

Abstract

TRUITT, MATTHEW JARROD. Mechanistic Investigations of Alkane Activation and Reaction on Zeolitic Catalysts. (Under the direction of Jeffery L. White.)

Alkylates are branched hydrocarbons used in motor fuels to provide octane enhancements. Unfortunately current production methods require the use of environmentally dangerous materials and produce large quantities of hazardous wastes. Zeolites could provide a safer process for alkylate synthesis, but mechanistic complications lead to a loss of selectivity, and eventually catalyst deactivation making their use impractical. Using a combination of variable-temperature solid-state NMR experiments which provide in-situ mechanistic information, and gas-phase pulsed microreactor experiments which provide information about the reaction selectivity and activity, alkane activation and reaction on zeolites has been investigated. Experiments from this work have shown: (1) H/D exchange can occur between perdeuterated isobutane and zeolites in the absence of olefins in adsorbed gas; (2) isobutane forms an adsorption complex with the catalyst selectively at the active Bronsted acid site; (3) there is insufficient residual carbon in the catalyst to initiate/mediate H/D exchange and it is unlikely such a species' presence would initiate/mediate exchange; (4) reactor data indicates structural isomerizations, cracking, alkylation, etc. do not occur for isobutane in H-ZSM-5 for the temperatures H/D exchange was monitored by the NMR work; (5) both the acid site and methyl peaks' kinetic data are in agreement; all of which give evidence of a direct protonation step for H/D exchange. The activation energy and mechanism of this direct H/D exchange were verified computationally. The mechanism was shown to involve a non-classical hydrogen bond between a methyl C-H of the adsorbed isobutane and an adjacent oxygen at the Bronsted acidic site.

Mechanistic Investigations of Alkane Activation and Reaction on Zeolitic Catalysts

by
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Dedication

I dedicate this work to my parents who have always encouraged me to strive for the best in all that I have done; and to my wife, who has given me all of her love and support.

Biography

Matthew Jarrod Truitt was born Thursday, July 1st, 1982 to Doug and Wanda Truitt in Burlington, North Carolina. In 4th grade while learning about different professions, Matthew, who had an interest in chemistry, asked his teacher if chemists were rich. His teacher answered “yes” and from that moment on, he aspired to be a chemist with the ultimate goal of obtaining his Ph.D. in the field. Fortunately, it was his love of science that would drive his aspirations, as some 10 years later he would discover he had been slightly misinformed. As a reward for obtaining high marks on his report card at the end of his 4th grade year, his parents purchased him a chemistry set, which further fueled his interest in science. It was also during his 4th grade year that Matthew became a brother. Kyle was born on April 10, 1992.

While attending Western Alamance High School, Matthew took all available chemistry and science classes, each of which further fueled his passion of chemistry and science. Matthew graduated in the spring of 2000, and began his undergraduate career that fall at North Carolina State University. In summer of 2002, Matthew began working for Dr. Jeffery L. White funded by the Dreyfus Undergraduate Research Fellowship which supported him for two summers of research; he also worked with Dr. White during the fall and spring semesters of the adjoining year. Matthew graduated summa cum laude in the spring of 2003. After the last summer of research, Matthew made the decision to return to NCSU and work for Dr. White for his Ph.D. While pursuing his doctorate degree, Matthew met his wife Rosimar Rovira Hernandez from Caguas, Puerto Rico, who was a fellow graduate student in Dr. White’s lab. In 2005, Dr. White moved his group to Oklahoma State University, speeding up the wedding ceremonies. Halfway to obtaining his degree, Matthew remained a student at NCSU, and completed the remainder of his graduate research at OSU.

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Chapter 1: Introduction

1.1 Alkylates:

Despite intensive research efforts to replace them, hydrocarbon fuels remain the bloodline of the energy supply for civilization. The 2008 Department of Energy's (D.O.E.'s) *Annual Energy Outlook* projects that these fuel types will be the primary source of energy well into the 21st century reporting that demand for these materials will increase.¹ The Federal Trade Commission has reported that demand for hydrocarbon fuels has remained virtually unchanged with current high market prices and crude oil market fluctuations and spikes, and would likely change little with further price increases illustrating society's current dependence on such fuels.² These predicted as well as current demands for hydrocarbon fuels have resulted in many improvements over the years in order to limit their environmental impact. These improvements include the elimination of various additives such as carcinogenic aromatic and olefinic additives; the additive tetraethyl lead which is toxic; and the suspected carcinogenic oxygenate additive methyl-tertbutyl ether, which may no longer be used as of 2004. The replacement for these additives are branched alkanes, typically 6-10 carbons in length, known as alkylates. These alkylates can be used to provide environmentally benign octane enhancements to motor fuels.

Gasoline is a mixture of aliphatic hydrocarbons obtained through the fractional distillation of crude oil. Gasoline is composed mostly of heptanes, octanes, nonanes, decanes, and undecanes. Depending on the contents of the gasoline, the gasoline/air mixture filled into the cylinder of a typical combustion engine can be compressed differing amounts prior to ignition. This difference in gasoline "grades" requires a rating for comparing its compressibility prior to spontaneously igniting. This rating is known as the fuel's octane

rating. This name arises from the fact that isooctane does not spontaneously ignite in very high compression ratios, whereas its seven carbon linear analog, heptane ignites at low ratios. A given aliquot of fuel is rated and compared to a mixture of only isooctane and heptane. Gasoline withstanding compression ratios comparable to that of a 93% isooctane, 7% heptane mixture is given an octane rating of 93, regardless of if the gasoline is actually only isooctane and heptane. The octane rating is independent of composition and functionalization. For saturated hydrocarbons, the octane rating's trend usually follows the surface area of the molecule. As the surface area of the molecule decreases, there is less space for oxygen to react with the molecule and combust. For this reason, as the surface area decreases, typically the octane rating of the pure substance increases. For example, linear hydrocarbons typically have a lower octane rating than a mono-branched isomer (n-hexane would most likely possess a lower octane rating than 2-methylpentane or 3-methylpentane. Similarly, 2,3-dimethylbutane would be expected to possess a higher octane rating than the mono-branched hexane isomers.) The higher the amount of branching, the higher the octane rating would be suspected to be.

Increasing the compression ratio of a combustion engine typically results in greater power output from the engine, but forces the engine to use gasoline with a higher octane rating. For this reason, additives that can be placed in gasoline to enhance its octane rating are desired. In the early 1900's, it was found that by adding a Pb derivative called tetraethyl lead to gasoline, the octane rating could be enhanced. Unfortunately, Pb is toxic, and its use was later banned. Aromatic and olefinic additives as well as methyl-tertbutyl ether have also been used, but due to their carcinogenic properties, they have each been banned. Fully saturated alkylates, which are known to be environmentally benign, have also been found to

give octane enhancements, and they are the additives which are being used presently. **Figure 1** illustrates several different alkylates. Note that the alkylate 2,2,4-trimethylpentane (isooctane) is the basis for the octane ratings of gasoline.

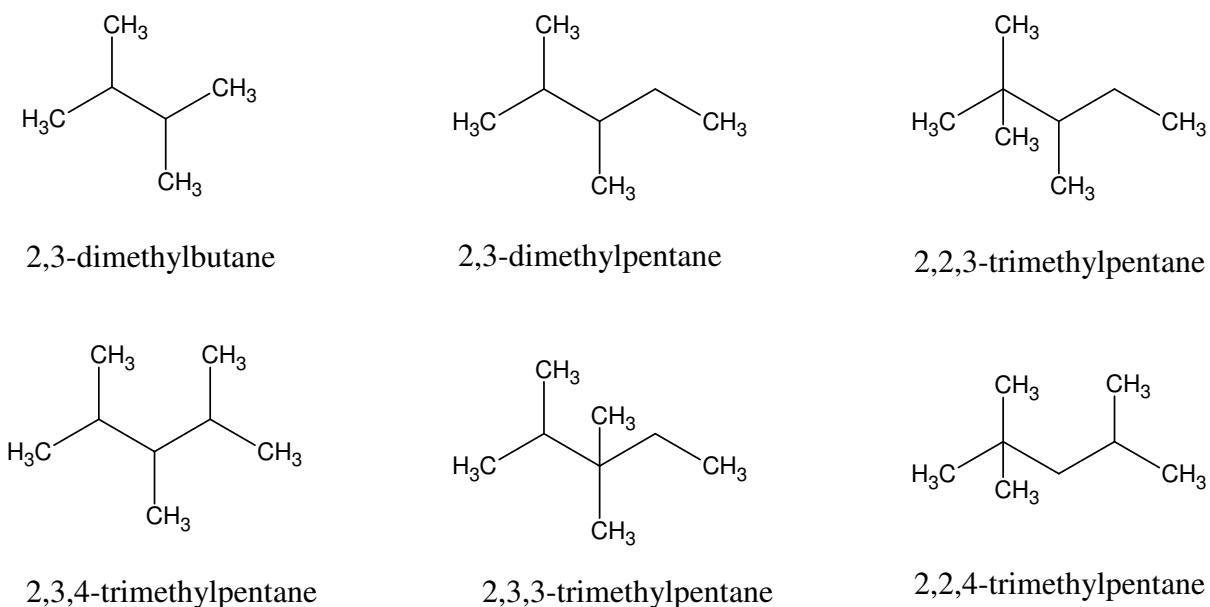


Figure 1. Some common alkylates

Unfortunately, while the alkylates themselves are environmentally safe, the current production methods for these additives (see **Figure 2**) involve the use of the environmentally hazardous materials sulfuric acid (H_2SO_4) and hydrofluoric acid (HF) as catalysts, and once spent, produce large quantities of potentially damaging waste. The basic steps of the alkylation process are: 1. Initiation of the reaction through protonation of an olefin by the acid to form a carbenium ion; 2. Attack of an olefin on the carbenium ion to form an oligomer; 3. C-H bond activation of isobutane and hydride transfer yielding the desired product and generating a smaller carbenium ion, thus continuing the catalytic cycle at step 2. The waste generated is the contaminated acid. As was already stated, the acid acts as a

catalyst; therefore, it is not consumed during the course of the reaction. The acid is unusable for further reactions as it contains large organics formed from secondary and side reactions such as oligomerization and cyclization. Not only is this waste dangerous, but refineries also must dispose of it, which further adds to the price of alkylates and hence gasoline. Hydrofluoric acid poses such high risks (corrosive, toxic, and relatively volatile) that many countries have stopped approving new alkylation processes involving its use.³ The consumption of these hydrocarbon based fuels continues to increase,¹ and so too does the amount of alkylates required. This causes an ever-increasing amount of this waste that sits in disposal facilities. Potentially, an environmental disaster could arise if their containment is ever compromised.

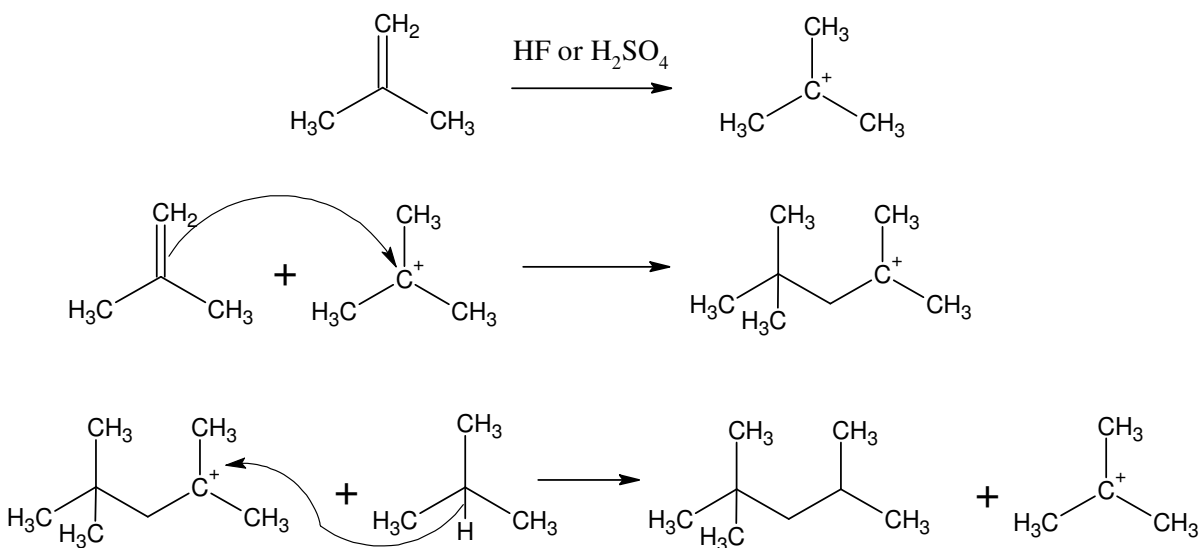


Figure 2. Mechanism of the current liquid acid catalyzed alkylation process. Though it is not readily apparent from the mechanism, the liquid acid also plays an important role in the activation of the saturated isobutane for the hydride transfer step.

Zeolites, a family of aluminosilicate materials possessing well defined microscopic channels, present a much more attractive route to alkylate synthesis. Zeolites are environmentally benign and can be reused, resulting in a safer process in addition to less waste generation. Zeolites possess a relatively high Bronsted acidity which is important for the alkylation process. As a result of their microporous structure, zeolites have a high surface area where chemistry can occur between themselves and adsorbed gases. The channels of zeolites are also known to sterically hinder the formation of some bulky products and are often used to selectively generate certain products from reactions whereas the same reaction performed without the zeolite's use could produce a mixture of products or a different product entirely.^{4,5} Zeolitic-based alkylate production is not commercial because the catalyst's alkylation activity is rapidly lost on-stream. While the exact reason for this loss of conversion is unknown, the unknown mechanistic factors lead to: 1) undesirable side-reactions, 2) loss of selectivity for the desired alkylates, and 3) "coke" formation in the catalyst that deactivates the catalyst via steric exclusion. Unfortunately, the small channels which enhance the zeolite's selectivity ultimately result in the catalyst deactivation by the blockage of the channels by this "coke". Weitkamp and others have pointed out that it is no longer appropriate to simply perform trial-and-error black-box reactions and that for this area to progress, mechanistic information must be obtained.³ With such mechanistic information, improvements in the catalysts could be made, allowing for better control of the reaction, and the commercialization of this process could proceed.

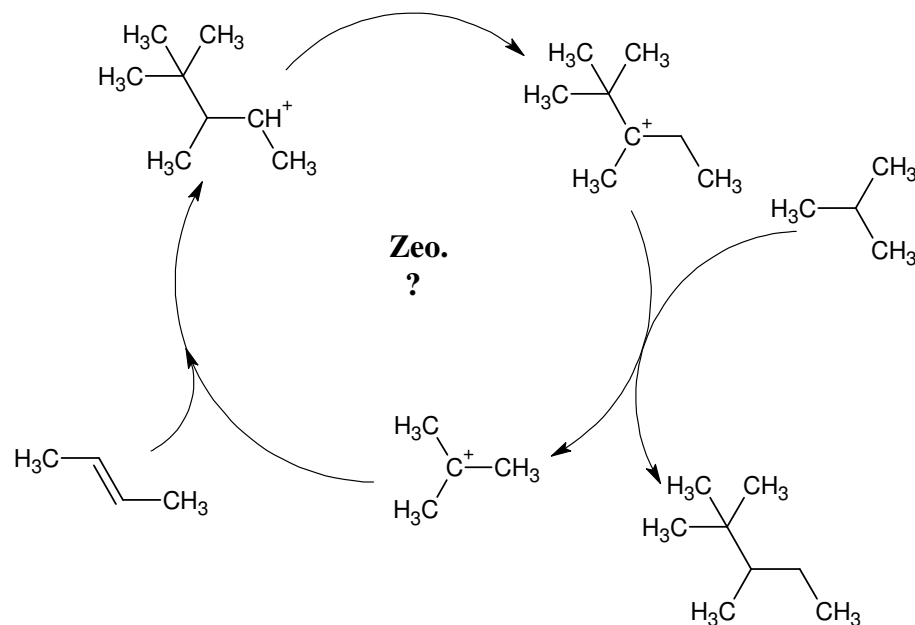


Figure 3. Proposed catalytic cycle for the isobutane/butene alkylation reaction in zeolites³

As previously stated, the simplest route to alkylate synthesis is the reaction of isobutane with an olefin in acidic media. Experiments have indicated that this reaction involves isobutane C-H bond activation through a pentavalent carbonium ion in highly acidic liquid solution,⁶ but as for how the reaction proceeds in zeolites, which are less acidic, the pathways are unknown.^{3,7} Sommer et. al. have investigated general mechanisms for the activation of small alkanes in solid acids,⁸⁻¹¹ while Corma et. al. have studied alkylate formation in many different zeolites such as Beta and USY.^{12,13} A proposed catalytic cycle (**Figure 3**) has resulted from these combined works, but it still lacks information concerning isobutane C-H bond activation, the cycle's hydride transfer, and in general what role the zeolite plays in the cycle. The role of the zeolite seems more than trivial as the actual process produces a variety of isoctanes rather than only the 2,2,3-trimethylpentane the cycle suggests, alluding again to the need for mechanistic information to advance the field.³ (While

the formation of many different isooctanes is not detrimental to the ultimate goal of the formation of alkylates as multiple structures can provide the desired octane enhancements, it is the absence of mechanistic reasoning which is the ultimate concern.)

This lack of an activation step has led to controversy with differing opinions of how small, saturated alkanes become activated on zeolitic catalysts. The first proposed initiation step involves activation of the isobutane through trace olefinic impurities in the feed. Such olefinic species are then believed to protonate to a carbocation at a Brønsted acid site, and then activate an alkane through hydride abstraction. This mechanism differs from others as the zeolite does not play a large role in the activation, but rather, the process is just the chemistry of impurities. This pathway has gained much favor since it is believed that zeolites do not possess enough acidic strength to directly protonate an alkane via traditional Olah superacid chemistry.⁶ Many researchers, however, still believe that the experimental evidence suggests a direct protonation step.^{14,15} Another possible mechanism involves hydride abstraction by the zeolite. An abstraction is believed to be performed by Lewis acid sites in the catalyst. These sites are more than likely extra-framework or terminating aluminum groups that could be generated during catalyst preparation. The resulting tert-butyl carbenium ion is an intermediate step in the catalytic cycle shown in **Figure 3** and hence, this proposed step as well as the olefinic impurity initiated step are seen as direct pathways to the catalytic process.

1.2 Zeolites:

Zeolites are a family of highly crystalline, aluminosilicate materials possessing a microporous structure. Several zeolites can be found in nature, however, many are synthetic.

While zeolites generally have the same elemental composition, being mostly silica tetrahedra connected to form the lattice with a small amount of alumina tetrahedra substituted in for the generation of acidity, the structure can differ greatly for two different catalysts. This is typically due to the templating agent used during the synthesis procedure. A zeolite's porosity can be in the form of channels, cages, or cages linked by a channel system. Channel systems are classified by the ability to move from one point in the system to another as 0, 1, 2, or 3 dimensional. **Figure 4** illustrates several different zeolitic framework types.

The pore size of a zeolite is important for selecting a catalyst to use for a specific reaction. Zeolitic pores are of the same order of size as molecules, zeolites can facilitate many interesting reactions. The physical steric constraints of a zeolite's walls can produce selectivities not observed in liquid phase catalysis. For example, the channels of the zeolite ZSM-5 fit the benzene molecule and mono-substituted benzenes. Di-substituted benzenes, however, become problematic. Para-substituted molecules typically can travel through the channels, while meta- and ortho-substituted benzenes cannot. If a reaction is performed inside the channels of the zeolite where one forms a di-substituted benzene, the selectivity is generally for the para- species, irrespective of if the reaction typically produces meta- or ortho- products in the homogeneously catalyzed case.

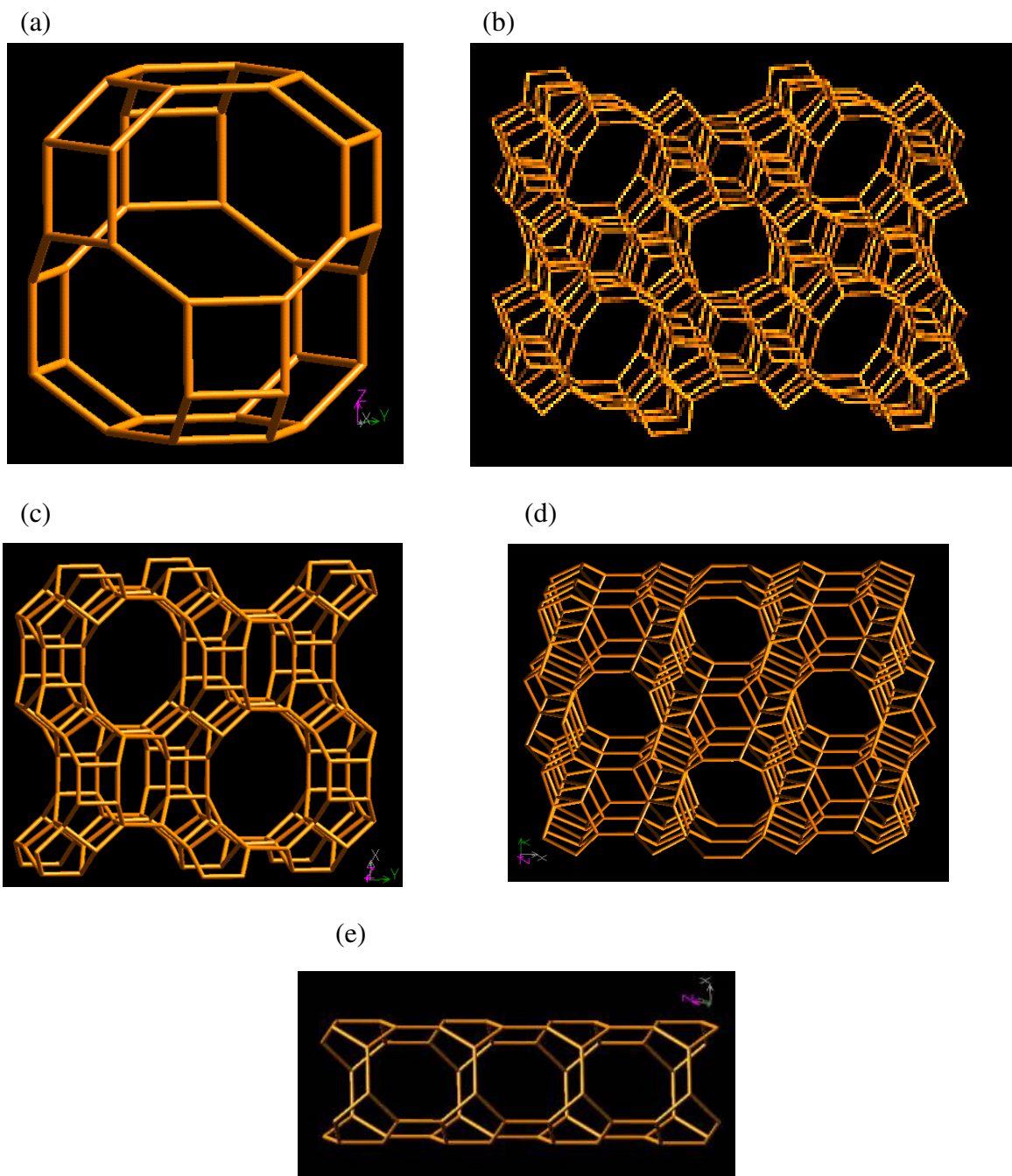


Figure 4. (a) Structure of SAPO-34 illustrating a cage in a zeolite; a 3-D framework (b) Structure of ZSM-5 showing a channel system in a zeolite, (c) MOR framework type; there are only 1 set of channels, which do not interconnect making MOR a 1-D framework, (d) FER framework type with two sets of channels interconnecting to form a 2-D framework, (e) FER interconnecting channel illustrating the 2-D framework. (Reproduced from the IZA structure database web site at <http://www.iza-structure.org>)¹⁶.

ZSM-5 is a well known synthetic zeolitic catalyst. It was discovered in the late 1960's by Mobil researchers, and was patented in 1972.¹⁷ ZSM-5 is of the MFI morphology, and its synthesis uses the tetrapropylammonium ion as a template (when synthesizing without the use of seed crystals.)¹⁸⁻²⁰ The template form is often a halide salt or hydroxide. ZSM-5 possesses 10-membered ring channels, with one set of straight channels, and one set of sigmoidal channels connecting the straight channel system. For this reason, ZSM-5 is sometimes classified as a 2 dimensional zeolite and other times as a 3 dimensional. The channels being referred to as 10-membered rings indicates the number of T-atoms in the cross sectional view of the channel (T-atoms are Si or Al in the lattice. There can be many crystallographically distinct T-atom sites in the same zeolite.) The channels of ZSM-5 are slightly oval, the measurements are 5.1Å x 5.5Å for the sigmoidal channels and 5.3Å x 5.6Å for the straight channels. **Figure 4b** depicts the structure of ZSM-5, and **Figure 5** illustrates the shapes of the channel systems. In **Figure 4b**, the straight channels are observed, with the sigmoidal channels lying in planes parallel to the page. **Figure 6** illustrates the interconnectivity of the channels.

The zeolite Beta was first synthesized by the Mobil Research and Development Laboratories in 1967. Beta is of the *BEA morphology (see **Figure 7.**)^{21,22} Beta synthesis uses tetraethyl ammonium ion as the structure directing agent. Beta possesses two interconnected straight channel systems, both consisting of 12 membered rings. There are two sets of channels that run perpendicular through the structure. The different sets of channels interconnect, making the structure 3-dimensional (see **Figure 7.**) Though both channels are made of 12-membered rings, their sizes are quite different (see **Figure 8.**) One of the channel systems have an oval shape with the diameter ranging from 7.7Å at its widest

to 6.6Å at its narrowest, while the other channels appear like squares with rounded corners, having a diameter at the smallest points of 5.6Å.

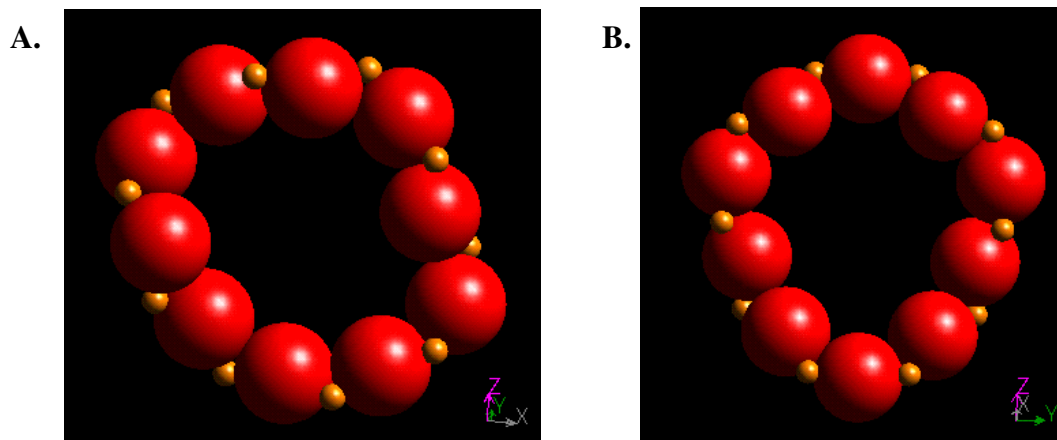


Figure 5. A. Straight channels, and B. Sigmoidal channels of the MFI morphology. Both rings contain the same number of T-atoms (Reproduced from the IZA structure database web site at <http://www.iza-structure.org>)¹⁶.

