Surface Energy of Alkyltrichlorosilane Modified Zeolites

Major Qualifying Project Proposal completed in partial fulfillment of the
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Abstract

The purpose of this project was to develop the methods for studying surface properties of alkyltrichlorosilanes modified zeolites. Unmodified zeolites have low tolerance to hot aqueous solutions. Crystal structures are destroyed and zeolites lose acid sites. Thus, bare zeolites are not good candidates as acidic catalysts in most biomass conversion reactions. Modified zeolites show promising catalytic ability and can survive under severe conditions. Alkyltrichlorosilane coating provides protection to delay coking and helps form emulsion in binary system. Surface properties of zeolites, especially the influence of outer surface, need to be studied to understand the macroscopic behaviors of zeolites during the reaction and the product separation processes. Glass slide surface was used as smooth, non-porous model. Silica beads were used as non-smooth, non-porous model. ZSM5, HY, and Beta zeolites were used in this study. All materials were coated with octadecyltrichlorosilane, hexyltrichlorosilane, and ethyltrichlorosilane. Powder materials were pressed into pellets. Contact angles were measured on glass slide surfaces and powder pellet surfaces with goniometer. Water, glycerol, formamide, bromonaphthalene, and bromobenzen were used in to form meniscus. Water-glycerol and water-formamide systems were used to develop the liquids that can be used in contact angle measurement and surface energy calculation. Surface energy was calculated with Owens and Wendt's approach. Results of glass slides were in good quality and reproducible. Results of powder materials, including silica beads and zeolites were not in good quality and not reproducible.

Acknowledgement

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1. Introduction

As a source of generating biofuel, biomass has been attracting people's attention for decades. An increasing amount of research work and commercial applications have been done recently because of the advantages of biofuels such as renewable sources, and eco-friendly production and consumption processes. Sugar and starch rich biomass, such as sugar cane and corn, are primary sources of fermented alcohol. Lately, celluloses and microalgae are frequently mentioned in research papers as additional sources to produce alcohol. Alcohol can further be dehydrated or react with lipid feed stocks, ideally with waste vegetable oils, to produce higher energy dense hydrocarbon products. [1, 2, 3]

Biofuel production involves many different chemical reactions. Reactions usually occur in the gas phase or liquid phase. Acids often act as catalysts to remove oxygen containing functional groups. The use of these acid catalysts intensively accelerates the reaction rates and reduces production costs. [4, 5] Solid acid catalysts stand out among various kinds of acid catalysts due to their unique properties. Solid state catalysts can be separated easily from the products compared to liquid acids, therefore reducing separation costs. Advantages such as efficient activity, high selectivity, and long catalyst life make solid catalysts more competitive. [6].

Zeolites are a family of porous solid acid catalysts that can be used in many biomass to biofuel conversion processes. The acid strength of zeolites can be controlled during the synthesizing process. Thus it is convenient to customize catalysts for different reactions to control the yields and rates. Since the porous structures expand the surface area of the materials, zeolites contain more active catalytic sites compared to nonporous materials. Porous zeolites, including the microporous and mesoporous kinds, are widely used. [5, 6, 7, 8]

Some reactions that zeolites can catalyze are esterification, transesterification, dehydration, hydrolysis, alkylation, and isomerization. Lipid feedstocks and low molecular weight alcohol can be used to synthesize biodiesel via transesterification. Inexpensive feedstocks contain high levels of free fatty acids, making alkaline bases not suitable for catalyzing. Acid catalysts are less sensitive to the level of free fatty acids, which allows them to simultaneously conduct esterification and transesterification. [5] Acid catalyzed sugar dehydration is an effective way to deoxygenate biomass to produce renewable chemicals and fuels. [7] H-form zeolites can be used in cellulose hydrolysis to decrease the crystallinity of cellulose and produce water soluble glucose. [9] Some zeolites are widely used as shape-selective catalysts because of the high selectivity. [8]

Most acid catalyzed reactions can have decent yields and reaction rates only at high temperatures and high pressures (e.g. in 200 ℃ aqueous solution). Under these conditions, crystal porous materials such as zeolites will coke and lose crystallinity. Changes in material structures will defunctionalyze the catalysts. [10] Improving the hydrophobicity of zeolites would make them less sensitive to high temperatures in aqueous solutions and more suitable.

Previous research has been done on modifying the outer surface of zeolites with alkyltrichlorosilanes to improve the hydrophobicity. [10, 11] Characteristics of the modified zeolites have been studied with FTIR, GC, TGA, in real chemical reactions, as well as with other technologies. The physical behaviors of zeolites in binary liquid systems, however, have not been studied in depth by many people. Surface properties of zeolites, especially the influence of outer surface, need to be studied to understand the macroscopic behaviors of zeolites during the reaction and the product separation processes. Only a few similar studies have been done in different fields such as geochemistry. [12] Studies on this topic will enhance our understanding of the behaviors of modified zeolites in binary liquid systems and further improve the modification process and technology.

2. Background

Zeolite

Zeolites are a family of porous, aluminosilicate minerals. Porous structure gives zeolite great absorptivity. Thus it is often used as commercial absorbents in situations such as absorbing oil spill. [13] The pore size varies with different zeolite frame work. Artificial zeolites are used as solid acid catalysts due to the abundance of acid sites, resulted by the extension of surface area, and their adjustable acidity. Generally, for the same type of zeolite, acid site density can be increased with decreasing Si/Al ratio of the zeolites. [14] Compared to liquid acid catalysts, heterogeneous zeolites can be separated from liquid products very easily and reduce environmental impacts.

Hydrolysis of cellulose, isomerization, and alcohol dehydration have been successfully conducted in aqueous solutions catalyzed by acidic catalysts. [7, 9] During these kinds of reactions, the yields and reaction time are usually related to reaction temperature. Within reasonable range, reaction rate and yield increase as temperature increases. [3, 10] High temperature aqueous solution, however, is fatal to crystal zeolites. [10] Crystal structures will be destroyed and zeolites will lose the acid sites. Part of the zeolites will dissolve in the hot aqueous solution.

