectivity” plays an important role in the properties of the platform which is prepared, from the number of remaining trimethyltin sites available for additional reaction, to the porosity of the matrix itself. It is the first step in understanding the composition of any platform. Gravimetric analysis continues to be important first as titanium is substituted for residual trimethyltin in the system, and then both during and after reduction to attempt to understand its mechanism. It is not, however, a stand-alone technique capable of independently yielding either structural or chemical information. Instead it offers an indirect analysis which can help to understand the results of other spectroscopic techniques.

The first independent technique capable of giving qualitative data about the chemical composition of an amorphous sample is Fourier Transform-Infrared Spectrometry (FT-IR). FT-IR can give

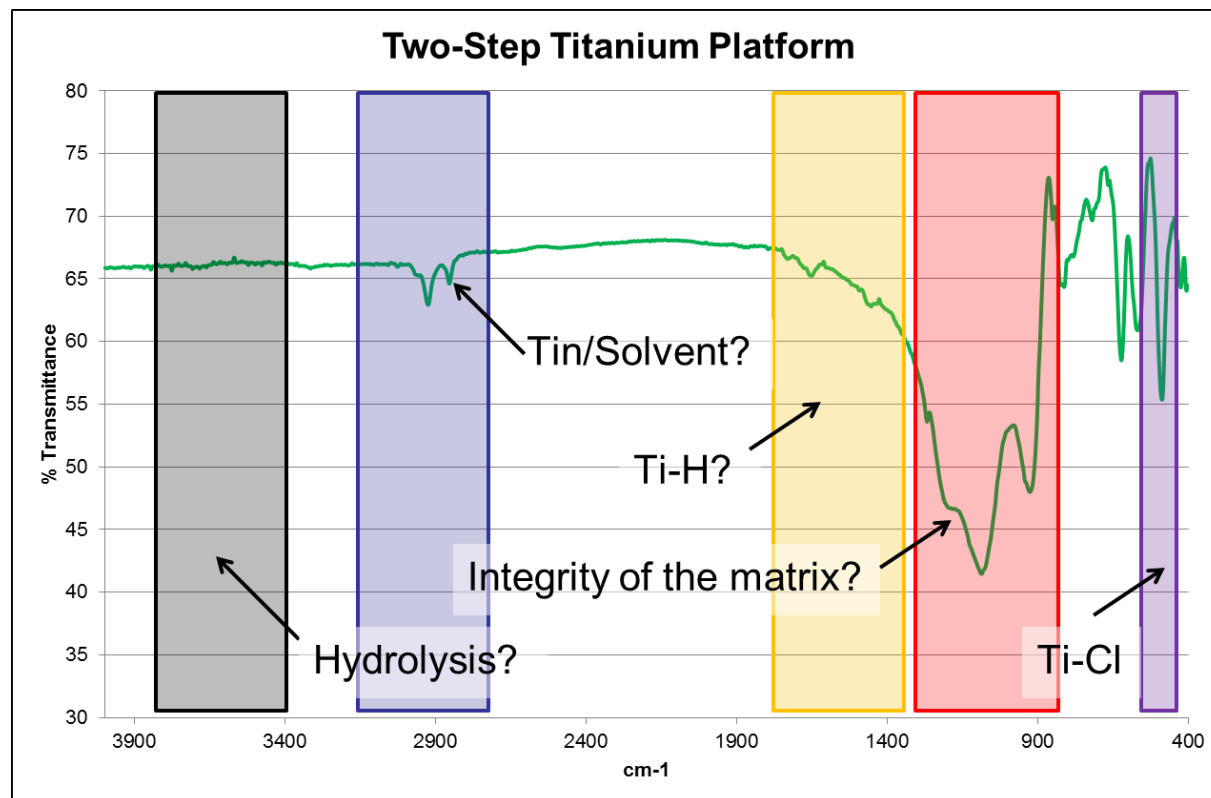


Figure 8: A sample FT-IR spectrum showing the main areas of interest

crucial information about the bonds present within a system and can also be used to monitor changes over the course of several reactions. Placing an IR instrument in the glove box makes it possible to easily obtain spectra of even the most air sensitive materials. The most important regions to monitor are shown in figure 8. Between 2800 and 4000 cm^{-1} two important stretches are seen. First, between 2800 and 3000 cm^{-1} C-H stretches are observed for organic groups (the methyl units of the tri-methyl tin) which decrease as trimethyltin chloride is lost during the synthesis. Also, between roughly 3400 and 3800 cm^{-1} it is possible to observe evidence of hydrolysis which would indicate the exposure of the sample to air. The next important region to observe is between 1500 and 1200 cm^{-1} which is where one paper indicates it may be possible to observe Ti-H stretches.²⁹ Additionally, between 1000 and 950 cm^{-1} are the Si-O and Ti-O stretches which form the foundation of the material. It is important that these bands be monitored to look for evidence of the breakdown of the sample in the form of leaching or the decomposition of the cube structure itself. Finally, at 495-490 cm^{-1} is the Ti-Cl stretch, which can be difficult to observe but gives further evidence as to the composition of the system. For all of these reasons infrared spectrometry is one standard component of the preparation of any sample.

Diffuse Reflectance Infrared Fourier Transform Spectrometry (DRIFTS) compliments standard FT-IR by providing a technique which permits the *in-situ* observation of a sample. Using a DRIFTS cell it is possible to monitor changes in a sample's IR spectrum while modifying the conditions around the sample or even performing a reaction, such as the reduction of a sample using ethylsilane. A final addition to the standard vibrational techniques is Raman Spectrometry. Pure hydrogen can be observed using a Raman Spectrometer, making it an invaluable technique for materials which hope to store H₂, as the H-H stretch of unbound molecular hydrogen is observed at 4160 cm⁻¹.³²

The second standard technique used to characterize porous amorphous systems is a BET analysis of the nitrogen adsorption isotherm for a given material. BET analysis uses a relatively simple

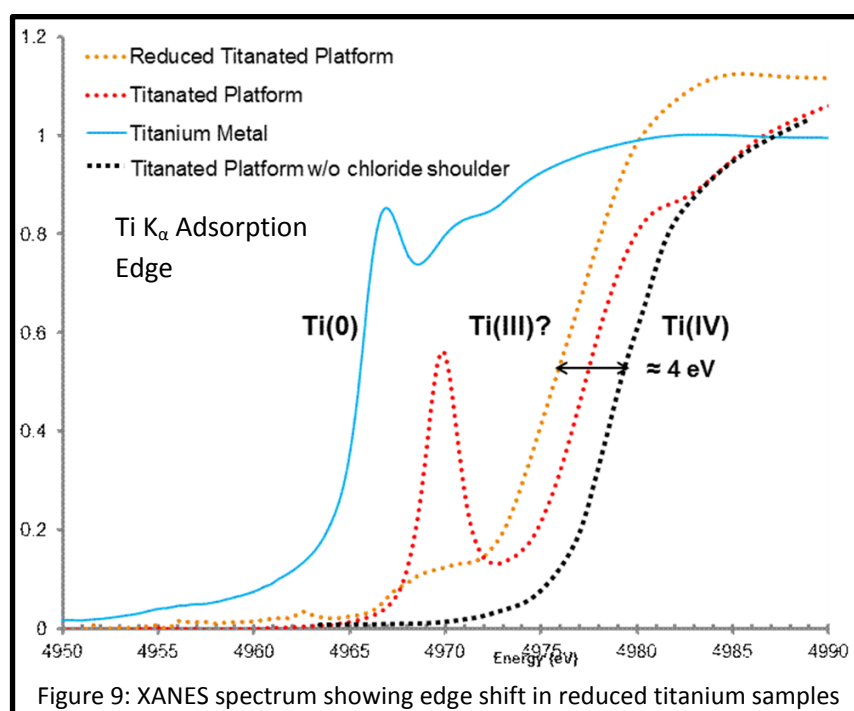
$$\frac{1}{v[(p_0/p) - 1]} = \frac{c - 1}{v_m c} * \left(\frac{p}{p_0}\right) + \frac{1}{v_m c} \quad \text{Equation 5}$$

equation (Eq. 5) to estimate the total surface area present within a sample³⁹. In this equation p/p_0 is the reduced pressure, c is the BET constant (extracted from the isotherm), v is the total adsorbed quantity of gas at the given reduced pressure, and v_m is the monolayer adsorbed gas quantity (also extracted from the isotherm plot). It is not extraordinarily precise (generally values for the actual surface area are only reproducible within a margin of 10%), but does give a reliable tool to determine whether or not a material has significant surface area and porosity. It can also be used to monitor changes in that porosity over the course of several reactions relatively easily. It is also possible to estimate the pore size distribution of a given sample using corrected BJH analysis (named for Barrett, Joyner, and Halenda, this method gives reasonable estimations of the pore size for large mesoporous materials), although some recent work has illustrated that this approach frequently underestimates the average pore radius for micro/mesoporous materials.⁴⁰ Chart 1 demonstrates the surface areas generally achieved in these novel titanosilicates. Regardless, nitrogen adsorption provides valuable insight into the nature of the porosity present in a given sample.

Nitrogen Adsorption Analyses of Titanosilicates			Chart 1: A comparison of the BET surface areas and BJH average pore radii for both reduced and unreduced samples
Sample	BET Surface Area (m ² /g)	Average Pore Diameter (nm)	
6.30:1 Ti:Sn 1-dose Platform	343	3.8	
2.5:1 Ti:Sn SiCl ₄ 1 st step Platform	624	2.8	
2.5:1 Ti:Sn SiCl ₄ Platform 2 nd step (with excess TiCl ₄)	401	2.6	
Titanated Platform treated with PhSiH ₃	522	2.6	
Titanated Platform treated with LAH	515	5.0	

A third technique used to confirm the gravimetric analysis as well as to quantify precisely the number of active sites present within a matrix is atomic emission spectroscopy (AES). Specifically Inductively-Coupled Plasma-AES (ICP-AES) serves to quantify the amount of any metal or other non-volatile components present in a sample. The very sharp nature of atomic emission lines means that each element has an entire set of resolvable bands which can be used to characterize a material with exceeding precision. In fact measurements of analytes with concentrations in the ppb regime are not uncommon. By knowing the exact concentration of metal centers within a sample it is possible to achieve much greater precision in the calculation of reduction equivalencies and also eventually as to the number of hydrogen molecules adsorbed per metal in a final material active toward the storage of hydrogen. ICP-AES does require significant sample preparation and also completely destroys the sample, so it is best reserved for use where the precise number of metal sites is of the utmost importance.

Electron paramagnetic resonance (EPR) is the first and, in many ways, most straightforward technique used to confirm an oxidation state change in the titanium sites located within these potential storage systems. EPR can detect the presence of unpaired electrons within any material and, under the appropriate conditions, can even be used to determine the environment surrounding the atom which contains this electron.⁴¹ In the case of the ill-defined, complex materials, which could result from the reduction of the titanium sites located within the silicate matrix, it is generally only possible to confirm that the titanium centers have been reduced from the +4 oxidation state to some other lower oxidation



state. Despite these limitations EPR provides the first level of information confirming a successful reduction.

To begin to quantify the degree of reduction which has been achieved for a given sample a different set of spectroscopic techniques are required. Two complimentary methods can be used to further characterize the reduced titanium center. First, X-ray photoelectron Spectroscopy (XPS) can be used to measure changes in the core electron binding energies of a titanium center. XPS measures the kinetic energy of the ejected electrons from a material after exposure to x-rays of a given energy. The energies of these electrons are characteristic of the atom from which they come, and also depend on the oxidation state of that atom. By comparing the spectra of unreduced and “reduced” samples it is possible to correlate the shift in binding energy for the titanium centers to the change in oxidation state of the titanium. Finally, XPS spectra can be integrated to obtain information about the composition of the sample.⁴² This has been and will continue to be an important method for confirming the information gained from the gravimetric analysis and ICP-AES measurements. To be confident in the changes in oxidation state observed with XPS it is important to use a second independent measurement which supplements these data. X-Ray Absorption Near Edge Spectroscopy (XANES) is a technique which can be used in this capacity. Whereas XPS ionizes the 2p shell of the titanium, XANES uses much higher energy tunable x-ray radiation to ionize the 1s core electrons of the titanium atoms.⁴³ By observing slight changes in this ionization energy and comparing them to a set of standards with known oxidation state it is possible to quantify the degree of reduction present in the titanium centers. Figure 9 illustrates how this technique may be used.

