A Study on the Hydrophobicity of Organosilane-Modified Zeolites

A Major Qualifying Project Report
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Submitted by: Jingtian Kuang and Chenming Li
Project Advisor: Professor Michael Timko
Co advisor: Professor John C. MacDonald
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Acknowledgement

As the contributors of this *A Study on the Hydrophobicity of Organosilane-Modified Zeolites* Major Qualifying Project Report, we sincerely would like to recognize the significance of Professor Timko for his extensive help, patience and guidance to this work. We also appreciate the help from our co. advisor Professor MacDonald for being so inspirational and letting us use his laboratory equipment.

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Abstract

Zeolites are a class of microporous materials that exhibit high external surface area, extraordinary molecular sieving capacity and microporous structure with selective pore sizes. Control of zeolite external surface properties, in particular hydrophobicity, is desirable for many applications in catalysis and separations. To control the hydrophobicity of zeolite surface, we modified the outer surfaces of four types of zeolites by covalently bonding organosilane molecules of varying alkyl chain length. We then characterized the hydrophobicity of the external surfaces by measurement of static contact angle, finding that zeolite hydrophobicity increased after silanization. To quantify the effect, we then performed gravimetric measurements to estimate the mass of coating acquired by the zeolites during silanization. When combined with external surface area measurements, the coating mass measurement allowed estimation of the surface density of the silane coating. We found that even modest coatings (>10 mg/cm^2) transformed the zeolite surface hydrophobic; increasing the coating density beyond this critical loading had little effect. This work provides a rational basis for determining the optimal coating density required for a given application.

Introduction

Zeolites are porous materials with hierarchical structures that exhibit the property of acting as sieve on a molecular scale. Among several types of molecular sieve materials, zeolites are a well know category which have already been synthesized in laboratories and industrial scales for more than half a century due to their unique catalytic, absorptive and separation properties (Durrani, Akhtar, Ahmad, & Moughal, 2005). In the field of biomass production, reactions often happen within micro porous materials (such as zeolites), with reactant molecules diffusing into the pores, reacting at the active sites and then diffusing out(Aho et al., 2008); the various selective pore sizes, as well as the Lewis and Bronsted acid site strength provide the flexibility and a wider range of choice in different reactions(B. Li et al., 2015). In theory the introduction of zeolites in biomass reactions should promote the reaction speed and, therefore, improve yield; however, for reactions that take place in a liquid water phase the use of most zeolites is not feasible for those which taken place at over 150 °C since the crystalline structure of zeolite would collapse easily and lose its catalytic ability (Zapata, Faria, Ruiz, Jentoft, & Resasco, 2012). To overcome this limitation, a new technique to extend hydrothermal stability has been shown to be coating the external surface of zeolite with a hydrophobic organosilane, as confirmed by Resasco et al., who reported that octadecyltrichlorosilane treated H-ZSM-5 was an effective catalyst for the hydrolysis of water-insoluble esters in toluene-water solvent system(Resasco, 2015).

Professor Timko's research group has been focusing on understanding the surface characteristics of organosilane modified zeolites as well as their performance in potential future applications including catalytic ability in biofuel upgrading reactions and absorption capability in chemical spill remediation processes, etc (Blanker, 2014). From previous research progress, we have proposed suspected that several parameters that would govern the hydrophobicity of zeolites, were the length of silylating material, the pore sizes of the zeolites. The amount of silane used and so on. Unfortunately, all these guesses remain on the level of hypothesis and lack experimental data or scientific calculation and analysis; therefore, this project is mainly designed to test those hypothesis and try to give more convincing conclusions.

To expand our research on studying the factors that influence the hydrophobicity of zeolites, this MQP project developed a series of control experiments and focused on investigating how each control variable would affect the hydrophobicity of functionalized zeolites. Important questions that we attempted to answer in this project included what is the relationship between the thermal stability and surface wetting properties, what is the coverage of coating on the surface for each type of zeolite and what are the corresponding performances when in contact with water. And most importantly, what is the optimum amount of silane needed to tune zeolite from hydrophilic to hydrophobic?

Background

Zeolite Modification

As illustrated above, the key challenge for the development of liquid-phase upgrading reactions for biofuel production is to prevent the collapse of the zeolite structure. Various modification methods has been investigated to enhance the tolerance of zeolites in severe environments (Dyer & Keir, 1989; Valadabadi, Shiranirad, & Farahani, 2010; Xavier, Chacko, & Mohammed Yusuff, 2004), especially when in contact with hot aqueous solutions at high pressure (Eroshenko, Regis, Soulard, & Patarin, 2001). Literature reviews show that the stability of zeolite in hot liquid water is strongly related with the density of Bronsted and Lewis acid sites (Xue et al., 2007), which in turn is governed by the Si/Al ratio in their framework configuration. Therefore, increasing the Si/Al ratio would be an effective way to make the zeolite structure last longer in aqueous environment since it increases the hydrophobicity character of the zeolite. Unfortunately, Moliner et al,who have recently used hydrophobic zeolites to isomerize glucose to fructose in an acid aqueous environment(Moliner, Román-Leshkov, & Davis, 2010), proposed that the increment of Si/Al ratio requires the compensation of Bronsted acid sites, which would inhibit the performance of zeolite in catalytic reactions(Zapata et al., 2012).

