

Study on the Formation and Testing of a Fenton Nanocatalyst using SBA-15



A WPI Major Qualifying Project

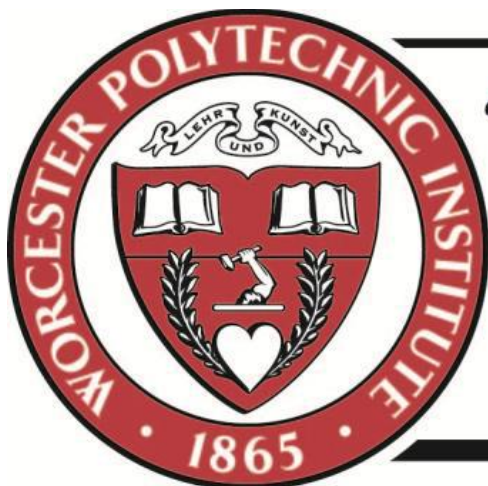
By Justin McLaughlin

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School of Environmental Science and Engineering



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Study on the Formation and Testing of a Fenton Nanocatalyst using SBA-15

*A major Qualifying Project Report submitted to the faculty of
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By

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On

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Abstract

With collaboration from Shanghai Jiao Tong University, a study of the formation and testing of a Fenton nanocatalyst utilizing SBA-15 mesoporous material was conducted. The main goals of this study were to find if different sources of iron and aluminum had an effect on the catalyst and to characterize the catalysts formed. Through the characterization it was found that the synthesized catalysts were not in the correct crystal formation and the main goal was therefore altered to find a procedure that formed the correct mesoporous structure with ferrous iron. Through testing and characterization it was found that increasing the period the catalysts were heated within the muffle furnace, was the best procedure for the formation of this mesoporous material with ferrous iron.

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Chapter 1: Introduction

In recent years there has been a growth in many industries. These industries create a variety of pollutants that can affect the environment. Many pollutants can be difficult to dispose of and can be dangerous if they are not dealt with correctly. If left unchecked, pollutants could be dumped into the environment at high concentrations which can be extremely dangerous, and some of the most troublesome pollutants are phenols. Some industries that produce these harmful pollutants are pharmaceuticals, petrochemical, and pulp mill (Xia et al., 2011). Many pollutants, such as phenols, must be treated properly or removed so that there is no risk to the surrounding environment. One of the main ways in which organic pollutants can be removed from waste material is through oxidation. Within this study it is attempted to form and test a Fenton Nano catalyst with the mesoporous material SBA-15. It is hoped that this catalyst can improve the process of oxidizing phenols (Gad, 2008).

Oxidation of phenols was studied, specifically oxidation through the use of hydrogen peroxide. The oxidation process requires a catalyst to quickly and efficiently oxidize material. Use of these catalysts has become known as advanced oxidation techniques (AOT). AOT are sometimes considered to be expensive but they can also be extremely effective. These techniques work by breaking down hydrogen peroxide to hydroxyl radicals to oxidize a material. These radicals are very reactive and can oxidize many pollutants efficiently. There are a few AOTs such as the use of ozone, a Fenton catalyst, and UV light (Neyens & Baeyens, 2003).

For this work we focused on the use of a Fenton catalyst, the use of ferrous iron to separate hydrogen peroxide into hydroxyl radicals. This process can be very effective at

improving the oxidation of a material but it has a maximum efficiency at a PH of about 3 or 2; this procedure also has the drawback of being unable to oxidize materials which are at high concentrations. These drawbacks within this procedure have led researchers to experiment with the use of different materials along with iron in order to improve the procedure(Xia et al., 2011). Within this lab the use of iron and the use of iron along with aluminum ions will be tested. One main reason of this lab is to test the effectiveness of the source of aluminum; aluminum can affect the charge upon iron. This is an important aspect of this procedure since ferrous iron (a 2+ charged iron ion) is effective to break down hydrogen peroxide to hydroxyl radicals while ferric iron (a 3+ charged iron ion) tends to break hydrogen peroxide down to hydrogen and water. By testing different aluminum sources it is hoped to find a source that will effectively leave iron with a 2+ charge.

The use of nanoparticles has been explored for quite a few years. Nanoparticles have unique properties that make them advantageous as catalysts. They are known to have an extremely high surface area which makes them perfect to improve the rate of a reaction. Within this lab the mesoporous material of SBA-15 will be used. This material allows for an easily recoverable catalyst while still providing the iron with a large surface area (Astruc, Lu, & Aranzaes, 2005; Nandiyanto, Kim, Iskandar, & Okuyama, 2009). This material was formed with different sources of iron as well as different sources of aluminum. Once this material was formed with iron or iron and aluminum it was tested as a catalyst to see if it will improve the oxidation procedure.

The initial study of this lab was the formation of the catalysts and the different sources of iron would affect the activity of the catalysts. However the catalyst did not react properly; it was found through characterization that the mesoporous structure did not form correctly. This led to a switch of objectives within this study. It was decided to focus on the formation of the correct mesoporous structure rather than the effects of different sources of iron since finding a better source of iron would mean very little if it was implemented within an incorrect structure.

Chapter 2: Background

Motivation

As stated above industrial processes can create dangerous pollutants. One of the most dangerous pollutants and the focus of this study are phenols. Phenols are compounds with an aromatic ring containing a hydroxyl group. These chemicals in high concentrations can be particularly intrusive to living beings. There have been many studies which have concluded that if organic beings are exposed to a high concentration of phenols it can cause many chemical problems with in the environment. One such study was conducted in Egypt on fish that were exposed to different phenols typically found in industrial waste water. It was found that the phenols caused problems with in the fish such as endocrine dysfunction, liver dysfunction, reduced growth rate, and phenol accumulate (Gad 2008). Phenols have also been known to be difficult to break down into less dangerous materials since they are a carbon double ring. To do this many methods have been developed to reduce phenols and other pollutants from industrial waste water.

There are quite a few ways to remove pollutants such as extraction, biodegradation, membrane-immobilized enzymes and oxidation. These separation techniques all have positive and negative effects.

Biodegradation is the breakdown of chemicals through the use of bacteria. In the area of biodegradation microbes are very good for removing pollutants. Many microbes belonging to the genus of *Pseudomonas* have been proven to break down phenols efficiently. The bacteria are able to accomplish this through the use of enzymes in their metabolic pathways (Mai,

Majcherczyk, Schormann, & Hüttermann, 2002). Another example of microbes being used to break down pollutants are the bacteria *Cryptanaerobacter phenolicus* which was proven to transform phenol into benzoate (Juteau, 2005). Microbes have proven to remove phenols fairly cheaply without introducing any unnatural chemicals to the environment; however, microbes have not been able to encompass a large range of pollutants. This is not beneficial for the treatment of most industrial waste since it will require the use of more processes in order to remove the other toxic material.

There have also been studies within cross flow filtration with the use of membrane immobilized enzymes to try to improve the degradation of phenols. Cross flow filtration is different from a normal filtration in the fact that the flow runs tangentially to the surface of the filter, this process helps in the fact that it is harder for material to build up. The species *Pseudomonas syringae* was used to create an enzyme which allowed for the breakdown of phenol rings. The purpose of this particular experiment was to find if cross flow filtration could improve the ability of the enzyme. It was found that in this process once the concentration reaches a certain point the rate of degradation begins to decrease (Akay, Erhan, Keskinler, & Algur, 2002). It can also be seen that just like the bacteria from which the enzyme was taken came. There is a limited variety of pollutants that this enzyme is able to effectively break down.

Extraction of phenols has also been explored, but these are mainly for the removal of phenols, and not the breakdown of the phenols. Extraction is a technique in removing a substance from a matrix; a simple example of extraction is using boiling water passing through coffee grounds to make coffee. This method does seem to be beneficial in the removal of

phenols in the food industry. One such branch is the olive oil industry which produces olive mill waste water which contains many organic compound including phenols (Jerma n Klen, 2011). The method of extraction offers the removal of phenols without the introduction of harmful chemicals or bacteria. The fact that the phenols are removed and not destroyed allows for a purification of the extract to obtain pure samples of different phenols. This process has not been fully explored especially for the removal of phenols from industrial waste.

One area that has gotten quite a bit of interest is the oxidation of phenolic compounds. Oxidation is the well-known reaction in which a material gives up electrons to another material such as oxygen. The oxidation of pollutants breaks the material down to simpler molecules which are less dangerous to the environment. Hydrogen peroxide has been used in many applications of waste removal as an oxidizer. It has been used in many applications for the removal of pollutants such as phenols, pesticides, cyanides, and sulphites. Hydrogen peroxide may be an excellent oxidizer but it becomes ineffective at high concentrations of some pollutants. The main method that is focused on within this study is Advanced Oxidation Techniques (AOT); these methods are very useful for improving the oxidation reaction. Three of the main methods for AOT are the use of ozone, UV light, and Fenton reaction (Acero & Gunten, 2000; Neyens & Baeyens, 2003; Shawaqfeh & Al Momani, 2010).

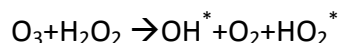
Basics of Advanced Oxidation Techniques

AOT is the use of a catalyst to form hydroxyl radicals from hydrogen peroxide which are better oxidizers than hydrogen peroxide. A few ways to form hydroxyl radicals are to use ozone, UV- light, and transition metals. The hydroxyl radicals are then able to oxidize the phenols and

other pollutants taking them apart to smaller and less intrusive chemicals such as carbon dioxide and water.

Ozone

The first of these AOT methods is the use of ozone. This process works by breaking down the hydrogen peroxide molecules as shown below.



This method splits the hydrogen peroxide into a hydroxyl radical and a deprotonated hydrogen peroxide radical while changing the ozone into an oxygen molecule. The process of using ozone and hydrogen peroxide is most widely known for its use in the treatment of drinking water. Although it is a good method it cannot completely oxidize all materials at normal conditions. This inability to oxidize completely has led to research in improving the process through the use of catalytic ozone (Acero & Gunten, 2000; Gulyas, von Bismarck, & Hemmerling, 1995; Neyens & Baeyens, 2003; Volk, Roche, Joret, & Paillard, 1997).

UV light

The use of UV light has also been explored to improve the degradation process of phenols. Just as the use of ozone this process is based upon improving oxidation by creating hydroxyl radicals.