From model compounds and others for which other data have given some initial insight into the structure surrounding a metal center, it is possible to extend the observation begun in the XANES region further to confirm a suspected structure. This technique is known as Extended X-Ray Absorption Fine Structure (EXAFS) and relies upon the backscattering of ionized electrons from atoms near the ionized absorber atom (e.g. titanium). The scattered and backscattered electron waves interact with each other producing an interference pattern which appears as oscillations in the baseline beyond the initial ionization energy of the target element. By extracting this component of the spectrum and analyzing it, the positions and distances of the atoms surrounding the central target element can be determined. The problem is that, unlike X-ray diffraction in crystalline materials, it is generally not possible to easily define these structures without a significant amount of *a priori* information about what is expected. As such EXAFS serves mainly as a confirmation of a model rather than an investigative technique for an

unknown system. An advantage in the context of our studies, however, is that hydrogen does not scatter x-rays effectively, so if a system contains hydrides or molecular hydrogen it would appear to have few backscatterers surrounding it. This would be strong indirect evidence that the system was in the appropriate configuration to store hydrogen.

For a system which appears to hold promise as a hydrogen storage medium one further technique must be used to quantify its ability as a sorbent: Hydrogen Adsorption Measurements. Hydrogen adsorption studies performed at low pressure either at 78 K or room temperature provide a final piece of information about the characteristics of the prepared material. Here the target is simply to measure the amount of hydrogen adsorbed (in cm^3/g at STP) by a sample at a given temperature and pressure, convert that amount to a weight percentage, and compare that value to other materials which are recognized as hydrogen carriers. To quantify the degree to which the metal center itself plays a role in this process it is also crucial to compare samples with and without inserted metals before and after activation through reduction toward hydrogen storage. The goal here is to observe no significant difference between samples which carry metal versus those which are simply a silicate matrix but to simultaneously observe a major enhancement of storage capacity after the reductive step. This would validate the targets of this work and would prove the feasibility of isolated titanium centers located within a porous silicate matrix as potential hydrogen storage materials.

1.7 Progress

This thesis describes the advances achieved over the past four years toward developing a material capable of meeting the hydrogen storage challenges preventing the implementation of a hydrogen based economy for vehicular applications. In the course of this research significant progress has been made toward the ultimate goal of developing a synthetic methodology which will permit the development of a hydrogen storage material based on weak chemisorption of hydrogen to a metal center chemically isolated in a porous silicate matrix. A system has been developed which contains roughly twenty-five weight percent titanium in a porous material, where each titanium center is spatially isolated from the others. Additionally, evidence has been collected showing that it is possible to reduce these materials using a variety of reductants without destroying the porosity of the matrix. Finally, attempts have been made to characterize these reduced materials to understand both the mechanism of the reduction and the coordination sphere surrounding the reduced titanium centers. Once this work is completed it will be possible to further tailor the system to enhance its ability to reversibly bind hydrogen in an efficient manner.

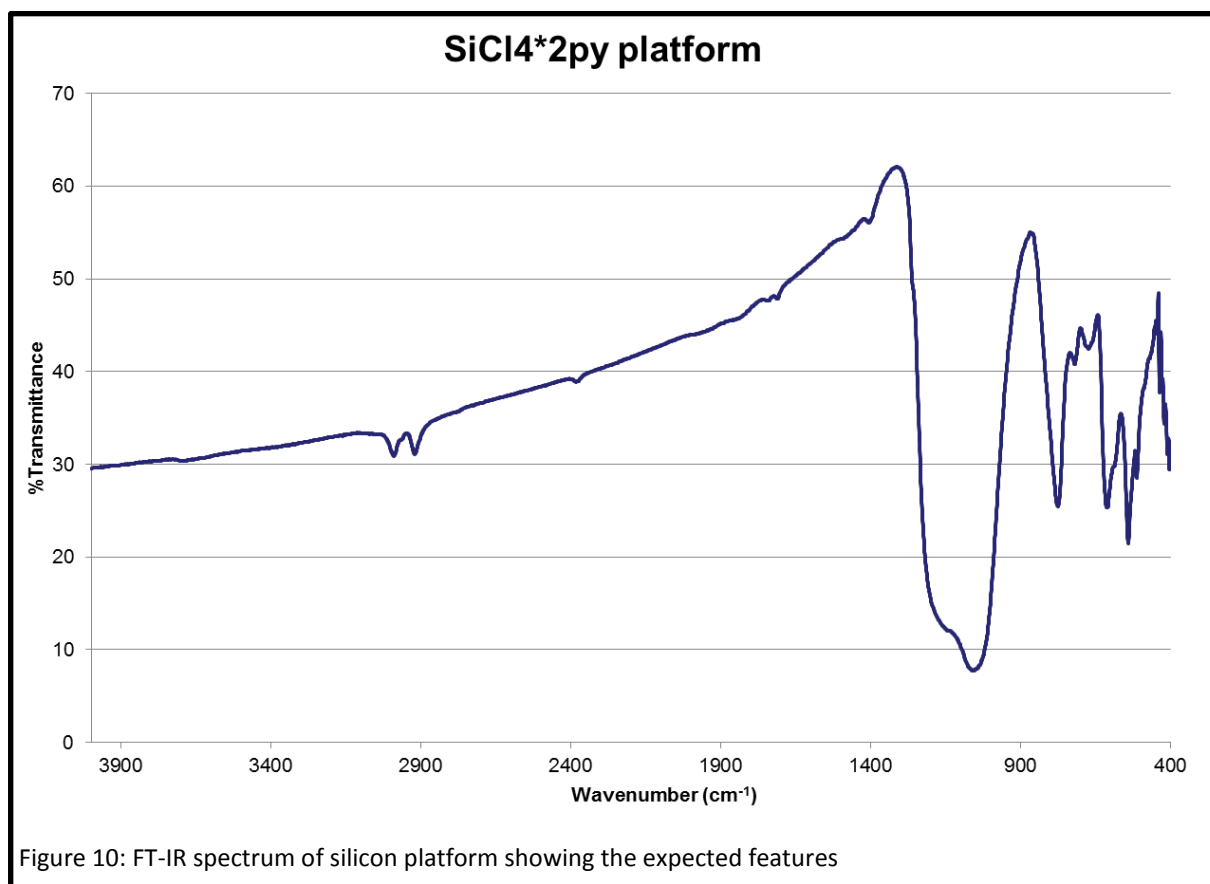
2. The Use of Molecular Silicates as Supports for Isolated Titanium Centers:

The main problem preventing most systems from achieving high loadings of any metal within a material is that it is difficult to achieve a homogeneous distribution of sites within a matrix in which each site is also isolated from the others. This generally leads to systems which have low loadings (<5 wt%) of metal in the system.⁴⁴ With such a low loading of active sites it is impossible to achieve a significant amount of hydrogen storage; for a system which is composed exclusively of titanium the theoretical maximum storage of hydrogen is 20.2 wt%. This means that to meet the department of Energy's targets a material which relies exclusively on the interaction between titanium and hydrogen must have roughly 25 wt% titanium. For almost any system this is impossible to achieve while still maintaining site isolation, as deposition based methodologies frequently lead to site aggregation at high metal loadings. The synthetic methodology of the Barnes group however ensures site isolation by fixing each active site ~ 10 Å apart from the next. Additionally, using one variation of this approach it is possible to achieve titanium loadings of about 25 wt%. For these reasons the use of the Barnes group methodology naturally lends itself towards addressing this problem. There are three different variations of this synthetic methodology of which two are important here: the two-step platform approach, which leads to a single type of metal site at lower loading, and the one-step platform approach, which results in a distribution of sites with a higher density of active metal. Here platform is defined as an amorphous, porous silicate or mixed metal oxide matrix.

2.1 Two-Step Titanium Platforms

The synthesis of a two-step platform begins with the same fundamental precursor as do all reactions within the Barnes group: the tin cube $((\text{Me}_3\text{Sn})_8\text{Si}_8\text{O}_{12})$. As the name implies synthesizing a two-step platform requires two separate reactions, and results in a material which has only a single type of titanium site. In the first step, shown in figure 5, the tin cube is reacted with silicon tetrachloride bispyridine (in most cases this ratio is 2.5 $\text{SiCl}_4 \cdot 2\text{py}$: 1 tin cube) using Schlenk line techniques to assure the complete elimination of water and oxygen from the system. This reaction is performed in toluene which has been dried over NaK alloy and vapor transferred to the Schlenk reaction vessel and generally requires several hours to progress to completion. Michael Peretich studied the time required and found that generally 12-24 hours of refluxing at 80 °C was sufficient to complete the reaction and that continuing the reaction beyond this point could lead to the loss of surface area due to the decomposition of the matrix (especially when the bispyridine adduct was not used). For this reason

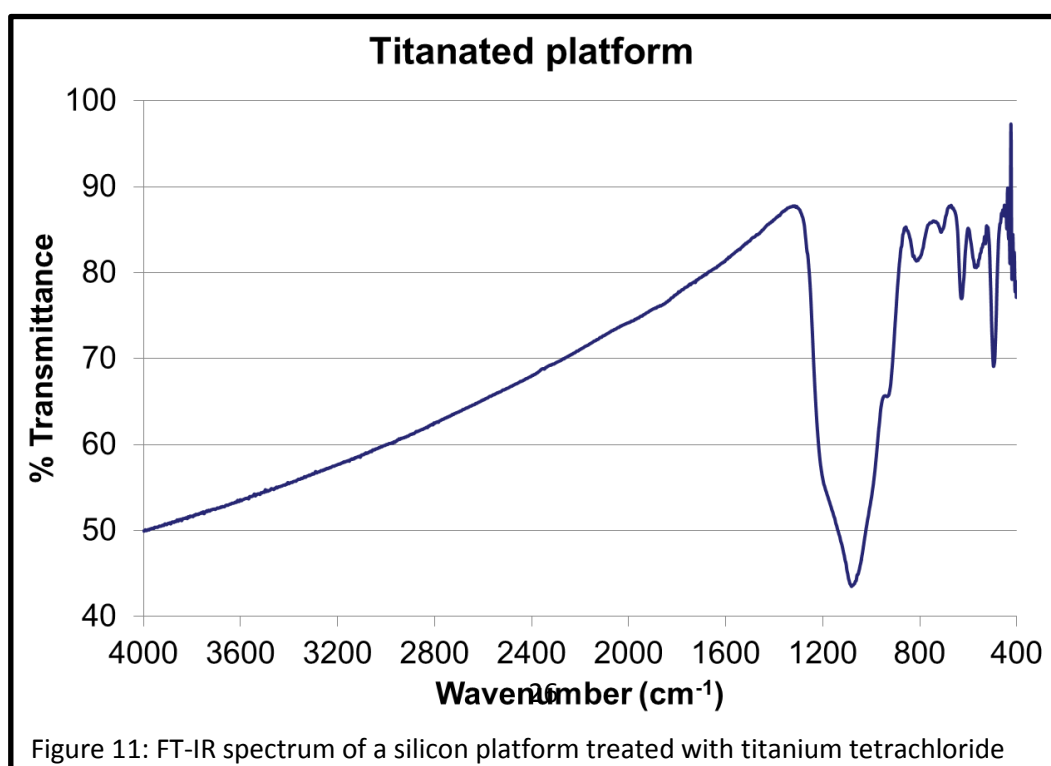
reactions are run for between 12 and 15 hours, resulting in translucent gels. The volatile components are then removed under vacuum while heating at 100 °C. ^1H NMR spectra of these volatiles can be used



to confirm the presence of the expected by product of the reaction, trimethyltin chloride, which appears as a singlet with a shift of 0.22 ppm (C_6D_6) along with the associated $^{119}\text{Sn}/^{117}\text{Sn}$ satellites. At this stage the dried product is a blocky white powder which can be ground to a fine powder if desired. These materials generally have surface areas of between 500 and 1000 m^2/g using BET analysis of the nitrogen adsorption isotherm. The silicon tetrachloride which is added to the system will have formed on average 2.5 connections within the matrix during this cross-linking process, which means that on average there are 1.75 tin groups remaining for each tin cube located within this matrix. The precise number of remaining tin groups is determined based on a gravimetric analysis of the sample after it has been dried. The presence of these tin groups has also been confirmed by ICP-AES analysis of these samples. Infrared spectra of the platform prepared in this first step shows the alkyl C-H stretches indicative of the trimethyl tin groups remaining in the system as well as the expected Si-O bands between 1200 and 1000 cm^{-1} (Fig. 10). The properties can be modified if a different composition is desired, but generally this is a robust system which can be easily studied and is adequate for further reaction.

