

Sorption and Diffusion Parameters of Organosilane-Functionalized Zeolites

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Abstract

The purpose of this project was to modify the surface of Zeolite Y catalysts with organosilanes and investigate the diffusion rates and overall uptake of hexanol and cyclohexanol in the modified zeolites. Unmodified zeolite catalysts have a low tolerance to liquid water at high temperatures, but recent studies have shown that functionalizing the surface of zeolites with organosilanes increases the hydrophobic character and the hydrothermal stability of the zeolite. The modified hydrophobic zeolites have the potential to improve the efficiency of high temperature liquid phase reactions. Zeolite Y was coated with octadecyltrichlorosilane, hexyltrichlorosilane, and ethyltrichlorosilane to explore how different alkyl chain lengths affect diffusion through the zeolite. Extensive tests were performed to characterize the native and modified surfaces, including FTIR, Nitrogen Sorption, and contact angle measurements. Adsorption tests using hexanol and cyclohexanol as probe molecules were performed to measure the overall capacity of native and modified zeolites. Diffusion coefficients were calculated for each target molecule in the zeolites. Results showed that the chain length of the zeolite coatings did not greatly affect the rate of diffusion but did affect the overall uptake of the target compounds.

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Chapter 1: Introduction

In recent years, increasing attention has been given to the derivation of specialty chemicals and fuels from biomass. Solid acids used as heterogeneous catalysts, such as Zeolite Y, have become increasingly important in biomass upgrading reactions. Unlike liquid acids, solid acids have the special properties of varying Lewis and Bronsted acid site strength, selective pore sizes, and recoverability (Corma and Garcia, 1997). Theoretically, these properties can be tailored to produce higher reaction selectivities and yields. However, many of these liquid phase reactions occur at high temperatures to promote a reaction speed that is economically feasible. Zeolites are an important heterogeneous acid catalyst in industry. For example, the majority of the world's gasoline is produced via catalytic cracking using zeolite catalysts (Cundy and Cox, 2003). Zeolites are an appealing choice to catalyze these reactions; however, the crystalline structure of many zeolites can be compromised in the presence of condensed water above 150° C.

Recent experiments have discovered that functionalizing zeolites with organosilanes gives the zeolites hydrophobic properties without the loss of any Bronsted acid sites, which are vital for catalyst activity (Resasco, 2012). The study demonstrated that NaY zeolite functionalized with octadecyltrichlorosilane is hydrothermally stable up to 200°C. Organosilane functionalized zeolites may be better suited to high temperature reactions in water-rich solvents, but more research is needed on the effects of organic coatings on diffusivity, adsorption, and thermal stability.

This study aimed to characterize three different organosilanes with varying chain lengths using methods such as TGA, FTIR, contact angle measurements, SEM, Nitrogen Sorption and biphasic emulsions. Using experimental data obtained through characterization and sorption experiments, parameters to study the diffusion of organic compounds in the zeolites were developed, which can be used to describe how the coating chain length will affect diffusivity. These parameters included analyzing the rate of diffusion and determining the diffusion coefficients for each modified zeolite. This allows for the discovery of the

optimal coating chain length for the surface modification of zeolites, leading to greater reaction selectivities, conversions, and efficiencies for any catalytic process for which the use of coated zeolites is desirable.

Chapter 2: Background

This chapter provides information on some of the current uses of zeolites and the information necessary to understand these uses. Potential applications of zeolites in industry are also explored. To provide an understanding of the importance of modified zeolites as solid acid catalysts and their diffusive properties, this chapter describes the potential use of zeolites and its applications in industry. Recent studies on the effect of coating zeolites and what is currently known on the diffusive and sorptive properties of zeolites are discussed in this chapter.

2.1 Biomass

Biomass is renewable biological material, deriving from plants or animals. Biofuels and biochemicals are important products that derive from biomass. Common examples of biomass feedstock include corn, manure, switch grass and wood. Biomass can be used to create eco-friendly and renewable alternatives to fossil fuels and fossil fuel derived chemicals. For example, the carbon dioxide released when biofuels are burned is recycled directly back into plant material instead of being stored in the atmosphere. However, for biomass-derived chemicals to be economically competitive with fossil fuels, the efficiencies of biomass conversion technologies must be improved. Unfortunately, this has become a challenging hurdle for scientists because bio-oils are generally not suitable for thermal fractionation after being condensed from pyrolysis vapors (Paula A Zapata, Huang, Gonzalez-Borja, & Resasco, 2013). Therefore using a catalytic conversion in the liquid phase at moderate temperatures appears to be the best approach. Zeolites are a potentially useful catalyst for breaking down biomass feedstock and converting it into biochemicals.

2.2 Components of Biomass

Biomass is composed of the same building blocks regardless of what the feedstock is ("Biofuels," 2013). It consists of three main components; hemicellulose, cellulose and lignin. These components are carbon-based materials and primarily consist of a mixture of

atoms including hydrogen, oxygen and nitrogen. Hemicellulose is composed of polysaccharides and makes up 20-40% of the biomass by weight. Hemicellulose is a branched compound that is made from five and six carbon sugars. Cellulose is a linear polymer composed of repeating glucose units that makes up 40-60% of the biomass by weight. Lignin is a complex, cross-linked polymer that consists of aromatic rings. Lignin has high energy content and makes up 10-24% of the biomass by weight



Figure 2.1: Biomass Components (U.S. Department of Energy, 2010)

To convert biomass into usable fuels, hemicellulose, cellulose and lignin must first be broken down into five and six carbon chain sugars and other molecules via catalyzed hydrolysis reactions. These molecules can be subsequently converted into highly useful chemicals, such as ethanol via fermentation. The bio-ethanol can be used in combination with gasoline as a fuel, or dehydrated to produce ethylene. The process for converting raw biomass into bioethanol can be seen in the process diagram Figure 2.1.2.



Figure 2.2: Biomass to Ethanol Process (Hahn-Hägerdal, Galbe, Gorwa-Grauslund, Lidén, & Zacchi, 2006)

Currently, ethanol is used to blend into gasoline for motor vehicle fuel, reducing the amount of oil required and improving emissions ("Biofuels," 2013).

2.3 Liquid Phase Reactions of Biomass Using Solid Acid Catalysts

Due to the increasing interest in renewable biomass, many different conversion strategies have been studied (Corma, Iborra, & Velty, 2007). Vegetable oil, lignin and sugars can be used as reactants and converted into useful biochemicals through different liquid phase reactions (Corma et al., 2007). These reactions include, but are not limited to, the fermentation of glucose, dehydrations of monosaccharides and ethanol, the transformation of sucrose using hydrolysis, esterification, or oxidation, and transesterification of oils for biodiesel production. There are also many different liquid phase reactions that can transform triglycerides, which are found in vegetable oils and animal fats. Triglycerides can be transformed into chemicals through liquid phase reactions of the carboxyl group or through reactions of the fatty chain. Similarly, terpenes can also be transformed through various liquid phase reactions, which include isomerization, epoxidation, and hydration of various parts of the terpene.

