Low Temperature Template Removal of Fe-ZSM-5

Major Qualifying Project completed in partial fulfillment
Of the Bachelor of Science Degree at
Worcester Polytechnic Institute, Worcester, MA

Submitted by:

Nathaniel Peterson
David Sun
Adam Thibault

Professors Robert Thompson and John MacDonald, Faculty Advisors

March 12th, 2013

Acknowledgements

We would like to thank our advisors, Professor Robert W. Thompson and Professor John C. MacDonald for their help and guidance along the course of our project. We would also like to thank Professor Fred Greenaway from Clark University for his assistance with Electron Paramagnetic Resonance, Professor Boquan Li for taking SEM photos for us, Giacomo “Jack” Ferraro for his help in running our experiments, Doug White for training us to use X-ray Diffraction, and Professor Destin Heilman for providing us with a UV source.

Abstract

Our project recognized the inefficiencies of current industry standards and investigated new, more effective ways to remove the organic backbone from Fe-ZSM-5 near room temperature. One step towards the inclusion of Fe-ZSM-5 in industrial processes is mass production. Large corporations are concerned about energy consumption taxing their process monetarily, and currently, the conventional method is to burn off the template at 600°C. Oxidation techniques were proposed to remove the template from within the zeolite, specifically ultra-violet radiation in the presence of peroxide and ozone treatment. The experiments illustrated that neither of these techniques, at the prescribed conditions, were adequate to remove the template from the Fe-ZSM-5 framework.

Contents

Table of Figures

Background

A Brief History

Alex Fredrik Cronstedt, a Swedish scientist, is credited with first publishing information about zeolites in his work "*An Essay towards a System of Mineralogy"* in 1758. In this article, he described zeolites as "minerals which either occur naturally or can be synthesized in the laboratory with many of them having no known natural counterparts". The word zeolite comes from the Greek words '*zein'* (to boil) and '*lithos'* (rock) after he noticed that heating these zeolites produced a steam product. Despite Cronstedt's interest and the unknown nature of these zeolites, they ended up going unstudied for the better part of 200 years after their discovery. Cronstedt would never know that he had really discovered a uniquely selective molecular sieve that would be used widely throughout the petroleum and water treatment industries (Masters et al 2011).

In 1925, Weigel and Steinhof reintroduced the zeolite by showing the "molecular sieve effect" which demonstrated that after the water was removed from the zeolite's pores, the crystals could be used to separate gas molecules by molecule size. Undergoing no chemical reaction, these zeolite crystals were then able to separate materials at the molecular level, and could be of great use if used on an industrial scale. This profound conclusion sparked interest among many other scientists, and interest in zeolites was rekindled (Masters & Maschmeyer 2011) .

In 1948, Richard Maling Barrer attempted to construct the naturally occurring zeolites chabazite and modernite in a laboratory. Other scientists had been able to recreate naturally occurring zeolites in the laboratory before, however, this time Barrer came across something unique. He reacted the materials known to form these zeolites, but this time with barium and potassium salts at high temperature. What Barrer found was a material that had the same molecular sieve properties as zeolites, but with no naturally occurring counterpart. This synthesis breakthrough paved the way for scientists to create aluminosilicate sieves in the laboratory that possessed controllable selectivity, and further enhanced their utility and commercial applications (Masters & Maschmeyer 2011) .

Applications

Scientists have discovered many uses for zeolites since their discovery. A lot of these applications have been towards water treatment and zeolites are good alternatives to reverse osmosis and waste water treatment.

Fe-ZSM-5 has been experimented with in many practical applications across many disciplines. Environmentalists have investigated the use of zeolites in removing NO_x from the air with the largest contributor being the burning of fossil fuels. Studies have shown that the use Fe-ZSM-5 reduced the amount of NO_x in the exhaust of fossil fuels by 90%. This discovery is useful because of its relatively low temperature (350-500K) and high conversion rate (Qi et al).

Fe-ZSM-5 has also been used as a pretreatment in wastewater. Fenton's advanced oxidation can be used to soften the load of organics on the rest of the processes in the treatment plant and reduce the amount of harmful byproducts that exit the plant untreated. At 30°C, Fenton's oxidation was effective at removing harmful organics from the water (Guedes et al 2003). This provides a great source of a powerful oxidant with little to no risk of harmful byproducts, and low start-up/maintenance costs.

Hydrogen peroxide is a powerful oxidation tool when dealing with the removal of organic compounds. In light or dark reactions, the peroxide acts as both an oxidant for the organic and a regenerative compound for the iron. In the specific case of phenol compounds, quinone acts as a transport for hydroxyl radicals to phenol sites for degradation. Additionally, quinone decreases the waiting time between reactions, speeding the kinetics and enhancing the conversion. Quinone is preserved in this transportation, and acts as a catalyst for the reactions occurring within the framework of the zeolite (Chen et al).

Fenton's oxidation

In recent years, Fenton's oxidation has been studied as a method for purifying liquid solutions containing harmful organics. This process generates hydroxyl radicals from the degradation of hydrogen peroxide, and regenerates these radicals using iron as a catalyst. These radicals are extremely effective in mineralizing organic matter, and in most cases, rendering them harmless.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO\bullet + HO^- \qquad (1)$$

Equation 1 above shows the initiation of hydroxyl radicals using iron as the catalyst. This reaction begins many initiation reactions between organics. Hydroperoxyl radicals can also be formed according to the mechanisms below (equations 2 and 3):

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \qquad (2)$$

$$HO\cdot + H_2O_2 \rightarrow HO_2\cdot + H^+ \qquad (3)$$

Radical reactions initiated by these produced hydroxyl and hydroperoxyl radicals will non-selectively oxidize organics present in the water. These reactions are advantageous because they can be carried out at a reasonable temperature, pressure and in an efficient amount of time. This makes this oxidation practical for water treatment facilities. Furthermore, the lack of selectivity ensures that all organic molecules are reacted with and removed (Melián-Cabrera, Kapteijn, & Moulijn 2005) .

Crystallization

Zeolite synthesis occurs via crystallization, but is significantly more complicated than ionic crystallization. Silica can be formed into a variety of different shapes and sizes all with different pore sizes and framework structures. The structure is often directed by an organic template, and by changing this template the crystal structure can be altered (Bell and Chang 1991).

There are two major phases in the crystal growth process. The first step is nucleation, and during this step, the reactant gel is formed into building blocks of the zeolites. The initial gel is broken up by hydroxide ions to create aluminate and silicate ions. These, in turn, create aluminosilicate and polysilicate species. These species remain in equilibrium during the nucleation process. During the next step, these species form and reform around the organic ions. One of the theories behind the kinetics of this reaction is called hydrophobic solvation. The proposed mechanism is that the organic structuring agent orders the water molecules around it creating negative entropy. This negative entropy acts as the driving force for the nucleation. The water molecules are slowly replaced by the silica polymers and this creates the nuclei (Beelen et al 1997) (Cundy and Cox 2005). During nucleation, OH^- ions play an important role in removing impurities. The OH^- ions break the silica and aluminum bonds (Si-O-Si, Si-O-Al) even after the nucleation starts so bonds that form incorrectly can be broken and reformed correctly (Chao et al 1980).

The second step in the process is crystal growth. During this step the nuclei and solution species combine, break apart, and recombine, again facilitated by the hydroxide ions, until they obtain the final crystal structure. One of the theories behind the mechanism of this reaction is that the cations bind to the structure and draw the silica species around them using the entropy mechanism proposed for the previous step. This reaction creates another active site that a new cation can bind to repeat the cycle. The nuclei can also come together and bond with the solution with free silica species (Cundy and Cox 2005).

Specifically for the ZSM-5 structure the silica species react to create the MFI framework pieces around the TPA^+ ions as shown in Figure 1. The individual species then combine with other species and unreacted nuclei to form the ZSM-5 crystals as shown in Figure 2.

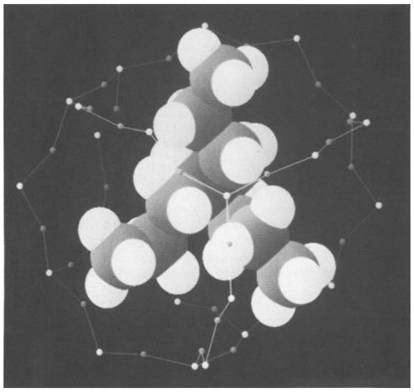


Figure 1. Zeolite growing into MFI framework around backbone (Image adapted from Chang and Bell 1991)

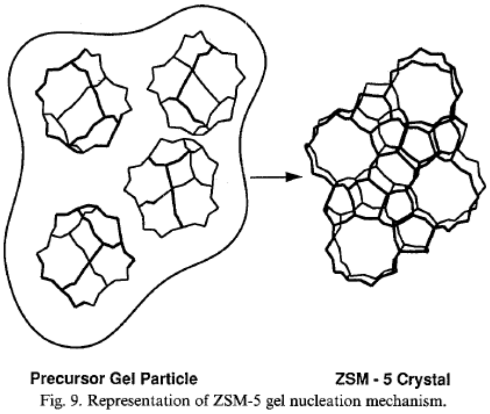


Figure 2. Zeolite crystals conglomerating out of gel. (Image adapted from Chang and Bell 1991)

Many different factors affect the size of the final crystals, the speed of crystallization, and the amount of product formed. One of the main controlling factors is the pH, specifically the concentration of OH^- ions. These ions break the silicon bonds and allow the mixture to reform and reset which is imperative to the synthesis. The more ions present in the early stages, the faster the reaction proceeds, allowing the silica species to form the base units needed. However, the OH^- ions will also pull desired bonds apart which will slow the overall nucleation step so a balance must be maintained. On the other hand, once the nucleation has reached its critical limit, the OH^- concentration seems to have little effect on the speed of crystallization. In addition, experimental evidence shows that lowering the pH also decreases the size of the crystals, the size of the pores, and the surface area (Larson et al 2010) (Cundy and Cox 2005).

Another factor that plays a role in the synthesis is aging of the silica gel. The two phases of the synthesis, nucleation and crystal growth, can be better divided by changing the temperature that the different steps operate at. One of the most common techniques is to have the nucleation occur at room temperature. The longer the solution sits, the more product produced but also the smaller the crystal size. However, aging at lower temperature also tends to give a higher yield. Finally in certain cases, if a high purity zeolite structure is desired, a high aging temperature, over 200°C, can lead to a higher quality product.

Another method studied in aiding the in the crystallization of zeolites is the use of seed crystals. The idea behind this method is that by adding the seed crystals, there will be more surface area for the reactants to bind to. This should accelerate the process as the nuclei can bond to the crystals as soon as they form rather than waiting until enough nuclei have formed to come together and make a bigger crystal. If the ions in solution do in fact act bond to seed crystals, it is best to have many small seed crystals, as they will provide the most surface area on which the silica can bind. In addition, the seed crystals may act as better partials for the silica to bind to than the nuclei that the reaction creates, because the template-free crystals have more available surface area than the nuclei (Cundy and Cox 2005) (Gora et al 1997).

Spectroscopy

After the synthesis of our zeolites we must characterize our final product. There are several methods that are typically used to analyze zeolite crystals which include x-ray powder diffraction (XRD), energy-dispersive x-ray spectroscopy (EDX) and thermogravimetric analysis (TGA). The issue with most of these characterization techniques is that they do not reveal the oxidation states of the atoms. This is important because the iron in the structure has to be in the 3+ state in order to act as a catalyst in Fenton's Oxidation. Thus, we need to use other imaging techniques such as Mössbauer spectroscopy and electron spin resonance (ESR) to characterize our product.

X-ray Powder Diffraction

XRD takes into consideration how x-ray wavelengths interact with crystalline solids. The x-rays are generated and filtered towards the sample and the resulting diffraction pattern is collected and analyzed. Peaks will be observed at the angles that satisfy Bragg's Law ($n\lambda=2d \sin \theta$), which relates the wavelength to the diffraction angle and the spacing within the crystal lattice. These graphs can then be compared to references to determine if they are the same.

Energy-Dispersive X-ray

Another method in determining whether or not our product contains iron is EDX, which is an elemental analysis tool. Because each element has a unique atomic structure, each will have its own x-ray spectrum. In EDX, a high-energy beam is directed at the sample in question which causes an electron to be ejected from the inner shell. An electron from a higher energy level will then replace the ejected electron and the energy loss associated with this shift is measured. Since each element has specific difference between their electron shells, the elemental composition of the sample can be determined by the energy released (Corbari et al 2008).

Thermogravimetric Analysis

TGA measures change in weight in relation to temperature. Essentially, the sample is heated until the components decompose and turn into gas lowering the total weight. Because we are not using the typical method of calcining the final zeolite product, TGA will help us determine if the organic backbone of tetrapropylammonium bromide (TPABr) has been removed successfully. The typical method is the calcine the final Fe-ZSM-5 product at 550°C to remove the TPABr and after using a different treatment, we can test if there is still a weight loss around 550°C signifying the presence of TPABr.

Electron Spin Resonance

ESR spectroscopy is based off the similar physical properties as NMR, but NMR focuses on the atomic nuclei whereas ESR focuses on electron spin. Because of this, ESR is limited to studying paramagnetic species and each unpaired electron will give off a unique signal. In our case, we are interested in two particular species: Fe^{2+} and Fe^{3+}. Fe^{2+} is paramagnetic so it can be analyzed with ESR, but Fe^{3+} is diamagnetic so it cannot be analyzed via ESR. To that end, if we run an ESR on our sample, we will either receive a spectrum or we will not.

Case Studies

Template Removal

As previously shown, calcination to remove the template of Fe-ZSM-5, has the potential to cause iron leaching. Alternative methods of ozone treatment to remove the template have been analyzed for zeolite membranes and macro-porous crystal powders as they have a tendency to crack during calcination (Heng et al 2004). The template could be removed from ZSM-5 membrane pores using an ozone flow rate of approximately 50 g/m^3 and heating between 150°C and 200°C. A treatment time of 2 hours was needed to remove templates that are 2 micrometers thick; the time of heating increases as the template thickness increases. Using ozone to remove the catalyst from mesoporous zeolites was also studied (Kiricsi et al 2000), and the templates could be removed without damaging the more delicate mesoporous structure. Again, temperatures between 150°C and 200°C were used; however, some of the mesoporous crystals required a longer reaction time to remove the template, up to 6 h.