Researchers have been trying to solve this problem and apply zeolite catalysts to large scale industrial productions. In previous studies, hydrophobicity of zeolites is usually manipulated to prevent structure destruction in hot aqueous solutions. [10, 11] In these studies, alkyltrichlorosilanes were used to modify the surface of zeolites to improve the hydrophobicity, thus prevent or reduce the structure damages. Three chlorine atoms are bonded with silicon atom at the head of alkyltrichlorosilane. The carbon chain tail can be short or long. Once alkyltrichlorosilane attaches to zeolite, it loses three chlorine atoms and forms Si-O-Si bond with the Si-O-H site on the surface of zeolite. Coating can thus be performed, as Figure1 shows.

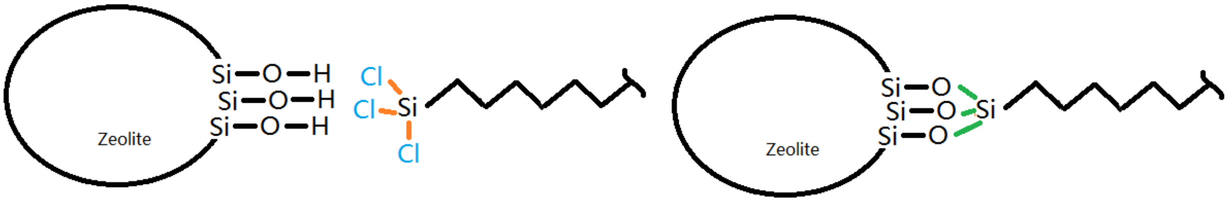


Figure 1. Concept of Coating Procedure

Characteristics of alkyltrichlorosilane modified zeolites were successfully studied by previous researchers. Technologies such as Fourier transform infrared (FT-IR) spectroscopy, X-ray photoelectron spectroscopy (XPS), Thermal Gravimetric Analysis (TGA), electron microscopy (EM), and detection of products after catalyzed reactions were used to characterize zeolites. [10, 11]

FT-IR spectra revealed C-H stretches of CH_2 and CH_3 as shown in Figure2. Weight loss in TGA spectra in Figure 3 indicated the loss of alkyltrichlorosilane at 500 to 600 ℃. [11] EM and Scanning EM (SEM) results showed decrease of destruction of crystal structures in Figure 4 and 5. Table 3 shows that overall conversion and product distribution of m-Cresol alkylation provides the evidence of better performance of zeolite after modification. [10]

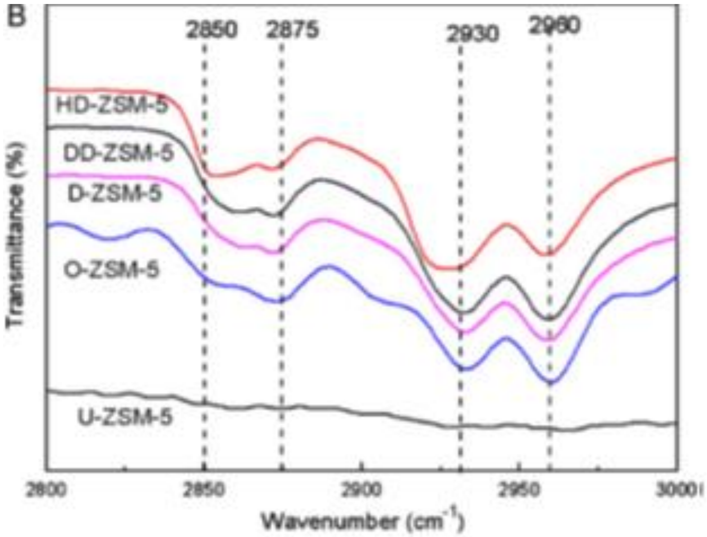


Figure 2. FT-IR Spectra of Coated Zeolites [11]

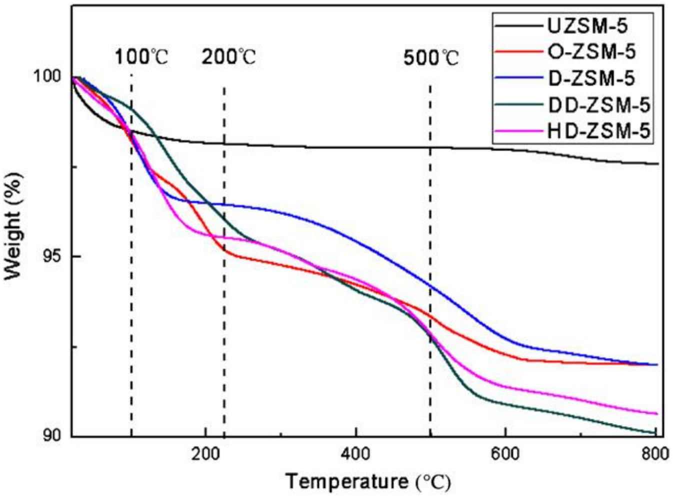


Figure 3. TGA Spectra of Coated Zeolites [11]

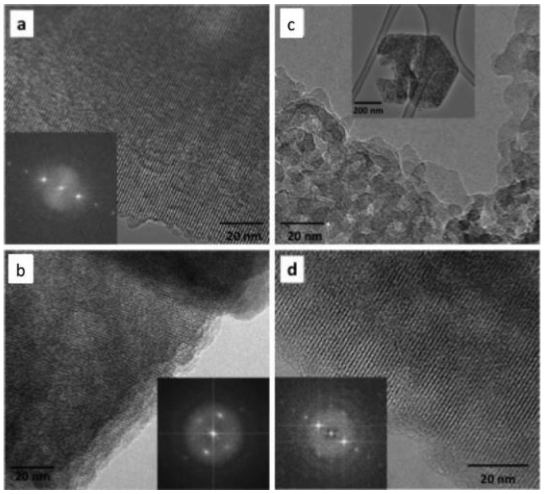


Figure 4. Electron microscopy (HRTEM) of the HY zeolites. Untreated zeolite, before (a) and after reaction (c); OTS functionalized zeolite, before (b) and after reaction (d). [10]