This method has been shown to be beneficial for the oxidation of pesticides and other pollutants. Although this method is effective, it is considered expensive due to the cost of the

UV light. There have been multiple studies to maximize the efficiency and bring the price to a more manageable level (Neyens & Baeyens, 2003; Shawaqfeh & Al Momani, 2010).

Fenton catalysts

One AOT method that has been gaining interest is the use of ferrous iron as a catalyst for the formation of hydroxyl radicals; this method is known as using a Fenton catalyst. The ferrous iron as a catalyst breaks the H_2O_2 down to hydroxyl ions. Iron is normally shown as an ion, or iron salt, in water as seen below. This is known as a homogeneous catalyst since the catalyst is in the same state as the reactants.



The use of transition metals is by no means a perfect method of oxidation for the breakdown of phenols. Through testing it has been found that the ideal conditions for the use of transition metals as a catalyst is at a pH of about 3; this is a condition that makes the process of oxidation more difficult to achieve. The pH level must be brought down to 3, and then, before the waste water can be discharged the pH must be neutralized to not introduce a strong acid to an environment. The use of iron as the catalyst for the oxidation process can be expensive and also introduces heavy metals into the process which need to be removed before the waste water is discharged. These disadvantages have encouraged a variety of studies within the transition metal catalysts (Bautista, Mohedano, Casas, Zazo, & Rodriguez, 2008).

The homogeneous reaction described above has been known to work incredibly well but does have a major drawback. In the reaction above the iron is dissolved into the solution; this form of reaction was found to be impractical as the iron cannot be easily recovered and

requires additional steps to remove it. This has led into research of heterogeneous Fenton catalysts; a heterogeneous catalyst is a catalyst that is in a different phase than the reaction. These catalysts are not as effective as a homogeneous catalyst but the removal of iron is much easier. Many studies have been done to study the use of a heterogeneous catalyst such as zeolites, pillared clays, and mesostructured SBA-15(Chen et al., 2007; Park, Han, & Kim, 2012).

The most recent of studies have been on the testing of different metals along with iron. This research has mainly been done with iron as a heterogeneous catalyst, so that the iron is not dissolved within the phenol solution. The hope is that by testing new additional metals and new heterogeneous forms a catalyst can be found that is cheap, effective, and reusable. Some metals that have been tried are copper and aluminum along with iron. Copper was chosen because due to its properties it could lower the pH dependence of the reaction. This could lead to a better reaction at higher pH levels which could reduce the cost of the procedure drastically. Aluminum was chosen in the hopes that it could improve the activity of the catalyst. It was expected that aluminum might donate an electron to the iron to ensure that the iron remain as ferrous iron rather than ferric iron to maximize the efficiency of the catalyst. It was also expected that aluminum would provide additional support to a mesoporous structure. Both of the metals were found to be good additions for the Fenton catalyst and require further investigation (Xia et al., 2011). Some other metals that have been looked into include gold, manganese, and palladium (Navalon, Martin, Alvaro, & Garcia, 2010).

TOC measurements

The analysis machine that will be used in this experiment is a TOC-Vcpr(combustion catalytic oxidation/NDIR method, PC controlled, standard model). TOC stands for total organic



Figure 1 TOC-Vcpn machine used to measure total organic carbon

carbon, A TOC analysis machine can be very useful and applied to many areas; it can be used for measurements in drinking water, industrial waste water, semiconductor industry, and other areas as well. The method of TOC is used in many areas because it has such a wide range 0.05 to 250000ppm of carbon; the machine used in this study has a range of about 0 to 50 mg/L (Cooper, 2001). The analysis machine for this

experiment utilizes a method of

combustion catalytic oxidation/NDIR method; the machine does not directly measure TOC it measures TC (total carbon) and subtracts the amount of IC (inorganic carbon) to find the amount of TOC.

The way a TOC analysis machine works is by first analyzing the amount of CO_2 then oxidizing all of the carbon into CO_2 and then analyzing the final amount CO_2 . The oxidizing of carbon can be achieved in a number of ways, such as high-temperature combustion, UV light, or combustion catalytic oxidation. The method of combustion catalytic oxidation is a very common method to use in TOC analysis and utilizes a catalyst to oxidize all the carbon with in a

sample. After the sample has been oxidized it is then necessary to analyze the amount of CO₂. This can also be done in a few different ways such as NDIR (nondispersive infrared), and conductivity. The method of Conductivity measures CO₂ in the form of carbonate and bicarbonate species which increase the conductivity of water. The method of NDIR measures CO₂ in gaseous form at a specific wave length; this is the method that was utilized in the machine for this study (Cooper, 2001).

Nanoparticle catalysts

Some of the most interesting materials that are being looked into as catalysts are the use of nanoparticles. Nanoparticles are simply particles that are on the scale of about 1 to 100nm. Nanoparticles have unique properties; as a catalyst they have more surface area than larger particles. This provides a great improvement over a homogeneous catalyst which can be difficult to recover and even an improvement over previous heterogeneous catalysts which were not nearly as effective as a homogeneous catalyst. Due to its unique properties nanoparticle materials improve upon previous types of catalysts. (Xia et al., 2011) In this experiment we will be using SBA-15 a mesoporous material as the support for the chemicals. A Santa Barbara Amorphous (SBA) material has pore sizes that can range from 200nm to 3000 nm.

Mesoporous materials can be found in nature such as coral, charcoal, and fossilized remains. One mesoporous material is the sand found on the beach of Cancun. This material was found to have a larger surface area than normal sand (through the use of methods such as SEM and BET). These naturally found mesoporous materials are beneficial since the formation of

mesoporous particles can sometimes be difficult or expensive using a material that is found in nature would be beneficial; however the major drawback of using natural material is the fact that the pore size cannot be altered(Chen et al., 2007). The method that will be utilized within this study is the formation of a mesoporous silicate.

Chapter 3: Methodology

The method used for creating a mesoporous silicate is widely used with different sources of surfactants and silica sources. Figure 2 shows the procedure. First a micelle is created by using a surfactant. Silicate and a polymer are then used to form a nucleate within the micelle, within this study iron and aluminum sources were also added at this time. The surfactant is then removed this results in what is called a composite particle. In the final step the polymer is removed from the particle leaving a porous particle. The size of the pores within this material can be controlled by using different concentrations of styrene and silica (Nandiyanto et al., 2009).

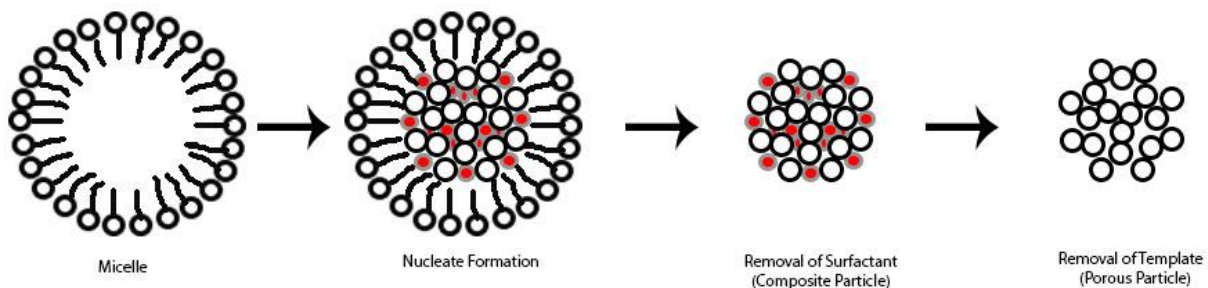


Figure 2. Formation of a Porous Material; 1) Formation of a micelle through the use of a surfactant 2) Formation of a nucleate within the micelle 3) Removal of the surfactant to leave a composite particle 4) Removal of template, usually a polymer, to form a porous particle

Materials

- P123(pluronic-123)- surfactant
 - $\text{HO}(\text{CH}_2\text{CH}_2\text{O})_{20}(\text{CH}_2\text{CH}(\text{CH}_3)\text{O})_{70}(\text{CH}_2\text{CH}_2\text{O})_{20}\text{H}$
- TEOS(tetraethyl orthosilicate)- silica source

- $\text{Si}(\text{OC}_2\text{H}_5)_4$
- Acid (HCl, H_2SO_4)
- Iron source ($\text{Fe}(\text{NO}_3)_3$, FeSO_4 , $\text{NH}_4\text{Fe}(\text{SO}_4)_2$)
- Aluminum source (Al powder, $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$)

Method 1 for the formation of the catalyst

The formation of the catalyst is very important. If the material is formed incorrectly it can result in the iron being inaccessible, which would reduce the effectiveness of the catalyst, or it could result in the iron being separated from the silicate which would result in a homogeneous catalyst. In this procedure the surfactant P-123 is used to create a micelle. Then the tetraethyl orthosilicate and iron are used to form the nucleate within the micelle. The surfactant is then removed through heating and filtration. Finally the polymers are removed from the catalyst through heating to high temperatures. The original procedure we used is as follows.

1. 2 g P123 was dissolved with 4mL of HCL and 75mL of water
2. 4.4g(4.7mL) of TEOS was slowly added with constant stirring
3. Iron and/or aluminum were dissolved into the solution with constant stirring
4. The pH of the solution was altered to about 3.5



Figure 3. Dissolving of iron and TEOS in a solution containing the surfactant P-123



Figure 4. Solution after having been stirred for 24 hours and ready to be heated to 130°C 1) left front flask is the formation of control SBA-15 2) right front flask is the formation of SBA-15 loaded with iron nitrate

5. The solution was stirred for 24 hours at 40°C Heated to 130°C for 24 hours

6. The material was then washed and the precipitate was filtered out



Figure 5. Formation of SBA-15 loaded with ferric nitrate after being heated at 130 degrees C to separate polymers from the mesoporous material



Figure 6. Vacuum filtration of SBA-15 loaded with ferric nitrate with distilled water to help remove polymers from particles

7. The material was then left to dry over night at 60°C

8. Once the material was completely dried it was ground in a crucible
9. Finally the material was placed in a muffle furnace to be heated at 500°C for 3 hours

Testing the degradation of methyl orange

In order to obtain reasonable parameters for the testing of the degradation of phenols we used the methyl orange as a trial pollutant. We used a simple procedure of dissolving the catalyst in solution and then pouring hydrogen peroxide and the pollutant in a flask and shaking in a heated bath. A spectrometer is then used to measure the wave length to see how well the pollutant was broken down. Our procedure for these tests is as follows.