Leaching

One major issue with Fe-ZSM-5 is the stability of the iron in the structure. The iron is usually incorporated into the structure at first, but after being used as a catalyst in Fenton’s oxidation, the zeolite is often regenerated with peroxide treatment. The typical method to regenerate the zeolite is the remove the organic that has been adsorbed. This entails using hydrogen peroxide followed sometimes by calcination at 500°C. Though the amount of iron that leached after one cycle has a negligible effect on its catalytic activity, over time the iron leaching out into solution will render the catalyst ineffective (Centi et al 2000). One issue to note is that the synthesis procedure tested in the iron leaching experiments was different than the synthesis we used. The samples in the papers dealing with iron leaching were made by ion exchange in solution rather than crystallization. Whether or not this will affect the leaching iron has yet to be determined.

Catalytic Activity

Water and wastewater treatment processes are gaining more attention in communities within the United States and worldwide. The desire to mass produce drinking water is only increasing as years pass and natural resources for this water are becoming scarcer. Fe-ZSM-5 has been shown to aid in catalytic degradation of organic material in water through Fenton’s oxidation. The heterogeneous presence of iron within the zeolite crystal has been shown to reduce the total organic carbon (TOC) within a wastewater solution at much greater rates in the presence of hydrogen peroxide than its homogeneous counterpart (Perathoner & Centi 2005). This discovery has led to further exploration of zeolite properties with respect to water remediation and Fenton’s oxidation.

One case study looked into the effect of pumping peroxide through a Fe-ZSM-5 packed bed to remove TOC from wastewater through Fenton’s oxidation. The zeolites could be used with great efficiency to remove TOC from the solution and under certain circumstances the zeolite crystals could be reused. By adding iron solutions into the column, less leaching occurs and the catalyst activity coefficient is retained longer. Furthermore, as the presence of oxalic acid, a byproduct of hydrogen peroxide oxidation of aromatic compounds, accumulated into the system, the leached iron molecules also increased (Perathoner & Centi 2005).

The reaction rate of the method used was tested, which included pumping hydrogen peroxide at a rate of 115% required for total oxidation with air at 70°C with varying proportions of excess oxygen and other oxidants. The method involving hydrogen peroxide as specified produced the best reaction rate, and required 15 minutes to reach the minimum TOC obtainable in the solution. (Perathoner & Centi 2005). Smaller organic molecules, such as acetic acid and ethanol, required different conditions to fully oxidize, and were left unreacted in solution. These findings support the potential of Fe-ZSM-5 being used as a catalyst for Fenton’s oxidation to remove harmful organics from wastewater in a pretreatment scenario requiring further treatment before release into the environment. This process could be used in an industrial setting to pretreat service water and wastewaters from the process.

Hartmann et al. studied the effect of incorporation of iron by various techniques into the zeolite crystal and compared them with iron salts as a catalyst for Fenton’s oxidation. Iron salts have a higher rate of reaction, but accordingly form more harmful byproducts. Iron incorporated into the zeolite by any means exhibits a lower reaction rate, and more specific conditions (pH, temperature, etc.) to prevent formation of harmful oxidation byproducts. Additionally, the iron is noted to leach out of the system and form harmful iron complexes that are difficult to remove. Of all methods of iron incorporation, the method of introducing the iron into the initial synthesis and replacing silica or aluminum in the framework results in the least amount of leaching from the system (Hartmann, Kullmann, & Keller 2010).

The group next looked at the effect of Fenton's oxidation on a known carcinogen, in this case phenol, and studied the effect of temperature and pH on the reaction rate using Fe-ZSM-5 as a catalyst. They found that a pH of 3.5 and a temperature of 90°C produced the least amount of byproducts relative to the amount of phenol oxidized. This process was noted to be able to be completed three times before catalyst activity was nearly zero. Regeneration of the catalyst could be obtained by calcining the zeolites at 450°C (Hartmann, Kullmann, & Keller 2010).

Methodology

Synthesis

Water (10.00 mL), sulfuric acid (2.40mL), and iron (III) sulfate (0.562g) were mixed together in solution until completely the iron salt was dissolved. In a separate beaker water (16.30mL) and sodium metasilicate pentahydrate (8.530g) were mixed until fully dissolved. The metasilicate mixture was then added drop-wise to the iron sulfate mixture with good mixing. When the mixture seized it was broken up and stirred until uniform. TPABr (1.130g) was then slowly added and again mixed until uniform. The mixture was poured into Teflon lined autoclaves and heated in an oven at 170°C for between 3 and 7 days. The autoclaves were removed from the oven, quenched, and the sample was washed until the pH was 7.

The predicted batch composition was 30 Na_2O : Fe_2O_3 : 30 SiO_2 : 1040 H_2O : 5 (TPA)Br : 25 H_2SO_4

Characterization

XRD

The x-ray diffraction pattern was taken using Rigaku Geigerflex X-ray Diffractometer at room temperature from 3° to 50°, with a 2 second step time and 0.05° intervals. The results were compared to the known spectra for ZSM-5 and Fe-ZSM-5.

SEM

To see if crystals had developed and if iron had made it into the structure SEM with EDX analysis was done on the samples. The EDX analysis was done on both the well-defined crystals and the amorphous material found in the sample to compare the relative elemental compositions.

ESR

In order to verify the oxidation state of the iron in the structure of our zeolite, we performed ESR with the assistance of Professor Fred Greenaway from Clark University. ESR was performed at room temperature running from 1 to 6000 gauss to determine the valence state of iron. The sample was run using a power of 20 mw and .2 mW to see if the if power would change the intensity of the peaks.

TGA

In order to determine if the template had been removed, TGA was done on the samples before and after different removal techniques had been completed. The samples were heated to 600°C at 10°C/min in air and the resulting weight loss curves were compared to see if the template had been successfully removed.

Template Removal

Ozone Treatment

0.10g of Fe-ZSM-5 was weighed and incased between two pieces of filter paper. The zeolite was then placed in an in-line filter and attached to a L-25 Ozonology Labzone ozone generator. Ozone was blown through the filter holder for 2 hours at 6.2 cuft/hr at 30°C. The packet was then removed and analyzed with a TA instruments Hi-Res-TGA 2950.

0.116 g zeolite was massed and incased in filter paper again. This time the ozone being passed over the zeolite was heated with Omega heating tape wrapped around the tube. The ozone was passed over the zeolite for 3 hours at 10 cuft/hr and reached a maximum of 60°C for 1 hour during the test. The sample was removed and analyzed with TGA.

0.141 g of zeolite was massed and incased in filter paper. Copper foil was wrapped around the 1/8” schedule 40 stainless steel pipe that the ozone was flowing through so the heating tape temperature could be maximized without damaging itself. The pipes leading to the filter holder were also insulated to retain as much heat as possible. The ozone was run through the system at the maximum flow rate (>10cuft/hr). The ozone reached 66°C for 1 hour at this flow rate. The sample was then removed and analyzed using TGA.

UV- Treatment

Initially, a 600mL beaker was filled with 400mL of 3% hydrogen peroxide and between 0.1-0.16 grams of synthesized Fe-ZSM-5. These samples were filtered and dried after being exposed to UV light at 254 nm in a Fisher Scientific FB-UVXL-1000 UV cross linker for 3600 and 9999 seconds in two separate runs. Finally, TGA was used to determine the presence of the organic backbone using a TA instruments Hi-Res-TGA 2950.

When the results of the 3% peroxide solution provided no results, 40-70 mL of 35% peroxide solution (Acros Chemical) was used to treat 0.1-0.16 grams of sample submerged in a 6 inch diameter petri dish to minimize the depth of the liquid and reduce the diffusion volume of the hydroxide radicals. The petri dish containing the solution was run for varying times and intensities. The first run was run for 3600 seconds and the second for 9999 seconds, machine maximum. The third sample was set to run at 9999 intensity, the maximum of the machine. All samples were filtered and dried in an oven overnight at 100°C immediately after completion. The fourth and fifth runs were repeats of the second and third runs for completeness, but these samples were filtered and dried after being allowed to sit for three days in solution. All samples were also analyzed using a TA instruments Hi-Res-TGA 2950.

Results and Discussion

SEM

The first step we took in verifying that we synthesized crystals of Fe-ZSM-5 was to physically inspect our sample with SEM. If we had successfully grown crystals, there would be planar faces in our sample as opposed to amorphous globs. As seen below in Figure 3, our sample is primarily constructed of many inter-grown, rectangular crystalline planar faces. Though there were amorphous particles present in our sample, they were few and far between, exemplifying that our sample was mostly crystalline product. This particular photograph was taken of a sample that was left in the oven for three days at 170°C. The final product that we used for our synthesis was left in the oven for seven days to ensure that no amorphous particles were present in the sample.

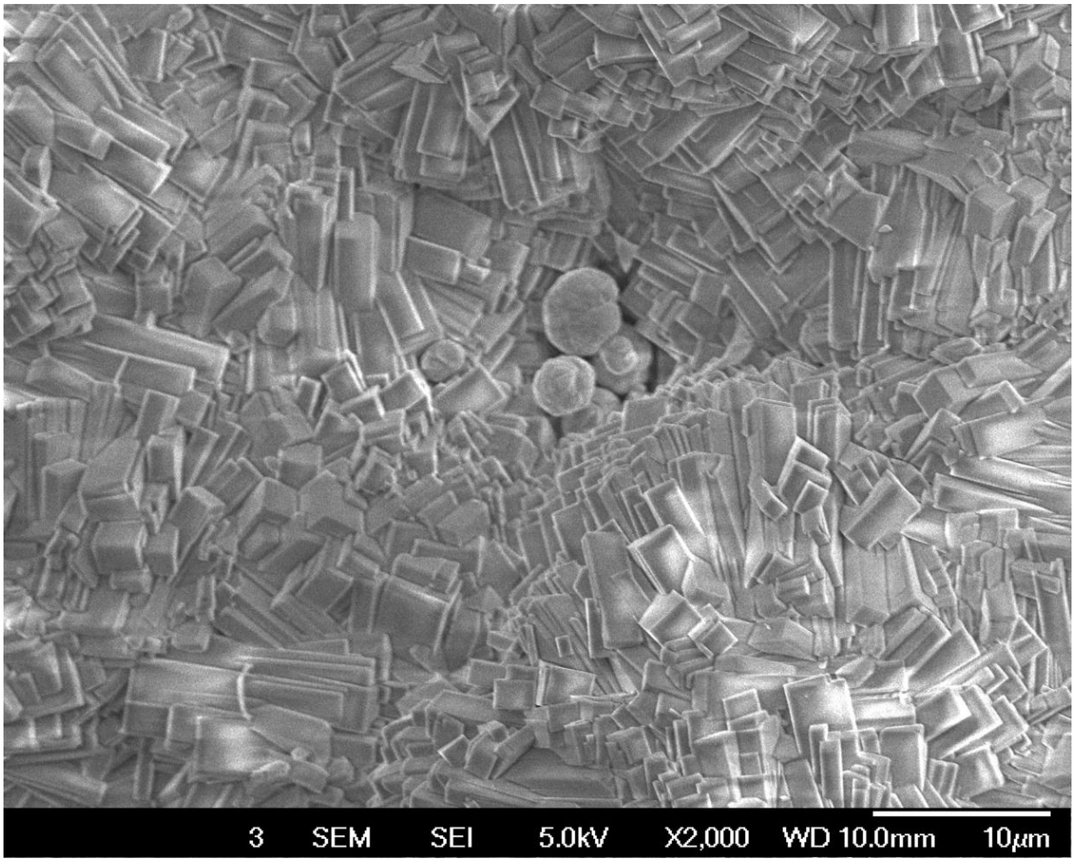


Figure 3. SEM photograph at 2000x magnification of crystals grown at 170C and 3 days

Additionally, as a preliminary test, we ran EDX of our samples to see if there was any iron present in our sample. We ran EDX at two difference places in the scan as seem below in Figure 4. The two resulting spectra of the EDX are found below in Figures 5 and 6.