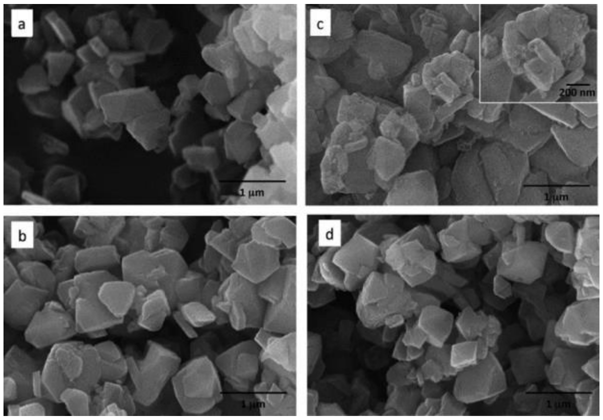
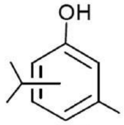
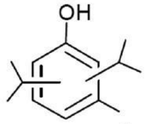


Figure 5. SEM. Untreated zeolite, before (a) and after reaction (c); OTS functionalized zeolite, before (b) and after reaction (d). [10]

Table 1. Catalyzed Alkylation of m-Cresol with 2-Propanol: Comparison of Overall Conversion and Product Distribution [10]

zeolite	single aqueous phase				emulsion (water/decalin)			
	untreated		functionalized		untreated		functionalized	
	1.33 h	3 h	1.33 h	3.h	1.33 h	3 h	1.33 h	3 h
	1.8	2.3	2.22	7.3	2.6	6.6	6.9	13.0
	0.2	1.1	0.6	3.0	1.0	2.5	3.0	6.5
m-cresol conversion (%)	2.0	3.3	2.8	10.3	3.6	9.1	9.9	19.5

Modified zeolites in binary emulsions can catalyze reactions better. However, there were only a few studies tried to quantify binding between zeolites and reactants or between zeolites and products. This quantification is important to understand material contribution in the mixture of reactants, products, solvents, and zeolite catalysts. It can further facilitate material separation and product recovery. Surface energy of the outer surface of modified zeolite is one of the properties needs to be studied to quantify the binding.

Contact Angle & Surface Energy

One direct way to study the surface energy of a specific material is to measure the contact angles of different liquids and then calculate. Since only the outer surface of the zeolite powder is the focus, contact angle measuring methods such as Wilhelmy plate technique and using the heat of immersion are not applicable. [15, 16] In previous studies, measuring contact angels on a compressed powder pellet surface have led to good results. [17]

Contact angle is shown in Figure 4 as θ. γ_{lv}, γ_{sv}, and γ_{sl} are the interfacial energies at the liquid-vapor, solid-vapor, and solid-liquid interfaces. [15] Surface energy can be calculated with the results of contact angle measurement data with Owens and Wendt's approach in equation 2 [18]:

$$\gamma_L(1 + cos\theta) = 2((\gamma_L^d\gamma_S^d)^{\frac{1}{2}} + (\gamma_L^p\gamma_S^p)^{\frac{1}{2}}) \qquad (2)$$

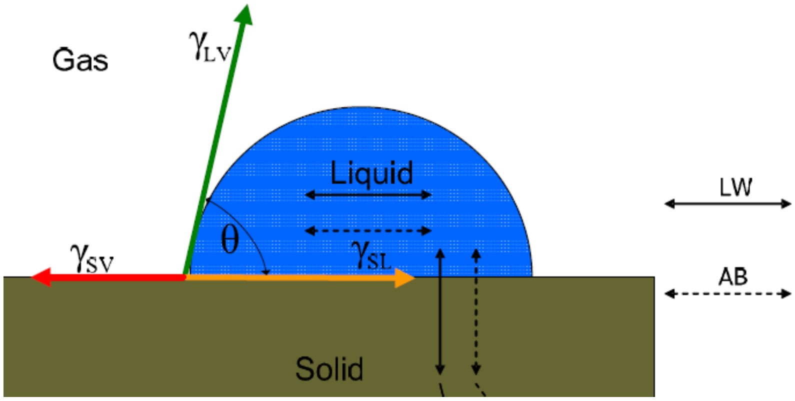


Figure 6. Contact Angle Measurement and Surface Energy [15]

In this approach, the surface energy of liquid or solid is considered as the attributions of dispersion force and polarity of the molecules. *d* and *p* represent dispersion portion and polar portion of the surface energy. γ_s, and γ_l are the surface energies of pure solid and pure liquid. [15-

Equation 2 can be rewritten as the following form for easy calculation:

$$W_a/(2*(\gamma_{LV}^{p})^{\frac{1}{2}} = (\gamma_{SV}^{d})^{\frac{1}{2}} * \left(\frac{\gamma_{LV}^{d}}{\gamma_{LV}^{p}}\right)^{\frac{1}{2}} + (\gamma_{SV}^{p})^{\frac{1}{2}} \qquad \text{(3), where}$$

$$W_a = \gamma_{LV} * (1 + cos\theta)$$

By plugging data in and plotting equation 3, γ_s, and γ_l can be easily calculated from the linear fit equations.

3. Methodology

Preparation of Glass Slides

22*40mm No.2 glass slides from Globe Scientific Inc. were used in this experiment as a smooth surface model with no pores. The glass slides were coated with ETS, HTS, and OTS. The first step was to clean the slides with piranha solution and rinsed with copious water and methanol. Piranha solution was a mix of concentrated sulfuric acid and 30% hydrogen peroxide at volume ratio of 3:1. 0.5 mmol of each kind of alkyltrichlorosilane was mixed with 100 mL toluene. One processed glass slide was then added to one solution and stirred using Teflon coated stir bar at 500 rpm for 24 h to obtain the coat. The coated slide was rinsed with toluene and then dried at 100 ℃ overnight. The contact angles of different solvents on the alkyltrichlorosilane coated glass slides were then measured.