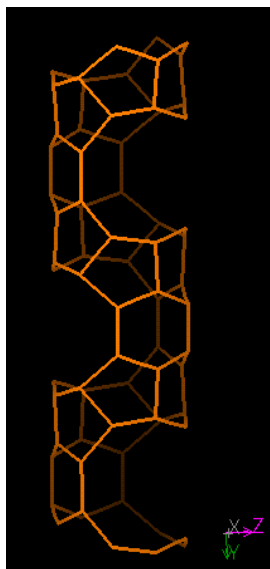


Figure 6. Illustration of the interconnectivity of the straight and sigmoidal channels of ZSM-5 (Reproduced from the IZA structure database web site at <http://www.iza-structure.org>)¹⁶.

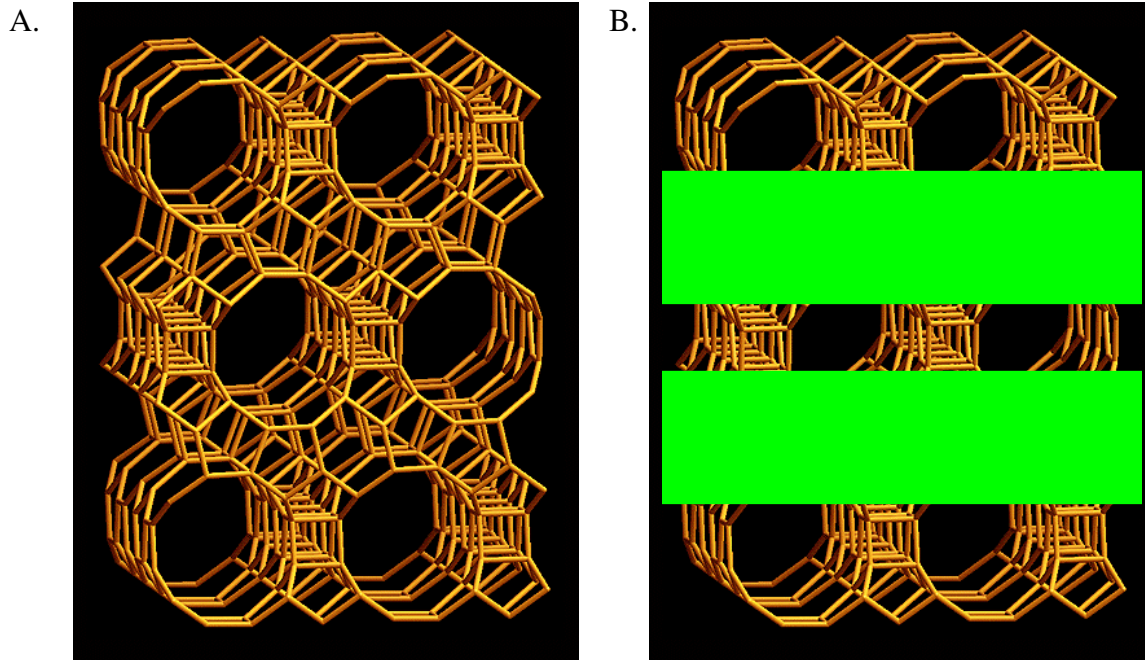


Figure 7. A. The *BEA framework morphology as viewed along the $\langle 100 \rangle$ plane. B. The same figure as A., but the green blocks indicate channels in the unseen set of channels. These channels connect separate rows in the first set, making the zeolite 3-dimensional. (Reproduced from the IZA structure database web site at <http://www.iza-structure.org>)¹⁶.

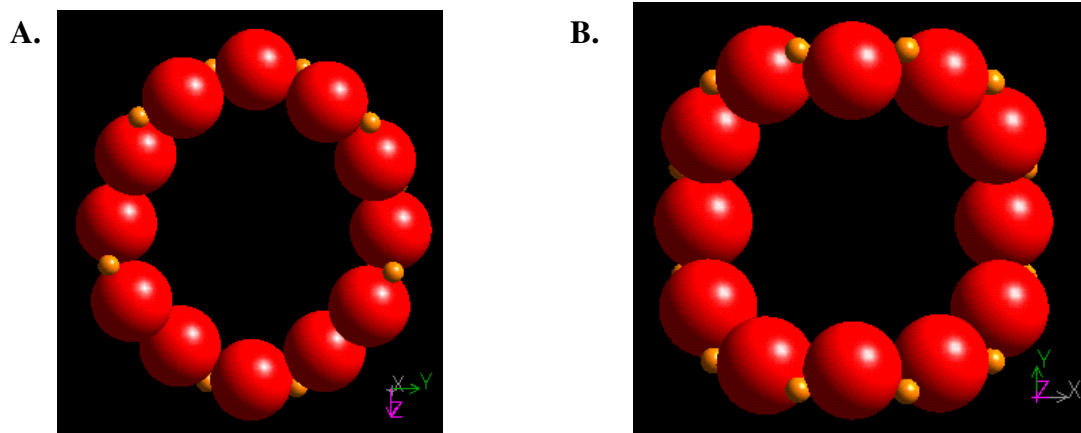


Figure 8. A. and B. illustrate the differing structures of the channel systems of the *BEA morphology. Both systems contain the same number of T-atoms (Reproduced from the IZA structure database web site at <http://www.iza-structure.org>)¹⁶.

Acidic Sites:

Acid site characterization is critical to understanding how all solid acids react. Multiple issues must be considered when trying to understand solid acids in the context of more established liquid acid reactions. One property of solid acids is the intrinsic strength of each of the individual acidic sites. This property is comparable to the pK_a of a liquid acid. This property differs from liquid acids as the same solid acid may possess several sites with varying intrinsic strength, whereas pK_a values are fixed for a liquid acid. Solids also possess a density of acid sites (quantity of sites per weight.) This is related to concentration and pH in liquid acids. In addition, not all catalysts possess a traditional Bronsted acidic proton (H⁺), but can have Lewis acidic sites (for example trivalent aluminum or gallium.) Solid acid catalysis also differs from liquid acid because of limited mobility of the activated reactant. In homogeneous liquid acid chemistry, reactants and catalysts are all in the same phase, and capable of moving over the course of reaction. In the heterogeneous solid acid case, the acid site is “tethered” to the catalyst, whether it is a Lewis acid or a Bronsted acid capable of protonating a reacting base. In the latter case, after protonation, the new species cannot travel far from the initial active site and relies on bimolecular collisions between other reagents for reaction propagation. Consequently, initiation and any subsequent reactions must occur in the general area of the acid site, and until the site is regenerated, the products cannot leave (products can leave if another balancing charge is available for the site). This alludes to the shape selectivity of zeolites.

Bronsted acidity in zeolites arises from the substitution of tetrahedrally coordinated aluminum in a SiO₂ lattice. Silicon in a tetrahedral environment possesses a formal charge of zero (arising from its 4 valence electrons for the parent element and 8 electrons shared in 4

bonds to give 4 electrons net in the tetrahedral environment.) Tetrahedrally-coordinated aluminum possesses one additional electron than the parent element. This leads to a formal charge of -1. In order to balance this charge, each framework aluminum must possess a proximate counter ion. This counter ion can be a variety of different cations, with the biggest constraint being the size restrictions of zeolite's structure. Common cations found in zeolites include Na^+ , K^+ , NH_4^+ , H^+ , etc., with the H^+ form being labeled the “acidic form” (see **Figure 9**). Multivalent cations may also be used. In this case, the cation may have additional anions to balance its charge (CaCl^+ , MgBr^+ , etc), or may satisfy more than one of the framework charges (this would require fairly low Si/Al ratios to ensure there are framework charges in close enough proximity.) As stated earlier, all of the zeolites used in this research are in their acidic form. Complex zeolites with many different T-atom sites can possess acidic sites which would appear to be of the same general structure as **Figure 9**; however, due to the constraints of the location, the sites could have different acidic strengths.

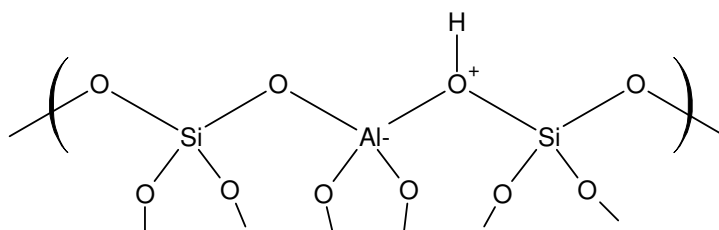


Figure 9. Scheme depicting a generic aluminosilicate material Bronsted acidic site

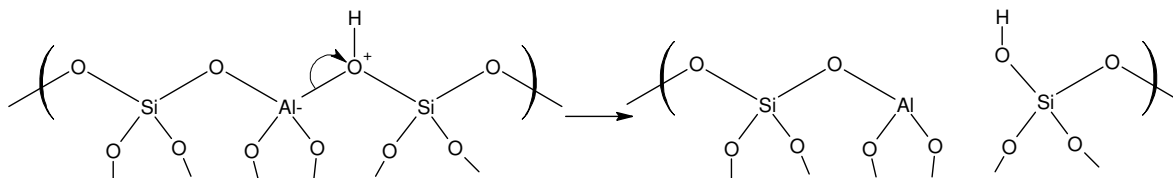


Figure 10. Scheme depicting a possible Lewis acidic site for an aluminosilicate material

In addition, zeolites can also possess Lewis acidity. In traditional aluminosilicate zeolites, this is trivalent aluminum which can be removed from the lattice by heating the catalyst in the presence of water. **Figure 10** illustrates one possible route to a framework Lewis acidic site from a Bronsted acid site, though most trivalent aluminum in zeolites is presumed to be extraframework. The exact structure of these extraframework species is still a matter of some debate. In some cases, as in “Ultra Stable Y” (USY), the Lewis acidic sites are created intentionally to increase both the stability of the catalyst and the intrinsic strength of the Bronsted sites remaining. While these Lewis acidic sites are interesting and can be quite useful, the present research to be discussed is interested specifically in the behavior of saturated alkanes in the presence of solid acid Bronsted sites. Lewis acidic site formation through the removal of framework aluminum can be avoided through calcination and dehydration via a gradual ramp soak procedure. This allows for the removal of water from the catalyst slowly and prior to the high temperatures required for template removal, and thereby prevents the generation of these sites.

In most cases, a zeolite’s Bronsted acidic site density is characterized by its silicon (Si) content divided by its aluminum (Al) content or its silica (SiO_2) content divided by its alumina (Al_2O_3) content. Since these two values differ by a factor of 2, it is important to specify which is being used in a reported value. While this practice is quite commonplace, it is obvious that it is not a perfect measure of the acid site density. The incomplete incorporation of aluminum into the lattice during crystallization, as well as the removal of framework aluminum during calcination/dehydration procedures can both lead to Bronsted acid site densities less than expected. For this reason, many methods for quantifying these densities have been developed. One of the most direct methods for this quantification is the

direct observation of the acidic protons using Magic Angle Spinning Nuclear Magnetic Resonance (MAS NMR) as well as an internal standard of known weight and composition for comparison. Using the integrated areas of internal standards such as polydimethylsiloxane which were ran with the zeolitic samples, and the area(s) of the Bronsted acid signal(s), White, et. al have calculated exact numbers for acidic site densities for various zeolitic catalysts.²³ Using IRMS-TPD and simulations, Niwa and coworkers have determined the quantity and strength of “strong acid sites” in the zeolite USY.²⁴ This phenomenon has been previously only studied qualitatively. USY is known to contain extraframework aluminum resulting from dealumination by steaming the catalyst. These sites are Lewis acidic, and can engender separate acid function for the catalyst as was previously discussed. In this case, it is the generation of this extraframework aluminum which makes the catalyst more active.

¹H MAS NMR should presumably be able to directly determine the intrinsic strength of differing catalysts. This, however, is often not the case. Zeolites containing Bronsted acidic protons more downfield than another zeolite’s might not actually possess more “acid strength”. Hence, indirect methods are often used in conjunction with MAS NMR or other types of spectroscopy for this purpose. Typically, a probe molecule is adsorbed on the zeolite and the molecule’s spectroscopic response is compared and referenced to its unabsorbed spectrum. In this manner, different zeolites can be compared based on their effects on the probe molecule. Trimethylamine has been used as a probe of acidity by using IR methods to monitor its interactions with various acidic sites in the zeolite HY.²⁵ Using this method, the authors found that the wavenumbers of some specific IR bands from the adsorbed TMA-protonated species depend on the acidic strength of the adsorption site. Test

reactions are also often performed using a reactant of choice and characterizing each sample by conversion rates or total conversion. Bokhoven, et al, have studied the catalytic activity of the acidic sites in various zeolites using the conversion of propane.²⁶ By using this choice of reactant, the authors were able to probe both the acidic strength and the local structure around the site as there are two independent reactions which propane undergoes, cracking and dehydrogenation. These different reactions have separate rate limiting steps that depend on these two characteristics respectively. Computational methods may also be used to estimate the strength of acid sites. Fujita, et al, have performed DFT calculations on the zeolite beta using one unit cell and periodic boundary conditions.²⁷ Using these methods, the authors have found that aluminum atoms in beta are in close proximity to allow for hydrogen bonding between the acid sites.

Until this point the two acid site classifications have been treated as independent. Typically, as the Si/Al ratio decreases (as the acidic site density increases), the intrinsic acidic strength of each individual site decreases. Lowenstein's Avoidance Rule states that in aluminosilicate materials, aluminum atoms cannot occupy adjacent T-atom positions. Although Lowenstein's rule prohibits so called "next-nearest neighbor" aluminum incorporation, there is some effect on each site when the neighboring sites are proximate. Drastic changes in the intrinsic strength are not common, however, and even for moderate Si/Al ratios, the effect on sites is minimal.

Zeolites are presently used in a variety of different applications. One of the largest uses of zeolites is in the detergent industry. Zeolites are added to various detergents as water softening agents. The cations in "hard" water (such as Ca^{+2}) can diffuse into the zeolitic channels where they exchange with the cation at the acidic site, thus "softening" the water.

Zeolites are widely used by the petroleum industry. The process of fluid catalytic cracking (FCC) employs zeolitic catalysts. In the FCC process, higher molecular weight oil is introduced into zeolitic catalysts at elevated temperature. The catalyst breaks the large hydrocarbon molecules down into smaller components such as gasoline and diesel fuels. The petroleum industry uses zeolites for a variety of other processes such as hydrocracking. Zeolites are used as molecular sieves for purifying gas streams.

1.3 NMR:

The birth of modern Nuclear Magnetic Resonance (NMR) was in 1945. Concurrently and independently, Edward Purcell and Felix Bloch monitored radiofrequency signals from atomic nuclei; the first observation of a nuclear property for matter in its ground state.^{28,29} Since its discovery, the field of NMR has grown tremendously. NMR is non-invasive and non-destructive, both of which have been important to its success. The main driving force behind NMR, however, is simply the vast quantity of information one can obtain by determining the precession frequencies of nuclei. Many know someone who has used a form of NMR data in medical treatment known as Magnetic Resonance Imaging (MRI). MRI is an extremely powerful tool for studying macroscopic, three-dimensional objects. In non-medicinal uses, this technique is commonly referred to as Nuclear Magnetic Resonance Imaging; but because of society's negative and fearful connotations with the term "nuclear", for medical purposes simply MRI is used. In MRI, gradient magnetic fields are used to monitor the precession frequencies of nuclei in selected regions of the sample. The precession frequencies are used to produce a cross-sectional image of the sample. This

allows for the study of the sample without destroying or opening it. In the case of MRI for medical use, doctors can use this information to detect and monitor tumors in a patient.

From a chemist's perspective, NMR's structural elucidation capacity at the molecular level is unparalleled. The ability to identify products synthesized in a reaction is of the utmost importance to organic chemists whether by simple proton or carbon experiments, or advanced techniques such as two-dimensional HETCOR or COSY experiments. In these experiments, detailed information is acquired. For example, nuclei of the same type in different electronic environments produce slightly differing precession frequencies in a magnetic field, B_0 (this interaction is called the chemical shift and will be discussed in detail later.) These subtle differences can be used to identify each nucleus' location and the structure of the molecule to which it belongs. In MRI, these differences are not resolved; only the main precession frequency from the Zeeman interaction is detected. In addition, NMR can be used to monitor the other interactions such as dipole-dipole coupling, J-coupling, and quadrupole coupling, all of which are ignored in the case of MRI.

Spin angular momentum, or simply "spin", is unique among the various types of angular momentum in that it is an intrinsic property of a particle, rather than the result of motion by the particle. For example, an orbiting electron in a nucleus possesses angular momentum due to its mass and motion around the nucleus (this is known as orbital angular momentum.) An electron also possesses a spin angular momentum. An electron at rest would have no orbital angular momentum. It would, however, still possess spin angular momentum and would behave according to the quantum angular momentum rules as if the particle were spinning rapidly. Many other particles also have spins including protons and neutrons. In atoms, these spins can combine to give the overall nucleus a net spin, or they

can cancel one another to cause no net spin. Spin (I) relates to the magnetic moment (μ) of a species by the formula:

$$\hat{\mu} = \gamma^* \hat{I} \quad (1)$$

where γ is the magnetogyric ratio. It is apparent from the formula that γ is simply a proportionality constant between the magnetic moment and spin. γ is specific to each nucleus (ie. hydrogens all have the same value, all carbons have the same value, etc.) Both positive and negative values of γ exist, with the difference being that positive values result in spins that are parallel to the magnetic moment of the nucleus, while negative values result in antiparallel spins and magnetic moments. In a magnetic field, the spins begin to precess about the field (see **Figure 11**). The frequency of precession (ω) in radians per second is given by:

$$\omega = -\gamma B_0 \quad (2)$$

where B_0 is the magnetic field (we will assume that the magnetic field is oriented along the positive z-axis.) The reason for this precession as opposed to simple reorientation along the field is due to the angular momentum the particle possesses. This can be thought about macroscopically as a top spinning with its angular momentum axis tilted. Rather than spinning stationary, the top wobbles around a precession cone. The spins maintain this angle with respect to the field, and would not change if it were not for the subtle fluctuations in the effective B_0 at each individual spin's location.

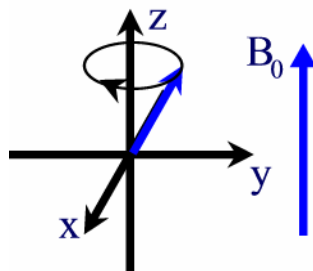


Figure 11. A precessing spin

Changes in the angle of the precession cone are brought about by the magnetic fields of other nuclei and electrons and the rapid movement of molecules. These microscopic fields interact with the spin, and change the angle gradually over time. Eventually, this allows for spins to find an energy minimum and develop an equilibrium spin polarization. The energy of a spin in a magnetic field is given by:

$$E = -\hat{\mu} \cdot B_0 = -\gamma \cdot \hat{I}_z \cdot B_0; \quad \hat{I}_z = \hbar \cdot m_I \quad (3)$$

$\hbar$ is Planck's constant divided by 2π , and m_I is the quantum number corresponding to state of the spin. The z subscript of I_z indicates that this term corresponds to the z -axis component of this operator. In the case of a proton, $I_z = \hbar/2$, leading to $m_I = +1/2$ or $-1/2$. The $m_I = +1/2$ is commonly referred to as the α state and the $m_I = -1/2$ is known as the β state. By plugging in m_I values for the proton, it is clear that the $+1/2$ state is lower in energy than the $-1/2$. It is possible to calculate the energy of transition between these two quantum states by subtracting their energies to obtain:

$$\Delta E = -\gamma \cdot \hbar \cdot B_0 \cdot \Delta m_I \quad (4)$$

Selection rules limit the value of Δm_I to $+1$ or -1 for I_z greater than $1/2$ leaving the equation as:

$$\Delta E = \gamma \cdot \hbar \cdot B_0 \quad (5)$$

for the absorption of energy between states, and:

$$\Delta E = -\gamma^* \hbar^* B_0 \quad (6)$$

for the emission of energy for positive values of γ . Negative γ nuclei result in (5) being for emission and (6) being for adsorption. Notice that according to these formulas, the energy of transition scales directly with the strength of the magnetic field.

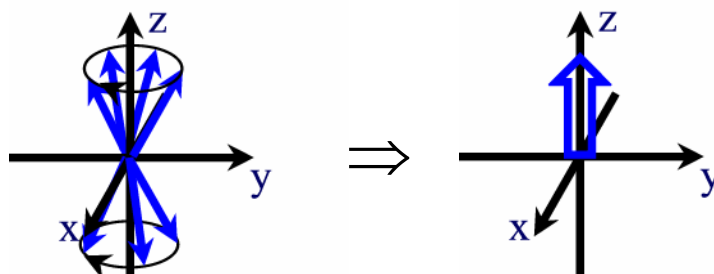


Figure 12. Equilibrium spin distribution leading to bulk magnetization (N_α/N_β greatly exaggerated)

Values of ΔE for transitions between spin states are quite low for nuclei. The proton, which possesses one of the highest magnetogyric ratios of all nuclei, has $\omega = (-9.00 \times 10^8 * 2\pi)$ rads/sec in some of the strongest magnetic fields presently used in NMR. This frequency gives an energy of transition of 5.96×10^{-25} J. When this is plugged into the Boltzmann equation:

$$\frac{N_\beta}{N_\alpha} = e^{\frac{-\Delta E}{k^*T}} = 0.999855 \quad (7)$$

where N_x represents the number of spins in the corresponding state, k is the Boltzmann constant, and T is the temperature (in this case we assumed 298K.) This number is much higher than in other types of spectroscopy where the ground state is more populated. Effectively, there is almost no population difference at equilibrium. Astonishingly, this small population difference is enough to create a detectible bulk magnetization, M_B , in a sample as is illustrated by **Figure 12**. For this reason, NMR is now performed by monitoring the

resonance properties of the bulk magnetization rather than direct absorption or emission studies as performed in infrared or UV-Vis spectroscopies. (For many years, direct observe continuous wave (CW) NMR was performed. This involved sweeping the field through the transition range and detecting the absorption of radiation. This method is slow and gives poor signal-to-noise ratios.) M_B is the overall sum of the individual spins. At equilibrium, M_B is oriented along the positive z-axis as can be determined by the calculated number (slightly more aligned parallel to the field rather than antiparallel.) There is transverse magnetization (magnetization in the XY plane) which is important for relaxation in NMR, however there is no net transverse magnetization. The net magnetization is manipulated and detected via a series of radio frequency pulses in the process of Fourier Transform NMR.

1.3.1 FT-NMR:

FT-NMR is a process by which all frequencies over a given range may be excited and detected at the same time. A short square pulse of a radiofrequency is sent through a coil in which the sample resides. When radiofrequencies are applied over short periods of times, the pulse actually contains components of all frequencies in close range to the main frequency. What this means is that a single frequency applied for a short period of time excites a range of frequencies. By performing a Fourier transform on the square wave pulse, one may obtain the range of frequencies which are excited. For short pulses, a broader range of frequencies are excited than with a longer pulse. This radiofrequency wave generates a magnetic field, B_1 , perpendicular to B_0 inside the coil. The phase of this wave can be altered to generate the B_1 in differing directions. The result of this field is to cause the M_B to rotate to a rough approximation as if in the absence of B_0 (the larger B_1 is with respect to B_0 , the better this

approximation is.) For example, if B_1 is applied along the x-axis, M_B will rotate in the y-z plane counter clockwise (see **Figure 13**). If the B_1 is applied for the appropriate length of time, the M_B can be rotated 90° into the x-y plane, oriented along the $-x$ -axis. This is commonly known as a 90° or $\pi/2$ pulse, because of the angle the bulk magnetization was rotated. M_B will now begin to precess about the B_0 field similar to the individual spins precession. The same coil which generated the magnetic field B_1 can now be used to detect this precessing field perpendicular to the static B_0 . This signal generated by the precessing spins of the sample in the transverse plane is known as free induction decay (FID). If the radiofrequency pulse had been applied for longer, the bulk magnetization would reach the $-z$ -axis. This is referred to as a 180° or π pulse. In this case, the bulk magnetization would have no net precessing transverse component as it is aligned antiparallel to the B_0 field, and the magnetization would not be detectable (there would be no FID.)

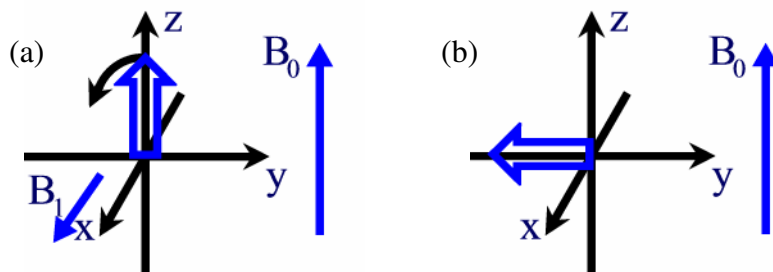


Figure 13. (a) Bulk magnetization rotating as a result of an applied B_1 field and (b) Bulk magnetization following a 90° pulse

Using this vector picture of FT-NMR, it is convenient now to switch from one frame of reference to another. Until now, we have been visualizing the system as if directly observing it. This is known as the laboratory frame of reference. When M_B tilts from its equilibrium position and has a transverse component, the magnetization begins to precess

around B_0 . While this is correct, it would be more convenient if we could monitor the precession from the central resonance's point of view. To do this, the x-y axis system must precess at the same frequency as the central frequency of the pulse, we will call this frequency ω_1 . If the bulk magnetization is on resonance, it will remain at its position in the x-y plane. This does not imply that M_B is not precessing, it is; this just indicates that it is precessing at the same frequency as the axes, ω_1 . If M_B is off-resonance, then it will precess at the frequency it differs from the central frequency ($\omega_{RF} = \omega_1 - \omega_M$, where ω_{RF} is the precession frequency of M_B in the rotating frame and ω_M is the precession frequency of M_B in the laboratory frame).

1.3.2 Internal Interactions:

Until now, the discussion has been about nuclear spins interacting with external magnetic fields. There are four fundamental internal interactions in NMR originating from the microscopic fields in the sample (neighboring spins, electrons, etc.) These interactions are quadrupole coupling, dipole-dipole coupling, scalar coupling, and chemical shielding. The quadrupolar interaction only exists in nuclei with spin greater than $\pm \frac{1}{2}$. It involves the interaction of the nuclear spin with the surrounding electronic field generated by the electron density. In highly spherical coordinations, the quadrupolar interaction magnitude averages to zero. However, in most environments, the quadrupolar interaction is second in magnitude only to the Zeeman interaction. Some of the most common nuclei monitored by NMR, ^1H , ^{13}C , and ^{19}F , are all spin $\frac{1}{2}$ nuclei, and thus do not exhibit this interaction.