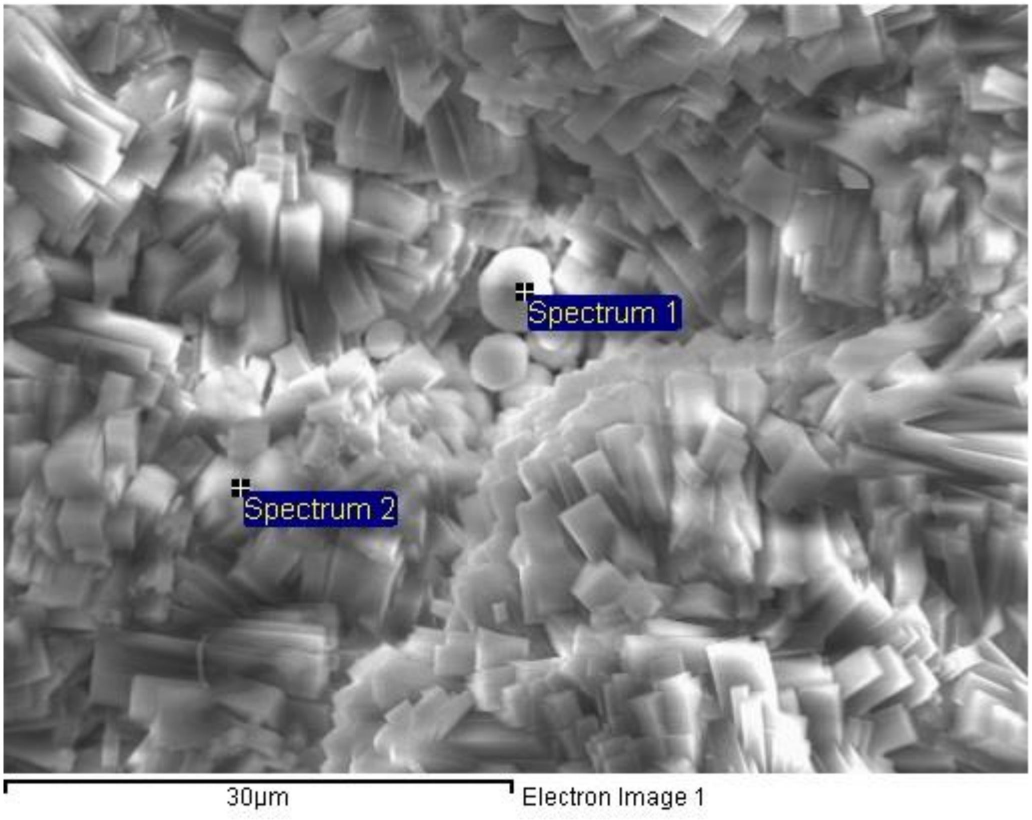


Figure 4. Locations where EDX was taken

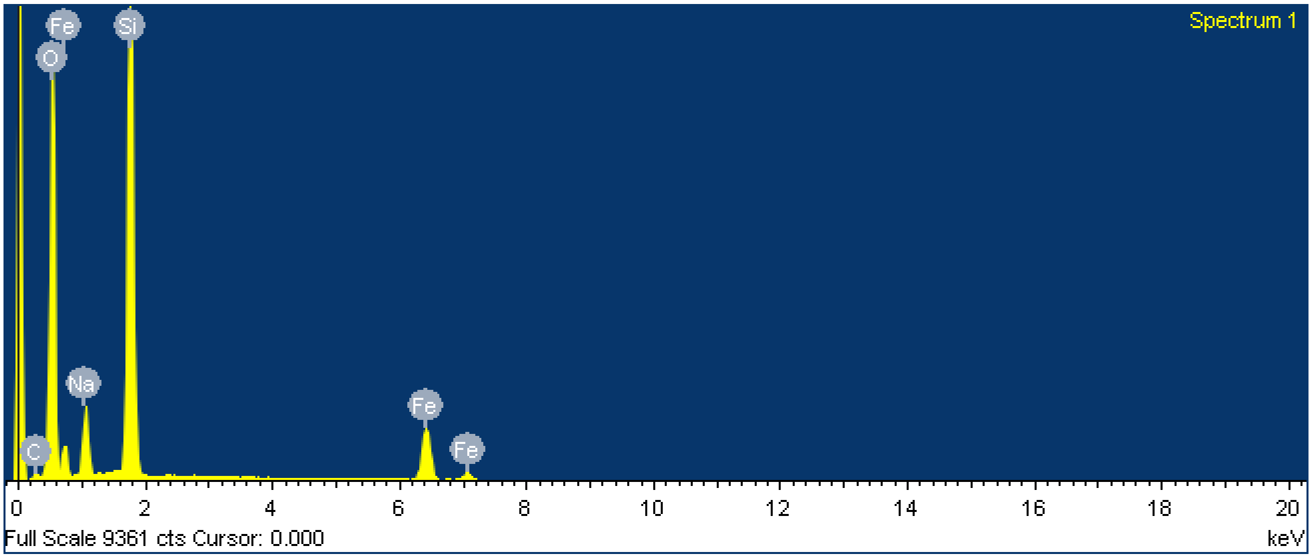


Figure 5. EDX of the amorphous particle present in our sample in Figure 4

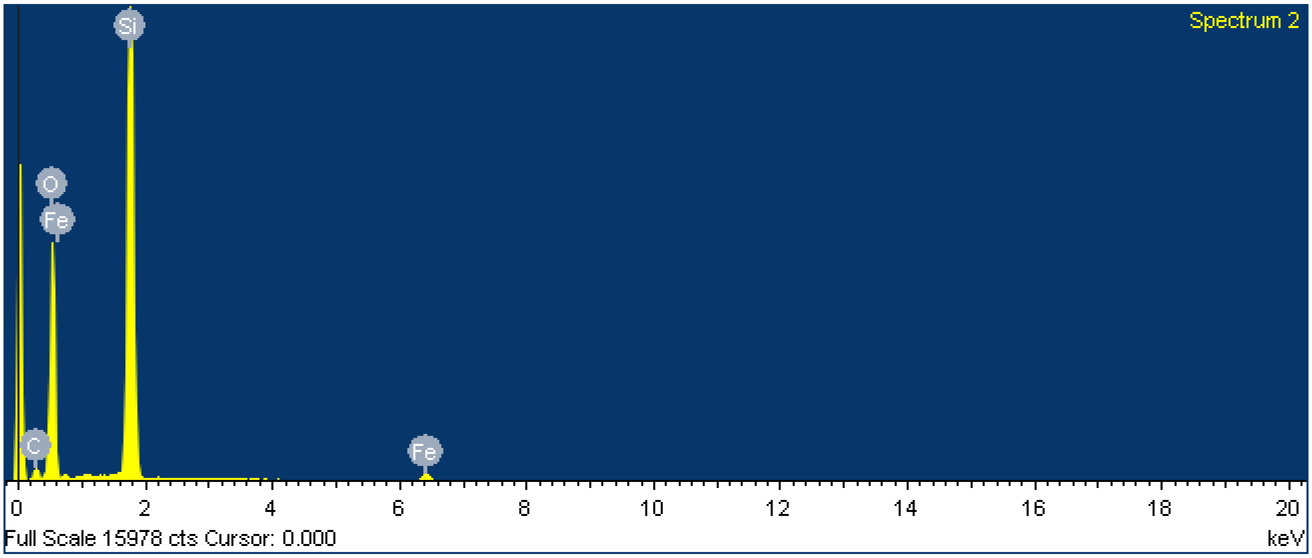


Figure 6. EDX of our crystalline product in Figure 4

As seen in the two resulting EDX spectra, there is a lot more iron present in the amorphous glob in our sample than in the crystalline product. Also, the peak around 0.5 keV labeled O and Fe only represents oxygen. The resolution of the peak is difficult to separate, and since oxygen is in so much abundance, the iron concentration represented by this peak is negligible. Overall, EDX is not a good quantitative method to determine the amount of iron incorporated into the structure, but it does verify that we have successfully incorporated iron into the crystalline structure of our zeolite.

XRD

In order to verify the crystalline structure of our sample, we conducted XRD and compared our spectrum, found below in Figure 7, with a reference spectrum, Figure 8. Our spectrum is not as clean as the reference spectrum since we still had the backbone present when we took our spectrum, but all of the characteristic peaks are present and there are no extra peaks. The relative intensity of the peaks in our spectrum were also different from the peaks in the reference spectrum because we ran x-ray powder diffraction so the random alignment of our crystalline structure could have been different. But since all the peaks were there, even if they are at different intensities, our crystalline structure still matches the reference, verifying that we successfully synthesized Fe-ZSM-5.

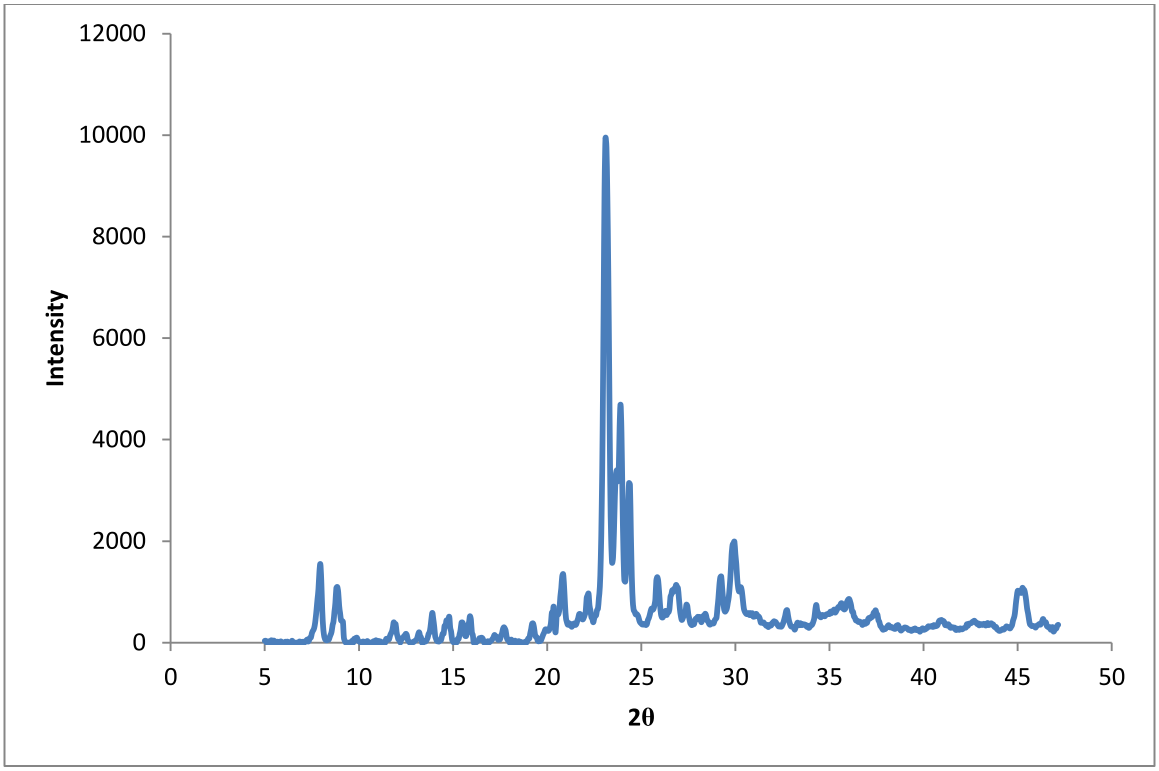


Figure 7. XRD of our synthesized zeolite sample

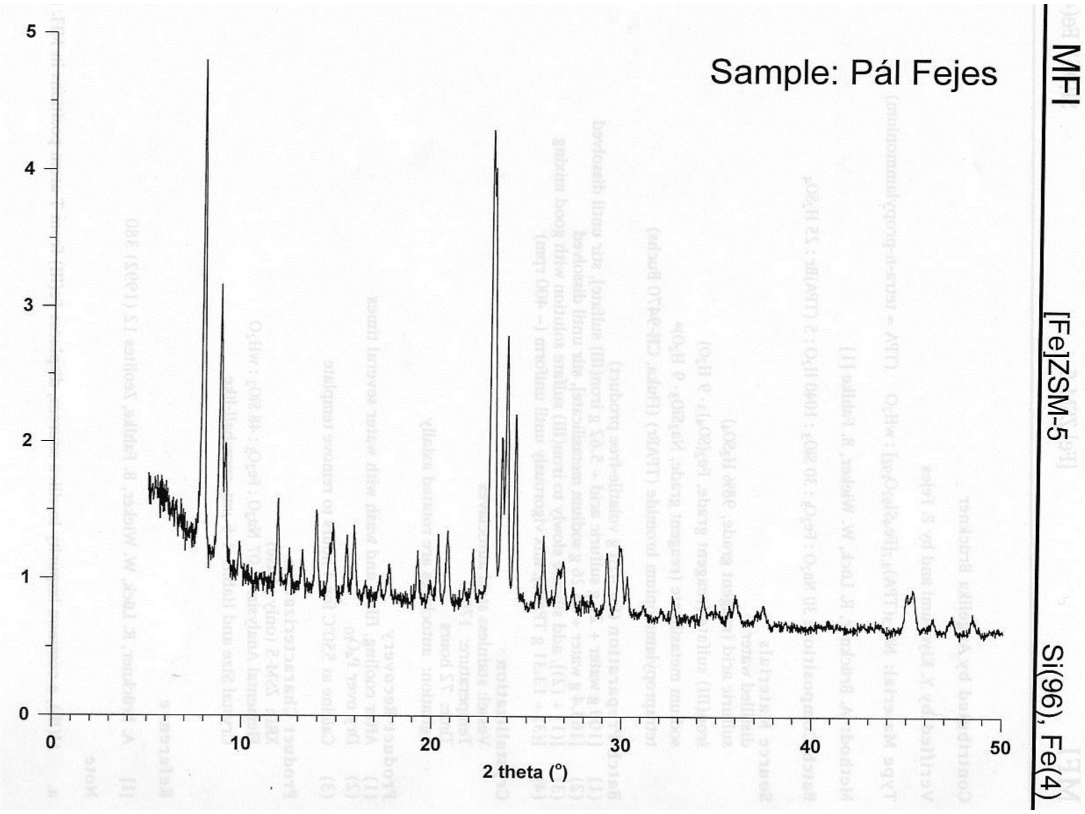


Figure 8. Reference spectrum for Fe-ZSM-5 (Brückner 1992)

ESR

After we had verified the crystalline structure of our sample, we needed to determine if iron in the structure of our zeolite was in the correct valence state to catalyze Fenton's Oxidation. For this we used electron spin resonance technology. According to the graph below, the characteristic Fe^{3+} peak shoots through at a large intensity, indicating its presence. If compared to a sample with a known concentration of iron, this peak could indicate how many grams of iron are present in the system. Further tests will need to be done to determine the presence of the iron within the crystalline structure, and the amount of iron in the structure.