Preparation of Silica Bead Powder and Zeolites

Silica beads from Evonik were used in this experiment as a powder pellet model with no pores. Type ZSM5, HY, and Beta zeolites from Zeolyst were used in this study. Unit cell size and SiO_2/Sl_2O_3 of three kinds of zeolite were summarized in Table 2. The powder was first calcined at 500 ℃ overnight. 0.5 mmol of each kind of alkyltrichlorosilane was mixed with 100 mL toluene. 1 g of calcined each powder was added to 20 mL toluene and sonicated with VC750 sonicator for 30 min at 25% amplitude to make a good suspension. The silica or zeolite suspension was then added to the solution and stirred with the same stirring procedure above to obtain the coating. This new suspension was then vacuum filtered using 0.22 um nylon filter paper and rinsed with toluene while being filtered. The coated powder was then dried overnight in the oven at 100 ℃.

Table 2. Information of Zeolites

Type	SiO_2/Al_2O_3	Unit Cell size (Å)	Product Number
ZSM5	358	N.A.	45883
HY	60	24.24	CBV760
Beta	150	N.A.	N.A.

Pellet making & Contact angle

Silica and zeolite pellets were made with CrushIR digital hydraulic press by PIKE. 5 to 10 mg of powder was loaded into the model every time. Silica, HY zeolite, and Beta zeolite pellets were pressed under 6 ton with 2-minute duration. ZSM5 pellets were pressed under 7 ton with 5-minute duration.

Contact angles were measured with goniometer by ramé-hart instrument. Sessile drops of water, glycerol, formamide, bromonaphthalene, and bromobenzen were added on the surface of glass slides and powder pellets to form the droplet. Every drop was added on fresh site for precise measurements. 2 μL drops were added on glass slides. For powder samples, one newly pressed pellet were placed on the sample stage of the goniometer. Then a drop of solvent was added on the sample surface and contact angles were then measured. For powder pellets, volume of the drops varied between 6 μL to 15μL based on pellet conditions. Five measurements were done on the surface of every kind of coated sample per one experiment. Numeric average and standard deviation was then calculated for every sample in one experiment.

Solvents and Solvent Mixtures

Five different pure liquids were used to form meniscus for contact angle measurements. Surface energies of water, glycerol, and formamide are listed in Table 3. [19]

Table 3. Surface Energy of Solvents

Solvent	γ_l	γ_d	γ_p
Water	72.8	21.8	51
Glycerol	63.4	37	23.4
Formamide	58.2	39.5	18.7

Different mole ratio mix of two different solvents were used to provide additional data points between the results of two pure solvents. Water-glycerol system and water-formamide system were used to examine this method. Water to organic ratios were set as 3:1, 1:1, and 1:3 molar ratios. Calculated volume ratios of the two water-organic systems were listed in Table 4 below.

Table 4. Volume Ratios of Water-Organic Systems

Water:Organic	Molar Ratio	1:1	1:3	3:1
Water:Glycerol	Volume Ratio	1:4.05	1:12.2	1:1.35
Water:Formamide	Volume Ratio	1:2.21	1:6.63	1:0.74

Surface energy of different ratios of the water-organic systems were calculated with different methods. Total surface energy of the liquid mix was calculated with equation 1 [20]:

$$\gamma = \gamma_1 - \left(1 + \frac{bx_1}{1-ax_1}\right) x_2(\gamma_1 - \gamma_2) \qquad (1)$$

1 represents organic solvent in the system and 2 represents water. γ is the total surface energy of the mixture. x is the molar fraction of each liquid in the binary system. a and b are surface tension parameters of binary water-organic systems. For glycerol, a= 0.958, b= 0.448. For formamide, a= 0.698, b= 0.78.

Dispersion portion of surface energy was calculated by taking the geometric average of γ_d of water and the organic solvent in the system. This calculation method was derived from the calculation of dispersion portion of the Van der Waals energy coefficient of two dissimilar molecules. [21] Polar portion of surface energy was the difference between γ_l and γ_d. Table 5 summarizes the surface energy values of pure liquids and binary liquid systems.

Table 5. Surface Energy of Pure Liquids and Binary Liquid Systems

dyne/cm	γ_l	γ_d	γ_p
Water	72.80	21.80	51.00
Glycerol	63.40	37.00	23.40
formamide	58.20	39.50	18.70
Water-Glycerol			
3:1	67.65	24.88	42.76
1:1	66.08	28.40	37.68
1:3	64.71	32.42	32.30

Table 6. Cont'd Surface Energy of Pure Liquids and Binary Liquid Systems

dyne/cm	γ_l	γ_d	γ_p
Water-Formamide			
3:1	64.67	25.29	39.38
1:1	61.13	29.34	31.78
1:3	59.26	34.05	25.22

Reproducibility

Three contact angle experiments were done with every kind of substrates, including every kind of base material and every kind of coating. In each experiment, every modified material was freshly coated and was only used in one experiment. Five measurements were performed for every liquid on every kind of substrate per experiment.

4. Results and Discussion

Glass Slides

Table 6 shows the contact angle measurement results of glass slides. Liquid drops could not from meniscus on bare glass slides, thus no measurable contact angle. It is clear to see that with the coating carbon chain increasing, the contact angle increases with the same measuring solvent. Compared with bare glass slide, all coatings can enhance the hydrophobicity of the substrate. Figure 1 is the calculation plot of surface energy of coated glass slides. The results were in good quality and reproducible.

Table 7. Contact Angle on Glass Slides

Degree	Solvent				
Coating	Water	Glycerol	Formamide	Bromonaphthalene	Bromobenzene
Bare	\	\	\	\	\
OTS	107.7 ±0.55	100.3 ±0.26	95.7 ±0.45	69.2 ±1.30	51.6 ±0.55
HTS	106.5 ±0.62	98.7 ±0.43	94.8 ±1.23	62.2 ±1.38	40.38 ±1.84
ETS	104.0 ±2.42	94.7 ±2.71	85.8 ±1.38	40.2 ±0.771	\

Table 7 shows the surface energy of glass slides with different coating. In Figure 7, data points of each coating could fit into a straight line. Thus, the calculated surface energy is in good quality. Shorter carbon chain coating provides more surface energy to the glass surface. The dispersion portion of surface energy decreases as the length of coating carbon chain increases. ETS coating provides less polar portion of surface energy compared to HTS and OTS.