1. First 0.1 g of the FE-SBA-15 catalyst was combined with 50mL of methyl orange and the mixture was stirred in a thermostatic oscillator at 40degrees C.
2. The pH of the solution was then adjusted to about 3.
3. The absorbance was measured through the use of a spectrometer (505nm wave length) before the hydrogen peroxide was added and at 30 min intervals for 3 hours afterwards.

Testing the degradation of phenol with a catalyst

Degradation of phenol is the main process of interest for this project. By using different catalysts it was hoped to study the effects of different catalysts and different metal sources on the degradation of phenols. The catalyst was first dissolved in the phenol solution and then the hydrogen peroxide was added. Samples were taken at 30 minute intervals and the catalyst was

removed. The solution was then diluted with water and measured using the TOC analysis machine. The TOC analysis machine does not measure just phenols it measures all organic carbon molecules, therefore within this study there will not be a total loss of TOC. What should be seen from an efficient catalyst is a significant loss of TOC. Below is the detailed procedure.

1. The phenol solution was altered to a pH of about 3.5.
2. 0.25g of catalyst was measured and dissolved into 50mL of phenol solution (concentration 100mg/L).
3. 0.25mL of hydrogen peroxide was added to the solution after a sample was taken for time zero.
4. Samples of 8mL were taken from the flask at 0,30,60,90,120 min.
5. The sample was then centrifuged to separate the catalyst. 5ml of the solution was diluted with 15mL of water and analyzed using the TOC analysis machine.

Method 2 for the formation of the catalyst

During the experiment it was found that the original method for the formation of the catalyst did not form a mesoporous structure. Because of this it was necessary to modify the process. Method 2 is modified from the original process by increasing the muffle furnace temperature to 600 degrees Celsius rather than 500 degrees Celsius and the time in the muffle furnace was increased from 3 hours to 5 hours.

1. 2 g P123 is dissolved with 4mL of HCL and 75mL of water
2. 4.4g(4.7mL) of TEOS was slowly added with constant stirring

3. Iron was dissolved into the solution with constant stirring
4. The pH of the solution was altered to about 3.5
5. The solution was stirred for 24 hours at 40°C
6. Heated to 130°C for 24 hours
7. The material was then washed and the precipitate was filtered out
8. The material was then left to dry over night at 60°C
9. Once the material was completely dried it was ground in a crucible
10. Finally the material was placed in a muffle furnace to be heated at 600°C for 5 hours

Method 3 for the formation of the catalyst

For the third method the muffle furnace temperature was kept the same at 500 degrees Celsius but the time was increased to 10 hours rather than 3 hours. Also a much smaller amount of HCl was used to dissolve the P-123, so this meant a longer time waiting for the P-123 to dissolve but the solution would have a higher pH. The way the iron source and TEOS was added was also slightly altered; the TEOS and iron source were first dissolved in water and then slowly added to the P-123 solution below is the total procedure.

1. 2 g P123 is dissolved with 0.2mL of HCL and 75mL of water
2. 3.2mL of TEOS and iron were slowly dissolved in water
3. The TEOS and iron were then added to the dissolved P-123 dropwise

4. The pH of the solution was altered to about 3.5
5. The solution was stirred for 24 hours at 40°C
6. Heated to 130°C for 24 hours
7. The material was then washed and the precipitate was filtered out
8. The material was then left to dry over night at 60°C
9. Once the material was completely dried it was ground in a crucible
10. Finally the material was placed in a muffle furnace to be heated at 500°C for 10 hours

Characterization

Once the catalyst of this study had been formed it was necessary to determine if the correct structure was formed from the procedure. It was also necessary to determine the properties of the created catalyst such as particle size and chemical composition. This can be achieved through procedures such as diffuse reflectance UV-vis spectrometry, x-ray diffraction, and SEM imaging.

X-ray diffraction

X-ray diffraction is an analytical method used to study materials and can give information on unit cell dimensions of the crystal material. X-ray diffraction is used mainly for identifying crystalline material. This type of identification is necessary in fields such as geology, material science, and environmental science.

An X-ray diffraction machine has three pieces, an x-ray tube, a sample holder and x-ray detector. The process starts by producing an x-ray and accelerating it through the x-ray tube; x-rays are generated by heating a filament to produce electrons. The electrons are then accelerated by applying a voltage. The electron ray then hits the material that is sitting on the sample holder. As the ray hits the sample the platform is rotated to a range of degrees. The sample typically diffracts the x-rays which are determined by the detector. The detector records the different angles of diffraction, giving spectra and intensities and is able to help identify certain qualities of the material (Dutrow & Clark, 2012).

Scanning Electron Microscope (SEM)

SEM images were the most helpful characterizations within this study. They provided a highly magnified picture of the particle so that we are able to determine the particle size and textures of the particles. An SEM works by firing an electron beam at a prepared sample, which has been coated by a layer of gold so that the electrons that are fired at the material will be scattered when they hit the sample. The scattered electrons are then detected as either secondary electrons, backscattered electrons or diffracted backscattered electrons depending on their interactions. The SEM machine is then able to take information on these scattered electrons and form them into an image of the sample (Swapp, 2012).

Chapter 4: Results and Discussion

Originally nine catalysts were formed using the first catalyst formation method; the various catalysts can be seen in Table 1. When the catalysts were formed they had distinct colors. A sample of pure SBA-15 was plain white while the samples with iron or iron and aluminum were various shades of brown and reddish brown, the difference can be seen in figure 7. This would indicate that the samples did contain iron. Since the catalysts had been ground into a fine powder they were easily stored in plastic test tubes and labeled as seen in figure 7.



Figure 7 comparison of catalysts 1) left tube contains control SBA-15 2) right tube contains SBA-15 loaded with ferrous sulfate

Table 1. Catalysts Formed from left to right 1) control SBA-15 2) Al-Fe-SBA-15 loaded with ferric nitrate and aluminum powder 3) Al-Fe-SBA-15 loaded with ferric nitrate and aluminum nitrate 4) Fe-SBA-15 loaded with ferric nitrate 5) SBA-15 control made with sulfuric acid rather than hydrochloric acid 6) Fe-SBA-15 loaded with ammonia ferric sulfate used sulfuric acid instead of hydrochloric acid 7) Fe-SBA-15 loaded with ferric nitrate (ran out of previous batch) 8) Fe-SBA-15 loaded with ferrous sulfate 9) Al-Fe-SBA-15 loaded with aluminum sulfate and ferric nitrate

No.	102801	103002	110601	110701	111001	111101	112002	112003	112701
Material Composition	SBA-15	Al-Fe-SBA-15	Al-Fe-SBA-15	Fe-SBA-15	SBA-15	Fe-SBA-15	Fe-SBA-15	Fe-SBA-15	Al-Fe-SBA-15
acid used in synthesis	4ml HCL	4ml HCL	4ml HCL	4ml HCL	1.3 ml H2SO4	1.3ml H2SO4	4ml HCL	4ml HCL	4ml HCL
Source/ amount of Fe used	\	Fe(NO ₃) ₃ ·9H ₂ O 0.524g	Fe(NO ₃) ₃ ·9H ₂ O 0.524g	Fe(NO ₃) ₃ ·9H ₂ O 0.524g	\	NH ₄ Fe(SO ₄) ₂ 2.15g	Fe(NO ₃) ₃ ·9H ₂ O 0.524g	FeSO ₄ * 7H ₂ O 0.404g	Fe(NO ₃) ₃ ·9H ₂ O .572g
Source/ amount of Al used	\	Al powder 0.035g	Al(NO ₃) ₃ ·9H ₂ O 0.851 g	\	\	\	\	\	Al ₂ (SO ₄) ₃ ·18H ₂ O 0.472
Measured pH during synthesis	\	3.47	3.36	3.55	3.45	3.4	3.59	3.55	3.38
Theoretical iron percent by weight	0%	5.26%	5.17%	5.40%	0%	5.40%	5.40%	5.40%	5.40%

Table 1 shows all the variations of the catalysts that were created. The material's row shows what each catalyst should contain. SBA-15 refers to the fact that each of the catalysts should be a mesoporous structure and the Al and Fe refer to each catalyst was loaded with. The row denoting acid specifies which acid was used to dissolve the surfactant P-123. For almost all the catalysts hydro chloric acid was used, except for when sulfate was used within the catalyst; for these situations sulfuric acid was used to not interfere with the iron source. The iron source and aluminum source are specified in the fourth and fifth rows. The pH was supposed to be adjusted to about 3.5 after the iron and aluminum were added; the specific pH that was achieved is shown in the sixth row. The final row specifies the theoretical percent of iron by weight in each of the catalysts. The goal of the iron wt. % for the catalysts containing iron is 5.4%, although some of them did not have the correct wt. % due to a mathematical error. The mathematical errors came from neglecting the amount of aluminum that was added.

Each catalyst was designated a specific number according to the date and sequence in which they were started. They were also labeled with the materials that they theoretically contain. A control was the first catalyst that was created, this catalyst was labeled No. 102801 and had no metal added to it. Another control was later created and was labeled No. 111001. This control group was chosen to ensure that there were no differences between the use of hydro chloric acid and sulfuric acid for adjustments.

The material Fe-SBA-15 made from ferric nitrate was created at two separate times because the first amount of the specified catalyst was depleted due to extensive testing with

methyl orange to determine parameters. These catalysts were labeled No. 110701 and No. 112002. These catalysts were made for testing and comparison purposes since ferric nitrate had been used and tested in similar catalysts. The material Fe-SBA-15 was also made with ammonia ferric sulfate and ferrous sulfate and was labeled No. 111101 and No. 112003 respectively for two samples. These catalysts were made to test how well the different sources of iron would affect the catalyst and if the charge of the iron introduced to the mesoporous material had any effect on the efficiency of the catalyst.

Since part of the original goal was to test the addition of aluminum, three additional catalysts were formed with the composition Al-Fe-SBA-15. The iron used for each of these samples was ferric nitrate; the aluminum source used for these catalysts was aluminum powder, aluminum nitrate, and aluminum sulfate, and each was labeled No. 103002, No. 110601, and No. 112701 respectively. These catalysts were created in order to find if the source of aluminum had any effect on the catalyst. Three sources were used: one with solely aluminum (aluminum powder), one with nitrate the same material that was used to supply the iron that theoretically was removed in the process (aluminum nitrate), and one with sulfate a material that would theoretically not be removed during the process (aluminum sulfate).