An alternative approach to increase the hydrophobicity of zeolites without deactivating the acid sites present on the external surface is via external surface modification using organosilane (Campbell, Hertzenberg, & Sherry, 1981; Kawai & Tsutsumi, 1998; Y. Li, Guan, Chung, & Kulprathipanja, 2006). The chemistry occurring at the surface can be illustrated by the following scheme:

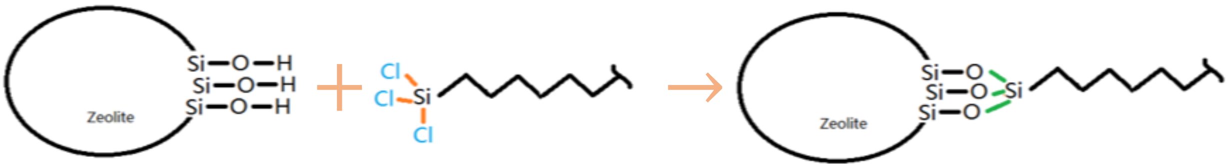

Figure 1 Scheme of Silylation Procedure(Wang, 2015)

The above figure represents the reaction process between zeolite and organosilane, where the –OH groups the zeolite are bonded with one end of silane and form the new Si-O-Si bonds.

The hydrophobicity of alkyltrichlorosilane functionalized zeolites have been studied by previous researches. Figure 2 shows that modification of the zeolite with organosilane successfully prevents water droplet from getting into the inner structure of H-USY zeolite; and figure 3 is an experiment where both untreated and treated zeolites are suspended into a mixture of oil and water and only treated zeolite is able to stay repelled from the aqueous phase whereas the untreated zeolite is entirely submerged by water.

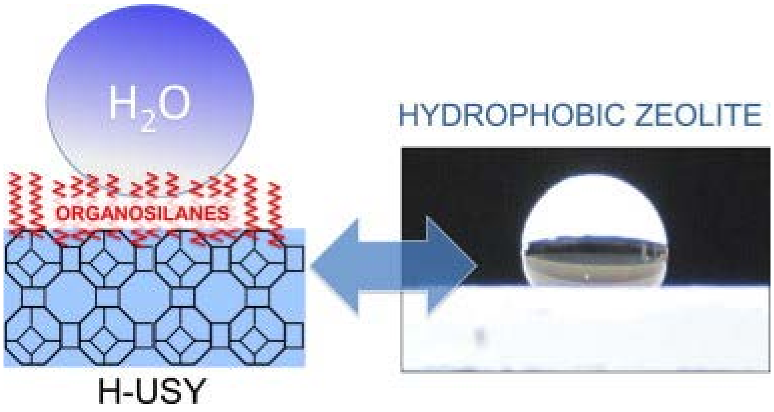

Figure 2. Organosilane prevents water getting sucked into the surface of H-USY zeolite(Zapata, Huang, Gonzalez-Borja, & Resasco, 2013)

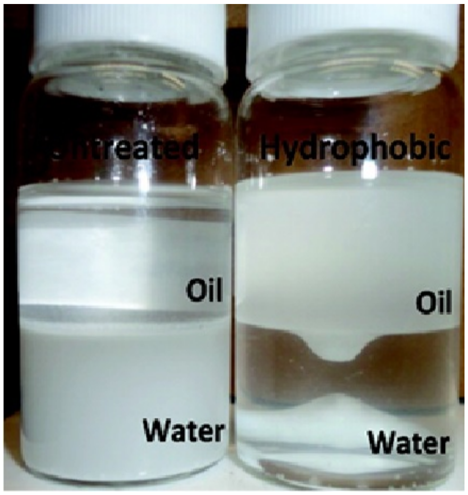

Figure 3. Distribution of the untreated and OTS-functionalized HY(Zapata et al., 2013)

Wetting Properties and Contact Angles

Wetting refers to the ability of a liquid to maintain contact with a solid surface and the degree of wetting directly reflects the level of hydrophilicity of the measured sample(Zaher & Caron, 2008). The simplest way to study the wetting property of zeolites is to measure its contact angle, as seen in figure 4:

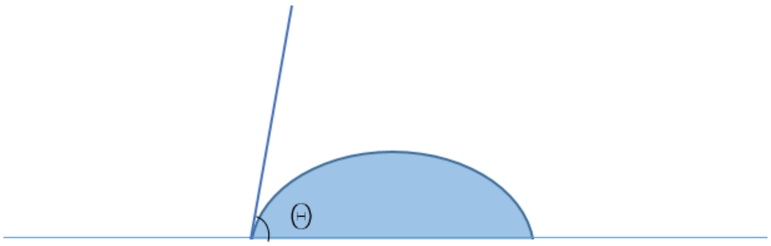

Figure 4. Contact angle for a liquid droplet on a solid surface

The truncated sphere represents a liquid droplet on the horizontal surface and theta is the contact angle that is determined by the adhesive and cohesive forces. The flatter the droplet, the smaller the contact angle and the more hydrophilic the surface is; thus contact angle is inversely related with wettability of the material.