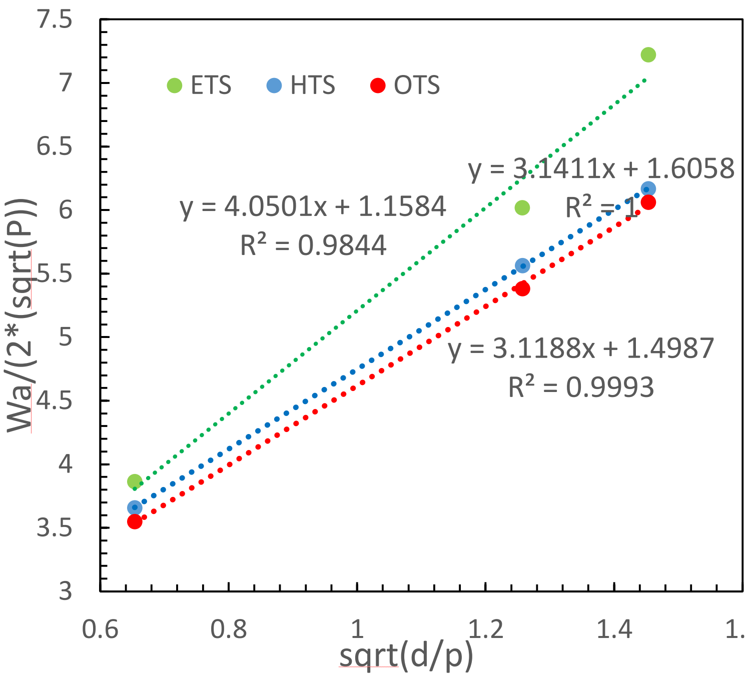


Figure 7. Calculations of Glass Slide

Table 8. Surface Energy of Glass Slides with Different Coating

Dyne/cm	γ_s	γ_d	γ_p
ETS	17.7	16.4	1.3
HTS	12.4	9.9	2.6
OTS	12.0	9.7	2.2

Silica Beads

Table 8 shows the contact angle measurement results and the standard deviations of silica bead pellets. None of bare silica, ETS coated silica, or HTS coated silica provided adequate measurement results. All three solvents were sucked into the powder pellets of bare silica and ETS coated silica. Water is the only solvent that could form meniscal droplets on HTS coated silica. This could be due to the capillary force caused by the large inter-particle pores. Bromonaphthalene and bromobenzen could not form meniscus on silica pellets. Rather, they were absorbed by the powder pellets.

Table 9. Contact Angle on Silica Bead Pellets

Degree	Solvents		
Coating	Water	Glycerol	Formamide
OTS	113.8 ±3.06	101.7 ±0.855	73.4 ±1.78
HTS	50.1 ±1.77	\	\

The calculated γ_s of OTS coated silica beads was 40.4 dyne/cm, with dispersion portion γ_d as 38.6 dyne/cm and polar portion γ_p as 1.8 dyne/cm. However, the line fit of calculated data points was not in good quality. More data is needed to derive the final result of the surface energy of coated silica beads. Curve fitting plot can be found in the Appendix section.

Zeolites

Table 9 shows the contact angle measurement results and the standard deviations of three kinds of zeolite pellets with different coatings. Pellets of bare zeolites of all three kinds and ETS coated ZSM5 and Beta absorbed liquids fast. No measurable contact angle can be obtained.

Table 10. Contact Angle on Zeolite Pellets

Degree	Water	Glycerol	Formamide
ZSM5 OTS	156.7 ±3.45	155.0 ±3.31	152.6 ±4.45
ZSM5 HTS	157.1 ±3.82	154.3 ±4.05	153 ±2.62
HY OTS	115 ±5.45	116.5 ±4.92	87.7 ±2.81
HY HTS	112.8 ±4.32	85.9 ±3.15	\
HY ETS	112.5 ±4.81	95 ±4.15	\
Beta OTS	109.3 ±2.45	117.2 ±6.83	76.5 ±4.95
Beta HTS	105.4 ±3.15	66.4 ±3.61	\

Table 10 shows the surface energy of glass slides with different coating. There was only small difference in surface energy between OTS coated and HTS coated ZSM5. OTS coated ZSM5 had much smaller surface energy compared to OTS coated HY and Beta. The line fit of calculated data points was not in good quality. More data is needed to derive the final result of the surface energy of coated zeolites. Curve fitting plots can be found in the Appendix section.

Table 11. Surface Energy of Zeolites with Different Coating

Dyne/cm	γ_s	γ_d	γ_p
ZSM5 OTS	0.18	0.16	0.021
ZSM5 HTS	0.19	0.17	0.017
HY OTS	17.18	17.17	0.015
Beta OTS	22.34	22.3	0.044

In general, γ_d is much smaller than γ_p for glass, silica, and zeolites. Longer coating chain provides larger contact angles and results in smaller surface energy.

Solvent Mixture

Reproducible contact angle results for water-organic systems are shown in Table 11 and 12. Contact angle decreased as concentration of organic solvent increases. Figure 8 and 9 present the decrease of the contact angles more visually.