Bio-derived ethanol and other biomass-derived chemicals also have uses for things besides fuels. For example, the dehydration of ethanol yields ethylene, which is used as the raw material for manufacturing polymers such as; polyethylene, polyethylene terephthalate, polyvinyl chloride and polystyrene ("Ethylene Uses and Market Data," 2010). These polymers are used for a variety of different markets and industries such as transportation, construction, chemicals, and electronics. The dehydration of ethanol is shown in the reaction below:

$$C_2H_5OH \rightarrow C_2H_4 + H_2O$$

Currently, ethylene is produced from fossil fuels. Bioethanol is a potential alternative source of ethylene. The reaction can be operated in the gas phase using a solid acid catalyst, or in the liquid phase at high temperatures. The latter is a more attractive option because it avoids the added energy cost needed for the latent heat of vaporization. However, solid acid catalysts may degrade under such process conditions.

2.4 Solid Acid Catalysts

Solid acid catalysts have recently been used for promoting hydrolysis and dehydration reactions of many biomass constituents and biorenewable molecules.

Sorbitol is an example of one useful biomass-derived chemical, and dehydrating sorbitol can give isosorbide, which is a useful chemical for polymers and medicines (Ahmed et al., 2013). Mineral acids can be used as catalysts for this type of reaction; however the best catalysts will not be harmful to the environment or people's safety and can be easily separated from the reaction mixture. The solid acid catalyst investigated in sorbitol dehydration was sulfated titania, where it was found that at 210°C 0.1 grams of the sulfated titania catalyst lead to 100% conversion of sorbitol, compared to only 20% conversion with no catalyst.

For many liquid phase reactions, including hydrolysis, hydration and esterification, there are a limited number of solid acid catalysts that are successful (Okuhara, 2002). There are many solid acid catalysts that will lose their catalytic activity in aqueous solutions, due to strong solubility and instability. However, catalytic reactions in aqueous systems are nontoxic, inflammable, safe, and often low in cost. HPAs have been found to be active in several aqueous phase organic reactions, as they were similarly found to be quite active for biodiesel production. HPAs are formed from the condensation of two or more different types of oxoanions (Corma & Garcia, 1997). Solid HPAs have strongly acidic sites due to the large size of the polyanion and low and delocalized surface charge density. The number of acidic sites on the surface can be relatively low if the HPA has a small surface area. They are also highly soluble in water. HPAs have been used for many different reactions, including the synthesis of diphenyl-methane, hydration reactions and esterification processes.

2.5 Zeolites

Zeolites are a type of solid acid catalyst that are used in oil refining, petrochemistry, and production of fine chemicals (Corma, 1997). Zeolites are silico-aluminates that have a crystalline structure with well-defined pores and cavities of molecular dimension, which greatly affects their reactive properties. Typical properties of zeolites include high surface areas, ability to control the number and strength of acidic sites, and a high adsorption capacity. One important characteristic of zeolites is the well-defined pore structure with characteristic dimensions similar to other molecule sizes. The acid strength of the zeolite depends on the density of acid sites and the Si to Al ratio.

Different types of zeolites have varying surface areas, pore sizes, and Si to Al ratios. These parameters have an effect on the catalytic activity in certain reactions (Sasidharan & Kumar, 2004). One example of this was found in a study of the transesterification of different alcohols to make β -Keto esters, which are widely used in many different industrial processes for product synthesis. This liquid phase reaction can be efficiently carried out over different zeolite catalysts. Zeolite β , Zeolite Y, ZSM-5 and mordenite were investigated, and it was found that the larger-pore zeolites, such as Zeolite β and Zeolite Y, are the best for transesterification. It was further discovered that when these large-pore zeolites were

dealuminated, their catalytic activity was higher due to increased acid strength and hydrophobicity.

2.6 Modified Zeolites

Zeolites are a nearly ideal candidate for catalyzing the biomass upgrading reactions mentioned in Section 2.3 because of their high surface area, acidic strength, and controlled pore structure. Unfortunately, under extreme conditions, including high temperatures in the liquid phase, the crystalline framework of zeolites breaks down. These conditions often occur in reactions important to upgrading of bio-oil in the liquid phase.

2.6.1 Zeolite Coatings

Zeolite coatings have been studied since the 1990s with the purpose of ion exchange between aqueous and organic solutions, as well as to improve zeolite incorporation in polyimide films (Singh et al, 1999). For use as a catalysts, applying a hydrophobic coating on the zeolite gives it greater resistance to hot liquid water and causes the mineral to float between the water/oil boundaries (Zapata et al, 2013). The main role of a hydrophobic coating is to provide a barrier to prevent contact between the zeolite and liquid water. This stabilizes the water/oil mixture while also increasing the mass transfer of both the reactants and the products. For example, bio-oils have a high concentration of water-soluble compounds compared to the low water solubility of the yielded products. Therefore using biphasic emulsions stabilized by catalytic zeolites is encouraging because the system amplifies the interfacial exchange area for simultaneous reaction and separation (Paula A. Zapata, Faria, Ruiz, Jentoft, & Resasco, 2012).

Choosing the type of coating is essential in maintaining the integrity of the zeolite. Silylation of the zeolite has been studied as an effective coating method because it does not alter the acidity of the mineral (Paula A. Zapata, Faria, Ruiz, Jentoft, & Resasco, 2012). Trichlorosilane reagents with long carbon chains are generally used in practice because of their hydrothermal stability.

2.6.2 The Effect of Chain Length

Previous work at the University of Oklahoma has examined several different silane coatings on Zeolite Y (Paula A. Zapata et al., 2012). These studies showed large difference in the degradation of the crystalline structure depending on the coatings. The research team ran reactions for 22 hours at 200°C and saw a great tolerance to the operating conditions from the silane-functionalized zeolites. The group found interesting results where there seemed to be a "give and take" between the carbon chain lengths of the coating agents. The organosilane coatings with longer carbon chain lengths increase the hydrophobic character of the tested zeolites. However the effect the carbon chain length of the coating has on the rate of diffusion and overall uptake of target molecules is poorly known. Therefore there is the need to find the optimal chain length in order to maximize the stability of the emulsion while maintaining high hydrophobicity. There is also a need to assess the effect of chain length on pore size, diffusivity, and adsorption. To find the ideal chain length for zeolite coatings, three agents will be tested:

- 1. Octadecyltrichlorosilane
- 2. Hexyltrichlorosilane
- 3. Ethyltrichlorosilane

Results from the study conducted at the University of Oklahoma showed the OTS functionalized zeolite to be the most hydrophobic. Their studies also showed that functionalizing a zeolite with OTS resulted in a slight loss of microporosity in the zeolite. The authors suggest that the loss in microporosity occurs due to pore blockage of the zeolite by the functional group. As the chain length increases it was seen that there was a higher loss of microporosity, therefore of the three organosilane coatings, OTS caused the lowest microporosity. However, the longer chain length of the OTS seems to best protect the zeolite from water keeping its catalytic activity throughout the whole reaction.

