## RICE UNIVERSITY

# Adsorptive Removal of Sulfur Containing Compounds from Fuels using Metal Loaded Zeolite Y

by

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## A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE

## **Master of Science**

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HOUSTON, TEXAS MAY 2017

#### ABSTRACT

# Adsorptive Removal of Sulfur Containing Compounds from Fuel using Metal

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The removal of sulfur containing compounds from liquid fuels is becoming increasingly important. The International Maritime Organization (IMO), the governing body that regulates international maritime trade, has recently passed regulation that significantly decreases the total allowable sulfur content in fuels in order to reduce  $SO_x$  emissions from merchant vessels. Furthermore, certain applications, such as the operation of fuel cells, require exceptionally low sulfur fuel in order to mitigate catalyst poisoning in the reformer. To this end, the two fuels that were investigated in this work were Intermediate Fuel Oil 380 (IFO380), a common heavy marine fuel, and Jet Propellant 8 (JP – 8), a military logistic fuel desirable for use with fuel cells.

The primary desulfurization method used at refineries is hydrodesulfurization (HDS), which is highly effective for sulfur removal of aliphatic sulfur compounds, but remains inefficient at removing refractory sulfur compounds. Therefore, alternative desulfurization methods have been heavily researched which aim to more efficiently remove these compounds after the refining process. In this work, adsorptive removal of sulfur compounds via a batch reactor was chosen for investigation using sodium zeolite Y loaded with copper or nickel (NaY, CuY, and NiY, respectively).

It was found that adsorptive desulfurization with metal loaded zeolite Y is capable of removing sulfur compounds from IFO380. The sulfur removal decreased as follows:

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CuY = NiY > NaY. The sulfur removal, however, was limited as compared to the JP – 8 results. Presumably, the decreased performance was due to the active sites in the zeolite being inaccessible to the large sulfur compounds that likely exist in IFO380, including the asphalthenes, which account for approximately 14% of the total sulfur in the fuel. A two-step batch reactor desulfurization technique was used to adsorb sulfur compounds in JP – 8, with the most effective two – step series being CuY – CuY. It was concluded that CuY is the most effective adsorbent for this fuel due to its bonding mechanism allowing it to selectively remove sulfur compounds over competing non-sulfur compounds.

Prior to conducting desulfurization experiments, the adsorbents are activated at high temperature under helium gas. During activation, it is well known that the Cu<sup>2+</sup> ions within the CuY partially reduce to Cu<sup>+</sup>. However, there is much disagreement in literature as to the extent of this reduction and which activation conditions contribute. This work investigates the reducibility of copper species within CuY, after various activation conditions under inert gas or reducing agent, using hydrogen – temperature programmed reduction. Through this method, the location of Cu<sup>2+</sup> species within the zeolite frame work can be determined, as well as the relative amounts of Cu<sup>2+</sup>, Cu<sup>+</sup>, Cu<sup>0</sup>, and CuO that exist. It was shown that the reducibility of copper species is a strong function of activation temperature and gas and not a function of activation time.

#### <u>Acknowledgments</u>

On Halloween of 2014 I was accepted into the post – graduate program of the U.S. Coast Guard for Chemical Engineering, under which I was given two years and funding to receive a Master of Science degree from a university of my choosing. Rice University was my top choice. I called the CHBE department chair, Dr. Michael Wong, and had a lovely conversation with him where I explained that I had no background in chemical engineering or any lab experience whatsoever (I received my Bachelor of Science in Naval Architecture) and that I would only have four semesters to earn my MS. Looking back on the conversation two and a half years later, I must first thank Dr. Wong for not laughing in my face and hanging up on me! After several rounds of emails and follow on conversations, Dr. Wong agreed that if accepted to the school, he would be happy to have me enter his group. I will forever be grateful to Dr. Wong, for without his support, I would not have ever had the opportunity to attend this University. Furthermore, his guidance and mentorship throughout this process have been invaluable to my success over the last two years and to my overall growth as an individual.