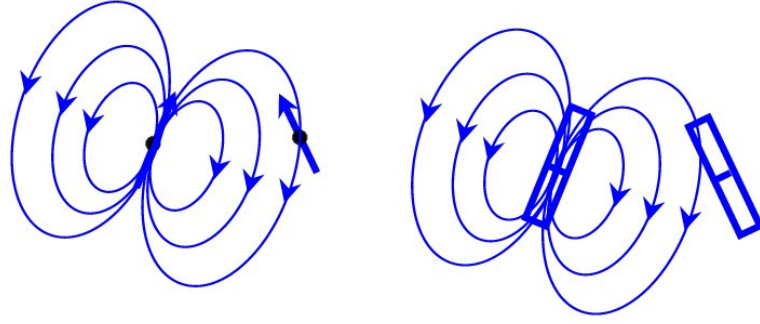


Figure 14. Dipolar coupling interaction illustrated as bar magnets

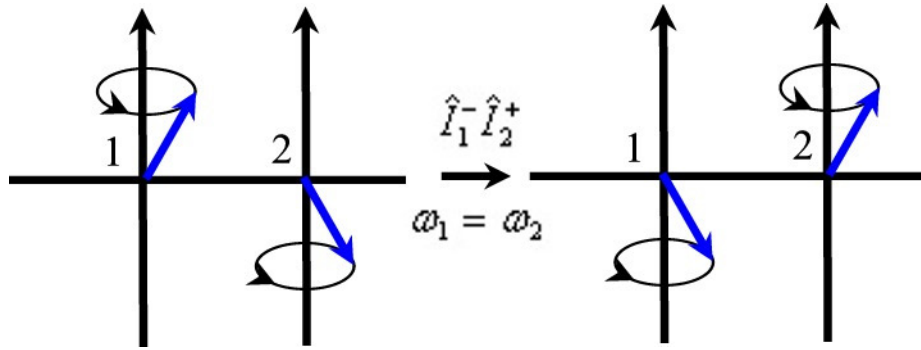


Figure 15. Energy conserving spin flips

Dipole coupling is the direct, through-space interaction of a magnetic moment with another. This interaction can be visualized macroscopically as two bar magnets interacting (See **Figure 14**). When the magnets are in close proximity, they interact with one another. If the magnets are aligned parallel, the magnets repel one another. If they are aligned antiparallel, they attract each other. While this analogy is not exactly the same as for nuclear spins, it illustrates the general idea of how this interaction occurs. The secular dipolar Hamiltonian, which is used to calculate the magnitude of this interaction, is as follows:

$$\hat{H}_{DD} = \left(\frac{-\gamma_1 \gamma_2 \hbar \mu_0}{4\pi r^3} \right) (3 \cos^2 \theta - 1) \left(\hat{I}_{1z} \hat{I}_{2z} - \frac{1}{4} (\hat{I}_1^+ \hat{I}_2^- + \hat{I}_1^- \hat{I}_2^+) \right) \quad (8)$$

where the subscripts 1 and 2 refer to two nuclei, μ_0 is the permeability of free space ($4\pi \times 10^{-7}$ H/m), r is the distance between the two spins, θ is the angle between the line connecting the

two spins and the magnetic field, I_z terms represent the z components of the respective spin, and I^+ and I^- represent step up and step down ladder operators from quantum mechanics. In the homonuclear case, the ladder operators give energy conserving spin flips also known as spin diffusion (see **Figure 15**). In the heteronuclear case, the equation reduces to:

$$\hat{H}_{DD} = \left(\frac{-\gamma_1 \gamma_2 \hbar \mu_0}{4\pi r^3} \right) (3 \cos^2 \theta - 1) (\hat{I}_{1z} \hat{I}_{2z}) \quad (9)$$

as the spin flips are not equal in energy for nuclei with differing magnetogyric ratios. The r term in both formulas illustrates that just as in the bar magnet example, the interaction scales inversely with the distance between the spins. Notice that the Hamiltonian for both cases possesses a space term of the form $(3 \cos^2 \theta - 1)$. This term goes to zero as θ approaches 54.74° . In the liquid state, rapid tumbling motion causes this term to average to 0, thus eliminating dipolar coupling. In the solid state, this term may be averaged by rapid rotation about 54.74° which causes the term to go to zero. The ability to average out this interaction by spinning (as well as the chemical shift anisotropy which will be discussed later) has led to the creation of Magic Angle Spinning NMR (MAS NMR). Unfortunately, not all dipolar interactions may be averaged in some solid state samples because of current limits in rotation speeds. The dipolar interaction leads to broadening of the NMR spectrum, giving, in general, much larger peak widths for MAS NMR as opposed to liquid state NMR. The dipolar interaction may also be averaged in spin space by rapid flipping of the coupled nuclei through radiofrequency irradiation. The observed nucleus “feels” all spin states of the coupled nucleus at the same instant, averaging the interaction to zero.

Scalar coupling is an indirect coupling of nuclear spins through the bonding electrons. This interaction is not through space like dipolar coupling, so coupling can only occur

between bonded nuclei. Scalar couplings can occur between nuclei which are not directly bonded, but are connected through multiple bonds. Though their overall magnitude is relatively small, scalar couplings can propagate through 3 or more bonds. Scalar couplings produce fine structure (splitting) in the NMR spectrum. They are not usually observed in MAS NMR spectra unless the magnitude is large (such as for directly bonded nuclei,) compared to the line widths associated with solids.

Chemical shielding, while not the largest interaction is one the most useful for the molecular applications of NMR. Chemical shielding is sometimes referred to as the chemical shift. The interaction arises from the effect the electrons, both bonding and core, have on the amount of the B_0 field “felt” by the nuclear spins. When placed in a magnetic field, a current is induced in the electron clouds by that field. The circulating current generates its own magnetic field, B_{ind} , which is then felt by the nucleus. The result is that the overall field the nucleus “feels” at its local environment is given by:

$$B_{loc} = B_0 + B_{ind} \quad (10)$$

While B_{ind} is small, it is still large enough to cause slight shifts in the precession frequencies of nuclei in differing electronic environments. When the new B_{loc} is used in **Formula 2**, we obtain:

$$\omega = -\gamma B_{loc} = -\gamma(B_0 + B_{ind}) \quad (11)$$

B_{ind} relates to the original external field strength as:

$$B_{ind} = \delta \cdot B_0 \quad (12)$$

where δ is the chemical shift tensor of site of the spin. δ represents a 3 x 3 matrix of values which correspond to the magnitude of the induced field in a given direction when a magnetic field is applied in a specific direction. For example, the δ_{xz} component corresponds to the

induced field's component in the x direction when a magnetic field is applied along z. Each δ term is dependant on the orientation of the molecule with respect to the external field. If the magnetic field is along the z-axis, B_0 consists of a vector with the first two components (the B_x and B_y components) being equal to zero, and the last (B_z) being equal to B_0 .

$$\begin{pmatrix} B_{ind,x} \\ B_{ind,y} \\ B_{ind,z} \end{pmatrix} = \begin{pmatrix} \delta_{xx} & \delta_{xy} & \delta_{xz} \\ \delta_{yx} & \delta_{yy} & \delta_{yz} \\ \delta_{zx} & \delta_{zy} & \delta_{zz} \end{pmatrix} \cdot \begin{pmatrix} 0 \\ 0 \\ B_0 \end{pmatrix} = \begin{pmatrix} \delta_{xz} \cdot B_0 \\ \delta_{yz} \cdot B_0 \\ \delta_{zz} \cdot B_0 \end{pmatrix} \quad (13)$$

While it is clear that the full chemical shift Hamiltonian would contain all three of these components, the secular approximation eliminates all but the δ_{zz} component. In an isotropic liquid, rapid tumbling causes a new term, δ_{iso} , to take the place of δ_{zz} ; where δ_{iso} is δ_{zz} averaged over all possible orientations.

$$\delta_{iso} = \frac{\delta_{xx} + \delta_{yy} + \delta_{zz}}{3} \quad (14)$$

This isotropic chemical shift causes the Larmor frequency to become:

$$\omega = -\gamma(B_0 + B_{ind}) = -\gamma B_0(1 + \delta_{iso}) \quad (15)$$

for isotropic liquids. Each nucleus in a different electronic environment in a molecule would possess its own value for δ_{iso} . This results in the nuclei of the same element having slightly shifted Larmor frequencies for a given molecule.

These shifted Larmor frequencies can be detected and used to distinguish between nuclei such as a proton in a $-CH_3$ group, and one in a $-CH_2X$ group. Unlike the other internal interactions, the chemical shift scales with the strength of B_0 as evidenced by **Formula 12**. The x-axis of NMR spectra is typically plotted in units of parts per million (ppm) to avoid complications when switching between field strengths. The frequency of the peak is divided

by the precession frequency of the nucleus at the magnetic field strength divided by 10^6 . This makes the chemical shift uniform at different field strengths.

In the solid state, there is usually no isotropic tumbling motion. The sample retains its orientation dependence and the chemical shift does not reach an average value for the sample. The orientation dependence is referred to as the chemical shift anisotropy (CSA). For a single crystal, the precession frequency changes as the crystal is rotated in the magnetic field. For a powder sample, one observes all different orientations of the small crystals at once. The sum of all the tiny signals from the differing orientations gives a broad spectrum. This is referred to as a powder pattern. Like dipolar coupling, the CSA possesses an angular dependence of $(3\cos^2\theta-1)$ which may be averaged to zero. Rapid spinning at the “Magic Angle” of 54.74° removes the effects of CSA. As with dipolar coupling, however, not all of the CSA can be removed from some samples due to current limits in spinning speeds. The result of this is to produce spinning side bands with residual signal at the distances of integer multiples of the spinning speed away from the isotropic peak. For example, when spinning at 5kHz, spinning side bands can appear at $\pm 5\text{kHz}$, $\pm 10\text{kHz}$, etc., over an energy range equal to the $|\text{CSA}|$.

1.3.3 NMR Experiments:

The 90° pulse experiment has already been discussed (see **Figure 16** for an illustration of this sequence), though for direct excitation and detection of dilute spins it is sometimes useful to perform an echo experiment to eliminate background signal. Such an experiment is as follows: $90^\circ - \tau - 180^\circ - \tau - \text{acquire}$, where τ is a wait time. **Figure 17** illustrates this pulse sequence. In this experiment, M_B is transferred into the xy-plane. The

magnetization is allowed to precess, causing some loss of phase coherence as the individual isochromats precess at their slightly different frequencies and due to inhomogeneities in B_0 . After this τ period, the 180° pulse flips the isochromats in the xy-plane. During the last τ period, the isochromats precess in the same direction as before, converging on the desired axis (the axis can be determined by the phases of the 90° and 180° pulses.) It is important that the τ periods be identical in order to observe this refocusing. A train of these flips can also be performed, where after subsequent 180° pulses, a τ period is allowed. With each subsequent flip, there is some loss of magnetization due to relaxation mechanisms. This echo pulse sequence has numerous applications, ranging from T_2 relaxation rate to diffusion rate measurements.



Figure 16. Simple one pulse NMR experiment followed by FID acquisition. The section to the left of the vertical line indicates the period during which the radiofrequency pulse is applied; and the section to the right indicates the oscillating signal detected from the sample during acquisition. The vertical line indicates the point at which the radiofrequency pulse is shut off, and the coil switches modes from transmitter to receiver.

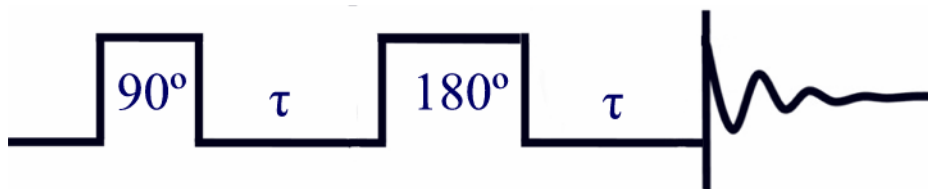


Figure 17. Echo pulse sequence

NMR of many low natural abundance spins such as ^{13}C and ^{29}Si poses a variety of complications. Low sensitivity arises from low natural abundance. In addition, many dilute

spins also have low magnetogyric ratios, as well as long T_1 relaxation times meaning that the delay between subsequent NMR pulse sequences must be longer. Many of these issues can be addressed through an experimental technique known as cross polarization (CP).³⁰ As was stated earlier, energy conserving spin flips are not possible in the laboratory frame for nuclei with different magnetogyric ratios. In the rotating frame, however, precession frequencies are adjustable as:

$$\omega_0 = \gamma B_1 \quad (16)$$

In this case, we can effectively transfer polarization from abundant, high magnetogyric ratio spin to a dilute spin to gain sensitivity per scan, and have pulse delays corresponding to the faster relaxing abundant spins. One of the most frequently used CP nuclei pairs is ^1H and ^{13}C . Often protons are abundant in carbon samples, and they possess a high magnetogyric ratio and high natural abundance. The condition for CP (known as the Hartmann-Hahn match)³¹ is for:

$$\omega_{0,^{13}\text{C}} = \omega_{0,^1\text{H}} \quad (17)$$

Substituting in **Formula 16** gives:

$$\gamma_{^{13}\text{C}} * B_{1,^{13}\text{C}} = \gamma_{^1\text{H}} * B_{1,^1\text{H}} \quad (18)$$

The magnetogyric ratio of each nucleus is fixed, so B_1 strengths must be adjusted to equate. Experimentally, this pulse sequence consists of a 90° pulse on ^1H , followed by a contact pulse where both the ^1H and ^{13}C channels are irradiated at the same time, at the power levels determined by the match condition. After this contact pulse, the signal is acquired on the ^{13}C channel, while the ^1H channel is continuously irradiated for high power decoupling. This pulse sequence is illustrated in **Figure 18**. This method gives a maximum gain of $(\gamma_{^1\text{H}} / \gamma_{^{13}\text{C}})$

in signal per scan compared to a simple 90° pulse, in addition to shorter pulse delays. Some drawbacks with this method are that because of the $(3\cos^2\theta-1)$ angular dependence, the samples must be spun rather slowly, causing more and larger spinning sidebands. Also, since dipolar coupling scales as the inverse of the distance between the nuclei cubed, the CP transfer efficiency decreases greatly with increasing distance. Lastly, some signals can be lost altogether if there are no close protons, or if rapid motion averages out the dipolar interaction. Even so, the benefits of CP usually outweigh the drawbacks.

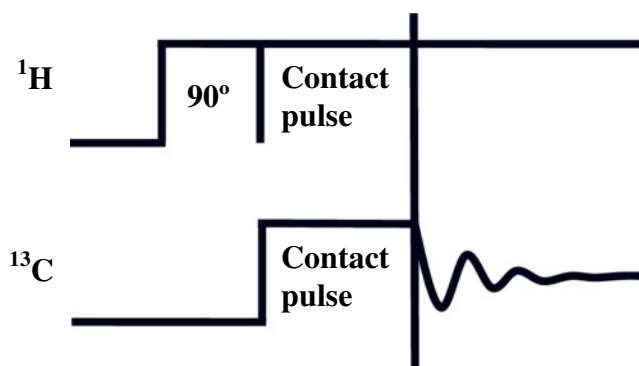


Figure 18. Cross polarization pulse sequence

1.4 Objectives:

The purpose of this research project is to determine the mechanism of how small alkanes react on zeolitic catalysts, including key initiation steps and subsequent reaction pathways. To address both of these problems, a two-fold approach is used. The first employs in situ, solid-state, magic-angle spinning Nuclear Magnetic Resonance. Gaseous reagents are adsorbed on zeolitic catalysts inside MAS NMR rotors. Subsequent reactions and interactions are monitored in the instrument as they occur. This area of the project probes the initiation of adsorbates on the catalyst. Because this is a closed system (ie. after

adsorption, no additional species are introduced to the system) and the upper temperature limit of the instrument around 150°C, this method is not suited for determining ultimate mechanistic information for alkylation. A combination of a pulsed micro-reactor system and Gas Chromatography analysis of products is used to determine active pathways during the alkylation process. The pulsed-type experiments are more representative of actual industrial processes as the system is dynamic (ie. the system isn't "closed" and, due to the continuous flow, is constantly changing) and the temperature range of the reactor is more similar to that found in such processes. These two methods can be used independently to address the process of alkylation in zeolites, or in conjunction. In cage type zeolites, organic co-catalysts can form during the reaction process which are too bulky after forming to leave the "cage" of the catalyst via the "windows" connecting the cage to the rest of the catalyst.³²⁻³⁴ Such species would be "invisible" to the GC analysis as they would never reach the instrument, but would remain in the catalyst, even after experimentation. In these cases, the sample from the reactor could be later analyzed by NMR to reveal these species and determine intermediates or co-catalysts during the process.

Chapter 2: Identification of an Adsorption Complex Between Isobutane and H-ZSM-5

2.1 Introduction:

The mechanism of alkane activation on acidic zeolitic catalysts remains controversial. Many attribute the initiation of alkanes to trace olefinic impurities since direct protonation pathways seem unlikely; this is because zeolites are not thought to possess the acidic strength required to form traditional Olah type pentavalent carbonium ions.^{6,35,36} The absolute quantity of these impurities remains small, precluding direct detection of the impurities by spectroscopic methods. The low concentrations also prevent traditional olefinic chemistry on the catalyst like oligomerization. These olefins would readily activate in the presence of acidic media, generating an active carbenium ion. Additionally, direct protonation activation seems even less probable due to the fact that recent experimental data has indicated a regioselectivity for proton exchange between branched alkanes and zeolites with exchange occurring preferentially/only at the primary and/or secondary positions neighboring tertiary locations.^{10,37,38} This is in direct contrast to traditional Olah type chemistry which would predict the exchange to favor more substituted carbons as ultimately they would form more stable carbenium ions. Still, numerous publications propose a direct protonation step.^{14,15,39,40} Other authors have suggested that olefinic species are formed by the catalyst.^{41,42} These alkenes may be generated by Lewis acidic sites on the catalyst through hydride abstraction. The presence of Lewis acidic sites in the catalyst is quite probable as some zeolites readily dealuminate during calcination and dehydration procedures, even when very gradual temperature ramping programs are used.

Each of these proposed mechanisms describes the activated alkane as a carbenium ion. Only the direct protonation mechanism illustrates a means by which an alkane can

exchange protons with the zeolite in the absence of a carbenium ion intermediate. Even this mechanism, however, inevitably generates olefinic species through the loss of H₂ gas which could exchange in the same manner. Recent key mechanistic discoveries have been found to be the result of trace impurities in reactant streams.^{43,44} In the example of methanol-to-olefin chemistry using zeolites, it was found that trace species in the methanol played a key role in the initiation reaction, as opposed to the formation of surface methoxy groups.⁴⁵⁻⁴⁷ It is clear that mechanistic understanding is vital to the progress of zeolite catalyzed alkylation. In the case of alkylation of isobutane in zeolites, mechanistic complications have prevented the development of a process due in part to side reactions leading to loss of selectivity and catalyst deactivation.³ The main goal of this chapter is to study the initial interactions between alkane molecules and zeolitic catalysts that subsequently lead to activation and reaction.

2.2 Experimental:

Silica samples were obtained from Grace-Davidson, and ZSM-5 (Si:Al=15) samples were obtained from Zeolyst International. Hexamethylbenzene was used to calibrate ¹H and ¹³C pulse widths, and for the cross polarization Hartman-Hahn match condition calibration. HMB was also used as a ¹³C chemical shift standard. Polydimethylsiloxane (PDMS) was used as a ¹H NMR chemical shift standard and was obtained from Rheometrics Scientific, Inc. Isobutane (99% purity) was obtained from Aldrich, Inc., isobutane-d₁₀ (99.1% D) was obtained from CDN Isotopes, and isobutane-2-¹³C (99% ¹³C) was obtained from Icon Isotopes. Purity of the gaseous samples was verified by GC analysis using a HP 5890 GC FID. Samples free of trace olefins were obtained by treating the as received reagents with D₂

(99.8% D) obtained from Isotec over a 0.5% dispersed Pt catalyst on alumina obtained from Alfa Aesar. These “cleaned” samples were analyzed by GC to verify the removal of olefinic impurities.

ZSM-5 samples for NMR experiments were prepared by heating via a stepwise procedure in a stainless steel reactor under dry, flowing air. The temperature controller was a 6-zone ramp/soak controller, model CN616 purchased from Omega Engineering, Inc. The ZSM-5 samples were heated via the following procedure: room temperature to 150°C at 2°C per minute, hold at 150°C for 2 hours, heat the sample from 150°C to 450°C at 6°C/min, hold at 450°C for 12 hours, and then power off. The samples were then closed under a positive pressure of the flowing dry air and transferred into a glovebox for loading. Silica samples were prepared by heating the samples under vacuum. The samples were placed in a quartz tube and attached to a vacuum line. The samples were evacuated to 10^{-3} torr and were heated by the temperature controller using a stepwise procedure. The heating procedure for preparing silica was as follows: room temperature to 100°C at 1°C per minute, hold at 100°C for 1 hour, heat from 100°C to 200°C at 1.7°C per minute, hold at 200°C for 1 hour, heat from 200°C to 300°C at 1.7°C per minute, hold at 300°C for 1 hour, heat from 300°C to 400°C at 1.7°C per minute, hold at 400°C for 1 hour, heat from 400°C to 450°C at 1.7°C per minute, hold at 450°C for 6 hours, and then power off. The samples were then closed under vacuum and transferred into a glovebox for loading. Zeolite sample preparation methods were verified after each preparation via ^1H magic angle spinning (MAS) NMR. This verification is important because the zeolites are prone to dealumination if heated too rapidly in the presence of moisture.

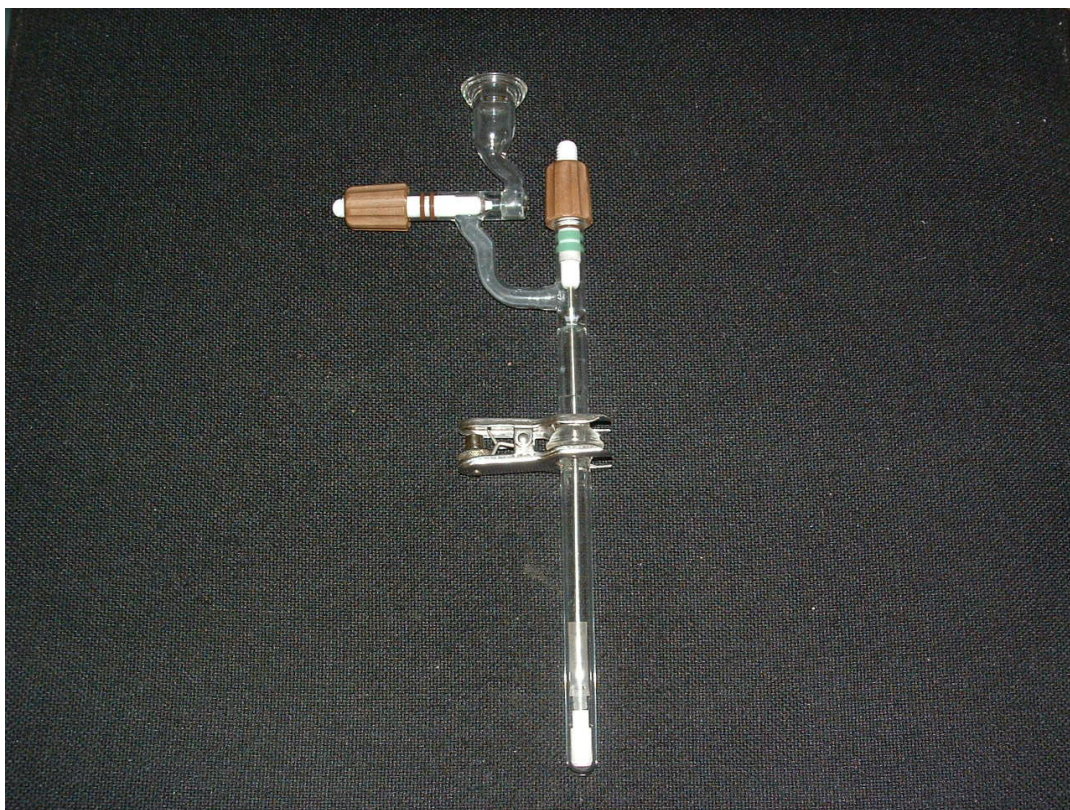


Figure 19. CAVERN-type apparatus⁴⁸

For NMR adsorption experiments, 50-55 mg of the prepared catalyst were loosely loaded into a 7 mm MAS zirconium oxide rotor and placed in a CAVERN type apparatus (see **Figure 19**).⁴⁸ This device allows the sample to be loaded with a gaseous reagent and sealed in the MAS NMR rotor without being exposed to the external atmosphere. The CAVERN is critical to this work as trace amounts of moisture can cause detrimental effects in the ^1H spectrum through both rapid exchange with the acid site, causing broadening of the peak, as well as the added complexity of an additional signal from the water itself. The CAVERN was attached to the vacuum line and evacuated to 10^{-3} torr. A slight overpressure of the gas was then delivered to the line. The test gas was allowed to adsorb onto the sample. Stoichiometric adsorptions were performed of one adsorbate molecule per Bronsted acid site

using an overpressure of the adsorbate. Fractional loadings were also performed using the ratios 0.25 and 0.5 molecules per acidic site to explore loading dependent phenomena. Exact absorption amounts were determined using acid site densities from White, et al.²³ When the desired pressure drop was registered, the rotor was sealed and taken to the spectrometer. Silica samples were loaded using liquid nitrogen to cryo-pump the adsorbates onto the samples as the gases did not readily adsorb on the silica in the desired amounts. A Kel-F plunger-type plug was sometimes used to seal the rotors in addition to the Kel-F cap to prevent moisture contamination and loss of adsorbate during low temperature experiments. After sealing the rotor, low temperature samples were submerged in liquid nitrogen prior to being placed in the pre-cooled NMR probe, whereas room and high temperature samples were kept at room temperature prior to inserting them into the spectrometer.

NMR data were obtained on a Bruker DSX 300 MHz spectrometer using MAS at the rate of 7.7 kHz or 8 kHz with 4 mm zirconium oxide rotors and rates of 4.5 kHz with 7 mm zirconium oxide rotors. ¹H NMR spectra were acquired using two different pulse sequences. The single-pulse experiment involved a simple $\pi/2$ pulse followed by acquisition, and the echo-pulse was a Carr-Purcell type echo pulse consisting of a $\pi/2_x$ pulse, a delay, τ , a π_y pulse, and lastly another delay for the refocusing of the magnetization. The τ periods used were equal to one period of the rotor. ¹³C NMR spectra were also acquired via two different pulse sequences; a Bloch decay sequence of a simple $(\pi/2)_x$ pulse and acquisition with ¹H decoupling, and the standard MAS cross polarization sequence.³⁰ Reverse CP spectra were acquired using a sequence consisting of a ¹³C $(\pi/2)_x$ pulse, followed by a contact pulse of both ¹H and ¹³C to transfer magnetization from the ¹³C nuclei to ¹H nuclei. The FID was acquired on the ¹H channel with ¹³C decoupling.