The HTS modified zeolite also tested to be highly hydrophobic being slightly less than the OTS sample. Again the microporosity of the zeolite decreased with the addition of the coating, however slightly lower than the OTS. The modified zeolites retained most of its

crystallinity after being exposed to a biphasic structure at extreme conditions. HTS was shown to be highly stable in the emulsion, allowing the zeolite to remain highly catalytic throughout the whole reaction.

ETS provided an interesting study by varying the coating concentration and studying the differing results. At lower concentrations the zeolite remained hydrophilic and quickly broke down when in emulsion. However, when the concentration was increased the modified zeolite became as hydrophobic as the two longer chained samples. The coating with a higher concentration of ETS proved to be comparable to the longer chained organosilane in retaining the crystallinity of the zeolite. The short alkyl-chains allow greater coverage of the zeolite, reaching small pockets within the zeolite that the longer chains cannot. However, the shorter chain is less stable when put into the biphasic water/oil emulsion.

2.7 Diffusivity and Adsorption

Diffusion parameters must be measured for different coating lengths so that a mathematical model may be developed that accounts for adsorbent characteristics and determines the optimum coating length. The diffusion of organic molecules within the void volume of zeolites has been a research topic for more than seven decades (Keipert & Baerns, 1998). Knowledge of diffusivities in zeolites is essential for catalytic processing and sorption separations. Past studies have shown the ability to successfully model the diffusion of organic molecules through zeolites by obtaining model parameters from experiments using direct and indirect analytical methods. Indirect methods include measuring the concentration of the diffusing species in the solvent with transient techniques such as gravimetry, volumetry, or chromatography. Direct methods use spectroscopic techniques such as polarimetry, IR, NMR, and DEXAFS, and determine the mean square displacement of the diffusing molecules. Pulse response experiments have also been used to model the diffusivity and adsorption of gaseous molecules in microporous materials. By modeling pulse responses it is possible to simultaneously determine the diffusion parameters, equilibrium

adsorption constant, and absolute rate constants for adsorption and desorption (Delgado, Nijhuis, Kapteijn, & Moulijn, 2004).

Less work has been done to model the diffusivity and sorption of molecules through zeolite coatings. Tatlier used the effective medium theory (EMT) to determine the effective diffusion coefficient of water in inhomogeneous open zeolite 4A coatings prepared by the substrate heating method (Tatlier & Erdem-Şenatalar, 2004). This study confirmed that estimated diffusivities increased with the void fraction of coatings. They also determined that lowering the ambient pressure in the EMT equation resulted in increased diffusion coefficients above a void fraction of 1/3 and that an increase in temperature increased the diffusion coefficients independent from the void fraction.

A study done by Chao et al. aimed to study the sorption of different organic molecules on octadecyltrichlorosilane modified NaY zeolites (Chao, Peng, Lee, & Han, 2012). They found that the modified zeolite behaved like an amphiphilic adsorbent. Organic molecules with high water solubility were able to adsorb onto the inner surfaces of the zeolite while molecules with low water solubility were able to partition to the OTS monolayer on the outer zeolite surface. The sorption capacities of molecules with low water solubility were much higher for OTS modified NaY zeolite than the unmodified NaY zeolite.

The purpose of our experiment was to further develop an understanding of the diffusivity of organic molecules of different sizes and polarities through organosilane zeolite coatings of different chain lengths.

Chapter 3: Methods

Untreated zeolites have shown a low tolerance to hot liquid water. However, functionalizing the zeolite surface with organosilanes creates a hydrophobic surface, greatly improving their stability in water. This chapter will describe the experimental methods used to develop a greater understanding of the diffusivity of two select target molecules through coated and uncoated Zeolite Y. The project focuses on three hydrophobic zeolite coatings; OTS, HTS and ETS, and measures the diffusion of Cyclohexanol and hexanol through the coatings and zeolite. The surface of zeolite samples was coated with three different organosilanes; ETS, HTS, and OTS. The resulting zeolites were characterized using oil/water emulsions, contact angle measurements, FTIR, TGA, Nitrogen Sorption, and SEM. Next, Uptake experiments were conducted to measure and evaluate how varying the alkyl chain length of the organosilanes affects the character of Zeolite Y.

3.1 Coating Procedure

The zeolite used in this study was Zeolite Y (Zeolyst International) with a Si/Al ratio of 60. The modification of the zeolite's surface using ETS, HTS and OTS was done following methods from a recent study (Zapata, 2012). First, 10 grams of the zeolite were placed in crucibles and put in the oven for 24 hours at 500 °C for calcination. This was done to remove impurities in the zeolite. In a flask, 5 g of zeolite and 100 mL of toluene were mixed. To break up agglomerated zeolite particles and to create a suspension of the zeolite and toluene, a VC750 sonicator was used. The mixture was sonicated for 15 minutes at 26% amplitude, stirred then sonicated for another 15 minutes, in order to ensure zeolite was fully suspended in the liquid. Next, the organosilane molecule was added to the suspension in a ratio of 0.50 mmol per gram zeolite. Three coating molecules were used: ETS, HTS, and OTS. The volume of organosilane injected into the suspension is shown in Table 3.1.1.

	c of ofganoshane nuucu (to Suspension for 5 gr	am Zeonice Sample
Organosilane	Molecular Weight	Density (g/mL)	Volume (mL)
	(g/mol)		
ETS	163.51	1.238	0.330
HTS	219.61	1.107	0.495
OTS	387.94	0.984	0.985

Table 3.1: Volume of Organosilane Added to Suspension for 5 gram Zeolite Sample

In addition to the three samples made with the organosilane coatings, one sample was preserved without surface modification as a control. Silane-zeolite solutions were placed on a stirring plate and stirred using a Teflon-coated stir bar coupled to a magnetic stirrer at 500 rpm for 24 hours. The zeolites were separated from the toluene by filtration (0.45 μ m) and rinsed with methanol. The methanol rinse was repeated two to four times until the majority of the zeolite sample was recovered from the solution. The recovered zeolite was placed in the oven dried for 24 hours at 100°C.