Upon entering the University in August 2015, I met a group of first year Ph.D students who were hard-working, dedicated, brilliant, and thankfully, extremely understanding to my situation and very willing to help me through the difficult course load. Mitchell, Mitch, Chelsea, Oliver, Eric, Annie, Jin, Yi-Lin, Yash, Amit, Narmadha, and Reza, you guys are all wonderful people, and I wish you all the best in life and in your careers! Within Dr. Wong's group I was introduced to Dr. Mayank Gupta and Ms. Priscilla Dias da Silva, who I would work closely with over the next two years. I will be forever grateful to these two individuals for their patience while teaching me general lab

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practices and the attention to detail required in becoming an efficient and competent researcher. These two have spent countless hours of their own time in the last two years helping me with "many many things". Without these two, my time at Rice would surely have not been successful! Dr. Wong's lab manager, Dr. Kim Heck also proved to be most helpful and willing to assist me through a variety of difficulties, ranging from how to order lab equipment to numerous research based discussions. In truth, all the members of Dr. Wong's group assisted me at one point in time, and I owe each member a debt of gratitude!

Finally, I would like to extend my gratitude to Dr. Kyriacos Zygourakis, "KZ", and Dr. Clarence Miller for serving on my thesis committee. Their comments and helpful discussions resulted in a much stronger, more complete body of work. It is impossible to truly acknowledge all the hands and hearts that went into ensuring my successful completion of this thesis and other department requirements for graduation, but to those I have not specifically mentioned, thank you for all the support and attention! As I move forward in my Coast Guard career, I will always look back on these two years as a most challenging, yet rewarding, period, where my mental abilities were pushed to their limit and my endurance was tested. And through it all I thank God for giving me the strength to get through all the long nights and rough mornings, and allowing me to cross the finish line on my feet.

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#### Introduction

Over the last couple of decades, the removal of sulfur containing compounds from liquid fuels has been gaining attention from global leaders.<sup>1,2</sup> Internationally and domestically, governing bodies have increased regulation designed to require the use of low sulfur fuel.<sup>1,3</sup> Such regulations are intended to reduce air pollution by limiting the SO<sub>x</sub> produced by fuel combustion. Furthermore, certain applications, such as the operation of fuel cells, require exceptionally low sulfur fuel in order to mitigate catalyst poisoning.

In this thesis, two fuel types were examined: intermediate fuel oil (IFO) 380 and jet propellant (JP) 8. Research was conducted as to the types of sulfur compound and overall composition of these fuels. Of the various methods of desulfurization, selective adsorption for the removal of sulfur containing compounds using metal loaded zeolite Y was chosen to be the primary focus. Finally,  $H_2$  – Temperature Programmed Reduction (TPR) analysis was performed on zeolite Y loaded with copper to determine and quantify the oxidation state of the copper ions.

#### 1.1 Maritime Transportation Fuel – Intermediate Fuel Oil 380

International maritime shipping is regulated by the International Maritime Organization (IMO) which is a body of the United Nations (UN). All internationally recognized countries, called States, are eligible to join the IMO, which currently boasts a membership of 171 States. All member States comprise the General Assembly which is then further divided into Committees. Each Committee has a defined role and mission.

The Committee charged with the regulation of maritime generated pollution is the Maritime Environmental Protection Committee (MEPC), which originates and consolidates all regulations in effect into the International Convention for the Prevention of Pollution from Ships (MARPOL).<sup>1</sup> Annex VI of these consolidated MARPOL regulations addresses the mitigation of shipboard air pollution and defines Emission Control Areas (ECA), areas deemed sensitive and requiring more stringent regulation. Beginning in 2005, the IMO has implemented a step by step reduction in the maximum total sulfur content of fuel used on board a ship inside and outside an ECA, culminating in a drastic reduction on 1 January 2020.



Figure 1.1: Graphical representation of the maximum total sulfur content allowed for use on board maritime vessels inside and outside an ECA<sup>1</sup>.