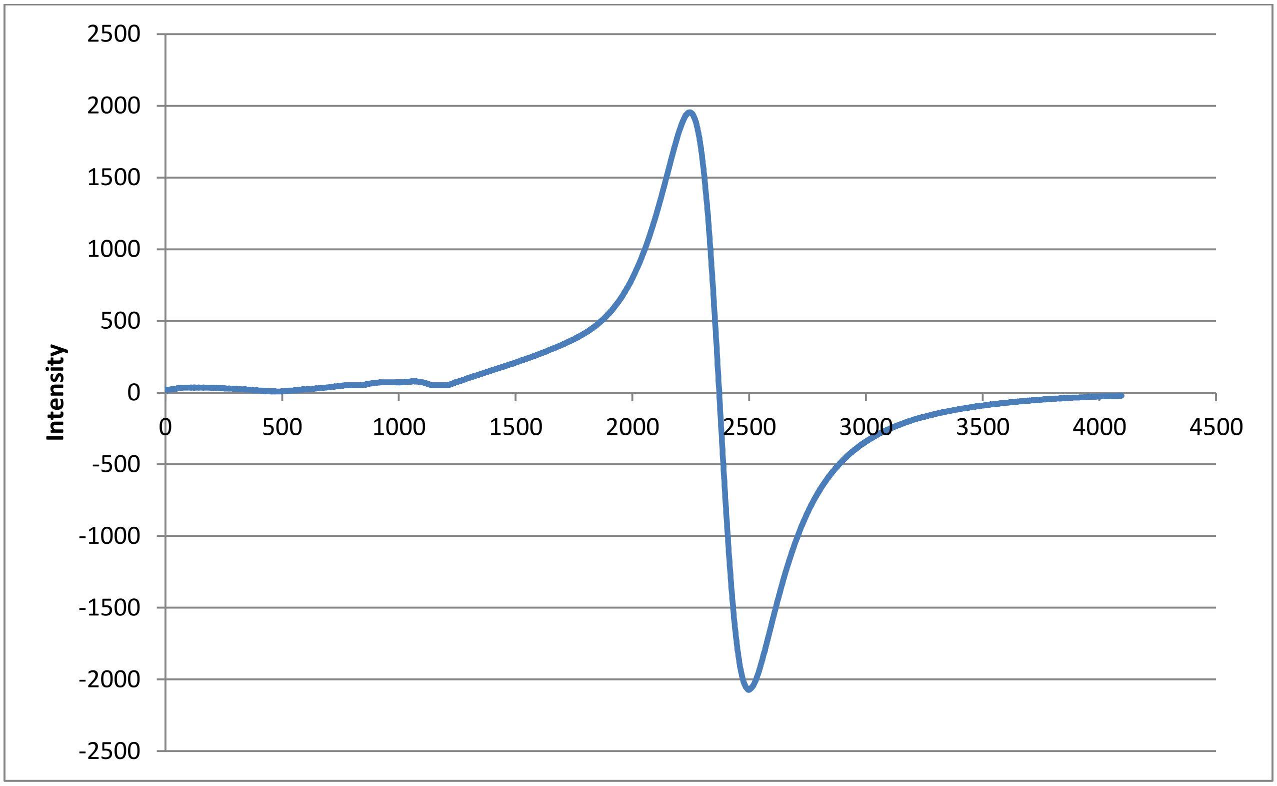


Figure 9. ESR spectrum of our Fe-ZSM-5 sample.

TGA

After verifying that we had synthesized Fe-ZSM-5, we tested various methods of template removal. After each test, the primary method we used to determine if the backbone had been removed was with TGA. Untreated, the template typically burned out around 500°C and the resulting weight loss was around 10% of the total weight as seen below in Figure 10. Initially the TGA was run in nitrogen however significant charring was observed. The TGA was then run in air, which significantly decreased the discoloration (Wilson). We attempted to remove the template with ozone at room temperature and at 66°C and also 3% and 27.2% hydrogen peroxide by volume under 254 nm UV. Both methods produced no visible physical changes and the resulting TGA graphs yielding no differences than the untreated sample which means that our attempts at oxidizing the backbone out of the structure were ineffective. Had our experiments been successful we expected to see no weight change at all across the TGA, or see a weight change at a lower temperature illustrating that the backbone had been broken into smaller pieces and were burning off at a lower temperature (Figures 10-12).

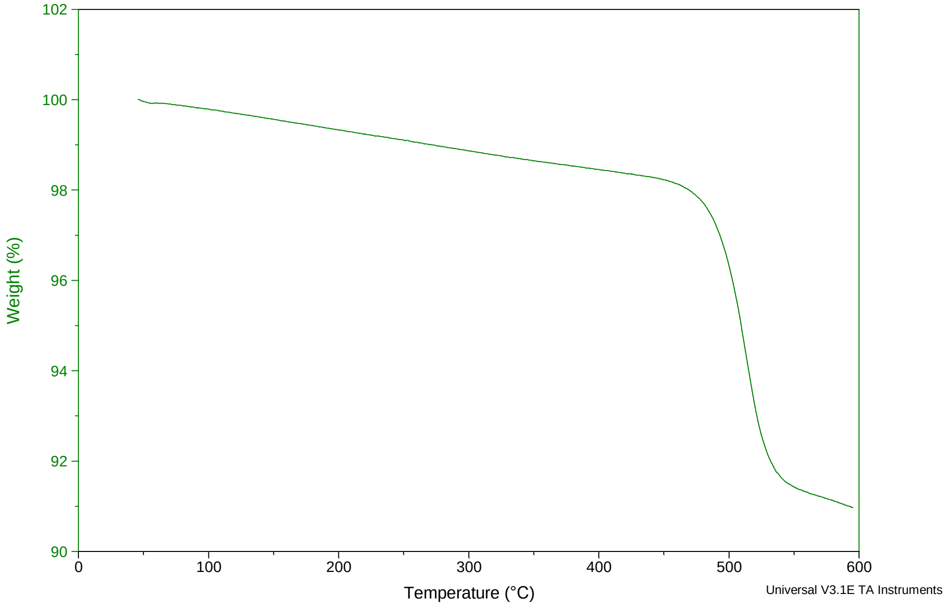


Figure 10. TGA spectrum of untreated Fe-ZSM-5

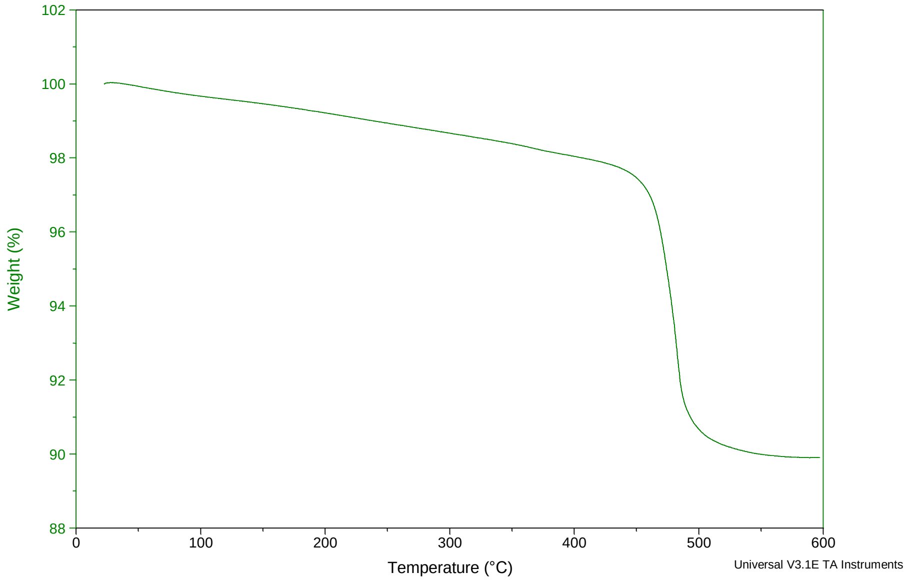


Figure 11. TGA spectrum of sample after 27.2% peroxide-UV treatment

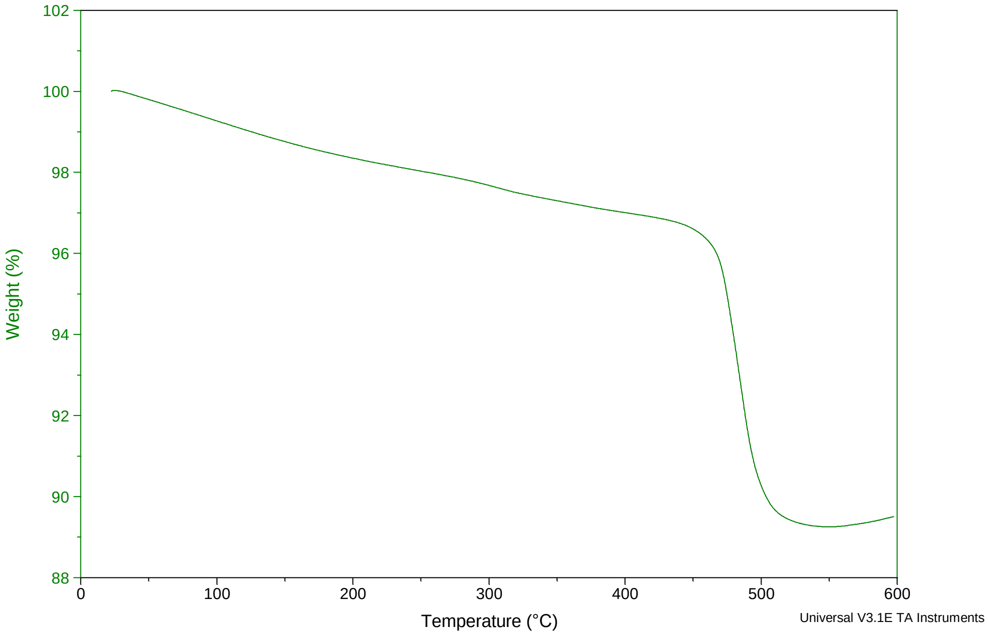


Figure 12. TGA spectrum of Fe-ZSM-5 after hot ozone treatment

Conclusions and Recommendations

After we completed all our experiments we were unable to remove the tetrapropylammonium bromide backbone from the crystalline structure of Fe-ZSM-5. We did successfully verify the synthesis of the zeolite and the 3+ oxidation state of the iron allowing for Fenton's oxidation.

The secondary goal of our project, to remove the organic backbone at a lower temperature, was unsuccessful despite our best efforts. On the other hand, we determined that using ozone at less than 66°C and 35% peroxide at room temperature were ineffective.

We did have some hardware limitations in our attempts to remove the backbone. Our research led us to believe that using at least 150°C ozone would oxidize the backbone out, but the highest temperature we could reach was only 66°C. If the backbone oxidation reaction proceeded in the presence of hot ozone, we were not able to witness it as we could not reach a high enough temperature with our setup.

It is recommended for further experiments to be done using a higher grade of peroxide and stirring the mixture to increase diffusion and contact area between the zeolite and the hydroxide radicals. Using a higher temperature of ozone is also recommended to initiate the reaction. A tube furnace would be preferable to accomplish this goal.

Bibliography

Brückner, A., et al. "E.p.r. Study on the Incorporation of Fe(III) Ions in ZSM-5 Zeolites in Dependence on the Preparation Conditions." *Zeolites* 12.4 (1992): 380-5. Web.

Calsavara, Valmir, Mauro Luciano Baesso, and Nádia Regina Camargo Fernandes-Machado. "Transformation of Ethanol into Hydrocarbons on ZSM-5 Zeolites Modified with Iron in Different Ways." *Fuel* 87.8–9 (2008): 1628-36. Web.

"Catalytic Oxidation of Trichloroethylene Over Fe-Zeolites." *Catalysis Today* 176.1 (2011): 357-60. Web.

Chang, C. D., and A. T. Bell. "Studies on the Mechanism of ZSM-5 Formation." *Catalysis Letters* 8.5 (1991): 305-16. Web.

Coker, Eric N., et al. "Zeolite ZSM-5 Synthesized in Space: Catalysts with Reduced External Surface Activity." *Microporous and Mesoporous Materials* 46.2–3 (2001): 223-36. Web.

Corbari, L., et al. - *Iron Oxide Deposits Associated with the Ectosymbiotic Bacteria in the Hydrothermal Vent Shrimp Rimicaris Exoculata*. - Copernicus PublicationsWeb.

Cundy, C. S., and P. A. Cox. "The Hydrothermal Synthesis of Zeolites: Precursors, Intermediates and Reaction Mechanism." *Microporous and Mesoporous Materials* 82.1 (2005): 1-78. Web.

Divakar, Duraiswami, et al. "Catalytic Oxidation of Trichloroethylene Over Fe-Zeolites." *Catalysis Today* 176.1 (2011): 357-60. Web.

Giannetto, G. "Synthesis and Characterization of [Cr, Al]-ZSM-5 Zeolites." *Zeolites* 19.2-3 (1997): 169. Web.

Hartmann, Martin, Simon Kullmann, and Harald Keller. "Wastewater Treatment with Heterogeneous Fenton-Type Catalysts Based on Porous Materials." *JOURNAL OF MATERIALS CHEMISTRY* 2.41 (2010): 92-917. Web.

Heng, Samuel, et al. "Low-Temperature Ozone Treatment for Organic Template Removal from Zeolite Membrane." *Journal of Membrane Science* 243.1–2 (2004): 69-78. Web.

"The Hydrothermal Synthesis of Zeolites: Precursors, Intermediates and Reaction Mechanism." *Microporous and Mesoporous Materials* 82.1 (2005): 1-78. Web.

Jiménez-Cedillo, M. J., et al. "Adsorption Capacity of Iron- Or iron–manganese-Modified Zeolite-Rich Tuffs for as(III) and as(V) Water Pollutants." *Applied Clay Science* 54.3–4 (2011): 206-16. Web.

Kiricsi, Imre, et al. "The Advantages of Ozone Treatment in the Preparation of Tubular Silica Structures." *Applied Catalysis A: General* 203.1 (2000): L1-4. Web.

Li, Chunjie, et al. "Surfactant Modified Zeolite as Adsorbent for Removal of Humic Acid from Water." *Applied Clay Science* 52.4 (2011): 353-7. Web.

"Surfactant Modified Zeolite as Adsorbent for Removal of Humic Acid from Water." *Applied Clay Science* 52.4 (2011): 353-7. Web.

Li, Zhaohui, et al. "Combination of Hydrous Iron Oxide Precipitation with Zeolite Filtration to Remove Arsenic from Contaminated Water." *Desalination* 280.1–3 (2011): 203-7. Web.

Machado, Francisco J., et al. "Spectroscopic and Catalytic Evidence for the Incorporation of Gallium in the AEL Framework." *Zeolites* 19.5–6 (1997): 387-94. Web.

Masters, Anthony F., and Thomas Maschmeyer. "Zeolites – from Curiosity to Cornerstone." *Microporous and Mesoporous Materials* 142.2–3 (2011): 423-38. Web.

Melián-Cabrera, I., et al. "Utilizing Full-Exchange Capacity of Zeolites by Alkaline Leaching: Preparation of Fe-ZSM5 and Application in N2O Decomposition." *Journal of Catalysis* 238.2 (2006): 250-9. Web.

Melián-Cabrera, I., F. Kapteijn, and J. A. Moulijn. "Innovations in the Synthesis of Fe-(Exchanged)-Zeolites." *Catalysis Today* 110.3–4 (2005): 255-63. Web.

