Testing the Stability of Cation Exchanged Zeolite ZSM-5 in Hot Liquid Water

A Major Qualifying Project submitted to the Faculty of Worcester Polytechnic Institute in partial fulfillment of the requirements for the Degree in Bachelor of Science in Chemical Engineering

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Date: March 24, 2017
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Abstract

This project studied the effects that cation exchanges have on both the framework stability and the crystallinity of zeolite ZSM-5 as a catalyst used in the ethanol dehydration process. Sodium, iron and gallium were the cations used in this experiment and were exposed to various treatment times in hot liquid water at 300°C in a batch reaction. Supporting data from X-Ray Diffraction, Infrared Spectroscopy, and pH measurements indicate sodium-exchanged ZSM-5 to be most favorable due to its high stability and crystallinity.
Acknowledgements

The BreakingCAD team would like to thank our advisor, Professor Michael T. Timko, for overseeing this project and providing feedback and support. We would also like to recognize and thank Chemical Engineering PhD student, Alex Maag, who spent countless hours helping us both inside and outside the laboratory. He gave us constant support and guidance in all areas of this project. We appreciate all of the time effort both of them have put forth into helping us have a successful project. We also want to thank Saudi Aramco (6600023444) for purchasing the catalyst for this study. Finally, our team would like to express our gratitude to the WPI Chemical Engineering Department and the rest of the Timko lab for their support.
Table of Contents

Abstract .......................................................................................................................... 2
Acknowledgements ........................................................................................................ 3
Table of Contents ......................................................................................................... 4
List of Figures ............................................................................................................... 6
1. Introduction ............................................................................................................ 7
2. Background ............................................................................................................. 10
   2.1 Zeolites ............................................................................................................. 10
   2.2 ZSM-5 ........................................................................................................... 10
      2.2.1 Acid Sites ............................................................................................... 11
   2.3 Zeolite Framework Stability .......................................................................... 12
   2.4 Cation Exchange ........................................................................................... 13
      2.4.1 Sodium Cation Exchange ................................................................... 14
      2.4.2 Iron Cation Exchange .......................................................................... 15
      2.4.3 Gallium Cation Exchange .................................................................... 16
3. Methodology .......................................................................................................... 17
   3.1 Batch Reaction ............................................................................................... 17
      3.1.1 Reactor Components ............................................................................ 17
      3.1.2 Start-up Procedure ............................................................................... 18
      3.1.3 Shutdown ............................................................................................... 19
   3.2 Catalyst Preparation ....................................................................................... 19
      3.2.1 H-ZSM-5 Calcination .......................................................................... 19
      3.2.2 Sodium Ion Exchange .......................................................................... 20
      3.2.3 Iron Ion Exchange .............................................................................. 20
      3.2.4 Gallium Ion Exchange .......................................................................... 21
   3.3 Analytical Tools ............................................................................................... 21
      3.3.1 Infrared Spectroscopy .......................................................................... 21
      3.3.2 XRD ......................................................................................................... 22
      3.3.3 pH Test .................................................................................................... 24
   3.4 Safety .............................................................................................................. 25
4. Results .................................................................................................................... 26
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.1 X-Ray Diffraction</td>
<td>26</td>
</tr>
<tr>
<td>4.1.1 Further XRD Investigation on 7-9° Peaks</td>
<td>32</td>
</tr>
<tr>
<td>4.2 Infrared Spectroscopy (IR)</td>
<td>33</td>
</tr>
<tr>
<td>4.2.1 Na-ZSM-5</td>
<td>33</td>
</tr>
<tr>
<td>4.2.2 Fe-ZSM-5</td>
<td>36</td>
</tr>
<tr>
<td>4.3 pH</td>
<td>40</td>
</tr>
<tr>
<td>5. Discussion</td>
<td>43</td>
</tr>
<tr>
<td>6. Conclusion and Recommendations</td>
<td>47</td>
</tr>
<tr>
<td>6.1 Conclusion</td>
<td>47</td>
</tr>
<tr>
<td>6.2 Recommendations</td>
<td>48</td>
</tr>
<tr>
<td>References</td>
<td>49</td>
</tr>
<tr>
<td>Appendices</td>
<td>53</td>
</tr>
<tr>
<td>Appendix A. Material Safety Data Sheets</td>
<td>53</td>
</tr>
<tr>
<td>Appendix B. Quantitative value tables for 7-9.5° XRD peaks</td>
<td>69</td>
</tr>
<tr>
<td>Appendix C: Quantitative pH results</td>
<td>71</td>
</tr>
</tbody>
</table>
List of Figures

Figure 1. Molecular structure of MFI zeolite showing pores (Kumar, 2014) ........................................ 11
Figure 2. Structure of the Brønsted Acid Sites (BAS) in ZSM-5 ....................................................... 11
Figure 3. Chemistry of the different methods of degradation ............................................................... 12
Figure 4. Autoionization of water ........................................................................................................ 14
Figure 5. Temperature controller of the Parr Model .......................................................................... 17
Figure 6. Batch reactor labeled components a) front and b) rear view .............................................. 18
Figure 7. Set-up of the iron ion exchange ......................................................................................... 20
Figure 8. Set-up of Fourier Transform Infrared spectroscopy ........................................................... 21
Figure 9. X-Ray Diffraction overview (Flowers et al., 2016) ............................................................. 23
Figure 10. Integrated Peak Area Method on Na-ZSM-5 residual 18-hr treatment sample ............. 24
Figure 11. VWR Scientific Model 8000 used for pH testing ............................................................. 25
Figure 12. Diffraction peaks for Na-ZSM-5 samples at 300°C at various treatment times ........... 27
Figure 13. Residual material on 18-hr Fe-ZSM-5 sample .................................................................. 27
Figure 14. Water solubility residue test (left to right): ................................................................. 28
Figure 15. Comparison of Na-ZSM-5 residual & powdered sample at various treatment times . 29
Figure 16. Diffraction peaks of various treatment times for Ga-ZSM-5 ........................................... 29
Figure 17. Diffraction peaks of Fe-ZSM-5 sample under HTW conditions ....................................... 30
Figure 18. Degree of crystallinity as a function of time for all treated samples .............................. 31
Figure 19. Degree of crystallinity for all crystalline and residual samples ...................................... 32
Figure 20. Diffraction peaks for a) Na-ZSM-5 b) Fe-ZSM-5 and c) Ga-ZSM-5 .............................. 33
Figure 21. Comparison of sodium ion exchanges with 3-hr treated Na-ZSM-5 ............................... 34
Figure 22. IR of different treatment time Na-ZSM-5 samples at 300°C .......................................... 35
Figure 23. IR comparison of treated and residue peaks for a) 24-hr and b) 72-hr ............................... 36
Figure 24. IR for Fe-ZSM-5 ion exchanges ..................................................................................... 37
Figure 25. IR peaks of Fe-ZSM-5 at various treatment times ............................................................. 38
Figure 26. Peaks at various heat-up temperatures of ........................................................................ 38
Figure 27. IR for Ga-ZSM-5 ion exchanges ...................................................................................... 39
Figure 28. IR peaks for gallium samples of different treatment times ............................................. 40
Figure 29. pH as a function of time for treated samples ................................................................. 41
Figure 30. Zeolite cation exchange mechanism with sodium nitrate wash example ..................... 44
Figure 31. IR for a) 3-hr and b) 18-hr runs of all cation-exchanged samples ................................. 45
Figure 32. Catalytic activity for zeolite samples ............................................................................. 46
1. Introduction

Companies in industry today rely heavily on the aid of a catalyst. Approximately 75% of chemicals produced across all industrial sectors are made through the use of catalysis (Wilczura-Wachnik, 2015). Catalytic reactions provide an alternative pathway for the breaking of bonds and require lower activation energy than an uncatalyzed reaction (Catalysis in Industry, 2013). Another beneficial component of catalysts is its selective nature. For example, in industrial practices, the same feed material can be used with multiple catalysts to obtain a variety of desired products. With research and improvements in catalytic activity, desired temperature and pressures may be obtainable; for example, a company can save money by lowering its operating conditions which in turn lowers energy and fuel consumption. Other industrial benefits of the catalytic process include less pollution and fewer side products (Armor et al., 2008).

There are many applications in which catalysts can be utilized. In the petroleum industry catalysis is applied through a process known at Fluid Catalytic Cracking (FCC). Oils are transformed into more usable products such as gasoline, butane and different plastics (Armor et al., 2008). Almost every human activity in the modern world is dependent upon plastics; this can range from clothing to cars to health care products (Why Plastics, 2011). Polyethylene, one of the main components of plastics, is formulated from ethylene (X. Zhang et al., 2008). As of 2015, resins based off of polyethylene sold in North America accounted for 42.3% of all resin sales (Plastics Industry Producers’ Statistics Group, 2016). A resin is a synthetic polymeric compound that is used for the manufacturing of petrochemicals and plastics. Human reliance on ethylene corresponds to many economic benefits in the organic chemistry industry.

The industry’s application of traditional steam cracking to manufacture plastics and other products however, has negative impacts on the environment with the emission of carbon dioxide. Alternatively, many researchers have been examining the process of ethanol dehydration to produce green ethylene. Furthermore, if the source used for this process is bioethanol, the final plastic product is able to be produced from a renewable feedstock as compared to coming from limited fossil fuel sources. Besides helping to eliminate a dependence on petroleum, using bioethanol helps prevent additional emission of greenhouse gases into the atmosphere (Fan et al., 2012).

Over 30% of the world’s bioethanol originates from Brazil with more than 37 billion liters produced in the 2013-14 crop year (Ethanol, 2017). Braskem, a large petrochemical company located in Brazil, invested $290 million dollars into its green ethylene plant, where bioethanol, from sugarcane, is transformed into green ethylene with the aid of a catalyst (Where it is Produced, 2017). Some catalysts utilized in the production of green ethylene include alumina, silica, molybdates, SAPO-34, and zeolites. Zeolites have been recommended for ethanol dehydration, because they operate at lower temperatures than alumina catalysts. Results show that coke formation was observed at the Brønsted acid sites along with catalyst deactivation.
(Luiz et al., 2013). Strives have been made recently to improve the current condition of zeolites for the use of ethanol dehydration.

Ethanol dehydration uses a variety of catalysts to produce ethylene. The addition of a catalyst to this process has been demonstrated to be more appealing than without one because it “requires lower temperature and offers higher ethylene yield.” With lower temperatures the process becomes more cost efficient which is vital from an economic and commercial standpoint (X. Zhang et al., 2008). In recent studies, zeolites have shown to be a promising catalyst for ethanol dehydration.

Zeolites are crystalline aluminosilicate based compounds that are of great use in facilitating reactions in the petrol industry. Their structure is formed through the interconnection of tetrahedrons composed of oxygen with either silicon or aluminum as the core atoms. When zeolites were first discovered during the 18th century, they were used as drying agents. As more of their properties were discovered, the uses of zeolites became diverse, ranging from cation exchangers to adsorbents. It was not until the 20th century, when synthetic zeolites became readily available for research purposes, that their catalytic properties were uncovered (Van der Gaag, 1987). Zeolites have found great use as catalysts because of their selective nature due to their porous structure. Zeolites are unique in that molecules of interest have definitive pore sizes, which allow for reactions to be selective based off of confinement. Zeolite Socony Mobile-5 (ZSM-5) is a general term for a pentasil type zeolite. It is characterized by high silica to alumina ratio in the framework (Van der Gaag, 1987). The conversion of ethanol to ethylene using ZSM-5 is typically performed in gas phase reactions. However, there are benefits to performing this conversion in the liquid phase. This alternative process can be considered economically and commercially more desirable because it has the potential to provide lower operating conditions than that of steam which in turn saves companies money. This specific zeolite provides a sustainable energy alternative and potential in the energy industry. Currently, ZSM-5 is used under steam conditions, which poses an economic challenge. Some research has explored the possibility of turning this process into a liquid phase reaction using hot liquid water (HLW) (Abu Muti et al., 2016).

Previous research has given us insight into a variety of ZSM-5 characteristics at different operating conditions. When comparing the activity and stability of four catalysts, X. Zhang et al. (2008) noted that at 300°C, 95% of ethylene in the reaction using a ZSM-5 variant, H-ZSM-5, as a catalyst was produced from a conversion level of 98% of ethanol. Zeolites that are referred to as “H-ZSM-5” are zeolites that have their ion exchange sites, located near the aluminum in the structure, occupied by H⁺ ions. The name “H-ZSM-5” is simply an example of a more specific notation; the same notation is used for other cation exchanges (i.e iron cation exchanged zeolites are represented by Fe-ZSM-5). Research from the Fan et al. (2012) review paper on catalytic dehydration indicates H-ZSM-5 catalyst to be a viable candidate for ethanol dehydration because
testing nanocatalyst H-ZSM-5 zeolites resulted in 99.7% ethylene selectivity at a temperature of 240°C and a lifetime of 630 hours using a microreactor. The nanoscale H-ZSM-5 in this study was the most ideal catalyst compared to the current ones being studied. Understanding the analysis of the chemistry of ethanol in vapor phase from these studies will allow our team to gain insights into any improvements that could be made in the liquid phase.

Although H-ZSM-5 has high initial activity for ethylene yield, there is a noticeable decrease over time. Literature has stated coking deactivation in the vapor phase may be a result of H-ZSM-5’s strong acidic property (X. Zhang et al., 2008). Studies with liquid phase conditions also resulted in zeolite stability worsening. Specifically in HLW, zeolites can collapse and lose their crystallinity after only a few hours (L. Zhang et al., 2015). The decrystallization of H-ZSM-5 in hot liquid water (HLW) occurs from the autoionization of water. It has also been proposed that decrystallization is heavily dependent on temperature. H-ZSM-5 zeolite stability is believed to be dependent upon thermal and ionic effects. Dissociation of acid sites occurs as temperature increases under HLW treatment. Additionally, data from infrared spectroscopy (IR) indicates that decrystallization generates extra-framework aluminum (EFAI) as well as the loss of Brønsted acid sites and silanol groups under HLW treatment (Abu Muti et al., 2016). A potential hypothesis of increasing stability is to perform a cation exchange. By studying the catalyst without the presence of the proton, we may be able to discover more information in regards to the framework stability.