In order to meet the stringent regulations while within ECA boundaries and reduce fuel costs, many marine operators directed ships in their fleet to maintain two fuel types on board: high-cost, low-sulfur distillate fuel to be consumed inside the ECA and low-cost heavy fuel oil (HFO) or HFO blend to be consumed outside the ECA.<sup>4</sup> Ship

masters are required to ensure that if two fuel types are carried onboard, the ship must maintain fuel transfer procedures documenting a standardized process. The U.S. Energy Information Administration conducted a study of overall fuel consumption by category in 2015 that showed an increase in distillate fuel usage in North American ECAs by 18.5 million barrels, for a total cost increase of over 370 million USD.<sup>5</sup> Furthermore, vessel propulsion, electrical plants, and fuel transfer systems have been specifically designed and optimized for the use of heavy fuel, which has drastically different thermal and viscous properties than distillate fuel. The process of switching from one fuel to another can cause problems ranging in severity from minor fuel leaks to total propulsion loss. For these two primary reasons, vessel operators strongly desire a HFO or HFO blend with sulfur content that meets the ECA threshold. Additionally, looking ahead to January 1<sup>st</sup>, 2020, there will also be a need for such a fuel that meets the less than 0.5wt% sulfur content threshold for consumption outside the ECA.

HFO, otherwise known as bunker-C or fuel oil number 6, is the lowest cut obtained from crude oil atmospheric distillation that has direct shipboard applications. Many ships are designed to consume HFO directly, but it is more common that the HFO is blended with distillate fuel. The resulting fuel is termed Intermediate Fuel Oil (IFO) and maintains much the same thermal properties as residual fuel but with a reduced viscosity, desirable for ease of internal transfer.<sup>6</sup> There are various blends of IFO, with one of the more common blends being IFO380, which contains approximately 98% HFO. Depending on its geographic origin, the HFO, and thus similarly the IFO380, can have a total sulfur content which ranges from 0.5wt% - 6.0wt%.<sup>7</sup> For comparison, as of June 1<sup>st</sup>, 2010, automotive diesel fuel, called ultra low sulfur diesel (ULSD), is required

to be less than 0.0015wt% or 15ppmw, and as of January  $1^{st}$ , 2017, automotive gasoline is required to be less than 0.001wt% or 10ppmw.<sup>3</sup>

Sulfur containing compounds come in two distinct forms: inorganic, such as hydrogen sulfide, and organic, such as thiols, sulfides, and thiophenic compounds. The most abundant and variant form is organic.<sup>8</sup> Common organic sulfur compounds are shown below in Figure 1.2.











Figure 1.2: From top left to bottom right: Dimethyl - disulfude; Enthanethiol; Thiophene (Maximum Diameter of 5.3Å) ;Benzothiophene (Maximum Diameter 6Å); Dibenzothiophene (Molecular Volume 189.06 Å<sup>3</sup>) ; and 4-6, Dimethyl - dibenzothiophene (Molecular Volume: 226.3 Å<sup>3</sup>)<sup>9,10</sup>

The hydrocarbon content of IFO380 is approximately 22% saturate, 49% aromatic, and 29% resin and asphaltene<sup>11</sup>; however, the total sulfur in each component is unknown. The predominant form of sulfur found in IFO380 is dibenzothiophene (DBT) and its alkylated derivatives.<sup>12</sup>

#### 1.2 Military Logistic Fuel - Jet Propellant 8

Outside the scope of government regulation, there also exists a strong application based drive for extremely low sulfur transportation fuel, such as gasoline, diesel, or jet fuel, for use in fuel cells. These power sources can be either portable or stationary and are seen as a promising alternative to generators due to their high energy efficiency, energy density, and noise reduction. In general, fuel cells create electricity by passing hydrogen gas through catalyst in the anode side of the cell. The result is free electrons which form electrical current and free protons which are combusted to form water.<sup>13</sup> Significant research has been conducted in recent years for the improvement and field use of solid-oxide fuel cells (SOFC).<sup>14–16</sup> The operational concept is similar, except SOFCs use hydrogen-rich synthesis gas, or syngas, which is catalytically reformed from one of the above mentioned transportation fuels. This fuel cell type is preferred as there is no longer a need for vast tank farms of hydrogen gas. However, the reforming catalysts can be poisoned by sulfur compounds in the fuel. For proper operation, it is essential that the transportation fuel chosen for use is desulfurization to less than 1ppmw of total sulfur, preferably less than 0.1ppmw.<sup>17,18</sup>

