Zeolite Catalyzed Ozonolysis

A Major Qualifying Project Proposal
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in Chemical Engineering
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Abstract

The goal of this project was to investigate the active sites of zeolites catalyzing the reaction of ethanol and ozone, to determine the importance of the alumina to silica ratio, external surface chemistry, and to consider if this process can be acceptable for the treatment of waste water. An experimental method was developed and implemented, including the use of zeolites with varying silica content. It was determined that the Si/Al ratio and external surface area are responsible for speed of catalysis.

Contents

Introduction

The main focus of this project was to determine the active sites of zeolites when catalyzing degradation reactions. Zeolites are useful catalysts in helping to degrade organic chemicals such as ethanol (Bell). However, it is important to gain an understanding of the important characteristics of zeolites in order to determine which could be useful on an industrial scale. Zeolites have varying molecular structures which create channels, or pores in the zeolites themselves. It is thought that these pores, and the sizes associated with the pores, play a large role in determining the effectiveness of the specific zeolite to catalyze these reactions (Baerlocher). Contrary to this belief, this project shows that the exterior surface chemistry plays the largest role in the effectiveness of a zeolite. More specifically, the importance of the Si/Al ratio of the exterior surface area was studied. The usefulness of zeolites to catalyze large scale reactions will also be discussed.

Across the country there exist many areas contaminated by chemical spills. Some of the most concerning spills are where chemicals have leached into the ground water, or drinking water sources. Even in areas where commercial spills have not occurred, domestic chemicals are accumulating at dangerous rates. With a growing concern over pollution in the environment, removing these chemicals has become a highly researched field. Researchers are continuously looking for methods to remove chemicals from the environment, but many methods are too costly to implement on a large scale. There is also the problem that the large majority of the contaminated water cannot easily be brought to a treatment facility and must be treated on site. One such affected area is the Massachusetts Military Reservation in Bourne, Massachusetts (Chemical Spill). Here they have experienced a problem with effluent from the base leeching into the ground, and spreading into an underground plume that extends over much of the base. The plume consists of trichloroethylene (TCE) and perchloroethylene (PCE), common chemicals used in degreasing machinery. These chemicals are extremely dangerous when humans are exposed to them in even minor quantities. Figure 1 shows that the plume reached as far as Ashumet Pond, which is a common recreational area for the surrounding towns (Chemical Spill).

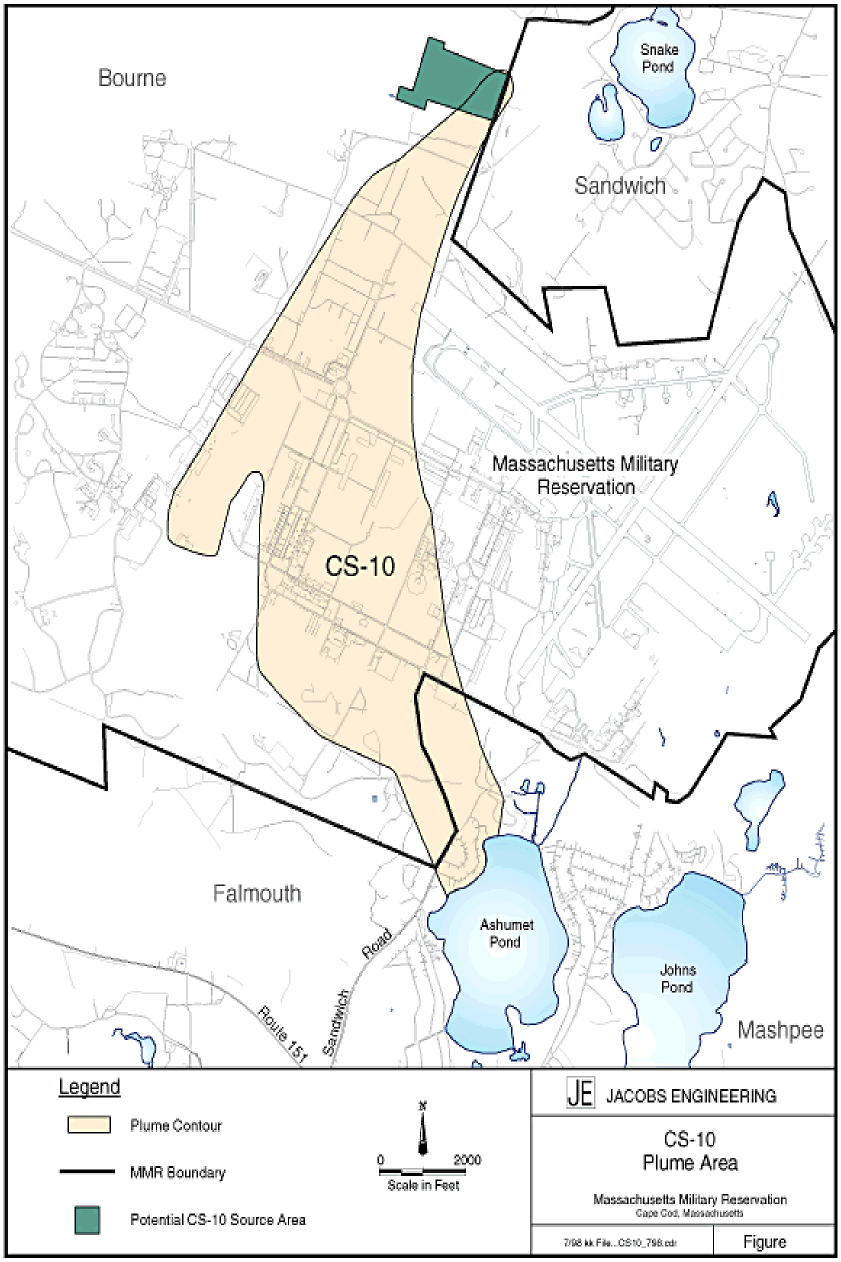

Figure 1 - Military Base Contamination (Chemical Spill)

This spill caused significant problems for both the military base and the surrounding towns, as the chemicals in the plume could not be allowed to enter the drinking water sources for those towns. The Air Force Center for Environmental Excellence (AFCEE), Environmental Protection Agency (EPA) and the Massachusetts Department of Environmental Protection (DEP) came up with a strategy of using underground fences and wells to contain, remove, and treat the majority of the groundwater in the affected regions. The problem with this method is that contaminants can leak through or around the fences, and treating all of the affected water will not be accomplished for many years (Chemical Spill).

Much research has already been done on zeolites. Their ability to catalyze reactions makes them very desirable for research into water treatment. Zeolites can also adsorb large amounts of chemicals due to their pores, which can trap the chemicals (Bell). Trapping contaminants is not the main concern of this project though, as the degradation of these chemicals is the ultimate goal. This project is focused on the ability of the zeolites to catalyze reactions, while determining the role of the surface chemistry of the zeolites and the differences in effectiveness between zeolites with varying ranges of silica versus alumina content. Existing research shows that zeolites with higher silica contents offer faster reaction times than zeolites with higher alumina contents. One paper, discussed more fully later, written by Professor Hirotaka Fujita et. al, discussed that ZSM-5, a specific zeolite, offered a faster and more complete degradation of TCE than the same zeolite with a lower silica to alumina ratio (Fujita). The data in the report does not fully support this conclusion however, and the experiments conducted for this paper were designed to take another look at these conclusions.

More research also needs to be done to determine the effectiveness of using zeolites on a large scale. Experimentation using zeolites has been accomplished on small scale projects using small vials and relatively low volumes of chemicals. These results are then extrapolated and used to estimate what would happen if zeolites were used on large scale applications. While it is easy to determine if the reactions taking place will remain unchanged if expanded, it is not as easy to determine if the method is feasible to use. The major concerns of any new implementable methods are the cost of implementation as well as sustainability and maintenance costs. In 1995 a TCE spill occurred in Orlando, Florida, which cost the responsible company in excess of five million dollars, and the state more than three million for investigation and clean-up of the contaminants (Quintana). With the costs associated with cleaning these spills being so high, any new methods must be studied to determine their cost-effectiveness.

Experiments were performed to determine where the reactions are occurring on the zeolites. The main reaction that was studied was the degradation of ethanol by ozone. Varying packed beds of different zeolites were used to catalyze the reaction. The zeolites were of varying types and silica contents to determine the active sites. Low amounts of the ethanol was mixed with water saturated with ozone gas and run over the zeolite bed. The effluent was then tested using Chemical Oxygen Demand (COD) analysis. These data were used to determine if the pore sizes of the zeolites are playing a role in the degradation of the ethanol. These data were also used to determine the effects of varying the silica content of the zeolites to see if higher silica content zeolites are better catalysts than high alumina content zeolites.

Background

Zeolites

Zeolites are compounds with crystalline structures. These structures also have large pores. Zeolites are mainly composed of aluminum, silicon and oxygen atoms. The pores are attractive to cations and other molecules such as water. Zeolites form in nature when high mineral content water crystallizes, forming the well defined crystal structures and pores of the zeolites. The actual molecular structure of zeolites is tetrahedral, with a silicon or aluminum atom in the center surrounded by four oxygen atoms to form a tetrahedral shape. These tetrahedra then bond together to form over 130 different known zeolites, both natural and synthetic (The Zeolite).

Zeolites have been used as far back as the early 1700s in agricultural applications to exchange ions in farming soil. Today they are used in a variety of applications. One such application is the treatment of water. A major problem in household drinking water is the buildup of bacteria. These bacteria can live in the water system, mainly in filtration systems, and are typically removed by chlorination. However, constant chlorine exposure tends to degrade filtration systems which can become costly to continuously replace. Zeolites remain unchanged in the presence of chlorine, and if used as the filtration medium do not need to be replaced. Zeolites also soften drinking water by removing metal ions such as iron, magnesium and calcium, and trapping them in their pores. With the ability of zeolites to adsorb high amounts of metal ions they also need less frequent upkeep, and can also be recycled or “cleaned” for further use. This ability to exchange ions also allows zeolites to be used in laundry detergents.