Our project specifically focused on establishing a fundamental understanding of the hydrothermal stability of ZSM-5 in hot liquid water when exchanging hydrogen (H⁺) with various cations: sodium (Na⁺), iron (Fe⁺) and gallium (Ga⁺). We measured the crystallinity of the ZSM-5 catalyst after each cation substitution and made comparisons with previous work as well as repeated trials of H-ZSM-5 to see the effects of degradation. The experiments were run using hot liquid water at temperatures and times lengths similar to prior research. The Na-ZSM-5, Fe-ZSM-5 and Ga-ZSM-5 samples were analyzed and compared to H-ZSM-5 samples using various techniques including Infrared Spectroscopy (IR), X-ray Diffraction (XRD) and pH testing.
2. Background

2.1 Zeolites

Zeolites are useful for a variety of functions, including petrochemical cracking, ion exchange, separation of gases and solvents, and agriculture and construction. With many applications and the ability to be formed from abundant, low cost material, it is important to understand the material in order to be able to compete in industry.

These catalysts are microporous crystalline solids usually formed of silicon, aluminum, and oxygen, and often contain cations, water, and a variety of other molecules in their pores. One of the reasons for their versatility is because of the large amount of variations that exist based on this structure. To date, over 130 different configurations have been identified, for use in environmental remediation, separation, ion exchange, and catalysis (Van der Gaag, 1987).

Zeolites have been used as a replacement for harmful alternatives for sorbents, detergents, and catalysts. Their nature as a solid acid means reducing the use for more corrosive and harder to handle liquid acids. As absorbent compounds, they can be used to separate out pollutants from gas streams and remove organics from water. Additionally, by exchanging ions that are pre-existing in some varieties’ pores, zeolites can be used to remove heavy metal ions from water (Bell, 2001). These traits are useful not only for environmental clean-up, but can be applied to many industrial processes requiring the purification of a product.

As a catalyst, zeolites enable reactions inside its internal cavities. Zeolites find a niche as a catalyst due to their ability to exert a steric influence on molecules that enter their pores as well as select products that form based on the size of the transition sites that form during reactions. Additionally, due to their microporous structure, zeolites possess a fairly large surface area, greatly increasing their effectiveness as a catalyst. This large surface area proves useful especially for multiphase reactions, in order to provide for effective contact between liquids and gases (Bell, 2001).

Among the wide array of zeolites, there is a type of hydrogen-exchanged zeolite that are especially useful for organic reactions including oil cracking, fuel synthesis and producing chemicals for feedstock in plastic production. The zeolite of interest for this project is H-ZSM-5, a zeolite variation with high acidity useful for catalyzing the ethylene production process.

2.2 ZSM-5

ZSM-5 is a pentasil type zeolite characterized by a very high silica to alumina ratio. It is composed of eight five-membered rings. The normal Si/Al ratio for zeolites is between 1 and 5 and in ZSM-5 it is 11 or greater with no more than 8 aluminum atoms in the crystalline structure.
It is formed in a tetrahedral shape composed of Al\(^{3+}\) and Si\(^{4+}\) surrounded by four oxygen molecules. See Figure 1. The metals form the vertices of the ring and the oxygen between them. It forms a straight channel that has a diameter of about 0.5-0.56 nm. Through this channel are pores which adsorbed species can fill in. Unbranched carbons are the only species that can fit through (Van der Gaag, 1987).

![Figure 1. Molecular structure of MFI zeolite showing pores (Kumar, 2014)](image)

**2.2.1 Acid Sites**

ZSM-5 contains acid sites next to aluminum atoms in the structure. Brønsted sites are the sites that ZSM-5 can donate a proton that is attached to an oxygen atom that is connected to the base tetrahedral shape as seen in Figure 2 below. The “T” in the figure below stands as a placeholder for either Al or Si in order to show the structure. These are important locations for catalytic activity in many ZSM-5 reactions.

![Figure 2. Structure of the Brønsted Acid Sites (BAS) in ZSM-5](image)

These are strongly acidic hydroxyl groups that allow protons to easily dissociate from the zeolite and allow ion exchange to occur. The other type of acid sites present in this catalyst is Lewis acid sites which are places that can accept electrons. There are present at the metals, Al and Si in the crystal. Acid strength of these sites varies based on bridge geometries. These geometries cause a change in bond length and bond angles which can alter the availability of a proton to be donated and electron space for additional electrons (Deka, 1998).
2.3 Zeolite Framework Stability

Zeolite framework stability is the ability for a zeolite to maintain its crystallinity under the presence of steaming, organic solvents, or hot liquid water conditions. Degradation entails the removal of the Si/Al species within the zeolite crystal. There are two forms of degradation: acid dealumination and desilication. Dealumination occurs via either steam or acid treatment that cleaves Al-O bond. Desilication using NaOH solution splits the Si-O-Si bond (Goen et. al., 2005). See Figure 3.

![Chemistry of the different methods of degradation](image)

Previous studies have proposed that the base-catalyzed mechanism, desilication, is the more dominant degradation pathway compared to the acid-catalyzed mechanism, dealumination, under hot liquid water conditions of ZSM-5. The process of dealumination under steaming conditions removes the framework aluminum (Al) atoms from the lattice in ZSM-5. The removed framework aluminum atoms then form the extra framework aluminum (EFAI), which is an independent alumina phase, outside the zeolite crystal. The degree of steaming can be dependent on the silica to alumina ratio within the zeolite crystallinity. Thus, as the Al content increases, the zeolite stability decreases in steaming. Furthermore, studies showed dealuminated H-ZSM-5 samples under severe steaming conditions do not contain any kind of relatively strong acidity, neither Brønsted nor Lewis. Dealumination via steaming showed twenty or less percent of structural breakdown with respect to their relative crystallinity (XRD) (Triantafillidis et al., 2001).
The decrystallization of zeolites yields different results under base conditions in hot liquid water using the base-catalyzed desilication method. Hydrothermal water (HTW) is characterized as hot liquid water (HLW) under either conditions of temperatures above 200˚C, or supercritical conditions, which occur at temperatures of 374˚C and above as well as pressures higher than 218 atm. The terms hydrothermal water and hot liquid water are used interchangeable throughout this report. Some factors that can affect the stability of ZSM-5 in HLW are Brønsted acid sites, framework type, silanol defects, and EFAI.

Previous research on the decrystallization of ZSM-5 using HTW has been analyzed using several different methods. In a previous study performed in 2015, X-Ray powder diffraction was used to analyze the crystallinity of the treated zeolite sample, H-ZSM-5 (Abu Muti et al., 2016). Analysis of the graphed results led to the conclusion that the decrease in crystallinity began to occur as treatment time and temperature increased. Further quantitative analysis showed that the relative crystallinity as a function of time. Furthermore, higher temperature runs showed a higher decrystallization rate and no stability. The stability tests concluded that the stabilization effect may be due to the effect of the extra-framework aluminum (EFAI). Furthermore, literature has suggested that the EFAI preserves the zeolite framework as it blocks the silanol groups from water molecules. Silanol groups are vulnerable to water molecules. Higher temperature runs are able to surpass the energetics of EFAI protection. The previous research group speculated that decrystallization occurs during the heat-up period to the desired temperature (Abu Muti et al., 2016).

2.4 Cation Exchange

Zeolites have well-defined pore structure and high activity per acid site. Many reactions are catalyzed by the acid sites of zeolites so they play a very important role (Ravenelle et al., 2010). The autoionization of water can contribute to high levels of both hydronium and hydroxyl species in solution. As previous studies have shown, due to these zeolites’ tendencies to breakdown under both acid and base conditions, these ions can contribute to decrystallization in the catalyst (Abu Muti et al., 2016). In autoionization, water molecules react with one another to form hydroxyl and hydronium ions (OH⁻ and H₃O⁺); the hydroxide acts as a base and is willing to accept a proton (Acids and Bases, 2016). Figure 4 shows the stoichiometry of autoionization of water. As the temperature in reaction increases, the number of dissociated ions increases which gives rise to the pH of the solution (Bandura & Lvov, 2006). The dissociated ions attack the porous surface and change the nature of the material; the increased acidity deactivates the ZSM-5 catalyst which impacts its long-term performance (Abu Muti et al., 2016).
Currently in zeolite studies, metal cations are used to keep the material charge neutral. As stated in the Introduction, ZSM-5 has high silicon to aluminum ratio. The structure of ZSM-5 includes the interconnection of tetrahedron composed or oxygen with the core atoms being silicon or aluminum. Silicon atoms exit naturally in a 4+ oxidation state while aluminum exits in a 3+ oxidation state (Price, 2015). The difference in the valences of silicon and aluminum create this negative charge that needs to be balanced out. The aluminum-oxygen form requires an additional positive charge to ensure electroneutrality; this positive charge can either come from a proton or a metal cation (Deka, 1998).

The ion-exchange process for the proton (H⁺), results in a much more acidic solution. As stated previously, the acidity directly relates to the content of the aluminum. When the zeolite undergoes dealumination, the material is more vulnerable and is more likely to be attacked by liquid water which results in structural collapse and loss in crystallinity (L. Zhang et al., 2015). Thus the function of the catalyst worsens making it less desirable. In order to improve upon the performance and stability of ZSM-5 over time, metal exchanged cations can replace the hydrogen cations so that the framework is not altered in a detrimental way. A metal cation exchange can potentially prevent the protons from causing a self-degradation of ZSM-5. The metal cations rather than protons are to be removed from the catalyst and placed into the solution; therefore our research hypothesizes less degradation will result from this. Three cation exchange ZSM-5 zeolites were studied and used in this project; the cations include sodium, iron and gallium.

### 2.4.1 Sodium Cation Exchange

Literature has shown several studies on metal cation exchanged zeolites. First, it is important to note that the crystalline structure of the zeolite remains intact during cation exchange because of the zeolite framework and the ionic nature of the bond (Deka, 1998). The crystallinity of ZSM-5 and the framework influence its stability and ultimately the catalyst’s performance (Ravenelle et al., 2010). In Chu et al. (2011), ZSM-5 is studied through its sodium cation location and aluminum distribution. The paper states that recently there has been expressed interest in metal cation exchanged zeolites. The location of the cation strongly influences the catalytic performance of zeolites as documented by previous research. In the ZSM-5 zeolite, there are 12 different aluminum sites. Each are associated with various Na-sites (labeled T1, T2, etc). This study surveyed the cation (sodium) locations, along with the aluminum distribution, in order to
further understand the catalytic properties of ZSM-5 using ONIOM (Own N-layer Integrated molecular Orbital molecular Mechanics) and XO (newly developed extended ONIOM) methods. Results show that in most Al-sites, Na\(^+\) prefers to occupy the six-membered ring site which allows for further comparison of relative stabilities of different Al substitution sites. Additionally some sites (T8, T4, and T10) are energetically more favorable in terms of cation location energies; they were the lowest. It was predicted that these three sites are preferentially occupied by an Al atom while sodium cations are being transferred into the zeolite structure. With further study of the sodium locations and aluminum distributions, more and more catalytic properties of zeolites can be discovered on the molecular scale.

Another paper investigates H-ZSM-5 zeolite going through partial exchanges with Na\(^+\) cations (Martinez & Peris, 2016). The aim of the study was to depress coke-forming tendencies and improve stability of the Mo/ZSM-5 catalyst in the non-oxidative methane dehydroaromatization reaction. Results show that neutralizing the OH groups with the sodium catalyst reduced both the amount and average strength that was remaining in the Brønsted acid sites. Additionally, the proton exchange with the sodium cation resulted in not only a “reduction in the total amount of acid sites, but also in the average of the remaining one.” This can correlate to our area of study because if there is a reduction in acidity, there is a smaller chance of hydrogen detaching from the catalyst and causing self-degradation. According to the recorded X-ray diffraction (XRD) patterns, the crystalline structure of the original H-ZSM-5 zeolite is preserved after the metal cation exchange of sodium as is expected.

2.4.2 Iron Cation Exchange

While research on sodium ion exchange has been well established, the deactivation method for iron exchanged ZSM-5 has not been studied in depth long enough to understand the complexity of the mechanism completely. However, studies have shown that hydrothermal aging yields the loss of active iron sites as well as a lower Brønsted acidity of the catalyst. The presence of water aids the reduction of active iron sites as it promotes the iron to migrate out of ion exchange sites. The migration of iron allow for the development of metal-oxide clusters and low activity particles (Shi et al., 2015).

A study performed by Brandenberger, Kröcher, et al. in 2011 showed that less hydrothermally stable Fe-ZSM-5 zeolites have a Fe/Al ratio of less than or equal to value of 0.8. Furthermore, the results of this study have predicted that an increase in the H\(^+\) to Fe\(^{2+}\) ratio could be responsible for a weaker iron bond strength at nearby ion exchange sites because of the hardness of H\(^+\) cations. The study then further investigated hydrothermal deactivation; results revealed that Al sites bearing an iron ion showed to have a higher stability under hydrothermal aging than Aluminum sites bearing a Brønsted acid proton when tested for the same duration. Al sites bearing Fe ions are less influenced by hydrolysis. The final conclusion from the results of this experiment revealed the correlation between the amount of isolated iron sites in Fe-ZSM-5 and
its hydrothermal stability, with a high amount of isolated iron sites yielding a higher hydrothermal stability. Overall, the study of iron-exchanged zeolites is not as focused on as other ion exchanges due to its poor hydrothermal stability compared to other ions (Brandenberger et al., 2011).

2.4.3 Gallium Cation Exchange

In addition to iron and sodium exchanged zeolites, research has been conducted investigating the catalytic properties of Ga-ZSM-5. One study by Shao et al. (2016) discusses the ability of gallium oxide based catalysts to have high activity for the dehydrogenation of alkane species, such as propane to propylene and ethane to ethylene. Their research goes on to test the activity of several gallium based catalysts for the propane to propylene process, one being Ga-ZSM-5. In the results, it was determined that out of all studied catalysts, Ga-ZSM-5 had the highest initial conversion of propane.

Ga-ZSM-5 is also used widely as an aromatisation catalyst, useful for converting alkanes into aromatic groups. H-ZSM-5 is also able to be used as such a catalyst, and a study by Tagliabue et al. (2003) compares it with Ga-ZSM-5. In their paper, it is discussed how H-ZSM-5 is not the best catalyst for aromatisation, and is more useful with a promoter cation. One of the reasons for this is that with H-ZSM-5, there is a risk for a side reaction, hydrogenolysis, to occur. While Ga-ZSM-5 is less active compared to H-ZSM-5, it is less susceptible to causing hydrogenolysis and so is still considered a viable catalyst.

With gallium based catalysts and Ga-ZSM-5 known to be good catalysts for a variety of reaction pathways, including ones that normally rely on H-ZSM-5, interest lies in how the stability of the compound compares to that of the other zeolites in this study.