3.2 Characterization of Modified Zeolites

Once the coating procedure was completed, it was necessary to run experiments confirming the success of the surface modifications. The experiments included surface contact angle measurement, IR absorbance, thermogravimetric analysis, and surface area, pore size and volume analysis. The experiments performed to achieve these measurements were:

- Oil and water emulsions
- Contact angle measurement
- Fourier Transform Infrared spectroscopy
- Thermogravimetric Analysis
- Scanning Electron Microscopy
- Nitrogen Sorption

3.2.1 Oil-Water Emulsions

The first test done was to observe how the organosilane coated zeolites interacted with a biphasic solution consisting of equal volumes of a hydrophobic (toluene) and hydrophilic (water) component. Toluene-water suspensions were created by adding 100 mg of the treated zeolite samples to 20 mL of toluene and 20 mL of water. Each mixture was sonicated

for 15 minutes using a VC750 sonicator at 26% amplitude and then left to settle for 24 hours. Hydrophobic zeolites were not wetted by water but instead become suspended in the toluene, while hydrophilic zeolites partition to the water phase.

3.2.2 Contact Angle

Contact angle measurements were performed to complement the qualitative hydrophobic/hydrophilic characterization provided by emulsion formation observations. First, the zeolite samples were crushed into a thin powder using mortar and pestle. Then, the zeolite samples were made into thin pellets using the CrushIR Digital Hydraulic Press. Using the small end of a spatula, two scoops of the sample were loaded onto the bottom anvil in the evacuable pellet press. The second anvil was placed on top of the sample and the piston inserted above that. The rubber O-ring was placed on the top of the piston to seal the column. Once loaded up, the evacuable pellet press was secured in the hydraulic press with the vacuum hose on the base and the screw on the piston. The pressure was manually increased to 8.0 tons of force, making sure not to operate too close to the maximum of 10.0 tons of force. The pressure was held for one to two minutes and then released using the pressure release knob. The center column of the pellet press was removed, and the pellet was carefully extracted from in between the two anvils. The pellets were extremely delicate and had rough surfaces because no organic binder was used.

To test the wettability of the different silvlated zeolites a 0.1 microliter water droplet was placed on the pellet using a rame-hart dispenser. The contact angle was then measured using a NRL C.A. Goniometer and DROPimage Standard software. The contact angles of the three coated samples and uncoated sample were compared to determine the relative hydrophobicity of each sample. This procedure was also repeated for modified, uncalcined zeolite samples to compare the effect of precalcination on the hydrophobicity of modified samples.

3.2.3 Fourier Transform Infrared Spectroscopy

The Fourier transform infrared spectroscopy (FT-IR) was performed to generate an infrared spectrum of absorbance of the samples. The goal of FT-IR was to compare the spectra unmodified Zeolite Y with those coated with ETS, HTS, and OTS. The machinery used was a Burker Vertex 70 instrument on the attenuated total reflectance (ATR) setting. For FT-IR ATR, there was no pretreatment of the samples required. First, the crystal area was cleaned with acetone and Kim-wipes in preparation for the 15 minute background scan. This background was taken to set the baseline for the sample scan. Enough of the zeolite sample was loaded on the platform to completely cover the crystal. The anvil was tightened on top of the zeolite forcing the sample into the diamond surface. The sample was then scanned for 1200 scans (approximately 15 minutes). This method was performed for all four treated samples of zeolite. Similar to the protocol in the contact angle measurement, the IR spectra of the calcined and uncalcined samples were compared to one another. This was done to observe the effect calcination has on zeolite modification. The spectra were viewed using OPUS software.

3.2.4 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was used to determine the thermal stability of our four modified Zeolite Y samples. A TA Instruments 2950 was used to determine the mass loss of organics within the zeolite and on its surface over a temperature range of 20 to 600 °C with a heating ramp of 10 °C per minute. A platinum pan was heated with a blow torch for several seconds to remove residual organic material on the surface. A small amount of zeolite sample ranging from 6 to 20 micrograms was placed in the pan for analysis. Data obtained from TGA was analyzed using TA Universal Analysis. TGA was performed to observe mass loss due to bound water vapor, water formation due to the decomposition of S-O-H bonds, residual solvent, and surface organics in the samples of coated and uncoated zeolite.

3.2.5 SEM

Scanning Electron Microscopy (SEM) images were taken of the ETS-modified, HTS-modified, OTS-modified and uncoated zeolite samples at 2500, 5000, 10000, and 25000 times magnification using a JEOL JSM-7000F Field Emission SEM. This was performed to observe the surface and particle size of the modified and unmodified Zeolite Y samples. A Sputter Coater using gold platinum alloy was used because of a lack of conductivity of the samples.

3.2.6 Nitrogen Sorption

Nitrogen sorption experiments were run to determine the pore sizes of the three modified zeolite samples along with two uncoated zeolite samples using Micromeritics ASAP 2020. The first uncoated sample was run through the same coating procedures as the modified zeolites with no organosilane added. The second uncoated zeolite was used straight from the manufacturer without any alterations aside from being calcined.

3.3 Diffusion Experiments

The final experiments conducted were used to measure adsorption of two target molecules in the modified and unmodified zeolite samples. The goal of the diffusion experiments was to measure the diffusion coefficients which can be used for future research when using these modified zeolites as catalysts. These adsorption experiments helped to understand how the alkyl chain lengths of the organosilane coatings affect diffusivity. More specifically these experiments were used to determine the adsorption rates of the different modified zeolites.

3.3.1 Sorption Experiments

The target molecules used to study the sorption through the zeolite samples were hexanol and cyclohexanol. These two molecules were chosen based on their different shapes and water solubilites. Both molecules allowed to study the difference in diffusion between a straight chain and cyclic chain. Also, the water solubility of hexanol is 5.9 g/L water, while the water solubility of cyclohexanol is much lower, at 0.36 g/L water. With these differing characteristics, the interactions between the zeolite coatings and the different shapes and solubilities can be observed. For these experiments, 20 microliters of the target molecule were dissolved in 20 mL of isopropanol. This gave a starting concentration of 1mL of target molecule per L of isopropanol. To begin the sorption, 0.50 grams of each zeolite sample was added to the target molecule and Isopropyl alcohol solution. Each mixture was shaken for a 5 hour period with samples taken every 5 minutes for the first half an hour, then every half hour for the first two hours and then every hour for the last three hours. Samples were taken using disposable sterile syringes equipped and nylon 0.2 microliter in-line filters, which ensured that there was no zeolite in the collected sample.