The use of zeolites in laundry detergents is also environmentally friendly as they replace phosphate compounds that contributed largely to environmental pollution (Bell).

Faujasite

One zeolite being studied in this report is Faujasite, most commonly caused naturally by volcanic activity. Faujasite is commercially sold by the Natural Faujasite Company. Their main supply is found in northern Jordan, but smaller, less economic deposits of Faujasite have been found in southern California, Hawaii and Germany. Faujasite can also be synthesized, and because of its structure is relatively simple to produce. Faujasite has many qualities that make it attractive for chemical processes. One of the most important qualities is that it has a "high cationic-exchange capacity" (Natural), which means that it can effectively catalyze reactions by facilitating the decomposition of an organic molecule by attracting cations. Faujasites are also naturally resistant to degradation, allowing them to be used multiple times for the same experiment without needing to be replaced. Simply heating them to burn off any residue will keep Faujasite active for long periods of time. This is also important to the study of feasibility in implementing this kind of water treatment in industry. The lack of needing to replace large quantities of Faujasite will lend itself to low maintenance costs over the lifetime of the zeolites and the process. Experiments have also been conducted to investigate the thermal resistance of Faujasite. The tests determined that unlike some zeolites, Faujasite has little to no reaction to intense heating. Temperatures upwards of two hundred degrees Celsius have been used to test Faujasite's limitations, but no structural or chemical changes occurred (Natural).

Another reason Faujasite was selected is its apparent resistance to acidic degradation. Many chemicals being leaked into groundwater supplies contain highly acidic compounds. Although the experiments conducted in this paper do not involve the zeolites coming into contact with acidic solutions, real world applications are being considered for this process, and the zeolites need to be chemically stable to promote good functionality. Experiments conducted with Faujasite show that it resists degradation at acidity levels down to a pH of 3 for extended periods of time, ranging up to forty eight hours of contact with the acid. This means that Faujasite can catalyze reactions involving highly acidic solutions without needing to be frequently replaced. Synthetic Faujasite outperforms the natural Faujasite from the Jordan deposit in every way, except for the cost. Synthetic Faujasite costs five to ten times as much per ton to have synthesized. The reason why synthetic Faujasite outperforms naturally occurring Faujasite is due to the percent of the compound that is actually made up of the Faujasite crystals. As with any naturally occurring mineral, imperfections and impurity phases occur in nature, not often in labs. The imperfections in natural Faujasite cause the compound to be less resistant to degradation, as the portions that are not strictly the Faujasite crystals are more reactive and less stable (Natural). The differences are not so disparaging that natural Faujasite should not be considered however, as the cost being so much less could overcome the fact that they need to be replaced more often.

The structure of Faujasite, shown in Figure 2 (Schmidt), also lends itself to Faujasite being useful for many commercial applications. It has a pore opening of 7.4 angstroms, which is relatively large for a zeolite. This large pore diameter allows the Faujasite to remove relatively large

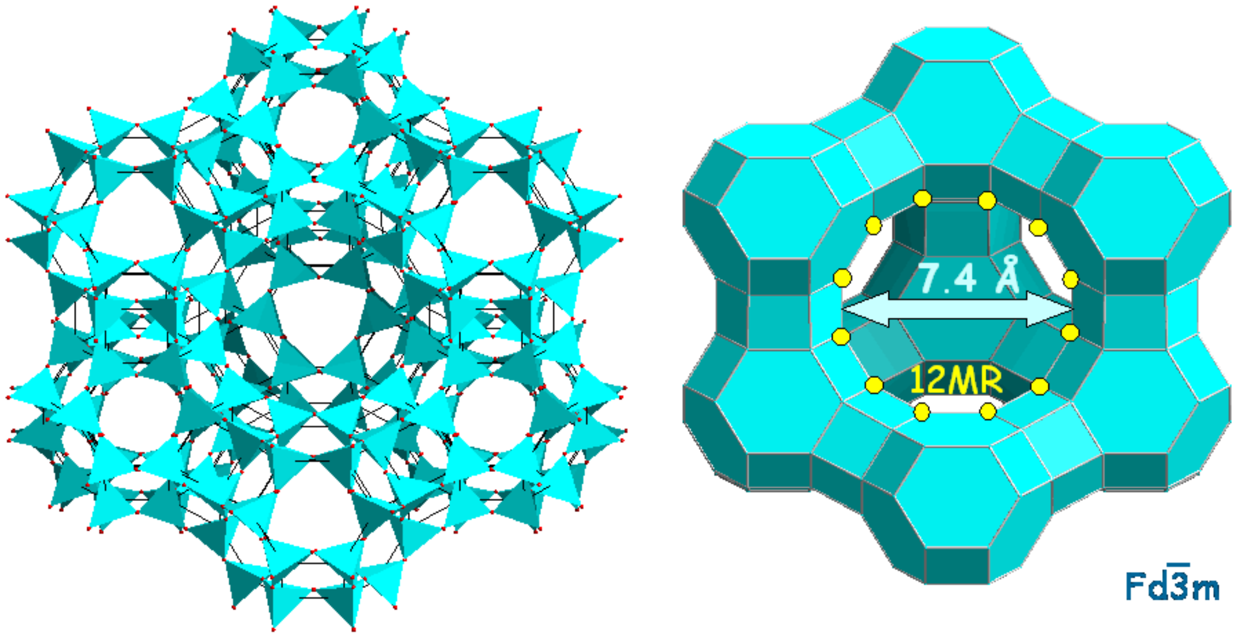

Figure 2 - Faujasite Structure (Schmidt)

chemicals from mixtures through simple adsorption. The internal cavity also measures 12 angstroms in diameter, which means that Faujasite has the ability to retain a large amount of the compound it has adsorbed inside the crystal structure. The tetrahedral structures in the left half of Figure 2 represent the tetrahedral coordination of the silica and alumina sites with oxygen molecules at their vertices. The right half of Figure 2 gives a solid picture of the arrangement around the pores, with silica and alumina sites represented by the intersections of the lines. For processes only requiring the adsorption of small compounds, Faujasite would seem to be extremely attractive because of its large pore openings and internal cavity size, which would allow it to adsorb large quantities of small compounds. The attractive properties of Faujasite that make it applicable to this paper however, are its large external surface area and low Si/Al ratio. Since the Si/Al ratio is what this paper is most concerned with, it is this parameter that needed to be varied between zeolites with otherwise similar structures.

Silicalite

The second zeolite chosen was a silicalite, HISIV 3000. HISIV 3000 has an MFI structure that contains channels with intersecting tunnels (see Figure 3 (Baerlocher)), and thus is part of the ZSM-5 species of zeolites. ZSM-5 was originally developed by Mobil Oil Company as an aluminosilicate zeolite with a high silica and low aluminum content. ZSM-5 was created and mostly used for hydrocarbon interconversion by the petroleum industry, but is also used for alkylation of aromatic compounds (Harrison). HISIV 3000 was chosen because it is an inexpensive synthetic zeolite (Roostaei). In Figure 3 the pores of HISIV 3000 are clearly viewable, as well as the crystalline structure, comprised of silica and alumina at the intersections of the lines. The lines themselves represent oxygen atoms.

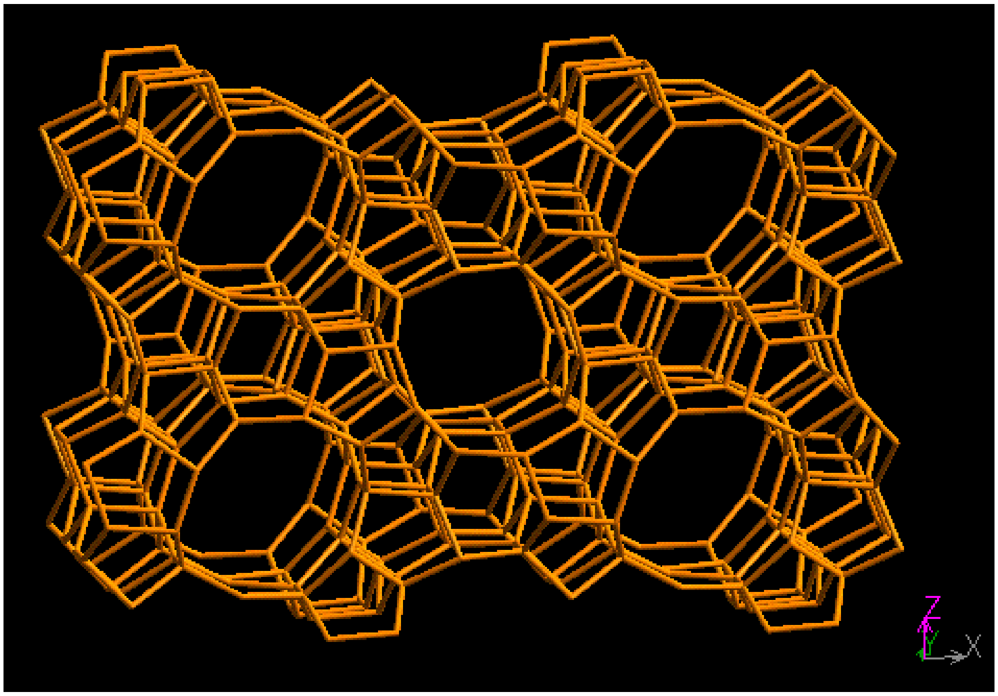

Figure 3 – HISIV 3000 (Baerlocher)

Mordenite

The third zeolite tested was Mordenite. One reason why Mordenite was an attractive option is that it is very cheap to obtain in large quantities. The cost of natural Mordenite is the same as that of Faujasite, making the two compounds comparatively economical (Hawkins). At an average of $100 per ton, natural Mordenite can be easily mined and shipped from many locations across the planet (Virta). Zeochem, a company based in Switzerland and Kentucky, is one of the largest producers of commercial grade Mordenite. They produce Mordenite with silica to alumina ratios ranging from twelve to sixty, the higher of which was considered to contrast the lower silica alumina ratio of the Faujasite (Zeochem). Mordenite has a different structure than that of Faujasite, but is still used in many of the same applications as the pore sizes found in Mordenite are only slightly smaller than that of Faujasite, approximately 5.5 angstroms (WolframAlpha). The structure of Mordenite can be seen in Figure 4 (Baerlocher).