The U.S. military is specifically interested in SOFC application using a jet fuel called Jet Propellant 8, or JP-8.<sup>15,19</sup> As a military logistic fuel, JP-8 is regulated by military specifications or MILSPECs, specifically MILSPEC 83133E. It is a kerosene based turbine fuel with a complex mixture of hydrocarbons that also contains certain additives for corrosion inhibitor, static dissipater, biocides and anti-icing.<sup>20</sup> The composition of JP-8 is approximately 60wt% paraffins, 2wt% olefins, 20wt% napthenes, and 18wt% aromatics, with a carbon distribution of C<sub>6</sub>-C<sub>18</sub> centered around C<sub>12</sub>.<sup>21</sup> MILSPEC 83133E sets the total sulfur limit of 3000ppmw. Unlike IFO380, JP-8 does not contain resins or asphaltenes and thus all sulfur compounds are either saturates or aromatics. The predominant sulfur compounds by weight are benzothiophene and its alkylated derivatives.<sup>2,21</sup>

#### 1.3 Fuel Desulfurization Processes

Significant advancements have been made in the field of liquid fuel desulfurization. This section will serve to differentiate between desulfurization during the refining process versus post processing. The case will be made that achieving sulfur contents in IFO380 of 5000ppmw and in JP-8 of 0.1ppmw during the refining process using current methods is highly inefficient and there exists a need to develop a viable method for post processing desulfurization. The desire is not to provide an exhaustive review of this field as a whole, as it is widely researched with thousands of articles written over the last few decades, but to provide enough understanding as to why the specific desulfurization technique used in this thesis was chosen and how it is applicable to both IFO380 and

JP-8. Other liquid fuels, such as gasoline or diesel, will not be discussed as they are not the focus of this thesis.

#### 1.3.1 Desulfurization during the Refining Process

The most commonly employed desulfurization technique used in industry today during the refining process is hydro-desulfurization (HDS). This technique is currently used on a large scale to produce low sulfur transportation fuels as well as upgrading heavy oil. In the conventional HDS process, the fuel is fed into a fixed bed reactor along with hydrogen gas. The reactor normally operates at between 200 - 425°C and 1 – 18MPa. The catalyst used is typically an supported metal, such as NiMo/Al<sub>2</sub>O<sub>3</sub> or CoMo/Al<sub>2</sub>O<sub>3</sub>.<sup>8</sup> This process is highly effective for converting aliphatic sulfur compounds to gaseous hydrogen sulfide as follows:

Thiols:  $R - SH + H_2 \rightarrow R-H + H_2S$ Sulfides:  $R_1 - S - R_2 + 2H_2 \rightarrow R_1 - H + R_2 - H + H_2S$ Disulfides:  $R_1 - S - S - R_2 + H_2 \rightarrow R_1 - H + R_2 - H + 2H_2S$ 

The sulfur contained within thiophenic, benzothiophenic, and certain dibenzothiophenes can also be removed through HDS.<sup>22</sup> The gaseous  $H_2S$  is usually then converted to elemental sulfur via the Claus Process, which is well known to be as follows:

$$2 \text{ H}_2\text{S} + \text{O}_2 \rightarrow 2 \text{ S} + 2 \text{ H}_2\text{O}$$

These processes and reactions are well understood, making HDS a viable method for use on a large scale industrially for desulfurization. Using HDS, refiners are able meet the current regulatory requirements for transportation fuels mentioned in section 1.1. However, larger aromatic compounds, such as 4,6- Dimethyldibenzothiophene, are much less reactive than other sulfur compounds.<sup>2,23</sup> These sulfur compounds are called refractory compounds. There are two predominant methods used to remove refractory compounds using conventional HDS: direct hydrodesulfurization or hydrogenation. These mechanisms are shown below for 4,6 - dimethyldibenzothiophene as follows:

**Direct Desulfurization Route:** 



Hydrogenation Route:



Figure 1.3. The two common methods for removal of sulfur from 4, 6 – dimethyl - dibenzothiophene.  $^{\rm 24}$ 