For our modified zeolite samples, we expect the contact angle to be greater than 90°, which is the typical delineation point separating low and high wettability. However, despite the capillary force which is already known to have influence on the measurement of contact angle, other factors such as the roughness(Marmur, 2003) of the surface is also influences observations of contact angle, and hence hydrophobicity, of zeolite samples.

Experimental

This section describes the silylation procedure that uses organosilane to modify the zeolite surface, and the scientific techniques used to characterize the modified samples, namely contact angle measurement, thermogravimetric analysis, scanning electron microscopy, light scattering, nitrogen adsorption, surface roughness measurement, and magic angle spinning Si^{29} nuclear magnetic resonance.

Sample Preparation

The four types of zeolites used in this study are ZSM5, Beta, HY, and SAPO-34; their physical properties as well as manufacturer information are summarized in the following table. All the zeolites appearances are weight powder in this study.

Table 1 Zeolite Information

Zeolite	**Manufacturer**	**SiO_2/Al_2O_3 ratio**	**Total Surface Area (m^2/g) from manufacturer**
ZSM-5 Zeolite	Alfa Aesar Lot#45883	200-400:1	400
Beta Zeolite	Zeolyst International Lot# CP 811E-150	150:1	620
HY Zeolite	Zeolyst International CBV760	60:1	720
SAPO-34 Zeolite	ACS Material	SiO2~10% Al2O3~42%	≥550

The organosilane coating materials were obtained commercially from SIGMA-ALDRICH and was directly used in synthesis without further modification. Table 2 shows the properties of the coating materials. All information are obtained from SIGMA-ALDRICH product website.

Table 2 Organosilane Coating Material.

Name	**Linear Formula**	**Bp °C**	**Density g/mL (@25 °C)**	**Molecular Weight (g/mol)**
Ethyltrichlorosilane (ETS)	$CH_3CH_2Cl_3Si$	99	1.238	163.51
Hexyltrichlorosilane (HTS)	$CH_3(CH_2)_5Cl_3Si$	191	1.107	219.61
Octadecyltrichlorosilane (OTS)	$CH_3(CH_2)_{17}Cl_3Si$	223	0.984	387.93

The coating method was published in the previous literature (Zapata et al., 2013). The detailed procedure is described below: Each of the parent zeolites was calcined at 550 °C overnight prior to silylation to remove any impurities in the pores and external surface. Then 2g of each type of zeolite was dispersed in 20ml toluene. The mixture was sonicated with a VC750 type sonicator operated at 25% amplitude for 45 minutes. This process disrupted agglomerated particles in the solution to achieve a uniform suspension of separate zeolite particles in the solvent. After sonication, organosilane coating material was added in with a ratio of 0.5mmol silane per gram of zeolite. The mixture was stirred using a magnetic stirrer at 500 rpm for 24 hours. The final solution was filtered through a nylon filter with 0.22 micrometer pore size. Zeolite sample obtained was washed completely with ethanol solution and dried at 80 °C overnight.

Characterization

The hydrophobicity of organosilane coated zeolites was measured using contact angle measurement. Since the contact angles of ZSM-5, BETA, HY samples were already determined by previous MQP student in the Timko Group, we followed the procedure described in the old MQP report and performed the measurement for only SAPO-34 zeolite; then we combined our data with those from previous MQP report (Wang, 2015) to compare the hydrophobicity of the four zeolites.

Briefly in the contact angle measurement procedure, the modified zeolites power were pressed into relatively smooth pellet using the CrushIR Digital Hydraulic Press (PIKE Company). To ensure the pellet was thick enough for contact angle measurement as well as for easier transfer, 5-10 mg of zeolites were used to prepare the pellets. The sample pellet was subjected to a constant froce of 7 ton force for 5 minutes, and the control of the press was adjusted manually to ensure a stable pressure. After a pellet was formed, it was carefully placed on the goniometer stage, and a water droplet of 6μL to 15μL dropped on the surface of the pellet in the sample stage. To obtain the best result, the exact volume of the droplet was determined based on the pellet condition by trial and error.

Quantification of silane loading on the functionalized zeolites was done by thermogravimetric analysis using a TA Instruments equipment (model #2950). Before each trial, the platinum pan was burned to glowing red to remove any residuals and then tared. A small amount of zeolite sample (7-20 mg) was placed in the tared pan and treated in air at 100 °C, followed by a ramp rate of 15 °C/min to 700 °C. The TGA profile and measurement of the variation in weight loss with respect of temperature was obtained by software automatically.

Morphology and external diameter of the samples were evaluated using a JEOL JSM-7000F Field Emission Scanning Electron Microscopy, and all samples were coated with gold platinum alloy by a Sputter Coater to increase the conductivity for relatively high resolution SEM images. Next, the particle size was determined using ImageJ software and compared to the result that was manually measured using the scale bar on the SEM images. In a typical trail of manual measurement, 50 particles were taken as samples and the average value was used for further calculation. For ZSM-5, HY and Beta zeolites that are spherical aggregates, we calculated the external surface area using the formula for spheres; whereas the structure of SAPO-34 was shown as a cubic from SEM result, we measured the side length in order to find the surface area.