In Figure 4 the pores of Mordenite are clearly viewable, as well as the crystalline structure, comprised of silica and alumina where the lines intersect, with oxygen in between.

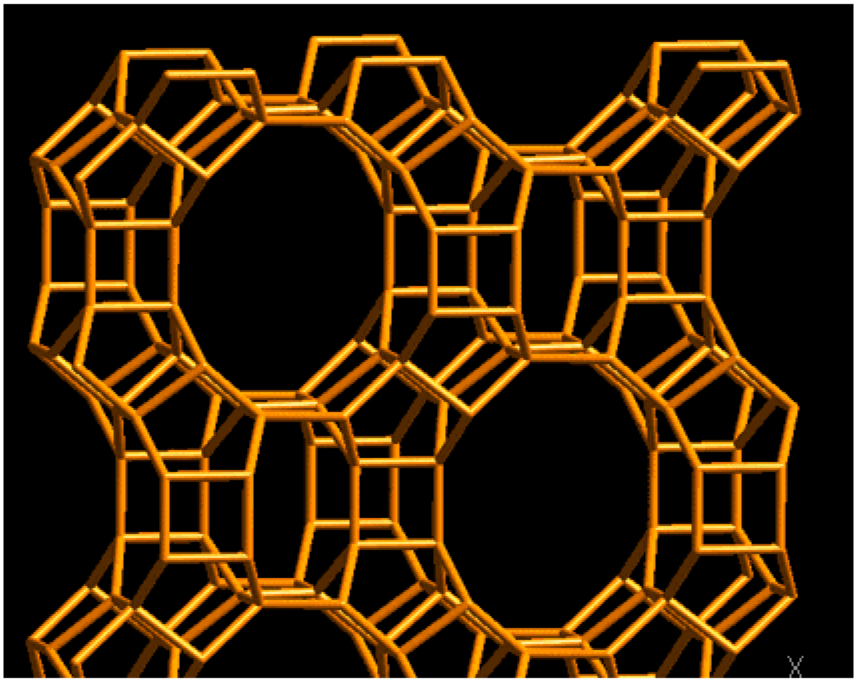

Figure 4 - Mordenite Structure (Baerlocher)

Reactants

Ethanol

Ethanol, shown in Figure 5 (Cotton), was used as the organic compound to be degraded in the experiments. It was chosen for several reasons. First, many of the chemical contaminants found in nature are volatile organic compounds (VOC's), such as the TCE and PCE found in the spill outside of the Massachusetts Military Reservation. Since these compounds all share the fact that they are made up of varying lengths of carbon chains, many of them undergo the same degradation mechanisms. They also have very similar byproducts when broken down, due to their similar structures. Ethanol is a relatively safe, stable compound that can be easily worked with in a lab, making it ideal to carry out reactions (Fisher). With little to no hazard to researchers, small-scale VOC degradation reactions could be studied, and the data extrapolated and scaled up for other VOC's.

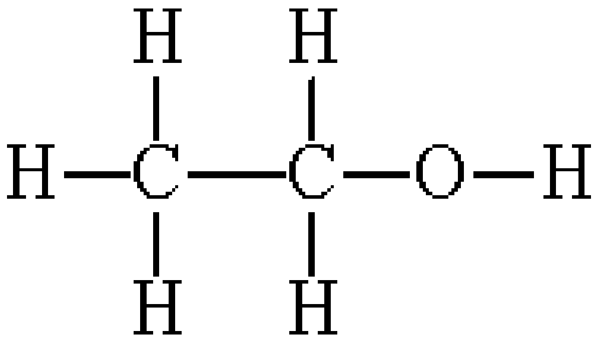

Figure 5 - Ethanol Structure (Cotton)

Ozone

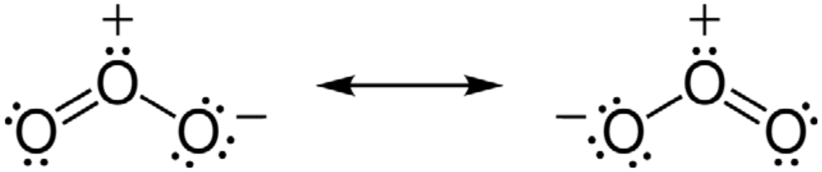

Figure 6 - Ozone (With Resonance) Structure (Wikimedia)

Ozone, shown in Figure 6 (Wikimedia), was chosen as the reactant because it is highly volatile. It is a superior oxidizing agent, and has been shown to easily degrade organic compounds. If inhaled, ozone can cause immediate damage to lung cells by breaking down the cell walls and damaging cellular structures, but under controlled settings it is easy to work with through saturation into water. These qualities make ozone a perfect reagent for carrying out the decomposition of ethanol, as it could simply be saturated in water, then mixed with a molar solution of ethanol and run over a bed of zeolites.

Reaction

The reaction between ozone and ethanol starts with ozone reacting with a hydroxide anion to form an oxygen radical anion and a hydroperoxy radical. This is the initiation reaction for a chain of reactions that form radicals. Primary and secondary alcohols can also propagate this reaction. Carbonate and bicarbonate can terminate this chain of reactions. The products from these reactions are oxygen, water, and carbon dioxide if the ethanol is oxidized completely. If this reaction doesn't proceed to completion methane and methanol can be produced as products instead (Lenntech).

Fujita Et. Al

Research has been done to determine the active sites of zeolites when catalyzing degradation reactions. One study was done by Professor Hirotaka Fujita at the University of Tokyo, Japan. The main goal of his research was to determine if the zeolites he was testing would be useful in catalyzing the reaction between ozone and TCE. Another focus of his research was to decide whether a higher or lower Si/Al ratio was preferable to act as a better catalyst. Fujita and his colleagues used a continuous experimental system, shown in Figure 7 (Fujita), where TCE in water was run through a tubular flow reactor containing the zeolite bed. Ozone was bubbled into water and the dissolved ozone solution was combined with the TCE solution prior to being exposed to the zeolites. By introducing the ozone and TCE into a mixing vessel before being run over the packed bed, Fujita ensured the sample was well mixed and there was a constant concentration of ozone as well as the TCE.

Measurements were taken to determine the TCE concentration before and after the packed zeolite bed, which yielded a conversion rate of the TCE. Fujita found that the degradation was taking place very rapidly, and that most of the TCE that was being degraded was doing so in approximately seven seconds. Another conclusion he drew was the zeolite that

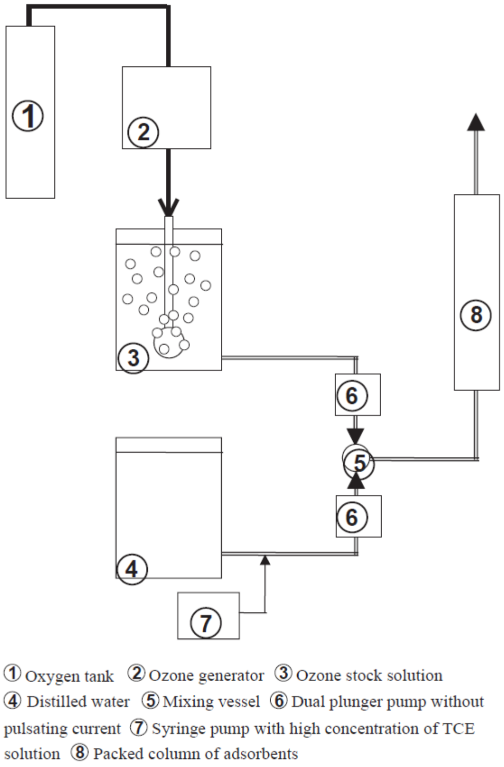

Figure 7 - Fujita Experiment (Fujita)

performed the best was ZSM-5 with a silica to alumina ratio of 3000.

Figure 8 (Fujita) is a graph of his results from the experiments which show the zeolites tested, and how much of the TCE was converted for each. The main problem with this conclusion is that by looking at the graph, it appears that the ZSM-5 with Si/Al ratio of 30 performs comparably to the ZSM-5 with Si/Al ratio of 3000. Along with this apparent incorrect conclusion it also appears that the Mordenite that was studied showed to have an increase in TCE conversion with an increase in Si/Al ratio. Since the correct conclusions were not drawn from these data, it was necessary to develop another experimental procedure in an attempt to determine what parameters were actually important to this reaction.

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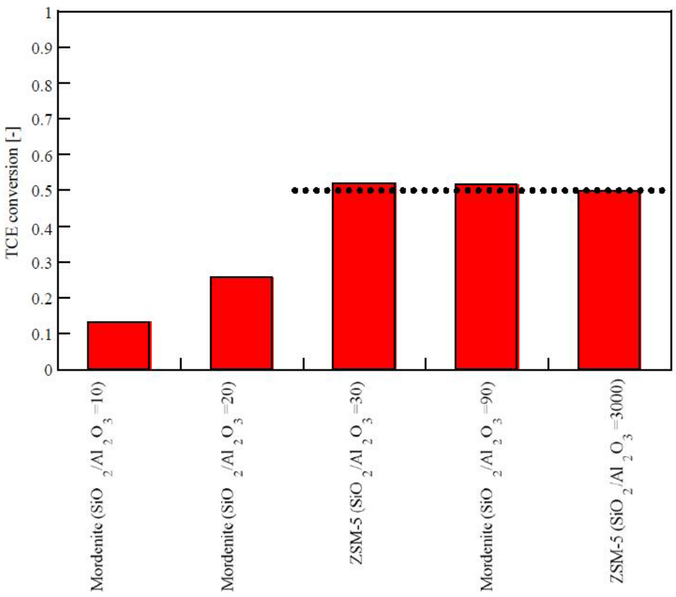

Experimental conditions: Flow rate: 10 mL/min; Reaction time: 3.77 s; Particle diameter: 500-590 μm; Ozone concentration: 1.5 mg/L; Aqueous TCE concentration: 1.27-3.0 mg/L.