3.3.2 Gas Chromatography

To be able to determine the amount of these molecules sorbed into the zeolite, gas chromatography (GC) and respective calibration curves for the molecules were used. A Gas Chromatograph GC-2010 Plus by Shimadzu was used. The GC was originally set at 30°C for the first 10 minutes, then increased 10°C per minute until it reached 140°C after 21 minutes. The GC continued to run for a total of 20 minutes. To make the calibration curves, known concentrations of the molecules in isopropanol were analyzed in the GC. A linear correlation between the response of the molecules on the GC and the concentrations of the molecules were found. Graphs of this correlation were created and used to relate the peak response of the molecules shown on the GC to their respective concentrations for the rest of the sorption experiments.

To measure how much of the target molecule sorbed into the zeolite samples, the samples taken over the 5 hour period were analyzed in the GC. The area of the peak was taken for each sample to measure the response of the target molecule left in the sample. Using the calibration curves, the concentration of the target molecules left in the sample were determined. This amount is what was not sorbed into the zeolite, therefore the amount of the target molecule sorbed into the zeolite was determined using the starting concentration of 1mL/L. These results were analyzed over time for each treated zeolite sample for both target molecules.

Chapter 4: Results and Analysis

The objective of this study was to characterize each of the modified and unmodified zeolite samples using different methods. Once it was determined coating was on the surface of the zeolite sorption test were run to explain how the alkyl chain length of the organosilanes effected the diffusion of alcohols and cyclo-alcohols. The data was analyzed to create recommendations on choosing an appropriate organosilane coating for the zeolites.

4.1 Characterization of Modified Zeolite Samples

Each sample was characterized using methods earlier described to ensure zeolites were coated with the different organosilane agents.

4.1.1 Oil/Water Emulsions

The OTS, HTS, ETS-modified and uncoated zeolite samples were put in a toluene-water suspension to determine hydrophobicity. Figure 4.1 shows the zeolites in the toluene-water suspensions. The left two vials show the zeolite samples settling in the water on the bottom half of the vial, where the right side of the figure shows the zeolite is in the toluene in the upper half of the vial. These emulsions were a qualitative way to determine if the organosilane coatings were sticking to the surface of the zeolite. The concentration of organosilane to zeolite was 0.5 mmol/g zeolite.



Figure 4.1: Water/Toluene Zeolite Y Suspensions

These results were expected as the hydrophobicity of the modified zeolites should increase with the length of the alkyl chain length of the organosilane. As shown in study in the Journal of Catalysis done by Zapata et al, the ETS does not create a thick enough barrier at this concentration to prevent water from penetrating the zeolite (Zapata e al., 2013). However, increasing the concentration of the ETS covering the zeolite will enhance the hydrophobic effects of the coating. The HTS and OTS results confirm our initial beliefs as the alkyl chain lengths are long enough to create a suitable barrier against water.

4.1.2 Contact Angle Measurements

Figure 4.2 shows the contact angle results of both calcined and uncalcined zeolite samples. The unmodified and the ETS modified calcined zeolites were so hydrophilic that the water droplet absorbed into the pellet instantly; therefore no image was captured resulting in a contact angle of 0°. The contact angle for the calcined zeolite with HTS and OTS surface modifications was 80° and 100° respectively. As shown in the figure, the OTS modified calcined zeolite better repels the water droplet than the HTS; however both are hydrophobic. The uncoated uncalcined and the ETS coated uncalcined zeolites are both hydrophilic with small contact angles that were unmeasurable using the DROP Image Standard Software. The

HTS and OTS modified uncalcined zeolites were extremely hydrophobic with contact angles of 123° and 127° respectively.

	Uncoated	ETS modified	HTS modified	OTS modified
Modified Using Calcine Zeolite	[Unable to capture photo because droplet absorbed into pellet instantaneously]	[Unable to capture photo because droplet absorbed into pellet instantaneously]	80°	100°
Modified Using Uncalcine Zeolite			^{123°}	127°

Figure 4.2: Contact Angle Measurements

As shown in the figure, uncalcined zeolites have higher contact angles than calcined zeolite. During calcination, where the zeolite was put in an oven at 500 °C for 24 hours, the impurities and trace organics in the zeolite were burned out. These results show that burning out the trace organics actually decreases the hydrophobicity of the catalyst. Therefore, these measurements show that not calcining the zeolite samples will lead to a higher hydrophobicity, as well as confirming that the longer alkyl chain length coatings are more hydrophobic.

4.1.3 Fourier Transform Infrared Spectroscopy

Fourier Transformation Infrared Spectroscopy (FTIR) was used to confirm that the zeolite sample surfaces were coated with the organosilanes. Figure 4.3 shows the general spectra of Zeolite Y before modification. The 2700-3100 cm⁻¹ range shows the effects of the coatings and the 3700 cm⁻¹ range shows the effects of calcining the samples.



Figure 4.3: Complete FTIR Spectra of Zeolite Y

Figure 4.4 shows the C-H stretching region in the spectra from 2700 cm⁻¹ to 3200 cm⁻¹ (Zapata et al., 2012). The spectra represents the C-H bonds of the organosilane on the zeolite surface. The intensity of each peak varies with the chain length of the organosilane. For the ETS-modified zeolite, there is a signal at around 2880 cm⁻¹ and 2890 cm⁻¹. The size of this band shows frequencies that would be expected by the dominant methyl groups in the short chain of ETS. Of the three functionalized zeolite samples, the ETS signals are the least intense. The HTS-modified zeolite has signals that are much more intense than the ETS-modified zeolite, and the OTS-modified zeolite has similar signals that are the most intense. Here, the bands are at about 2860 cm⁻¹ and 2920 cm⁻¹. These more intense bands show the C-H stretching of methylene groups, which are more dominant in longer chains. The uncoated sample of the zeolite does not have any intense peaks in this region, showing that its surface does not contain an alkyl group that are present in the modified zeolites. Comparing these

four spectra confirms that the each sample of zeolite had a successfully modified surface by the organosilanes.



Figure 4.4: FTIR Spectra of coated zeolite samples comparing C-H stretching

Because we noticed the difference in hydrophobicity between the calcined zeolite samples and the uncalcined zeolite samples when measuring the contact angles, we also used FTIR to characterize the zeolite samples that had not been previously calcined. This spectra is shown in Figure 4.5. Comparing the spectra over the same range of 2700 cm⁻¹ to 3200 cm⁻¹ shows the same intense peaks for the modified zeolite samples, and the lack of intense peaks for the uncoated samples. This means that calcining the samples affected the zeolite to make it less hydrophobic, rather than an inconsistent coating procedure.