The particle external surface area determination was complemented with light scattering using a Zeta-Sizer equipment. The zeolites were dispersed in DI water, with a VC750 type of sonicator operated at 25% amplitude for 20 minutes to make the sample distribute evenly in the mixture. 2 mL of the mixture was then added in a new disposable plastic transparent square cuvette and placed in the equipment for scanning. The scan was set to 10 trails per measurements, and the scanning time was 1.5s/ time. Software were used to analysis the data and we took the median diameter of the particles and compared the data with those from SEM.

Nitrogen adsorption of the coated zeolites was performed by Professor Goldfarb at Boston University using Quntachrome instrument. BET curve and T plot was acquainted and produced automatically, and the surface area was calculated using the BET equations in the 0.05 to 0.3 pressure range.

Surface roughness measurements were performed to detect the roughness of zeolites surface that may influence the contact angle measurement. Prior to each measurement, both the uncoated and coated samples were made into pellets and the roughness of zeolite pellet was then determined using a Raman spectroscopy. In a roughness measurement, the pellet was handled carefully with a squeezer to avoid the contamination on the surface for accurate measurements. The pellet was placed on the stage and light was used to make the filed easier to see. The focus of the camera was adjusted to focus on the top and the valley of a local point. The height difference was recorded as the roughness of the surface. Five points were measured for each sample.

Magic angle spinning Si^{29} nuclear magnetic resonance (MAS NMR) measurement was performed and provided by Prof. Smith at Clark University to determine any chemical changes of the silicon atoms due the reaction with organosilane.

Result

The results of this project study are presented and analyzed in several parts, each corresponded with a type of characterization technique we used. We first dealt with the surface characterization of the zeolites after modification using silane reagents of varying carbon chain lengths. We confirmed the successful bonding of silane by conducting CP-MAS NMR and analyzed the zeolite hydrophobicity using contact angle measurement to investigate the effect of carbon chain length on the hydrophobicity level. Then we determined the exact coating density of each type of zeolite using a combination of methods including TGA, SEM, Nitrogen Adsorption and Light Scattering.

Contact Angle Measurement

The contact angle directly reflects the hydrophobicity of the modified zeolites, and from literature reading, we know the alkyl chain length has a positive effect on the hydrophobicity of zeolite (Zapata et al., 2013), but this trend is obviously unclear to see on the graph we plotted using our data, as shown in Figure 5. It is interesting to notice that for HY zeolite, the samples functionalized with OTS, HTS and ETS exhibit almost the same hydrophobicity, which does not follow the trend of increasing hydrophobicity with increasing carbon chain length. literature(Han et al., 2011). In addition, the ETS modified Beta and ZSM-5 samples remain essentially hydrophilic despite the presence of the hydrophobic coating

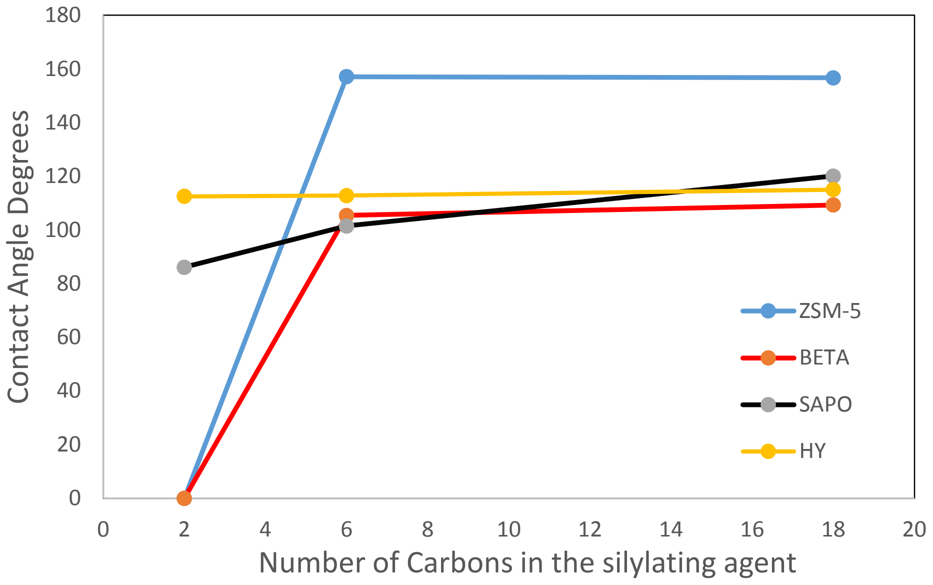

Figure 5. Relationship between carbon chain length and hydrophobicity

Thermogravimetric Analysis (TGA)

To determine exactly how much coating was present on the zeolite, thermogravimetric analysis (TGA) was performed to quantify the amount of silane anchored on the external surface. Below is the TGA graph of ZSM-5 modified zeolite and the graph were plotted from 110 °C, since we suspected that only loosely bonded water was evaporated off from the surface below that temperature. From 110 to roughly 300 °C, there is a 1% weight loss, which should attributed to the desorption of tightly bonded water; from 300 up to 700 °C, the most pronounced weight loss was observed, and this is contributed by the decomposition of organosilane. Since the decomposition temperature of organosilane is higher than its boiling point, it indicates that strong chemical bonds have formed between silane and zeolite(Han et al., 2011). The graph also shows a trend that the longer the carbon chain length of the silane, the greater the observed weight loss, which may be consistent with similar molar loadings of the different chain length coatings. Another concern is the incomplete removal of ETS and HTS by the end of the TGA experiment since the slope of both lines is going downward, and this problem may induce a slight error in our silane mass determination. The graph below is an example to show the TGA graph. Different coatings of ETS, HTS and OTS coated ZSM-5 weight loss is compared in Figure. 6.