Figure 8 - Fujita Results (Fujita)

Hypothesis

The experiments designed for further evaluation of zeolite catalyzed degradation were designed with a two part hypothesis in mind. The first part of the hypothesis was that the external surface chemistry of the zeolites, and not the internal chemistry or pore sizes, was important to how effective of a catalyst the zeolite was. The second aspect of the hypothesis was that a lower silica to alumina ratio would outperform a higher one as it was believed the alumina sites on the surface of the zeolite are the active sites in the reaction.

Methodology

In order to test the hypothesis presented, experiments needed to be designed to determine the effectiveness of the zeolites to catalyze the reaction between ozone and ethanol. It was decided that a batch process where the reactants would be mixed over a bed of zeolites would be used to simulate a similar reaction environment to that used in the paper by Professor Fujita. The same initial concentration of ethanol was used in all experiments, and the final concentration of ethanol was determined using the Chemical Oxygen Demand (COD) analysis method. This would produce data that showed which zeolite was most effectively catalyzing the reaction.

Preparation

Ethanol

In order to create the same starting ethanol concentration, solutions were made using 200 proof, denatured ethanol and water. The ethanol was obtained from the Worcester Polytechnic Institute (WPI) Goddard Hall storage room. Measured quantities of ethanol were combined with quantities of water to create the molar solutions to be used for the experiments. All degradation experiments began with an initial concentration of 3.315 mol% ethanol in solution (see Table 4, Appendix B).

Water

Both pure water and water saturated with ozone were needed for the experiments. In all cases where pure water was used, E-pure water was used due to the fact that it was the purest water available. This water was obtained through the use of a Barnstead E-pure water filtration system in the Water Lab of Kaven Hall, WPI. For all cases of ozone saturated water, ozone was supplied by a Labozone Model L-50 ozone generator, manufactured by Ozonology Inc. The output of this generator was pure ozone, which was bubbled through E-pure water in order to saturate the water with the ozone. Ozone levels present in the water could not be determined so an estimate on how long the ozone would take to saturate the water was used. This was estimated using the flow rate of the ozone, 2 standard cubic feet per hour or 111.2 grams per hour, and the maximum solubility of ozone in water at 25 degrees C, which is 40mg/L (Haas). Since solutions were made using 200mL of E-pure water, the maximum amount of ozone that could be dissolved was approximately 8mg. Using these values, an estimate of one hour of exposure for saturation was assumed, as this would expose the water to many times the amount of ozone that could possibly dissolve. With no way to test the amount of ozone dissolved in the water this estimate had to be used and remain constant throughout all experiments.

Zeolites

The zeolites used in the experiments were HISIV 1000, HISIV 3000, and Mordenite. In all experiments 3g of the zeolites were weighed using an Ohaus model 1500D scale and put into 50mL glass beakers, which were used as the reaction vessels. It was important to ensure the purity of these zeolites as zeolites can become clogged with contaminants over time, and can even adsorb water from the atmosphere if not stored properly. In order to ensure clean zeolites, they were placed in ceramic dishes and allowed to be heated to 150°C for no less than five hours in a Thermolyne 6000 furnace. This process would burn off any contaminants present on or in the zeolites, and would ensure that any adsorbed water would be evaporated. This process was repeated before and after every trial to ensure consistency in the purity of the zeolites.

Control Experiments

Ozone Interference

It was also necessary to prove that ozone, which could be present in solution after the experiment was run, would not skew the readings from the spectrophotometer. For this reason ozone saturated water was run through the spectrophotometer, model Cary50 made by Varian, and showed essentially zero readings (see Table 3, Appendix B). Error in these measurements can most likely be attributed to the delivery method of the ozone into the water, which used a hose that could have contained trace amounts of contaminants.

Reactions

Before the degradation reactions could be studied it was necessary to prove that without either ozone or the zeolites no reaction would occur. This was to be certain that all degradation of the ethanol was due to the catalyzed reaction with ozone present, not another secondary reaction. If secondary reactions were occurring simply between the ozone and ethanol in water for instance, the ethanol concentration readings would be thrown off during the degradation experiments since the reaction would continue to occur even when the solution was removed from the zeolite bed. Two experiments were conducted, one without ozone and one without zeolites. In the experiment without ozone, zeolites were combined with a solution of ethanol in water and agitated for 600 seconds. The liquid was then separated from the zeolites and run through the COD procedure to determine the amount of ethanol left in solution. These data are summarized in Table 3, Appendix B.

The other experiment was run using a mixture of ozone saturated water and ethanol. 10mL of 20 vol% ethanol solution was mixed with 10mL of ozone saturated water and agitated for 600 seconds. The resulting solution was then run through the COD procedure to determine the amount of ethanol degraded by the ozone. These data are summarized in Table 3, Appendix B.

Calibration Curve

To determine how much ethanol was left in solution a calibration curve needed to be made using the spectrophotometer in order to convert the absorbency readings from the spectrophotometer into concentrations of ethanol. Solutions of varying ethanol volume concentrations ranging from 20% to 0% were mixed and then run through the COD analysis, detailed later, to determine their absorbency. Each concentration was run a minimum of 3 times for accuracy. Appendix D contains the calibration curve created from the data obtained (see Table 7, Appendix D).

Degradation Experiments

Time Scale Experiments

The second set of experiments was conducted over a large time scale to ensure that the reactions went to completion. They were also necessary to show how quickly and effectively each of the zeolites acted in catalyzing the reactions considered. The same type of zeolite sample was used for these reactions. 10mL of 20 vol% ethanol solution was added to the beaker, along with 10 ml of ozone saturated water in all cases. The beaker was again covered with Parafilm, and shaken for 15 seconds. A pipette was used to collect 2.5 ml of solution immediately after the 15 second time limit. The sample was then run through the COD analysis to record its absorbency. This experiment was repeated with all zeolites, and the time was varied from 30 to 600 seconds. See Tables 4 and 5, Appendix B for data from these experiments.

Ozone Concentration Experiments

After completing these preliminary steps the degradation reaction experiments were then conducted. The first set of these experiments were conducted to show that the degradation did not depend on the concentration of ozone used in the experiment. A catalyst sample of 3g of a specific zeolite was added to a 50mL glass beaker. A starting quantity of 10 ml of 20 vol% ethanol solution was added to the beaker, along with 10mL of ozone saturated water. The beaker was covered with a film in the laboratory, Parafilm "M" produced by the Pechiney Plastic Packaging Company, and agitated for 10 minutes. The liquid portion of the sample was separated from the zeolites, then run through the COD analysis to record the absorbency readings. This experiment was repeated four times using 8mL of ozone saturated water mixed with 2mL E-pure water, 6mL ozone and 4mL E-pure, 4mL ozone and 6mL E-pure, and finally 2mL ozone and 8 ml E-pure. Each of the three types of zeolites, HISIV 1000, HISIV 3000, and Mordenite, were tested in this experimental process. The experimental system can be seen in Appendix E. See Table 6, Appendix B for data from these experiments.

Chemical Oxygen Demand Analysis

Every spectrophotometer reading was obtained after using the COD analysis method to prepare the reaction effluent. This was accomplished by carefully adding 2.5mL of the effluent down the side of the low range COD vials so that it created a layer on top of the reagents. These vials were received from Bioscience, Inc. The active ingredients contained in the vials were 77% sulfuric acid, .05% potassium dichromate, .4% silver sulfate, and .002% Sulfamic Acid. Once the cap was securely tightened back on the vial, the contents were thoroughly mixed and placed in the COD reactor, made by the Hach Company, for 2 hours at 150°C. The reactor was essentially a heater with holders designed especially for holding the vials. After reacting in the heater, the vials were removed and allowed to cool down to room temperature. If the vials were filled with solution which contained zeolites, they were run through the centrifuge, an Eppendorf 5804, for 5 minutes at 2700 RPM to remove any particulate matter. The spectrophotometer was then set to zero absorbance at 440 nm by using an empty cell. The cell was then filled with the sample and the absorbance read by the spectrophotometer.

Disposal of Waste

Special disposal considerations were made for all materials involved. The zeolites were cleaned by heating and stored in separate storage containers, as they could not be reintroduced into the stock material. All glass beakers were thoroughly cleaned and returned to the same storage facility. All liquids mixed and reacted during experiments were placed into hazardous material containers for proper disposal through WPI. All vials used during COD analysis were emptied of liquid, and disposed of in the hazardous glass wastebasket in the Water Lab in Kaven Hall, WPI.

Results and Discussion

Control Experiments

The results of the control experiments were what was expected for the process being analyzed in that ozone did not affect the spectrophotometer readings, and without all three reaction components no reaction occurred. When ozone saturated water was run through the spectrophotometer there were negligible absorbency readings. The error on these readings, as they should have been zero, was most likely attributed to how the ozone was delivered to the water. Since the hose attached to the ozone generator had to be submerged in the beaker of water, trace particulate matter probably transferred from the hose into the ozone solution. These particles most likely caused the COD analysis to register the trace amounts of ethanol seen in Table 3, Appendix B. These numbers should all read zero, meaning a concentration of ethanol of zero, but in fact have low values representing low concentrations of ethanol not present in the tested solution.

When one material or reactant was removed from the experiment little to no change was observed in ethanol concentration. After analyzing a mixture of ozone and ethanol it was determined that no changes had occurred after 600 seconds, which was the maximum degradation experiment time considered. When zeolites and ethanol were combined there was a small drop in ethanol concentration. There was a change of 3-15% in the ethanol concentrations after 600 seconds of exposure. This was most likely due to the adsorptive properties of the zeolites. Since no reaction was taking place, the ethanol had time to orient itself and enter the pores of the zeolites, where it was removed from solution, lowering the reading that should have been obtained for that particular solution. See Table 3, Appendix B for data concerning all control experiments.