Degradation of Methyl orange

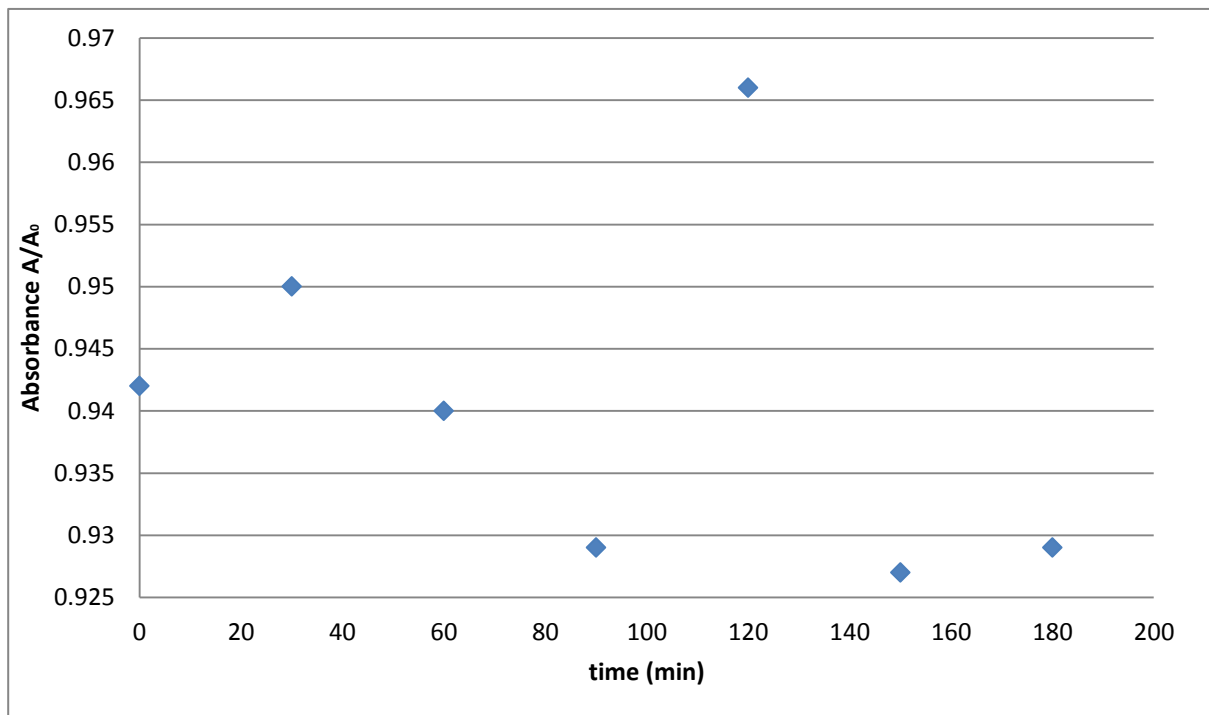


Figure 8. Test of Degradation of methyl orange using Fe-SBA-15 loaded with ferric nitrate; y axis is the absorbance measured by the spectrometer a higher absorbance indicates a higher concentration of the methyl orange.

To determine reasonable parameters for pollutant degradation test methyl orange was used. In figure 8 the results of the tests can be seen. A spectrometer was used to obtain these results. The spectrometer was used to view how much light at a specific wave length was absorbed by the solution at any given time. It can be seen that as time progressed the methyl orange was degraded. The catalyst was effective at activating the hydrogen peroxide to break down the methyl orange. The reaction came to an end at about 100-120 minutes; where the plot levels out (figure 8). It was difficult to determine the exact time as there were outliers at both time zero minutes and 120 minutes. These outliers were most likely due to an incorrect wavelength setting on the spectrometer because the samples continually changed color because of catalyst that could not be separated; it was difficult to establish a wavelength that

would give consistent readings. The fact that the wavelength changed indicates that the catalyst became homogenous with the reaction which was trying to be avoided. This fact was not fully realized until further testing was completed. Since this was only a test to decide parameters the outliers and incorrect measurement process were disregarded. It was decided to run the phenol degradation tests for only 2 hours since the hydrogen peroxide would not be active after about 90 minutes.

Testing of catalysts' activity for phenol degradation

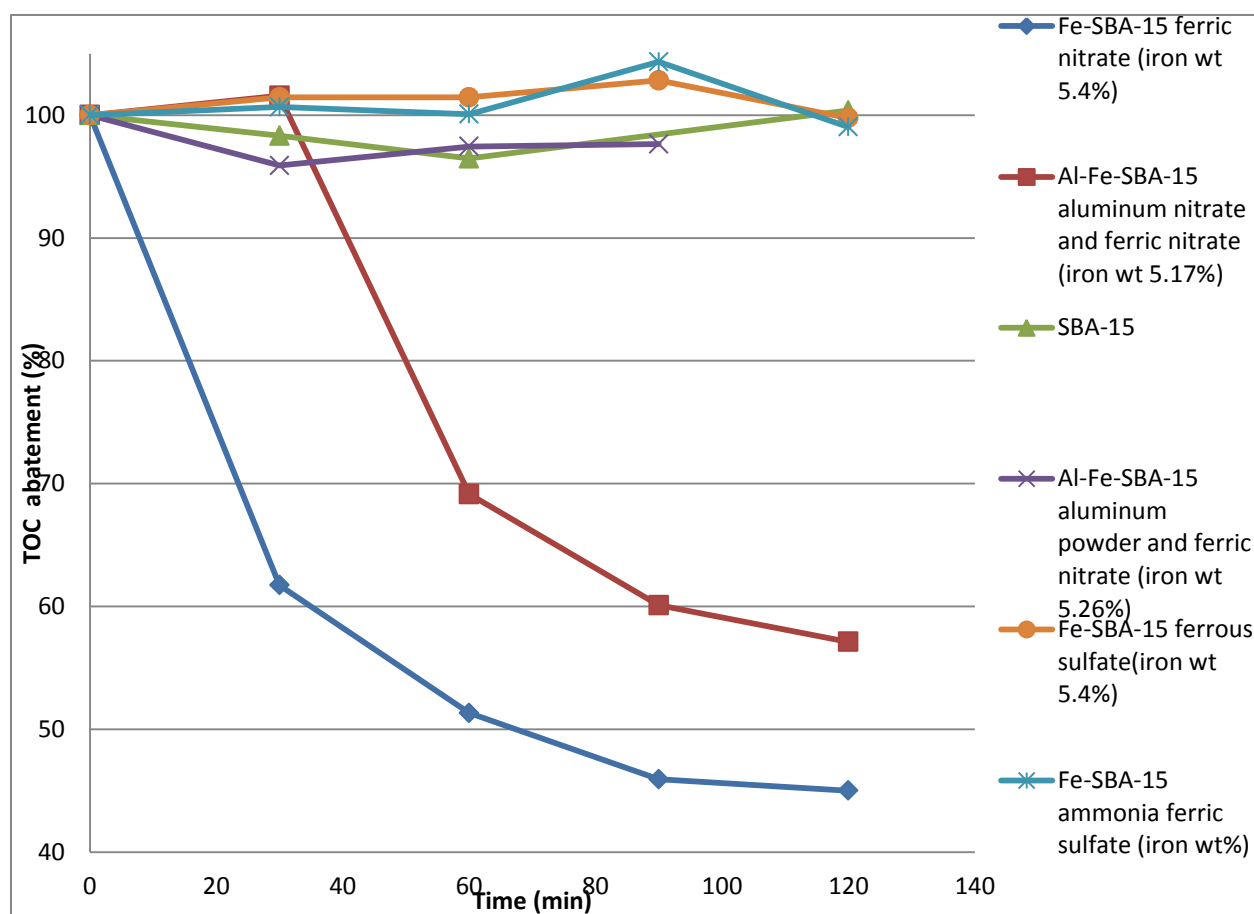


Figure 9. The TOC results from the use of the catalysts TOC abatement % refers to the percentage of TOC left in the solution for a reaction after a given time.

In figure 9 it can be seen that several of the catalysts were tested on how effective they are for the degradation of phenols. In this graph the y-axis shows TOC abatement which refers to how much total organic carbon is left during that point in the reaction. This is the measurement we used for how much phenol was degraded in each solution; this measurement does not measure solely phenols but all total organic carbon. The TOC abatement will not reach zero in this experiment since there is other organic carbons within the solution. The x-axis displays how long the phenol solution was allowed to react with a catalyst present. After the catalyst was removed the samples were stored in a refrigerator. In this experiment it was expected to see that the materials that contained iron would act as catalysts releasing the hydrogen radicals and initiating the breakdown of the phenolic solution. It was also expected that materials with both aluminum and iron would experience less TOC abatement since these materials were supposedly superior due to the addition of aluminum.

Figure 9 displays that only a few of the catalysts were effective. SBA-15 was the control in this experiment which did not degrade the phenol at all, as expected. Materials which were loaded with metals from sources of ferric nitrate or ferric nitrate and aluminum nitrate were effective in degrading phenols. The tests these catalysts were involved in reached lower TOC %. It was seen during the degradation tests that these 2 materials in the final solution had a reddish tint even after centrifugation. This could indicate that iron had been dissolved into the solution and would be difficult to remove. When iron is dissolved into the solution it becomes a homogenous catalyst and even though it is effective as a catalyst it is difficult to remove from the solution. The use of a homogeneous catalyst is not part of the study; it was desired to test a mesoporous catalyst.

The other catalysts that were loaded with ferrous sulfate, ammonia ferrous sulfate, and aluminum powder and ferric nitrate did not show any degradation of phenols. It seems that instead of degrading the phenols these catalysts inhibited the reaction and saw high TOC % even after 2 hours. This was a very curious outcome for the aluminum powder; this material should have been only slightly different from the material with an iron source of ferric nitrate which did act as a catalyst. This could be an indicator that the aluminum powder source inhibits the reaction because it is improperly integrated into the mesoporous structure. Further study is required to find how aluminum powder acts with a mesoporous material and iron.