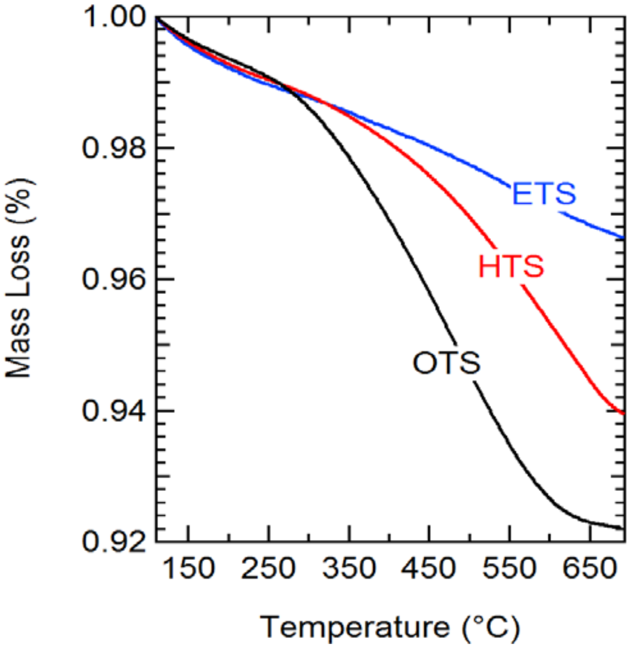

Figure 6. ZSM-5 Modified Zeolite TGA Comparison

Scanning electron microscopy (SEM)