Research from the Han & Qiao (2009) paper on high-pressure cation exchange states that cations can diffuse into the zeolite network and can effectively deactivate framework defect sites. Hydrophobicity of the zeolite increases which can correspond to fewer protons being removed from the catalyst. If the catalyst is less prone to losing H+ ions then the water solution is less acidic which can result in less self-degradation. More research needs to be done on the effects of metal cation exchanged zeolites in the process of ethanol dehydration; specifically how the cation exchange affects the stability of the catalyst.
3. Methodology

This section of the report describes the experimental methods used to establish a fundamental understanding of the hydrothermal stability of multiple cation exchanged ZSM-5 catalyst samples in hot liquid water. The ZSM-5 zeolite underwent substitution to form Na-ZSM-5, Fe-ZSM-5 and Ga-ZSM-5 samples, which were run in a batch reactor and then characterized using Fourier Transform Infrared Spectroscopy, X-ray Diffraction, and a pH meter. Experiments were conducted to measure and evaluate how varying the cations in the ZSM-5 zeolite affects the crystallinity and its catalytic activity.

3.1 Batch Reaction

3.1.1 Reactor Components

The system used for batch experimental runs was called the Parr Reactor System, Model 452HC2. The reactor utilized has six major components to its structure. The first component is prongs that connect to a thermocouple; it has a process controller, which allows for temperature monitoring and the prevention of overheating. Figure 5 displays a temperature reading on the Parr Model indicating the desired temperature (300˚C), as well as the control temperature on the right (208˚C) and the actual temperature above the desired (208˚C). The control temperature slowly increases to the desired temperature to ensure safe heat up of the reactor.

![Temperature controller of the Parr Model](image)

The second component is a pressure gauge which ensures desired operating conditions were met. The reactor also has third component with an inlet line with a valve to allow nitrogen gas to flow from a tank into the system and pressurize the reactor. Two metal spouts on the reactor attach to plastic tubes as the fourth component; this allows for cooling water to flow through the system to prevent the internal mixer from overheating. A rupture disk is the fifth component which is utilized to prevent over pressurization of the system. The sixth and final component is a mixture
head attached to the top of the reactor which permits internal mixing. The system uses magnetic drive to allow internal mixing without rotating seals to avoid leaking and to ensure gas tight continuous runs (Magnetic Drives, 2017). Figure 6 below provides a front and rear view image of the components of the batch reactor system.

![Figure 6. Batch reactor labeled components a) front and b) rear view](image)

### 3.1.2 Start-up Procedure

Using a mass scale, 0.5 g of our calcined zeolite sample were measured and placed into the batch reactor cylinder. A beaker filled with 100 mL of distilled water was added to the zeolite sample. The batch reactor was then closed by screwing in six bolts in a star pattern to ensure a tight seal. The batch reactor was positioned into the experimental setup and a Teflon ring was placed on the top and right below the resting plate to minimize heat transferred to the plate. The reactor was connected to a wired pipe, which allowed the system to be pressurized by flowing nitrogen into it from a tank. The thermocouples were plugged into the prong, and the mixer head on the reactor was also secured and connected to the Parr Model. Cooling water tubes were also plugged into the reactor. An aluminum cylinder cut-out was fitted around the reactor in order to provide heat flow; the aluminum is conductive so heat travels well through it. A heating ring was placed on the outside of the aluminum and covered with a white fiber heat wrap to provide insulation and minimize the amount of heat loss to the surroundings.
After the reactor was completely set up, the valve connected to the pressure tank containing nitrogen, N\textsubscript{2}, was opened to a specified pressure of 1300 psi. The pressure valve connected to the reactor was opened to allow the 1300 psi of nitrogen into the system and then closed once the reactor reached the specified pressure. To check for any escaping gas, SNOOP was used; the solution begins to bubble if a leak is found. The reactor was observed for ten to fifteen minutes to ensure that pressure was held, before turning on the heater. The pressure was adjusted to 2900 psi once the reactor reached 300°C. All runs were held at this specified low temperature because prior research confirms that at 300°C H-ZSM-5 selectivity to ethylene was maximal (X. Zhang et al., 2008). The overall goal of this research is to utilize a catalyst that produces the highest yield possible of ethylene from ethanol so selecting 300°C for our reactor temperature optimizes the ZSM-5 catalyst for the process.

3.1.3 Shutdown

After the experiment was completed, the reactor was cooled down by preparing an ice bucket and unplugging the heater from the Parr Reactor system; the switch to the mixer was also turned off. Ice was added to the bin where the cooling water lines were connected to allow the internal reactor temperature to lower quicker. The insulation, along with the heating ring and aluminum cut out, was removed from the reactor using heat resistant gloves, and the reactor bottom was placed inside the ice bucket. After the temperature of the reactor dropped to below 100°C, the pressure valve was slowly opened to release pressure. Once completely depressurized, the Parr Reactor System was disabled. Following cooling, the reactor was opened and a small liquid vial of the sample was labeled and kept for pH testing; the remaining sample was placed into a crucible and dried in the oven for 24 hours at 60°C. The test sample was then placed into vials and labeled using the following identification method: vial number, type-temperature-test time-sample number/total number of samples after 24 hours of drying time. Upon removing all of the test sample, the reactor was cleaned with Alconox three times. All parts of the reactor were wiped down using a Kimwipe before putting the reactor away.

3.2 Catalyst Preparation

3.2.1 H-ZSM-5 Calcination

H-ZSM-5 was supplied by ACS Materials with 38 as the silica to alumina ratio. Using a mass scale, 5 g of the zeolite was measured in a crucible and placed into a low temperature oven for one hour at 100°C. This step in the calcination process removes any trace amounts of water from the sample to allow for easier access to the active sites. The zeolite sample was then removed and placed into a high temperature oven at 550°C overnight for approximately 16 hours. The second step in the calcination process removes any organic residue in the H-ZSM-5 sample (Abu Muti et al., 2016).
3.2.2 Sodium Ion Exchange

For our experimental runs using H-ZSM-5 substituted with sodium ions, the Na-ZSM-5 samples to be tested underwent a three time wash process. A mass of 10 grams of H-ZSM-5 was measured and added to a 1.0 M solution of sodium nitrate. This mixture was then heated to 50 °C and allowed to stir in a flask for 1 hour. Following this hour, the solution was strained using vacuum filtration, transferred to a crucible, and set to dry in a 60 °C oven for 24 hours. The process of placing the zeolite in a sodium wash was repeated twice for a total of three washes to remove any trace amounts of protons (H⁺). After each wash, a small sample of dried zeolite was tested using IR spectroscopy to confirm the decreasing appearance of peaks at 3600 cm⁻¹ which indicate the presence of H⁺ acid sites in the zeolites. The method used for the preparation of catalyst Na-ZSM-5 was taken from the sodium ion exchange detailed in “Quantitative analysis of IR spectra of carboxylic species in alkali–metal exchanged ZSM-5 and FER zeolites” (Bulánek & Koudelková, 2015).

3.2.3 Iron Ion Exchange

The Fe-ZSM-5 catalyst was prepared by carrying out an exchange process between H-ZSM-5 and the iron ion in ferric chloride (FeCl₃). First, 10 g of of H-ZSM-5 was measured and added to a beaker filled with 400 mL of deionized water. 0.2 M of FeCl₃ • 6 H₂O was added to the mixture which was then stirred and heated to 55 °C for a time frame of 24 hours. Figure 7 represents the set-up utilized for the mixing process. The mixture was filtered, washed with deionized water, and dried overnight in a 60 °C oven. IR spectroscopy was tested in order to confirm the ion exchange; the process of placing the zeolite in an iron wash was repeated two more time for a total of three to fully exchange the protons for iron ions. The method used for the preparation of catalyst Fe-ZSM-5 was taken from the iron ion exchange detailed in “Fe-ZSM-5 for selective catalytic reduction of NO with NH₃: a comparative study of different preparation techniques,” (Long & Yang, 2001).

![Figure 7. Set-up of the iron ion exchange](image)
3.2.4 Gallium Ion Exchange

The Ga-ZSM-5 zeolite was prepared by carrying out an exchange process between H-ZSM-5 and gallium nitrate. For each batch created, 10 g of zeolite was added to a 500 mL solution of 0.04 M GaNO₃. This mixture was then heated to 70 °C and stirred for 20 hours before being removed from heat and separated by vacuum filtration. The solid was then dried for a minimum of 24 hours in a 60 °C oven. IR spectroscopy was used to determine the success of the exchange. The process of placing the zeolite in a gallium wash was repeated once for a total of two exchanges. The procedure used in this experiment was based off of a gallium ion exchange detailed in “Production of Renewable Aromatic Compounds by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with Bifunctional Ga/ZSM-5 Catalysts.” (Cheng et al., 2011).

3.3 Analytical Tools

3.3.1 Infrared Spectroscopy

Fourier Transform Infrared (FT-IR) spectroscopy was used to investigate the functional groups on the treated zeolite samples. Infrared spectroscopy studies how molecules absorb infrared radiation and convert it to heat (Infrared Spectroscopy, 1997). Chemical bonds absorb varying intensities at varying frequencies, and the data collected is then analyzed in the form of a spectrum (Introduction to IR Spectra, 2000). Each molecule provides unique IR data, which can serve as a signature to identify the molecule. Additionally, the non-destructive quality of this instrument is another reason why this instrument plays a significant role in the analysis of treated zeolite samples (Infrared Spectroscopy: Introduction, N.d).

The FT-IR spectroscopy instrument that was utilized during this project was the Nicolet Magna IR 560 device 1-2. See Figure 8. The Nicolet Magna IR 560 device 1-2 held the test sample in a drift cell, which is a key component of the IR reader. The terms Fourier Transform Infrared, FT-IR and IR will be used interchangeably throughout this paper.

![Figure 8. Set-up of Fourier Transform Infrared spectroscopy](image-url)
Liquid nitrogen was first added to the FT-IR instrument to ensure pretreatment cooling of the detector; a minimum of twenty minutes was allotted before collecting spectra. The glass inserts from the drift cell were washed with acetone and dried using a Kimwipe prior to testing. The IR reader was also vacuumed to ensure any residual component that may have been left in the reader was removed. The dried test sample from the batch reactor was removed from the oven and crushed up using a spatula to form a fine powder. A portion of the test sample was then loaded into the IR reader and flattened at the top. A small piece of aluminum foil was cut and placed on top of the IR reader sample using a spatula and tweezers. The O-rings, glass inserts, and metal rings were placed back on the IR reader and fastened with M2 knot screws. The top of the IR reader was then closed. The IR instrument was plugged into a thermocouple, water pump, and nitrogen tank and the sliding plastic door was closed to enclose the system. The Nicolet Magna IR 560 device 1-2 was connected to the software program called OMNIC. The nitrogen valve was turned on, and the flowmeter was adjusted until it read 20 psig. Nitrogen is introduced to purge the system, which eliminates any carbon dioxide, CO\(_2\), present. Removing carbon dioxide is ideal, because the peaks can interfere with important functional groups and information from a specific sample that is needed for analyzing data. The water pump was turned on. OMNIC software was used to collect the background once the carbon dioxide peak was settled which takes approximately an hour.

Following background collection, the aluminum foil was removed from the top of the test sample to begin sample collection. The temperature was adjusted to the desired temperature of 500˚C, starting at 30˚C and building up incrementally. The purpose of this was to boil off any excess water or organic compounds to expose structure modes of the zeolite. Set time intervals were allotted between each specified temperature to allow for proper and safe heating as well as collection of IR sample information. Upon completion of data collection, the Nicolet Magna IR 560 device 1-2 was unplugged from the thermocouple, water pump, and nitrogen feed. The water pump was powered off. The nitrogen supply tank was shut off. The analyzed IR spectra includes both calcined and ion exchanged ZSM-5 zeolites hydrothermally treated at various time intervals, which can be found in the Results and Discussion portion of this report.

### 3.3.2 XRD

As the Background previously states, X-Ray powder diffraction (XRD) is an analytical tool that examines the relative crystallinity of ZSM-5. In this study XRD is used to detect any crystalline structural changes caused by hydrothermal treatment with the cation exchanged zeolites. The process of XRD is fairly simple requiring only three parts: an X-Ray tube, a sample holder and the X-Ray detector. For powdered XRD, X-Ray waves are generated in the cathode tube by heating a filament that creates electrons which then move toward a target with aid from applied voltage. The energized electrons then displace the inner shell electrons of copper atoms which produces X-Ray spectra. The X-Ray is then compiled and placed onto the sample holder where it is rotated with an angle, \( \Theta \), corresponding to the X-Ray. It is then rotated with twice the angle,
2θ, of the sample holder and the sample detector documents the X-Ray pattern. The pattern is then outputted to a computer for viewing and analyzing (Dutrow & Clark, 2016).

Figure 9 depicts the overall process of X-Ray powder diffraction from the web source matter.org.uk. To simplify the process even further, an incident beam passes through a crystalline structure sample (in our report, various cation exchanged ZSM-5 zeolite powders) and the X-Rays interfere with one another as they leave and a diffracted beam is captured on a film and is then recorded and analyzed (X-Ray Diffraction, n.d.).

![Figure 9. X-Ray Diffraction overview (Flowers et al., 2016)](image)

XRD is a nondestructive technique and its applications include identifying crystalline phases and orientations as well as determining structural properties (X-Ray Diffraction, n.d.). The equipment used for XRD in this research is a Rigaku instrument with a serial number GD2820. XRD is vital to our project as it currently is known to be the optimal method of indicating ZSM-5 stability under HTW conditions. It has the capability of identifying any decrystallization to the treated ZSM-5 sample in comparison to the control.

Due to the complexity of the XRD instrument and risk to personal safety, the team did not directly interact with the equipment.

In order to quantify the relative crystallinity from XRD results, Integrated Peak Area Method was used as seen in Figure 10. The software MDI Jade 6 used this method to add the area under the peaks between the angles 22.5° and 25.0° of the treated and untreated samples. The sum of the area under the peaks of the hydrothermally treated samples was then divided by the corresponding cation-exchanged untreated ZSM-5 peak area. The quotient of this yielded the relative crystallinity of the hydrothermally treated ZSM-5 sample.
3.3.3 pH Test

Following each of the Batch Reactor runs, a portion of the liquid sample was removed before the drying step to be placed in its own vial. These liquid samples were then tested with a pH meter to determine their acidity level. To determine pH measurements at zero hour, stock and exchanged zeolites were dissolved in water with a concentration of 0.005 g/mL which is equivalent to the original concentration of zeolite in the reactor.