The other two materials, with metal sources of ferrous sulfate and ammonia ferrous sulfate, which did not act as catalysts both contained sulfate. With the catalysts that had a nitrate source the nitrate should have evaporated off during the formation process. Sulfate on the other hand was not removed from the catalyst; it would remain as part of the material catalyst. In principle sulfate should not have affected the materials capability as a catalyst, but unfortunately this did not seem to happen. The materials with sources of metal from sulfate did not act as catalysts; there was no indication that the iron material dissolved in solution and acted as a homogeneous catalyst like the material with metal sources from nitrate. It would be expected that if the incorrect structure was created at least some of the iron would have been dissolved and acted as a catalyst, but the sulfate source did not allow the iron to be used as a catalyst at all. With this result it can be inferred that sulfate inhibited the reaction for this catalyst.

The results shown in figure 10 reveal the fact that the catalysts that were created either blocked the iron from the reaction or allowed the metals to dissolve in the solution, neither of which would indicate catalyst had formed.

Characterization of the catalysts

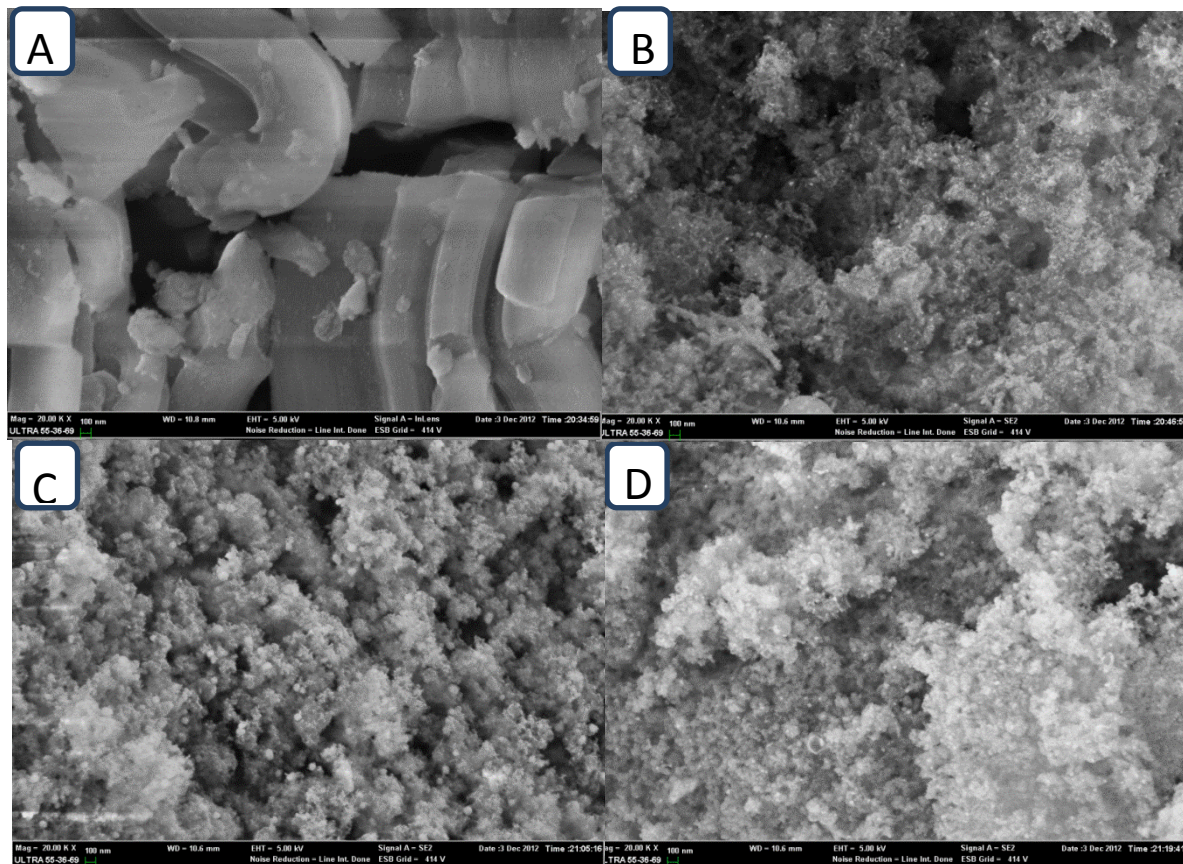


Figure 10. SEM images 20000X of materials A) SBA-15 B) Al-Fe-SBA-15 (aluminum nitrate, ferric nitrate) C) Fe-SBA-15 (ammonia ferric sulfate) D) Fe-SBA-15 (Ferric Nitrate)

It was very important to characterize the catalysts in order to know if the mesoporous materials were formed correctly. A sample of four materials that were created were taken and looked at through a scanning electron microscope and studied through x-ray diffraction, both large and small angles. The four materials that were chosen to be characterized were the SBA-

15 control, Al-Fe-SBA-15 (aluminum nitrate, ferric nitrate), Fe-SBA-15 (ammonia ferric sulfate), and Fe-SBA-15 (ferric nitrate). The SBA-15 control was chosen as a reference to compare the structure of materials; the control would have no interference and therefore should have the best mesoporous structure. Al-Fe-SBA-15 (aluminum nitrate, ferric nitrate) and Fe-SBA-15 (ferric nitrate) were chosen because these were the only materials that were effective as catalysts. It was necessary to characterize these catalysts to see if they formed the correct structure and if they acting as homogeneous catalysts. Finally Fe-SBA-15 (ammonia ferric sulfate) was characterized to understand why the materials that included sulfate did not act as a catalyst.

In figure 10 the SBA images of four separate catalysts can be seen at 20000x magnification. The catalysts were supposed to form into structured particles with pores of 50-500nm wide. The pores would only be visible through the use of a transmission electron microscope which was not used.

The upper left image is of the control catalyst SBA-15, this sample formed very large and structured particles; this is the outcome that was hoped for while trying to form a mesoporous structure. The SBA-15 control sample formed strands with a width of 500-1000nm. The other catalysts where not nearly as well structured as the control SBA-15. The other samples created small conglomerations rather than the structured material that was desired. The small conglomerations show that the materials were formed incorrectly and lead to incongruities which may explain some of the phenol degradation tests. This result could be due to the addition of the metal source which may not have been completely removed during formation

of the process. If chemicals such as the polymers, nitrates, sulfates, and ammonias were not removed they could cause detrimental damage to the structure of the material. The extensive array of small particles could also be due to an incorrect addition of TEOS and iron; if these substances are added too quickly it could lead to incorrect formation within the micelles which would result in the structures being incorrect as well.

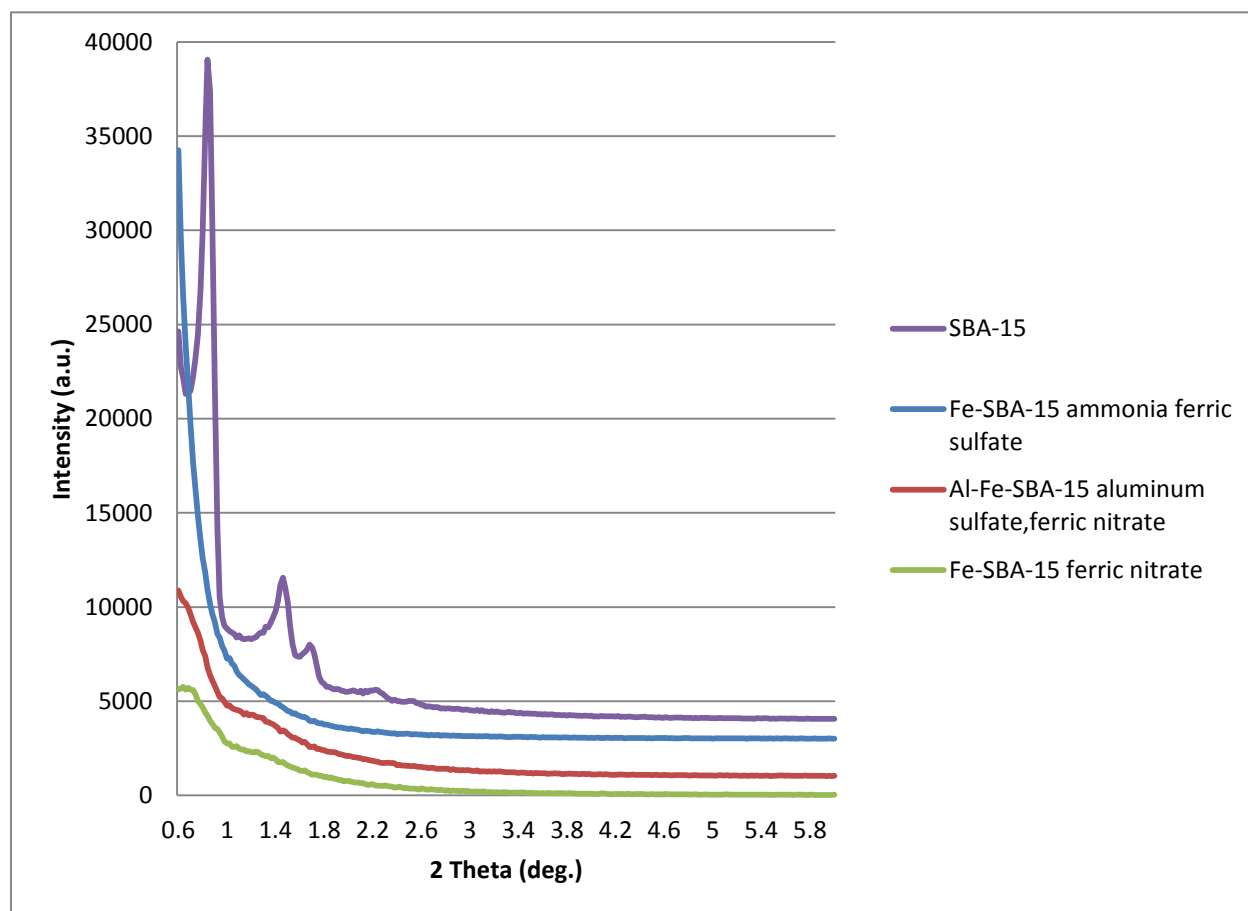


Figure 11. Small angle XRD of catalysts typical peaks of a mesoporous structure would be at about 1, 1.6, and 1.7