The challenges of conventional HDS for removing refractory compounds are attributable in part to the steric hindrance caused by the methyl groups.<sup>25–29</sup> Because of this low reactivity, refractory compounds are the most prevalent sulfur compounds remaining in JP-8 treated by HDS.<sup>2,30–32</sup> In the case of IFO380, refractory compounds are the most prevalent sulfur compound prior to any treatment.<sup>12</sup> Therefore, achieving ultra-deep desulfurization of JP-8 and desulfurization of IFO380 would require the removal of refractory compounds. In the case of JP-8 or IFO380, the use of conventional HDS would be highly energy intensive and require significant amounts of

hydrogen feed. These extreme conditions reduce the economic feasibility of HDS for ultra – deep desulfurization of JP-8 and desulfurization of IFO380.<sup>26–28</sup>

For these reasons, an alternative method of fuel desulfurization post processing is needed. Significant efforts have been made to develop and improve alternative desulfurization methods, namely: oxidative desulfurization, extractive desulfurization, bio-desulfurization, and selective adsorption for removing sulfur.<sup>2,8,24,33–36</sup>

#### 1.3.2. Desulfurization Post Refining

Selective adsorption for removing sulfur (SARS) is an emerging method for ultra – deep desulfurization, with early work by Song and coworkers and Yang and coworkers on transportation fuel gaining much attention.<sup>2,36,37</sup> SARS is an appealing desulfurization method due to its ability to be performed at low temperature (<200°C) and pressure while remaining effective at removing larger thiophenic sulfur compounds. Simply put, the process of SARS is to flow liquid fuel over an adsorbent bed, specifically designed and optimized for adsorbing sulfur compounds. The difficultly in adsorbent development is that it must: 1) preferentially adsorb the sulfur containing compounds over competing hydrocarbons, namely aromatics, 2) have a high adsorption capacity such that it will have a high ratio of sulfur removed per gram of adsorbent 3) be capable of regeneration such that the adsorbent can be reused. There are many types of adsorbents that have been heavily explored in literature, primarily: supported metals, metal oxides, activated carbons, ionic liquids, and metal loaded zeolites.<sup>33</sup> For this thesis, it was chosen to investigate metal loaded zeolite Y, as discussed in the following section. This technique of using metal loaded zeolite Y for SARS has been directly applied to desulfurization of JP-8, but it has not been used in the study of IFO380 because of its high viscosity and composition. <sup>8,33</sup>

#### 1.4 Introduction to Zeolite Y and its Structure

The International Zeolite Association (IZA) maintains a database of 232 natural and synthetic zeolites. This database organizes these various zeolites alphabetically by three letter framework types. Of particular interest in adsorptive removal of sulfur containing compounds is faujasite, FAU. There are two types of faujasite, denoted zeolite X and Y, which are comprised of 192 aluminosilicate cubic unit cells, (Si, AI)O<sub>4</sub>. Early work in this field by Breck distinguishes zeolite X as having a Si/AI ratio of less than 1.5, and zeolite Y having a Si/AI ratio of 1.5 or greater.<sup>38</sup>



Zeolite Y

Figure 1.4. The structure of a faujasite unit cell with dimensions specifically for Zeolite Y. Figure adapted from the database of zeolite structures, maintained by the IZA.<sup>39</sup>

The aluminosilicate framework forms two secondary building units (SBUs), octahedral cages called sodalite cavities, and hexagonal prisms. The combination of these SBUs forms a large supercage. During synthesis, the crystalline structures are formed from aluminosilicate gel that has been formed in aqueous solution, along with a template such as sodium hydroxide. The general formula for faujasite is therefore

$$M_{x/n}[(AIO_2)_x(SiO_2)_y \cdot w H_2O$$

where M is the cation of valence n, w is the number of water molecules and y/x is the given ratio of Si/Al, ranging from 1 - 5. The total sum of x + y for the case of faujasite is equal to the aforementioned total number of tetrahedral,  $192.^{38}$  Also note that the ratio of O/(Si+Al) must equal 2.

The ratio of Si/Al is therefore a variable chosen during synthesis which greatly influences the adsorptive properties of the faujasite. A hypothetical framework consisting of 192 SiO<sub>4</sub> tetrahedra, with Si<sup>4+</sup>, would have no electrostatic charge. As the Si<sup>4+</sup> is tetrahedrally substituted by  $Al^{3+}$ , the polyanionic framework, as described by Breck, has the composition  $[(Al_xSi_{1-x})O_2]^{x-.38}$  Thus, a cation is needed to return the electrostatic charge back to neutral.