2.3 Results and Discussion:

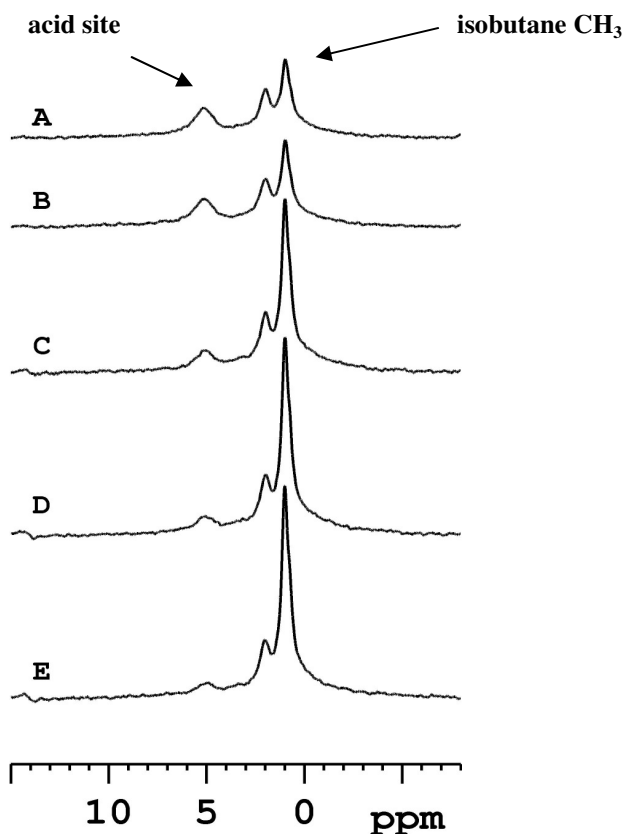


Figure 20. In-situ CAVERN ^1H NMR experiment for adsorption of isobutane- d_{10} on zeolite H-ZSM5: (A) 298 K immediately following adsorption; (B) same as (A), after five minutes; (C) 320 K; (D) same as (C), after 15 minutes; (E) same as (C), after 45 minutes.

Perdeuterated isobutane was adsorbed onto H-ZSM-5, and the exchange of deuterium for a proton from the zeolite's Bronsted acid site was monitored. **Figure 20** shows a stack plot of the exchange process as is monitored by the ^1H spectrum over time. In the ^1H -NMR spectrum of neat zeolite H-ZSM-5, there are two dominate peaks; one from the Bronsted acid sites (around 4.2 ppm), and one from the non-acidic terminal Si-OH groups (around 1.9 ppm) (see **Figure 21**.) The methyl groups of isobutane have a shift of approximately 1.0 ppm and the methine group approximately 1.8 ppm. In **Figure 20A**, it is apparent that the reaction has

already begun at room temperature at the time of the first spectrum. The Bronsted acid peak has a smaller intensity in the adsorbed spectrum than the neat H-ZSM-5. There is also a substantial methyl peak that is too large to be from residual protons in the adsorbed gas. H/D exchange at room temperature is surprising since previous reports had indicated that the exchange occurs at higher temperatures.¹⁰ The gases had been “cleaned” as described earlier, and GC analysis indicated that the samples were free of trace olefinic impurities which could serve as carbenium ion pathway initiators (see **Figure 22**). Olefinic species can undergo a number of reactions at room temperature when adsorbed on acidic zeolitic catalysts including rapid H/D exchange and oligomerization. A second, low temperature adsorption of the gas on the catalyst was preformed. The temperature was slowly increased from 230 K. The exchange reaction initiated at 273 K (see **Figure 23**.)

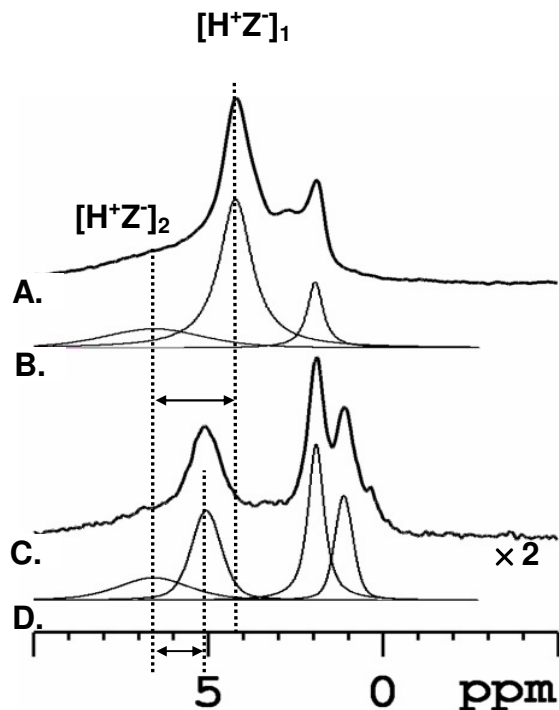


Figure 21. (A) ^1H MAS spectra of neat, dehydrated H-ZSM-5 at room temperature; (B) deconvolution of (A); (C) H-ZSM-5 with 1 eqv of isobutane- d_{10} adsorbed at 298 K; (D) deconvolution of (C). Individual peak assignments, and peak shifts, are discussed in the results and discussion section. The small peak at 0.5 ppm in (C) is a background signal from the probe.

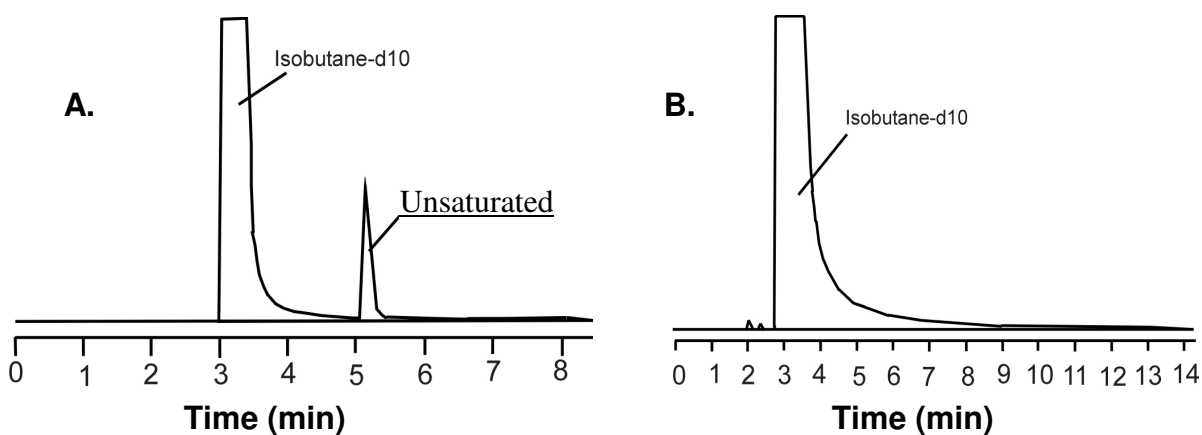


Figure 22. GC analysis of (A) 99.99% purity isobutane- d_{10} vs. (B) the same sample after treatment with D_2 gas over a dispersed Pt hydrogenation catalyst. The isobutane peak is deliberately shown off scale. In (B), the vertical scale is expanded by a factor of two relative to (A) to emphasize the absence of the unsaturated peak.

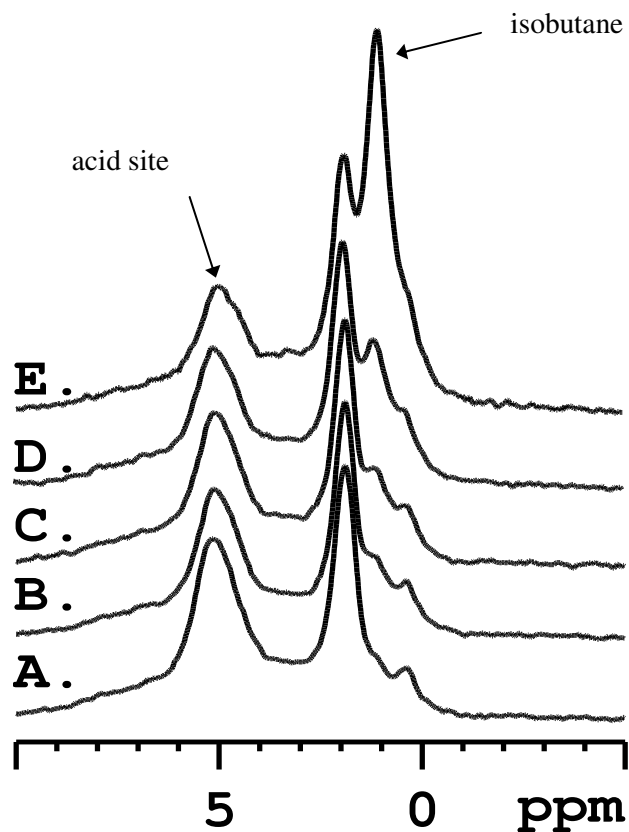


Figure 23. ^1H MAS spectra of H-ZSM-5 following adsorption of 1 eqv. of isobutane- d_{10} . The temperature was gradually increased and the spectra were collected at (A) 230 K, two minutes after adsorption; (B) 270 K, 75 minutes after adsorption; and showing the onset of H/D exchange; (C) 273 K, 85 minutes after adsorption; (D) 273 K, 135 minutes after adsorption; (E) 298 K, 175 minutes after adsorption. The small peak at 0.5 ppm is a background signal from the probe.

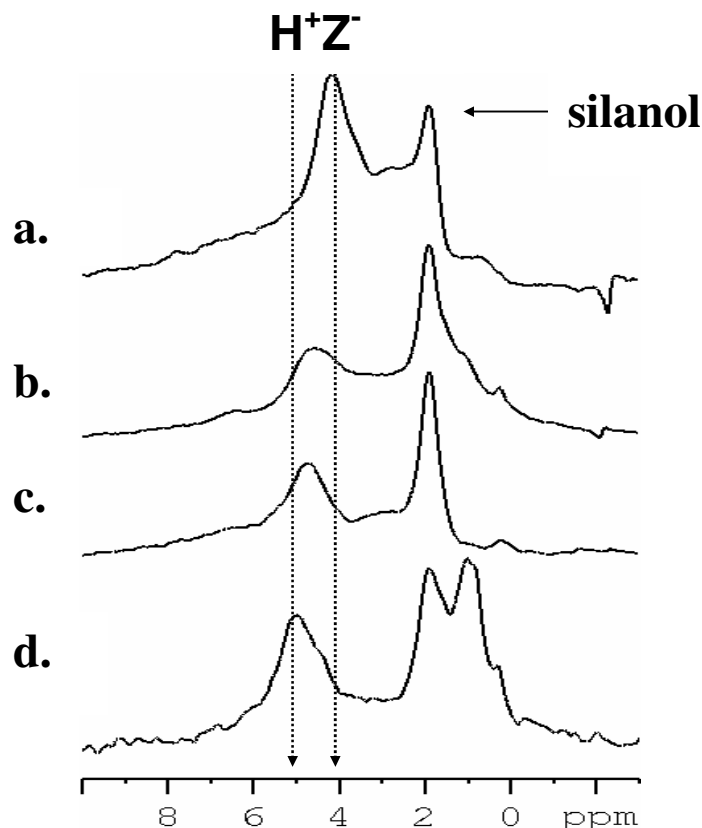


Figure 24. Comparison of Bronsted acid site peak chemical shift in (a) neat, dehydrated, and activated HZSM-5 vs. HZSM-5 with (b) 0.25; (c) 0.5; and (d) 1 equivalents isobutane- d_{10} . The peak at 0.9 ppm in (d), is protonated isobutane resulting from H/D exchange with the acid site.

A second surprising feature of the stack plot is that after the adsorption, the acid peak is at 5.1 ppm rather than at the typical shift of 4.2 ppm. **Figures 21A and 21B** show the ^1H spectrum of neat H-ZSM-5 as well as its deconvoluted component peaks, while **Figures 21C and 21D** show a spectrum of 1 equivalent of isobutane- d_{10} per acid site adsorbed on H-ZSM-5 and its deconvoluted component peaks. The second acidic peak downfield on both spectra denoted $[\text{H}^+\text{Z}^-]_2$ is the second acidic site for H-ZSM-5.⁴⁹ The peak in **Figure 21C** at 1.0 ppm is from isobutane which has exchanged prior to acquisition. The downfield shift of the primary acid site is very apparent in this stack plot; as is the fact that the second acidic site

doesn't seem to shift at all. Being further downfield, one would expect that this site would be more acidic than the primary acid site as it has less electron density around the proton, but for the purposes of H/D exchange with isobutane-d₁₀, the site seems less active. One possibility is that it could be inaccessible to the isobutane molecule as the second acidic site is thought to be at a defect location in the zeolite's lattice. The downfield shift of roughly 1 ppm for the primary acidic site, however, is quite significant in the ¹H spectrum. Such a shift has previously only been documented for unsaturated species.⁵⁰ Stoichiometric titration of the acid sites by fractional loadings with isobutane-d₁₀ (**Figure 24**) illustrates that the shift process directly depends on the amount of the alkane adsorbed. Excessive loadings of test gas also result in the final spectrum (Figure 3d) indicating that all sites are saturated when there is 1.0 equivalent of alkane per acid site. Control experiments performed with natural abundance ¹H isobutane were performed and gave similar titration results. These results rule out the possibility of trace olefinic impurities causing this shift, as the sites would not be saturated until the trace species was at a 1.0 equivalent ratio, thus requiring a large excess of the bulk alkane. This result leads to the idea that the alkane adsorbs specifically at the primary Bronsted acid site, and interacts in such a manner to cause a deshielding effect on the acidic site. This is a promising discovery for the goal of making alkylates in zeolites as it indicates that the alkanes do not simply wander around the channels of the zeolite, but rather they specifically adsorb close to the active sites. This allows a greater amount of time and a higher probability for them to encounter another species at that site and react.

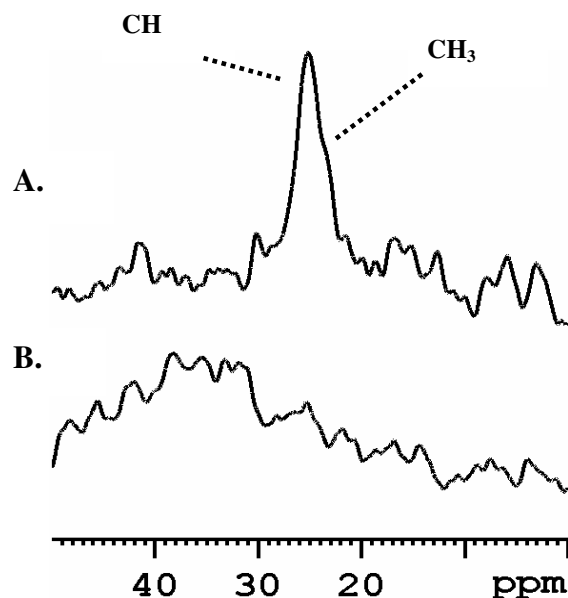


Figure 25. Results from in-situ $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS experiment performed with one equivalent of isobutane- d_{10} per acid site on (A) HZSM-5 and (B) dehydrated silica.

Further experiments were carried out to verify the existence of an adsorption complex between a saturated alkane and the Bronsted acid site in zeolites. The first experiment was adsorbing isobutane, d_{10} onto H-ZSM-5 and performing a low temperature-natural abundance $^1\text{H} \rightarrow ^{13}\text{C}$ CP/MAS experiment. If the adsorption complex existed and the isobutane were in close enough proximity to the acid site, then this experiment should give rise to a peak for isobutane in the ^{13}C spectrum. The sample was kept at low temperatures at the time of adsorption and throughout the experiment to prevent H/D exchange from occurring. In **Figure 25A**, there is a prominent peak at ~ 25 ppm which is the chemical shift of the isobutane carbons. Signal to noise ratios are poor in this experiment due to the small amount of gas adsorbed onto the catalyst, as well as the low natural abundance of ^{13}C . Control experiments on silica (**Figure 25B**) indicate that similar results are not obtained for the adsorption of isobutane, d_{10} on non-acidic species. The second experiment consisted of

adsorbing 2-¹³C-isobutane onto H-ZSM-5 and then performing a ¹³C → ¹H CP/MAS experiment (the reverse CP experiment). Much like the first experiment, if the adsorption complex existed and the isobutane is in close enough proximity to the acid site, then this experiment should give rise to a peak near the shift of the Bronsted acid site in the ¹H spectrum. (This experiment is not a traditional experiment as in the case of the regular CP, it is merely used to illustrate an interaction. In fact, this experiment gives much poorer signal to noise ratios than a simple one pulse ¹H, rather than the enhancements one sees with the CP over one pulse ¹³C experiments.) In **Figures 26A and 26B**, there is a clear peak in the 4-7ppm range which is not present in **26C** which is the control experiment on silica, giving further evidence of the existence of an adsorption complex. The large peak in each of the three spectra ~1.8ppm is from the methine proton which is directly attached to the ¹³C label.

2.4 Conclusions:

Evidence of the formation of an adsorption complex between a saturated alkane and a zeolitic catalyst has been presented and explored. Perturbations in the chemical shift similar to those observed upon the adsorption of olefinic species on zeolites were noted. Fractional and excess loadings of the alkane resulted in the predicted partial and saturated shifts based on pure stoichiometry. Additionally, polarization transfers from the alkane to the zeolitic lattice, and from the lattice to the alkane were found to be possible. The adsorption complex presumably forms only with the primary acid site of H-ZSM-5 as the secondary site gives no evidence of interaction with the adsorbed alkane. This could be due to inaccessibility of the secondary site due to defect sites in the lattice.

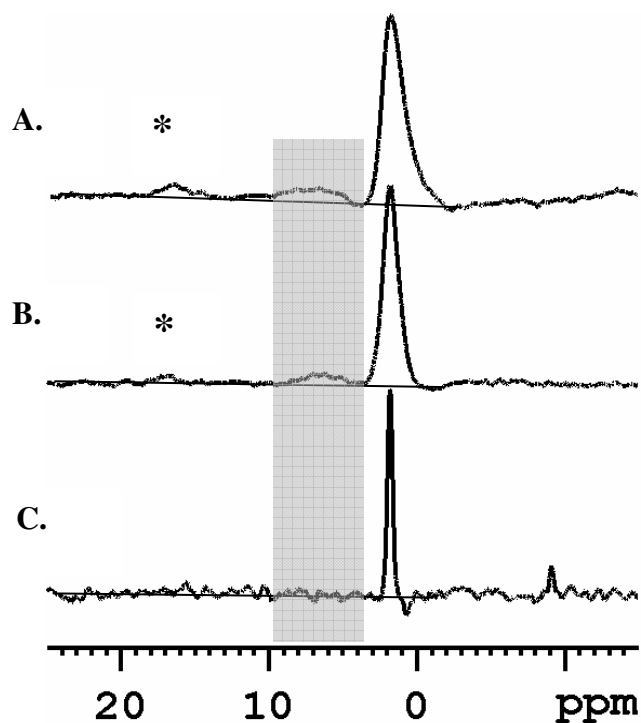


Figure 26. Spectra from in-situ reverse ($^{13}\text{C} \rightarrow ^1\text{H}$) CP/MAS experiment with one equivalent of labeled $^{13}\text{CH}(\text{CH}_3)_3$ on HZSM-5, obtained at (A) 220 K; (B) same sample as (A), obtained at 298 K; (C) 220 K spectrum following a similar sample preparation as in (A), except replacing the HZSM-5 with dehydrated silica gel.

Chapter 3: H/D Exchange Kinetics between Perdeuterated Isobutane and H-ZSM-5

3.1 Introduction:

Previously in the literature, the H/D exchange process between isobutane and H-ZSM-5 catalyst has been monitored only at elevated temperatures.¹⁰ Recent results from our current projects has indicated that this exchange initiates and proceeds at much lower temperatures.⁵¹ Additionally, previous reports have only monitored the evolution of product signals, and the samples were often analyzed off-line following reaction.^{8,10} For the purposes of determining mechanistic information, it is important to monitor reactant and product evolution simultaneously during reaction. As has been previously illustrated, following the reactant and product peaks can provide vital clues to operative mechanisms and intermediate steps.^{50,51} In this chapter, kinetic information for both the decay of the reactant acidic peak as well as for the evolution of the product methyl peak will be presented, and this information will be used to obtain an activation energy for the H/D exchange process.

3.2 Experimental:

ZSM-5 (Si:Al=15) samples were obtained from Zeolyst International. Hexamethylbenzene was used to calibrate ^1H and ^{13}C pulse widths, and for the cross polarization Hartman-Hahn match condition calibration. HMB was also used as a ^{13}C chemical shift standard. Polydimethylsiloxane (PDMS) was used as a ^1H NMR chemical shift standard and was obtained from Rheometrics Scientific, Inc. Isobutane- d_{10} (99.1% D) and neopentane- d_{12} (99.4% D) were obtained from CDN Isotopes. Purity of the gaseous samples was verified by GC analysis using a HP 5890 GC FID. Isobutane samples free of trace olefins were obtained by treating the as received reagents with D_2 (99.8% D) obtained

from Isotec over a 0.5% dispersed Pt catalyst on alumina obtained from Alfa Aesar. These “cleaned” samples were analyzed by GC to verify the removal of olefinic impurities.

ZSM-5 samples for NMR experiments were prepared by heating via a stepwise procedure in a stainless steel reactor under dry, flowing air. The temperature controller was a 6-zone ramp/soak controller, model CN616 purchased from Omega Engineering, Inc. The ZSM-5 samples were heated via the following procedure: room temperature to 150°C at 2°C per minute, hold at 150°C for 2 hours, heat the sample from 150°C to 450°C at 6°C/min, hold at 450°C for 12 hours, and then power off. The samples were then closed under a positive pressure of the flowing air and transferred into a glovebox for loading. Zeolite sample preparation methods were verified after each preparation via ^1H magic angle spinning (MAS) NMR. This verification is important because the zeolites are prone to easy dealumination if heated to rapidly in the presence of moisture.

For H-ZSM-5 NMR adsorption experiments, 50-55 mg of the prepared catalyst were loosely loaded into a 7 mm MAS zirconium oxide rotor. The rotor was then placed in a CAVERN apparatus.⁴⁸ This device allows the sample to be treated with a test gas and sealed in the MAS NMR rotor without being exposed to the external atmosphere. The CAVERN is critical to this work as trace amounts of moisture can cause detrimental effects in the ^1H spectrum through both rapid exchange with the acid site, causing broadening of the peak, as well as the added complexity of an additional signal from the water itself. The CAVERN was then attached to the vacuum line and evacuated to 10^{-3} torr. The test gas was then adsorbed onto the sample, allowing the gas to adsorb on the catalyst freely under slight positive pressure. Stoichiometric adsorptions were performed of one adsorbate molecule per Bronsted acid site using an overpressure of the adsorbate. Exact absorption amounts were

determined using acid site densities from White, et al.²³ After the desired pressure of gas had been delivered, the rotor was sealed. A Kel-F plunger-type plug was used to seal the rotors in addition to the Kel-F cap to prevent moisture contamination and loss of adsorbate during low temperature experiments. After sealing the rotor, low temperature samples were then submerged in liquid nitrogen prior to being placed in the pre-cooled NMR probe, whereas room and high temperature samples were kept at room temperature prior to inserting them into the spectrometer.

NMR data were obtained on a Bruker DSX 300 MHz spectrometer using MAS at the rate of 7.7 kHz or 8 kHz with 4 mm zirconium oxide rotors and rates of 4.5 kHz with 7 mm zirconium oxide rotors. ¹H NMR spectra were acquired using the Carr-Purcell type echo pulse consisting of a $\pi/2_x$ pulse, a delay time, τ , a π_y pulse, and lastly another τ delay time for the refocusing of the magnetization. The τ periods used were equal to one rotor period.

3.3 Results and Discussion:

3.3.1 Perdeuterated Isobutane and H-ZSM-5:

Perdeuterated isobutane was adsorbed onto H-ZSM-5 catalyst and isothermal NMR experiments were performed. Exchange was monitored at much lower temperatures than in previous literature.¹⁰ Exchange was detected just a few degrees above the boiling point of the gas. Similar to what was observed by Sommer, et. al., H/D exchange was found to occur exclusively at the methyl position. This type of selectivity would be expected for olefinic H/D exchange with an acidic catalyst. **Figure 27** illustrates the mechanism of this process. For a saturated alkane, however, this selectivity would not be expected for an Olah superacid catalyzed reaction.⁶ Such a reaction would be expected to preferentially exchange at the

methine position. Zeolites, however, differ greatly from liquid acids in their solvation effects and steric constraints. It is most likely these forces and interactions of the lattice with the isobutane that produce the observed exchange selectivities. More discussion about this selectivity will be presented in Chapter 5. Additionally, the second acidic site of H-ZSM-5 appears to be excluded from H/D exchange with the alkane. This gives further evidence that this site could be sterically hindered due to a structural defect so as to prohibit adsorbed molecules of the size of isobutane from adsorbing and reacting at these sites. Their more downfield chemical shift suggests that they might be more acidic than the primary acid sites if they were accessible.

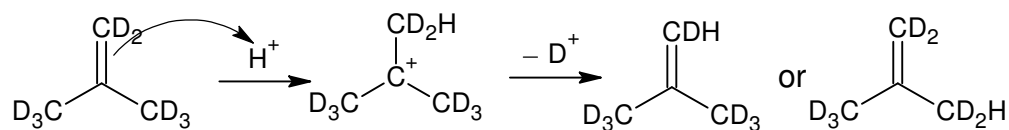


Figure 27. H/D exchange mechanism for isobutene

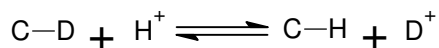


Figure 28. Simplified schematic reaction for H/D exchange for a methyl CD bond in the presence of an acid

The general reaction for H/D exchange between a zeolite and isobutane can be simplified as depicted in **Figure 28**. The scheme shows a C-D bond rather than the complete isobutane molecule as this makes the balancing coefficients less complicated. Ultimately, the simplified scheme better represents the system as it avoids the complications of isobutane molecules which exchange with the catalyst multiple times, and those that don't exchange labels (though such species will still exchange with the catalyst; it is just not visible in these experiments as the deuterium labels are in excess.) These molecules with varying extents of

exchange do not affect the results as they all are all the same chemical species, just with different quantities of labels. The only important information is exchange site (already shown to be exclusively at the methyl position) and the total extent of exchange.