Table 12. Contact Angle on Glass Slides with Water-Glycerol System

Degree	Water	W/G 3:1	W/G 1:1	W/G 1:3	Glycerol
Glass OTS	107.1 ±0.57	104.5 ±1.61	102.2 ±0.79	100.3 ±1.50	99.6 ±0.36
Glass HTS	105.3 ±0.26	103.2 ±0.38	100.8 ±0.61	98.7 ±1.37	96.4 ±0.43
Glass ETS	102.3 ±0.45	98.3 ±1.41	96.8 ±1.20	94.3 ±0.62	92.8 ±1.23

Table 13. Contact Angle on Glass Slides with Water-Formamide System

Degree	Water	W/F 3:1	W/F 1:1	W/F 1:3	Formamide
Glass OTS	107.1 ±0.57	104.3 ±0.71	101.6 ±1.04	99.7 ±1.45	95.7 ±0.63
Glass HTS	105.3 ±0.26	98.3 ±1.12	95.4 ±4.34	93.3 ±2.71	93.2 ±0.55
Glass ETS	102.3 ±0.45	95.8 ±0.74	93.2 ±0.92	89.6 ±1.38	85.8 ±0.55

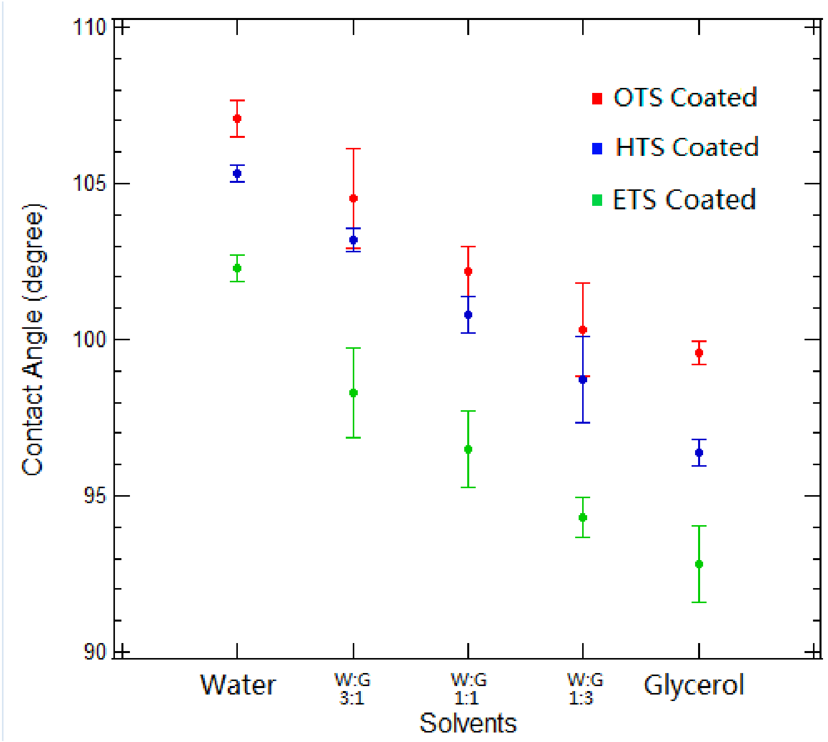


Figure 8. Contact Angle on Glass Slides with Water-Glycerol System

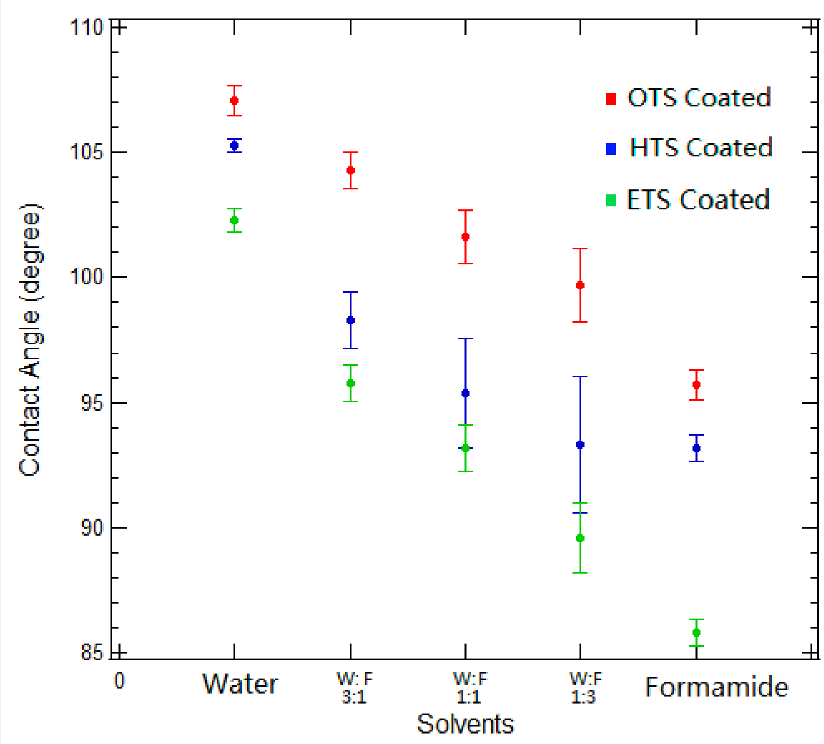


Figure 9. Contact Angle on Glass Slides with Water-Formamide System

Table 13 shows the surface energy of coated glass slides derived from different water-organic systems. Comparable results from two systems were very close. This might represent that the water-organic systems and their calculated surface energy values can be used to study the surface energy of zeolite powders. Data points of each coating could fit into a straight line. Thus, the calculated surface energy is in good quality.

Table 14. Surface Energy of Glass Slides with Water-Organic Systems

dyne/cm	Water- Glycerol System			Water- Formamide System		
	γ_s	γ_{sd}	γ_{sp}	γ_s	γ_{sd}	γ_{sp}
Glass OTS	12.11	9.77	2.34	11.64	9.56	2.08
Glass HTS	14.1	12.19	1.91	13.41	10.27	3.14
Glass ETS	16.04	13.47	2.57	17.7	15.77	1.93

5. Conclusions and Recommendations

All three kinds of alkyltrichlorosilane coating improved hydrophobicity of glass slides, silica beads, and zeolites based on the contact angle experiments. Most of the coated materials could form larger contact angles with water, glycerol, formamide, and the two water-organic system. Some coated powders absorbed liquids might be caused by the capillary force generated by the large inter-particle spaces. The coating could also help prevent the attachment of hydrophobic organic solvents based on the results of contact angles of glass slides. Contact angle generally decreases as the length of coating carbon chain decreases.

Surface energy of coated materials decreases as the length of coating carbon chain decreases. Thus, liquid needs more energy to attach on longer carbon chain coated surface than shorter carbon chain coated surface. This also improved the changing of contact angles with respect to the length of coating carbon chain.