For characterization through x-ray diffraction measurements were taken for both large and small angles. The small angle measurements, seen in figure 11, were taken from 0.6- 6.0 (deg). The typical peaks for a mesoporous structure would be at about 1, 1.6, and 1.7 2θ (deg). SBA-15 was the only material which exhibited these peaks. The other materials formed very

small peaks or barely any peaks at all which reveals that the mesoporous structure was not created properly. The catalyst with the iron source of ferric nitrate formed the least mesoporous structure. This would allow for iron to be separated from the silicate structure and therefore dissolve in the solution or be trapped within the silicate structure and unable to react. The catalyst with metal sources of ferric nitrate and aluminum nitrate formed a slightly better structure which is what was hoped for. Aluminum was added to create a more stable mesoporous structure which was accomplished but the structure was a well-defined mesoporous structure. The material with an iron source of ammonia ferric sulfate showed the best peak besides the control and this could mean that the mesoporous structure was beginning to form but did not fully form correctly. Unfortunately none of the materials with iron sources formed a well-defined mesoporous structure

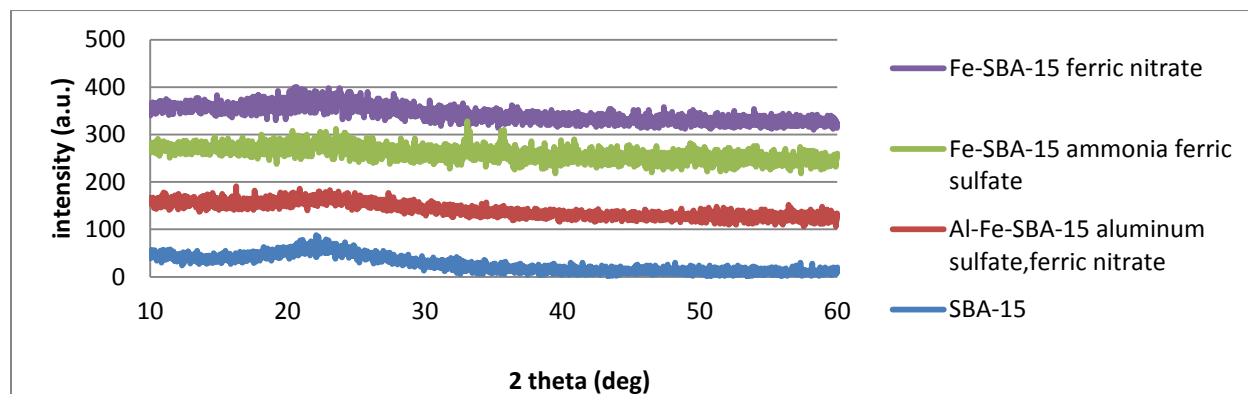


Figure 12. Large angle XRD of Catalysts

Within the large angle X-ray diffraction, seen in figure 12, many of the same results from the small angle x-ray diffraction were reaffirmed. In this type of measurement for a mesoporous structure a peak at about 22 2θ (deg) is typical (Li et al., 2005). Again, SBA-15 was the only catalyst to show this peak clearly defined. The other catalysts did not show a clear enough peak to even warrant that a mesoporous structure had been created. The catalyst that

was loaded with ammonia ferric sulfate showed peaks at around 33 and 35 2θ (deg). These peaks are typical of an iron oxide as seen in previous studies (Xiang et al., 2009). These peaks show that the formation of this catalyst did not happen correctly and formed other materials that could be detrimental to the mesoporous structure or could have resulted in the inhibition of iron as a catalyst. These characterizations show that these materials did not form the correct mesoporous structure and that this method of formation was flawed.

Testing of improved synthesis methods

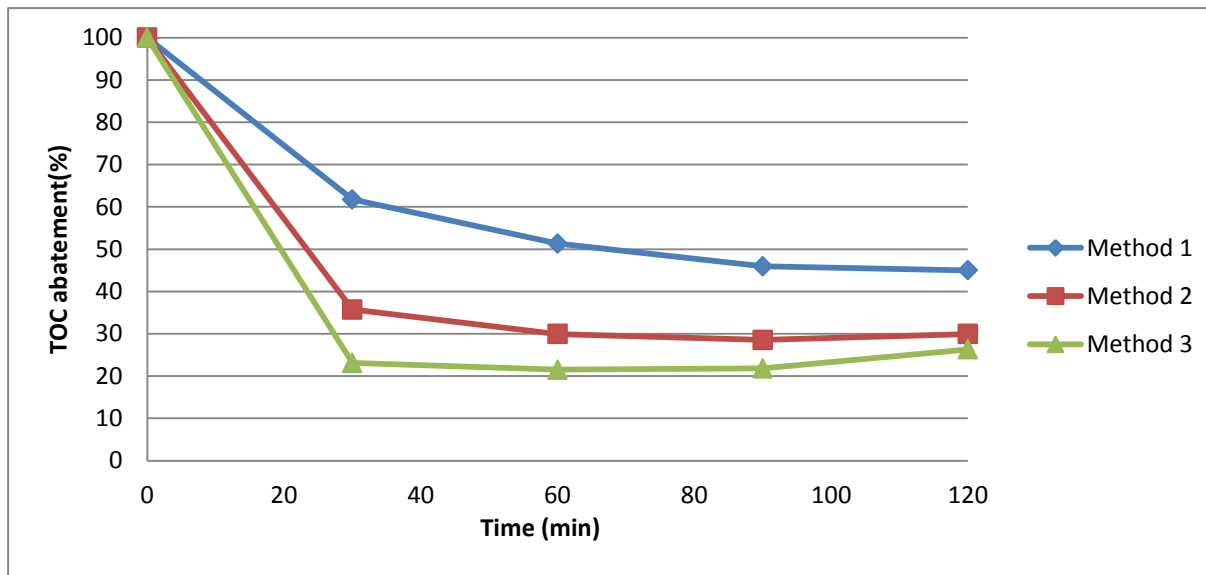


Figure 13. TOC abatement with catalysts formed through the 3 different methods all using ferric nitrate as the iron source Method 1) the original method used to form the catalyst. Method 2) improved method formation by increasing calcination and time. Method 3) improved method formation by increasing calcination time.

To improve the formation method two additional methods were developed and tested. The methods were only tried to form the material Fe-SBA-15 with an iron source of ferric nitrate. Only one iron source was used because there was not enough time to form materials with different metal sources and it was more important to establish a correct formation method. Similar materials have also been studied in the past and have given significant

indication that a correct mesoporous structure could be created (Li et al., 2005; Xiang et al., 2009). In method 2 the calcination temperature and period were increased from 500 to 600 degrees C and 3 to 5 hours respectively. In method 3 the calcination period was increased from 3 to 10 hours. Also in method 3 the way of adding TEOS and iron was slightly changed to introduce them more slowly to the dissolved P-123. The calcination period was focused on due to the belief that extra substances had not been completely removed within the last stages.

In fig. 13 the results for the degradation tests of each of the methods can be seen. The figure shows that method 2 created a material that was a more effective catalyst than the material from the original method. Method 2 however did have a final solution that was tinted by iron, it was slightly red, but the color was much less intense than in previous tests of the material formed by method 1. These results indicate that the mesoporous structure was more well-defined.

It can also be seen that method 3 was even more effective than method 2 at creating a catalyst. The catalyst formed by method 3 improved the degradation of phenols in the first half hour by about 80%. It should also be noted that during the testing of the materials made from method 3 there was no signs of the iron being dissolved in the final solution. The improved method of adding the TEOS and iron together drop wise allowed for an easier entry into the micelles created by the surfactant. This establishes better formation of a structured particle that was looked for in the SEM images. The higher calcination also helped to remove any unwanted material that the previous calcination could not remove.

Characterization of New Methods

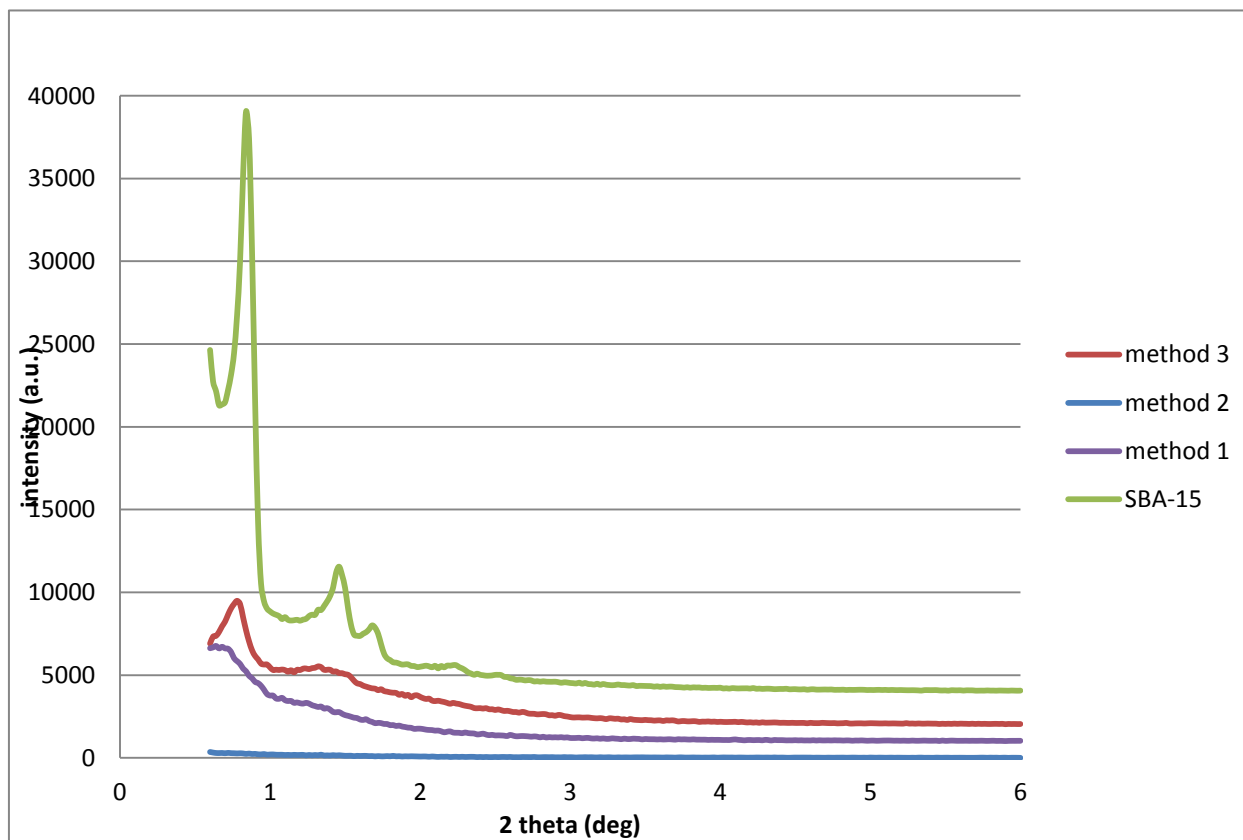


Figure 14. Small angle XRD of the 3 different methods for forming catalysts, methods 2 and 3 had increased calcination temperatures and time

Characterization of methods 2 and 3 were also conducted although due to time constraints only the small angle x-ray diffraction was completed; the results can be seen in figure 14. It can be seen that the control SBA-15 was the best formed mesoporous structure most likely due to minimum interference from loading with ferric nitrate. Method 2 showed no peaks at all which is unexpected because it was believed to be an effective catalyst from the degradation tests and the fact that very little material dissolved in the solution indicates the possibility of at least some form of mesoporous structure. All previous materials showed at least a single peak across the range. The flat result could be due to an incorrect packing of the sample since it is inconsistent with all previous characterizations of the developed materials.