Since this reaction is an isotopic exchange, the equilibrium constant should be equal to 1. The full rate law would be as follows:

$$Rate = k_1 [CD]^m [H^+]^n - k_{-1} [CH]^o [D^+]^p = -\frac{d[H^+]}{dt} = \frac{d[CH]}{dt} \quad (19)$$

where the exponents m, n, o, and p all correspond to the orders of their respective concentrations. Only the derivatives of the ^1H NMR observable species were included. We can simplify this equation by only using the initial data obtained from the exchange. In the initial case, $[CH]$ and $[D^+]$ are very small, causing that term to be approximately zero. This makes the expression:

$$Rate = k_1 [CD]^m [H^+]^n = -\frac{d[H^+]}{dt} \quad (20)$$

The expression can also be simplified by using an excess of one of the reactants. In this case, we used one isobutane per acid site. This corresponds to a 9:1 excess of $[CD]$ with respect to $[H^+]$ as each isobutane has 9 methyl C-D bonds. Assuming this excess and an equilibrium constant of 1, at equilibrium there will be 8.1 C-D bonds remaining per isobutane, and only 0.9 C-H bonds. Since the change in this reactant is approximately zero, we can treat the concentration as a constant, making the equation:

$$Rate = k_1' [H^+]^n = -\frac{d[H^+]}{dt} \quad (21)$$

where,

$$k_1' = k_1 [CD]^m \quad (22)$$

While the determination of this rate constant will not be the actual value for the reaction, it can be used to determine the activation energy, and is useful for comparing the relative rates of reaction at different temperatures.

Assuming the reaction will be first order in $[H^+]$, the equation is integrated to give:

$$\ln \left(\frac{[H^+]}{[H^+]_0} \right) = -k_1' t \quad (23)$$

where $[H^+]_0$ is the initial concentration of acidic sites. Because this is an equilibrium reaction, using such a large excess of $[CD]$ will, by Le Chatelier's principle, drive reactions toward the products side. This means that at equilibrium, $[CH]_\infty$ will approximately equal $[H^+]_0$ (using 1 as the equilibrium constant shows that 90% of the initial acidic sites will be incorporated into C-H bonds at equilibrium.) Also, $[H^+]$ can be given by:

$$[H^+] = [H^+]_0 - [CH] = [CH]_\infty - [CH] \quad (24)$$

Plugging these into **Equation 23** gives:

$$\ln \left(1 - \frac{[CH]}{[CH]_\infty} \right) = -k_1' t \quad (25)$$

This means that the relative rate constants can be easily determined by either of the observable signals; provided the data is from the initial reactions.

Figure 29 shows a representative stack plot of selected spectra from kinetics runs at 298 K (the other exchanges were similar.) Rate constants for the acidic peaks were found by deconvoluting the spectra in the program PeakFit, and plotting $\ln[I(t)/I(0)]$ verses time (where $I(t)$ represents the integrated area of a peak at time t) and determining the slope. This

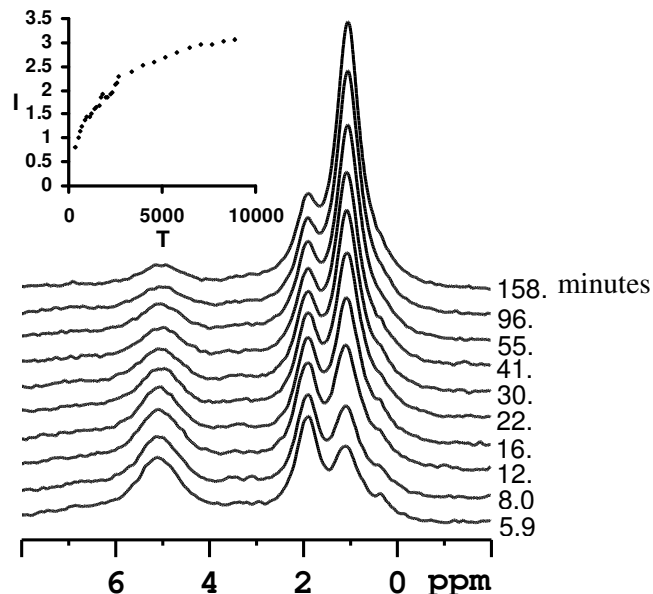


Figure 29. Series of selected in-situ ¹H MAS spectra acquired at 298 K following the adsorption of 1 equivalent of isobutane-d₁₀ per acid site on H-ZSM-5. The time shown to the right of each spectrum is the total time following adsorption. The top left insert shows the peak area for the CH₃ peak vs. time.

is better than single point calculations because using a linear regression fit gives the average value for the rate constant over the points as the slope of the regression line. Only the initial linear regions were used for regression determined rate constants to ensure the system followed the criteria of the rate law. The rate constant for the methyl peak was determined similarly, but by plotting $\ln[1 - I(t)/I(\infty)]$ versus time and finding the slope. Monitoring the fates of both the active site as well as the product has been shown to be imperative in studies such as these.^{50,51} **Figure 30** shows the initial points of the 298 K kinetics plot for both the acidic and methyl peaks. The slopes of the two lines, 4.6 and $4.1 \times 10^{-4} \text{ s}^{-1}$ respectively, are equal within error. **Figure 31** shows the kinetics plots for the 273 K and 285 K runs; only the methyl peaks are shown for clarity. The plot at 273 K appears to follow the proposed

first order rate law reasonably well and a rate constant of $5.0 \times 10^{-5} \text{ s}^{-1}$ was calculated. When the temperature is increased slightly to 285 K, a different result is observed. The 285 K kinetics plot was found to have an initial rate of $2.2 \times 10^{-4} \text{ s}^{-1}$. In the 285 K plot, the breakdown of the rate law is observed. This is due to the initial assumptions determined (no reverse reaction and the concentration of C-D bonds does not change) no longer being valid. This breakdown was also observed in the 298 K plot. It is probable that this feature may also be present in the 273 K data, but it was not observed because the reaction proceeds so slowly. As the temperature rises, the exchange constants follow the expected trend of increasing, but the large change in initial rates from 273 K to 285 K is quite surprising.

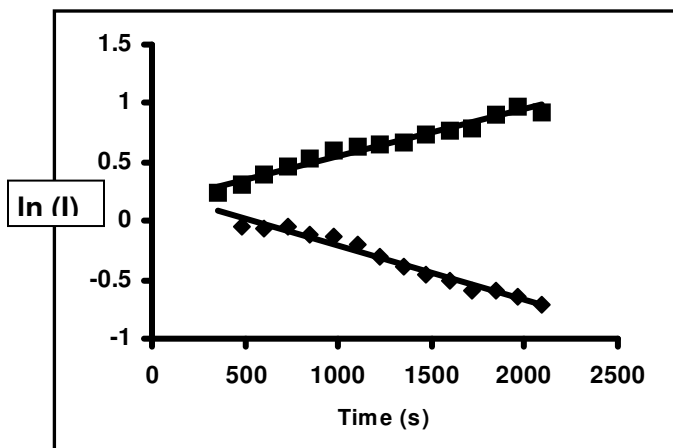


Figure 30. Semi-logarithmic plot of peak area versus time for the spectra acquired at 298 K. The (■) represent the areas of the 1.1 ppm isobutane peak and the (◆) represent the areas of the 5.1 ppm acid site peak. The exchange rate constants equal 4.1×10^{-4} and $-4.6 \times 10^{-4} \text{ s}^{-1}$ for the isobutane and the acid peaks, respectively. The decaying acid site peak is plotted as $y = \ln[I(t)/I_0]$, while the rising isobutane peak as $y = -\ln[1-I(t)/I_\infty]$.

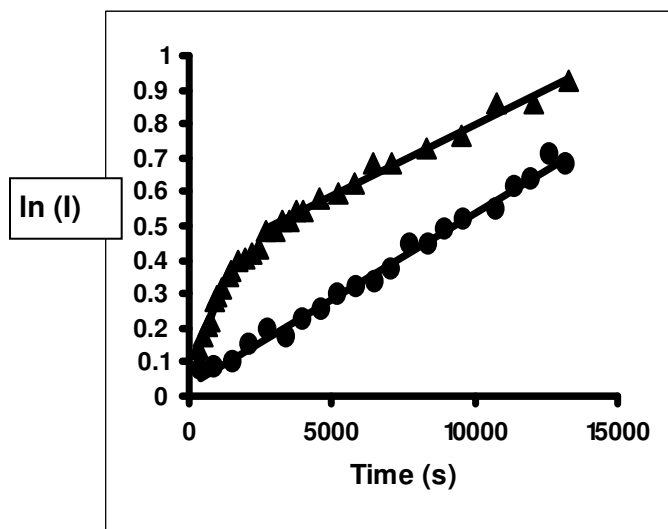


Figure 31. Rate plot for the H/D exchange experiment between isobutane-d₁₀ and HZSM-5 at 273 K (●) and 285 K (▲) (only the methyl's are shown.) The 273 K data gives a single rate constant of $5.0 \times 10^{-5} \text{ s}^{-1}$. At 285 K, the initial rate constant equals $2.2 \times 10^{-4} \text{ s}^{-1}$, while the second component equals $4.2 \times 10^{-5} \text{ s}^{-1}$. The linear regression results are shown as trendlines.

Figure 32 is an Arrhenius plot for the rate constants calculated at 273 K, 285 K, and 298 K. For the data collected at 285 K, only the initial rate constant value was used. The activation energy for the H/D exchange process between isobutane and H-ZSM-5 was found to be 57 kJ/mol (13.6 kcal/mol). This value is considerably lower than the calculated theoretical value for the dehydrogenation of isobutane as performed by an Olah type superacid of 222.6 kJ/mol.⁵² Additionally, the initial protonation step of olefinic H/D exchange with the zeolite has been found to have an activation energy of approximately 30 to 45 kJ/mol.^{53,54} This low value compared to our experimentally determined one indicates that this process is not the activation step as it would be evident in both the trace olefin case and the Olah dehydrogenation step.

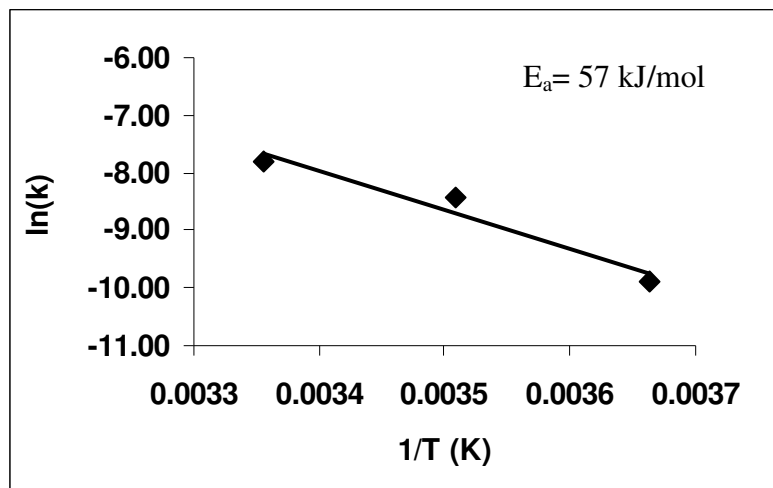


Figure 32. Arrhenius plot for H/D exchange between H-ZSM-5 and perdeuterated isobutane

3.3.2 Perdeuterated Neopentane and H-ZSM-5:

Neopentane is an ideal test molecule for direct H/D exchange between a methyl group and a zeolite. Neopentane has no option for a mechanism involving a carbenium ion, ruling out any trace olefins as mediating species in the exchange process. Upon exposing the CAVERN to a slight overpressure of neopentane-d₁₂, the gas did not readily adsorb onto the catalyst as did the isobutane. Cryo-pumping of the gas into the catalyst using liquid nitrogen also failed as verified by ¹³C NMR of the sample. Recent reports have found that neopentane will readily enter the channels of ZSM-5 at elevated temperatures. These authors found that neopentane will H/D exchange with the catalyst, but not at temperatures our spectrometer is currently able to achieve (513 to 543 K).⁵⁵ The inability of neopentane to adsorb as readily at room temperature is most likely due to sterics causing slow diffusion rates into and through the channels. The kinetic diameter of neopentane is slightly larger than the pore size of ZSM-5 at room temperature.⁵⁶ At higher temperatures, the increased dynamics of the

molecules as well as flexibility of the lattice facilitates neopentane's entry into the channels.^{57,58}

3.3.3 Role of Residual Carbonaceous Species Presence in Catalyst:

To effectively eliminate the possibility of residual carbonaceous species residing in the catalyst from the template used in synthesis, total carbon analysis was performed on a calcined sample of H-ZSM-5 (analysis was performed by Galbraith Laboratories by combusting all carbon into detectible CO₂.) It is important to rule out the presence of such species as they may act to initiate and/or mediate H/D exchange. The results of the analysis were that the sample contained less than 0.1 weight % carbon. Using this value as an upper limit and the SiO₂/Al₂O₃ ratio for the sample, this translates into 0.08 carbons per acid site. (Using the SiO₂/Al₂O₃ ratio of 30 for the zeolite, the catalyst contains a theoretical maximum of 1.04 mmol of acid sites per gram based on the Al content used in synthesis.) One would suspect that the carbon remaining in the catalyst would be proximate to an acid site since it is the structure directing template which forms the acid site. This ratio of 0.08 C/acid site must be further divided by a factor of 2 to obtain the smallest olefinic contaminate, resulting in the possibility of 0.04 ethylene/acid site. This number is sufficiently small to rule out the carbon contamination in the catalyst from having a role in exchange in stoichiometric ratios, especially with the added fact that it would be highly unlikely that ethylene would remain in the catalyst after our calcination procedure. In reality, remaining hydrocarbons in the catalyst would probably be aromatic, leading to the smallest possible unit of six carbons, and thus reduce the ratio by an additional factor of 3. If aromatic species were present in the catalyst, it is unlikely that they would initiate or mediate H/D exchange between the catalyst

and isobutane. It is more likely that the aromatic would exchange with the catalyst itself, excluding the isobutane from the process. From the H/D exchange work, since the aromatics would be natural abundance (their protons would be 99.985% ^1H and 0.015% ^2H (D)), there would be no loss of the acidic site of the zeolite. In addition to preferential exchange with the aromatic ring, if we again limit the rings to being the smallest size, six carbons, it is known that this molecule fits snugly inside the channels of H-ZSM-5. For this reason, the presence of such an aromatic at the acid site would sterically prohibit the adsorption of isobutane at the acid site thereby prohibiting exchange.

3.4 Conclusions:

Isothermal H/D exchange was monitored between perdeuterated isobutane and H-ZSM-5 by ^1H MAS NMR spectroscopy. Both the reactant signals and product signals were monitored, and consistent kinetic data was obtained from each signal suggesting a direct exchange mechanism. The rate law was found to be first order in the concentration of $[\text{H}^+]$. Rate constants were calculated for a range of temperatures allowing for the determination of the activation energy through the use of an Arrhenius plot. The activation energy was determined to be 57 kJ/mole, considerably lower than traditional Olah carbonium ion chemistry, yet significantly higher than the energy of protonating an olefin. The zeolite samples were also found to be free of a sufficient amount of residual carbon following calcination to facilitate exchange.

Chapter 4: GC/Micro-Reactor Pulsed Alkane Reactions

4.1 Introduction:

For the mechanism under study, carbon-carbon bond reactions could interfere with the obtained H/D exchange results. A concerted mechanism for carbon skeletal rearrangement in addition to H/D exchange could complicate the H/D exchange mechanism. Although this type of carbon-carbon bond breaking/forming chemistry would not be expected at the low temperatures monitored, neither was the H/D exchange expected. The following pulsed reactions were performed to rule out the possibility of skeletal rearrangements.

4.2 Experimental:

Reactor data were collected on an in-lab built micro reactor system (see **Figure 33.**) The system contains one six-port two-position Valco injection valve for loading and injecting the test gas (in the future, a second valve will be added to allow for dual feeds), a stainless steel reactor which is heated in a tube furnace, a thermal conductivity detector (TCD) allowing for timing of sample collection, and a second six-port two-position Valco valve used in conjunction with a Valco multi-position collection valve with six 250 μ L collection loops after the reactor which is used to collect up to 5 samples of the reactor effluent and analyze them offline. There is also a bypass valve before the second Valco six-port two-position valve which can be used to send the effluent from the reactor straight to the GC for analysis. The injection loop on the first Valco valve can be changed to allow for various amounts of test gas to be injected onto the catalyst bed. The amount of gas used varied both with the amount of catalyst loaded in the bed and with the desired stoichiometric ratio of

acidic sites in the catalyst per molecule of test gas. ZSM-5 samples were calcined in the reactor for 12 hours at 500°C at a flow rate of 40 SCCM. Experiments were performed by maintaining the catalyst bed at a set temperature and pulsing an amount of test gas through the bed. The catalyst bed was allowed to equilibrate at the experimental temperature no less than 30 minutes prior to injection.

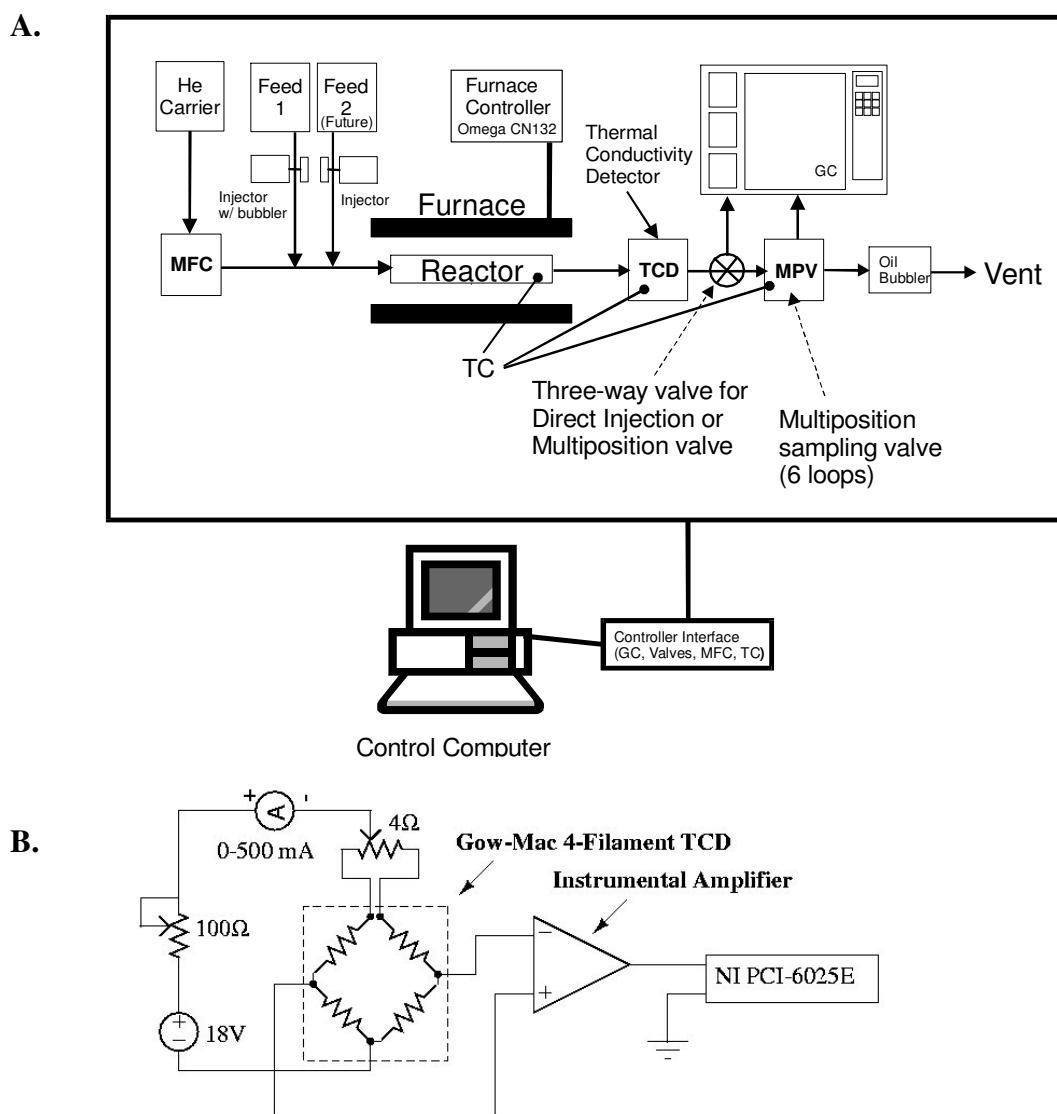


Figure 33. A. Schematic of microreactor configured for computer-controlled pulsed reagent/fixed catalyst bed and multi-loop sampling operation. B. Schematic of TCD device constructed from individual components.

The effluent samples were either sent to the collection loops for off-line analysis after completing the experiment, or were sent directly into the GC using the bypass valve. The GC was a model HP 5890 GC FID fitted with a Restek 50 meter, 0.53mm ID Rt-Alumina column. The heating program for the GC was to maintain the temperature at 40°C for 3 min after the start of the run, ramp up 5°C/min to 180°C, and maintain 180°C for 12 min. To allow for injection from the reactor system, the carrier gas for the GC was routed through the second Valco six-port two-position valve and back to the GC column. The bypass valve was also connected to the tube returning the carrier gas back to the column for the direct injection runs. Using the carrier gas as the carrier for both the GC column and the second Valco six-port two-position valve eliminates the backpressure problem which could arise from having two carriers meet at the column. The Valco six-port two-position valve allows the carrier to flow through the GC in both of its positions, with the only difference being in one of the positions it is directly routed to the column, and in the other, the gas flows through the multi-position valve, then back to the column.

Sample collection using the multi-position valve was triggered by the TCD (see **Figure 34** for representative images of typical TCD output.) The timing for maximum sample collection was determined by picking an arbitrary trigger value on the TCD, in our case 2.00 V, and then collecting samples at various times after the trigger to determine which time would give the largest sample of the effluent for GC analysis. The process of changing position on the multi-position valve takes around 2 seconds, so this dictates how close two samples can be taken to one another. Normally this is not an issue as only one sample is taken per pulse, but for this calibration where it is necessary to collect samples in rapid succession, one must take this into account. For this reason, three sets of experiments were

performed using 8 mg of HZSM-5 at a temperature of 450°C and pulsing isobutane over the catalyst. Previous direct injection tests had indicated that a variety of chemistry takes place with these reactants at this temperature, and a large number of products result. The collection timings for these experiments were as follows: Experiment 1: the position of the valve was changed 3 s after a 2.00 V signal on the TCD, and then 6 s, 9, 12, and 15; Experiment 2: 4 s, 7, 10, 13, and 16; Experiment 3: 5 s, 8, 11, 14, and 17. The injection amounts were the same for each experiment, and GC was performed immediately after collection for each experiment.

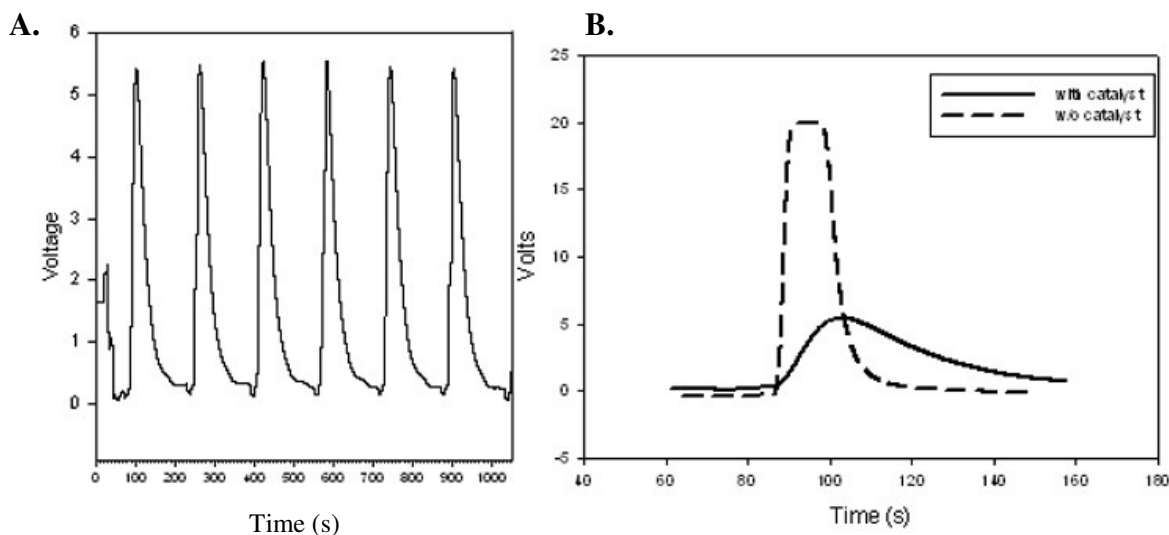


Figure 34. A. Output from thermal conductivity detector (TCD) for repetitive pulses of isobutane over a reactor filled with catalyst at 150°C. (B) Expanded TCD output of a single pulse for a reactor filled with catalyst (solid line) versus an empty reactor (dashed line).

Retention times were calibrated by loading the multi-position valve with a standard gas mixture followed by GC Analysis of the sample. Three standard gas mixtures were used, the first was a mixture of 1000 ppm each of methane, ethane, propane, n-butane, n-pentane, and n-hexane in He; the second was a mixture of 1000 ppm each of ethene, propene, 1-

butene, 1-pentene, and 1-hexene in He; and the last was a mixture of 15 ppm each of 2,2-dimethylbutane, 2,2-dimethylpropane, isobutane, 2-methylbutane, 2-methylpentane, and 3-methylpentane in N₂. GC analysis was performed immediately after loading the valve and the retention times of each peak were noted.

4.3 Results and Discussion:

The multi-position valve collection calibration procedure allowed for a sampling of effluent from 3s to 17s in 1s intervals after the thermal conductivity detector (TCD) trigger. Inspection of the chromatograms indicated that the “largest” peaks were in the one 6s after the trigger. In this chromatogram, the 15 peaks with the largest integrated areas were noted, and their areas were recorded for each of the other chromatograms. Plotting these values verses time gave the “effluent” pattern for each species showing how each species eluted from the reactor over time (see **Figure 35A**). Because of the large diversity in peak areas, each set of peak data was normalized by dividing each area by the peak’s largest area. Plotting these values verses time showed that not all species were collected at their maximum amounts at the same time. There were two times that peaks reached their maximums, some peaked at 6 seconds, the others at 8 seconds (see **Figure 35B**). More peaks reached their maximum values at the 6 second collection time, so this was the collection time used for all subsequent experiments.