The second step involves replacing the remaining tin groups within the system with the desired titanium centers; titanium tetrachloride (TiCl_4) is used to achieve this substitution. As each tin group within the matrix is completely isolated from the others there is no way for more than one of the four reactive chlorides on the titanium to react with a tin group. This leads to a unique titanium site which has a single connection to the silicate matrix and retains three chloride groups. This reaction is shown in figure 6. An excess of titanium is used to assure that every accessible tin site is converted to a titanium site; a standard ratio is two titanium units for each remaining tin group. Any lower loading of titanium can be achieved simply by limiting the amount of titanium tetrachloride which is added to the reaction vessel. The conditions for this reaction are the same as in the first step although no gel is formed here. Instead a fine off-white powder results after the sample has been dried under vacuum. Gravimetric analysis supported by ICP-AES indicates that a ratio of roughly 40 titanium groups for every remaining tin is achieved in this reaction. This ratio means that of the initial eight tin groups for each building block there is now only one tin group for every 23 cube structures within the matrix.

This very low presence of tin is confirmed by FT-IR spectra which show little to no alkyl C-H stretches in these samples. Additionally, there is also no evidence of O-H stretches which would be present in a sample which had been exposed to the atmosphere. Finally, these “titanated” platforms contain a new band at 980 cm^{-1} , which is indicative of a Ti-O stretch. A spectrum illustrating these points is shown in figure 11. Frequently this process results in a slight reduction of surface area in these materials, although given the relatively imprecise nature of BET analysis this reduction is only rarely statistically significant (>10% surface area loss).



Once the silicate platform has been titanated it is ready to be activated toward hydrogen storage. While it is not possible to obtain as high a loading of titanium using this methodology it has several advantages with respect to its characterization. First, in theory each titanium site is the same as every other. Having a single type of titanium center within the matrix is crucial for either XANES or EXAFS analysis, as any differences in the local environment surrounding the titanium are superimposed making the spectra exponentially more difficult to solve. Second, because it is possible to easily control the amount of titanium within the matrix, samples can be prepared which are already at the appropriate concentration for a variety of spectroscopic techniques, especially EPR analysis which is very sensitive and requires a lower loading of titanium to prevent saturation. Finally, the rigid silicon platform formed in the first step of the synthesis is quite stable and is not likely to be affected by any further activation steps. For these reasons the two-step platform is used as a model to eliminate as many potential variables as possible and ease the process of grappling with the already complex processes observed when the titanium sites undergo reduction.

2.2 One-Step Titanium Platforms

While the two-step titanium platform is excellent as a model it does not represent a material which has the potential to meet the guidelines established by the department of energy. Additionally, it is a more complicated process requiring two separate synthetic reactions, which must be separated by a drying step to prevent the formation of unwanted by-products (the bispyridine adduct of titanium tetrachloride). For both of these reasons a much simpler and more direct methodology was developed which permits the rapid and effective synthesis of a porous material which contains 25 wt% titanium and is ready for activation toward hydrogen storage. This process again begins with tin cube, however this time instead of adding silicon tetrachloride, a large excess of titanium tetrachloride is used to both cross-link the cubic precursors (generating the porous framework), and remove any remaining tin groups by replacing them with capping titanium units with only one connection to the matrix. The ratio of titanium tetrachloride to tin groups in this synthesis is normally one TiCl_4 for every Me_3Sn group present in the system, which corresponds to a ratio of eight TiCl_4 units for each cube. To effect the reaction the mixture of tin cube and titanium tetrachloride is refluxed while stirring at 80 °C in dry toluene. An orange gel is formed very quickly (frequently before the solution reaches a stable temperature) and studies have shown that the reaction is generally complete within one hour. However to ensure that the maximum number of titanium units to react, this reaction is generally run for at least six hours before the solvent and other volatile components are removed at 100 °C under vacuum. Once

all volatiles have been removed the resulting off-white powder can be characterized. Figure 12 outlines the process involved in synthesizing this matrix.

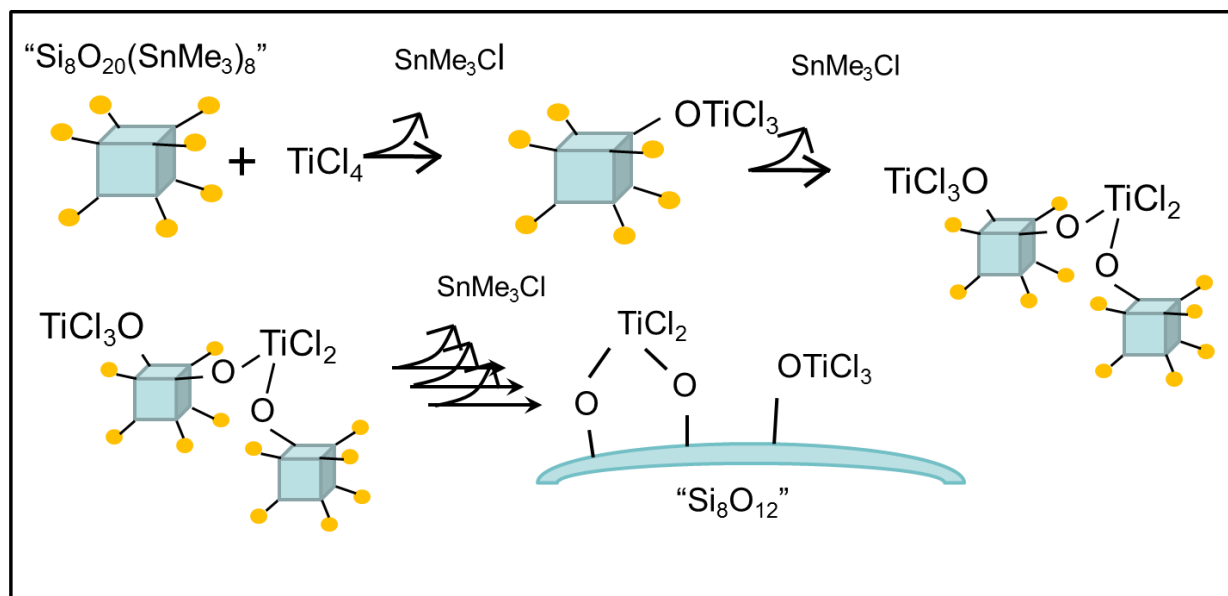


Figure 12: Synthetic diagram for a one-step titanium platform.

The first issue with characterizing the one-step process is that the gravimetric analysis is much less precise. While in the two-step process it was assumed in the first step that each silicon reagent reacted at least once, which meant that it was possible to know how many total potentially reactive chloride units were in the system. Here that is not the case, because the solution remains orange during the course of the reaction indicating that there is at least some unreacted TiCl_4 in the reaction flask at the end of the synthesis. As the amount of TiCl_4 which actually reacted with the system is unknown the connectivity of the incorporated titanium units must be estimated by calculating what the expected mass change would be for a given connectivity of titanium and then comparing that value with the actual data obtained. Although this process is not as precise as a direct calculation it does give a good idea of the degree of cross-linking present in a one-step titanium platform. In general this value is around 1.3 connections per titanium. This value again correlates well with the values obtained using ICP-AES analysis which gives a direct measure of the amount of titanium in the system and permits a direct calculation of the connectivity when combined with the gravimetric analysis. ICP also reveals that in these matrices there is even less tin remaining (relative to the number of titanium sites) than in the two-step platform. On average there are 100 titanium sites for every tin site left in the platform, which

corresponds to roughly one tin for every sixteen cube structures. Infrared spectrometry of the one-step platform shows the expected features indicating the Si-O and Ti-O stretches at 1020 and 980 cm^{-1} respectively and little else (Figure 13). Finally, these materials generally have specific surface areas of between 300 and 700 m^2/g indicating a significant degree of cross-linking is present in the matrix. Once

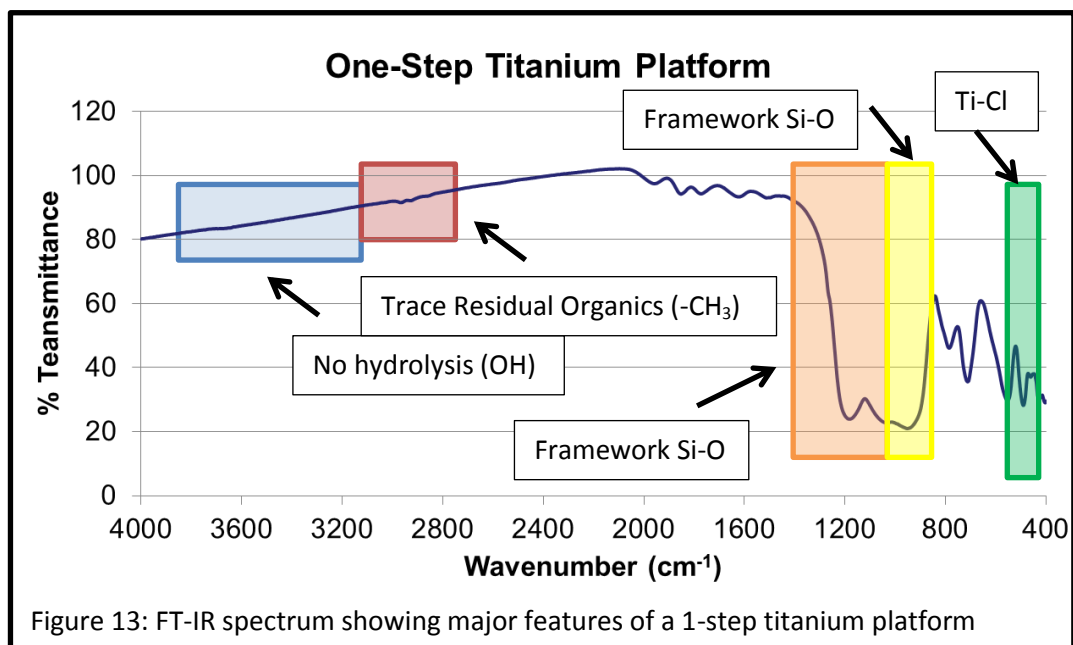


Figure 13: FT-IR spectrum showing major features of a 1-step titanium platform

the standard characterization steps have been performed on these materials they are ready to be activated toward hydrogen storage.