Method 3 shows peaks at the desired spots at a much higher intensity than the peaks of method 1. This shows that method 3 was the most effective method found in this study for creating a mesoporous material loaded with iron; further work would be needed to verify the nature of the catalysts formed by method 2.

Recommendations

One of the clear recommendations from this project is to use method 3 if possible to make sure that the mesoporous material is formed correctly and that the solution is properly heated to remove chemicals that can cause interference. This should ensure that the material is the correct structure and that the iron catalyst will not become homogeneous. Another recommendation is to continue this research by using method 3 and different sources of iron and aluminum. In this study due to time constraints it was impossible to do this; this is the next expected step for this study. It could also be beneficial to further study method 2

Although method 2 was not as good at forming a functional catalyst as method 3 it would still be beneficial to characterize the material created. It would be valuable to see if the material formed by method 2 had a better mesoporous structure than the material formed by method 3. It is difficult to determine how the material was affected by the higher temperature in the muffle furnace. Further characterization of the material is necessary to determine how the higher calcination temperature effected the material

An action that should always be taken in this type of study is to characterize the catalyst before testing if at all possible. This will ensure that the catalyst is in the correct formation and that there is not a waste of time and materials by testing the uncharacterized catalyst. In this

study multiple degradation tests were done with the materials created; it would have been beneficial to first characterize the materials to not waste time and focus on obtaining the correct mesoporous structure.

Due to time constraints it was impossible to finish all desired tests. If given the opportunity to continue the research I would recommend testing the mesoporous material created by method 3 with the iron sources we originally attempted to incorporate. I would also recommend testing an iron source of ammonia ferrous sulfate to compare with the iron source of ammonia ferric sulfate. I would strongly encourage these tests to compare how effective they are since the difference between ferric and ferrous ions are essential to how well the catalyst works.

Chapter 5: Conclusions

The first main conclusion was the fact that when making a catalyst with the original method the use of a sulfate source inhibits the reaction. Sulfate severely interferes with the degradation of phenols; as to how sulfate interferes with the reaction is not completely known at this point. Sulfate could have been left behind in the formation of the catalyst and could have interfered with the reaction or it could have been responsible for a formation of an incorrect structure blocking the iron which was necessary for the catalyst. Further study is required to discover how sulfate interacts with the SBA-15 structure.

Although the sulfate samples were not effective there were some effective formations of the catalysts. It was found that the formation of a mesoporous catalyst loaded with iron through a hydrothermal process is possible. The original method for the formation of the catalyst was ineffective and was seen to create an incorrect mesoporous structure; however method 3 appears to have created a mesoporous structure confirming that the process was on the right track but needed additional time in the calcination period to remove excess material. The formation of a mesoporous material from method 2 is unclear and needs further characterization.

Method 3 created the best catalyst in this study. The catalyst that was created showed the correct mesoporous structure and showed no signs of iron dissolving into the solution. The catalyst was also very effective at degrading phenols. When tested this catalyst showed a 70% decrease in TOC within the first 30 minutes of the test. It is difficult to say why method 3 created a catalyst that was more effective than method 1; method 1 created a homogeneous

catalyst which is supposedly the most effective kind of catalyst. Perhaps in method 1 iron particles were left as ferrous ions, making them less effective, or were blocked due to being trapped within the silicate mass. To determine the definite reason that method 3 was more effective than method 1 further study is required.

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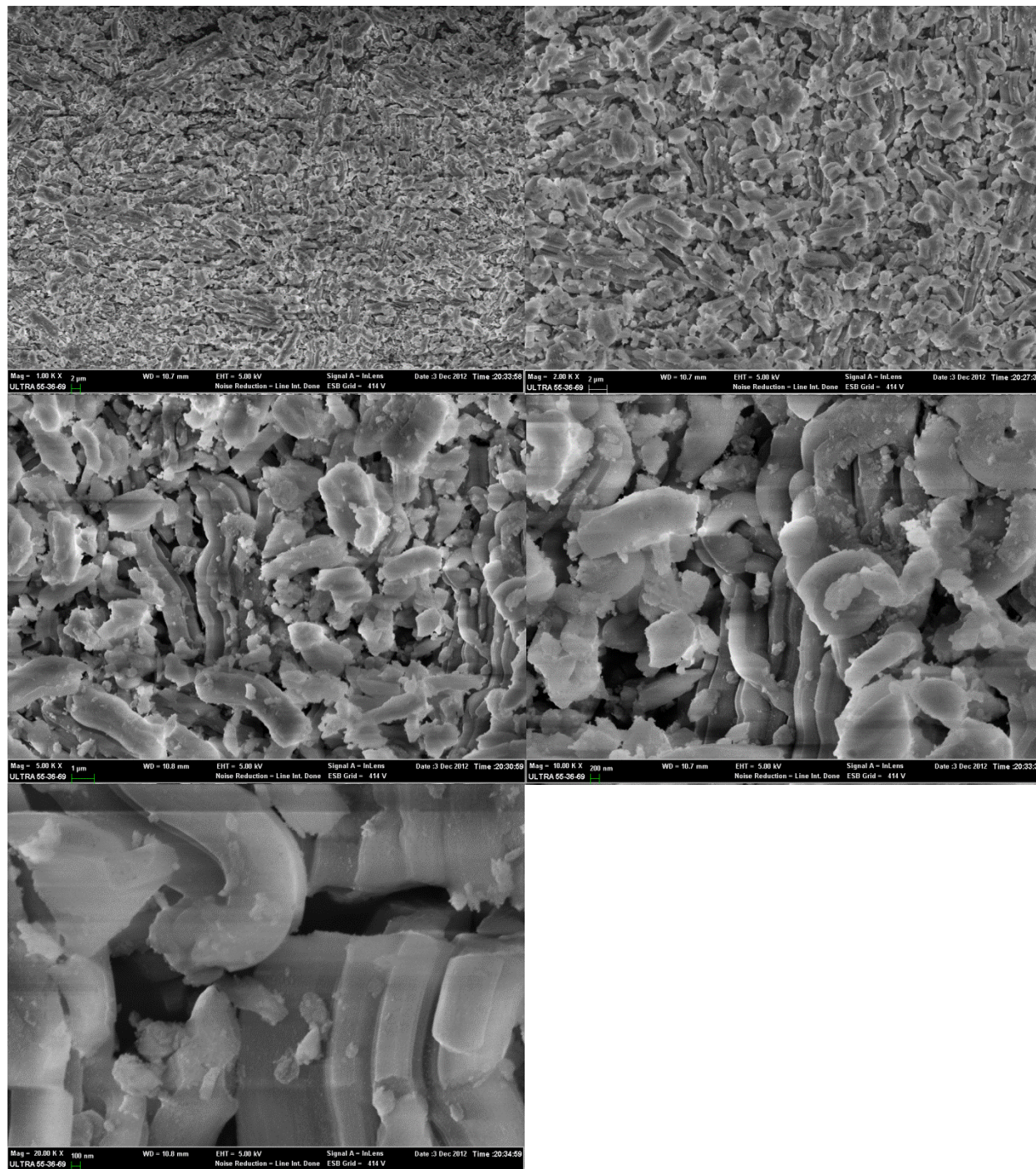
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Appendix