Mohamed, Mohamed Mokhtar, Ibraheem Othman Ali, and N. A. Eissa. "Effect of Thermal Treatment on Surface and Bulk Properties of Fe/ZSM-5 Zeolites Prepared by Different Methods." *Microporous and Mesoporous Materials* 87.2 (2005): 93-102. Web.

Perathoner, Siglinda, and Gabriele Centi. "Wet Hydrogen Peroxide Catalytic Oxidation (WHPCO) of Organic Waste in Agro-Food and Industrial Streams." *Topics in Catalysis* 33.1 (2005): 207-24. Web.

Petushkov, Anton, Suhyoung Yoon, and Sarah C. Larsen. "Synthesis of Hierarchical Nanocrystalline ZSM-5 with Controlled Particle Size and Mesoporosity." *Microporous and Mesoporous Materials* 137.1 (2011): 92-100. Web.

Tekbaş, Mesut, H. Cengiz Yatmaz, and Nihal Bektaş. "Heterogeneous Photo-Fenton Oxidation of Reactive Azo Dye Solutions using Iron Exchanged Zeolite as a Catalyst." *Microporous and Mesoporous Materials* 115.3 (2008): 594-602. Web.

Wącław, A., et al. "N2O Decomposition Over Iron Modified Zeolites ZSM-5." *Catalysis Today* 90.1–2 (2004): 21-5. Web.

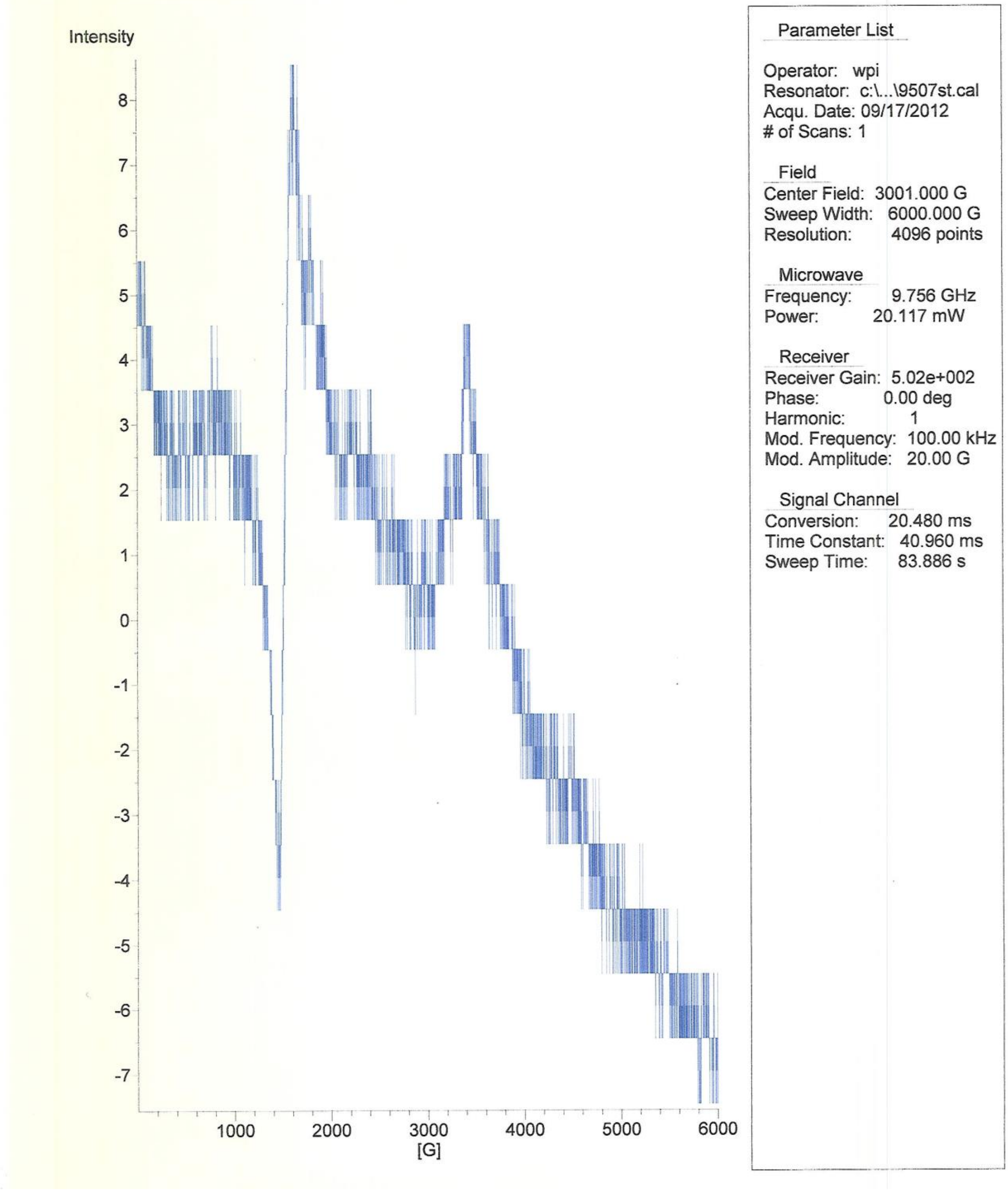
Wącław, A., K. Nowińska, and W. Schwieger. "Benzene to Phenol Oxidation Over Iron Exchanged Zeolite ZSM-5." *Applied Catalysis A: General* 270.1–2 (2004): 151-6. Web.

Wang, Shaobin, and Yuelian Peng. "Natural Zeolites as Effective Adsorbents in Water and Wastewater Treatment." *Chemical Engineering Journal* 156.1 (2010): 11-24. Web.

Weigel, O. "Adsorption of Organic Liquid Vapors by Chabazite." *Z.Kristallogr.* 61 (1925): 125. *OnlineLibrary*. Web.

Wilson, Steve. Personal Interview**.** November 19, 2012

Appendix A – ESR Spectrum



Parameter List

Operator: wpi
Resonator: c:\...\9507st.cal
Acqu. Date: 09/17/2012
# of Scans: 1

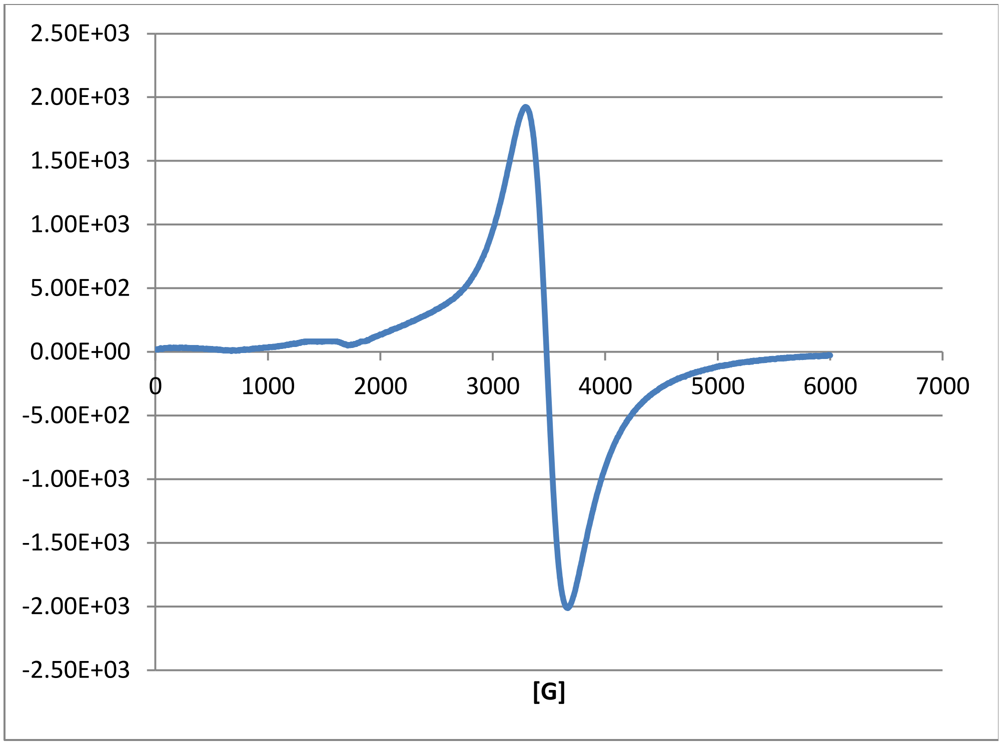
Field
Center Field: 3001.000 G
Sweep Width: 6000.000 G
Resolution: 4096 points

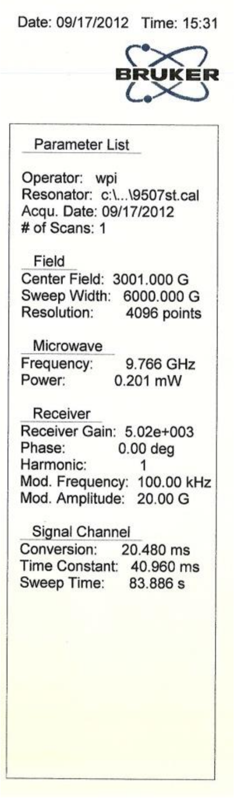
Microwave
Frequency: 9.756 GHz
Power: 20.117 mW

Receiver
Receiver Gain: 5.02e+002
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 20.00 G

Signal Channel
Conversion: 20.480 ms
Time Constant: 40.960 ms
Sweep Time: 83.886 s

Figure 13. ESR Fe-ZSM-5 Created in 5 days at 150 Days




Date: 09/17/2012 Time: 15:31

BRUKER

Parameter List

Operator: wpi
Resonator: c:\...\9507st.cal
Acqu. Date: 09/17/2012
# of Scans: 1

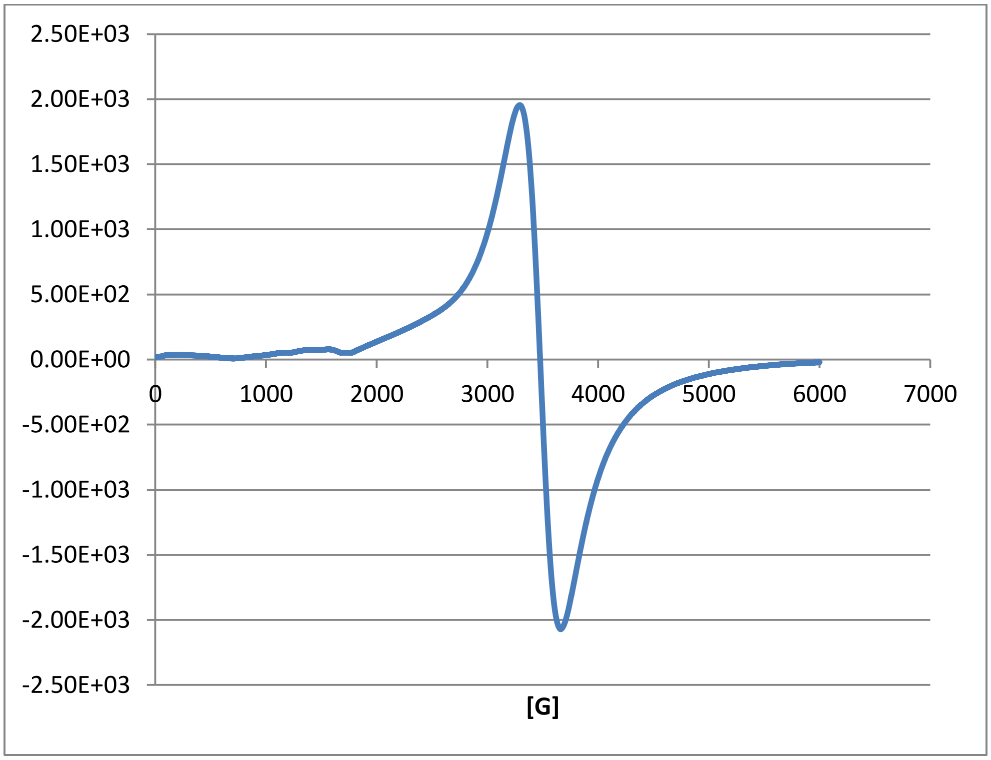
Field
Center Field: 3001.000 G
Sweep Width: 6000.000 G
Resolution: 4096 points

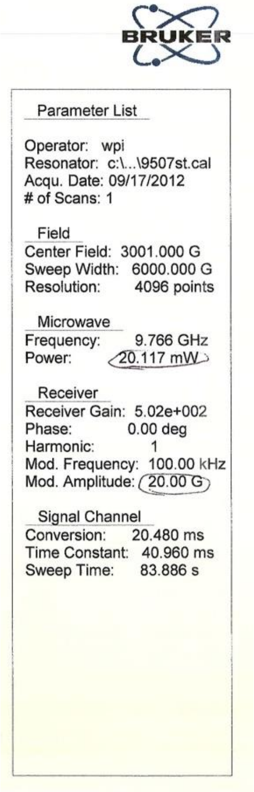
Microwave
Frequency: 9.766 GHz
Power: 0.201 mW

Receiver
Receiver Gain: 5.02e+003
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 20.00 G

Signal Channel
Conversion: 20.480 ms
Time Constant: 40.960 ms
Sweep Time: 83.886 s