The major advantages of the one-step synthetic methodology are two-fold. First, the process is easy and can be performed quickly in high-yield to give a reliable product. As such, it holds promise for in an industrial setting. The second, more significant advantage, is that this process leads to a much higher loading of titanium than can be achieved using a traditional two-step synthesis, while still maintaining site isolation. Although recent work within the group has begun to target a more controlled method to achieve this same result, the fact remains that there is currently no other system which could be found that can achieve as high a loading of titanium sites while still retaining site-isolation. The disadvantages are also significant, however. As titanium is used as both the cross-linking reagent and as the capping (one-connected) "active site" there is some risk that whatever process is used to activate the titanium active sites will also affect the units which form the backbone of the matrix. This could lead to degradation of the porosity in the system as a result of this process, and as will be mentioned this has actually been observed under certain conditions. The second major disadvantage is that this material

contains a distribution of titanium sites, which makes it very difficult to characterize using the X-Ray absorption techniques described above. If it is difficult to interpret and model the spectrum of a two-step titanium platform it would be nearly impossible to do the same for a one-step system.

3. Activating the System Toward Hydrogen Storage:

No matter which support is synthesized the next challenge remains the same; titanium (IV) has no d-electron density and is expected to have little to no affinity for molecular hydrogen. To be able to potentially store any hydrogen beyond the small amount which adsorbs simply due to physisorption on the pore surfaces these titanium sites must be reduced to some lower oxidation state. Once reduced it is hoped the electron density on the titanium centers will be able to interact with hydrogen molecules and could lead to the formation of weak reversible bonds to hydrogen in the so-called “sweet spot” for hydrogen storage. The problem is that effecting this reduction is not a simple process. There are many chemical reductants which hold the potential to achieve the necessary activated titanium sites. These are divided here into three categories: Hydrogen gas itself, molecular hydride sources, and traditional organic reductants. Each of these potential pathways has its own advantages and disadvantages, and, despite being a major focus over the course of the last two years, there is still no clear answer as to which system will prove to be the best.

3.1 Hydrogen Gas

When it comes to chemical reductants nothing is simpler than hydrogen gas. Molecular hydrogen is actually the most basic molecule possible (excepting its ion H_2^+) and also is the molecule which these systems are designed to eventually store. Hydrogen is not, however, a strong reductant, making it more challenging to use for activation of the titanium centers. There are two ways to overcome this difficulty, either the hydrogen and sample can be heated to very high temperatures (generally 500-600 °C) or the titanium center can be modified to be more reactive toward the hydrogen.³⁸ The organometallic titanium has been shown to react with hydrogen at roughly 150 °C, which is a significant improvement over the 500 or 600 degrees required when using pure hydrogen gas. The second consideration when running a reaction at an elevated temperature is what other side products might be possible under such energetic conditions. It is possible that the hydrogen could cleave other bonds in the system or that when HCl is generated it could attack the support itself. Both of these scenarios would result in a loss of porosity which could be detected using adsorption studies.

3.2 Molecular Hydride Sources

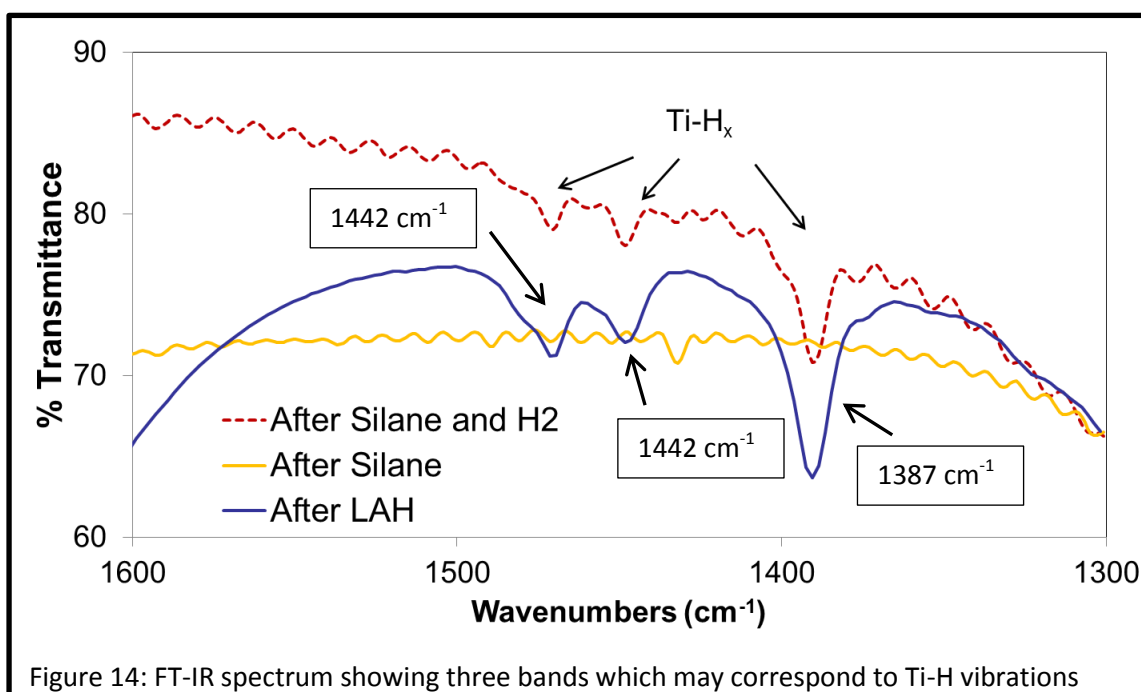
The bulk of this work has focused on using traditional hydride sources to effect a reduction at the titanium center. The two traditional hydride donors employed for this task were lithium aluminum hydride (LiAlH_4 , "LAH") and sodium borohydride (NaBH_4). Each of these systems has been studied exhaustively in organic systems, and some work has also been performed with both zeolites³⁷ and molecular titanium species.^{45,46} LAH has been shown in these investigations to be effective toward the reduction of titanium under mild conditions. A mechanism has even been proposed for the reduction of the molecular titanium species, although this model requires two titanium units to be in close proximity. The major advantage of either hydride reductant is the ability to perform stoichiometrically controlled reductions under ambient conditions with relative ease. When the initial work on these systems was being performed it was not known whether or not it would even be possible to reduce the titanium centers which had been placed into the matrix, and so, when it appeared that under mild heating hydrogen was not effective, a more powerful traditional reductant was chosen. Initially it appeared that LAH was not able to reduce the two-step titanium platforms, although it did show activity toward the one-step systems. After purification of the lithium aluminum hydride it was found to be effective in reducing both types of materials.

While both reductants have proven themselves capable of reducing the titanium centers located within the matrix there are still several drawbacks to these ionic reducing agents. First, they are non-volatile solids, making it very difficult to remove any unreacted reductant from the sample after the reaction has completed. Any excess material that remains after the system has been activated toward hydrogen storage is simply more mass unless it in some way enhances the storage capacity of the material. While there are studies indicating that it is possible to enhance the reversible binding characteristics of LAH toward hydrogen gas,⁴⁷ unless this effect is observed here then the LAH simply acts to clog the pores of the matrix and reduce the number of titanium sites which are accessible to hydrogen. The second concern with these traditional reductants is their low solubility in dry organic solvents. While lithium aluminum hydride theoretically has a solubility in ether in excess of 5 M many articles also indicate the difficulty in achieving a saturated solution even after many hours of stirring.⁴⁸ Additionally, the very reactive nature of these materials makes it difficult to obtain NMR spectra of prepared solutions. Therefore, to obtain pure LAH it was necessary to use a Soxhlet extractor ether and then to cannulate the resulting saturated ethereal solution to a Schlenk Vessel and remove the solvent under vacuum at 100 °C. Fortunately, it is possible to use the purified white LAH powder to reduce the

titanium centers without having to prepare a solution beforehand. It is likely that as the lithium aluminum hydride is consumed the remaining powdered LAH is solvated according to Le'Chatelier's principle. This discovery has made reductions based on either hydride much simpler experimentally. Despite these advances the limited solubility and non-existent volatility of both lithium aluminum hydride and sodium borohydride make them poor choices for use as reductants.

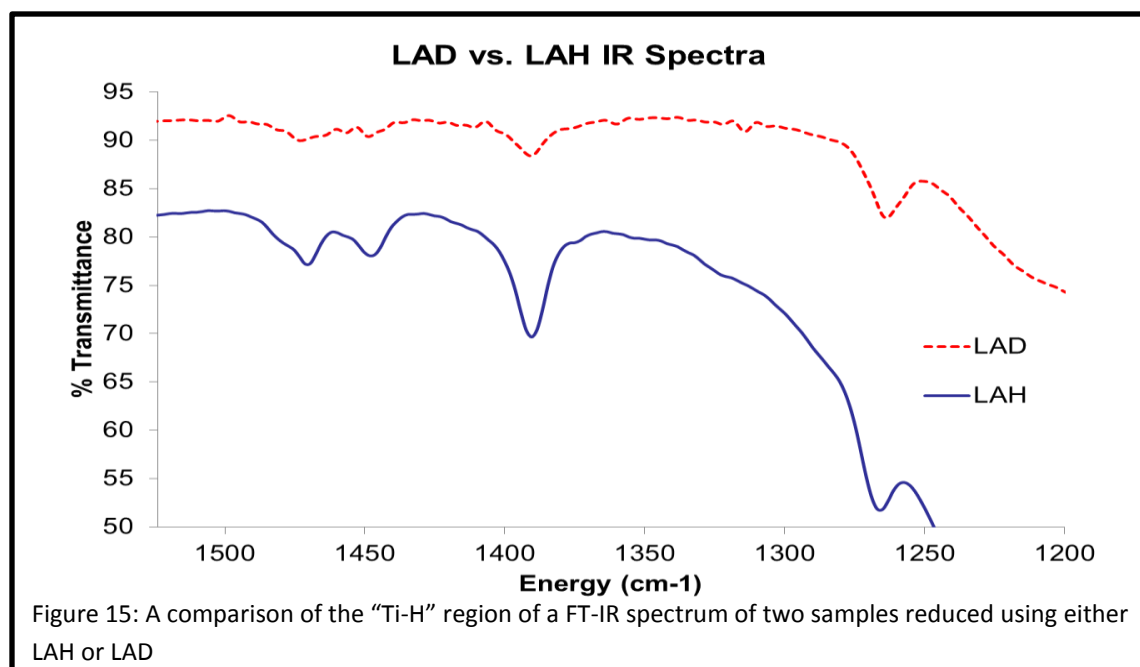
The last, and most important, issue concerning the use of traditional reducing agents is the mystery surrounding the mechanism of reduction. Recent evidence indicates that there is likely ether which is coordinating to the titanium site as part of the reduction process, however there is also a question as to how even having a hydride source present it is possible to achieve a reduction at the titanium. These issues continue to prevent a thorough understanding of the titanium centers that result from this process and limit our ability to make hypotheses about what steps to pursue in the future. Until some handle can be achieved on the method of reduction in these systems there is little hope of understanding whether or not they constitute viable hydrogen storage materials. Unfortunately, there are few ways to directly characterize amorphous materials and so it is unlikely that direct evidence will emerge to confirm any postulated final state for these systems. There are, however, some clues which can be used to establish the possible outcomes. An analysis of the available data is presented below.

The first tool available in any synthesis using the Barnes group methodology is the gravimetric analysis performed between each step. When there is only one variable in the system (i.e. only one component is changing during the course of a reaction) it is generally possible to accurately determine the degree of reaction simply by monitoring the mass changes associated with that process. In reductions using LAH a mass increase is generally observed. This is inconsistent with the observed gas evolution which occurs during the course of the reduction, as this evolved gas should actually produce a slight mass loss. The only other chemical which is present during these reductions is dry diethyl ether. Given the affinity of ether for lithium aluminum hydride it might be expected to form a complex with the LAH which could contribute to the observed mass change. The actual amount of mass gained is somewhat less than that predicted by the observed etherate species present in solutions of LAH⁴⁸ which also makes sense as some mass must be lost from the generated gasses. The actual ratio of "ether" units for each lithium aluminum hydride based simply on the observed mass change is 0.8:1.