Figure 1.5. The tetrahedral substitution of Al<sup>3+</sup> for Si<sup>4+</sup> creates a negative charge which is balanced through the synthesis process with a cation. In this case, the cation is Na<sup>+</sup>.<sup>38</sup>

The use of sodium hydroxide during synthesis in turn provides sodium as the cation for stabilization as shown above. The presence of sodium cations also contributes to the surface acidity of the faujasite, creating Lewis acid sites.

#### 1.4.1 Sodium Zeolite Y as a Molecular Sieve

The crystalline structure of zeolite opens the door for molecular sieve technology, in which the surface acidity, large surface area and pore volume can be utilized for the selective adsorption of size specific molecules.<sup>40</sup> Due to the aforementioned size of sulfur containing compounds such as dibenzothiophene, sodium zeolite Y (NaY) is the preferred type as its surface area of 700m<sup>2</sup>/g, largest pore diameter of 7.4Å, and total accessible internal volume of 3,953 Å<sup>3</sup> is the largest amongst all zeolites.<sup>38</sup> Amongst NaY, perhaps the most studied for the adsorption of sulfur containing compounds and

the choice of this thesis, is Na Y with Si/Al ratio of 2.55.<sup>15,37,41,42</sup> The specific formula for this hydrated NaY is therefore:

The presence of Na<sup>+</sup> on the surface on NaY becomes of paramount importance to understanding its behavior as a molecular sieve, and more so as an adsorbent. This concept will be explored further in the next section.

#### 1.4.2 Location of Sodium Ions within Faujasite

As discussed above, the presence of Na<sup>+</sup> on the surface of NaY creates Lewis acid sites. These active sites essentially enable the zeolite to become an effective adsorbent. However, the crystalline structure of zeolite and its varying pore size and diameter raise concerns about the accessibility of the active sites, or whether or not the desired molecule for selective adsorption can physically come close enough to the site to enable a bond to be formed. Therefore, the location of Na<sup>+</sup> becomes vitally important. While this concept of ion location has been widely researched since the late 1960's, there has yet to be a strong agreement among investigators. According to the widely used notation of Smith, there are 8 cationic sites in zeolite Y: I, I', II', II, II\*, III, V and U, shown below in Figure 1.6.<sup>43</sup>

Breck established that the position of Na<sup>+</sup> in hydrated and dehydrated NaY differs, and that the ions migrate during the dehydration process.<sup>38</sup> Breck also established that dehydrated zeolite Y maintains its crystalline structure up to 800°C, at

which point the structure collapses to an amorphous shape.<sup>38</sup> The concept of ion migration within zeolite was widely accepted.<sup>44–46</sup>



Figure 1.6. Possible cationic sites using Smith nomenclature.<sup>43</sup> Site I is at the center of a hexagonal prism, site I' is in a sodalite cage adjacent to an hexagonal face shared by a hexagonal prism and by a sodalite cage, site II is in a supercage adjacent to an hexagonal face of a sodalite cage shared by a sodalite cage and a supercage, site II' is in sodalite cage adjacent to an hexagonal face of a sodalite cage shared by a sodalite cage and a supercage, site II' is in sodalite cage adjacent to an hexagonal face shared by a sodalite cage and a supercage, site II' is like site II, but displaced toward the supercage, site III is in a supercage adjacent to a four-membered ring of a sodalite cage, site Vis near the center of 12-membered ring between supercages, site U is at the center of a supercage.<sup>47</sup> Figure from Berthomieu et al.<sup>47</sup>

Perhaps the most definitive early work for the specific location of the sodium ions was performed by Rubio and coworkers, who determined that the vast majority of the sodium ions in hydrated NaY reside on Site III of the supercage.<sup>48</sup> The sodium ions in dehydrated NaY migrate inwards towards the smaller pores as a function of dehydration temperature. Dehydration at 500°C under vacuum yields sodium ions at seven of the

eight locations, with the exception being II\*. The maximum sodium population on dehydrated zeolite Y was found on site II.  $^{48}$ 