Degradation Experiments

Figure 9 is a graph of the data obtained from the time varied experiments. One major result gained from these data is that the bulk of the reaction occurs in the first thirty seconds of the reaction. The reactions then begin to level out, and are essentially complete after 200 seconds, although in some cases small changes can be seen up to 600 seconds. The reaction time must then be limited by the instability of ozone in solution because the ethanol concentration should go to zero. After approximately 180 seconds, the ozone ceased to degrade more ethanol, which meant it was no longer present in solution. The ozone was being agitated out of solution by shaking, as well as consumed by the reaction. Once all of the ozone left solution, no more reaction could occur, which also supports the control experiment results where zeolites were mixed with ethanol and no ozone, and minimal changes occured.

This graph also shows that all three zeolites are active in catalyzing the degradation reaction, as all experiments showed a large decrease in ethanol concentration. The zeolite that performed the best was HISIV 1000, the zeolite with the lowest Si/Al ratio (see Table 1, Appendix A). HISIV 1000 showed a total conversion of approximately 79% of the ethanol in the solution. HISIV 3000 and Mordenite converted 59% and 56% of the ethanol in the solution respectively after the same reaction time. All data for conversion of ethanol can be found in Table 5, Appendix B. Figures 11 through 13 in Appendix C were made from the same data as Figure 9, but have been seperated to more clearly show the results that each zeolite gave.

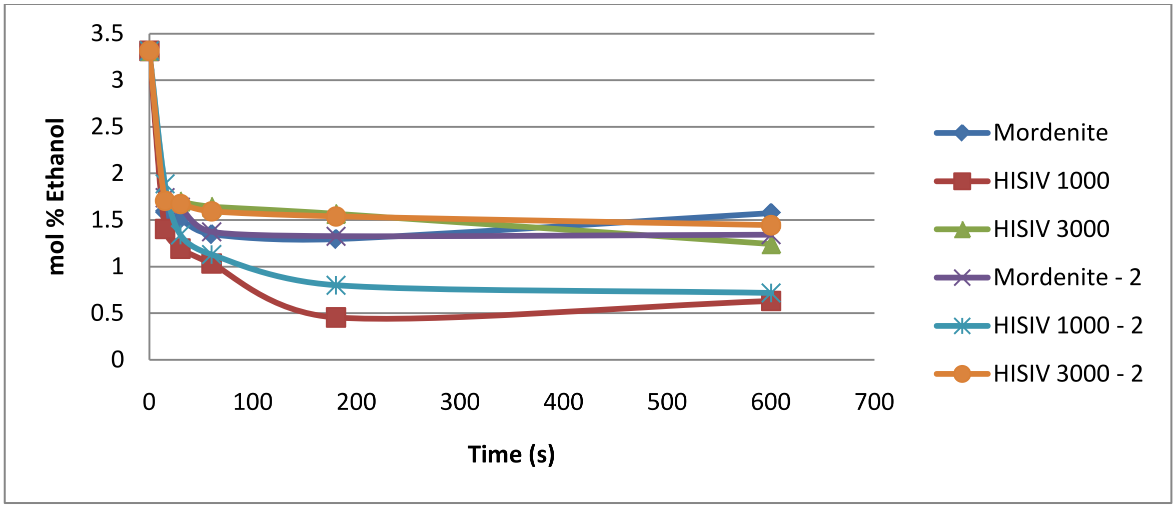

Figure 9 - Time Scale Experiments

Figure 10 is a graph of the data obtained from the experiments where the starting ozone concentration was varied. These experiments were run for 600 seconds with an initial ethanol concentration of 3.315 mol%. The graph shows that the concentration of the ozone across all of the experiments played no appreciable role in the extent of the reaction of ethanol after 600 seconds of reaction. If the ozone concentration was affecting the completion of the reaction in this time span, conversion of ethanol at lower concentrations of ozone would be less complete. The ethanol concentration values obtained for lower concentrations of ozone were comparable to those of higher ozone concentrations. This showed that the ozone was the limiting reagent in the reactions, but not because of its initial concentration. It was the limiting reagent because at some point during the experiments, all of the ozone in solution was used or lost, leaving excess ethanol. As previously discussed and shown in Figure 9, the ozone most likely ceased to be present in solution near 180 seconds of reaction. This is why the mol% ethanol left in solution during the ozone experiments is almost identical to the mol% ethanol present after 180 seconds of reaction in the time varied experiments. The fluxuations present in the data and subsequent graph are most likely attributed to the error in the experiment itself, where ozone concentrations could not be accurately determined, and contact time with the zeolite could not be maintained as constant, as agitation was accomplished through shaking of the beakers, which is not a constant process. Figure 10 also agrees with Figure 9 in that it shows that HISIV 1000 has the greatest degradation of ethanol, vastly outperforming Mordenite and HISIV 3000 during the same time span.

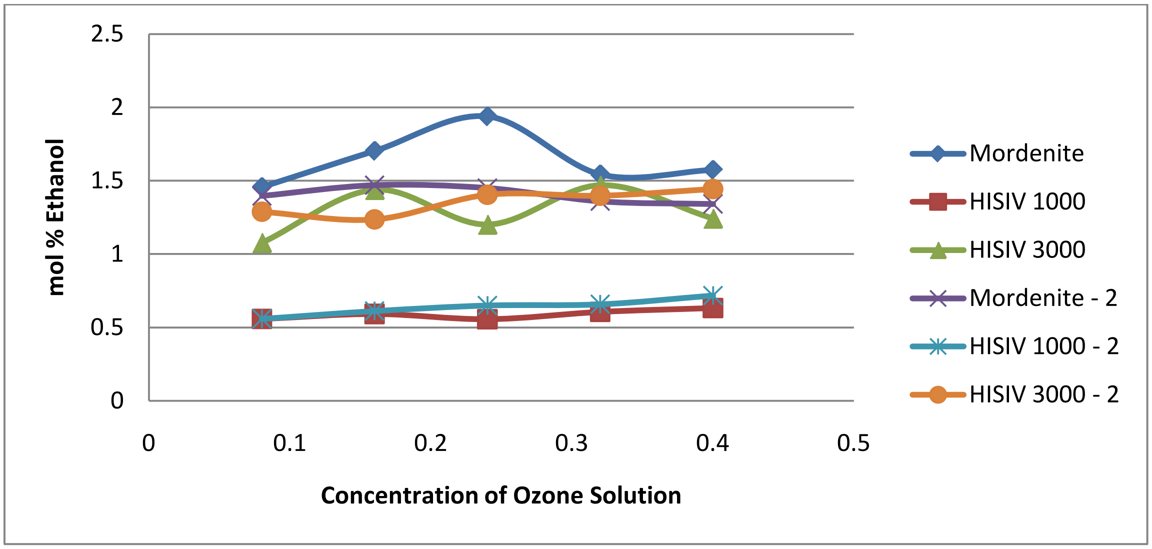

Figure 10 - Ozone Concentration Experiments

Conclusions

Although the zeolite with the lowest silica to alumina ratio was shown to outperform the higher silica zeolites, other factors must be taken into consideration if the best catalyst is to be determined. One major concern is the external surface area of the zeolites. Due to the fast reaction speed that the zeolites are supporting, the reactant to be degraded will not have enough time to appreciably adsorb into the pores of the zeolites, eliminating this property from concern. It was also shown through the control experiments that during the zeolite and ethanol experiments without ozone, only 3-15% of the ethanol could have been adsorbed (see Table 3, Appendix B). This means that most, if not all, of the reaction is taking place on the surface of the zeolite, which supports the hypothesis presented earlier.

As summarized in Table 1, Appendix A, Mordenite has the largest external surface area of the three zeolites studied. HISIV 1000 has the second most external surface area, followed by HISIV 3000 with a relatively low external surface area comparatively. HISIV 1000 has the lowest Si/Al ratio however, followed by Mordenite and finally HISIV 3000. The combination of external surface area and alumina sites most likely plays the largest role in how effective the zeolite functioned as a catalyst. Even though ozone was the limiting reagent, the experiments performed still allow a comparison between the zeolites and their catalytic efficiency. The results from the experiments show the differences in speed of the reactions, where HISIV 1000 has the fastest degradation, followed by Mordenite and finally HISIV 3000. These differences seem to be linked to the Si/Al ratios of the zeolites as well as the external surface areas. Since HISIV 3000 has a low external surface area, the reaction does not take place as fast due to the lower density of active sites. By the time the ozone leaves the solution, around minute three of the experiment, HISIV 3000 has not catalyzed as much reaction as the other zeolites, and therefore is outperformed. HISIV 3000 seems to have the least attractive combination of surface area and Si/Al ratio. Mordenite has the second most attractive combination of external surface area to Si/Al ratio, as the larger surface area allows it to catalyze the reaction faster than HISIV 3000 due to the higher density of active sites. HISIV 1000 then has the best combination of a large external surface area and the lowest Si/Al ratio. This allows HISIV 1000 to carry out a faster degradation of ethanol than the other zeolites. Figures 9 and 10 clearly show that across all experiments, with varying ozone concentrations and over differing time scales, HISIV 1000 has the ability to more efficiently catalyze the reaction considered. This leads to the conclusion that alumina sites and external surface area, and not silica sites or the internal chemistry of the zeolites, are responsible for catalyzing the degradation reaction, supporting the second part of the hypothesis presented earlier.

Although the results clearly support the hypothesis set forth, more experimentation needs to be done on the topic. When the results from Fujita Et. Al are compared to those summarized in this paper, the data are clearly contradictory. The Mordenite studied by Professor Fujita clearly shows, in Figure 8, that as the Si/Al ratio increased, the degradation of TCE also increased. As the Si/Al ratio of the ZSM-5 increased, the conversion of TCE fell, although the change is too minute to draw any conclusions from. It has been shown in this paper that as the Si/Al ratio of the zeolites decrease, the degradation of ethanol by ozone is catalyzed faster. These contradictory results lead to differing conclusions about what aspects of zeolites are truly important, and if they are to be fully understood, more experimentation needs to be completed.