To test the samples, the probe from the pH meter VWR Scientific Model 8000 shown in Figure 11, is removed from its storage buffer solution, rinsed with DI water into a waste jar and dried with a Kimwipe. After the probe is clean and dry, it is calibrated using both a pH 4 and a pH 7 buffer solution. The buffer solutions are prepared for each test by filling two beakers with 100 mL of DI water and adding a dissolvable capsule for the pH 4 or 7 solution in each beaker. The “Cal” button is pressed on the instrument and displays “4/7.” The pH 4 buffer solution is confirmed. Once the instrument is ready, the pH meter is cleaned and placed into the pH 7 buffer solution. These two buffer solutions are used for calibration since it is known and expected that the pH of the zeolite mixtures from the experimental runs will fall on the acidic side of the spectrum. Following confirmation of the second calibration, the pH probe is rinsed again with deionized water and the samples are ready to be tested.
3.4 Safety

Zeolite ZSM-5 is a white odorless powder, which can cause irritation to the skin, eyes or lungs if inhaled. Sodium nitrate, a white powdered solid, was used for the sodium cation exchange. This chemical is hazardous if ingested and may result in skin burns and ulcerations if it comes in contact with skin. For the iron cation exchange, ferric chloride was used as the source; it is an orange odorless solid that is very hazardous in the case of ingestion and corrosive to the eyes and skin. Ferric chloride can cause corneal damage or blindness. Gallium nitrate, a colorless solution, was used for the gallium cation exchange and can cause skin corrosion/irritation along with serious eye damage if it comes in contact. Please refer to the Material Safety Data Sheets of each chemical product in Appendix A for further information. Gloves along with safety glasses, closed-toed shoes and long pants were worn in order to ensure the use of personal protective equipment when handling these chemicals. Proper waste disposal was also implemented. Precautions were also taken when handling laboratory equipment. Safety shields were used during batch runs because the reactor was being run at a high pressure of 2900 psi. Heat resistant gloves were used when removing treated sample from high temperature ovens.
4. Results

This part of the report analyzes and discusses the data collected following the experimental procedures. This project began by investigating the effect of exchanging hydrogen atoms in the acid sites with sodium and comparing H-ZSM-5 to Na-ZSM-5 at various temperatures and time periods. After initial research and analysis, it was decided that focusing on one temperature would be most effective. The Zhang et al. (2008) paper determined that at 300°C selectivity to ethylene was maximal for ethanol dehydration with ZSM-5 as the catalyst. The overall goal of this study is to improve the ZSM-5 catalyst so that it can be used for the process of ethanol dehydration so it is logical to set operating conditions at 300°C for the batch reactor. After our team analyzed Na-ZSM-5 in HLW for various time frames, promising results led the team to question the specific effects that sodium had on the zeolite compared to other ions. Our team hypothesized that different cation exchanges could also affect the framework stability of the ZSM-5 zeolite catalyst. Our motivation for conducting more cation exchanges comes from a desire to test our hypothesis that the dissociation of hydrogen ions from acid sites in ZSM-5 in HLW causes dealumination to become more aggressive which thus adversely affects the zeolite framework.

Each cation-exchanged ZSM-5 catalyst sample was tested under HLW conditions at 300°C with various treatment times in a batch reactor. The ZSM-5 zeolite was subjected to sodium, iron, and gallium ion exchange to form Na-ZSM-5, Fe-ZSM-5, and Ga-ZSM-5 respectively. Various analytical tools were used to determine trends in hydrothermal stability and relative crystallinity including X-Ray Diffraction, Infrared Spectroscopy, and a pH meter.

4.1 X-Ray Diffraction

The X-Ray Diffraction instrument utilized in this project examined the crystallinity of the ZSM-5 zeolite and any changes that may have resulted from hydrothermal treatment. Figure 12 below shows Na-ZSM-5 samples ranging from 3 to 72 hours of hot liquid water (HLW) treatment at 300°C. As stated previously, 300°C was utilized as treatment temperature for all experimental runs for each cation (sodium, gallium and iron) due to its selective nature to ethylene (X. Zhang et al., 2008).

Figure 12 shows diffraction peaks for Na-ZSM-5 runs from 0-72 hour batch runs. Results from Figure 12 indicate little to no loss in crystallinity of Na-ZSM-5 subjected to various HLW water treatment time. Crystallinity can be measured by integrating from the angle 22.5° to 25.0° because this is the region that indicates crystallinity in ZSM-5 samples. The structure and area between the angles 22.5° and 25.0° remain almost identical to the untreated Na-ZSM-5; thus it can be inferred that the sodium-exchanged zeolite samples show no signs of degradation under HLW treatment.
Following extraction from the oven, a flaky residual material was discovered to be forming around the wall of the crucible; this material was found in all three cation exchanged zeolites. An image of the 18-hr Fe-ZSM-5 residue around the zeolite sample edges and the crucible wall is shown below in Figure 13 with flaky and dark orange characteristics.
Solubility tests were performed for the residual material taken from each sample by adding deionized water to each residue along with the heating of and mixing of each sample. Figure 14 shows samples from various treatment times and cation exchanges with solubility test results indicating that none of the residual material is water soluble.

Figure 14. Water solubility residue test (left to right): 3-hr Ga-ZSM-5, 18-hr Na-ZSM-5 and 6-hr Fe-ZSM-5

Figure 15 below compares the peaks of the 18-hour and 72-hour run for both residual and powdered samples. The low peak intensity of both the residue runs verify that the samples have low but some crystallinity due to zeolite mixing in with the residual material. The 18-hour and 72-hour Na-ZSM-5 show high crystallinity comparatively as peak intensity is amplified. This further supports the notion that the low intensity peaks were present on the residual samples as a result of zeolite mixing. The 3rd sodium ion exchange is on the graph as a control for comparison purposes and aligns well with both 18-hour and 72-hour Na-ZSM-5 peaks; this affirms the presence of high crystallinity, as well as supports that little to no degradation in the zeolite has occurred.
Furthermore, Figure 16 provides XRD data from the Ga-ZSM-5 samples at various treatment times. There is a clear decrease in peak intensity as the treatment time lengthened can be seen. Specifically, looking at the amplified peak intensity shown in the 3-hour run versus the low peak intensity in the 18-hour further emphasizes that treatment time has an influence on peak intensity. The untreated Ga-ZSM-5 sample is included to show the progression of decrystallization. Thus, longer exposure to hydrothermal water (HTW) conditions correlates to a loss in relative crystallinity and degradation of the zeolite catalyst.

Figure 15. Comparison of Na-ZSM-5 residual and powdered sample at various treatment times

Figure 16. Diffraction peaks of various treatment times for Ga-ZSM-5
Figure 17 shows the diffraction data for Fe-ZSM-5 following the cation exchange and batch runs. In this figure, the iron-exchanged zeolite samples also show decrystallization with increased treatment lengths. The transition from untreated to 3 hours in hot liquid water indicate some loss in crystallinity and degradation; the peak area between angles 22.5 and 25° decreases in this progression. The peak intensity lowers only minimally over the time frame of 15 hours. Therefore, treatment of this zeolite catalyst does indeed affect its crystallinity and stability.

![Figure 17](image_url)

**Figure 17.** Diffraction peaks of Fe-ZSM-5 sample under HTW conditions

Further analysis of the XRD data using the integrated peak area method provided more concrete, quantitative results of the treated samples’ relative crystallinity as shown in Figure 18 and 19. As detailed previously in section 3.3.2, by using Integrated Peak Area Method to compare treated to untreated samples, we are able to get a scale of degree of crystallinity where 0 is completely amorphous and 1 is completely crystalline based on comparison to the untreated samples. The relative crystallinity of each cation exchanged ZSM-5 sample was compared to the results from H-ZSM-5 sample runs of the previous MQP project’s research (Abu Muti et al., 2016). The data for H-ZSM-5 samples indicates that degradation occurs slowly overtime for the zeolite decreasing by 5% over a 12 hour timeframe. The H-ZSM-5 XRD data outlined in green corresponds to experiments done by our team. We expected to see a pattern following the previous group’s data, however, our data shows significantly higher crystallinity. This may be due to the presence of the residual material. When comparing relative crystallinity in this paper, the H-ZSM-5 runs taken from previous experimentation will be used. A discussion of the differences between new H-ZSM-5 data and results from previous experimentation will follow in the Discussion section. In contrast to the H-ZSM-5 data from last year’s project, the data
collected for Na-ZSM-5 do not appear to show the same apparent decreasing trend as H-ZSM-5. While some noise is present in the data, Na-ZSM-5 has maintained a relative level crystallinity around 1. Noise such as what is seen in the 18 hour run for Na could be due to inconsistent levels of residual material in the samples or could be due to instrumentation sensitivity. Overall, the degree of crystallinity for the sodium cation exchange shows promising results with minimal degradation.

The graph also shows that as treatment time increases, the degree of crystallinity for Ga-ZSM-5 samples decreases significantly more than H-ZSM-5. This relationship is the most evident of all three ion exchange samples as the 3-hour run shows a relative crystallinity of around 91% and the 18-hour run shows a significant decrease from that with around 45% relative crystallinity. The iron exchanged samples indicate an initial decrease in crystallinity followed by an increase after 6 hours of treatment and then another drop in crystallinity at the 18-hour run. Our team believes the reason for the high crystallinity in the 6-hour run, as compared to the 3-hour run, is likely due to some residual material being mixed in with the crystalline zeolite during the transfer of the 3-hour sample from the oven to the collection vial. This being the case, the degree of crystallinity of iron is expected to decrease with increasing treatment time. The 18-hour run confirms loss in crystallinity, and it is recommended that the Fe-ZSM-5, 3-hour batch run be repeated to validate this decreasing trend.

![Graph](image)

**Figure 18.** Degree of crystallinity as a function of time for all treated samples
Figure 19 includes all the crystallinity data for the residual materials as well as the data for the bulk samples from batch runs shown in Figure 18. All residues are significantly less crystalline than their zeolite counterparts which indicate that the sample is mostly in the form of amorphous material with a small amount of crystalline zeolite present.

4.1.1 Further XRD Investigation on 7-9° Peaks

To further investigate the stability of each cation exchanged zeolite, analysis of XRD was taken between the 7-9° peaks. The strong peaks around 7.94 and 8.9 provide fingerprints of the zeolite structure specifically the unit cell pore volume (Al-Dughaither & De Lasa, 2014). The area under these peaks corresponds to the aluminum in the framework of ZSM-5, so as the peaks decrease, the presence of aluminum in the zeolite framework decreases as well. It is observed that as treatment time increases, peak area decreases as seen above in Figure 20. Figure 20a shows the Na-ZSM-5 peaks, which show little to no indication of aluminum leaving the framework. Quantitative results founds in Appendix B indicate the area for the 72-hour run to equal less than 30% of the untreated Na-ZSM-5 area. The loss in area can potentially be due to dealumination. The iron-cation exchanged samples in Figure 20b show area diminishing in the 7-9° peak range for the 3-hour run. This may be due to the residual and crystalline material combination. All other sample runs have relatively the same intensity. The Ga-ZSM-5 samples in Figure 20c show diminishing peaks as treatment times progress and thereby support the notion that aluminum is being removed from the framework. Our team has proposed two hypothesizes for this aluminum
removal: the gallium ion is exchanging with the aluminum in the framework or the gallium ions are mixing into the solution instead of the zeolite pores. This exchange can provide some insight as to why the crystallinity in Figure 18 for gallium is drastically decreasing relative to the other cations. In order to determine if either hypothesis is correct, an acid site exchange back should be performed. XRD is a bulk crystallinity indicator technique, but it cannot tell you about specific chemistry, investigation the 7-9˚ can only provide an indicator for crystallinity, but more specific techniques are needed understand more about the changes occurring in samples, so infrared spectroscopy must also be used to achieve this end.

Figure 20. Diffraction peaks for a) Na-ZSM-5 b) Fe-ZSM-5 and c) Ga-ZSM-5 samples at 300˚C at various treatment times

4.2 Infrared Spectroscopy (IR)

Fourier Transform Infrared Spectroscopy is utilized to investigate the functional groups on the treated zeolite samples. Each molecule provides unique IR data, which can serve as a signature to identify the molecule. Infrared was first used to verify cation exchange within the pores of the zeolite catalyst. Cation exchanges were repeated until protons were replaced. These procedures can be found in section 3.2 of this report. Following this exchange, samples were tested at various treatment times and were once again examined using the FT-IR instrument. The data collected from IR was analyzed and compared to see how treatment time affected various functional groups in the ZSM-5 zeolite.

4.2.1 Na-ZSM-5

Before any experimental runs can be tested, it was important that Brønsted acid sites were exchanged with sodium ions. From research in the literature, H-ZSM-5 expresses hydroxyl stretching modes with IR peaks ca. 3590 cm⁻¹ and 3640 cm⁻¹ which are an indication of
Brønsted acid sites (BAS) (Ong, 2012). Eliminating the peaks for the Brønsted acid sites corresponds to hydrogens being exchanged with cations. Figure 21 shows the IR following the exchanging procedures with sodium. After each sodium exchange, it is clear that the BAS peak at 3590 cm\(^{-1}\) is decreasing. Based on the IR results, it was concluded that after the third wash, nearly all of these hydrogen ions were replaced and the sample was ready to undergo hydrothermal treatment. Figure 21 shows the comparison of the IR following the 1st, 2nd, and 3rd sodium ion exchanges including a 3-hr run. Figure 21 verifies that all protons were exchanged; little if any acid sites appear following this treatment.

![Figure 21. Comparison of sodium ion exchanges with 3-hr treated Na-ZSM-5](image)

Following validation of cation exchange, the Na-ZSM-5 samples were tested in a batch reactor with various treatment times and analyzing the results using IR. Figure 22 below depicts all Na-ZSM-5 runs at 300°C and compares it to both the calcined H-ZSM-5 and 12-hour treated H-ZSM-5 at 300°C samples. The peaks of interest in analyzing the IR data for sodium include peaks at 3735 cm\(^{-1}\), 3650 cm\(^{-1}\), and 3590 cm\(^{-1}\) which correspond to silanol groups, extra framework aluminum (EFAI) and Brønsted acid sites (Ong, 2012). Overall in the sodium samples there are minimal signs of a peak returning around 3600 cm\(^{-1}\) which is an indication of acid sites not returning to the catalyst; this is a good measure of stability because the sodium cations are not being dissociated into solution. Further verification can be seen in Figure 18 where Na-ZSM-5 samples have high degrees of crystallinity. One note to add is that there may be Brønsted acid sites present at 3590 cm\(^{-1}\) after 24 hours in the presence of hot liquid water. Other than this deviation, there is no significant change in IR spectra thus indicating that the zeolite did not structurally change after treatment. The slight return of the acid peak could occur by a mechanism in which the sodium detaches from the zeolite allowing any remaining hydrogens to reenter the acid site. In regards to EFAI, the only sample that shows any small
indication of this peak besides 12-hour H-ZSM-5 is the 72-hour treated sodium sample. Relative to H-ZSM-5, Na-ZSM-5 retains the aluminum in the framework, thus showing stronger stability.