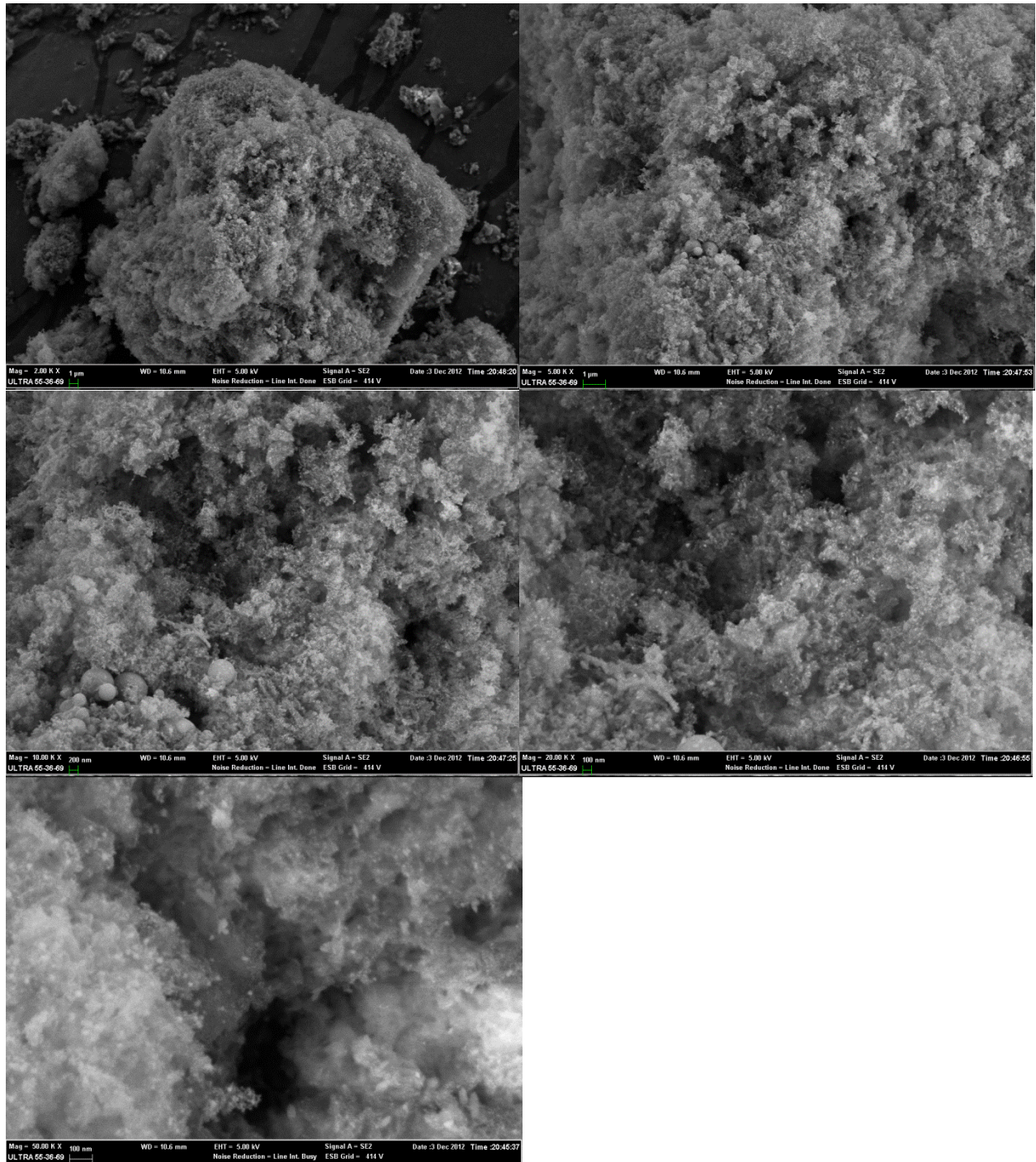
SEM Images

These are various SEM images that were not used in this paper they were taken of the 4 materials that were characterized at 2KX, 5KX, 10KX, 20KX, and 50KX magnification

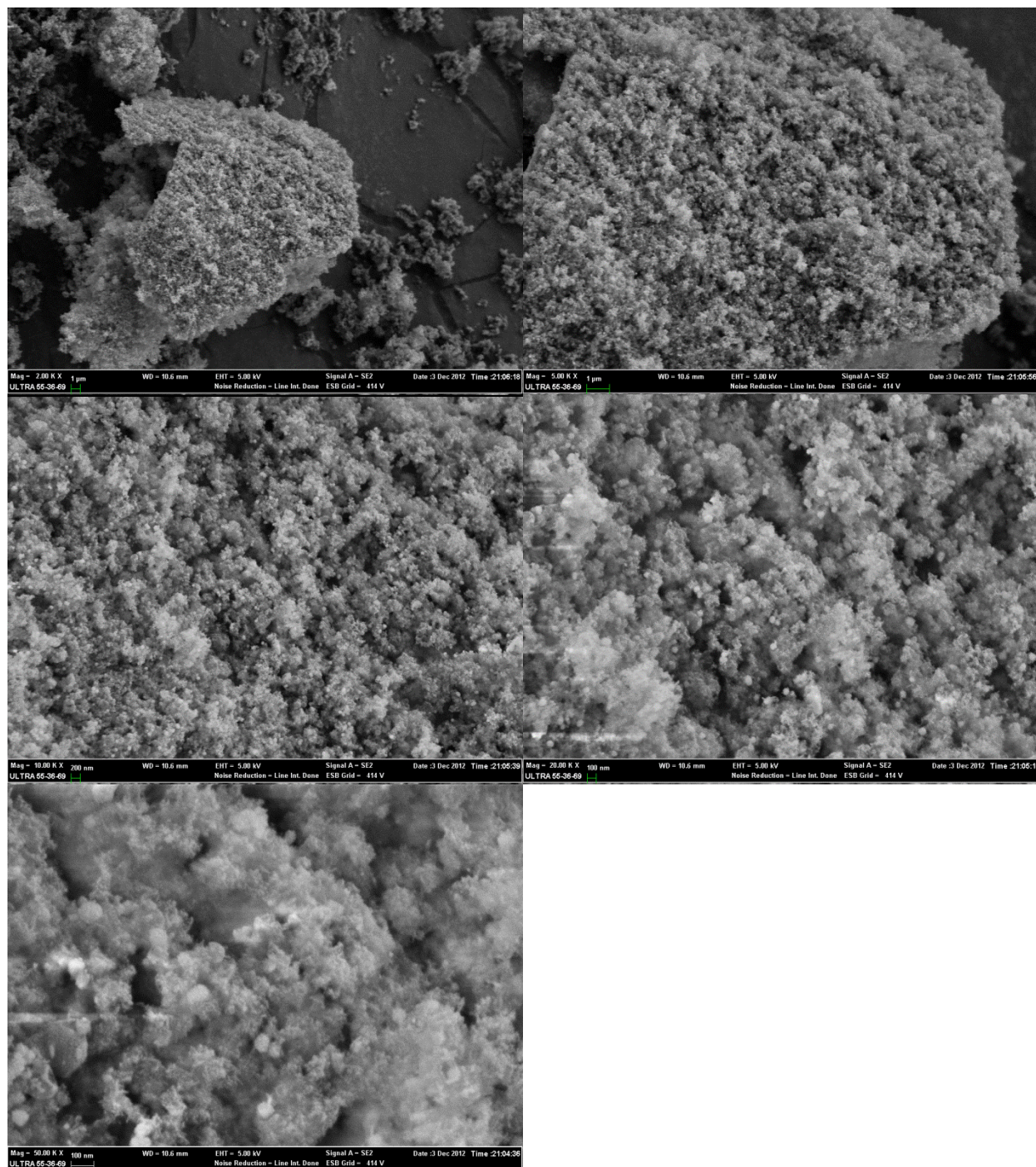
SBA-15



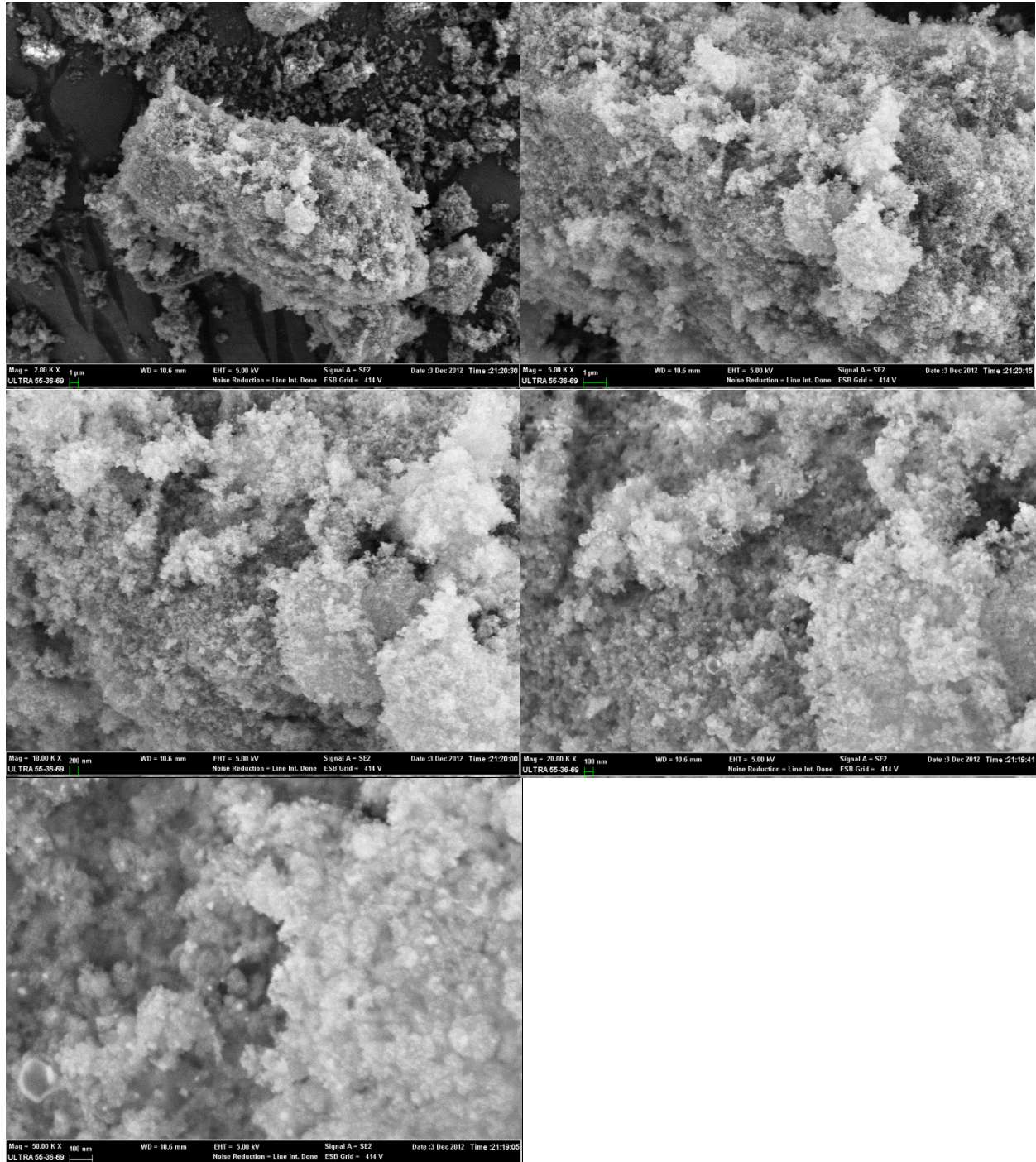
Al-Fe-SBA-15 (aluminum nitrate, ferric nitrate)



Fe-SBA-15 (ammonia ferric sulfate)



Fe-SBA-15 (Ferric Nitrate)



Analysis of solution after degradation process

This analysis was obtained from a separate lab and shows that with the original method an iron source of ferric nitrate led to over 20% of the iron being dissolved and with an iron source of ammonia ferrous sulfate almost no iron was dissolved.

Catalyst	Fe-SBA-15 ferric nitrate	Fe-SBA-15 ammonia ferrous Sulfate
Percent of iron dissolved	21.12%	0.232%