Figure 14. ESR Fe-ZSM-5 Created in 7 days at 150 Degrees C, Power: .201 mW




BRUKER

Parameter List

Operator: wpi
Resonator: c:\...\9507st.cal
Acqu. Date: 09/17/2012
# of Scans: 1

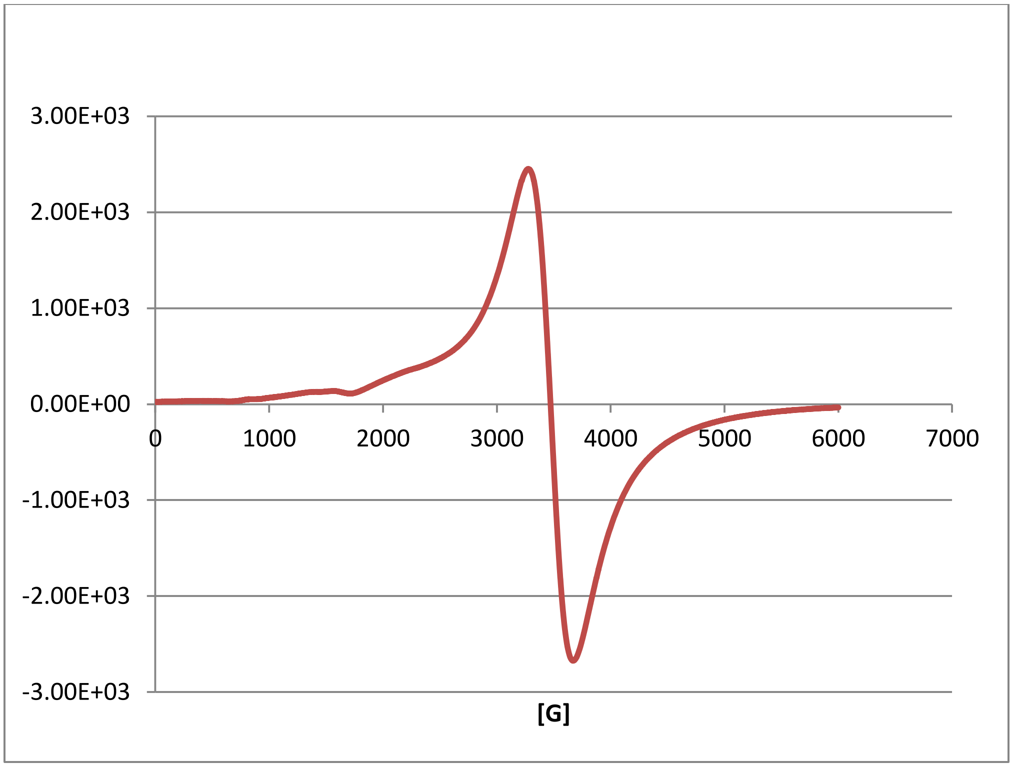
Field
Center Field: 3001.000 G
Sweep Width: 6000.000 G
Resolution: 4096 points

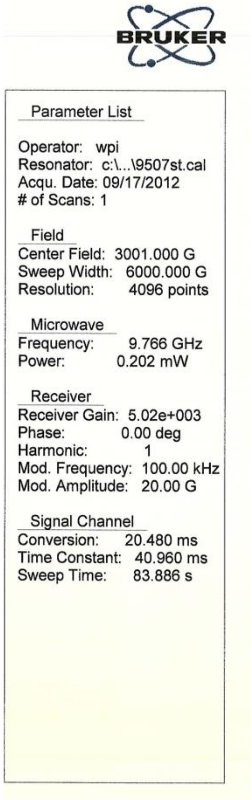
Microwave
Frequency: 9.766 GHz
Power: 20.117 mW

Receiver
Receiver Gain: 5.02e+002
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 20.00 G

Signal Channel
Conversion: 20.480 ms
Time Constant: 40.960 ms
Sweep Time: 83.886 s

Figure 15. ESR Fe-ZSM-5 Created in 7 days at 150 Degrees C, Power: 20.117 mW





Parameter List

Operator: wpi
Resonator: c:\...\9507st.cal
Acqu. Date: 09/17/2012
# of Scans: 1

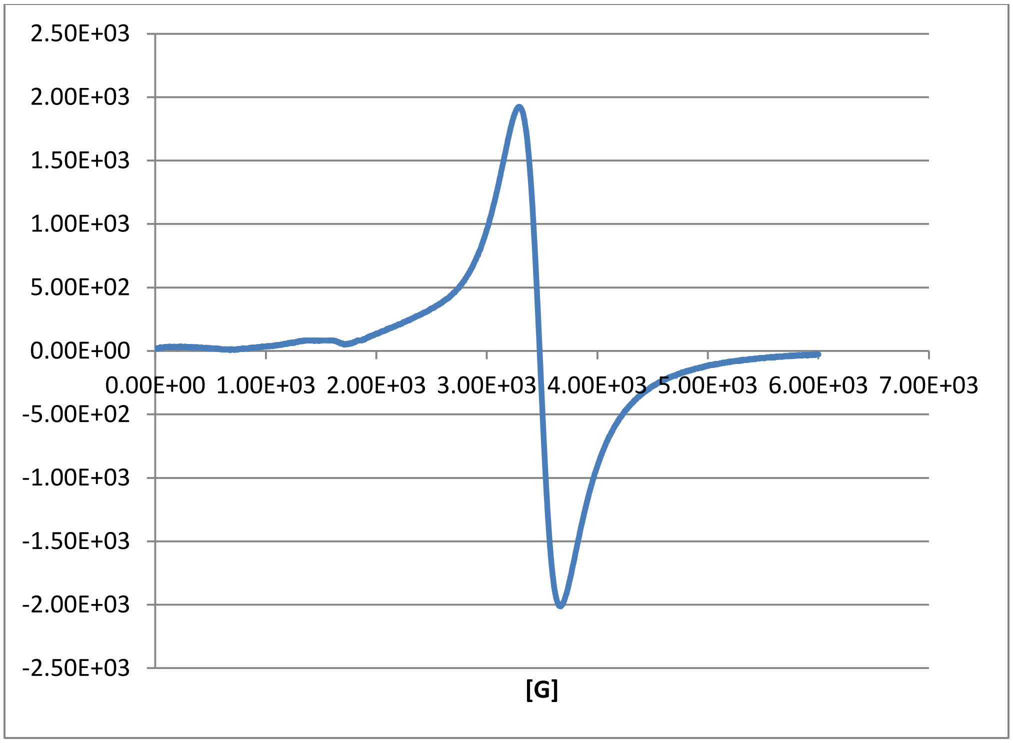
Field
Center Field: 3001.000 G
Sweep Width: 6000.000 G
Resolution: 4096 points

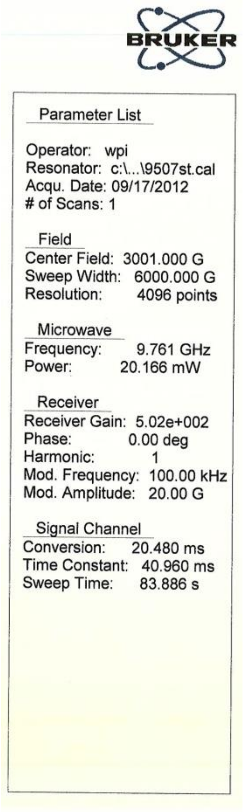
Microwave
Frequency: 9.766 GHz
Power: 0.202 mW

Receiver
Receiver Gain: 5.02e+003
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 20.00 G

Signal Channel
Conversion: 20.480 ms
Time Constant: 40.960 ms
Sweep Time: 83.886 s

Figure 16. ESR Fe-ZSM-5 Created in 5 days at 150 Degrees C, Power .202 mW





Parameter List

Operator: wpi
Resonator: c:\...\9507st.cal
Acqu. Date: 09/17/2012
# of Scans: 1

Field
Center Field: 3001.000 G
Sweep Width: 6000.000 G
Resolution: 4096 points

Microwave
Frequency: 9.761 GHz
Power: 20.166 mW

Receiver
Receiver Gain: 5.02e+002
Phase: 0.00 deg
Harmonic: 1
Mod. Frequency: 100.00 kHz
Mod. Amplitude: 20.00 G

Signal Channel
Conversion: 20.480 ms
Time Constant: 40.960 ms
Sweep Time: 83.886 s

Figure 17. ESR Fe-ZSM-5 Created in 5 days at 150 Degrees C Power: 20.166 mW

Appendix B – TGA Spectrum

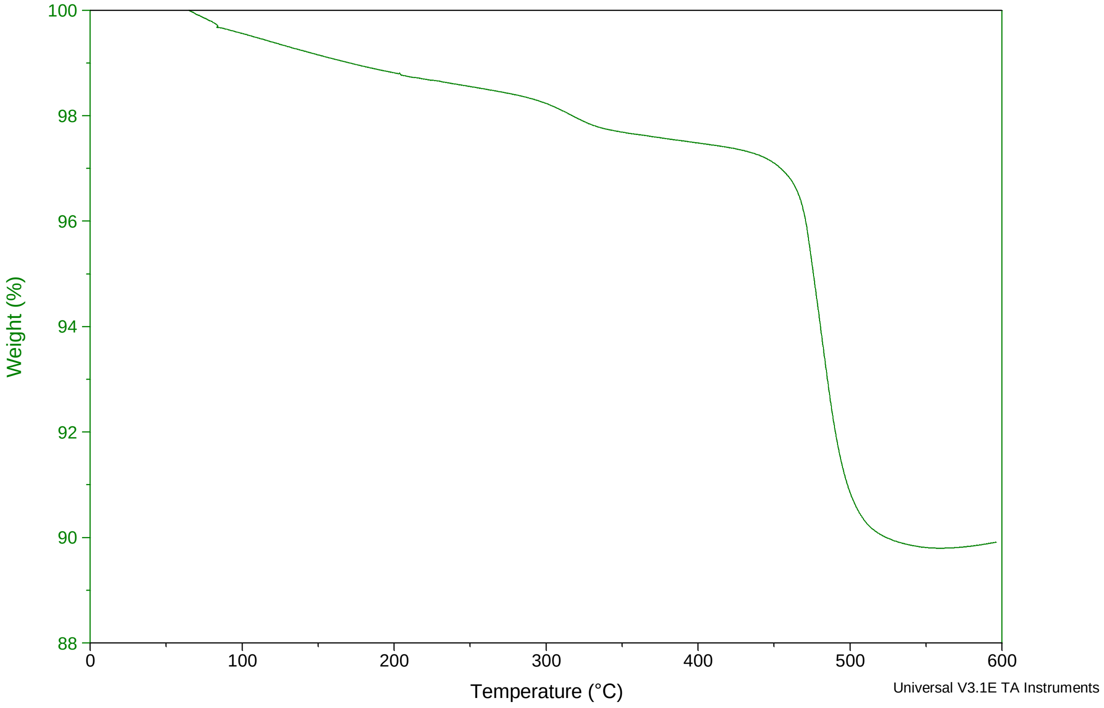


Figure 18. TGA in Nitrogen of Untreated Fe-ZSM-5 Created in 5 days at 150 degrees C

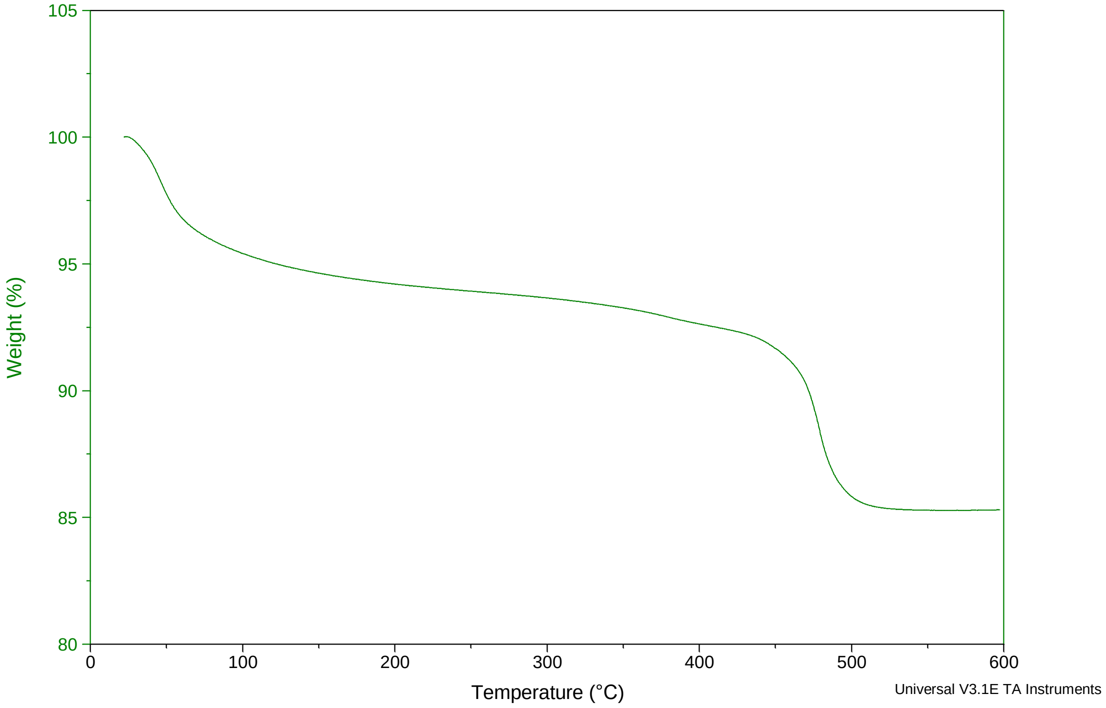


Figure 19. TGA in Nitrogen, Untreated Fe-ZSM-5 Created in 6 days at 150 degrees C (still wet)