#### 1.4.3. Ion Exchange with Transition Metals

The acidity of these active sites is enhanced if the sodium cation is replaced with a transition metal cation. This process of replacing cations is called ion exchange. There are three main types of ion exchange: solid state ion exchange (SSIE), vapor phase ion exchange (VPIE), and liquid phase ion exchange (LPIE). LPIE in aqueous solution will be the primary ion exchange type utilized in this thesis due to the simplicity of the ion exchange process, relatively high exchange rate, and no formation of hazardous byproducts such as HCI. Substantial work has been performed using copper and nickel as the transition metal due to their low cost and ability to selectively adsorb sulfur compounds as discussed in the following section.<sup>33,36,37</sup> The precursor used was copper nitrate or nickel nitrate. LPIE was thoroughly investigated early on by Breck, who summarizes the ion exchange process as follows:

$$Z_A B_{(z)}^{z_B^+} + Z_B A_{(s)}^{z_A^+} \leftrightarrow Z_A B_{(s)}^{z_B^+} + Z_B A_{(z)}^{z_A^+}$$

where  $z_A$  and  $z_B$  are the charges of the exchange cations A and B and the subscripts z and s refer to the zeolite and solution, respectively .<sup>38</sup> Therefore, if the divalent ion Cu<sup>2+</sup> is ion exchanged for Na<sup>+</sup>, two sodium ions must be exchanged for every copper ion. Complete ion exchange of Cu<sup>2+</sup> for Na<sup>+</sup> in hydrated zeolite Y (Si/AI = 2.55) would therefore be:

### Cu<sub>27</sub>[(AIO<sub>2</sub>)<sub>54</sub>(SiO<sub>2</sub>)<sub>138</sub> · 240 H<sub>2</sub>O

where the copper ions have an overall weight percentage of 13.1%. However, complete ion exchange is not achievable due to the hydration state of the copper ions and because of complex hydrolysis mechanisms that arise during exchange.<sup>49</sup> Breck generalizes divalent and trivalent ion exchange stating that the maximum degree of exchange at room temperature is near 68%, with site I sodium ions remaining in the zeolite. However, at elevated temperatures of 100°C, Breck achieved 92% ion exchange of La<sup>3+</sup> after stirring for 47 days.<sup>38</sup>

Because complete liquid phase ion exchange is not possible, the location of the exchanged transition metals becomes important with regards to active site accessibility, surface acidity, and overall adsorptive performance of the zeolite Y. This is a highly investigated topic with more recent studies with respect to copper and nickel ion exchange performed by Berthomieu, Yang, and Guesmi.<sup>37,47,50,51</sup> Copper ions in dehydrated zeolite Y can reside in sites I, I', II, II', and III; however, achieving ion exchange in the hexagonal prism is difficult and most authors report that sites II, II', and III dominate due to the accessibility and relative ease for ion exchange in these locations.<sup>49,52</sup> Conversely, nickel ions in dehydrated zeolite Y prefer sites SI, SI', SII, and SII'. <sup>49,50</sup> In the case of either ion, simultaneous occupation of adjacent sites, such as II and II' with respect to a single sodalite cavity, is not possible due to Coulombic repulsion.<sup>53</sup>

#### 1.4.4 Mechanism of Sulfur Adsorption on Zeolite Y

To be an effective adsorbent for removing sulfur containing compounds from IFO380 or JP-8, the active sites of the ion exchanged zeolite Y must be capable of attracting and bonding to these sulfur molecules. As discussed by Velu, thiophene, for example, has two pairs of electrons on the sulfur atom. One pair of electrons is in the six-electron  $\pi$  system, and the other lies in the plane of the ring. Therefore, thiophene can act as either an *n*-type donor by donating the lone pair of electrons of the sulfur atom to the adsorbent (direct S-adsorbent interaction or direct S-M bond) or as a  $\pi$ -type donor by utilizing the delocalized electrons of the aromatic ring to form a  $\pi$ -complex with the metal or metal ion.<sup>54</sup> Aliphatic sulfur compounds, such as dimethyl-disulfide, are not capable of bonding via  $\pi$ -complexation and must rely on direct S-M bonding. These concepts are explored further in the following sub-sections.