IR spectra are then obtained of each of these materials in an attempt to identify some of the expected groups that should be present within these reduced titanium systems. As mentioned previously, great attention has been paid to a series of bands occurring between 1500 and 1200 cm^{-1} which according to the literature²⁹ may be attributed to a variety of Ti-H_x stretching modes. Specifically, the band at 1387 cm^{-1} and those appearing at 1442 cm^{-1} and 1471 cm^{-1} were postulated to correspond to TiH , $\text{TiH}_2(\text{H}_2)_x$, and Ti_xH_y respectively. An IR spectrum showing the position of these bands is presented in figure 14. If these assignments are correct then it should have been possible to change their position by reducing the titanium centers using lithium aluminum deuteride (LAD) in a labeling study. The expected positions for the equivalent Ti-D stretches would be beneath the much stronger Si-O-Si bending bands at $\sim 1000\text{ cm}^{-1}$ (For the three different assignments mentioned above the exact values were predicted as 1020 cm^{-1} , $\sim 1050\text{ cm}^{-1}$, and 1071 cm^{-1} respectively), making it difficult to directly identify these features were they present. In any event, for a reduction completed with LAD the previously observed bands should be absent from the spectrum, but this was not found to be the case. The relative intensity of the features between 1200 and 1500 cm^{-1} was not significantly changed when the reduction of the titanium centers was completed using LAD. Spectra of two-step titanium platforms reduced with both LAH and LAD are shown in figure 15. When these data were obtained it was still not possible to quantify exactly the amount of reductant which had been added to the system and therefore there was no expectation that a mass change would indicate the potential coordination of solvent within the matrix.

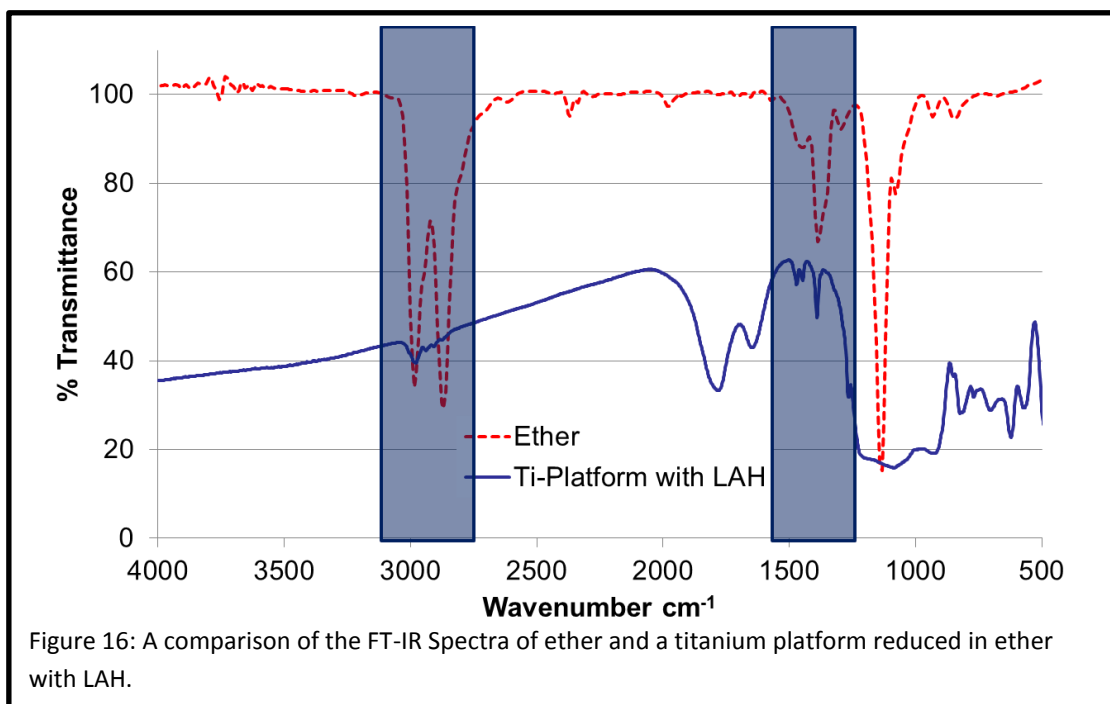
Once more accurate stoichiometric and gravimetric ratios of reductant could be calculated and it was observed that there was excess mass within the system other explanations of the new IR features could be explored. As ether was the only other chemical present during the reduction it was thought that perhaps this was coordinating to the system in some way. When an IR spectrum of ether obtained



from the spectral database⁴⁹ it was found that although the spectrum showed many of the same bands as those observed in the sample itself it also contained many other bands which were not observed. An independent spectrum was taken, but the band positions proved to be inconclusive. A comparison of the observed bands in the reduced titanium platform as compared to those observed in the pure ether is shown in figure 16.

No matter what the mechanism of reduction is there is strong evidence that the titanium centers within the matrix are, in-fact, undergoing an oxidation state change in the presence of either lithium aluminum hydride or sodium borohydride. To reduce a sample of either a two-step or one-step titanium platform the desired amount of reductant is added to the platform under an inert atmosphere in a Schlenk vessel. This mixture is then placed under vacuum and cooled in a liquid nitrogen bath. A small amount (~30 ml for 500 mg of titanium platform) of dry ether is added to the system using vapor transfer techniques, and the sample is allowed to return to room temperature while stirring. During this time the material will begin to emit a gas and will also darken. The mixture is stirred for several hours or until no more evolution of gas is observed and may be periodically evacuated to ensure that there is not

a buildup of pressure within the system. At this point the volatiles are removed from the sample under vacuum and the resulting dark powder is heated at 100 °C overnight to remove any residual volatile components. Once all of the volatiles have been removed the sample is massed and is placed in a glove-box under an inert atmosphere until all analyses can be completed.

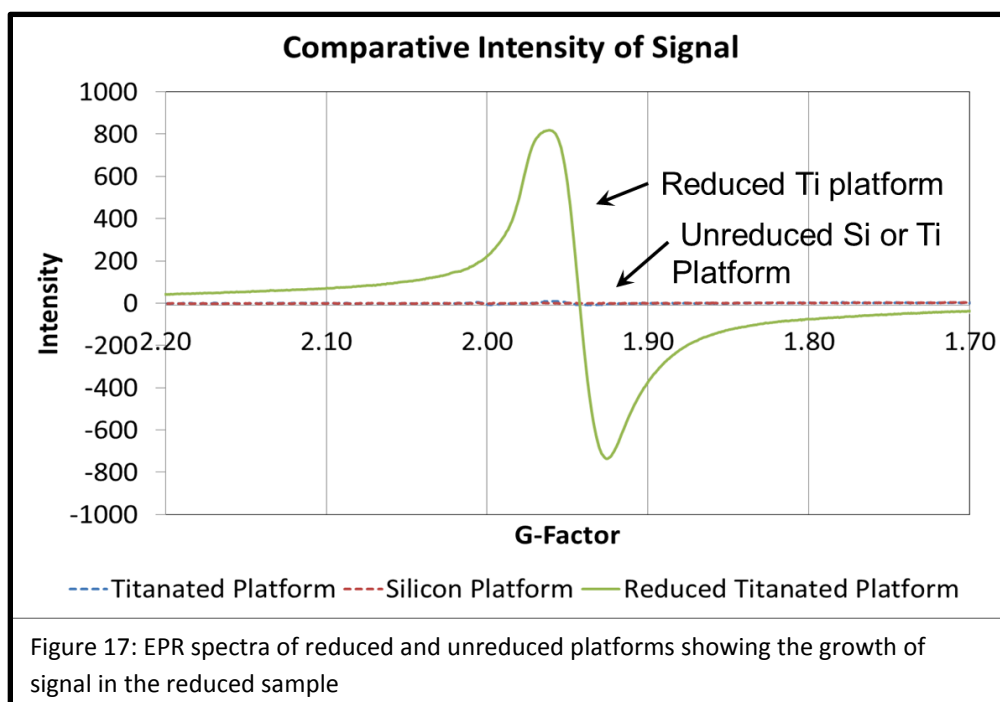


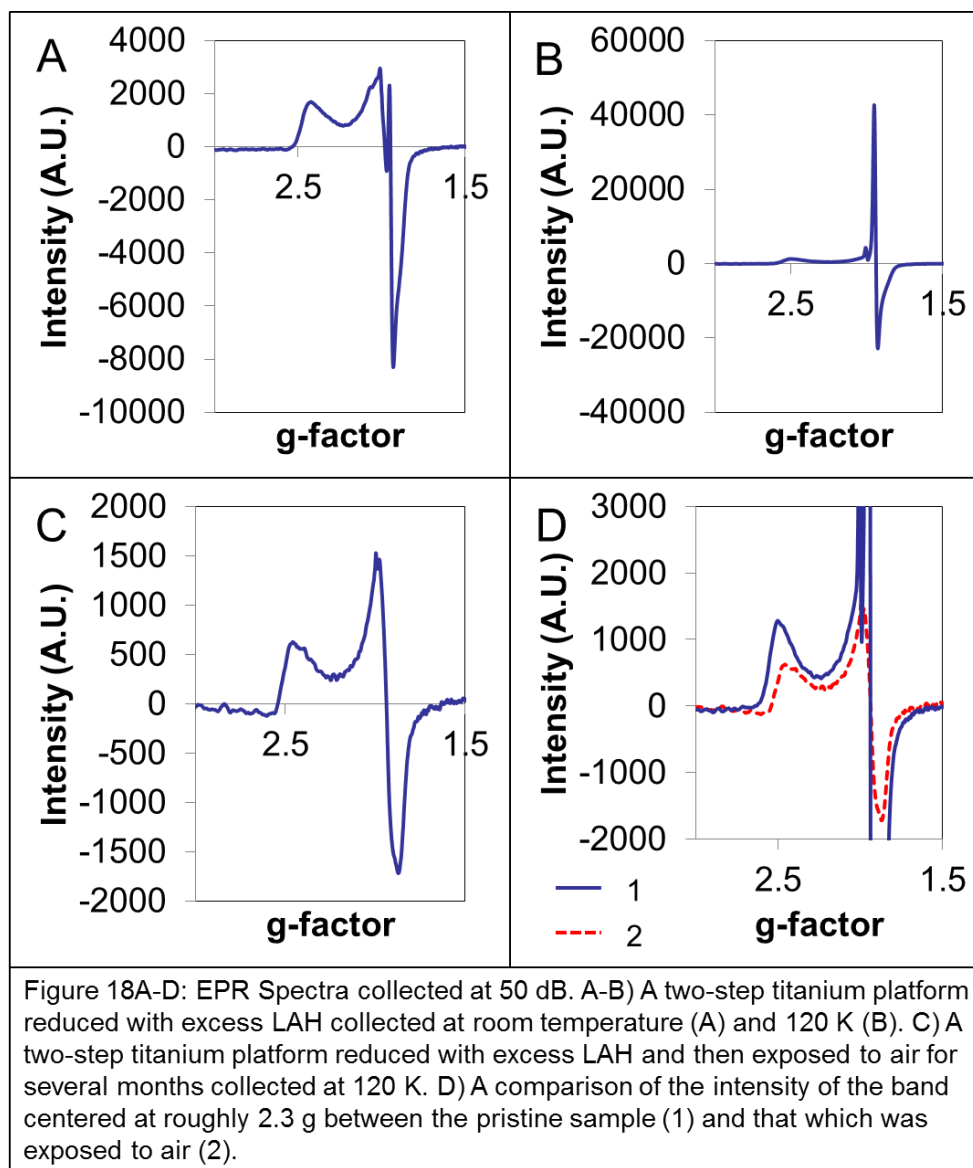
The first piece of evidence for the reduction of the titanium centers arises from direct observations during the reduction process. When exposed to LAH in ether (even at reduced temperature) a color change from tan to black is observed over the course of about 30 minutes as the sample warms to room temperature. This color change does not occur in samples which have no titanium. Figure 7 shows the difference in color from the beginning to the end of the reduction. There is also a direct correlation between the amount of reductant added to the system and the final color of the material. Finally, if the ratio of reductant to titanium is less than one then the samples will return to an off-white color when exposed to air, however if this ratio is significantly above one then it will take much longer for this reversal to occur, sometimes requiring hours of days in moist air, or not occurring at all.