All data of glass slides was in good quality and reproducible. Data of silica and zeolite powders was not in good quality and not reproducible. This was mainly caused by the surface geometry of the powder pellets. The surfaces of the pellets were not ideally smooth and had some local curves. This made the contact angle measurements way less precise. Thus, new methods to make powder pellets needs to be found for better pellet surface quality.

Water-organic systems were only examined on glass surfaces due to time restrain. Results were in good quality and reproducible. The systems could provide additional data points between two points of pure solvents. The calculated surface energies of water-organic systems should be close to reality based on the results. This method can be modified and used on powder zeolite surfaces to make better curve fit to calculate surface energy.

6. References

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7. Appendix

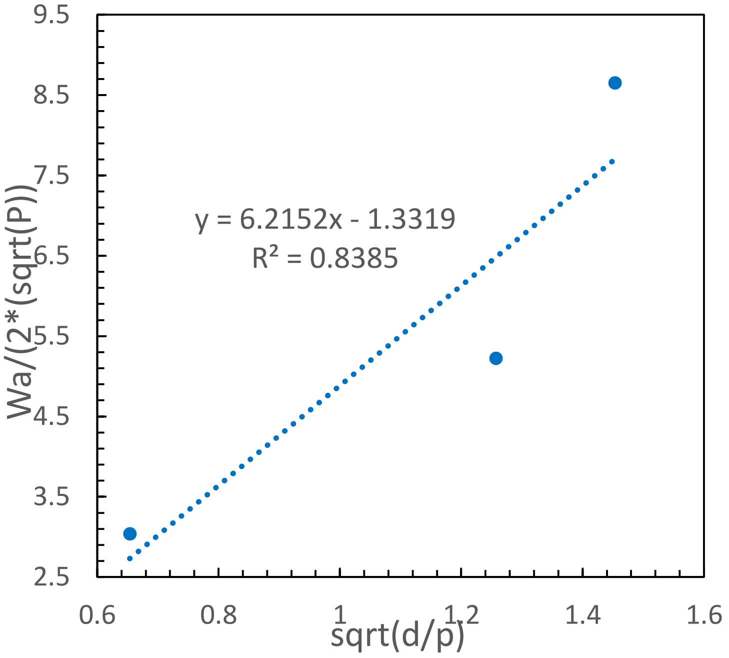

Figure 10. Calculation of Silica Beads

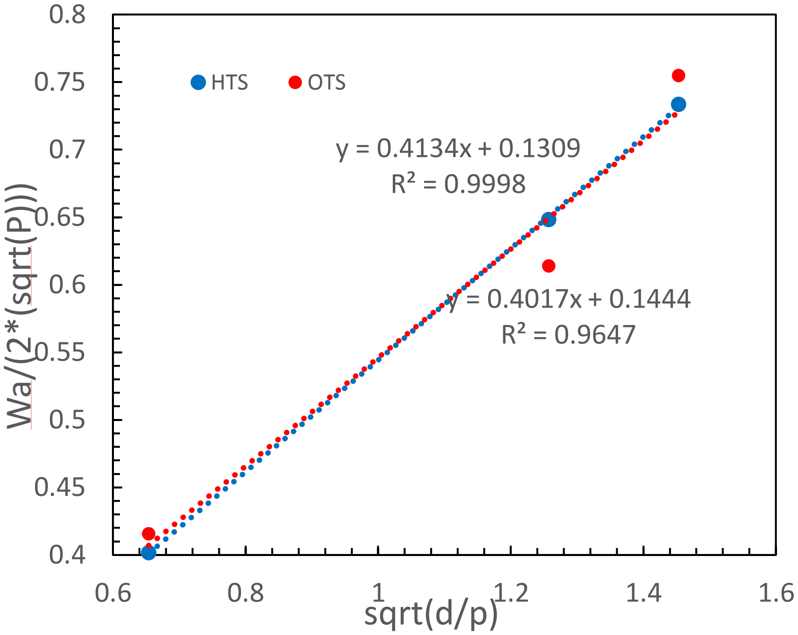

Figure 11. Calculations of ZSM5 Zeolite

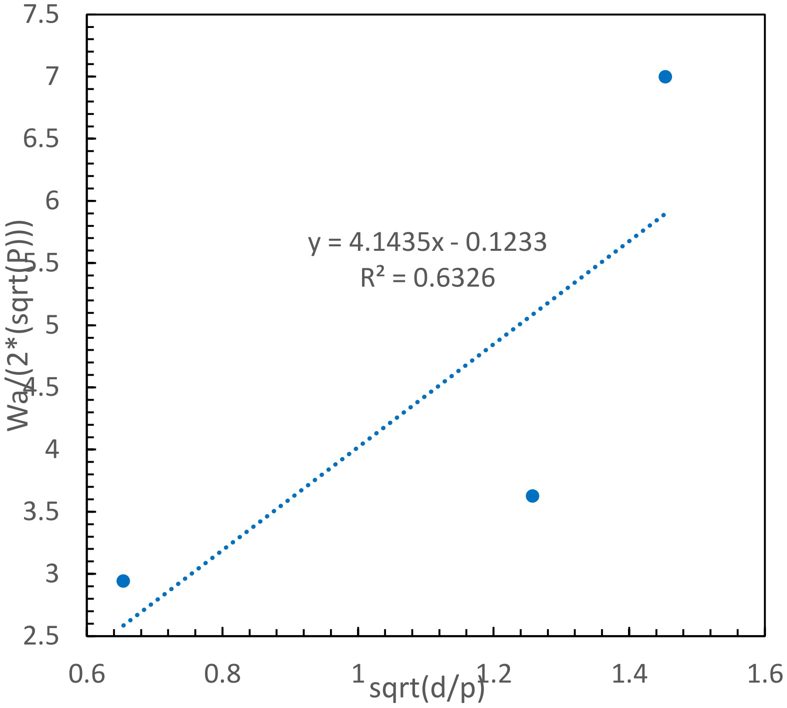

Figure 12. Calculations of HY Zeolite

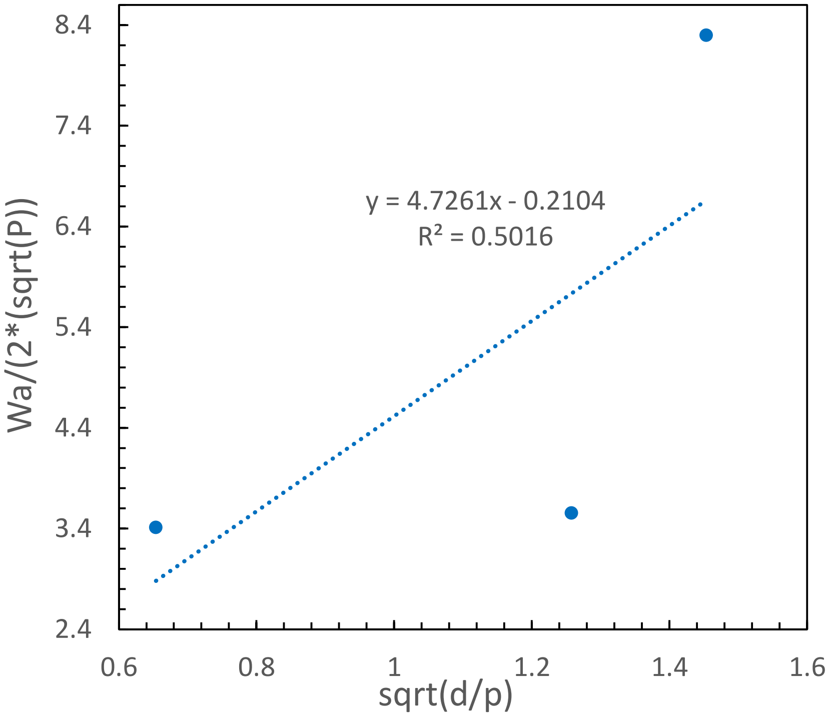

Figure 13. Calculations of Beta Zeolite

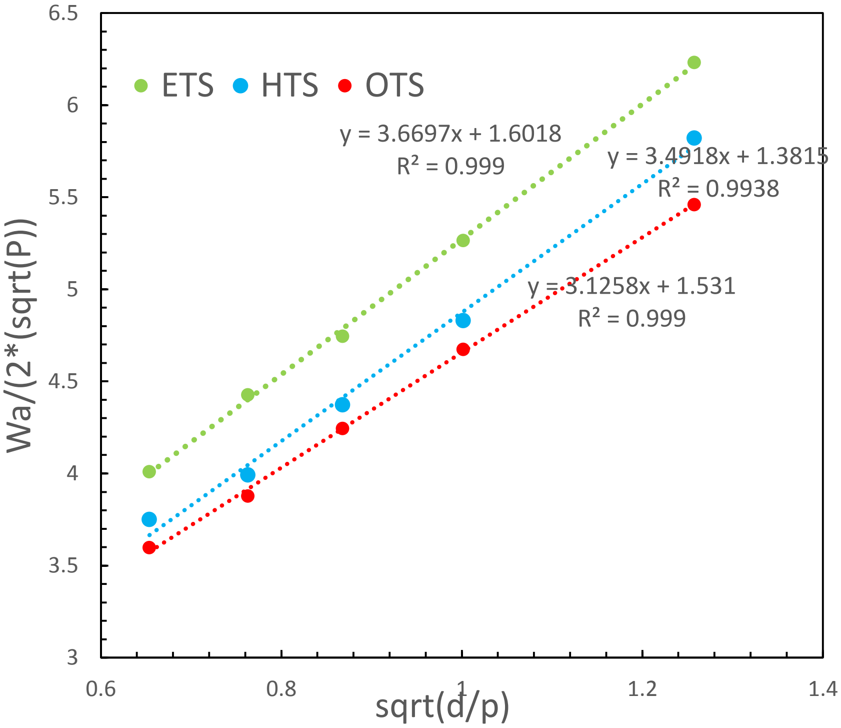

Figure 14. Calculations of Glass Slides with Water-Glycerol System

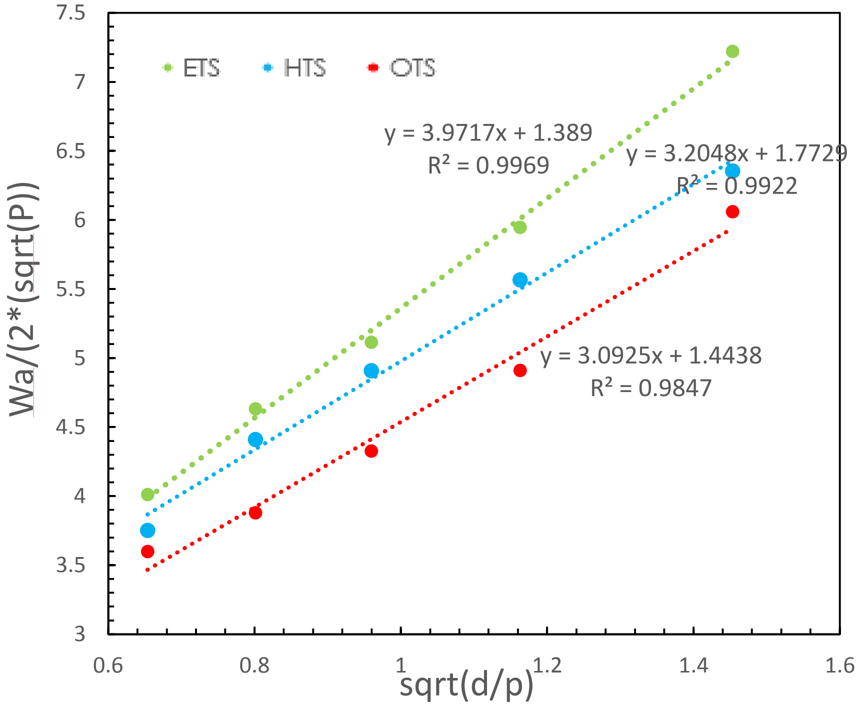

Figure 15. Calculations of Glass Slides with Water-Formamide System