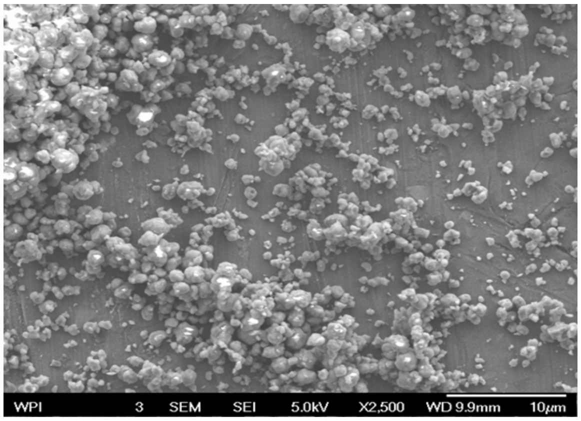

Figure 7a. ZSM-5 SEM Capture

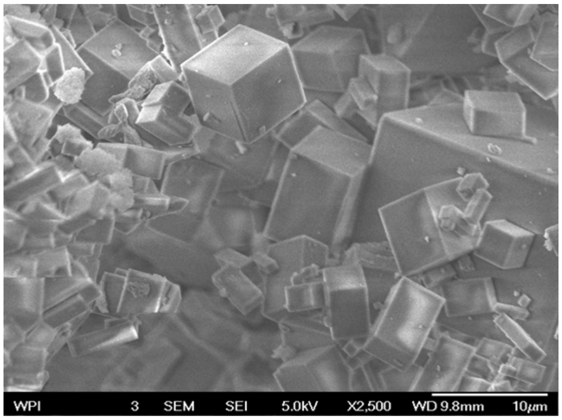

Figure 7b. SAPO-34 SEM Capture

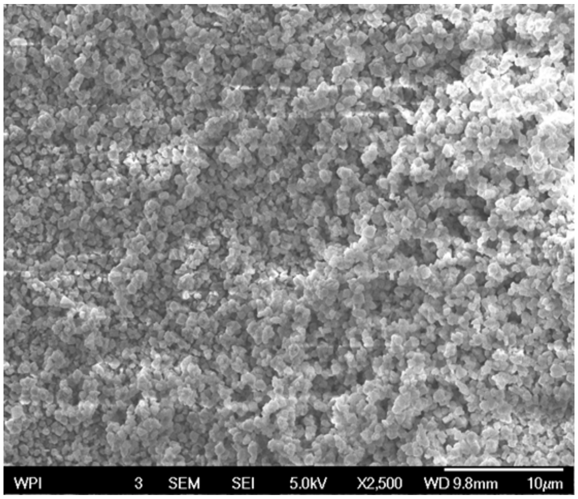

Figure 7c. HY SEM Capture

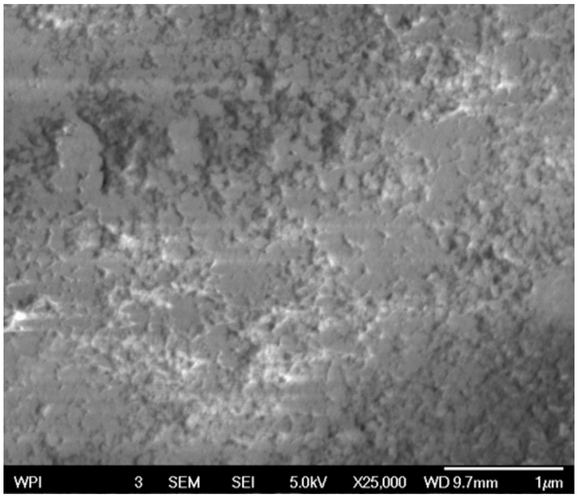

Figure 7d. Beta SEM Capture

From SEM results, we are able to evaluate the physical appearance, crystallinity and crystal morphology of each type of zeolite and from there external surface area of single zeolite particle can be determined using an automated software (ImageJ). However, the Beta zeolite surface area was difficult to determine by the software as the resolution was not good, and the agglomeration of particles result in unclear boundaries. The manually determined surface area was also limited by the image resolution. Even though the zeolite samples for SEM were pre-calcined, they were placed in room temperature for a while and were not dried again before use; this may lower the electricity conductivity of the sample so that the image resolution of SEM result images decreased as a result. Samples were coated with gold platinum alloy before taking the SEM images. However the conductivity of zeolites surface was still too low.

Other Particle Size Determination Method as references

To confirm the result of SEM experiments, we attempted to obtain the particle size data from other experiments. Light scattering and nitrogen adsorption were conducted as references. Light scattering results are shown in the table below. For HY and ZSM-5, the light scattering measurements of particle size are in reasonably good agreement with the SEM size estimate (within about 20%). On the other hand, the experiments show that the light scattering method is not suitable for BETA and SAPO-34 zeolites. The results of those two types of zeolite were out of the reasonable range for the instrument. The standard deviations were also very large. We suspect that, consistent with the aforementioned SEM images, that SAPO-34 and Beta zeolite were too strongly agglomerated for the ultrasound method to disrupt them prior to the light scattering measurement. For these reasons, the light scattering result was not used in calculations of outer surface area; however, the reasonable agreement between light scattering and SEM size measurements for weakly agglomerated HY and ZSM-5 zeolites improves our confidence in the use of SEM for estimating the external surface area of zeolite particles.

Table 3. Comparison of Light Scattering and SEM Result

Zeolite Type	Average Diameter from light scattering (nm)	STD	Average Diameter from SEM (nm)
HY	469.95	16.74	577.18
ZSM-5	426.45	15.73	508.09
Beta	3954.50	836.77	2645.09
SAPO-34	10187.33	5280.54	3665.46

Nitrogen adsorption was also performed in this study. However, the data indicates that, maybe it is powerful in determine the total area, nitrogen adsorption is not a good method the surface area of the zeolites. The external surface area could be calculated from BET equation but the result is too large and does not make any sense. Table 4 compares the external surface area calculated from SEM results to the nitrogen adsorption data, and there is a large difference in results. Also clearly shown in Figure 8, the SAPO-34 BET plot has a negative slope, which indicates a negative external surface area but this is entirely impossible.

Table 4. Comparison of External Surface Area from SEM and Nitrogen Adsorption

Zeolites	Surface Area from SEM (m^2/g)	Surface Area from BET plot (m^2/g)
ZSM-5	5.05	105.4
BETA	1.24	230.01
SAPO-34	0.92	-4.27
HY	3.99	148.6

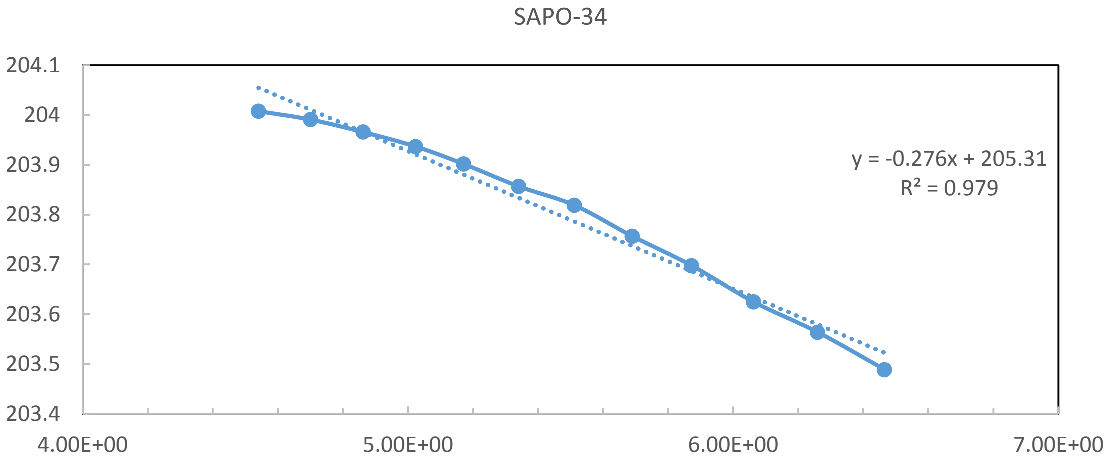

Figure 8 Nitrogen Adsorption Result for SAPO-34

Si^{29} magic angle spinning nuclear magnetic resonance (MAS-NMR)