The first spectroscopic technique which gives direct evidence for the oxidation state of the titanium center is EPR⁵⁰. EPR spectra showing the difference in signal between a silicon platform (the first step of the two-step titanium platform), a two-step titanium platform, and the same platform after reduction using an excess of LAH are shown in figure 17. As there are no other sources of unpaired

electrons present in any of these systems before reduction, there should be no significant EPR signal prior to the reductive step. Figure 17 illustrates this clearly, and also shows that upon reduction there are clearly unpaired electrons present within the system. As yet it has been impossible to elucidate what the geometry of the titanium centers within these systems are based solely upon the EPR spectra which have been obtained. Lastly it is important to note that a silicon platform will show no significant EPR signal even if treated with an excess of LAH.

One important point, however, is that in samples which return to a “white” coloration upon the exposure of the sample to a humid atmosphere, this signal disappears. In contrast, it was recently found that in samples which have been reduced with a higher ratio of reductant and maintain their dark coloration on exposure to a moist environment preserve the smaller of the two EPR signals observed. Additionally, this small feature does not show enhancement when the sample is cooled to 120 K. These two facts indicate that whatever this smaller signal is, it may be at least partially responsible for the coloration observed in the sample and it also is generated only under a different set of conditions than those observed for the samples prepared using a smaller ratio of reductant. Figure 18 summarizes this information.

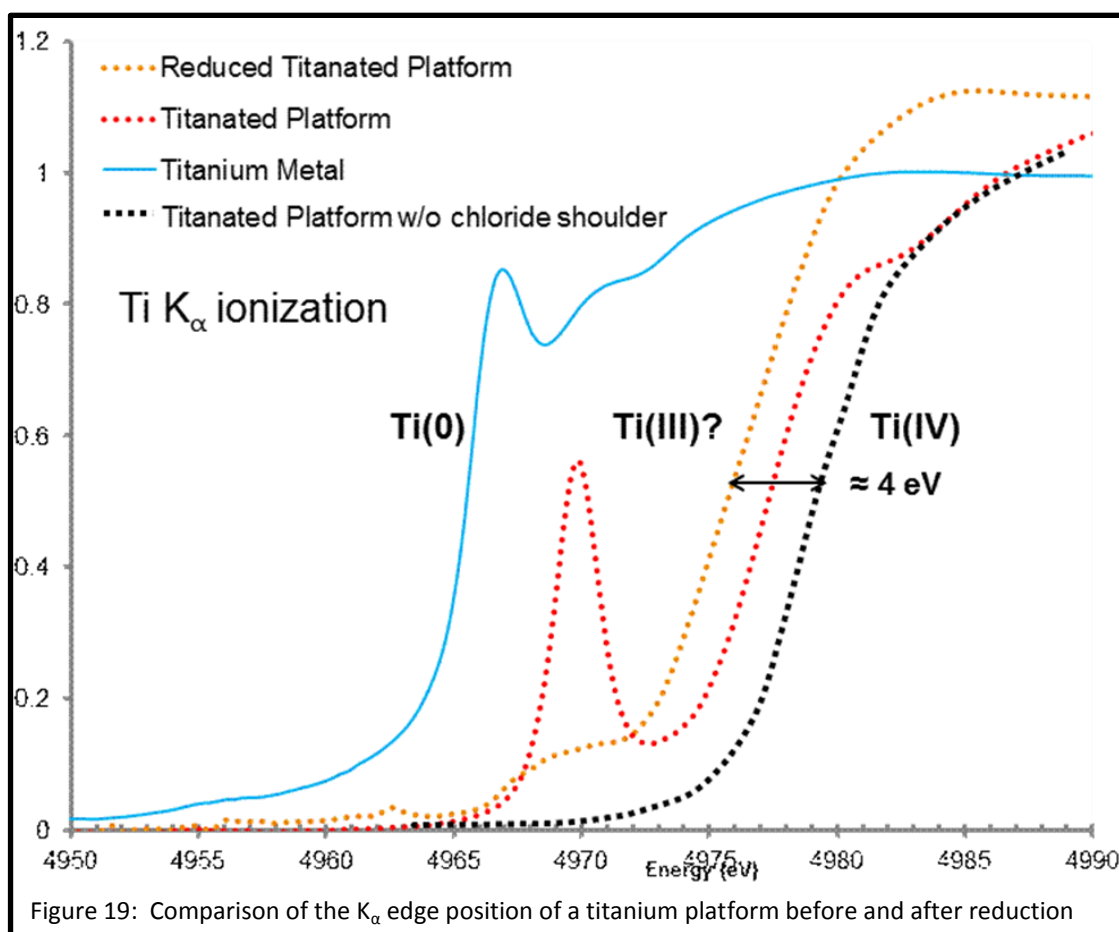




Further evidence corroborating that obtained from EPR can be gained using the two different X-Ray techniques available for use in amorphous systems. XANES analysis of the edge position in samples before and after reduction shows a shift in the inflection point of the edge of roughly 4 eV (Fig. 19). The position of the edge in the reduced samples closely matched that of a titanium (III) nitride standard which was run during the same data collection period. Additionally, a shift of approximately this amount has been shown in the literature⁵¹ to be consistent with a one oxidation state change in a metal center. With this oxidation state change there is also a significant decrease in the intensity of the pre-edge feature which, along with a very slight increase in the energy of this peak indicates a change in the coordination geometry of the titanium center.⁵² These data provide a strong correlation to the less

quantitative information gained from the EPR and give the first insight into the actual oxidation state of the final system.

Finally, XPS studies were performed to quantify the actual stoichiometry of the reductive process occurring with the use of hydride reducing agents. This work is ongoing, but data from Austin Albert indicates that there is a clear correlation between the stoichiometric ratio of NaBH_4 and the binding energy for the expelled electrons from the titanium centers. With an increased ratio of reductant there is a shift toward lower binding energy which is consistent with a reduced titanium



center, and again this shift is about 2 eV (1.68 eV). It also appears that when one sodium borohydride unit has been added for each titanium within the matrix then there is a nearly complete one electron reduction of the titanium center. This lends credence to the hypothesis that each unit of sodium borohydride is only able to reduce a single titanium site, despite the fact that it has four hydride groups. It is possible that once the reduction has been completed the borohydride is coordinated near the titanium center itself and so is unable to interact with any other sites.

All of these data provides a convincing argument that there has been a reduction of the titanium sites located within the silicate matrix. It is also apparent that during this process there is a change in the coordination geometry of the titanium from tetrahedral to some other state. There is some evidence that ether is coordinating either to the reductant or to the titanium itself. This information gives some clues as to the nature of the titanium sites, but does not provide a conclusive picture of their environment. Lacking this key piece of information it will be very difficult to ascertain the mechanism through which the titanium is reduced. The complicated nature of the traditional hydride reductants, LAH and NaBH_4 , means that they do not promote an enhanced understanding of the fundamental nature of the titanium centers here, but it has been shown that they are capable of achieving an end result which is comparable to that which has been proposed to be adept at storing molecular hydrogen. As such they continue to be an interesting synthetic tool.

3.3 Silanes

Silanes (RSiH_3) are another class of potential reducing agents which do not have many of the limitations of the more traditional organic reductants. First, many in this family of molecules exist as gases under ambient conditions but can also be liquefied with ease simply by lowering the temperature a few degrees. Others are liquids which remain sufficiently volatile to be transferred using vapor transfer techniques. Having a volatile material which may be able to act as a reductant is invaluable because they can be handled under air free conditions and, since they can also be liquefied and have known densities, may also be added in very precise ratios if desired. Finally, as they are either liquids or gases under ambient conditions, they may be employed without the need for any additional solvent and can be cleanly removed at the end of a reaction. For all of these reasons silane reagents make for a tantalizing chemical reductant.

Although the silanes might seem to be a very promising solution to the problems experienced with the complex hydride reagents, there are still some issues regarding their use. First, it was not initially clear that they would be able to achieve a reduction at the titanium center. In early work it appeared as though they were unable to reduce the titanium in a two-step platform, but that they could reduce the one-step system. This was confusing because while there are some differences between the two systems the titanium sites are, by and large, the same. Additionally silanes are, in general, pyrophoric. While this is not a problem if they are handled appropriately it does require special attention to be paid to the disposition of any excess reagent which is removed and will have to be exposed to air at the end of a reaction. As a result of the limitations observed during the first few

experiments performed using silane reagents it was decided that the major focus should initially be on the more effective traditional hydrides. It was only later when the problems with the traditional reagents emerged that attention was redirected toward silane reagents once again.

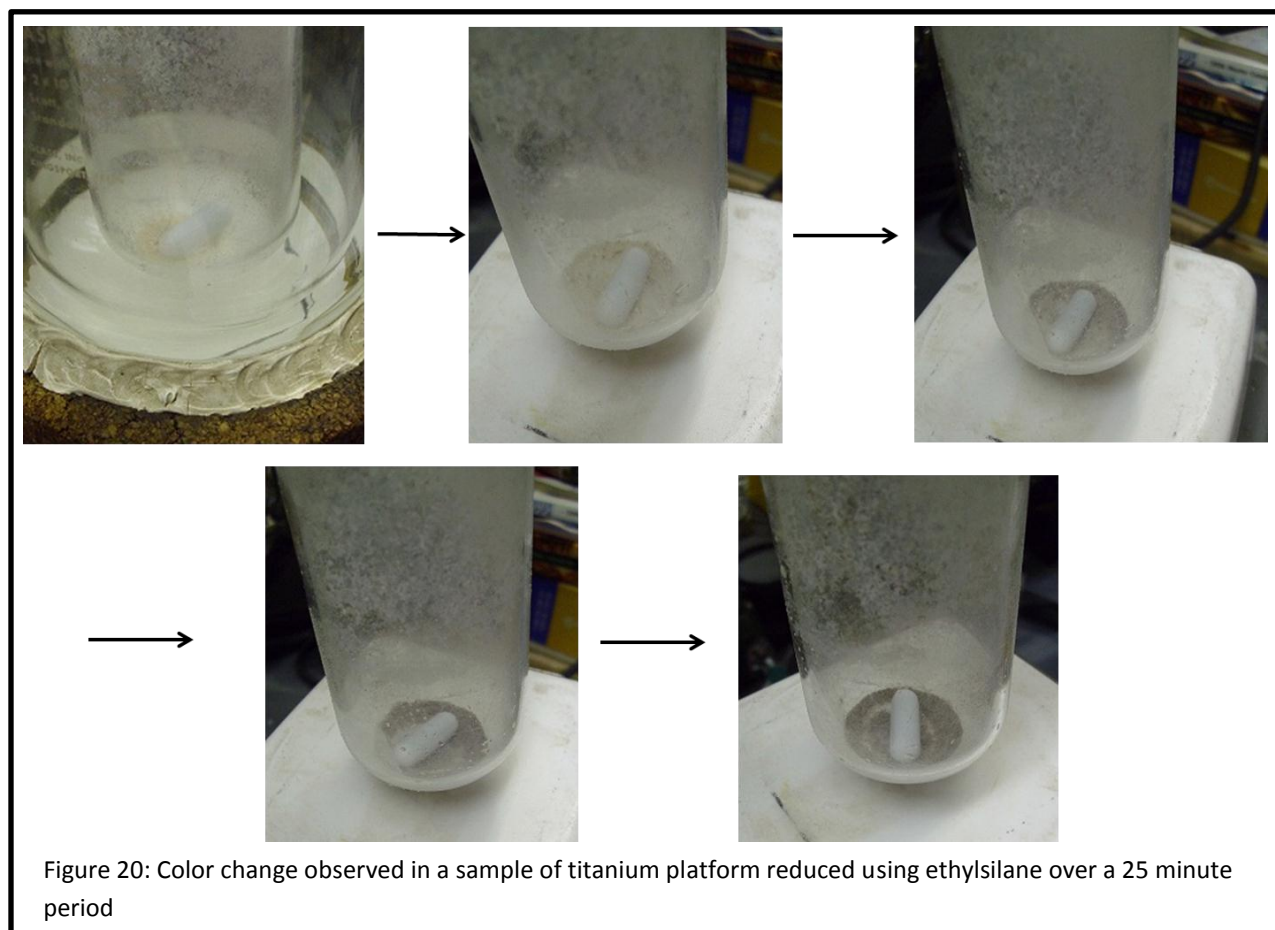
This work has focused on the use of two very similar silanes: ethylsilane (EtSiH_3) and phenylsilane (PhSiH_3). Phenylsilane is a liquid that boils at roughly 120°C , while ethylsilane is a gas with a boiling point of 19°C . Silane itself (SiH_4) was not chosen for study because of its extreme reactivity and pyrophoric nature. While both silanes have been shown to be effective in achieving a reduction of the titanium sites, the phenylsilane reacts much more slowly than the ethyl which is responsible for the earlier results which did not indicate reaction with the two-step platform. Recent work has focused on the EtSiH_3 as it is both more reactive and a gas at room temperature.