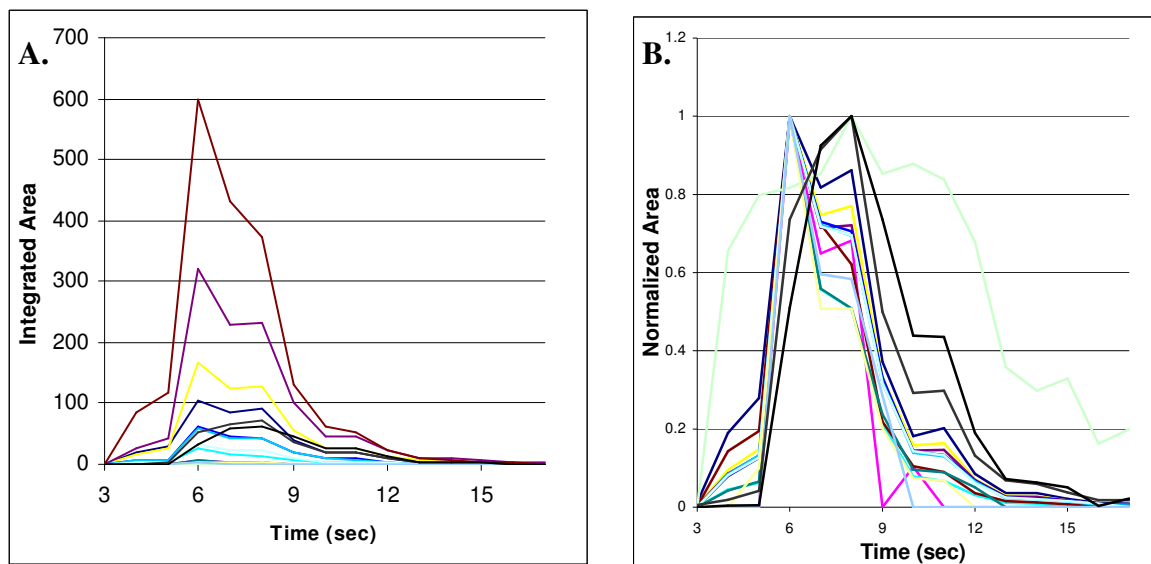


Figure 35. A. Elution pattern of effluent from reactor used for calibration. B. Normalized elution pattern of effluent from reactor used for calibration. From this plot it is apparent that there are two different maximum signal times.

Reactor experiments were carried out in 50°C increments from 100°C to 550°C, pulsing 1 equivalent of isobutane per acid site on H-ZSM-5. **Figure 36** shows a representative chromatograph at 500°C. These experiments revealed that at room temperature and below, no operative carbon-carbon rearrangements occur. The fact that these reactions do not occur at temperatures below 150°C rules out the possibility of carbon chemistry interfering with or playing a role in the previously observed H/D exchange mechanism results.^{51,59} Additional peaks become apparent in the chromatograph at temperatures greater than 200°C. The overall performance of the catalyst was evaluated by plotting percent conversion verses temperature (see **Figure 37**). At 500°C, a variety of different products are formed, including the aromatic species benzene and toluene. Unfortunately, while the percent conversion is high at 500°C (86.4%), the majority of the

products formed using H-ZSM-5 are from hydrocarbon cracking rather than alkylation (methane, ethene, and propene represent 86.5% of the products.)

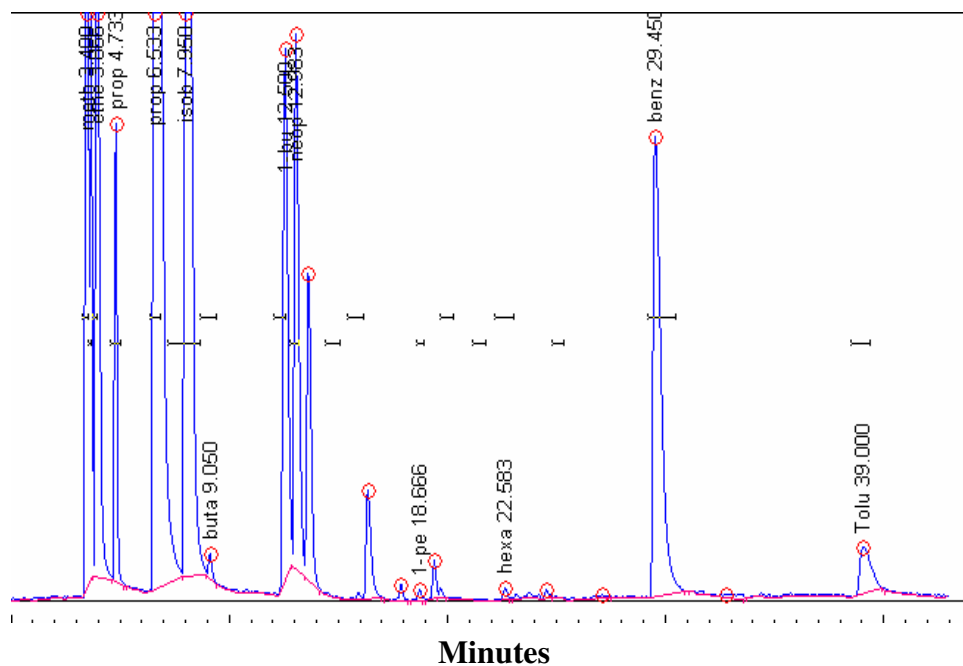


Figure 36. Gas Chromatogram of the effluent from the microreactor following a 1 equivalent of isobutane per acid site pulse while maintaining the catalyst bed at 500°C. There are many different mechanisms active during this experiment including hydrocarbon cracking, alkylation, and aromatization.

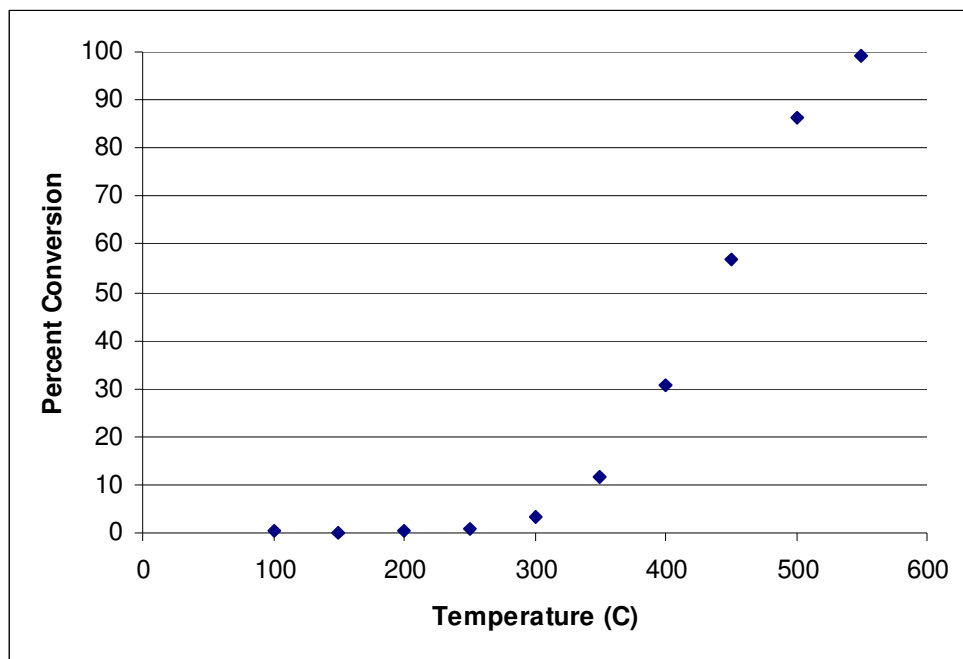


Figure 37. Percent conversion plotted as a function of temperature. Experiments at 100°C and 150°C show no conversion, but at 200°C, a couple of small product peaks become visible. At 300°C and above, there are numerous peaks present.

4.4 Conclusions:

Reactions of isobutane on H-ZSM-5 catalyst were monitored via GC analysis coupled with a pulsed microreactor system. The onset of carbon-carbon bond chemistry was determined to be around 200°C. At lower temperatures, a range of alkylation products were observed, in addition to some cracking products. At higher temperatures where total conversion was larger, cracking products were favored; conversion to benzene and toluene was observed. No appreciable carbon-carbon bond chemistries were found to be active at room temperature and below, indicating H/D exchange occurs in the absence of these rearrangements. The processes used for testing the total conversion of isobutane by the catalyst can now be repeated as a routine catalyst evaluation tool.

Chapter 5: Evidence for a Direct Protonation Exchange Mechanism

The key results mentioned in previous chapters (the absence of olefins in isobutane gas; the formation of an adsorption complex between the isobutane and the catalyst; the absence of sufficient carbon to initiate/mediate exchange and unlikeliness of such a species' presence initiating/mediating exchange; reactor data indicating that structural isomerizations, cracking, alkylation, etc. do not occur for isobutane in H-ZSM-5 at the temperatures H/D exchange was observed at by the NMR work; and the consistent kinetic data from the primary acid site and methyl peaks) all suggest a direct protonation step for the H/D exchange at the relatively low temperatures where exchange was observed. Classical superacid chemistry would predict that the protonation of the molecule would occur preferentially at the methine position forming a pentavalent carbonium ion which is stabilized by the three connected electron donating methyl groups (see **Figure 38**). This species would then lose H₂, or in this case H-D, and form a tert-butyl carbenium ion. The initial protonation would have an appreciable reverse reaction (illustrated with rate constant k_{-1} .) The reverse reaction should result in the evolution of a methine ¹H signal for isobutane (the methine's peak would be at 1.8 ppm.) The absence of exchange at the methine position rules out direct protonation of the tertiary site. The lack of exchange at the methine position is also reported in similar experiments in the recent literature giving further evidence against the reaction scheme in **Figure 38**.¹⁰ In addition, it would not be expected that the relatively bulky isobutane molecule would be able to accommodate this type of exchange at the methine position inside the channels of H-ZSM-5. Recent calculations have ruled out the possibility of the formation of tert-butyl carbenium derived alkoxy species from the reaction

of isobutene with the acid site because of the steric constraints of the rigid channel walls.⁶⁰ The researchers for the study mentioned found that rather than the formation of this alkoxy intermediate, the protonated isobutene remained a tert-butyl carbenium ion and was stabilized by the lattice. In the same publication, the authors found that at low enough temperatures, the alkoxy species does have a lower energy than the lattice stabilized carbenium ion, but the carbon-oxygen bond is formed at the methyl position rather than the methine. Though the isobutane would not have to adsorb as closely to the acidic site for the exchange in **Figure 38** as the alkoxy species, it would still have to be in very close proximity to the acid site and hence should encounter the same steric hindrance as the alkoxy, thereby prohibiting direct protonation of the methine position by the catalyst. Other recent studies have shown H/D exchange between perdeuterated propane and H-ZSM-5 at both the methyl and methylene positions.⁶¹ It is important to note, however, that the mentioned studies monitored exchange at temperatures of or greater than 210 K above the exchange we monitored for isobutane. At these high temperatures there are many other mechanisms of alkane activity

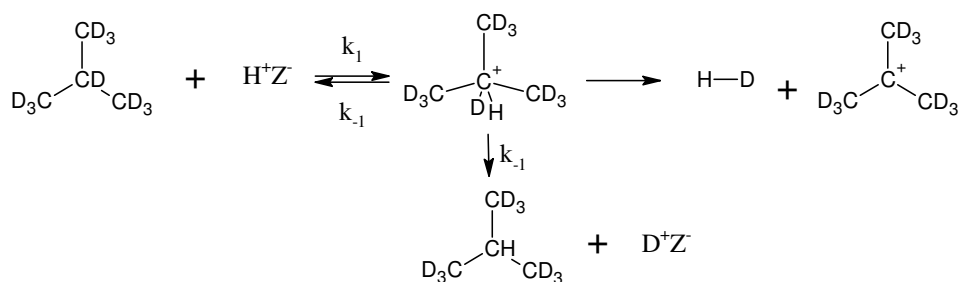


Figure 38. Proposed reaction scheme 1. Direct protonation via classical Olah superacid chemistry.

including skeletal isomerization/rearrangement. From our ^{13}C NMR data and pulsed microreactor experiments, we have seen that at temperatures for which we monitor H/D exchange, there are no backbone rearrangement mechanisms active. However, at temperatures only 150 K higher, reactions involving carbon-carbon bond cleavages and/or formations can occur (see **Figure 39**.) For this reason, the results at the higher temperatures could be the result of a multi-step process involving H/D transfer, followed by skeletal rearrangement giving the appearance of exchange at both positions, or it could be from true H/D exchange at both sites. Indeed, Stepanov, et. al. monitor ^{13}C label scrambling for propane in the publication at the same temperatures the H/D exchange is monitored.⁶¹ Our results eliminate the possibility of these rearrangement mechanisms and hence are more conclusive for the purpose of H/D mechanistic determination.

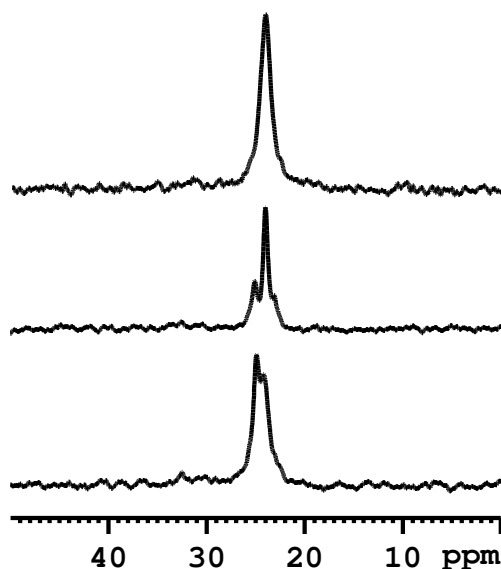


Figure 39. ^{13}C NMR (Bloch decay) spectra of 2- ^{13}C -isobutane adsorbed on H-BEA; (A) taken at room temperature immediately after adsorption, (B) taken after heating the sample to 423 K and allowing to equilibrate for 30 minutes, (C) taken at 310 K after allowing the sample to cool after (B).

An alternative to the previously discussed reaction scheme is illustrated in **Figure 40**. In this scheme, reaction occurs by direct protonation of the methyl groups of isobutane through a 5-center/4-electron bond transition state. The reaction initiates by adsorption of the isobutane at an oxygen adjacent to the acid site through a non-classical hydrogen bond of a C-H to the O.⁶² These weak interactions have been illustrated to be the driving force for the blending compatibility of certain polymers such as poly-(vinyl methyl ether) (PVME) and polystyrene (PS).⁶³⁻⁶⁶ (In the case of these polymers, it was found that the aromatic hydrogens interact with the oxygens of the ether linkages leading to an exothermic mixing.) This is followed by the formation of the 5-center/4-electron bond. After transfer, the isobutane emerges from the complex to yield $(\text{CHD}_2)\text{CD}(\text{CD}_3)_2$ and a deuterated acid site. The formation of the 5-center/4-electron bond is much less demanding on the system than traditional superacid carbonium ion, giving a virtually neutral carbon during the transition state, and never requiring more than a partially positive charge on the carbon from the hydrogen bonding leading up to and following the transition state. The adsorption of the methyl group is much less sterically hindered than the adsorption of the methine resulting in little/no steric interference for this process. Also unlike the previous scheme, the reverse reactions of any step in this scheme would not produce any H/D exchange at a position other than the methyl.

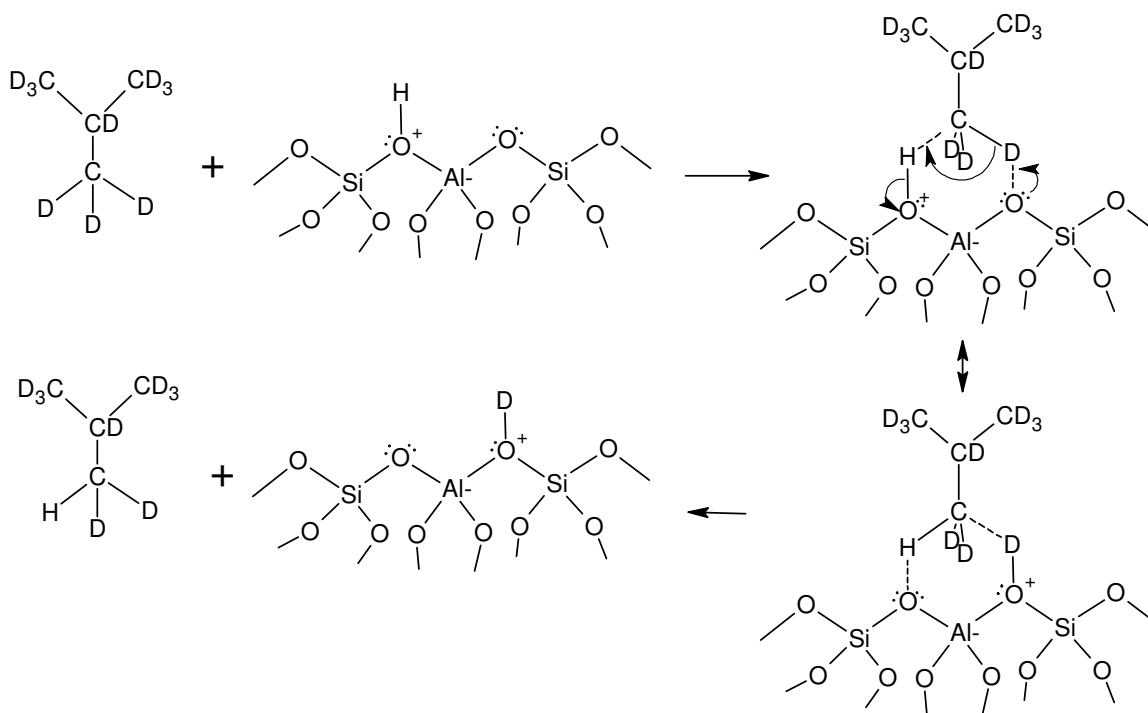


Figure 40. Proposed reaction scheme 2. Direct protonation at the methyl position invoking a 5-center/4-electron bond transition state.

Through collaboration with Dr. Laura S. Sremaniak and Dr. Jerry L. Whitten, the proposed mechanism illustrated in **Figure 40** was tested computationally.⁶⁷ Ab initio calculations were performed on a cluster model of the system at the Hartree-Fock self-consistent field/single determinant (HF-SCF) and the more rigorous configuration interaction multi-determinant (CI) levels of theory. The model invoked is illustrated in **Figure 41**, and consisted of two tetrahedrally coordinated silicon atoms with a tetrahedral aluminum joining. One of the bridging oxygens between the aluminum and silicon contained an attached proton, representing the Bronsted acidic site. Each of the dangling bonds was terminated with a realistic OH group to emulate an extended lattice structure. Other recent works have used terminating hydrogen atoms which are less realistic, but computationally less demanding. While this cluster model cannot represent all of the solvation and confinement effects of the

zeolite, it is necessary for this extensive level of computational theory. Sauer, et. Al. have recently illustrated the importance of modeling these effects as was previously discussed for the case of the protonation of isobutene.⁶⁰ For the purposes of this study, however, the importance of the interaction with the surface requires this stringent method to properly calculate an activation energy. Since the molecule isobutane fits comfortably inside the channels of H-ZSM-5, the most dominate interaction for this proposed mechanism should be that of the molecule with the acidic site and the closest atoms, and accurate calculation of this energy should give the desired values.

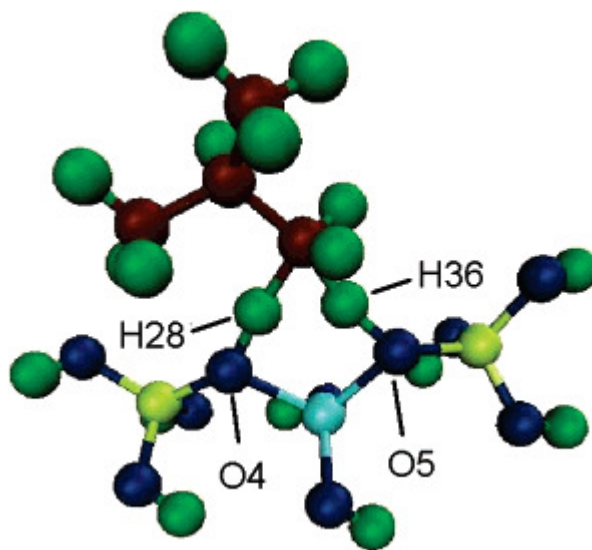


Figure 41. Optimized transition state of the model used in the discussed computations

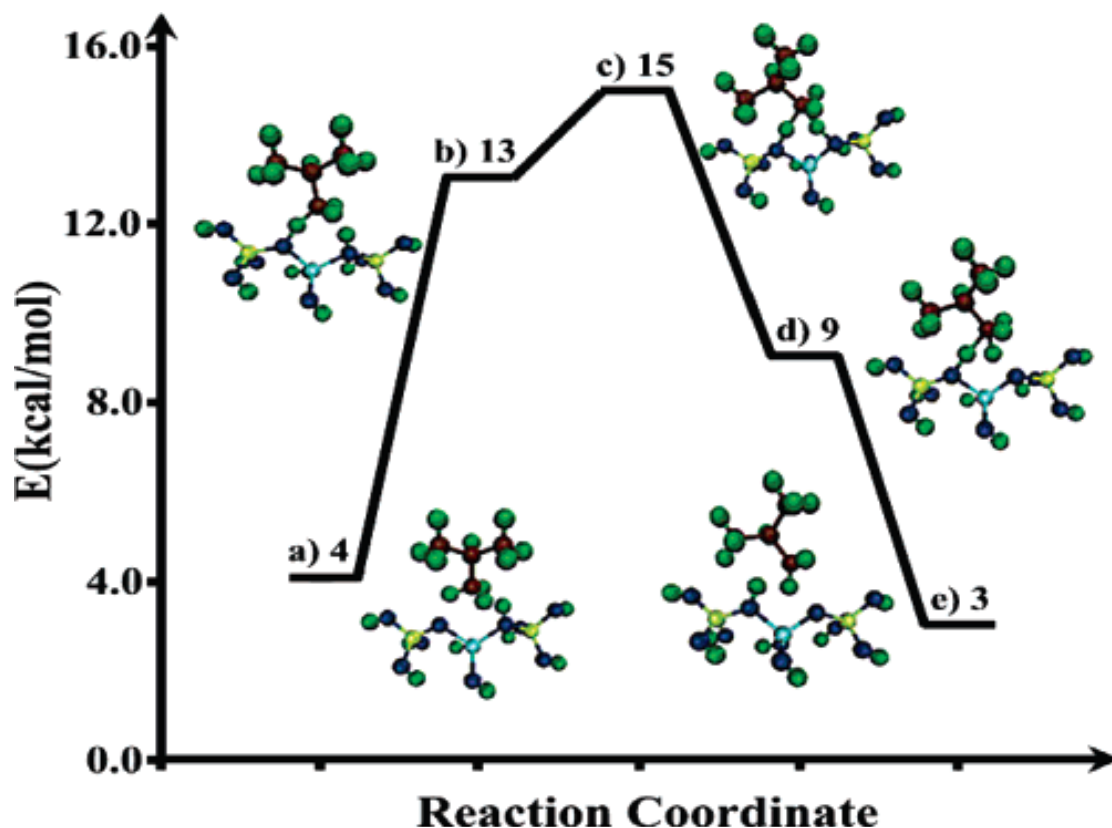


Figure 42. Calculated energy landscape for the proton exchange of isobutane and H-ZSM-5. Energies are relative to the values for desorbed isobutane.

Figure 42 illustrates the calculated energies of various points along the reaction pathway. The calculated activation barrier at the CI level was found to be 60.7 kJ/mol (14.5 kcal/mol). This number is in close agreement with the experimentally determined value of 57 kJ/mol. Interestingly, additional calculations performed where the molecule underwent more traditional Olah type carbonium ion chemistry without the stabilizing effects of the lattice resulted in an activation energy of 372 kJ/mol. This number is almost an order of magnitude larger than the observed barrier. This clearly indicates that the zeolitic lattice plays a more than trivial role in the overall exchange process. These results also show that even a small cluster model can be used to represent the main interactions between a zeolitic

Bronsted acid site and adsorbate, and can show the importance of these weak C-H to O hydrogen bonds to reaction mechanisms.

Chapter 6: H/D Exchange between Alkanes and Solid Acids Possessing Complex Acidic Functions

6.1 Introduction:

Much research has been conducted studying the utility of zeolites as acidic catalysts for a variety of reactions.^{3,68-72} Zeolites are cheaper and less hazardous than their liquid acid analogs. Zeolites are also easier to dispose of as they are environmentally benign. These benefits make zeolites highly desirable for processes for which they may be utilized, especially in high-volume industrial applications. Unfortunately, many mechanisms that are known for liquid phase catalysis are still unknown for the heterogeneously catalyzed case. These unknown pathways lead to undesirable side reactions, the formation of secondary products, and ultimately, catalyst deactivation through the formation of bulky polynuclear aromatics. Zeolites can be regenerated through relatively mild conditions, but for most processes, their useful lifetime between regenerations is too short for practical application. Only through the determination of alkane activation and reaction pathways on zeolitic catalysts can these side reactions be better controlled for the catalyst's broader implementation.

When considering the Bronsted acidic function of a zeolite, it is typically assumed that each site is identical for a particular catalyst. These sites should possess the same acidity and reactivity. This, however, is not always the case. In the zeolitic lattice, there are many different T-sites where aluminum may substitute. The zeolite ZSM-5, for example, possesses 12 crystallographically distinct T-sites. Theoretical studies have shown that in ZSM-5 there is no difference in acidity for Al in various T-site locations.⁷³⁻⁷⁸ Differential reactant accessibility to an active site may not be ruled out for example, the zeolite chabazite is a

typical “cage” zeolite possessing cages interconnected by a system of windows. There are two different sets of windows between the cages, differing by the number of T-atoms in the window. Al substituted in the larger window adjoining cages has been found to be more accessible to adsorbed probe molecules than in the smaller one.⁷⁹

The zeolite Y illustrates another complication of acidity in zeolites due to extraframework aluminum. When converting Y to what is referred to as “Ultra Stable Y” (USY), framework aluminum is extracted from the lattice, altering the acidity of the remaining sites. Authors have reported that after steaming and treating the catalyst with EDTA (ethylenediamine-tetraacidic acid), the predominate acidic site type in the catalyst was Bronsted. The intrinsic strength, however, of the sites was much higher than the original Y, more comparable to that of H-ZSM-5.²⁴ Recent reports have shown that the differences in acidity between USY and the parent Y are due to proximate Lewis and Bronsted acid sites.⁸⁰⁻⁸⁷ H-ZSM-5 possesses similar lattice defects that lead to differing acid sites.⁴⁹ In this case, two independent acidic sites are distinguishable via direct observation methods such as ¹H solid state NMR. These sites have been shown to exhibit different reactivities for certain adsorbates.⁵¹ This difference has been attributed to accessibility issues caused by the presence of the defect.