Figure 4.5: FTIR Spectra of uncalcined zeolite samples comparing C-H stretching

Figure 4.6 shows the spectra at 3700 cm-1 which shows O-H bonds on the surface. This spectra compared the uncoated calcined zeolite sample to the uncoated uncalcined zeolite. Figure 4.6 shows a reduction in surface O-H groups between the calcined and uncalcined zeolites. The intensity of the peaks of the uncalcined samples are more intense than the peaks of the calcined samples. Therefore, these results show that the calcination burned off some of the O-H groups that were on the zeolites, which explains the difference in the characteristics between the calcined and uncalcined zeolites.



4.1.4 Thermogravimetric Analysis

The thermal loss of the modified zeolite samples was measured using a TA Instruments 2950 thermogravimetric analyzer. In the 20°C - 200°C range, all samples experience moderate weight loss of 1-2%. This can be attributed to the loss of absorbed water molecules and other surface adsorbed species. Over the temperature range from 250°C to 600°C the modified zeolites experience further weight loss ranging from about 2% mass of the ETS-modified zeolite to about 7% weight loss for OTS-modified zeolite, shown in Figure 4.7. This weight loss consistent with vaporization of the organic coatings. At the higher temperatures, the difference in weight loss can be attributed to the difference in mass of the three organic coatings, as the ETS-modified zeolite loses less than the HTS-modified zeolite, which loses less than the OTS-modified zeolite. Only the ETS-modified zeolite follows the same weight loss pattern as the uncoated zeolite sample from the 20°C to 250°C temperature range. The HTS-modified sample experienced a larger weight loss. This may be due to different room and atmospheric humidity during the times when the modified zeolites were

created, stored, and analyzed. Further measurements are needed to determine if this is an effect of the coating or simply an anomaly in the data.



Figure 4.7: Thermogravimetric Analysis of Zeolite Y samples from 100°C-600°C

4.1.5 Nitrogen Sorption

Figure 4.8 shows the amount of nitrogen absorbed by each zeolite sample over the pressure range of 0mmHg to 700 mmHg. The graph shows a significant higher amount of nitrogen absorbed by the uncoated zeolite sample. As the alkyl chain length of the coating increases, the amount of nitrogen absorbed by the sample decreases. This is because the pore sizes become smaller with increasing alkyl chain length of the coating. These results coincided with previous studies performed by Zapata et al in the Journal of Catalysis, showing an increase in pore blockage with an increase in chain length of the modified zeolite (Zapata et al., 2013). Pores may become blocked by the larger coatings due to thickness of coating. Specifically, the longer alkyl may wrap back into adjacent pores, blocking access.



Figure 4.8: Nitrogen Sorption data of zeolite samples from 0 -700 mmHg

Table 4.1 shows the calculated pore size, BET surface and total pore volume from the nitrogen sorption.

Sample	Pore Size	BET Surface	Total Pore
	(nm)	(m^2/g)	Volume (cm ³ /g)
Uncoated Treated	2.97	688	0.510
ETS	2.99	555	0.414
HTS	3.00	527	0.395
OTS	3.13	522	0.408

Table 4.1: Nitrogen Sorption Analysis

4.1.6 Scanning Electron Microscopy

Figure 4.9 shows the zeolite samples magnified 10000 times, other images can be found in the Appendix. The images obtained from SEM alone are inconclusive in terms of differentiation. However using the J Image program we were able to estimate the average particle size. Coated and uncoated zeolite produced particles of a nearly identical average particle size of around 500 nm. These results were expected because the coating should only affect the zeolite on a molecular level.



Figure 4.9: SEM images of zeolite samples magnified 10,000 times

4.2 Diffusion

After coating samples of the zeolite and characterizing these coatings, the uptake of two molecules through these samples was studied. Two alcohols, hexanol and cyclohexanol, were used as the target compounds, which were mixed with isopropanol as a solvent. The total amount of the target compounds used was 1 mL. Samples were taken over a period of five hours and analyzed with gas chromatography to determine the amount of the target compound absorbed by the zeolite sample.



Figure 4.10: Amount of hexanol adsorbed over time



Figure 4.11: Amount of cyclohexanol adsorbed over time

Figures 4.10 and 4.11 show the amount of hexanol and cyclohexanol adsorbed over the five hour period. Looking at these figures within the first 15 minutes shows the relative rate of diffusion. In Figure 4.11, the amount of cyclohexanol adsorbed is shown, revealing that the rates of diffusion for the four samples are very similar. The main difference in this graph is the total amount adsorbed at equilibrium, which happens for most samples at about 30 minutes. A similar trend is shown in Figure 4.10 with the amount of hexanol adsorbed. The uptake rates of the uncoated, ETS and HTS coated samples all have a very similar dynamics in the first 15 minutes. However, there is a noticeable difference in the OTS coated sample, where both the rate of diffusion and the amount adsorbed at equilibrium is different from the other samples. The graph shows a slightly slower uptake rate in the first 15 minutes for the OTS coated zeolite sample.

Figure 4.10 shows that the OTS coated zeolite sample adsorbed the least amount of hexanol, adsorbing only 0.5mL at equilibrium. This is what would be expected due to the longer chain length of the OTS and the smaller pore volume of this sample. The uncoated zeolite sample adsorbed the most amount of hexanol, which also agrees with the idea of the negative correlation with the length of the carbon chain on the zeolite surface with the amount of the compound adsorbed. The uncoated zeolite sample adsorbed about 0.7 mL at equilibrium. However, the amounts adsorbed by the HTS coated sample and the ETS coated sample do not agree with this correlation, as can be seen in Figure 4.10, where the HTS coated zeolite sample adsorbed a similar amount of hexanol as the uncoated zeolite sample.

The data in Figure 4.11, which shows the amount of cyclohexanol adsorbed over time, is somewhat different than the results with hexanol. Instead, the OTS coated sample adsorbed the greatest amount of hexanol over the five hours, absorbing about 0.95 mL at equilibrium. Meanwhile, the zeolite with the shortest carbon chain length, ETS, and the uncoated zeolite adsorbed the least amounts of cyclohexanol, about 0.7 mL and 0.8mL of cyclohexanol respectively. The results of cyclohexanol diffusion were the opposite of what was expected, as zeolites with longer carbon chain lengths on their surface adsorbed more over time.

To better analyze the amount of target compounds adsorbed by each zeolite sample, the percent of available pore space that was occupied by the target compounds was calculated using the above values in Figures 4.10 and 4.11, along with the pore volumes shown in Table 4.1.