Based on previous research, the silanol peaks that form at around 3740 cm\(^{-1}\) in Figure 22 are likely more prominent due less BAS so the peak can be seen easier. There is a lack of BAS to be exchange and EFAI formed so the most prominent peak is at 3740 cm\(^{-1}\). The silanol peaks were hidden in the samples rather than the notion of a large amount of them forming. The small band at 3740 cm\(^{-1}\) stems from either the residue or the surface material of the crystal. More generally, the peak emerges from limiting, non-acidic OH band (Weitkamp, 2000). This peak is prominent in the sodium samples and shows a trend as treatment time increases. The result of this peak accounts for the noise seen in Figure 18.

![Figure 22. IR of different treatment time Na-ZSM-5 samples at 300°C](image)

In further attempts to identify the presumable residual material, IR testing was done for the 24 and 72-hr Na-ZSM-5 run. Figures 23a and 23b show the IR peaks of this residue. As seen in Figure 23a, there is an indication that this residual solid contains crystalline zeolite due to the similarity in peaks. The IR combined with the XRD analysis, indicates evidence that another compound is present; however it is unidentifiable by IR above the 2000 cm\(^{-1}\) wavelength. Raman spectroscopy data has revealed that it is unlikely the compound could be sodium aluminate. IR peaks that can identify this compound exist below 1000 cm\(^{-1}\), and the equipment available does not provide the accuracy needed in this region to support this hypothesis. One important observation to make is that the residue in both samples does not appear to have a definitive peak at 3590 cm\(^{-1}\) indicating a lack of Brønsted acid sites. It does maintain a peak at 3650 cm\(^{-1}\), which supports the conclusion that this may be a mixture of zeolite and another material. Figure 23b contains a singular peak around 3740 cm\(^{-1}\) for the 72-hr treatment, which indicates the presence
of silanol groups. This could indicate that the residue is actually silica leaving the ZSM-5 framework. At first it was hypothesized that this solid may be silicic acid and therefore was soluble, however according to the solubility study discussed in section 4.1, no residual materials were soluble therefore this hypothesis was rejected.

![Figure 23. IR comparison of treated and residue peaks for a) 24-hr and b) 72-hr](image)

4.2.2 Fe-ZSM-5

The iron cation exchange was performed during this study for the same purpose as the sodium ion exchange: to investigate the plausibility of exchanging the hydrogen atoms located at the Brønsted acid sites and replacing them with iron ions. The procedure to execute this exchange was similar to the exchange method used in the Na-ZSM-5 exchange. The exact procedure can be found in section 3.2.

The ion exchange results in Figure 24 shows the IR following the first, seconds and third iron ion exchange and three hour treatment compared to H-ZSM-5. The Brønsted acid sites (BAS) peak at 3590 cm⁻¹ for Fe-ZSM-5 appears to be at a higher intensity than that of the peak associated with calcined H-ZSM-5. This peak remained the same for the first and second wash which is why a third exchange was performed. The third wash yielded results where almost all previously seen peaks flattened with a only one low intensity peak at the 3590 cm⁻¹ line. This dramatic change clearly shows that the iron ions are exchanging out the hydrogen ions; however, after 3 hours of treatment the BAS sites reappear, which indicates how unstable the iron is in the pores. This can be further confirmed by performing an acid site exchange back after three hours of
treatment and comparing IR results in order to see how easily it is to remove iron indicating its instability.

![Figure 24. IR for Fe-ZSM-5 ion exchanges](image)

The results from the iron samples that underwent various treatment times can be seen below in Figure 25. Peaks already begin to form after three hours around 3590 cm\(^{-1}\) and 3740 cm\(^{-1}\) indicating the presence of protons exchanging back into Brønsted acid sites (BAS) and silanol groups forming. Furthermore, for the 6-hour run, the BAS and silanol group peaks are more prominent, thus indicating that as treatment time increases, peak intensity grows. The silanol peak present, similar to Na-ZSM-5, is also potentially the product of residual material; it is feasible that silica is leaving the framework of the zeolite. A small peak can be seen around 3650 cm\(^{-1}\) which accounts for extra framework aluminum. Since the iron in the zeolite pores is unstable, the framework of the zeolite is more prone to protons exchanging back. With the proton exchange and HTW treatment, the zeolite begins to dealuminate by removing framework aluminum atoms and thus degrades losing framework stability. The Fe-ZSM-5 sample that undergoes 18 hours of treatment shows weak signals at both BAS and the silanol group peaks. This weak signal may be due to some degradation of the zeolite. To investigate these spectra further, additional IR can be seen in Figure 26. This figure shows the sequence of IR spectra at increasing temperatures up to 500°C. Lower heat-up temperatures (200-350°C) show two EFAI peaks along with silanol and BAS peaks. Our team believes that as the temperature reading progressed to 500°C, the peaks combined to show the degradation of the sample. Future analysis could be performed by increasing the temperature to 500°C and then lowering it again to see if the stretching modes return.
Figure 25. IR peaks of Fe-ZSM-5 at various treatment times

Figure 26. Peaks at various heat-up temperatures of the treated 18-hr Fe-ZSM-5 300°C batch run

4.2.3 Ga-ZSM-5

Ga-ZSM-5 is the final cation exchange completed for this study. The method of exchange is an aqueous based procedure similar to the ones used for Na-ZSM-5 and Ga-ZSM-5. This procedure can be found under Gallium Ion Exchange within section 3.2 of this report.
Comparing the IR of the cation exchanges below in Figure 27, it can be seen that the relative intensity of the peak due to the presence of Brønsted acid sites at 3590 cm$^{-1}$ decreased as more washes were carried out. The Ga-ZSM-5 zeolite was ready to be tested under HLW treatment following the second ion exchange.

![Figure 27. IR for Ga-ZSM-5 ion exchanges](image)

For the batch runs on Ga-ZSM-5, the IR results can be viewed below in Figure 28. It can be seen from the 3 and 6-hour batch runs, that the acid peak at 3590 cm$^{-1}$ remains prominent. It is most likely that these are due to the acids sites not having been fully exchanged at the beginning. One note to make is that it appears that the peak due to acid intensifies on the 6-hour run. It may be possible that the acid sites are returning to the sample. Another explanation could be that the acid sites are not retaining well, and were not well exchanged initially. The method used for exchanging could have been done one of three ways. The gallium ions could have replaced the hydrogens at the Brønsted acids sites, they could have replaced aluminum in the framework, or it could have been impregnated onto the surface of the zeolite. The Sanchez paper entitled “Characterization of gallium-containing zeolites for catalytic applications,” suggests that aqueous methods of exchanging gallium into H-ZSM-5 are not as effective as others, and that this approach leaves gallium ions on the external surface, and does not allow them to replace the Brønsted acid sites in the micropores (Garcia Sanchez, 2003).
Similar to what was addressed above for Na-ZSM-5, Ga-ZSM-5 samples show the same peak at 3740 cm\(^{-1}\). It is possible that this peak is also the product of residual material. While the peak is not present in the second wash, the peak is prominent in the 3, 6, and 18-hour sample. Another point of discussion is the presence and lack thereof of the EFAI peak in the Ga-ZSM-5 samples. Compared to the peak that can be clearly seen in the 12-hour H-ZSM-5 sample, the 3 and 6-hour do not show a prominent peak at 3650 cm\(^{-1}\). However, in the 18-hour sample, as the peak at 3590 cm\(^{-1}\) disappeared completely, a peak corresponding to the presence of EFAI is clearly visible.

![Figure 28: IR peaks for gallium samples of different treatment times](image)

**Figure 28.** IR peaks for gallium samples of different treatment times

### 4.3 pH

A pH meter was used in our research to show us how hydrothermal treatment affects the acidity of each sample. Figure 29 below shows the pH reading of each sample as it relates to treatment time.
The trials in which sodium was cation-exchanged have the highest pH and therefore, are the most basic. Previous MQP research states that the presences of ions in the solution result from the disassociation of acid sites in the zeolite (Abu Muti et al., 2016). This being true, Na-ZSM-5 samples at treatment times of 6, 18, and 72 hours show the least dissociation out of all of the trials and therefore, correspond to higher stability. The sodium-exchanged zeolite removed a good portion of the hydrogen ions. It could be argued that dealumination occurred during the 6-hour treatment, removing hydrogen sites with it. This could have resulted in the pH rising to almost 7. The increase in pH from 5 to a little less than 7 for Na-ZSM-5 stemmed from sodium consuming protons during the reaction. The pH of the H-ZSM-5 samples is consistently acidic around 3.5 regardless of treatment time. This indicates that a large portion of the protons from the zeolite are dissociating into the solution as hydrogen ions. These ions lower the pH thus making the solution more acidic.

The pH of the Fe-ZSM-5 samples is consistently around three excluding the 6-hour run. This low pH value corresponds to the dissociated protons in solution. From the IR data, we have concluded that iron in the acid sites is very unstable so it is logical that the pH decreases from zero treatment time to 3 hours. Our team has multiple speculations for the jump in pH from the 3-hour treatment to the 6-hour. Instrumentation error is a possibility, but is highly unlikely as the pH meter was calibrated after each use. It is, however, possible that dealumination occurred during the 6-hour treatment, removing hydrogen sites with it and thus yielding a rise to the pH. The IR data from Figure 25 supports this because the 3600 cm\(^{-1}\) peak increases in intensity from the 3 to the 6-hour treatment indicating hydrogen exchanging back into the acid sites. The sharp decrease in pH from 6 to 18-hour for iron may be due to the hydrogens from the framework
exchanging into the solution causing it to become more acidic. The dissociation of hydrogen results in liquid water attack of the zeolite thus leading to degradation. The IR spectra in Figure 25 supports this notion as the 18-hour Fe-ZSM-5 sample shows weak peak intensity indicating signs of structural collapse.

The Ga-ZSM-5 sample show a small initial increase in pH, which stems from protons being consumed. From the 3 to 6-hour treatment time, the pH of the gallium-exchanged zeolite decreases making the solution more acidic. Based upon XRD results in Figure 18, the degree of crystallinity, and therefore the framework stability of Ga-ZSM-5, worsens with treatment time; the increase in protons in solution causes degradation of the zeolite. From the 6-hour treatment to the 18-hour treatment, the acidity decreases, which may correspond to the EFAI forming as indicated in Figure 28. Similar to the Na-ZSM-5 samples, dealumination is occurring during the 18-hour treatment and is removing hydrogen sites with it, which results in a pH rising. Improved hydrothermal stability can correspond to a better, more durable catalyst for potential commercial use in the process of ethanol dehydration. A table showing the specific measurement of the pH of each sample can be found in Appendix C.
5. Discussion

The framework stability as well as the cation exchange mechanism are important parameters in the characterization of ZSM-5 as a catalyst for Ethanol Dehydration. As section 4.1 states, sodium-exchanged zeolite yielded nearly 100% crystallinity for all treatment times, thus indicating a stable framework. While both methods of instrumentation displayed some noise in the data, further research and experimentation has linked the noise to the residual material captured in Figure 13. The residue is likely silica leaving the framework. The IR data in Figures 4.9 and 4.10 show strong peaks at 3740 cm$^{-1}$ where the silanol groups are present on the external surface. The Zhang *et al.* (2015) paper states that silanol group defects are the main characteristics responsible for water susceptibility. Our team believes that since these silanol groups are simply removed from the zeolite surface and what remains is still crystalline, this alteration could lead to a change in activity.

The treated H-ZSM-5 samples we tested also showed retention of its crystallinity, and we believe this could also be due to the silica in on the surface of the zeolite. This report compares Na-ZSM-5, Fe-ZSM-5, and Ga-ZSM-5 to data collected from previous work done on H-ZSM-5 that determined the non-Arrhenius rate of degradation of this zeolite in HLW. However, our research was unable to reproduce this H-ZSM-5 data. The results found in this lab did not show this significant decrease in crystalline structure but instead discovered that after treatment, the H-ZSM-5 zeolite formed a residual material around the edges of the crucible. It is possible that the previous research had not accounted for this material, which would have likely changed their results. If this material were to have formed and both the zeolite and the residual material were mixed and ran in the XRD instrument, the crystalline structure would most likely decrease explaining the observed trend which is a possible explanation for the results in the previous MQP research. The data from this experiment can support the claim that the zeolite crystallinity does decrease, however it may not be as dramatic as previously indicated.

Furthermore, our IR data for all zeolite samples presented inconclusive results for the Brønsted acid sites, because it cannot be confirmed that the acid sites disappear completely. Zeolite framework and acid sites are both dependent upon the amount of ions in the solution, so pH testing provided a good indication on how treatment affects acidity. The pH for sodium-exchanged zeolite provided to be the most basic and therefore the most stable. This is because fewer ions were in the water, which can result in framework attack and cause degradation. Figure 30 below shows the mechanism by which we believe sodium is exchanging. The sodium is inserted via ion exchange which results in improved stability and maintenance of crystallinity.
For Fe-ZSM-5, we saw lower retention of crystallinity as the duration of batch runs increased. One cause for this could be due to the remaining presence of protons at the acid sites within the catalyst. Following the first two aqueous washes, IR data showed a large peak at 3590 cm\(^{-1}\) correlating to BAS showing that almost no exchange occurred, and even after the third wash a minor peak still remained. In addition to this, once the batch runs were made, it can be seen that as the length of batch runs increased, a larger and larger peak was shown at 3590 cm\(^{-1}\), indicating that the hydrogen ions that had been exchanged were returning. Hydrothermal treatment of the Fe-ZSM-5 samples leads to dealumination which corresponds to a higher susceptibility of hot liquid water attack. The low pH of the iron-exchanged catalyst indicates that more protons are in solution increasing the acidity. These results align with research discussed prior, mentioned in Section 2.4.2 of the Background that iron-exchanged zeolites tend to have poor hydrothermal stability compared to zeolites exchanged with alternative ions.