6.2 Experimental:

Beta (Si:Al=12.5) samples were obtained from Zeolyst International. Hexamethylbenzene was used to calibrate ¹H and ¹³C pulse widths, and for the cross polarization Hartman-Hahn match condition calibration. HMB was also used as a ¹³C chemical shift standard. Polydimethylsiloxane (PDMS) was used as a ¹H NMR chemical

shift standard and was obtained from Rheometrics Scientific, Inc. Isobutane-d₁₀ (99.1% D) and neopentane-d₁₂ (99.4% D) were obtained from CDN Isotopes. Purity of the gaseous samples was verified by GC analysis using a HP 5890 GC FID. Isobutane samples free of trace olefins were obtained by treating the as received reagents with D₂ (99.8% D, obtained from Isotec) over a 0.5% dispersed Pt catalyst on alumina obtained from Alfa Aesar. “Cleaned” samples were analyzed by GC to verify the removal of olefinic impurities.

Beta samples were prepared for NMR experiments by a ramped dehydration procedure. Beta was loaded into a quartz reactor tube and evacuated to 10⁻³ torr. Samples were heated under vacuum using a temperature ramp/soak controller via the following gradual heating program: room temperature to 100°C at 1°C per minute, hold at 100°C for 2 hours, 100°C to 200°C at 1.7°C/min, hold at 200°C for 1 hour, 200°C to 300°C at 1.7°C/min, hold at 300°C for 1 hour, 300°C to 400°C at 1.7°C/min, hold at 400°C for 1 hour, 400°C to 450°C at 1.7°C/min, hold at 450°C for 12 hours, and then power off. The temperature controller was a 6-zone ramp/soak controller, model CN616 purchased from Omega Engineering, Inc. The zeolite samples were sealed under vacuum, and placed into a glovebox. Zeolite sample preparations were verified via ¹H magic angle spinning (MAS) NMR in a 4mm zirconium oxide rotor. Verification is important because zeolites are prone to dealumination if heated too rapidly in the presence of moisture.

40-45 mg of H-Beta were loaded into a 7 mm zirconium oxide rotor inside the glovebox. The filled rotor was placed in a CAVERN type apparatus.⁴⁸ This device allows the sample to be loaded with a gaseous reagent and sealed in the MAS NMR rotor without being exposed to the external atmosphere. The CAVERN is critical to this work as trace amounts of moisture can cause detrimental effects in the ¹H spectrum through both rapid

exchange with the acid site, causing broadening of the peak, as well as the added complexity of an additional signal from the water itself. The CAVERN was attached to the vacuum line and evacuated to 10^{-3} torr. A slight overpressure of the gas was delivered to the line and the test gas was allowed to adsorb onto the sample. Stoichiometric adsorptions were performed of one adsorbate molecule per Bronsted acid site. Absorption amounts were determined using theoretical acid site densities determined from the Si/Al ratio of the samples. After the desired pressure of gas had been delivered, the rotor was sealed and promptly inserted into the spectrometer.

NMR data were obtained on a Bruker DSX 300 MHz spectrometer using MAS at the rate of 8 kHz with 4 mm rotors and rates of 4.5 kHz with 7 mm rotors. ^1H NMR spectra were acquired using the Carr-Purcell type echo pulse consisting of a $\pi/2_x$ pulse, a delay, τ , a π_y pulse, and lastly another delay, τ , for the refocusing of the magnetization. The τ periods used were equal to one rotor period.

6.3 Results and Discussion:

H-Beta is known to have a complicated acidic function.⁸⁸ **Figure 43** indicates H-Beta's acidic function has a ^1H NMR signal which is much smaller and broader than in H-ZSM-5, and appears to have at least two different acidic site environments. **Figure 44** shows the spectra of H-Beta 5 minutes after the adsorption of 1 equivalent of perdeuterated isobutane per acid site. By comparison with the neat spectrum, it is apparent that at least one of the acidic sites forms an adsorption complex with the gas similar to that observed with H-ZSM-5. This is evidenced in the appearance of a signal at approximately 4.6 ppm and the absence of a signal at 4.2 ppm. The silanol at 1.8 ppm serves as a good reference for

comparing the two spectra as it does not interact with the adsorbate molecule. The small methyl peak at 0.9 ppm is from the small amount of exchange prior to acquisition of the first experiment. The second acidic site's interaction with isobutane is difficult to gauge as the signal is much broader, though it appears to not shift downfield. This behavior is similar to the case of ZSM-5, where the more deshielded acidic proton does not exhibit the same downfield shift as the primary.^{51,59} The 0.4 ppm downfield shift is considerably smaller than the 1.0 ppm shift observed for isobutane in H-ZSM-5.

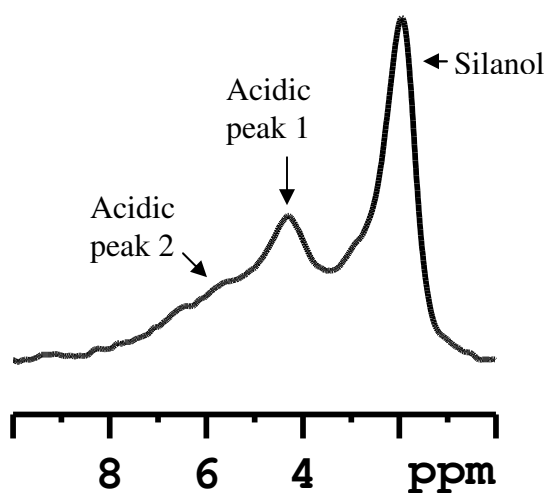


Figure 43. ¹H NMR spectrum of neat H-Beta

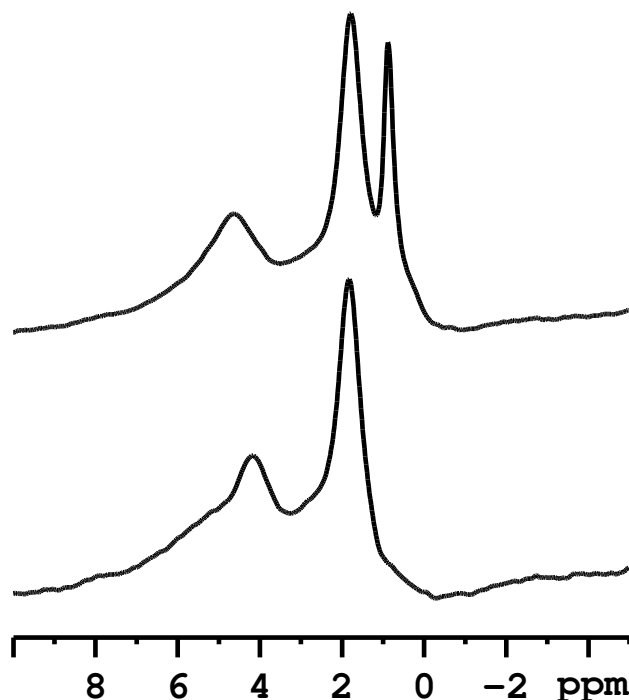


Figure 44. Top: ^1H NMR spectrum of H-Beta with 1 equivalent of isobutane- d_{10} per acidic site adsorbed. The peak at 0.9 ppm is from the methyl group of isobutane for the amount of exchange which has occurred. This spectrum was acquired 300 seconds after adsorption. Bottom: ^1H NMR spectrum of neat H-Beta for comparison.

After only 5 minutes at room temperature, there is already a substantial amount of exchange which has taken place. **Figure 45** follows the ^1H NMR spectrum of the sample as the reaction progresses in time. The equilibrium spectrum, taken after 24 hours, is not included in the stackplot as the methyl signal would be significantly off scale. Note that as the reaction progresses, both acidic peaks decrease. This is contrary to what was observed in the case of H-ZSM-5 where the secondary acidic site seemed not to participate in exchange. The H/D exchange results, however, do indicate that both sites are accessible to the isobutane. The H/D exchange process is regiospecific to the methyl groups of isobutane determined by the absence of a methine peak at 1.8 ppm. This regiospecificity is the same as observed for H-ZSM-5, suggesting that although the Beta possesses larger pore diameters

than ZSM-5, the steric constraints of the methyl groups approaching the wall still prevent exchange at the methine position.

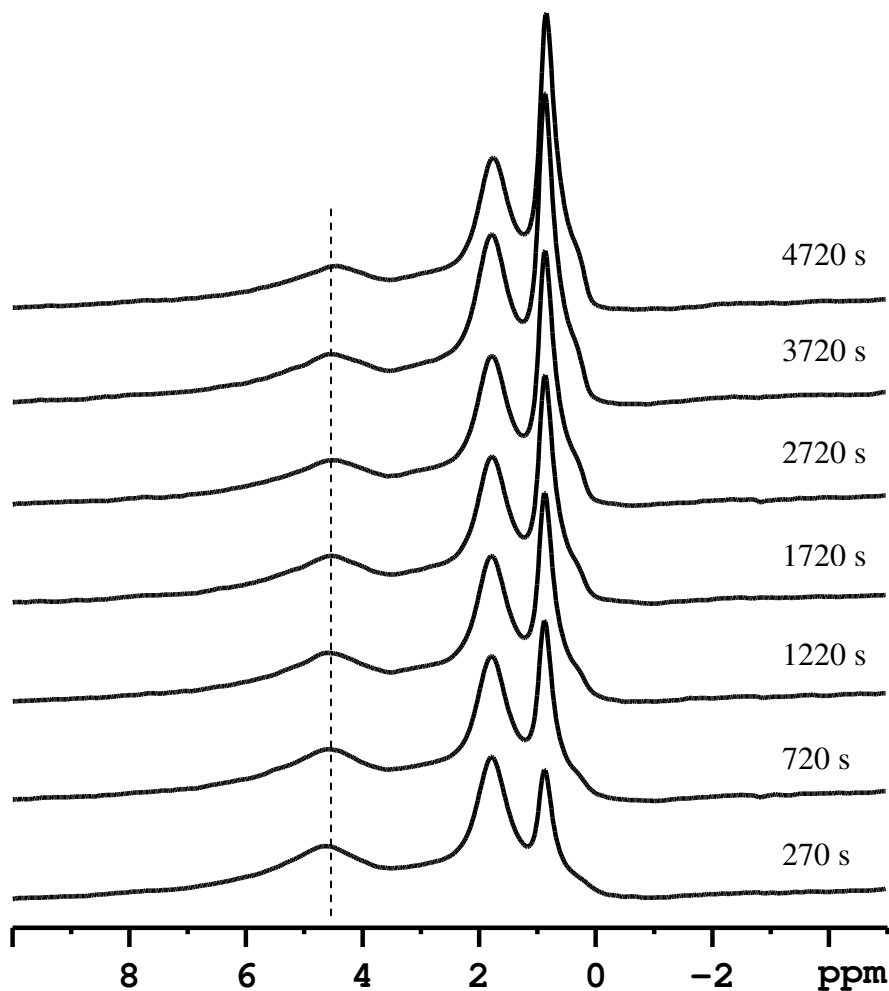


Figure 45. Series of selected in-situ ^1H MAS spectra acquired at 300 K following the adsorption of 1 equivalent of isobutane- d_{10} per acid site on H-Beta. The time shown to the right of each spectrum is the total time following adsorption.

Figure 46 shows the semi-logarithmic plot of the peak area for the methyl peak of isobutane at 300 K. The rationalization of the rate law follows the same concepts as for H-ZSM-5, yielding the same equation and limitations/conditions for the H-Beta data fitting. The complex acidic function of Beta makes the integration of the acidic sites difficult. For

this reason, only the methyl groups were used when calculating H/D exchange rate constants with adsorbed gases; though the fate of the acidic site was also monitored. The slope of the semi-logarithmic linear regression at 300 K is $-2.7 \times 10^{-4} \text{ s}^{-1}$. After the initial 5 points shown in the figure, the rate law reaches its breakdown point similar to that observed for H-ZSM-5.⁵⁹ When additional points were added to the regression, the R^2 value dropped off drastically, illustrating that the breakdown of the rate law had been reached. The value of the rate constant is slightly smaller than observed for H-ZSM-5 at room temperature ($4.1 \times 10^{-4} \text{ s}^{-1}$), consistent with H-Beta's lower acidic strength.^{55,89}

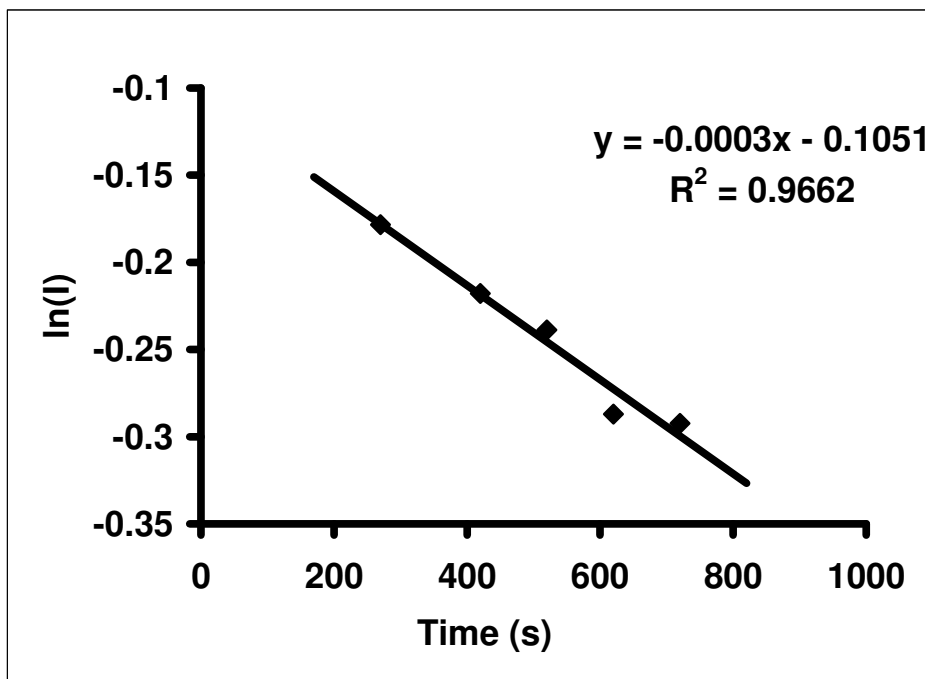


Figure 46. Semi-logarithmic plot of peak area versus time for the spectra acquired at 300 K. The isobutane peak is plotted as $y = \ln[1-I(t)/I_{\infty}]$.

Isothermal kinetics runs were also performed at 308 K and 315 K. The rate constants were determined to be $5.7 \times 10^{-4} \text{ s}^{-1}$ and $1.0 \times 10^{-3} \text{ s}^{-1}$, respectively. These values are in

reasonable agreement with the H-ZSM-5 data. An Arrhenius plot of these values (see **Figure 47**) was used to calculate an activation barrier of 16.8 kcal/mol (70.2 kJ/mol). This value is slightly larger than the barrier observed for H-ZSM-5. The higher barrier is indicative of slightly weaker acidic strength for Beta, and is still in close agreement with the theoretically determined value for a direct hydron exchange mechanism.⁶⁷ More importantly, this value is even more isolated in magnitude from some alternative pathways available for activation of the H/D exchange process. Olah dehydrogenation of isobutane performed by a superacid has a barrier of 222.6 kJ/mol,⁵² and the protonation of a contaminate olefin to a carbenium ion is 30 to 45 kJ/mol.^{53,54} The isolation of the activation barrier suggests a unique mechanism of exchange independent of these alternative pathways.

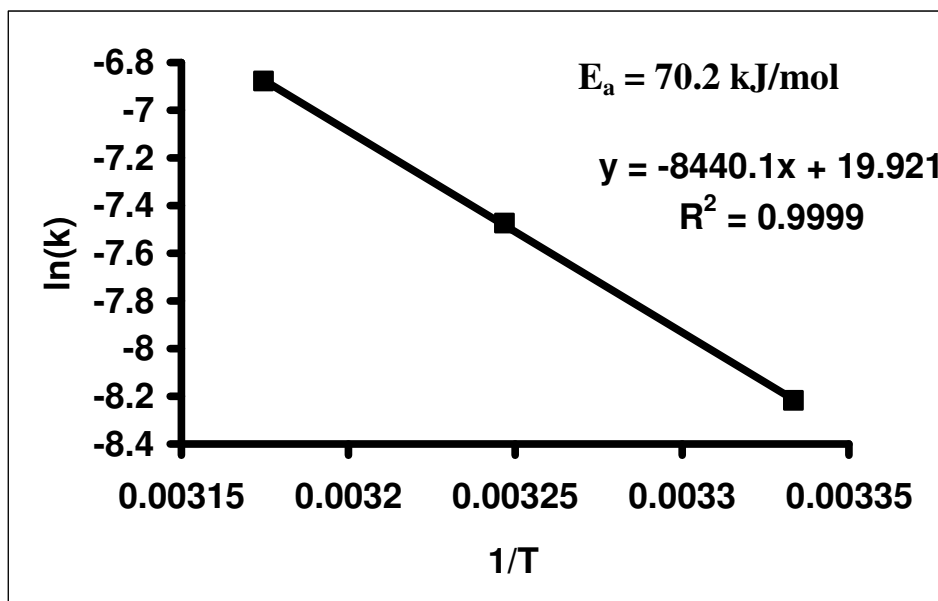


Figure 47. Arrhenius plot for H/D exchange between H-Beta and perdeuterated isobutane

Neopentane-d₁₂ produced a similar downfield shift of the first acidic site upon adsorption (see **Figure 48**.) The first acidic peak component appears at 4.8 ppm in the

adsorbed spectrum. This represents an approximate 0.6 ppm downfield shift. The second component remained at its neat spectrum location. While overall the adsorbed spectra of both isobutane-d₁₀ and neopentane-d₁₂ appear similar, neopentane produces a ~50% larger shift than observed for isobutane. Most likely this effect is due to neopentane's larger volume, forcing the molecule in closer proximity to the walls/acid sites.

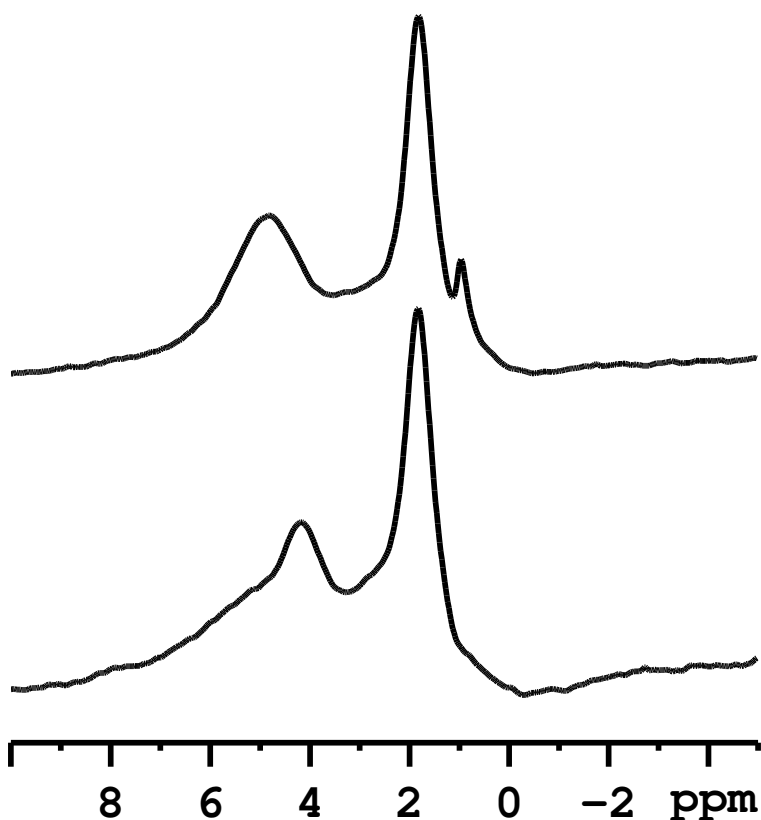


Figure 48. Top: ¹H NMR spectrum of H-Beta with 1 equivalent of neopentane-d₁₂ per acidic site adsorbed. The peak at 1.0 ppm is from the methyl group of neopentane from a trace amount of residual ¹H in the as received gas. This spectrum was acquired 180 seconds after adsorption. Bottom: ¹H NMR spectrum of neat H-Beta for comparison.

A small amount of a methyl signal was observed from residual hydrogen from the gas; no exchange was detected at room temperature. When heated to 350 K and maintained for an hour, no appreciable exchange was noted. The inability of neopentane-d₁₂ to

appreciably exchange with the catalyst at these elevated temperatures is probably due to steric interactions with the walls. Neopentane fits comfortably in the BEA framework. Though the two gases differ by only one methyl group, neopentane is more spherical than isobutane. The spherical shape most likely hinders it from adopting the necessary position for our direct exchange mechanism inside the channels. Indeed, a recent article presented an exchange rate of approximately $3.70 \times 10^{-9} \text{ s}^{-1}$ with neopentane on D-Beta (perdeuterated H-Beta) at a temperature of 523 K (a temperature unobtainable by our current NMR probes.)⁵⁵ At these higher temperatures where neopentane and the zeolitic lattice are much more flexible, the authors reported direct exchange in the absence of carbon-carbon bond chemistry.

6.4 Conclusions:

Isothermal H/D exchange was monitored between perdeuterated isobutane and H-Beta by ^1H MAS NMR spectroscopy. The product signals were used for kinetic data; and the fate of reactant signals was also monitored. The rate law was found to be first order in the concentration of $[\text{H}^+]$. Rate constants were calculated for a range of temperatures allowing for the determination of the activation energy through the use of an Arrhenius plot. The activation energy was determined to be 70.2 kJ/mole, considerably lower than traditional Olah carbonium ion chemistry, yet significantly higher than the energy of protonating an olefin. The activation barrier was slightly higher in energy than that observed for perdeuterated isobutane on H-ZSM-5, which is consistent with a weaker intrinsic acidic strength. Perdeuterated neopentane did not appreciably exchange with the catalyst at

temperatures up to 350 K. This was attributed to the molecule's sterically hindered shape not allowing for proper orientation for exchange at these temperatures.

Chapter 7: Zeolitic Aqueous Phase Catalysis

7.1 Introduction:

The field of acid catalysis is vast.⁹⁰⁻⁹⁴ Presently, many acid catalyzed reactions are carried out using strong liquid acids. These acids provide a high intrinsic acidic strength and an adjustable pH by simply varying the acid concentration, making such acids excellent catalysts for a wide range of reactions. Unfortunately, the same properties which make such species good catalysts also make them quite hazardous. Special precautions must be made for carrying out reactions involving such acids, as well as for the disposal of the catalysts after being spent. In the example of alkylate formation, H_2SO_4 and HF stand as excellent catalysts for the formation of these clean burning fuel additives. However, because of their dangerous nature, safer heterogeneous methods have been sought, though the goal of using a solid acid such as a zeolite for this process has not yet been achieved.

In the field of heterogeneous catalysis, there is typically an emphasis on keeping the catalyst moisture free. Indeed, few studies have been conducted on the behavior of solid acids in the presence of a reactant and water.⁹⁵ The studies that have been conducted have used minimal amounts of water, thereby treating it as a reagent, or performed simple liquid reactions such as water addition to an olefin. In some reactions such as dehydrations of alcohols in flow reactors, water arises in the system as a product, but it is produced in small quantities and quickly removed from the catalyst by the carrier gas. While keeping the catalyst dry is important for mechanistic studies not involving water, as well as in preventing dealumination when maintaining the catalyst at elevated temperatures, there is no reason preventing a zeolite's use in an aqueous catalytic reaction at moderate temperatures. In this study, we have monitored the use of the zeolite ZSM-5 as an aqueous phase acidic catalyst,

and have compared its reactivity for organic reactions to that of differing concentrations of strong liquid acids. In doing so, we have defined a new “effective pH” resulting from the concept of a “tethered” acidic site in a fixed volume, preventing the complete uniform dilution of the acid concentration into the total volume of solution. In addition, the tethered acidic site remains inside the channels of the zeolite, thereby maintaining the shape selectivity of the catalyst.

7.2 Experimental:

ZSM-5 (Si/Al=15) samples were obtained from Zeolyst, and 99.9% 2-butanol was obtained from Fisher. Purity of the 2-butanol was verified by GC analysis using a HP 5890 GC with flame ionization detection. Concentrated HNO₃ was obtained from Pharmco and was diluted to the desired concentrations. Calcined, acidic zeolite samples were prepared from the ammonium form in a stainless steel reactor body under flowing dry air. The temperature controller was a 6-zone ramp/soak controller, model CN616 purchased from Omega Engineering, Inc. The ZSM-5 samples were heated via the following procedure: room temperature to 150°C at 2°C per minute, hold at 150°C for 2 hours, heat the sample from 150°C to 450°C at 6°C/min, hold at 450°C for 12 hours, and then power off.

Batch reactions were carried out in a 125 mL acid digestion bomb lined with a Teflon cup obtained from Parr Instrument Company. The reactor used a modified cup top made from stainless steel. The top was fitted with a ¼” stainless steel tube attached at the center. The tube connected to the inside of the cup and protruded from the top of the bomb 3”. A ¼” Swagelok valve was attached to the tube, and a standard GC septum and nut were fitted to the valve. This apparatus allowed for reactions to be performed at elevated temperatures and

pressures in a tightly sealed vessel; then allowed for gas sampling for GC analysis by opening the valve to the septum.

Theoretical acid site concentrations obtained by using the Al content of the zeolite were used in determining the concentrations of the HNO₃ solutions. For Si/Al equal to 15, the corresponding acid density was 1.04mmol H⁺/gram. Solutions were prepared for a 1:1 acid site comparison between the zeolite and the liquid acid at the same total volume, producing the same theoretical concentration of H⁺. Concentrated HNO₃ solutions with 25 times more H⁺ per unit volume than the zeolite solution were also prepared. Fixed amounts of 2-butanol were added to each of the runs. In a typical run, 25.0 mL of 0.04 M HNO₃, 25.0 mL of 1.0 M HNO₃, or 25.0 mL of H₂O and 0.963 g of ZSM-5 were added to the bomb with 5.0mL of 2-butanol. The digestion vessel was heated to 150°C for 5 hours with stirring by a magnetic stir bar, and then cooled at room temperature. Liquid aliquots from the HZSM-5/water reactions were filtered with a 0.2 um filter prior to analysis. Liquid GC samples were acquired under vigorous stirring of the product solution to ensure sampling consistency. Sample volumes for liquid samples were 10 uL and gas samples were 5.0 mL. GC analysis was performed on a HP 5890 GC with flame ionization detection using a Varian PoraPlot Q column. GC/MS was performed on a HP GCD with electron ionization detection. Gaseous GC/MS sample volumes were 1.0 mL. Total conversion to gaseous species was determined by volume measurements of the products. Total liquid phase conversions were determined by comparing integrated areas of all GC peaks.