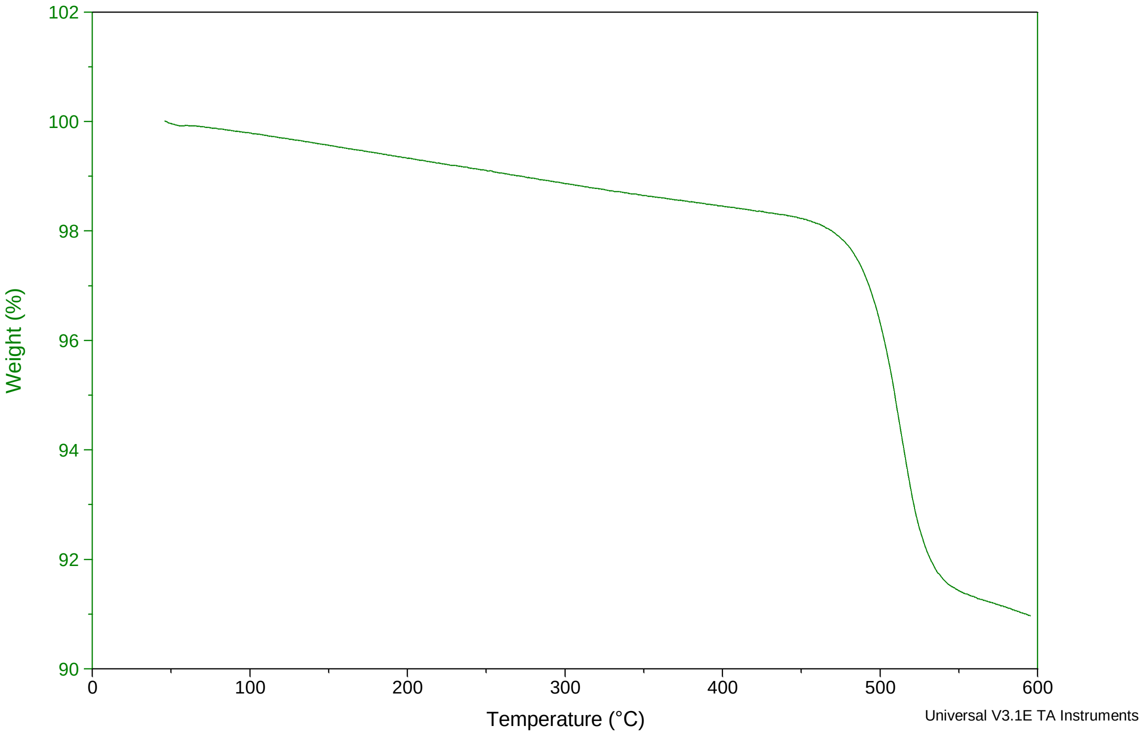


Figure 20. TGA in Nitrogen, Untreated Fe-ZSM-5 Created in 7 days at 170 Degrees C

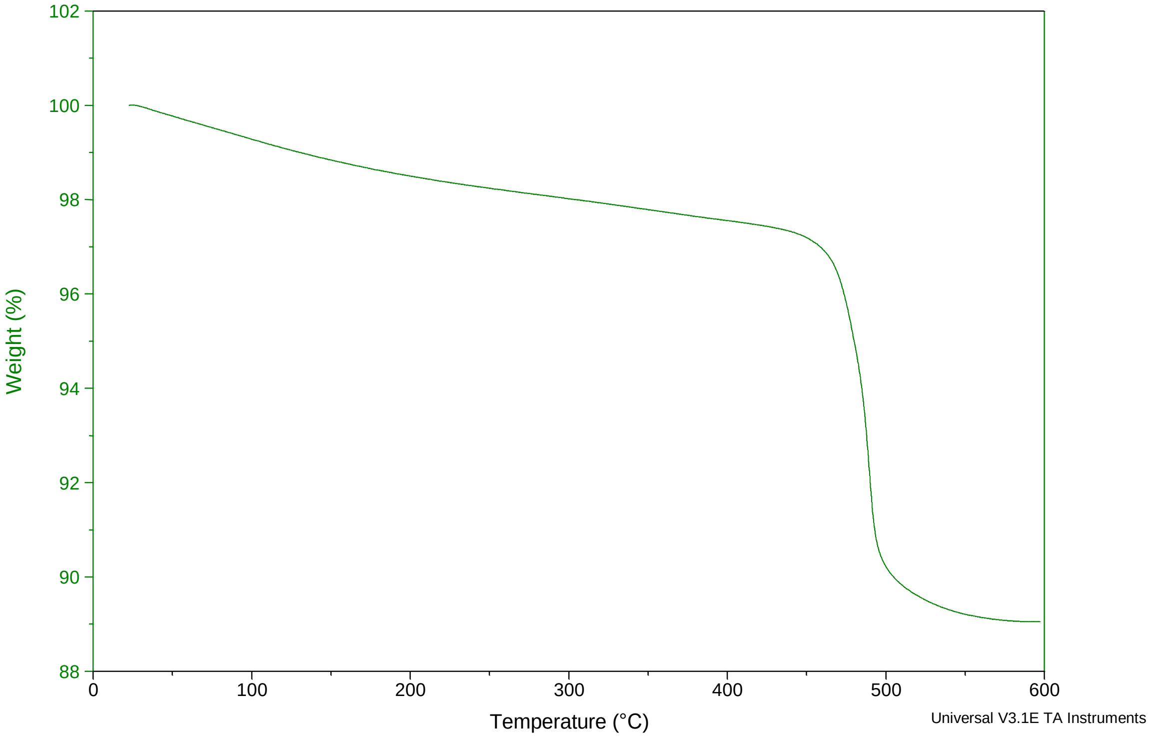


Figure 21. TGA in Air, Fe-ZSM-5 Treated with 3 Percent Peroxide and UV at 120 microJoules/cm^2 for 1 Hour

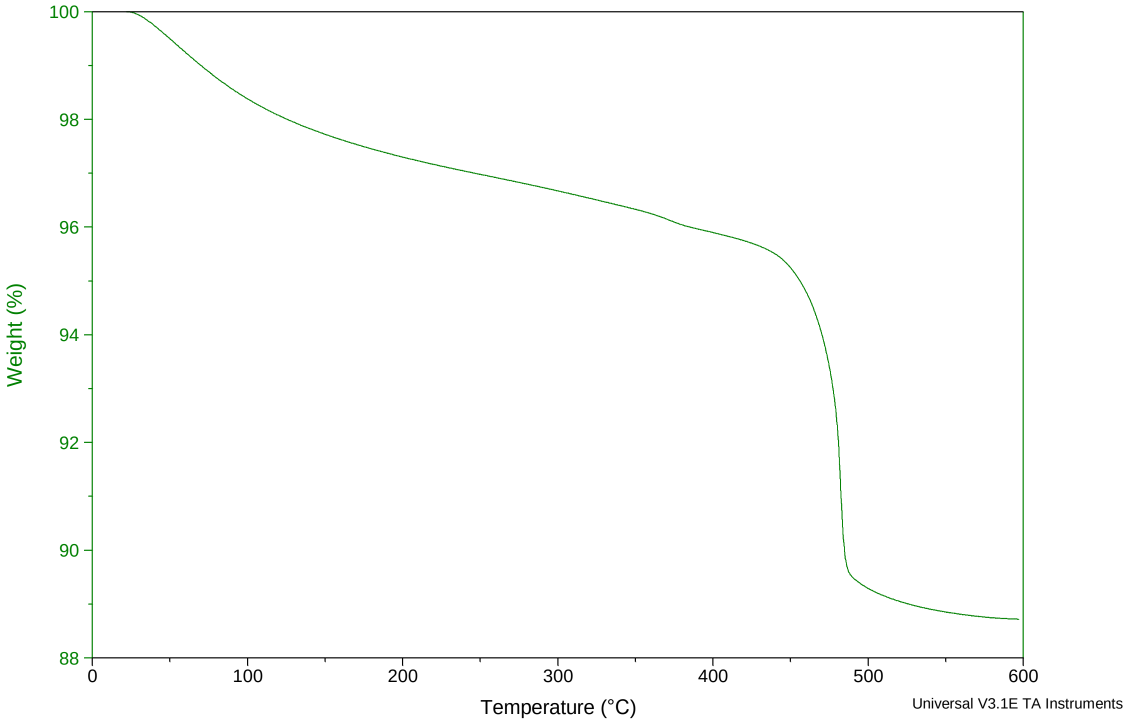


Figure 22. TGA Fe-ZSM-5 Treated with 3 Percent Peroxide and UV at 10,000 microJoules/cm^2 for 2 ¾ Hours

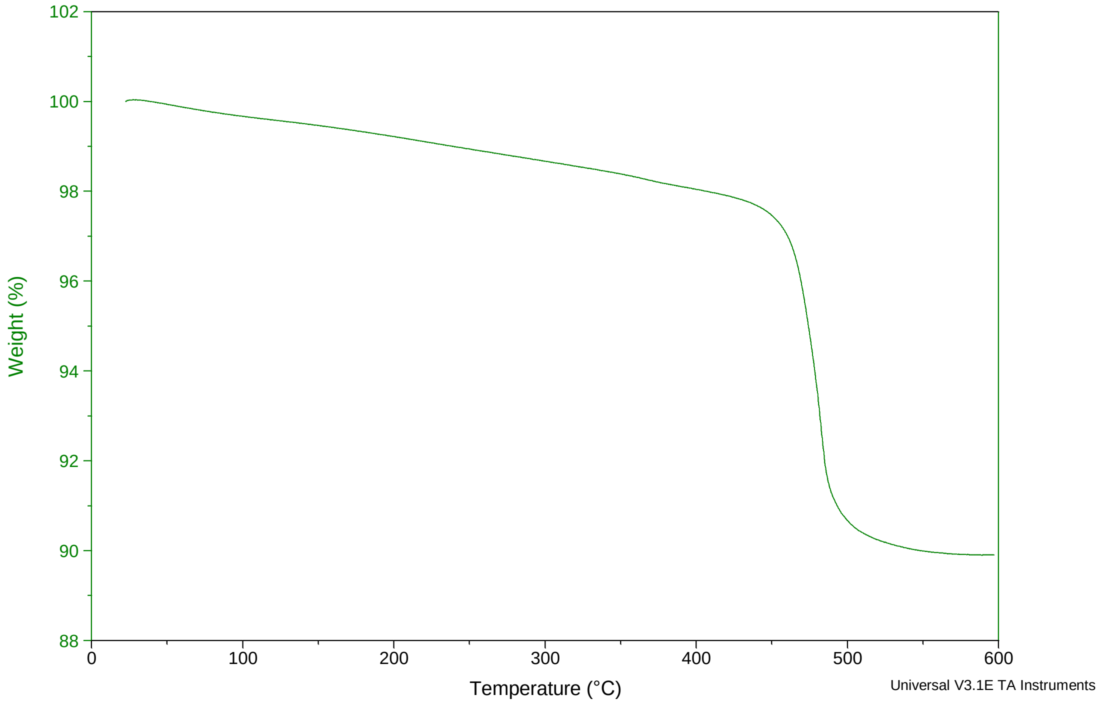


Figure 23. TGA Fe-ZSM-5 Treated with 27.3 Percent Peroxide and UV at 120 microJoules/cm^2 for 2 ¾ Hours

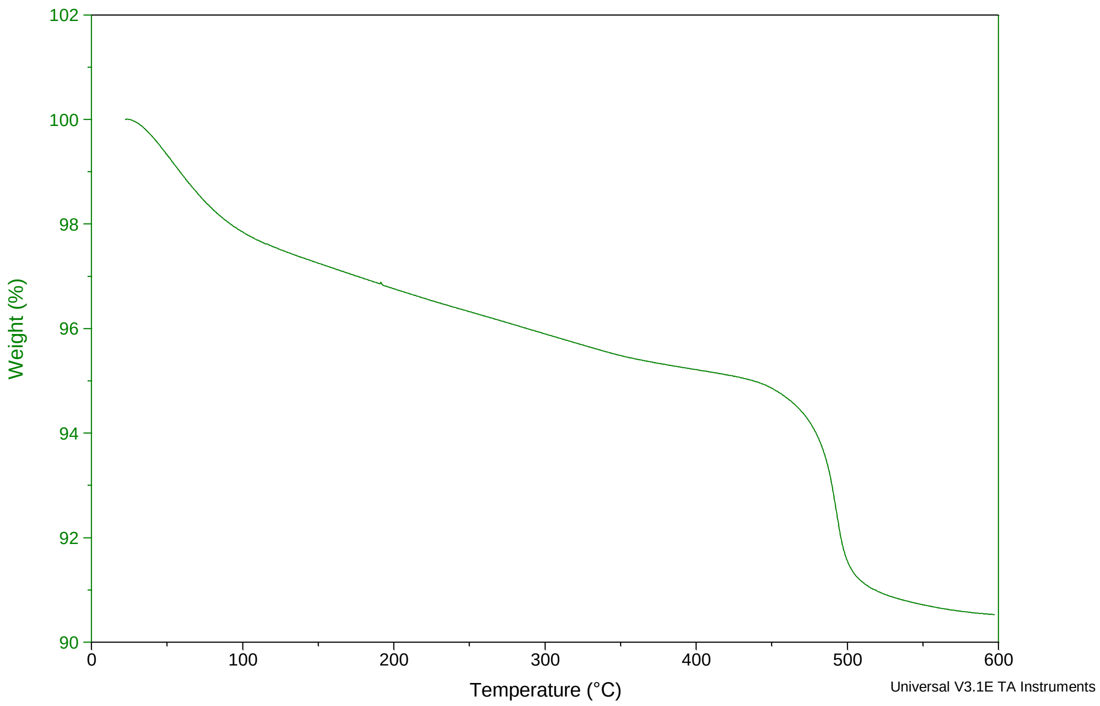


Figure 24. TGA Fe-ZSM-5 Treated with 27.3 Percent Peroxide and UV at 10,000 microJoules/cm^2 for 2 ¾ Hours refilled and run a second time