Most likely due to the presence of hydrogen ions in solution dissociating from retained acid sites and the possibility of gallium exchanging into the framework rather than the acid sites, Ga-ZSM-5 showed relatively fast degradation. If gallium was in fact in the framework instead of just in the acid sites, it could be greatly susceptible to attack by hydrogen ions, and an attack in that location would greatly destabilize the structure. Examining the XRD and IR results together, the 18 hour treatment for Ga-ZSM-5 sample appears to have resulted in loss of most structure. Leading up to this, we could see the progression to how this happened as gallium exchanged back with hydrogen ions according to the peaks seen in the 3 and 6 hour runs, as well as how the crystallinity dropped by a great percentage between both runs as well. It is definitive that the sample dealuminated completely and the structure was destroyed as there is no longer peak even indicating acid sites around the 3600 cm\(^{-1}\) line and the crystallinity dropped to below 50%. Dealumination of the sample from the 18 hour run corresponds to an increase in pH which is seen in Figure 29. The back-exchange most likely placed gallium in a more susceptible place to be attacked thus resulting in the emerging peaks around the EFAl line.

All three cation-exchanged zeolite samples, which were treated under the same temperature and treatment length, were compared against the calcined H-ZSM-5 control sample as shown in Figure 28. The IR peak at 3590 cm\(^{-1}\) is still apparent for all ion-exchanged zeolites except for

![Figure 30. Zeolite cation exchange mechanism with sodium nitrate wash example](image-url)
Na-ZSM-5. As stated earlier, the Na-ZSM-5 sample after three washes showed to have exchanged all its hydrogen ions and appeared to maintain this structure after treatment. Both Fe-ZSM-5 and Ga-ZSM-5, however, were not successful in completely exchanging all their acid sites making it difficult to compare across ions. Further washes, or different exchange methods could yield different results, but this cannot be confirmed without further experimentation. The inconsistency of the IR data for Fe-ZSM-5 indicated Fe-ZSM-5 lacks ion stability among the acid sites. Fe-ZSM-5 also showed little ion exchange compared to Na-ZSM-5. Once the exchanged Fe-ZSM-5 was tested in the batch reactor, it could be seen that over longer runs the acid sites returned, and the zeolite showed a downward trend in retention of crystallinity in contrast with the stability seen in Na-ZSM-5. Ga-ZSM-5 increases its intensity of the Brønsted acid sites with increasing treatment time indicating a lack of stability of the ion in these acid sites. Ga-ZSM-5 also showed little ion exchange compared to Na-ZSM-5. In sum, this data shows that of the three, Na-ZSM-5 is the most effective and easiest ion to exchange. Additionally, Na-ZSM-5 does not change its acid sites over time. However, this is a tradeoff, because the structure of the zeolite may be changing due to the presence of the residue which was assumed to be silica leaving the framework.

Overall, comparative analysis of all ions led to the following conclusions. Sodium is ion exchanged; therefore, it is expected that the data does not show signs of dissociation from the acid sites. Conversely, the results for Ga-ZSM-5 and Fe-ZSM-5 show that both exchanges are likely framework exchanges, as results show dissociation from the acid sites as well as a presence of hydrogen ions as indicated by BAS and EFAl peaks in Figure 31.

![Figure 31](image)

**Figure 31.** IR for a) 3-hr and b) 18-hr runs of all cation-exchanged samples
Additionally, activity of our zeolite samples was measured by a party outside of our project work using a continuous phase plug flow reactor setup. We explored the shift in activity for untreated H\(^+\), Na\(^+\), and Ga\(^+\) form ZSM-5 catalysts. A vapor phase reaction was performed by delivering pure ethanol at a rate of 1ml/min over a bed of 0.3 grams of zeolite sample at 375 °C. The ethylene product was quantitatively measured with online GC-FID using nitrogen as a carrier gas. The liquid product was analyzed ex-situ to verify mass balance closure ethanol conversion as well as any other reaction byproducts. Figure 32 shows the resulting yields using ethanol as a reactant for H-ZSM-5, Na-ZSM-5 and Ga-ZSM-5. Data for Fe-ZSM-5 was not obtained during a reaction run. The H-ZSM-5 zeolite shows highest conversion to ethylene, which is fitting because it is much more reactive than the ion exchanged zeolites due to its acid sites. Although the Na-ZSM-5 and Ga-ZSM-5 samples show lower yields, they still show some conversion activity. This is a positive result, because there is potential for the ion exchanged zeolites, especially the relatively stable Na-ZSM-5, for the process of green ethylene production in future studies; their composition can be changed to try and increase their yield for ethylene.

Figure 32. Catalytic activity for zeolite samples
6. Conclusion and Recommendations

Based on the analysis of our results, our team has utilized this section to conclude our findings and provide recommendations for future groups who chose to continue this study.

6.1 Conclusion

This study was able to compare Na-ZSM-5, Fe-ZSM-5, and Ga-ZSM-5 with H-ZSM-5 after being treated in hot liquid water. Using methods of IR, XRD, and pH analysis, the following key findings were made. Each cation-exchanged zeolite had different degradation and stability outcomes. Main takeaway points for each ion-exchanged zeolite are discussed below.

Sodium-exchanged zeolite, overall, showed to have a very stable framework with almost 100% crystallinity after being tested at various treatment times. However, IR results have shown ambiguous results for the Brønsted acid sites, thus it is inconclusive whether or not the acid sites disappeared completely. Results from pH testing indicate that Na-ZSM-5 samples dissociate the least out of all the sample type which correspond to lower acidity and higher stability of the framework. Furthermore, the residual material discovered during experimentation is believed to be silica leaving the framework. This is has not been verified, however; further testing should be done to identify what the residue is.

Fe-ZSM-5 expressed Brønsted acid sites (BAS) in its IR data leading to the suspicion that the protons most likely did not completely dissociate from the catalyst. This would contribute to the degradation seen to Fe-ZSM-5 over time, as the zeolite was able to be attacked by the protons that remained following the washes. Additionally, this destabilization process was most likely compounded by the protons that seemed to have been pulled out of solution and returned to the zeolite during the batch runs, as indicated by the IR data. The high acidity of the iron-exchanged zeolite samples from pH testing help to validate the idea that not all protons are dissociated from the catalyst initially; the low pH value shows that protons are still dissociating into solution even after the three cation exchange procedures.

Unlike Na-ZSM-5, data from the XRD experimentation for Ga-ZSM-5 displayed an unstable framework with significant loss in crystallinity. Possibilities for this are most likely due to the presence of dissociating hydrogen ions and gallium potentially could be performing framework substitution instead of exchanging into the acid sites. However, this needs to be confirmed with further experimentation. Ga-ZSM-5 also showed the presence of Brønsted acid sites. Thus, the protons also may not have completely detached or the acid sites may be returning back to the sample. Initially pH tests gave low values which correspond to the dissociation of acid sites in the zeolite and support the rapid loss in relative crystallinity. However after 18-hr of treatment, the pH rise is most likely due to the formation of extra framework aluminum outside the zeolite crystal. This independent alumina phase assists with removing hydrogen sites which gives rise to pH.
Final conclusions based on a cohesive analysis of all the cation-exchange zeolites are as follows. Sodium proved to be the most valuable and easiest ion to be exchanged of the three. Analysis showed sodium to be an ion exchange as there were no signs of dissociation from the acid sites. Meanwhile, both Fe-ZSM-5 and Ga-ZSM-5 appeared to most likely be framework exchanges. Both yielded results that displayed dissociation from the acid sites and the presence of hydrogen ions. Finally, the most stable of all was sodium-exchanged zeolite as the other two ions showed apparent degradation.

6.2 Recommendations
From an overall analysis, due to time constraints, our team was unable to test more cations to form a more complete study of cation exchanges. The more cation exchanges studied can provide a better insight into the best ion exchange to use as far as stability is concerned. We propose teams research other ions first in order to determine the best ions to further experiment with. Furthermore, our team recommends that the activity of the various cations be studied using the Ethanol Dehydration mechanism for the purpose of testing reactivity and ethylene yield.

Closer investigation of different cation exchanges led the team to make several suggestions for future teams who wish to continue this study. For each cation-exchanged zeolite we tested, we recommend testing the various treated samples at different temperatures for the purpose of further understanding the effects of crystallinity and degradation. Our team advises that future teams test Na-ZSM-5 at higher temperatures as based on MQP experimentation, higher temperatures have shown higher crystallinity. At this time, more experimentation should be done on both Ga-ZSM-5 and Fe-ZSM-5 in general. More washes for the exchange for both ions are recommended as they may yield more promising results like Na-ZSM-5 did after three washes. Additionally, we propose examining alternative methods of exchange for Ga-ZSM-5, such as using chemical vapor deposition of trimethyl gallium, as recommended in a study by Garcia Sanchez (2003). We also propose performing the iron ion exchange using iron nitrate instead of iron chloride as the method we used to exchange the iron did not yield promising results. Additionally, more research should be conducted to determine if the tests for different treatment temperatures of Ga-ZSM-5 and Fe-ZSM-5 should be higher or lower than 300°C. Even though past research indicates high conversion of ethanol using H-ZSM-5 and HLW occurs at 300 °C, this temperature may not be optimum for the gallium and iron zeolites. Along with treatment temperature, our team proposes that longer treatment times should also be taken into consideration when furthering this study. Longer treatment times will help to confirm or negate degradation. Specifically, based on Ga-ZSM-5 results, we would like to verify that degradation is correlated with longer treatment times. However, due to time restraints, we were unable to; thus, we propose testing Ga-ZSM-5 samples at 24-hour and 72-hour treatment lengths. Finally, based on the inconclusive IR results, our team also proposes future teams to perform the acid site exchange back in order to verify the type of exchange that occurred.
References


Appendices

Appendix A. Material Safety Data Sheets

**APPENDIX A: MATERIAL SAFETY DATA SHEET**

**Trade Name:** CBV2314  
**Product Description:** ZEOLITE AMMONIUM ZSM-5 POWDER  
**Manufacturer:** Zeolyst International  
**P. O. Box 830**  
**Valley Forge, PA 19482 USA**  
**Telephone:** 610-651-4200  
**In Case of Emergency Call:** 610-651-4200  
**For Transportation Emergency:** 800-424-9300

---

1. **CHEMICAL PRODUCT AND COMPANY IDENTIFICATION**

- **Product Name:** CBV2314  
- **Product Description:** ZEOLITE AMMONIUM ZSM-5 POWDER  
- **Manufacturer:** Zeolyst International  
  **P. O. Box 830**  
  **Valley Forge, PA 19482 USA**  
- **Telephone:** 610-651-4200  
- **In Case of Emergency Call:** 610-651-4200  
- **For Transportation Emergency:** 800-424-9300

---

2. **COMPOSITION/INFORMATION ON INGREDIENTS**

<table>
<thead>
<tr>
<th>Chemical and Common Name</th>
<th>CAS Registry Number</th>
<th>Wt. %</th>
<th>OSHA PEL</th>
<th>ACGIH TLV</th>
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<td>Zeolite</td>
<td>1318-02-1</td>
<td>100%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**OSHA PEL:**
- 15 mg/m³ total dust
- 5 mg/m³ respirable

**ACGIH TLV:**
- 10 mg/m³
- 3 mg/m³ respirable

(Particulates Not Otherwise Regulated)

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3. **HAZARDS IDENTIFICATION**

**Emergency Overview:** White, odorless, powder. Causes respiratory irritation. Causes mild eye irritation. May cause skin irritation. Ammonia released on contact with strong bases. Noncombustible. Ammonia or nitrogen oxides may be released at high temperatures.

**Eye contact:** Causes mild eye irritation.

**Skin contact:** Prolonged or repeated contact may dry skin and cause irritation.

**Inhalation:** Causes irritation.

**Ingestion:** No known hazards. Inedible.

**Chronic hazards:** No known hazards.

**Physical hazards:** Absorbs water from air and fluids. Generates heat when it absorbs water.

---

4. **FIRST AID MEASURES**

**Eye:** In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Get medical attention if irritation persists.

**Skin:** In case of contact, immediately flush skin with plenty of water. Remove contaminated clothing and shoes. Get medical attention if irritation develops.
and persists. Wash clothing before reuse. Thoroughly clean shoes before reuse.

**Inhalation:**
Remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

**Ingestion:**
Not applicable.

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### 5. FIRE FIGHTING MEASURES

**Flammable limits:**
This material is noncombustible.

**Extinguishing Media:**
This material is compatible with all extinguishing media.

**Hazards to fire-fighters:**
Ammonia or nitrogen oxides may be released at high temperatures.

**Fire-fighting equipment:**
The following protective equipment for fire fighters is recommended when this material is present in the area of a fire: self-contained breathing apparatus (SCBA), chemical goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots.

---

### 6. ACCIDENTAL RELEASE MEASURES

**Personal protection:**
Wear safety goggles, body-covering protective clothing, chemical resistant gloves, and rubber boots, NIOSH-approved dust respirator where dust occurs. See section 8.

**Environmental Hazards:**
Sink in water. No know environmental hazards.

**Small spill cleanup:**
Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.

**Large spill cleanup:**
Keep unnecessary people away; isolate hazard area and deny entry. Do not touch or walk through spilled material. Carefully shovel or sweep up spilled material and place in suitable container. Avoid generating dust. Use appropriate Personal Protective Equipment (PPE). See section 8.

**CERCLA RQ:**
There is no CERCLA Reportable Quantity for this material. If a spill goes off site, notification of state and local authorities is recommended.

---

### 7. HANDLING AND STORAGE

**Handling:**
Avoid contact with eyes, skin and clothing. Avoid breathing dust. Keep container closed. Promptly clean up spills. Wash thoroughly after handling.

**Storage:**
Keep containers closed. Store separated from strong bases in original containers or clean metal, plastic, or fiber containers.
8. EXPOSURE CONTROLS/PERSONAL PROTECTION

Engineering controls: Use with adequate ventilation. Safety shower and eyewash fountain should be within direct access.
Respiratory protection: Use a NIOSH-approved dust respirator where dust occurs. Observe OSHA regulations for respirator use (29 C.F.R. §1910.134)
Skin protection: Wear body-covering protective clothing and gloves.
Eye protection: Wear safety goggles.

9. PHYSICAL AND CHEMICAL PROPERTIES

Appearance: White powder.
Odor: Odorless.
\( \text{pH} \): Not applicable.
Specific Gravity: >1.
Solubility in water: Negligible.

10. STABILITY AND REACTIVITY

Stability: This material is stable.
Conditions to avoid: None.
Materials to avoid: Ammonia may be released on contact with strong bases.
Hazardous decomposition products: Ammonia, nitrogen oxides.