Recommendations

After conducting this research, some recommendations have arisen that should be discussed. First, when considering whether to use a batch process as performed in this paper, or to develop a continuous process for experimentation as in Professor Fujita's paper, the continuous process will provide more favorable conditions in a laboratory setting. Better control is offered in maintaining contact time of the ethanol and ozone solution with the zeolite bed in a continuous system. The ability to vary flow rates through the system can lead to better analysis of reaction times as well as concentration profiles. The open batch process also has the possibility of losing ozone while the mixing is being performed, an issue that a closed system would not be affected by. A multi-stage batch system could be designed in which ozone is added at intervals during the experiment to overcome the problems experienced with ozone leaving solution. However, custom vessels would need to be designed in order to add ozone and maintain a continuous closed system. Another advantage of a closed system would be the ability to achieve a steady state reaction. Multiple samples could be taken from the same set of conditions and compared. Attempting to compare results across multiple batch systems inherently adds error as there are too many factors to attribute to human precision in the lab. If this process were to be implemented on an industrial scale, a continuous process would be the only option for consideration. Industrial sized batch processes would take too long to perform to be economically viable when accounting for the time it would take to set each batch, run the experiment to completion, and reset the equipment for the next run.

Another recommendation that arose would be to select a larger assortment of zeolites to be tested. Zeolite samples obtained should have only one specification that differs, such as the

Si/Al ratio or the external surface area, as these parameters were shown to offer the greatest diversity of results. It is difficult to conclusively decide what parameters mattered to the reactions studied in this paper, as too many factors varied in the zeolite samples. Testing a larger assortment of zeolites, with different subgroups of similar zeolites, would allow for a better understanding of what aspects play the most important role in catalyzing degradation reactions. For example, if a group of Mordenite zeolites were selected, in which the external surface area remained nearly constant, and the Si/Al ratios were vastly varied, a more developed understanding of the effects of varying Si/Al ratios could be observed. If samples of Mordenite with the same Si/Al ratio, but differing external surface areas were then tested, it would provide the researcher with better organized data to draw conclusions from.

A minor recommendation that arose was the need to properly store all chemicals being used in the experiments. Specifically, if COD analysis is to be used, it is important to check that all COD vials have been stored properly and protected from light, as the acid in the vials undergo chemical changes when exposed to light. The spectrophotometer readings from the COD analysis can be extremely varied if the vials experience light damage.

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Appendix A –Material information

Table 1: Zeolite Specifications (From Table 1, Abu-Lail)

Sample name	$\frac{SiO_2}{Al_2O_3}$	Zeolite %	Nature	Bonding Material	Company Name	Lot Number	Surface Area (m2/g)	Micropore Area (m2/g)	External Area (m2/g)
Zeolite Mordenite	50	80	Granular		Engelhard	05001C-BWC2-06	472.6	304.3	168.3
HISIV 1000 (High silica Faujasite)	35-40	80	Granular	Clay	UOP	2006006135	379.9	247.1	132.8
HISIV 3000 (Silicalite)	800	80	Granular	Clay	UOP	2002001440	321.9	230.5	91.4

Table 2: Substance Property Data (Haas)

	Ethanol	Water	Ozone (in H2O)
Density (g/mL)	0.789	1	.040
MW (g/mol)	46.0684	18.0153	47.9982
mol/mL	0.017126707	0.055508	.000833

Appendix B- Experiment Data Tables

Table 3: Control Experiments After 600 Seconds of Contact

	Ozone and Ethanol Solution (mol% EtOH)	HISIV 1000 and Ethanol Solution (mol% EtOH)	HISIV 3000 and Ethanol Solution (mol% EtOH)	Mordenite and Ethanol Solution (mol% EtOH)	Ozone Solution (mol% EtOH)
Initial Concentration	3.315	3.315	3.315	3.315	0.000
Trial 1	3.401	2.843	3.092	3.043	0.104
Trial 2	3.061	2.976	2.792	2.998	0.010
Trial 3	3.542	3.001	3.217	3.106	0.035

Table 4: Ozone Concentration Variation Experiment With 600 Seconds of Agitation

		Mordenite (mol% EtOH)		HISIV 1000 (mol% EtOH)		HISIV 3000 (mol% EtOH)	
mL of Ozone	mL of H2O	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
10	0	1.574	1.342	0.632	0.718	1.243	1.444
8	2	1.543	1.636	0.606	0.658	1.470	1.398
6	4	1.939	1.450	0.557	0.650	1.202	1.405
4	6	1.704	1.470	0.592	0.612	1.439	1.237
2	8	1.457	1.397	0.558	0.559	1.078	1.289

Table 5: Reaction Time Experiment -Ethanol Remaining

	Mordenite (mol% EtOH)		HISIV 1000 (mol% EtOH)		HISIV 3000 (mol% EtOH)	
Time (s)	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
0	3.315	3.315	3.315	3.315	3.315	3.315
15	1.591	1.739	1.404	1.888	1.777	1.706
30	1.506	1.636	1.193	1.341	1.701	1.673
60	1.347	1.374	1.034	1.130	1.644	1.592
180	1.295	1.326	0.455	0.801	1.567	1.539
600	1.574	1.342	0.632	0.718	1.243	1.444

Table 6: Reaction Time Experiment - % Ethanol Converted

	Mordenite (%EtOH Converted)		HISIV 1000 (%EtOH Converted)		HISIV 3000 (%EtOH Converted)	
Time (s)	Trial 1	Trial 2	Trial 1	Trial 2	Trial 1	Trial 2
0	0.000	0.000	0.000	0.000	0.000	0.000
15	0.520	0.475	0.576	0.430	0.464	0.485
30	0.546	0.506	0.640	0.595	0.487	0.495
60	0.594	0.586	0.688	0.659	0.504	0.520
180	0.609	0.600	0.863	0.758	0.527	0.536
600	0.525	0.595	0.809	0.783	0.625	0.564