The Si^{29} MAS NMR data is shown below. The Si^{29} MAS NMR data was contributed by Prof. Smith from Clark University. According to the literature (Dědeček et al., 2009), the peaks at around 110 ppm is the silicon in ZSM-5 starting material. Q3 and Q4 peaks are connected to different kinds of aluminum atoms and have different linkage. As indicated in the pictures, both Q3 and Q4 sites were the silicon atoms in the zeolite. The T2 and T3 sites that appear only in the treated zeolite indicate the successful coating of organosilane groups on the zeolites surface. The ratio of T2 and T3 sites indicates two different bond structures. The ratio of those two (approximately 2:1) peak areas can be considered as the ratio of atoms that is in two different linkage. However, a direct polarization experiment did not reveal the ratio of T sites to Q sites as the intensity of the T sites signals were too low to be measured. Seen in the NMR, the chemical shifts of Q spots are not the equal area as before. It is possible the presence of coating on the zeolite surface changed the chemical environment of some of the silicon atom in the zeolite pores. Or it is maybe possible that the structures inside the pores has changed due to the thermal modification treatment of 100 ^{o}C for a relatively long time (12 hours) during silanization.

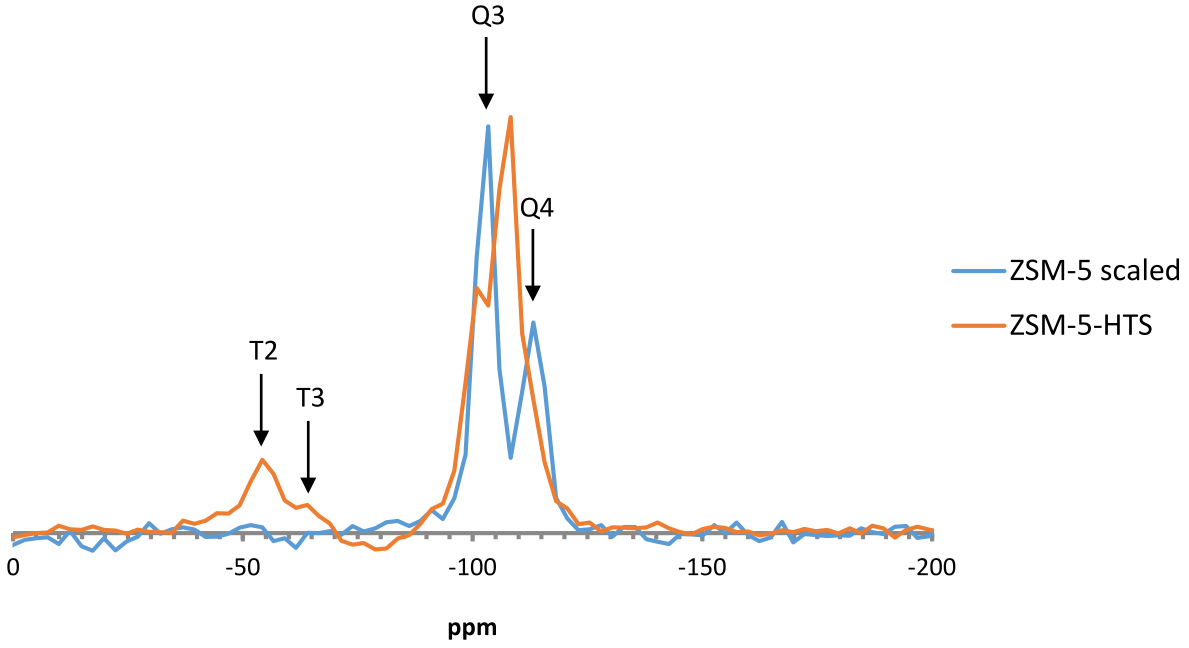

Figure 9. ZSM-5 and ZSM-5 HTS Si29 CP-MAS NMR

Discussion

Combining the surface area data from SEM experiments and the contact angle results, we observed a phase change at a specific coating density so that the zeolite would flip from hydrophilic to hydrophobic crossing that point. In figure 10, the critical point seems to be at around 10 mg/m^2; however since ETS coated Beta did not show a hydrophobicity character under a relatively high coating amount. Due to the inaccuracy in determination of surface area data for that specific zeolite and its high degree of agglomeration, it is possible that the estimated mass coating for this zeolite has been inaccurately determined.