11. TOXICOLOGICAL INFORMATION

Acute Data: When tested for primary irritation potential, similar materials caused mild eye irritation and were slightly irritating or non-irritating to the skin. Human experience with similar materials indicates that prolonged or repeated contact may dry skin and cause irritation. This material has not been tested for acute inhalation toxicity. It contains fine particles which can cause respiratory irritation. The acute oral toxicity of this material has not been tested. There are currently no reports of human toxicity for ingested zeolite.
Subchronic Data: This material has not been tested for subchronic toxicity potential.
Special Studies: This material has not been tested for chronic inhalation toxicity. Zeolite Beta is not listed by NTP, IARC, or OSHA as a carcinogen.
12. ECOLOGICAL INFORMATION

Eco toxicity:
This material has not been tested for ecotoxicity potential. There are no known reports of adverse environmental effects.

Environmental Fate:
Does not bioconcentrate in animals.

Physical/Chemical:
Sinks in water.

13. DISPOSAL CONSIDERATIONS

Classification:
This material is not RCRA Hazardous waste.

Disposal Method:
Dispose in accordance with federal, state and local regulations.

14. TRANSPORT INFORMATION

DOT UN Status:
This material is not regulated hazardous material for transportation.

15. REGULATORY INFORMATION

CERCLA:
See section 6.

SARA TITLE III:
This material is not a listed Toxic Chemical subject to the reporting requirements of SARA Title III §313 and 40 C.F.R. Part 372. Hazard Categories under SARA Title III §§311/312: Acute.

TSCA:
All ingredients of this material are listed on the TSCA inventory.

16. OTHER INFORMATION

Prepared by:
John G. Blumberg

Supersedes revision of:
10/29/03

THE INFORMATION ON THIS SAFETY DATA SHEET IS BELIEVED TO BE ACCURATE AND IT IS THE BEST INFORMATION AVAILABLE TO ZEOLYST INTERNATIONAL. THIS DOCUMENT IS INTENDED ONLY AS A GUIDE TO THE APPROPRIATE PRECAUTIONS FOR HANDLING A CHEMICAL BY A PERSON TRAINED IN CHEMICAL HANDLING. ZEOLYST INTERNATIONAL MAKES NO WARRANTY OF MERCHANTABILITY OR ANY OTHER WARRANTY, EXPRESS OR IMPLIED WITH RESPECT TO SUCH INFORMATION OR THE PRODUCT TO WHICH IT RELATES, AND WE ASSUME NO LIABILITY RESULTING FROM THE USE OR HANDLING OF THE PRODUCT TO WHICH THIS SAFETY DATA SHEET RELATES. USERS AND HANDLERS OF THIS PRODUCT SHOULD MAKE THEIR OWN INVESTIGATIONS TO DETERMINE THE SUITABILITY OF THE INFORMATION PROVIDED HEREIN FOR THEIR OWN PURPOSES.
Material Safety Data Sheet
Sodium nitrate MSDS

Section 1: Chemical Product and Company Identification

Product Name: Sodium nitrate
Catalog Codes: SLS1102, SLS3946, SLS1726
CAS#: 7631-99-4
RTECS: WC5600000
TSCA: TSCA 8(b) inventory: Sodium nitrate
Cl#: Not available.
Synonym: Chile salt peter; soda niter; Sodium salt peter;
Nitric acid, sodium salt; Nitrinate
Chemical Name: Sodium Nitrate
Chemical Formula: NaNO3
Contact Information:
Sciencelab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396
US Sales: 1-800-901-7247
International Sales: 1-281-441-4400
Order Online: ScienceLab.com
CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300
International CHEMTREC, call: 1-703-527-3887
For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

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<tr>
<th>Name</th>
<th>CAS #</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sodium nitrate</td>
<td>7631-99-4</td>
<td>100</td>
</tr>
</tbody>
</table>

Toxicological Data on Ingredients: Sodium nitrate: ORAL (LD50): Acute: 1267 mg/Kg [Rat]. 2680 mg/Kg [Rabbit].

Section 3: Hazards Identification

Potential Acute Health Effects:
Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Prolonged exposure may result in skin burns and ulcerations. Over-exposure by inhalation may cause respiratory irritation.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance may be toxic to blood. Repeated or prolonged exposure to the substance can produce target organs damage.

Section 4: First Aid Measures

Eye Contact:
Check for and remove any contact lenses. In case of contact, immediately flush eyes with plenty of water for at least 15 minutes. Cold water may be used. Get medical attention if irritation occurs.

Skin Contact:
Wash with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used.

Serious Skin Contact: Not available.

Inhalation:
If inhaled, remove to fresh air. If not breathing, give artificial respiration. If breathing is difficult, give oxygen. Get medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek medical attention.

Ingestion:
Do NOT induce vomiting unless directed to do so by medical personnel. Never give anything by mouth to an unconscious person. If large quantities of this material are swallowed, call a physician immediately. Loosen tight clothing such as a collar, tie, belt or waistband.

Serious Ingestion: Not available.

---

**Section 5: Fire and Explosion Data**

- **Flammability of the Product**: Non-flammable.
- **Auto-Ignition Temperature**: Not applicable.
- **Flash Points**: Not applicable.
- **Flammable Limits**: Not applicable.
- **Products of Combustion**: Not available.
- **Fire Hazards in Presence of Various Substances**: organic materials, combustible materials
- **Fire Fighting Media and Instructions**: Not applicable.

**Special Remarks on Fire Hazards**:
It may accelerate burning when involved in a fire. Increases the flammability of any combustible material. May ignite combustibles (wood, paper, clothing, etc.). Flames up when heated to 540 deg. C. Mixture with charcoal ignites on heating. Contact with combustible or organic materials may cause fire.

**Special Remarks on Explosion Hazards**:
It will react explosively with hydrocarbons. Interaction of nitrates when heated with amidoxides (sulfamates) may become explosively violent owing to liberation of dinitrogen oxide and steam. Mixtures of sodium nitrate with powdered aluminum or its oxide were reported to be explosive. Mixtures of sodium nitrate and barium thiocyanate may explode. Mixture with sodium nitrate and powdered antimony explode. Mixture of sodium nitrate and sodium thiosulfate or sodium phosphinate explode.

---

**Section 6: Accidental Release Measures**

**Small Spill**: Use appropriate tools to put the spilled solid in a convenient waste disposal container.

**Large Spill**: Oxidizing material. Stop leak if without risk. Avoid contact with a combustible material (wood, paper, oil, clothing...). Keep substance damp using water spray. Do not touch spilled material. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal.
Section 7: Handling and Storage

Precautions:
Keep away from heat. Keep away from sources of ignition. Keep away from combustible material. Do not ingest. Do not breathe dust. Wear suitable protective clothing. If ingested, seek medical advice immediately and show the container or the label. Keep away from incompatibles such as reducing agents, combustible materials, organic materials, acids.

Storage:

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection: Safety glasses. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Dust respirator. Boots. Gloves. A self contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits: Not available.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid. (Granular solid. Powdered solid.)
Odor: Not available.
Molecular Weight: 84.99 g/mole
Color: White.
pH (1% soln/water): Not available.
Boiling Point: Decomposition temperature: 380°C (716°F)
Melting Point: 308°C (586.4°F)
Critical Temperature: Not available.
Specific Gravity: Density: 2.26 (Water = 1)
Vapor Pressure: Not applicable.
Vapor Density: Not available.
Volvatility: Not available.
Odor Threshold: Not available.
Water/Oil Dist. Coeff.: Not available.
Ionocity (in Water): Not available.
Dispersion Properties: See solubility in water, methanol.
Solubility:
Easily soluble in hot water. Soluble in cold water. Partially soluble in methanol. Very slightly soluble in acetone. Very slightly soluble in glycerol. Very soluble in liquid Ammonia. Solubility in water: 92.1g/100 ml @ 25 deg. C.; 180 g/100 ml @ 100 deg. C. Solubility in Methanol: 1 g dissolves in 300 ml Methanol 1 gram dissolves in 125 ml Alcohol, 52 ml boiling Alcohol, 3470 ml absolute Alcohol.

Section 10: Stability and Reactivity Data

Stability: The product is stable.
Instability Temperature: Not available.
Conditions of Instability: Incompatible materials
Incompatibility with various substances: Highly reactive with combustible materials, organic materials. Reactive with reducing agents, acids.
Corrosivity: Non-corrosive in presence of glass.
Special Remarks on Reactivity: Fibrous organic material is oxidized in contact with sodium nitrate above 160 deg. C and will ignite below 220 C. Wood and similar cellulosic materials are rendered highly combustible by nitrate impregnation. Reacts with acids to emit toxic fumes of nitrogen dioxide. Also incompatible with boron phosphide, barium rhodanide, cyanides, sodium thiosulfate, hypophosphites such as sodium hypophosphate, sulfur plus charcoal, antimony, chlorides, aluminum and stannous chloride, esters, powdered metals such as zinc or aluminum or aluminum oxide, isothiocyanates, thiocyanates, phosphorus, organic materials, combustible materials, acids, pyrosulfites, sulfides, amides, bisulfites, hydrazine, ammonium sulfate, amides, amines, phospham. Sodium nitrate + amines may for nitroasamines which have been proven to be carcinogenic in animal tests.
Special Remarks on Corrosivity: Not available.
Polymerization: Will not occur.

Section 11: Toxicological Information

Routes of Entry: Inhalation. Ingestion.
Toxicity to Animals: Acute oral toxicity (LD50): 1267 mg/kg [Rat].
Chronic Effects on Humans:
MUTAGENIC EFFECTS: Mutagenic for bacteria and/or yeast. May cause damage to the following organs: blood.
Other Toxic Effects on Humans:
Hazardous in case of ingestion. Slightly hazardous in case of skin contact (irritant), of inhalation.
Special Remarks on Toxicity to Animals: Not available.
Special Remarks on Chronic Effects on Humans:
May affect genetic material (mutagenic). May cause adverse reproductive effects based on animal test data. May cause cancer based on animal test data.
Special Remarks on other Toxic Effects on Humans:
Acute Potential Health Effects: Skin: Causes skin irritation with redness, itching, and pain Eyes: Causes eye irritation with redness, itching, and pain. Inhalation: Causes respiratory tract and mucous membrane irritation. Symptoms may include coughing, shortness of breath. Ingestion: May be harmful if swallowed. Clinical signs associated with nitrate poisoning include: Gastroenteritis, abdominal pain, nausea, vomiting, diarrhea, metabolic acidosis, muscular weakness, dizziness, fatigue, headache, mental impairment, incoordination, convulsions, accelerated heart rate, orthostatic hypotension, dyspnea, and in severe cases, methemoglobinemia due to inadequate oxygenation of the blood leading to progressive cyanosis, and coma. Cyanosis is first visible as a bluish discoloration of the mucous membranes and unpigmented areas of the body. Purging and diuresis can be expected. Rare cases of nitrates being converted into more toxic nitrates.

Section 12: Ecological Information
Ecotoxicity: Not available.
BOD5 and COD: Not available.
Products of Biodegradation:
Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.
Toxicity of the Products of Biodegradation: The products of degradation are less toxic than the product itself.
Special Remarks on the Products of Biodegradation: Not available.

Section 13: Disposal Considerations

Waste Disposal:
Waste must be disposed of in accordance with federal, state and local environmental control regulations.

Section 14: Transport Information

DOT Classification: CLASS 5.1: Oxidizing material.
Identification: Sodium nitrate UNNA: 1498 PG: III
Special Provisions for Transport: Marine Pollutant

Section 15: Other Regulatory Information

Federal and State Regulations:
Connecticut hazardous material survey.: Sodium nitrate Rhode Island RTK hazardous substances: Sodium nitrate Pennsylvania RTK: Sodium nitrate Massachusetts RTK: Sodium nitrate New Jersey: Sodium nitrate TSCA 8(b) inventory: Sodium nitrate

Other Regulations:

Other Classifications:
WHMIS (Canada):
CLASS C: Oxidizing material. CLASS D-2B: Material causing other toxic effects (TOXIC).

DSCC (EEC):
R8- Contact with combustible material may cause fire. R22- Harmful if swallowed. S17- Keep away from combustible material. S36- Wear suitable protective clothing.

HMIS (U.S.A.):
Health Hazard: 2
Fire Hazard: 0
Reactivity: 0
Personal Protection: E

National Fire Protection Association (U.S.A.):
Health: 2
Flammability: 0
Reactivity: 0
Specific hazard:
Protective Equipment:
Gloves. Lab coat. Dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Safety glasses.

Section 16: Other Information

References: Not available.
Other Special Considerations: Not available.
Created: 10/10/2005 08:27 PM
Last Updated: 05/21/2013 12:00 PM

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Material Safety Data Sheet
Ferric chloride MSDS

Section 1: Chemical Product and Company Identification

Product Name: Ferric chloride
Catalog Codes: SLF1675, SLF2188
CAS#: 7705-08-0
RTECS: L79100000
TSCA: TSCA 8(b) inventory: Ferric chloride
Cl#: Not available.
Synonym:
Chemical Formula: FeCl3

Contact Information:
Scielab.com, Inc.
14025 Smith Rd.
Houston, Texas 77396
US Sales: 1-800-901-7247
International Sales: 1-281-441-4400
Order Online: Scielab.com
CHEMTREC (24HR Emergency Telephone), call:
1-800-424-9300
International CHEMTREC, call: 1-703-527-3887
For non-emergency assistance, call: 1-281-441-4400

Section 2: Composition and Information on Ingredients

Composition:

<table>
<thead>
<tr>
<th>Name</th>
<th>CAS #</th>
<th>% by Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferric chloride</td>
<td>7705-08-0</td>
<td>100</td>
</tr>
</tbody>
</table>

Toxicological Data on Ingredients: Ferric chloride: ORAL (LD50): Acute: 900 mg/kg [Rat]. 1278 mg/kg [Mouse].

Section 3: Hazards Identification

Potential Acute Health Effects:
Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of eye contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator). Corrosive to eyes and skin. The amount of tissue damage depends on length of contact. Eye contact can result in corneal damage or blindness. Skin contact can produce inflammation and blistering. Inhalation of dust will produce irritation to gastro-intestinal or respiratory tract, characterized by burning, sneezing and coughing. Severe over-exposure can produce lung damage, choking, unconsciousness or death.

Potential Chronic Health Effects:
CARCINOGENIC EFFECTS: Not available. MUTAGENIC EFFECTS: Not available. TERATOGENIC EFFECTS: Not available. DEVELOPMENTAL TOXICITY: Not available. The substance is toxic to lungs, mucous membranes. Repeated or prolonged exposure to the substance can produce target organs damage. Repeated exposure of the eyes to a low level of dust can produce eye irritation. Repeated skin exposure can produce local skin destruction, or dermatitis. Repeated inhalation of dust can produce varying degree of respiratory irritation or lung damage.