Appendix C – Graphs of Degradation Experiments

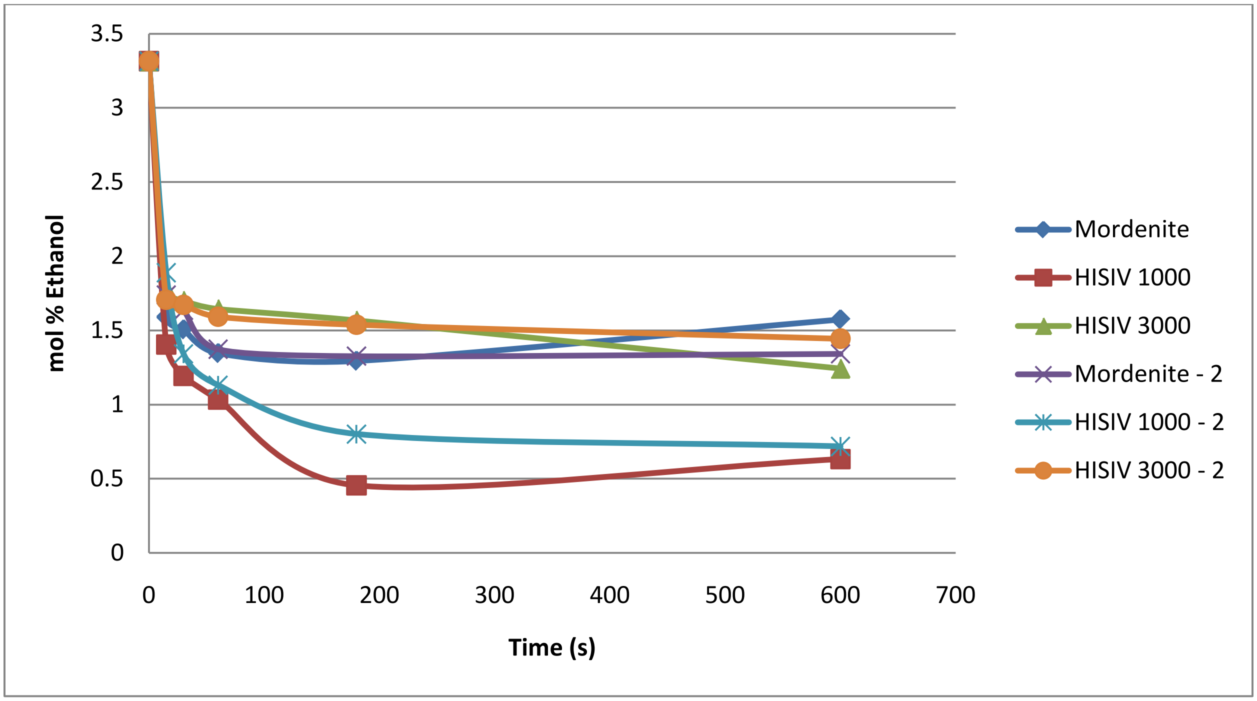

Figure 9 - Rate of Reaction for all Zeolites

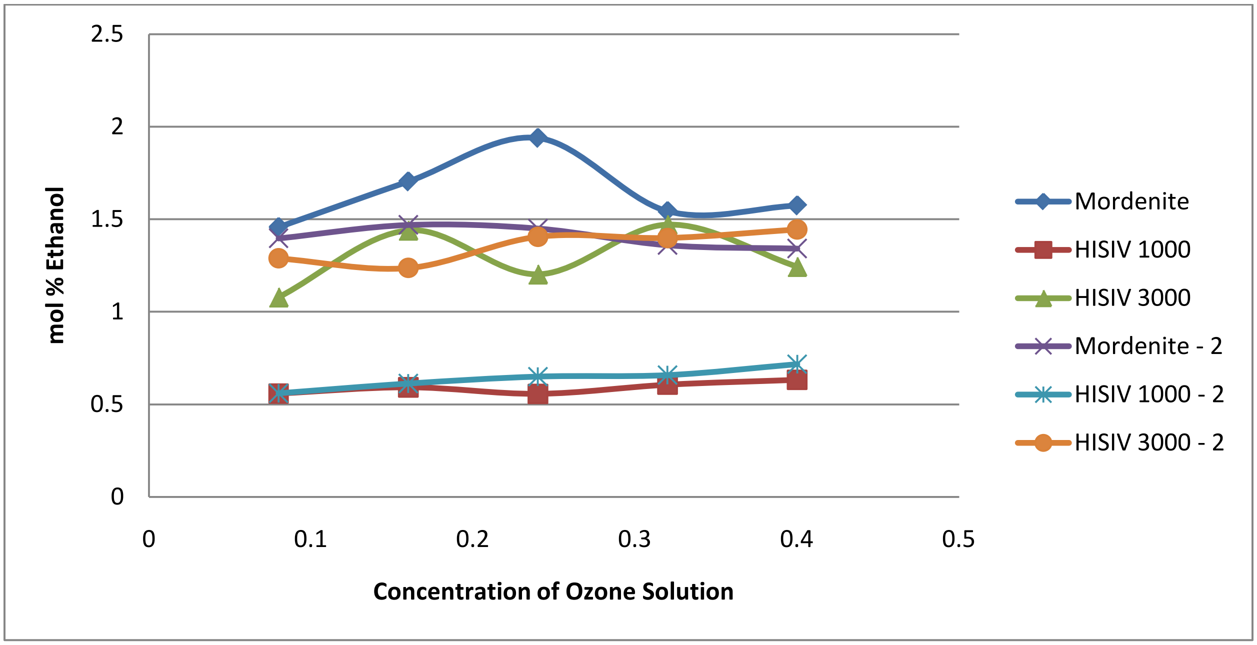

Figure 10 - Ozone Concentration Variation Experiments

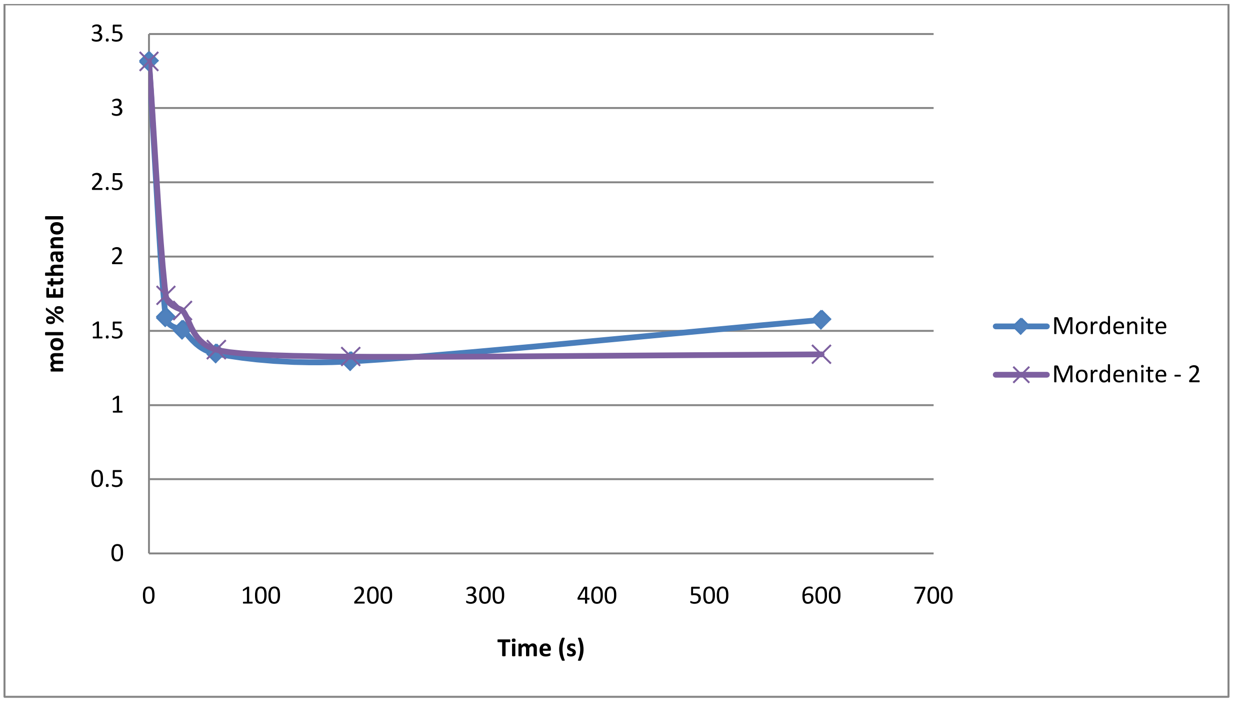

Figure 11 - Rate of Reaction for Mordenite

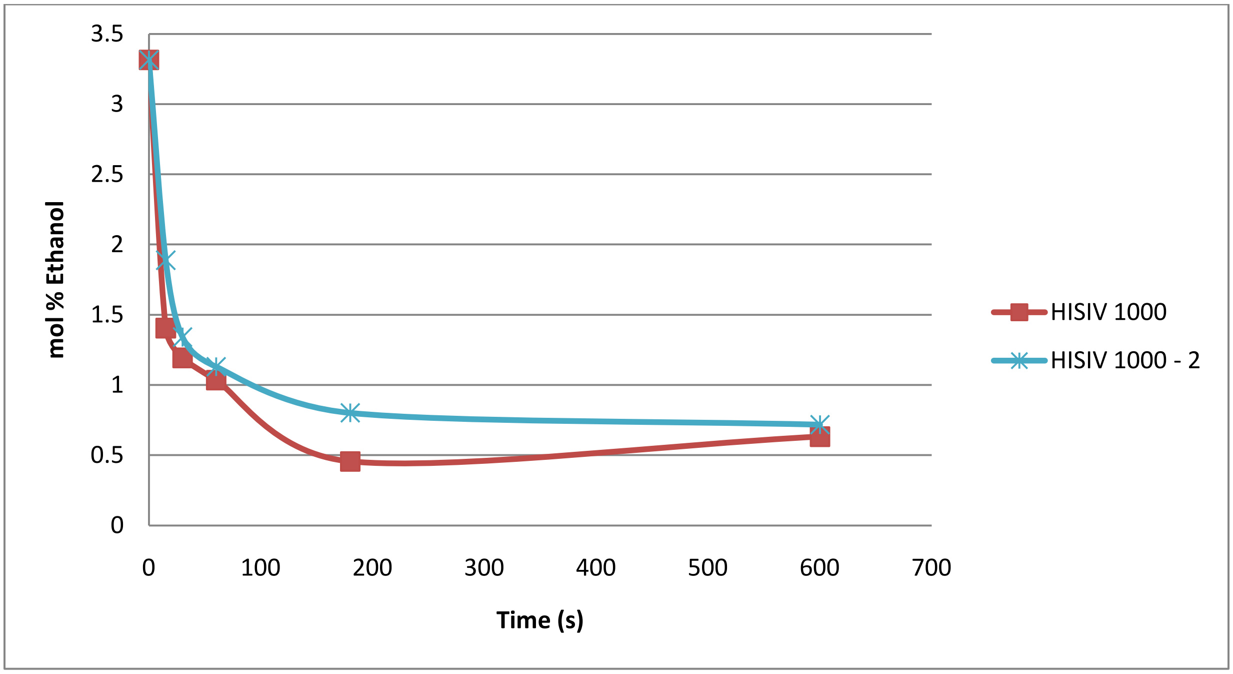

Figure 12- Rate of Reaction for HISIV 1000

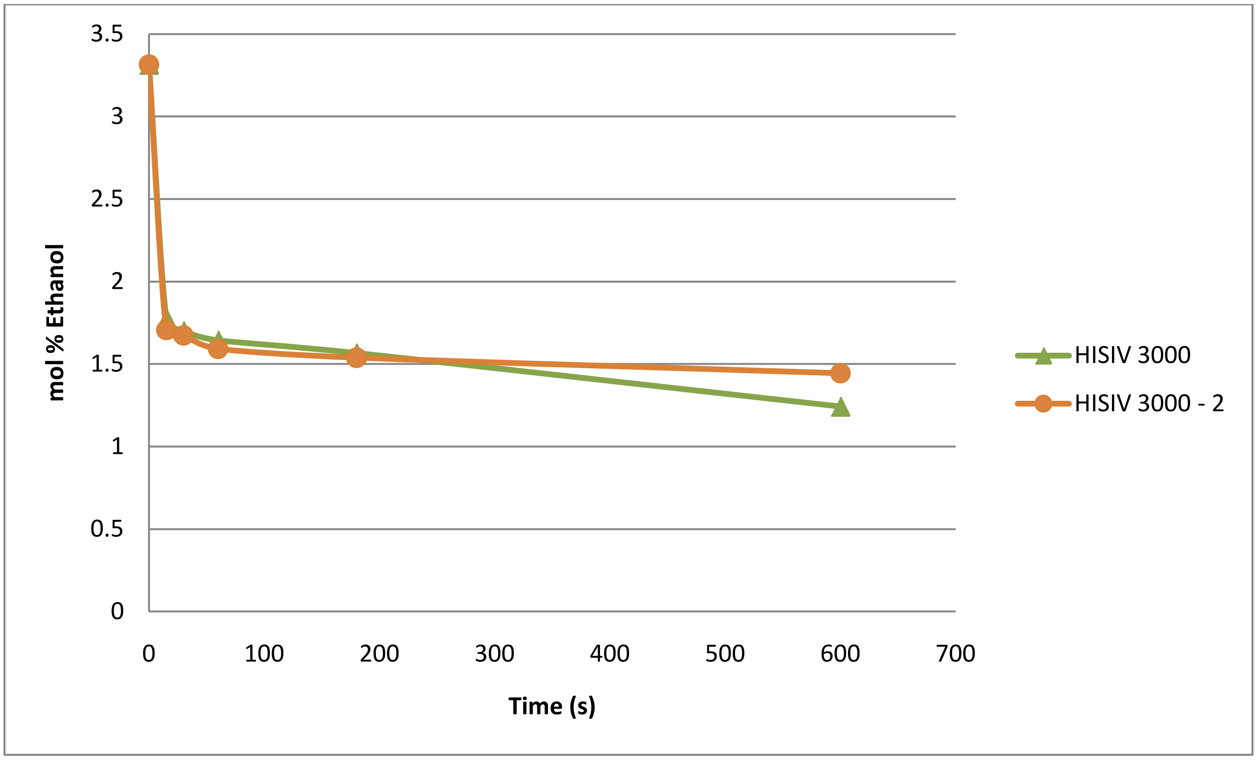

Figure 13- Rate of Reaction for HISIV 3000

Appendix D – Ethanol Calibration Curve and Data

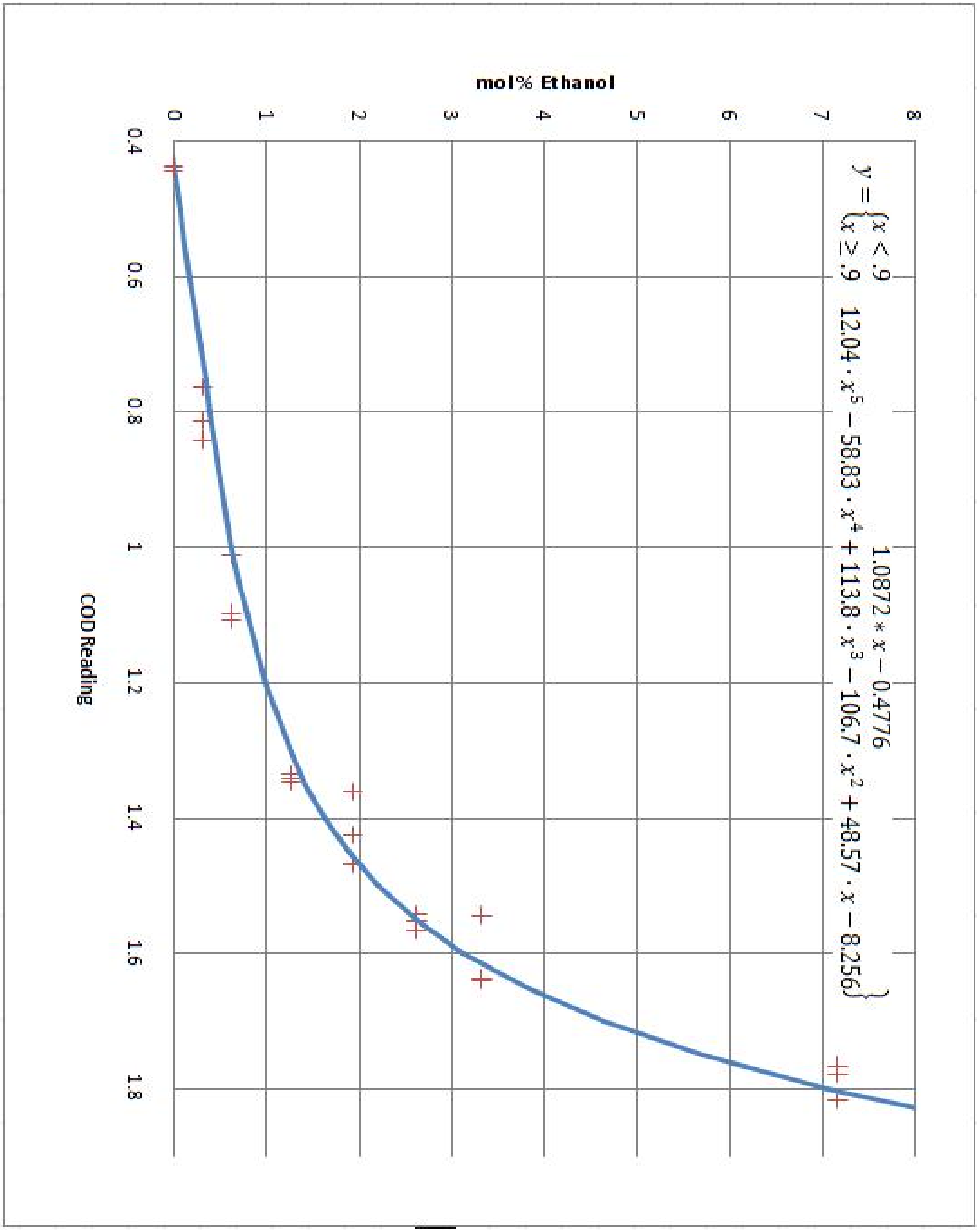

Figure 14 - Ethanol Calibration Curve

Table 7: Ethanol Calibration Curve Data

Vol % Ethanol	mol % Ethanol	COD Reading
20	7.161186173	1.778
20	7.161186173	1.8158
20	7.161186173	1.7664
10	3.314619449	1.6388
10	3.314619449	1.5451
8	2.612877601	1.5524
8	2.612877601	1.5416