Figure 4.12: Percent of available pore volume occupied by hexanol



Figure 4.13: Percent of available pore volume occupied by cyclohexanol

Figures 4.12 and 4.13 offer a better example of how much of the target compounds were adsorbed into the available pore space of the zeolite samples. Figure 4.12 shows that while the OTS coated sample adsorbed the least amount of hexanol, it adsorbed a similar amount in the pore space as the uncoated and ETS coated sample. However, there was a noticeably higher amount of hexanol adsorbed into the HTS coated zeolite, where about 3.5% of the available pore space was filled with hexanol, compared to the closer range of 2.3% - 2.8% of the other three samples. Therefore, this figure shows that there is not a strong relationship between the length of the carbon chain on the surface of the zeolite sample and the amount of hexanol adsorbed.

On the contrary, Figure 4.13 supports the relationship between the chain length of the coating and the amount of cyclohexanol adsorbed. This graph shows that the sample modified with a longer carbon chain length, OTS, adsorbs more cyclohexanol than all other samples, showing that about 4.7% of the available pore space was occupied by cyclohexanol.

Meanwhile, the uncoated zeolite sample adsorbed the least amount, shown in the graph that only 3.2% of the available pore volume was occupied by cyclohexanol. Although this is not what would be expected, these data suggests a positive relationship between the carbon chain length of the coating on the zeolite and the amount of cyclohexanol absorbed.

Comparison of Figures 4.12 and 4.13 shows that more cyclohexanol was adsorbed overall by the zeolite samples than hexanol. This is not what would be expected since cyclohexanol is slightly bulkier than hexanol. An idea that may explain this behavior is that the interactions between the O-H group and the zeolite may be stronger with the smaller butanol, hexanol, than the larger cyclobutanol, cyclohexanol. However, this idea is undefined and only a postulation, but may be worth studying in the future.

Using the uptake rates within the first 15 minutes as shown in Figures 4.10 and 4.11, the diffusion coefficients were found using the following equation:

$$\frac{M_t}{M_{\infty}} = \left(\frac{Dt}{a^2}\right)^{1/2} \left\{ \pi^{-1/2} + 2\sum_{n=1}^{\infty} ierfc \frac{na}{\sqrt{(Dt)}} \right\} - 3\frac{Dt}{a^2}$$

This equation solves for the Fickian diffusion in a sphere, which was assumed to be a good representation of the zeolite samples (Crank, 1975). As the time approaches 0, the ierfc function also approaches 0. Therefore at this short time, the simplified equation shown below is proportional to the uptake rates and can be used to find the diffusion coefficients.

$$\frac{M_t}{M_{\infty}} = \left(\frac{Dt}{a^2}\right)^{1/2}$$

Where M_t is the amount absorbed at time t, M_{∞} is the amount absorbed at equilibrium, D is the diffusion coefficient, t is time, and a is the particle size. M_t/M_{∞} was analyzed over time to get relative slopes for the diffusion coefficients.



Figure 4.14: Amount adsorbed at time t over amount adsorbed at equilibrium to determine diffusion coefficients for Fickian diffusion

Zeolite Sample + Target Compound	D/D _{hexanol}	$10^{11} \text{ D} (\text{cm}^2/\text{s})$
Uncoated + Hexanol	1	1.95
ETS + Hexanol	1.027	2.0027
HTS + Hexanol	1.017	1.9832
OTS + Hexanol	0.871	1.6985
Uncoated + Cyclohexanol	1.0303	2.0091
ETS + Cyclohexanol	0.992	1.9344
HTS + Cyclohexanol	1.025	1.9988
OTS + Cyclohexanol	1.0302	2.0089

Table 4.2: Diffusion Coefficients for all Zeolite Samples

The diffusion coefficient for the uncoated Zeolite Y and hexanol is known to be 1.95×10^{-11} cm²/s, which is shown in Figure 4.14 with a bold pink line (Choudhary, 1992). Using the slopes of all the lines of the samples shown in Figure 4.14, a ratio of the diffusion coefficients to the known could be found, therefore giving approximate diffusion coefficients as shown in Table 4.2. As seen in the table, the majority of the samples with the target compounds have very similar diffusion coefficients. The ratio of the diffusion coefficients to the known diffusion coefficient of the uncoated sample and hexanol mostly range from 0.99 to 1.03. The only sample that appears to have a significantly different diffusion coefficient is the OTS coated zeolite and hexanol. As shown in the previous figures, the rate of diffusion with this sample was slower than the other rates, and this lead to a smaller diffusion coefficient of about 1.69×10⁻¹¹ cm²/s.

4.2: Uncertainty in Uptake Measurements

The uncertainty measurement of the adsorption experiments was determined using the following equations:

$$x_{avg} = \frac{x_1 + x_2 + \dots + x_n}{N}$$
$$\Delta x = \frac{x_{max} - x_{min}}{2}$$

The diffusion experiments were repeated for the uncoated zeolites to determine the reproducibility of the data. From this simple statistical analysis, the percent error was found and is reported in Table 4.3.

Time	Percent error hexanol	Percent error cyclohexanol
0	0	0
15	42.9	0.537
30	12.6	0.286
60	0.244	0.412
120	0.967	0.367
180	0	0.157
240	0.237	0.590
300	0.331	0.0835

Table 4.3: Uncertainty of the uptake experiments

For the cyclohexanol trials, the percent error is well under 1%, meaning that the trials had little variation between them. Therefore, the results from the uptake of cyclohexanol with the zeolite samples should be reproducible. However, the percent error for the hexanol trials is much more sporadic. The error at times 15 and 30 minutes is 42.9% and 12.6% respectively. This shows such a wide variation between the trials. These uncertain measurements were during the initial uptake of the hexanol, therefore the initial rate of uptake for hexanol was not easily reproducible in this study. However, after 30 minutes, the error stays under 1% for the hexanol experiment, meaning these values were much more consistent.

There are many possible sources of error associated with the diffusion experiments. Specifically for hexanol, the initial uptake was not accurate. It is possible that there was some human error when taking the initial sample during the sorption experiments. It is also possible that there was some cross-contamination in one of the trials with the syringe and filter used for the sorption experiments.

Chapter 5: Conclusions and Recommendations

After a thorough analysis of the results, the following conclusions and recommendations were developed. First, after characterization the surface modification of Zeolite Y with OTS, HTS and ETS was shown to be successful. FTIR spectra showed increased signal intensity at the wavelength region of 2800-3000 cm⁻¹ correlating to the increasing chain length of each sample. The uncoated sample showed no peaks in the stretch while the intensity grew with each of the three coatings. This proved that the methodology for coating the zeolites was successful. The contact angle measurement and oil-water emulsion experiments showed that the hydrophobicity was increased with modification and more specifically with longer alkyl chain length. The nitrogen sorption results showed that the pore volumes were largest for the uncoated zeolite and decreased with increasing alkyl chain length. The continued testing of organosilane coatings with longer chain lengths to see if there is a point where the coating blocks the pores and inhibits diffusion may provide an interesting study.