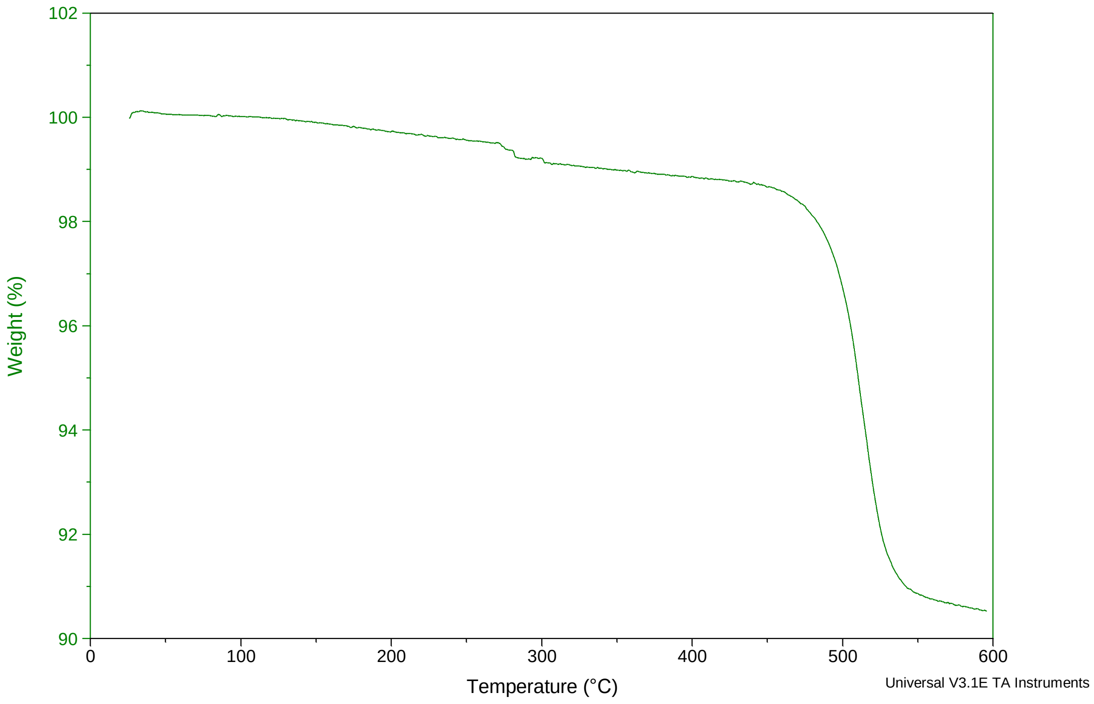


Figure 25. TGA Fe-ZSM-5 Treated with Ozone at 25 Degrees C for 1 Hour

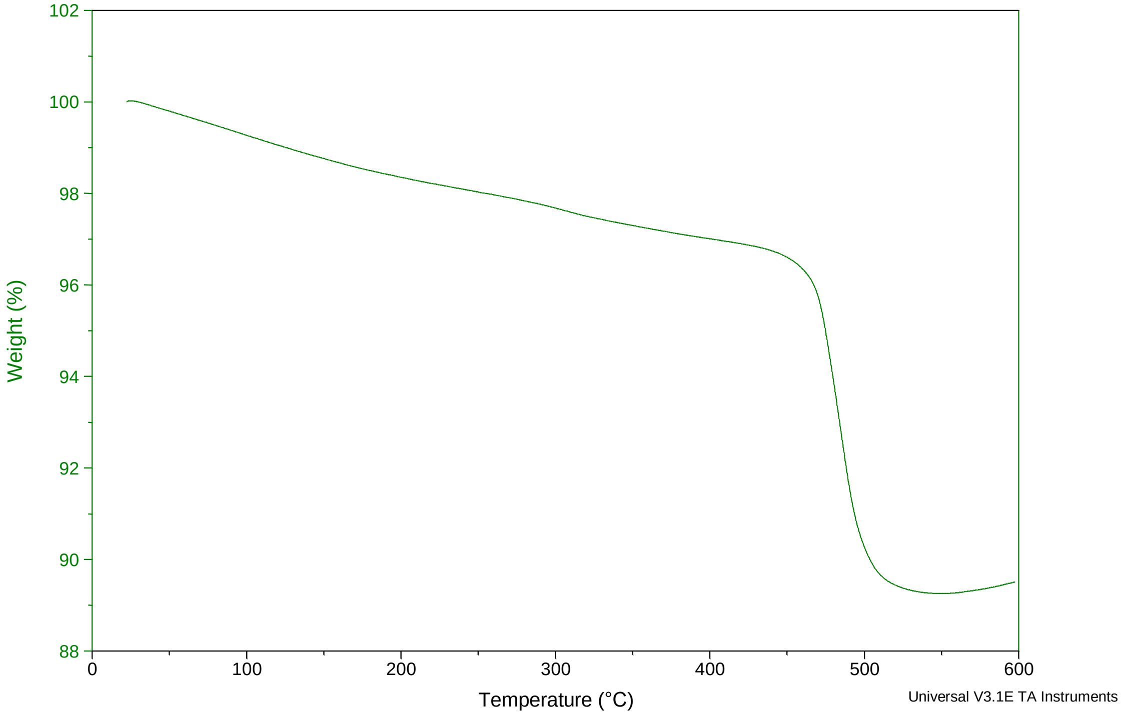


Figure 26. TGA Fe-ZSM-5 Treated with Ozone at 60 Degrees C for 1 Hour

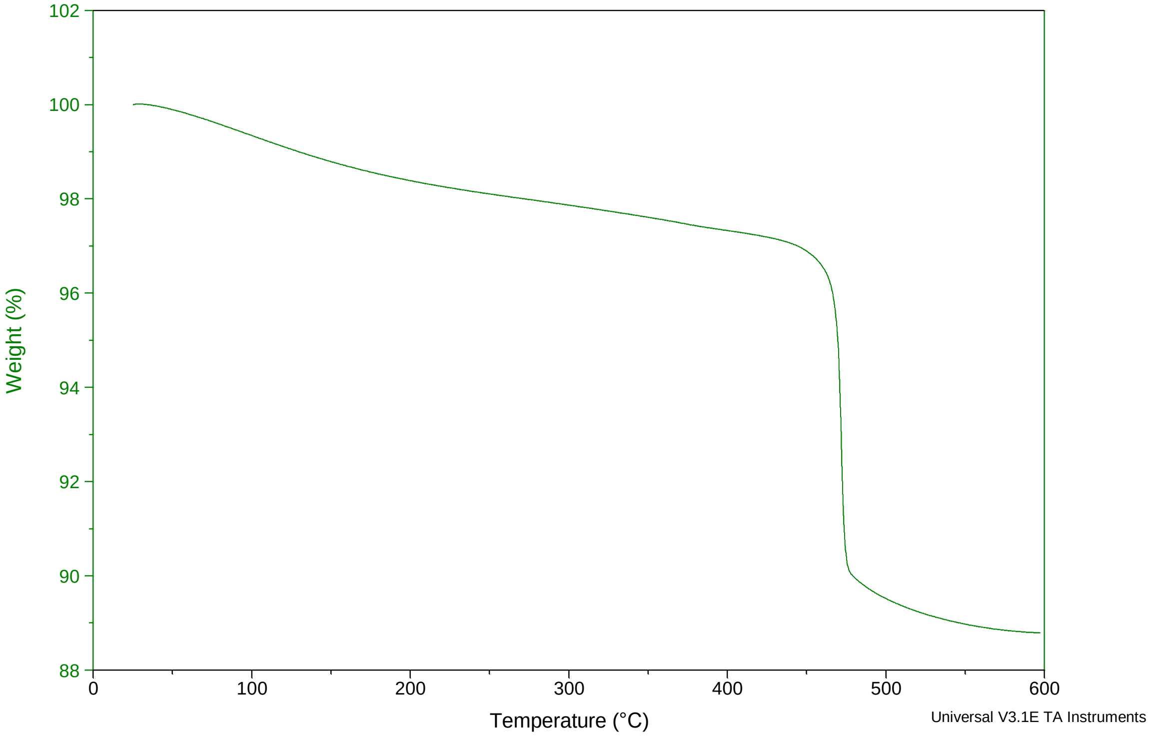


Figure 27. TGA Fe-ZSM-5 Treated with Ozone at 66Ddegrees C for 1 Hour

Appendix C – SEM Photographs

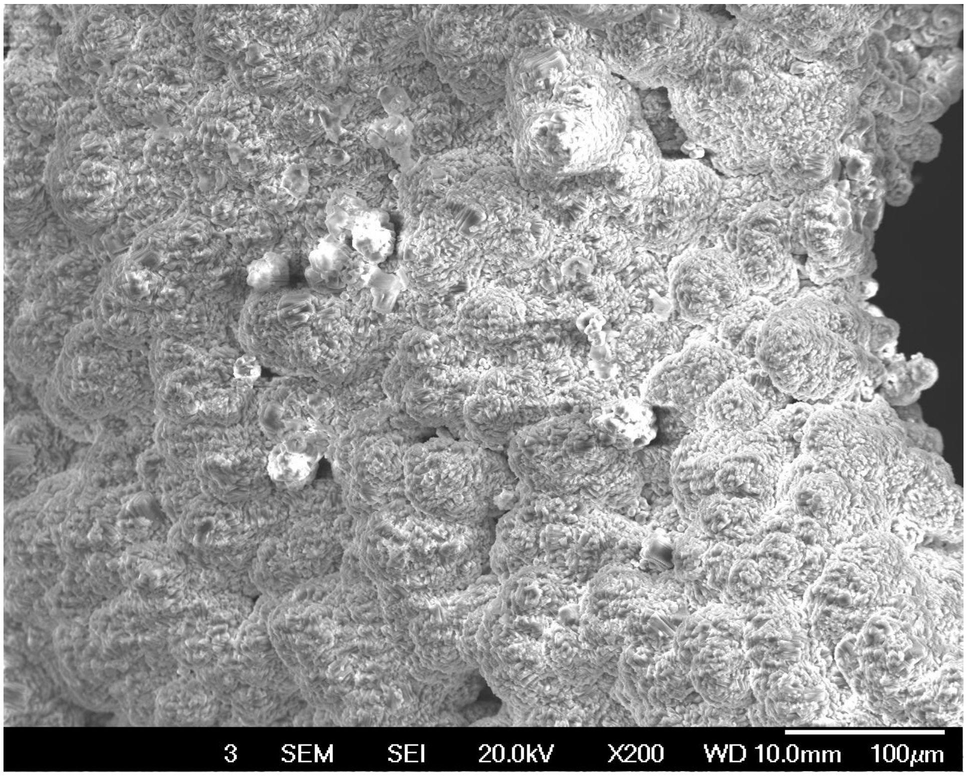


Figure 28. SEM at 200x magnification

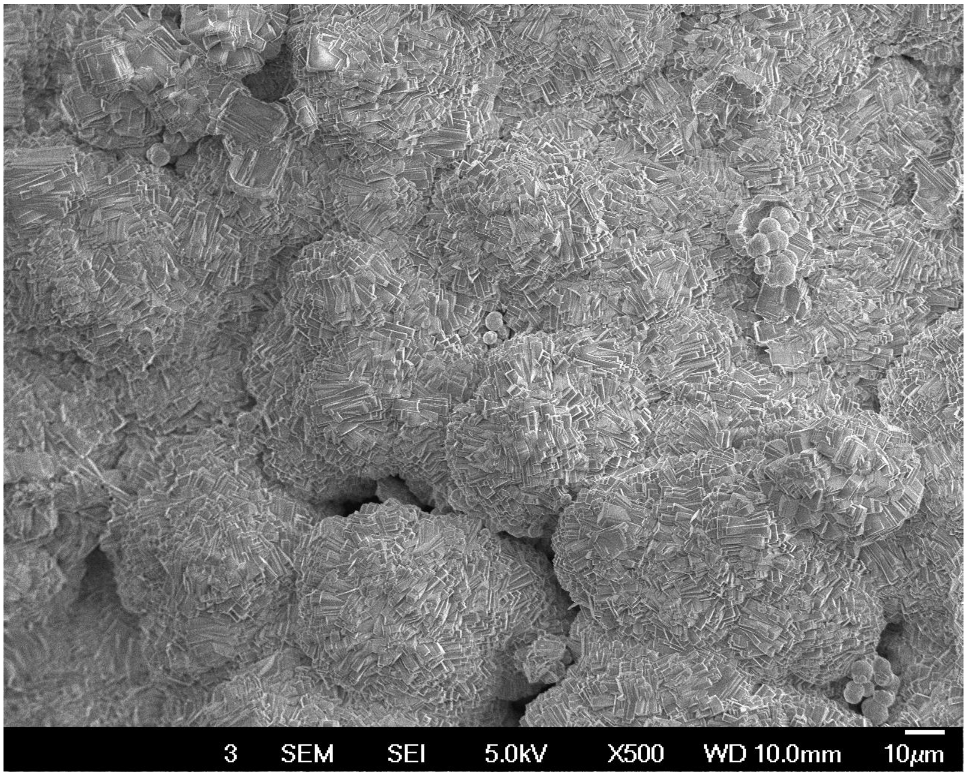


Figure 29. SEM at 500x magnification

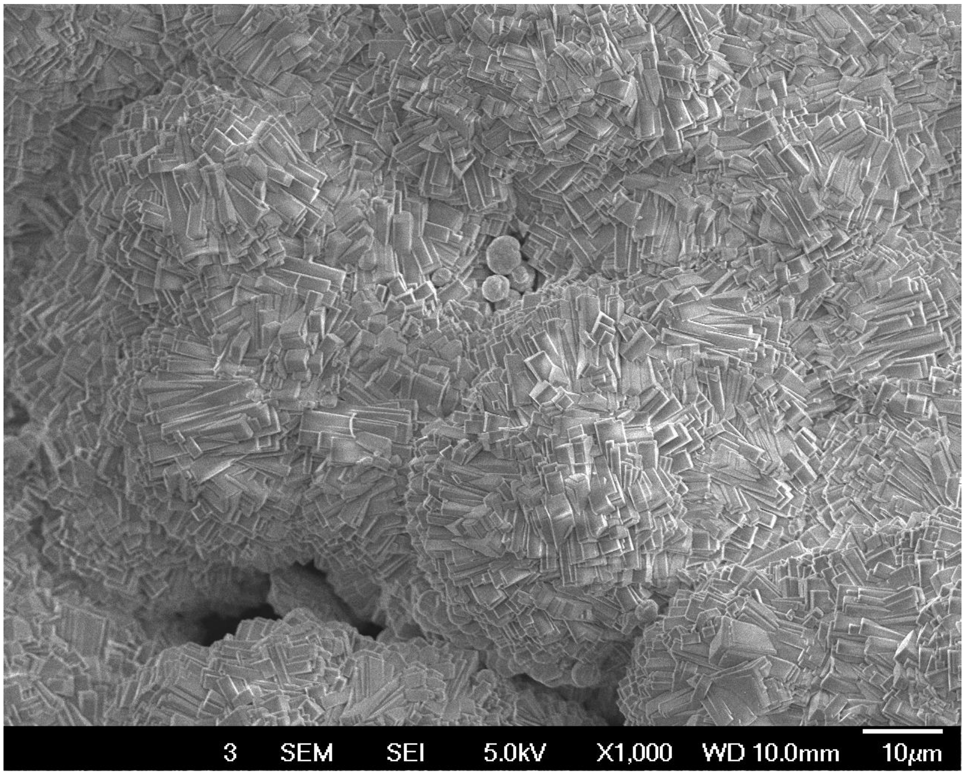


Figure 30. SEM at 1000x magnification