Reduction of a sample of titanium platform using ethylsilane is a straightforward process. For a 1:1 stoichiometric ratio of silane to titanium the appropriate volume of liquid ethylsilane ($\rho = 0.639 \text{ g/cm}^3$)⁵³ is calculated from the number of moles of reductant required. Using a capillary tube of known diameter it is then possible to determine the volume of silane required and equate that to a length of the capillary, cool the capillary using an ice bath, and fill it with only the desired amount of silane using vapor transfer techniques. Once this process is completed the silane may be transferred to the Schlenk vessel containing the sample to be reduced by cooling it using a dry ice/isopropanol bath to create a temperature gradient. If this process proceeds slowly it may be expedited by removing the ice bath from the capillary containing the ethylsilane and allowing it to return to room temperature. Once the ethylsilane has been added to the Schlenk, the isopropanol bath can be removed and the system sealed and allowed to return to room temperature. It is important to calculate the volume the silane will occupy to ensure that there is not a build-up of pressure within the vessel. Figure 20 shows the progress of the reaction over the course of twenty-five minutes. During the reduction the sample will slowly change from an off-white color to a dark grey as the reaction proceeds. To ensure that the process is allowed to continue to completion the reaction vessel is left sealed overnight at room temperature. The next morning the volatile components are removed under vacuum and the sample is heated to 100°C . The powder is heated to ensure that any residual unreacted silane is removed from the system. Once this process is complete a mass is taken of the vessel for gravimetric analysis and the sample may then be stored under an inert atmosphere to await analysis.

In some cases one further step is pursued in an attempt to activate these materials toward hydrogen storage. Once the sample has been reduced using either silane reagent it may be exposed to

either flowing or static hydrogen gas at elevated temperatures (and sometimes pressures). This is accomplished using either a sealed vessel where the sample is placed on a fritted disk and hydrogen is flowed through it or by placing the sample in a pressure cell and dosing it with the desired amount of hydrogen gas (generally about 2 atm at room temperature). In both cases the materials are then heated to at least 200 °C and allowed to react for several hours. This step is thought to be an important component of completing the activation of samples prepared using the silane reductants, however it has not been a major focus until recently.

Again the first clue that a reduction has been successful comes not from any analytical technique, but instead from direct observation of the sample. As the sample becomes more and more reduced there is an obvious color change from light to dark which cannot be attributed to any other source (fig. 20). In the case of ethylsilane this is most obvious as there is literally nothing else in the sample which could be responsible for the observed changes. While the same stoichiometric analysis which has been performed on the traditional hydride reductants has not yet been undertaken with the silanes it is possible to tell a qualitative difference in the degree of darkening based on the amount of

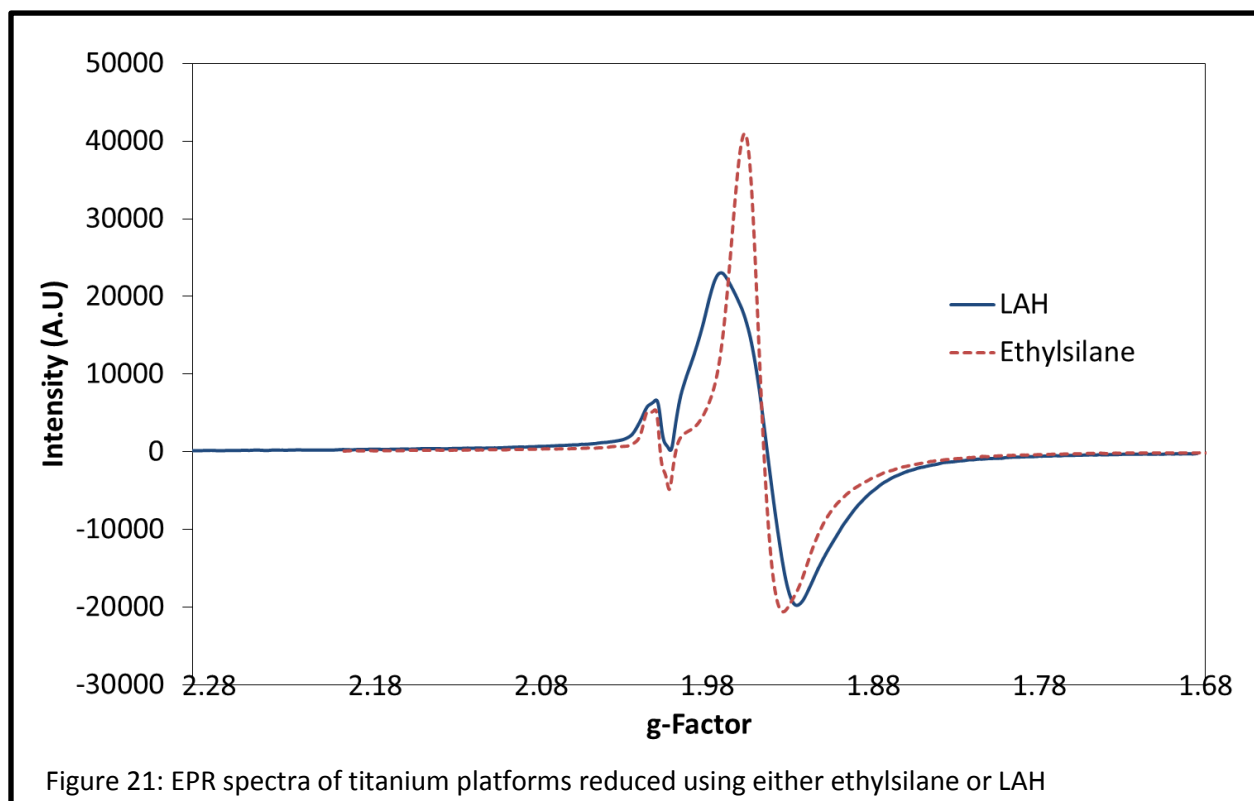


titanium which is present in a given sample. For those which have a lower loading of metal there is significantly less observable difference between the coloration of the platform before and after reaction with the silane. It is likely, therefore, that the same relationship between stoichiometric ratio and final color will hold true for this system as well. These samples also undergo the same process of color reversal upon exposure to air. Observation suggests that they are in fact more susceptible to this phenomenon than samples treated with the more traditional hydrides. It is therefore likely that a similar mechanism is operating for this system.

Interestingly, gravimetric analysis does not show any evidence of mass gain during reductions involving silane reagents. In fact there is generally a mass loss associated with this process. It is possible that this mass loss could be attributed to the exchange of chloride and hydride ligands, but as yet there is insufficient data to make a definitive judgment on this matter. The most interesting point however is that it is unlikely that there is a significant amount of residual ethylsilane remaining in the matrix after the reduction step. This is important not only because any added weight reduces the potential storage capacity of the system, but also because it makes it more likely that a volatile species is being produced as one product of the reductive step. If this species could be identified it could yield an important clue as to the mechanism which is operating in this reaction. As yet this species has not been identified using NMR of the volatile components, but further studies will attempt to isolate and characterize this unknown product.

Infrared studies of these materials have not shown the same degree of reproducibility as those performed with LAH. Initially there were some very promising results which showed a change in the spectrum of samples prepared using phenylsilane after treatment with hydrogen. It was later found that the bands which appeared also exactly matched those of samples reduced using lithium aluminum hydride in the key region which was identified as one location where Ti-H bonds might be expected to absorb.²⁹ Figure 14 illustrates the similarities between the two sets of bands. Once this was discovered an effort was made to replicate these results, as they would have provided strong evidence not only that both pathways could result in the same final material but also that hydrogen gas was playing a key role in the case of materials reduced using phenylsilane. As yet it has not been possible to replicate these results, casting doubt on their veracity. One reason for this is simply that the silane reducing agents have not been a major focus of work until recently and so not enough attention has been paid to pursuing this question. As work with the hydride reagents draws to a close more emphasis will be paid to this important issue.

EPR once again shows a distinctive difference between the platform before and after reduction with ethylsilane. Before reduction there is no appreciable EPR signal, but upon exposure to ethylsilane a feature which appears identical to that of a sample reduced using either LAH or sodium borohydride is noted. This feature is again subject to enhancement when the sample is cooled and also is resolvable into a band with two distinct maxima under these conditions. Figure 18 shows a comparison of spectra obtained at room temperature and those from 120 K. While it remains difficult to ascertain what, if anything, this enhancement signifies for the sample itself, the fact that matrices reduced using either method give rise to very similar radical systems suggests that both are proceeding to a similar endpoint. Figure 21 shows a comparison of samples reduced using ethylsilane and lithium aluminum hydride to illustrate the similarity in the lineshapes of these two sets of data. There has not yet been an opportunity to obtain either XANES or XPS spectra for these materials, but once these data are obtained it is hoped that they will give more insight both into the final oxidation state of platforms reduced using silane reagents, and that it may be possible to elucidate more information concerning the coordination geometry these systems exhibit.