Section 4: First Aid Measures
Eye Contact:
Check for and remove any contact lenses. Immediately flush eyes with running water for at least 15 minutes, keeping eyelids open. Cold water may be used. Do not use an eye ointment. Seek medical attention.

Skin Contact:
If the chemical got onto the clothed portion of the body, remove the contaminated clothes as quickly as possible, protecting your own hands and body. Place the victim under a deluge shower. If the chemical got on the victim's exposed skin, such as the hands: Gently and thoroughly wash the contaminated skin with running water and non-abrasive soap. Be particularly careful to clean folds, crevices, creases and groin. Cold water may be used. If irritation persists, seek medical attention. Wash contaminated clothing before reusing.

Serious Skin Contact:
Wash with a disinfectant soap and cover the contaminated skin with an anti-bacterial cream. Seek immediate medical attention.

Inhalation: Allow the victim to rest in a well ventilated area. Seek immediate medical attention.

Serious Inhalation:
Evacuate the victim to a safe area as soon as possible. Loosen tight clothing such as a collar, tie, belt or waistband. If breathing is difficult, administer oxygen. If the victim is not breathing, perform mouth-to-mouth resuscitation. WARNING: It may be hazardous to the person providing aid to give mouth-to-mouth resuscitation when the inhaled material is toxic, infectious or corrosive. Seek immediate medical attention.

Ingestion:
Do not induce vomiting. Examine the lips and mouth to ascertain whether the tissues are damaged, a possible indication that the toxic material was ingested; the absence of such signs, however, is not conclusive. Loosen tight clothing such as a collar, tie, belt or waistband. If the victim is not breathing, perform mouth-to-mouth resuscitation. Seek immediate medical attention.

Serious Ingestion: Not available.

Section 5: Fire and Explosion Data

Flammability of the Product: Non-flammable.
Auto-Ignition Temperature: Not applicable.
Flash Points: Not applicable.
Flammable Limits: Not applicable.
Products of Combustion: Not available.

Fire Hazards in Presence of Various Substances: Not applicable.

Explosion Hazards in Presence of Various Substances:
Risks of explosion of the product in presence of mechanical impact: Not available. Risks of explosion of the product in presence of static discharge: Not available.

Fire Fighting Media and Instructions: Not applicable.
Special Remarks on Fire Hazards: Not available.
Special Remarks on Explosion Hazards: Not available.

Section 6: Accidental Release Measures

Small Spill:
Use appropriate tools to put the spilled solid in a convenient waste disposal container. If necessary: Neutralize the residue with a dilute solution of sodium carbonate.

Large Spill:
Corrosive solid. Stop leak if without risk. Do not get water inside container. Do not touch spilled material. Use water spray to reduce vapors. Prevent entry into sewers, basements or confined areas; dike if needed. Call for assistance on disposal.
Neutralize the residue with a dilute solution of sodium carbonate. Be careful that the product is not present at a concentration level above TLV. Check TLV on the MSDS and with local authorities.

Section 7: Handling and Storage

Precautions:
Keep locked up. Keep container dry. Keep away from heat. Keep away from sources of ignition. Keep away from direct sunlight or strong incandescent light. Do not ingest. Do not breathe dust. Never add water to this product. Avoid shock and friction. Wear suitable protective clothing in case of insufficient ventilation, wear suitable respiratory equipment if ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes.

Storage: Corrosive materials should be stored in a separate safety storage cabinet or room.

Section 8: Exposure Controls/Personal Protection

Engineering Controls:
Use process enclosures, local exhaust ventilation, or other engineering controls to keep airborne levels below recommended exposure limits. If user operations generate dust, fume or mist, use ventilation to keep exposure to airborne contaminants below the exposure limit.

Personal Protection:
Splash goggles. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Gloves.

Personal Protection in Case of a Large Spill:
Splash goggles. Full suit. Vapor and dust respirator. Boots. Gloves. A self-contained breathing apparatus should be used to avoid inhalation of the product. Suggested protective clothing might not be sufficient; consult a specialist BEFORE handling this product.

Exposure Limits:
TWA: 1 CEIL: 2 (mg/m3) Consult local authorities for acceptable exposure limits.

Section 9: Physical and Chemical Properties

Physical state and appearance: Solid.
Odor: Not available.
Taste: Not available.
Molecular Weight: 162.21 g/mole
Color: Not available.

pH (1% soln/water): 2 [Acidic]
Boiling Point: 316°C (600.8°F)
Melting Point: 308°C (582.8°F)
Critical Temperature: Not available.
Specific Gravity: 2.9 (Water = 1)
Vapor Pressure: Not applicable.
Vapor Density: 5.61 (Air = 1)
Vapor Pressure: Not available.
Odor Threshold: Not available.
Water/Oil Dist.Coeff.: Not available.
Ionicity (in Water): Not available.
Dispersion Properties: See solubility in water.
Solubility: Soluble in cold water.

### Section 10: Stability and Reactivity Data

Stability: The product is stable.
Instability Temperature: Not available.
Conditions of Instability: Not available.
Incompatibility with various substances:
The product may undergo hazardous decomposition, condensation or polymerization, it may react violently with water to emit toxic gases or it may become self-reactive under conditions of shock or increase in temperature or pressure.
Corrosivity: Non-corrosive in presence of glass.
Special Remarks on Reactivity: Not available.
Special Remarks on Corrosivity: Not available.
Polymerization: No.

### Section 11: Toxicological Information

Routes of Entry: Eye contact. Inhalation. Ingestion.
Toxicity to Animals: Acute oral toxicity (LD50): 900 mg/kg [Rat].
Chronic Effects on Humans: The substance is toxic to lungs, mucous membranes.
Other Toxic Effects on Humans:
- Very hazardous in case of ingestion. Hazardous in case of skin contact (irritant), of inhalation. Slightly hazardous in case of skin contact (permeator).
Special Remarks on Toxicity to Animals: Not available.
Special Remarks on Chronic Effects on Humans: Not available.
Special Remarks on other Toxic Effects on Humans: Not available.

### Section 12: Ecological Information

Ecotoxicity: Not available.
BOD5 and COD: Not available.
Products of Biodegradation:
- Possibly hazardous short term degradation products are not likely. However, long term degradation products may arise.
Toxicity of the Products of Biodegradation: The products of degradation are more toxic.
Special Remarks on the Products of Biodegradation: Not available.

### Section 13: Disposal Considerations

Waste Disposal:
Section 14: Transport Information

DOT Classification: CLASS 8: Corrosive solid.
Identification: : Ferric chloride, anhydrous : UN1773 PG: III
Special Provisions for Transport: Not available.

Section 15: Other Regulatory Information

Federal and State Regulations:
Pennsylvania RTK: Ferric chloride Massachusetts RTK: Ferric chloride TSCA 8(b) inventory: Ferric chloride CERCLA: Hazardous substances.: Ferric chloride
Other Classifications:
WHMIS (Canada):
CLASS E: Corrosive solid. CLASS F: Dangerously reactive material.
DSCL (EEC): R36/38- Irritating to eyes and skin.
HMIS (U.S.A.):
  Health Hazard: 3
  Fire Hazard: 0
  Reactivity: 2
  Personal Protection: j
National Fire Protection Association (U.S.A.):
  Health: 3
  Flammability: 0
  Reactivity: 2
  Specific hazard:
Protective Equipment:
Gloves. Synthetic apron. Vapor and dust respirator. Be sure to use an approved/certified respirator or equivalent. Wear appropriate respirator when ventilation is inadequate. Splash goggles.

Section 16: Other Information

References: Not available.
Other Special Considerations: Not available.
Created: 10/09/2005 05:32 PM
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MATERIAL SAFETY DATA SHEET

Recapture Metals, Inc.
High Purity Gallium
1877 E. Harris Lane (102-7)
Blanding, Utah 84511
(435) 678-2734  FAX: (435) 678-3276

42% Gallium Nitrate Solution
Revision Date: November 23, 2005
Emergency Phone: CHEMTREC- (800) 424-9300

SECTION 1 - IDENTIFICATION

Substance: 42% Gallium Nitrate Solution
Trade Names/Synonyms: 42% Gallium Nitrate Mineral Water, Gallium (III) Nitrate; Nitric Acid, Gallium (III) Salt; Gallium (III) Nitrate (1:3); Nitric Acid, Gallium (3+) Salt; OH510300
Chemical Family: Metal Salt
Molecular Formula: Ga(NO₃)₃
Molecular Weight: 255.75
CAS#: 13494-90-1
NFPA Rating (scale 0-4):
Health = 1, Fire = 0, Reactivity = 0

SECTION 2 - INGREDIENTS

<table>
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<tr>
<th>Chemical</th>
<th>CAS#</th>
<th>% w/v</th>
<th>PEL</th>
<th>TLV</th>
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<tbody>
<tr>
<td>Gallium Nitrate</td>
<td>13494-90-1</td>
<td>42</td>
<td>Not established</td>
<td>Not established</td>
</tr>
<tr>
<td>Water</td>
<td>58</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
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</table>
(11.5% w/v equivalent Gallium concentration)

SECTION 3 - PHYSICAL DATA

<table>
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<tr>
<th>Description</th>
<th>Specific Gravity (H₂O = 1): 1.3</th>
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<tbody>
<tr>
<td>Boiling Point</td>
<td>110 °C, decomposes</td>
</tr>
<tr>
<td>Melting Point</td>
<td>No data</td>
</tr>
<tr>
<td>% Volatiles (by wt.): 58</td>
<td>Vapor Density (air = 1): No data</td>
</tr>
<tr>
<td>Solubility in Water: Very soluble</td>
<td>Vapor Pressure: No data</td>
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<tr>
<td></td>
<td>pH: 1</td>
</tr>
</tbody>
</table>

SECTION 4 - FIRE AND EXPLOSION HAZARD DATA

<table>
<thead>
<tr>
<th>Flash Point</th>
<th>Flammable Limits in Air, % by volume: Lower: No data; Upper: No data</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auto Ignition Temperature: None known</td>
<td></td>
</tr>
<tr>
<td>Extinguishing Media: Highly concentrated (&gt;60%) or solid gallium nitrate is a strong oxidizer whose heat of reaction with reducing agents or combustibles may cause ignition. Use water, carbon dioxide, dry chemical extinguishing agents, dry sand, or ground dolomite. Special Fire Fighting Procedures: No special fire fighting procedures needed. Use normal procedures, which include wearing NIOSH/MSHA approved self-contained breathing apparatus, flame and chemical resistant clothing: hats, boots, and gloves. If without risk, remove material from fire area. Cool container with water from maximum distance.</td>
<td></td>
</tr>
</tbody>
</table>

SECTION 5 - HEALTH DATA

OSHA (PEL): None  ACGIH (TLV): None

A. ANIMAL TOXICITY Half of the mice ingesting 4360 mg/kg died, with symptoms of paralysis, somnolence, and changes in their food intake.

B. EFFECTS OF EXPOSURE

ACUTE EFFECTS - Ingestion: Large amounts of concentrated nitrates taken by mouth may have serious or even fatal results. The symptoms are dizziness, abdominal cramps, vomiting, a metallic taste, itching, bone marrow depression leading to anemia, bloody diarrhea, blood damage with subsequent renal damage, weakness, convulsions, and collapse. May damage the mouth and gastrointestinal tract.

Skin and Mouth Contact: Gallium nitrate solution is readily absorbed through the skin. May cause skin irritation (itching and/or stinging), drying, and skin exfoliation, and will cause painful mouth irritation.

Eye Contact: Will cause painful irritation of the cornea and the conjunctivae.

Inhalation: Fumes from solid gallium nitrate will cause irritation of mucus membranes and respiratory passages.

Medical Conditions Aggravated by the Chemical: None known
Appendix B. Quantitative value tables for 7-9.5° XRD peaks

**Ga-ZSM-5**

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Area</th>
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<tr>
<td>0</td>
<td>36520</td>
</tr>
<tr>
<td>3</td>
<td>25579</td>
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<tr>
<td>6</td>
<td>23039</td>
</tr>
<tr>
<td>12</td>
<td>18626</td>
</tr>
<tr>
<td>18</td>
<td>13712</td>
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**Fe-ZSM-5**

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<thead>
<tr>
<th>Treatment Time</th>
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<tbody>
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<td>0</td>
<td>20393</td>
</tr>
<tr>
<td>3</td>
<td>16521</td>
</tr>
<tr>
<td>6</td>
<td>14969</td>
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</table>

**Na-ZSM-5**

<table>
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<th>Area</th>
</tr>
</thead>
<tbody>
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<td>0</td>
<td>32462</td>
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<tr>
<td>3</td>
<td>26905</td>
</tr>
<tr>
<td>6</td>
<td>26719</td>
</tr>
<tr>
<td>18</td>
<td>31508</td>
</tr>
<tr>
<td>24</td>
<td>29245</td>
</tr>
<tr>
<td>72</td>
<td>9178</td>
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</table>
### H-ZSM-5

<table>
<thead>
<tr>
<th>Treatment Time</th>
<th>Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>39345</td>
</tr>
<tr>
<td>3</td>
<td>38984</td>
</tr>
<tr>
<td>18</td>
<td>29568</td>
</tr>
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</table>
Appendix C: Quantitative pH results

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<thead>
<tr>
<th>Sample, Treatment Time</th>
<th>pH</th>
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<tbody>
<tr>
<td>H-ZSM-5, 0-hr</td>
<td>3.70</td>
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<td>H-ZSM-5, 3-hr</td>
<td>3.34</td>
</tr>
<tr>
<td>H-ZSM-5, 18-hr</td>
<td>3.63</td>
</tr>
<tr>
<td>Na-ZSM-5, 0-hr</td>
<td>4.93</td>
</tr>
<tr>
<td>Na-ZSM-5, 6-hr</td>
<td>6.71</td>
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<tr>
<td>Na-ZSM-5, 18-hr</td>
<td>6.46</td>
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<tr>
<td>Na-ZSM-5, 72-hr</td>
<td>5.97</td>
</tr>
<tr>
<td>Ga-ZSM-5, 0-hr</td>
<td>3.60</td>
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<td>Ga-ZSM-5, 3-hr</td>
<td>3.85</td>
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<td>Ga-ZSM-5, 6-hr</td>
<td>3.60</td>
</tr>
<tr>
<td>Ga-ZSM-5, 18-hr</td>
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<td>Fe-ZSM-5, 0-hr</td>
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<td>Fe-ZSM-5, 3-hr</td>
<td>2.96</td>
</tr>
<tr>
<td>Fe-ZSM-5, 6 hr</td>
<td>4.01</td>
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<tr>
<td>Fe-ZSM-5, 18 hr</td>
<td>2.96</td>
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