8	2.612877601	1.5656
6	1.931384814	1.4242
6	1.931384814	1.3594
6	1.931384814	1.4668
4	1.269277109	1.3334
4	1.269277109	1.3405
4	1.269277109	1.3464
2	0.625738973	1.011
2	0.625738973	1.0987
2	0.625738973	1.1067
1	0.310691065	0.8428
1	0.310691065	0.7624
1	0.310691065	0.8135
0	0	0.4356
0	0	0.4389
0	0	0.4433

Appendix E- Experimental System

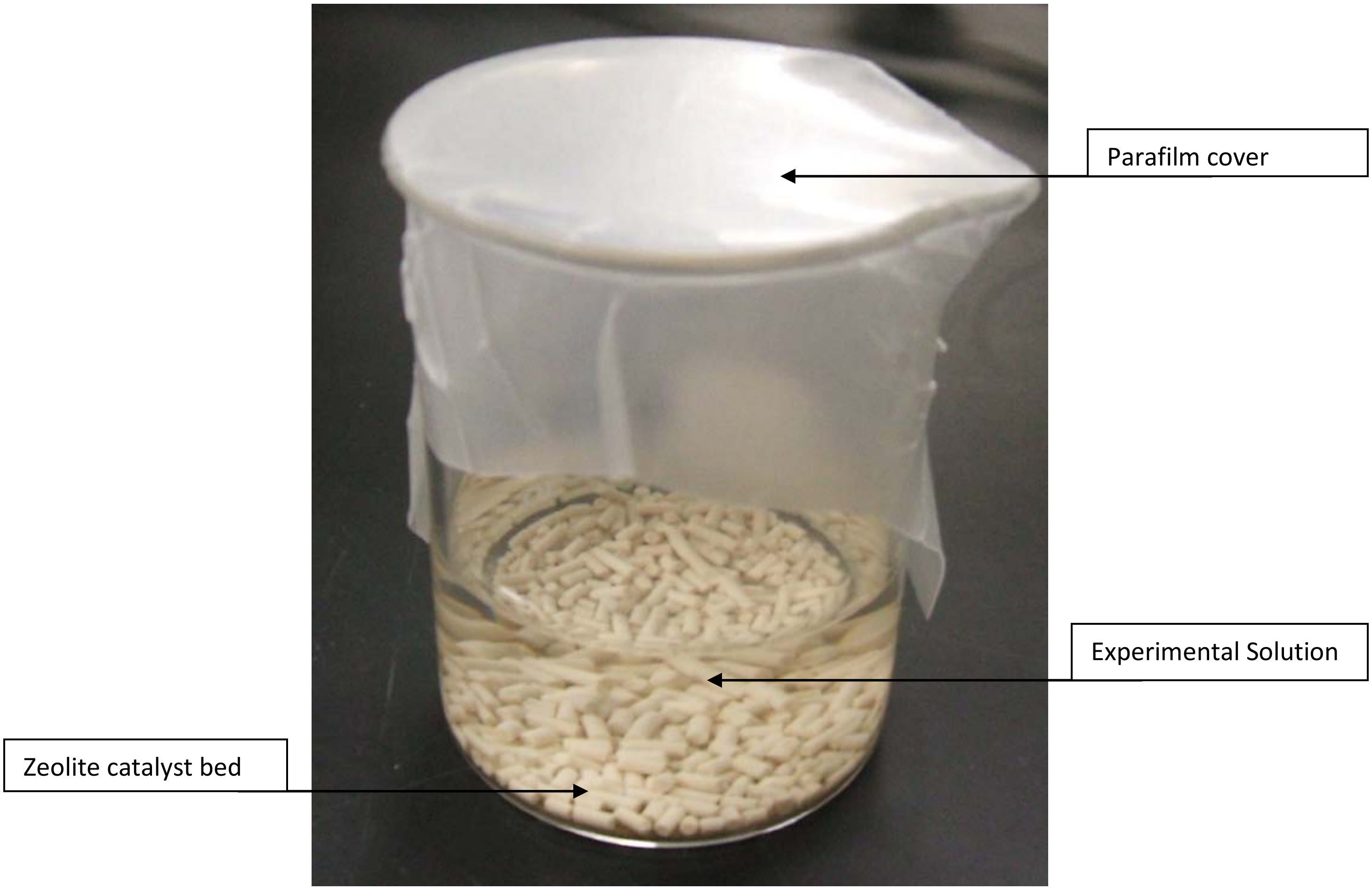

Figure 15 - Experimental System

Appendix F – List of Acronyms

AFCEE – The Air Force Center for Environmental Excellence

COD – Chemical Oxygen Demand

DEP – The Massachusetts Department of Environmental Protection

EPA – Environmental Protection Agency

EtOH - Ethanol

PCE - Perchloroethylene

RPM – Rotations per Minute

Si/Al – Silica to Alumina ratio

TCE - Trichloroethylene

VOC – Volatile Organic Compound

WPI – Worcester Polytechnic Institute

ZSM-5 – Zeolite Socony Mobile-5