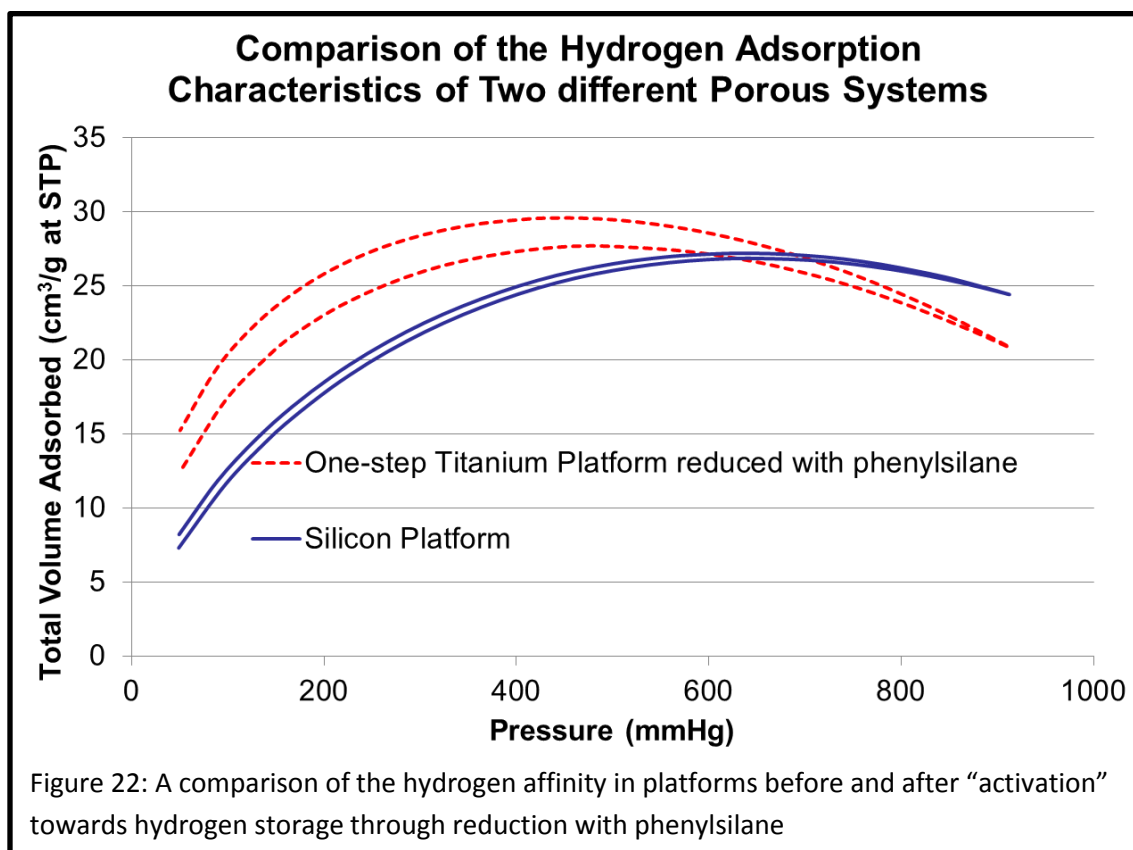
Given the ability of the silane systems to effectively reduce both titanium systems and the fact that they do not appear to coordinate to the titanium during the reductive process, it is believed that

silane reagents hold promise as an alternative to the more traditional hydride reagents. While further work is required to establish the precise nature of the titanium center in platforms prepared using either phenyl- or ethylsilane it is likely that these chemical reductants give rise to a site which is more open for interactions with hydrogen molecules. If this is the case then they should exhibit a more favorable binding toward hydrogen which would be shown through a larger weight percent adsorption when compared with matrices prepared using either LAH or NaBH_4 .

4. Hydrogen Storage, Conclusions, and Future Studies:

4.1 Adsorbing Hydrogen

Once the titanium centers have been activated toward hydrogen storage through a chemical reduction, the final step is to analyze their ability to actually adsorb hydrogen gas. While the hope is that atomically dispersed reduced titanium centers will be able to weakly chemisorb hydrogen gas at room temperature (the so-called “sweet spot”), until it can be proven that this is the case then this work simply constitutes an the world’s most expensive moisture detector. Hydrogen storage measurements



are necessarily the final step in the characterization of activated titanium platforms because it must first be established that they may be in the appropriate configuration to enable interaction with hydrogen. For materials which are believed to be in this state there is then there is cause to pursue hydrogen adsorption studies. While the department of energy has set standards for high temperature, high pressure loading of hydrogen gas, the more promising regime for a weak adsorber is at low temperature and high pressure. These measurements have been collected using a Micromeritics ASAP 2020 gas sorption analyzer in collaboration with the Jenkins group using low temperature and low pressure. It is not currently possible to obtain high pressure measurements using this system, but if a particular sample showed promise in the low pressure regime then the requisite data could be obtained externally.

Experiments have been performed to compare the ability of two-step platforms (both before and after treatment with titanium) as well as two-step platforms reduced with LAH to adsorb hydrogen. These measurements were taken at 77 K and were performed between 40 and 910 mmHg. Figure 22 shows the results which have been obtained thus far. Unfortunately, even the reduced titanium system shows only a fraction of the adsorption which would be required to be a successful storage material. The maximum adsorption observed for the titanium platform after reduction with LAH is 29.6 cm^3 hydrogen/g of sample at 246 mmHg. This corresponds to a weight percentage of hydrogen of 0.26. Obviously this is nowhere near the targets established by the department of energy and also shows only a small enhancement above the storage capacity of non-reduced samples (0.22 wt. % H_2). It is hoped that samples activated using silane reagents will show a much better hydrogen storage profile. Work in this area has only recently begun because until it is possible to make effective predictions about the nature of the titanium site there is little additional information to be gained from performing hydrogen adsorption analyses. This is especially true in the case of samples reduced using traditional hydrides where the understanding of the final system is poorly understood.

4.2 Future Work

Several experiments hold the key to determining whether or not these titanosilicate materials will ever have the ability to store appreciable amounts of hydrogen. Four areas of interest must be investigated further before it will be possible to finally answer initial question about whether or not exposed metal sites within a matrix hold promise as hydrogen storage materials. These are: can either

platform be reduced using hydrogen and then characterized?, is it possible to determine the identity of the gases being liberated during reductions involving phenyl- and ethylsilane?, do these systems approximate those resulting from reductions using LAH or NaBH_4 once they have been treated with hydrogen?, and can the IR stretches which appear in the reduced samples be assigned either as hydride stretches or as something else?. Once these four questions have been answered it should be possible to elucidate much more concerning the mechanism of reduction and the potential for optimizing the system toward hydrogen storage.

First, to establish the viability of reducing the system using pure hydrogen gas, studies must be performed to effect this reduction and observe the resulting system. Austin Albert has begun this investigation and results are forthcoming. If it proves possible to achieve a reduction in this manner (confirmed with EPR) it will be crucial to obtain a high-quality XANES and EXAFS data set for this material. When the only reagent within the system is hydrogen it becomes much easier to understand the possible outcomes and resulting systems. By quantifying the number of chlorides which remain bound to the titanium center after reduction it will be possible to begin formulating a mechanism which leads to this system. With both a coordination sphere and an oxidation state it may be possible to answer once and for all whether or not the basic premises upon which this work has been based are reasonable by obtaining hydrogen adsorption measurements on this system. These measurements, placed in the context of a known titanium site will be much more valuable in evaluating the potential for hydrogen storage.

Second, by identifying the gases which are being emitted during the course of the reductions using either hydride or silane reagents it will be possible to eliminate some of the potential mechanisms operating in the titanium reduction process. With molecular titanium chloride species both hydrogen chloride and hydrogen have been proposed as potential by-products during the reduction of these titanium sites with lithium aluminum hydride.^{45,46} By determining the gaseous products being produced it may be possible to grasp what the actual mechanism is and whether or not it is one which may lead to a system that could interact with hydrogen. A method has already been established in the lab which could be used to identify HCl by passing the evolving gases through a bubbler containing water and monitoring the change in pH during this process, but if the gas is not HCl this method may give misleading results. A better way to attempt to identify these gases is through the use of a real-time gas analyzer (RGA). This may be able to identify whatever gas is being generated and should play a role in future real-time characterization of the reaction mixture.

It is important that samples reduced with phenylsilane are also treated with hydrogen to reproduce the same changes in the IR spectrum which were seen previously. If these results cannot be replicated then the samples reduced using silane reagents will have to be analyzed completely independently. If, on the other hand, it is possible to reproduce the initial results then the preliminary assignment of the IR bands occurring between 1300 and 1500 cm^{-1} can be more assertively affiliated with Ti-H features. In this case hydrogen-deuterium exchange reactions will give a conclusive assignment of these peaks and they would then be able to be used as a standard for materials prepared using a variety of other reducing agents in the future. This would also answer one of the most important questions surrounding samples reduced using hydride reagents, which would be to show that they are capable of reversibly binding hydrogen under at least certain conditions.

Finally, as the building block approach permits the use of a wide variety of metals, studies must be performed which compare the ability of a variety of low valent metals to adsorb hydrogen under similar conditions. Many syntheses have to be modified to incorporate different transition metal species into a system, but the Barnes methodology allows the same procedure to yield a wide range of materials including those with more than one metal.^{36,54,55} This broad applicability makes it possible to easily investigate many metals simultaneously, and even to potentially incorporate two (or more) different metal sites within the same matrix under the appropriate conditions. Work has begun to introduce a small amount of platinum into matrices which contain a large amount of titanium to study the enhancement of the hydrogen storage capability of the titanium sites under these conditions. It has been shown that platinum sites can increase the storage capacity of systems which would not normally interact with hydrogen⁵⁶ By adjusting the ratio of platinum to titanium it will be possible to ensure maximum hydrogen storage capacity while minimizing cost.

4.3 Conclusions

Over the course of the past four years much progress has been made toward synthesizing and characterizing a new class of titanosilicates which contain a high loading of atomically dispersed titanium sites in a porous, amorphous matrix. Two different classes of materials have been studied: a two-step platform which contains a lower loading of titanium which can be prepared in a single-site configuration with each titanium center being essentially equivalent to every other and a one-step platform which contains a distribution of titanium moieties. It has also been shown that it is possible to reduce the titanium in both of these materials using a variety of reductants while maintaining surface area in the matrix as a whole. Finally, the majority of the work with these systems has focused on

characterizing the titanium center present in these systems to understand their composition. This final step continues to prove difficult, but there remain several experiments which may yet yield insight into the coordination sphere surrounding the titanium sites. Regardless, this work represents a novel system which may hold promise for hydrogen storage.

Even if porous titanosilicates do not prove to be a viable hydrogen storage material, hydrogen remains one of the most important energy carrying molecules available today. Hydrogen fuel cell systems also remain the only potential energy plants capable of completing fuel cycle easily. By electrolyzing water to generate hydrogen gas and then regenerating that water using fuel cell catalysts it is possible to have a completely balanced rotation. Even if the hydrogen is simply combusted it would still be a much cleaner alternative to fossil fuels, assuming that is generated using solar electrolysis. On a gram to gram basis hydrogen contains many times the amount of accessible energy as hydrocarbons and should compose at least one part of the future energy market.

5. Acknowledgements:

I would like to thank all of those who have helped to make these last four wonderful years possible. Dr. Kovac, who not only helped to strengthen my fundamental knowledge of chemistry and served as my academic advisor throughout my entire college experience, but also guided me toward joining Dr. Barnes' research group at the end of my first year. Who knows where I would have been without his help. Dr. Barnes, who introduced me to the magic of silsesquioxanes (still the coolest chemistry word I know) and "the most expensive sand in the world". I'm glad that we both now share the experience of roofing a building, because there is no more important job. Michael Peretich, who took me under his wing when I joined the group and educated me in the ins and outs of air sensitive inorganic chemistry, thank you so much for putting up with all of my questions and forgetting all of the times I asked the same one about ten times. Also, for those times when you threw the question right back at me and made me think a little harder. Austin Albert, who joined me in this crazy quest for a world without oil and made life so much more "interesting" in lab, here's to you, boss! Finally Josh Abbott, my literary guide and infinite resource on all things chemistry, thank you for showing me the ropes and helping me stay sane. Also thanks to Dan, Matt, Lena, Desta, Rich, and Katherine for all of your help and advice along the way. Lastly, thank you Art, Beverly, Trey, Gary, Gene, and Tim for literally making the tools I needed to do chemistry. There would have been no cube, platform, or anything really without your help.

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