Although the literature claimed to have used calcined zeolites, uncalcined zeolites were found to have a higher hydrophobicity. This is shown from the contact angle measurements where the uncalcined samples had much higher contact angles. This may be a result of calcination where the organic matter and impurities are burned out of the zeolite. Creating a zeolite with less sites for the organosilane coatings to adhere to, thus making the calcined samples more hydrophilic. To better understand this phenomenon, more research and experimentation should be done on the effects of calcination on zeolite properties. In the future, sorption experiments should be run on the modified uncalcined samples to compare with modified calcined samples.

With respect to the diffusion experiments, the different coatings did not greatly affect the rate of diffusion of the target molecules in the zeolite. However, the equilibrium amount of hexanol or cyclohexanol absorbed did vary depending on the coating. In all experimental runs, there was more cyclohexanol absorbed than hexanol, which contradicts the hypothesis that a more bulky and cyclic compound would not diffuse as easily as an alcohol chain.

Sorption of the target molecules occurred rapidly within the first minutes of immersion in the zeolite-isopropanol solution and reached equilibrium around ten minutes. The methodology used called for samples every 5 minutes for the first half hour of shaking. This meant that only the first two samples in the first ten minutes were used to determine the rate of diffusion. Because of this limitation, the resolution on the initial rate of diffusion curve was poor. In order to get a better understanding of the sorption period, it is recommended that these diffusion experiments be repeated using a greater time resolution so that many data points may be gathered for this initial period to produce an accurate and clear sorption curve. As previously mentioned, a greater amount of cyclohexanol was adsorbed by the zeolite samples than the hexanol. Researching possible explanations for this behavior would be beneficial to understand the diffusive behaviors of the organosilane coatings.

Due to time restraints, two target molecules, hexanol and cyclohexanol, were sorbed into the different zeolite samples. Additional molecules should be tested to gain a better understanding of the interaction of the modified zeolites with different molecular species. Testing a wide variety of molecules including alkanes, acids, and molecules of larger and smaller sizes is recommended for future experimentation.

Appendix A: Additional Data







Figure A.2: FTIR spectra of ETS coated Zeolite Y







Figure A.4: FTIR spectra of OTS coated Zeolite Y



Figure A.5: SEM images of Zeolite Y samples magnified 2500 times. (A is Uncoated, B is ETSmodified, C is HTS modified, D is OTS modified.)



Figure A.6: SEM images of Zeolite Y samples magnified 5000 times. (A is Uncoated, B is ETSmodified, C is HTS modified, D is OTS modified.)

SE

10.08

С

10.0kV

D

X5,000

WD 10



Figure A.7: SEM images of Zeolite Y samples magnified 25000 times. (A is Uncoated, B is ETSmodified, C is HTS modified, D is OTS modified.)



Figure A.8: Gas Chromatography calibration curve for hexanol



Figure A.9: Gas Chromatography calibration curve for cyclohexanol

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	6699906	0.3274	0.6726
30	6898982	0.3329	0.6671
60	6277713	0.3156	0.6844
120	6939475	0.334	0.666
180	5968681	0.307	0.693
240	6086289	0.307	0.693
300	5921876	0.3103	0.6897

Table A.2: Gas Chromatography data for uncoated Zeolite Y and Hexanol

Table A.2: Gas Chromatography data for uncoated Zeolite Y and Cyclohexanol

Time	GC Peak	Amount Left	Amount
(minutes)	Area	in Solution	Adsorbed
		(mL)	(mL)
0	0	1	0
15	17605643	0.1853	0.8047
30	18765650	0.1984	0.8016
60	18357558	0.1938	0.8062
120	19526887	0.2069	0.7931
180	18357023	0.1938	0.8062
240	19333391	0.2048	0.7952
300	19846374	0.2105	0.7895

Table A.3: Gas Chromatography data for ETS coated Zeolite Y and Hexanol

Time (minutes)	GC Peak Area	Amount Left in Solution	Amount Adsorbed
		(mL)	(mL)
0	0	1	0
15	10203573	0.4249	0.5751
30	10598752	0.4359	0.5641
60	10094728	0.4218	0.5782
90	10895693	0.4441	0.5559
120	12617048	0.492	0.508
180	11733854	0.4674	0.5326
240	11019953	0.4476	0.5524
300	11315474	0.4558	0.5442

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	26339135	0.2837	0.7163
30	23786923	0.255	0.745
60	26225479	0.2824	0.7176
120	25070253	0.2694	0.7306
180	26607957	0.2868	0.7132
240	26246188	0.2827	0.7173
300	26607762	0.2868	0.7132

Table A.4: Gas Chromatography data for ETS coated Zeolite Y and Cyclohexanol

Table A.5: Gas Chromatography data for HTS coated Zeolite Y and Hexanol

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	6598005	0.3245	0.6755
30	6241925	0.3146	0.6854
60	6846065	0.3314	0.6686
90	6604839	0.3247	0.6753
120	7279064	0.3435	0.6565
180	6564389	0.3236	0.6764
240	6706790	0.3276	0.6724
300	7170779	0.3405	0.6595

Table A.6: Gas Chromatography data for HTS coated Zeolite Y and Cyclohexanol

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	11670713	0.1184	0.8816
30	11421986	0.1156	0.8844
60	11587044	0.1175	0.8825
90	11812357	0.12	0.88
120	11099755	0.112	0.888
180	11473816	0.1162	0.8838
240	11348497	0.1148	0.8852
300	11452932	0.1159	0.8841

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	15558708	0.5739	0.4261
30	13077645	0.5048	0.4952
60	13802408	0.525	0.475
120	13397904	0.5138	0.4862
180	12728365	0.4951	0.5049
240	13298709	0.511	0.489
300	13060618	0.5044	0.4956

Table A.7: Gas Chromatography data for OTS coated Zeolite Y and Hexanol

Time (minutes)	GC Peak Area	Amount Left in Solution (mL)	Amount Adsorbed (mL)
0	0	1	0
15	6874310	0.0643	0.9357
30	7372474	0.0699	0.9301
60	6944271	0.0651	0.9349
120	7140086	0.0673	0.9327
180	7002864	0.0658	0.9342
240	6706865	0.0624	0.9376
300	7373358	0.07	0.93

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