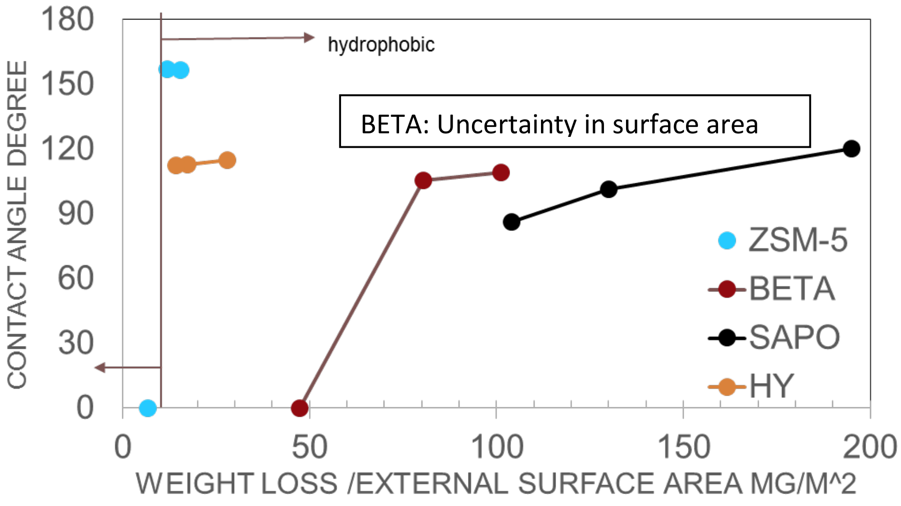

Figure 10. Contact Angle vs. Unit Surface Coating Amount

The roughness of the particle surface also effect the contact angle measurement. To determine the average roughness, the data of five points are shown for each zeolite. The data were obtained for uncoated fresh zeolites. The data for each point was obtained as the difference between a local top and valley point height. HY is the roughest zeolites among the 4. The resolution of the machine is not good enough to give the exact focus height. However, the relative relation between 4 data can be trust for the large difference of 10 times larger. Due to the resolution of the image and the equipment, the data is not very accurate. The larger roughness of zeolite HY contributes to the large contact angle result at low coating amount.

Table 5. Surface Roughness Measurement Results

Roughness	POINT 1	POINT 2	POINT 3	POINT 4	POINT 5	AVG	STD
BETA	1.5	5	2	3	2	2.7	1.67
SAPO-34	1	1	4	1	7	2.8	2.66
HY	31	24	14	25	30	24.8	11.79
ZSM-5	2	1	1	3	1	1.6	1.03

Conclusion

In conclusion, the coating density was determined for each zeolite to find the optimum coating amount. A phase change point of 10mg/m^2 is the optimum coating amount for most of the zeolites. However, zeolites with higher surface roughness can behave hydrophobic with a coating amount less than 10mg/m^2. At the same time, the relative high coating density indicates the possibility of multi-layer coating.

From the experiments we performed, presented below are some highlights of our study.

The surface of four types of zeolites was modified with hydrophobic trichlorosilane materials of varying chain lengths. When characterizing the wetting ability, contact angle experiments clearly show the increased hydrophobicity of the organosilane coated zeolites. The tricholorosilane coating acts as a protecting outer layer and successfully enhances the wetting ability of zeolites. We surely observed an obvious phase change from hydrophilic zeolites to hydrophobic modified zeolites, but the phase change coating amount is hard to determine, since it varies with the zeolite kinds.

Furthermore, the minimum coating amount required to achieve the hydrophobic performance is also influenced by roughness. In contact angle measurements, most of the ETS coatings fails to hold a droplet with a low coating density. The ETS coated HY was the only one that can hold a droplet in the contact angle measurement with a low coating amount; we suspected the reason to be the high roughness of the HY zeolite surface. Specifically speaking, Beta, SAPO-34 and ZSM-

5 zeolites that are not as rough as HY. They probably require a higher coating density to overcome the low surface roughness to be hydrophobic.

Multi-layer coating may be possible due to the unusual high coating density of Beta and SAPO-34 compared to other zeolites in this study. SAPO-34 shows a great coating capacity in the study. When modified with the same chain length of organosilane groups, the SAPO-34 zeolites has coating weight on unit surface area about 10 times greater than the coating weight of ZSM-5. Since it is unlikely that SAPO-34 would have about 10 times more acid sites on a unit area than the others, the high coating density may result from the multi-linkage of Si-O-Si group.

Future Study

At the time this report concludes, there are still some unclear points needed for further clarification. First of all, the proposed multi-layer coating on the surface of zeolite is still under investigation; since the coating reaction is kinetically controlled, we highly recommend that for future studies, either the reaction time need to be shortened, or the molar ratio of coating material and zeolites should be reduced in order to form a monolayer of coating on the surface. Moreover, if the multilayer assumption is true, there may or may not be a limit of the coating amount.

Secondly, even though we have tried at least three different methods to find the zeolite surface area, the results do not match each other very well and the error percentage is pretty large. The differences in results may be explained by the agglomeration of particles. For example, in light scattering the agglomerated particles kept settling down during the long period of measurement, which then gave out inconsistent results for the list of trials we ran. However, a shorter measuring time will force the number of measurement decreases in each trail and will make the result even less reliable. To avoid this situation in future studies, we suggest extending the duration of sonication prior to silylation process to break apart zeolite particles more sufficiently.

Lastly, we think that contact angle measurement may not be the best way to test the hydrophobicity of zeolites since we could not collect the contact angle data for ETS modified Beta and ZSM-5 zeolites. In this study, the contact angle of zeolites was first pressed as pellets, and the pellet preparing procedure may contain some error. The pressing time and the pressure applied on the pellet may affect the pellet surface. The stainless steel presser used as contact with the zeolites may have some defects that may change the surface roughness of the zeolites pellets. Considering the limit of contact angle measurement for hydrophobicity, some new method should be explored to determine the hydrophobicity of zeolites.

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