7.3 Results and Discussion:

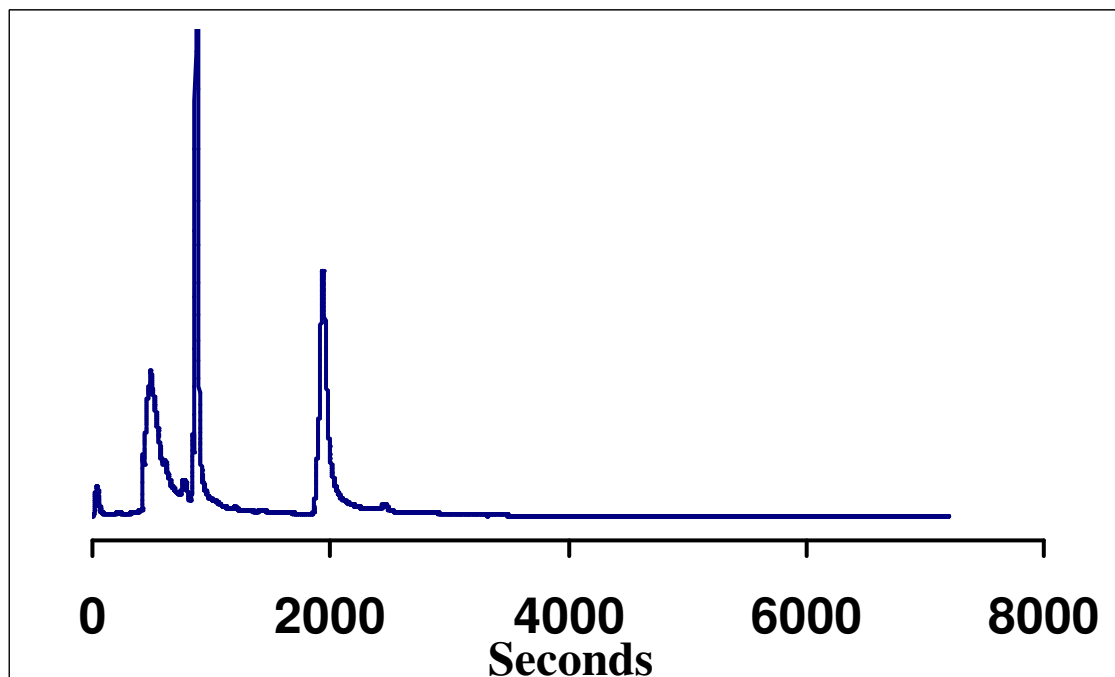


Figure 49. Aqueous phase products from a representative H-ZSM-5 run

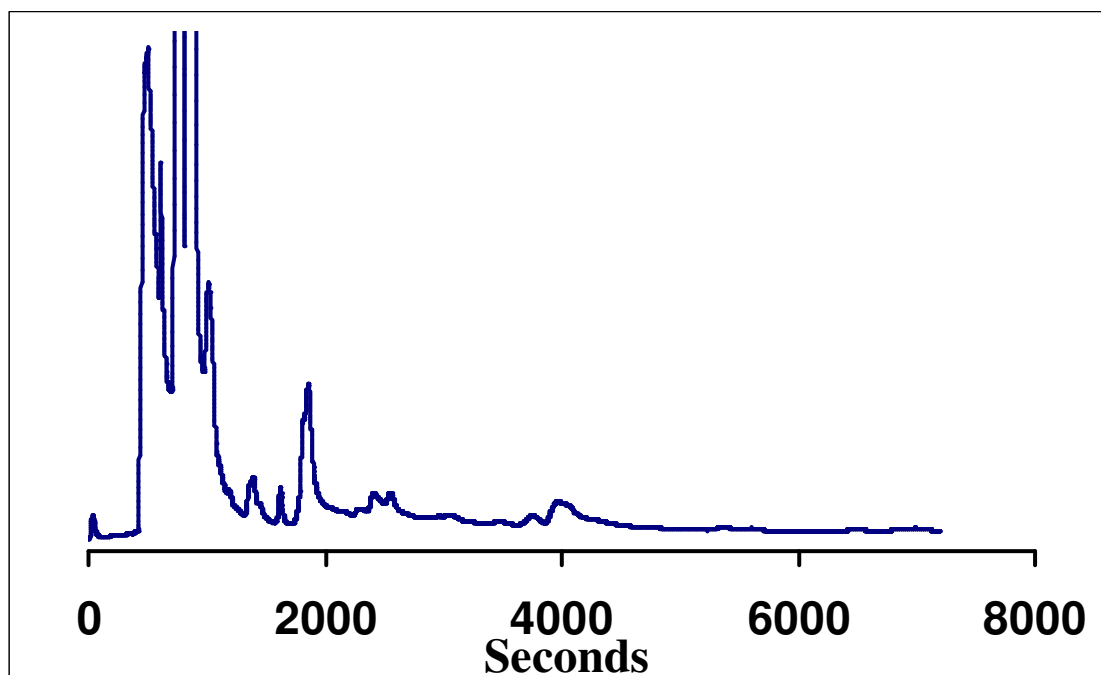


Figure 50. Aqueous phase products from a representative 1.00 M HNO₃ run

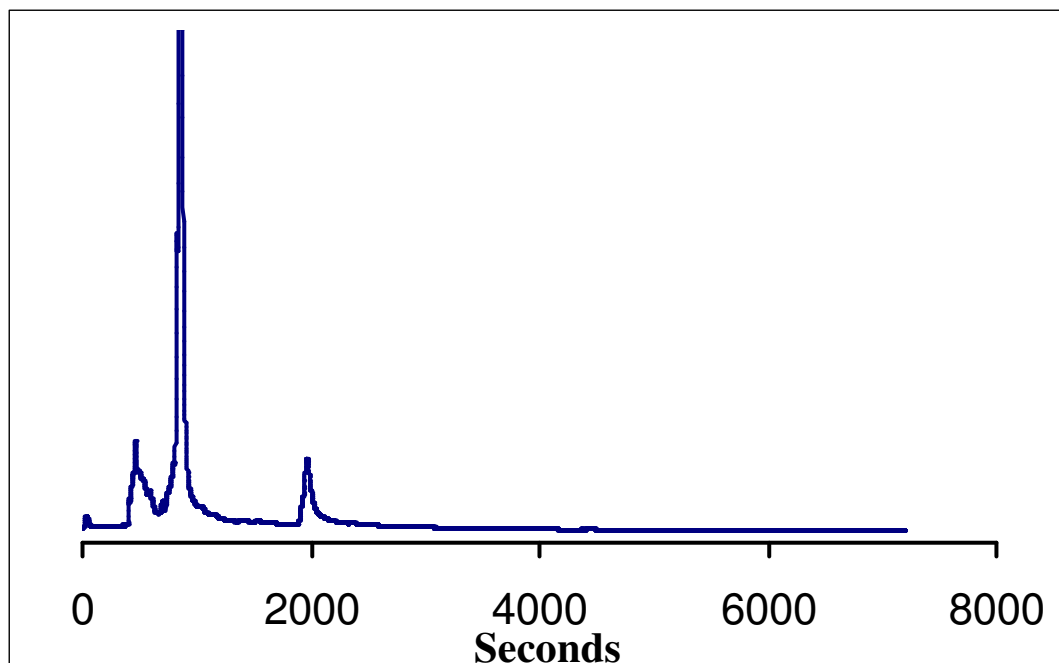


Figure 51. Aqueous phase products from a representative 0.04 M HNO₃ run

Figures 49-51 show GC/FID chromatograms for the aqueous HZSM-5, 1:1 HNO₃, and 25:1 HNO₃ reactions with butanol. In the ZSM-5 runs, alkylation/oligomerization products were typically in the C₈ range, while the HNO₃ runs had products over the broader C₅-C₁₂ range. The more dilute HNO₃ produced only very small amounts of the larger products, while the more concentrated produced much more. The more concentrated HNO₃ run also produced a small amount of non-soluble solid products on the inside of the cup as well as a considerable amount of cracking products. The aqueous non-soluble species were soluble in ethanol, but were too large for GC analysis with our column. There were also some cyclization and aromatization products. The liquid acid exhibited a greater extent of these two secondary reactions, whereas the ZSM-5 typically produced simpler alkylation/oligomerization products such as octanes/octenes. This result is not unexpected as in unconstrained liquid acid catalysis, larger, bulkier products are capable of forming while

in the sterically hindered ZSM-5 reactions, the size of the channel trends toward smaller products. In addition, upon reaction, it is plausible that the liquid acid would have a higher percentage of secondary reactions. In the ZSM-5 case, once reaction has occurred and the product has exited the channel volume, there is no acid function to catalyze further reaction. The product must return into the zeolite for subsequent reaction, which is increasingly difficult for larger species. In the liquid acid, reaction can occur numerous times as the products are continuously in the same acidic environment. The average total liquid phase conversion from the ZSM-5 runs was 40%, the 25:1 HNO₃ was 68%, and the 1:1 HNO₃ was 5%.

The gas phase products were similar for all runs with each containing one dominate peak (see **Figures 52-54.**) In all cases this peak contained more than 90% of the total peak area. This peak was assigned as butene and isobutene by GC/MS analysis. Upon magnification, more product peaks are observed in addition to a small 2-butanol peak. While the small products differ between the zeolite and HNO₃ runs somewhat, the dominate peak is the major product from all; and, as the smaller peaks also are apparent in the liquid phase, they may be attributed to the vapor pressures of the liquid products. The average conversion to all gaseous products for ZSM-5 was approximately 58%, the 25:1 excess HNO₃ was 2%, and the 1:1 HNO₃ was 23%. This trend is also most likely due to the increased likelihood of secondary reactions. After reacting in the ZSM-5, the gas phase products could quickly exit the channel and escape solution, where no further reaction could occur. Likewise, in the more dilute HNO₃, reaction could occur and the products could escape with less of a chance of secondary reactions. In the more concentrated acid, however, secondary reactions could

occur quite rapidly, leading to the oligomerization, cyclization, and aromatization observed by both the liquid GC analysis and the formation of waxy insoluble products.

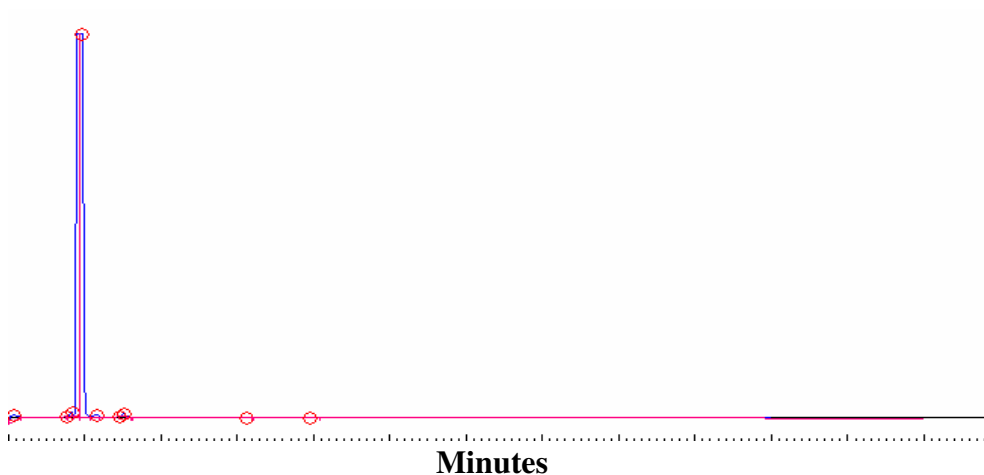


Figure 52. Representative chromatogram of gas phase products of ZSM-5 and 2-butanol reaction (dilute HNO_3 plot similar)

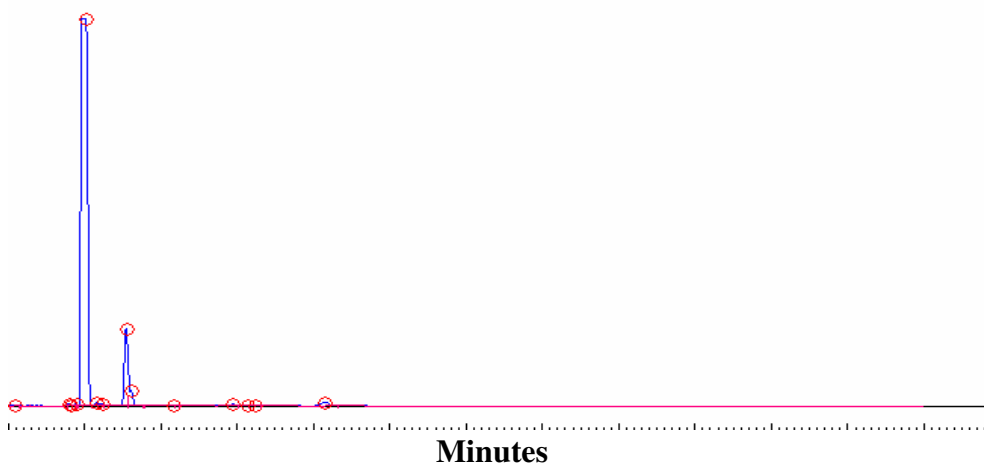


Figure 53. Representative chromatogram of gas phase products of HNO_3 (25:1) and 2-butanol reaction

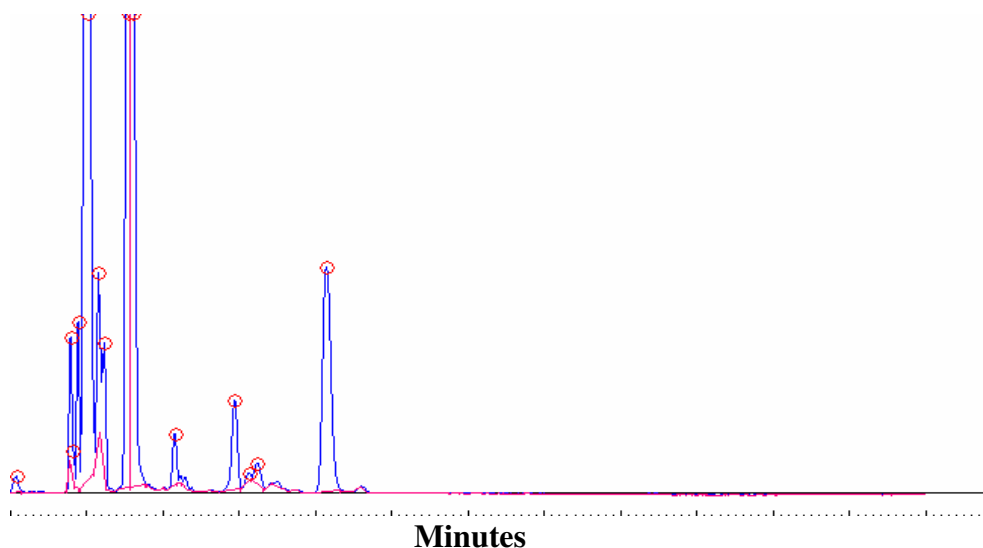


Figure 54. Gas phase products of HNO_3 (25:1) and 2-butanol reaction (Fig. 5 expanded)

Combining the liquid and gaseous phase conversions gives total conversions to all products for ZSM-5 of 78%, the 25:1 HNO_3 of 69%, and the 1:1 HNO_3 of 27%. The fact that a zeolite in aqueous solution has a much higher conversion of a reactant than a strong acid of equal H^+ concentration seems quite perplexing. Even more the fact that the zeolite's conversion rivals, much less exceeds, that of a strong liquid acid of much greater acid concentration. Additionally, quantitative spin counting techniques have indicated that just over half of the Al in H-ZSM-5 generates ^1H MAS NMR observable Bronsted acid sites.²³ There is obviously more than a simple dependence on the acid site quantity for conversion. Concentration effects of the zeolite could explain a small amount of the increase. By concentrating the reactants in channels, the reactants are in closer proximity to the acid sites. This would aid in the conversion slightly. In itself, this seems hardly enough to explain the large discrepancies. Consider now the idea of a tethered acid site. While recent studies have

shown that with as little as three waters of solvation, the acidic proton can be removed from the lattice,⁹⁶ still the balancing charge must remain in close proximity to the original site.

This concept of a tethered acid site is how a zeolite in aqueous media would fundamentally differ from a liquid acid. Using the channel volume of ZSM-5 from XRD data of $889.57 \text{ \AA}^3/\text{unit cell}$ and the average volume of a water molecule obtained from its density at room temperature of $29.984 \text{ \AA}^3/\text{molecule}$, we can calculate that 29.7 molecules of water are in each unit cell of the zeolite. While the calculated spherical volume of water does not truly represent the shape of water, we can take this number as an upper limit for further calculations, and any imperfect filling of the volume would only lead to a higher concentration of H^+ . From the Si/Al ratio, the catalyst contains approximately 6 acid sites per unit cell. This means that there are 4.94 water molecules available for solvation for each acid site. Using this to calculate concentration as for bulk, inside the pore volume the H^+ concentration is roughly 11.2 mol/L! This high concentration leads to an “effective pH” of -1.05 inside the channels of the zeolite, much different than the expected pH of 1.4 based on the total water volume and number of acid sites. A solution of ZSM-5 and water alone in the same amounts used in each experiment had a pH of 3; much less acidic than the “effective pH” or the expected pH.

While undoubtedly not every aluminum atom present in the lattice leads to an acid site, still the concentration inside the channels would be quite high due to their physical confinement. This difference in “effective pH” could easily explain the higher conversions of the zeolite with respect to the two liquid acid solutions. This could also extend to other zeolites of different sizes and structures as well. One could tailor the “effective pH” by two real means: (1) changing the pore volume by selecting a different zeolite framework, or (2)

altering the Si/Al ratio of the zeolite. In changing the pore volume, the smaller a zeolite's pore volume, the larger this "effective pH" effect is, while the larger the volume, the less the theoretical pH differs from the corresponding liquid acid. Altering the Si/Al ratio changes the "effective pH" in the same manner as in liquid acids; e.g. changing the Si/Al ratio from 15 to 30 would change the H^+ concentration from 11.2 mol/L to 5.6 mol/L and hence, the "effective pH" would be lowered to -0.75.

This poses many interesting possibilities for catalysis. Zeolites are much safer to use than liquid acid catalysts. They are environmentally benign, and even in these solutions, the bulk liquid's pH was measured to be only 3.0 while their activity and conversion was comparable to a much stronger liquid acid pH. Since the "effective pH" is only dependant on the channel volume of the zeolite, it is independent of the total volume of water. This means that whereas liquid acids depend on concentration, the zeolite would possess the same "effective pH" irrespective of the total volume of water. The activity of the zeolite would only be hindered by the concentration of the reactant(s) (which would be aided by concentration effects exhibited by the zeolite) and the time it takes for their diffusion into and out of the channels. The practical uses of this "effective pH" of zeolites show real promise.

7.4 Conclusions:

Zeolite catalyzed reactions were carried out in aqueous solvent and compared to conversions by corresponding liquid acid solutions. Total conversions for the zeolite exceeded that of a HNO_3 solution of equal H^+ concentration, in addition to one 25 times more concentrated. An "effective pH" of a zeolite was defined as the pH inside the zeolitic channel volume arising from a tethered acid site in a fixed volume. This pH was shown

theoretically and experimentally to be much greater than simple dilution as in the liquid acid case. The use of this property of zeolites can provide shape selectivity in acid catalyzed aqueous reactions, as well as safer processes not involving hazardous liquid acids.

Chapter 8: Conclusions and Future Work

Using MAS NMR, evidence of the formation of an adsorption complex between a Bronsted acidic site in a zeolite and a saturated alkane has been presented. Such complexes have previously only been observed in the case of unsaturated olefins and aromatics where π electron density can interact with the site. The interaction was proven to be more general as two different framework zeolites with differing channel sizes both exhibited evidence of this complex. In the larger pore zeolite, two differing alkanes produced this evidence as well meaning that the complex is also not specific to only one molecule. The fact that alkanes specifically adsorb at the active sites in zeolites provides insight to the main goal of how alkanes become activated on solid acid catalysts.

Following the evidence of a direct adsorption complex, H/D exchange rate constants were determined for adsorbed perdeuterated alkanes on the protonated catalysts. For isobutane- d_{10} , exchange was monitored at temperatures much lower than previously reported and the test gases were free of trace olefins. Rate constants at various temperatures were used for H-ZSM-5 to obtain an activation energy for the process of 13.6 kcal/mole. This energy is larger than the literature reports for the protonation of an olefin, but lower than the literature reported value for dehydrogenation of an alkane.⁵²⁻⁵⁴ Rate constants determined for the acidic peak and the methyl peak were equal. Carbon-carbon bond chemistry was proven inactive at the temperatures for which H/D exchange was monitored both by a pulsed GC/Microreactor system and high temperature ^{13}C MAS NMR. Additionally, the catalyst was shown to be free of trace carbon species which could facilitate or initiate exchange by total carbon analysis performed by Galbraith Laboratories.

All results suggested a direct protonation step for H/D exchange. Ab initio calculations performed by Dr. Laura S. Sremaniak and Dr. Jerry L. Whitten on a test system with a small cluster model of the zeolite's Bronsted acid site and an isobutane molecule produced a theoretical activation energy of 14.5 kcal/mole. The adsorption of the alkane and the H/D exchange process was determined to be initiated through a non-classical hydrogen bond from a methyl C-H bond to an oxygen of the lattice adjacent to the acidic proton and bonded to the aluminum of the site. The theoretically determined mechanism and activation energy are in close agreement with the observed experimental results and values.

Zeolite catalyzed reactions were carried out in aqueous solvent and compared to conversions by corresponding liquid acid solutions. Total conversions for the zeolite exceeded that of a HNO_3 solution of equal H^+ concentration, in addition to one 25 times more concentrated. An "effective pH" of a zeolite was defined as the pH inside the zeolitic channel volume arising from a tethered acid site in a fixed volume. This pH was shown theoretically and experimentally to be much greater than simple dilution as in the liquid acid case. Ultimately, the "effective pH" does not depend on the total amount of water added to the system, but only the acid site density of the zeolite and its channel volume. The use of this property of zeolites can provide shape selectivity in acid catalyzed aqueous reactions, as well as safer processes not involving hazardous liquid acids. Additionally, this illustrates that water does not necessarily inhibit the acidity of a zeolite as is commonly presumed in the literature.

Presently, calculations are being carried out using the same zeolite cluster, but using neopentane rather than isobutane. Experimentally, the activation energy for H/D exchange between a zeolite and neopentane is much higher. There is no obvious reason why

neopentane would behave differently than isobutane in this reaction, so hopefully the calculations will provide some insight into this difference. If the calculations return the same result as isobutane, it could be that the difference is due to the limits of the small cluster model we are using. In this case, the channel systems could be inhibiting reaction due to sterics. Other more immediate future works include better assignment of the acid sites in H-Beta. This work will seek to identify the differences between these multiple sites and any difference in reactivity/availability to reactants. This project will also study other relevant zeolites and zeotype catalysts which could hold promise for alkylation such as SAPO and AlPO catalysts to see if their behaviors are similar for activating an alkane. Both NMR and microreactor studies could test bimolecular reactions between the activated isobutane and a second reactant. Some initial NMR experiments using isobutane co-adsorbed with ^{13}C labeled carbon monoxide gas were performed, but no reaction was monitored at room temperature. Other small nucleophile reactants (or even CO at higher temperatures) may be able to attack the activated methyl group and result in reaction at low temperatures. For both the NMR and microreactor experiments, the most difficult part of this experiment would be choosing a second reactant and adsorption amounts. The difficulty is that a nucleophile will also adsorb selectively at the zeolitic acid site, resulting in a competitive adsorption process. If this difficulty is addressed, this reaction could produce a variety of interesting products, and give further evidence of our methyl exchange mechanism.

An area that holds promise for progress in alkylation chemistry in zeolites from this work is in the development and characterization of new catalytic materials. One of the mentioned problems that has prevented the commercialization of zeolites for alkylate synthesis is the secondary reactions which ultimately result in catalyst deactivation. In the

microreactor experiments, a “plug” of catalyst is used, and the test gas must pass through the entire plug before being analyzed. This long pathway could give rise to a variety of undesired secondary reactions as a single reactant might encounter several active sites and/or activated carbonaceous species before emerging. In addition, olefins such as butene undergo rapid oligomerization followed by cyclization in the acidic environment. This then leads to the production of aromatics and coke, thus deactivating the catalyst. These undesired reactions could be lessened by minimizing the distance the test gases must travel through the zeolite (using a smaller plug of catalyst in the reactor) or in the olefin case by reducing the percentage of olefin injected, but doing so would also lead to less of the desired product being formed and these undesired reactions would still occur.

One possible solution to these problems is to exchange a small number of the Bronsted acid sites in the zeolite with a metal which could provide a dehydrogenation function to convert a small amount of alkanes to olefins inside the catalyst. By using this method, small amounts of olefins could be generated in concentrations low enough that the undesired reactions would not occur, yielding mostly the primary desired product. Another benefit of this would be that the reaction would require no olefinic feed, only isobutane. Another option is to make use of a new mesoporous/microporous catalyst. Micropores, such as zeolites, are capable of offering the desired shape selectivity for the production of alkylates, but suffer because of their rapid deactivation. Mesopores do not exhibit the same rapid deactivation as zeolites, but their large sized pores do not offer the shape selectivity required for the formation of alkylates. The idea of these combined catalysts is to synthesize a mesoporous material that has tiny nanoclusters of zeolites coated onto the mesopore’s channel walls. Such materials have been recently synthesized and the results published in the

literature.^{97,98} Another possible alternative is to synthesize a mesopore which has a micropore as the walls. These materials have also been recently synthesized and characterized.^{99,100} These type materials will allow test gases to freely flow through the inactive mesopore and diffuse in and out of the active zeolite along the walls (whether the zeolite is coated on the walls or the actual walls themselves). The main difference with this catalyst design is that it would not require the gases to travel through a large section of active catalyst as does the zeolite plug. In this case, the high acidity and shape selectivity of the zeolite would be maintained for the alkylation chemistry, and the mesopore, along with the very small thickness of the zeolite layer (around 5 nm thick), allows for long lifetime of the catalyst as well as fewer secondary reactions. These future directions are presently being studied by beginning graduate students in Dr. White's group.

Additional research in the aqueous phase zeolitic catalysis is also being performed. Currently, glycerin conversion at elevated temperatures (250°C) is being investigated as a potential methanol source. Other possible projects include a more expanded study of water soluble reactants, most notably, determining the differences between the reaction of secondary or tertiary alcohols and primary alcohols. The solvation effects of the zeolitic lattice in addition to the water within the channels might result in differences in reactivity as compared to the gas phase. Changing the Si/Al ratio of the zeolite could also result in different reactivity. Lower ratios should produce a more hydrophilic surface, whereas higher ratios should result in a more hydrophobic surface. The higher ratios might result in higher selectivity to larger products as the primary products could more easily remain in the hydrophobic channel as opposed to exiting into the aqueous environment. The overall conversion would most likely be less because of the lower H^+ concentration.

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