#### 1.4.4.1. Coordination Geometries of Thiophene to Organometallic Species

Early work by Angelici and Sanchez – Delgado developed eight possible S-M coordination geometries of thiophene in organometallic complexes as shown below in Figure 1.7.<sup>55,56</sup>



Figure 1.7. Eight coordination geometries for thiophene in organometallic complexes:  $\eta^1 S$  and S- $\mu 3$  show thiophene coordinating directly with the metal through sulfur-metal interaction;  $\eta^1 C$ ,  $\eta^2$ ,  $\eta^4$ , and  $\eta^5$  show  $\pi$  – complexation through interactions between the C = C bond within the thiophene and the metal; and  $\eta^4$ , S-  $\mu 2$  and  $\eta^4$ , S-  $\mu 3$  show a combination of direct sulfur metal interaction and  $\pi$  – complexation.<sup>29,33,55,56</sup> Figure from Ma et al.<sup>29</sup>

These coordination geometries provide the theoretical background for the work performed by the authors in the following subsections, as different authors designed adsorbents specifically tailored to certain coordination geometries.

#### 1.4.4.2 $\pi$ -complexation

As discussed in Section 1.3.1, conventional hydro-desulfurization using traditional molybdenum based catalyst is inefficient method for removing refractory compounds. As shown below in Figure 1.8, molydenum based catalysts rely on direct sulfur to metal interaction for sulfur adsorption.



Figure 1.8: Schematic representation for desulfurization of 4,6-dimethyl-benzothiophene with a) molybdenum based and b) copper (I) based adsorbent. Case a) emphasizes the steric hindrance caused by the methyl groups and case b) corresponds to  $\pi$ -complexation. <sup>57</sup> Figure from Hernandez – Maldonado et al.<sup>57</sup>

Therefore, HDS is very effective for the removal of thiols and sulfides; however, as discussed by Yang and coworkers, remains ineffective for the adsorption of alkylated dibenzothiophenes due to the steric hindrance caused by the methyl groups.<sup>31,57-59</sup> Yang hypothesizes that such steric hindrance can be avoided if the sulfur compound is adsorbed through  $\pi$ -complexation.<sup>49</sup> Therefore, Yang and coworkers focus on designing adsorbents which selectively adsorb sulfur compounds via  $\pi$ -complexation, specifically the following coordination geometries:  $\eta^1 C$ ,  $\eta^2$ ,  $\eta^4$ , and  $\eta^{5.25}$  Among the adsorbents investigated were Cu<sup>+</sup> and Ni<sup>2+</sup> (Cu(I)Y and Ni(II)Y respectively).<sup>37,49</sup> Upon activation of LPIE of Cu(II)Y and Ni(II)Y, the Cu<sup>2+</sup> ions are partially reduced to Cu<sup>+</sup>, whereas Ni<sup>2+</sup> are not reduced. In a follow on article, Wang and coworkers emphasize that the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> is a critical step as Cu<sup>2+</sup> lacks the sufficient electron density needed to form  $\pi$ -complexes, and hence the adsorbents selectivity to sulfur containing compounds will

decrease as the ratio of  $Cu^{2+}$  to  $Cu^{+}$  increases.<sup>31</sup> The mechanism for  $\pi$ -complexation between  $Cu^{+}$  ions  $(1s^22s^22p^63s^23p^63d^{10}4s^0)$  and thiophenic aromatic rings is shown below in Figure 1.9.



Figure 1.9: Faujasite supercage with copper ions occupying 6-ring window sites, Site II. A)  $\sigma$ -donation of  $\pi$ -electrons of thiophene to the 4s orbital of copper (I) B); d- $\pi$ \* back-donation of electrons from 3d orbitals of copper (I) to  $\pi$ \* orbitals of thiophene. Here 3d represents d<sub>xy</sub>, d<sub>yz</sub>, or d<sub>xz</sub> or 3 of the 5 3d orbitals. <sup>49</sup> Figure from Hernandez – Maldonado et al.<sup>49</sup>

As shown in Figure 1.9, through the  $\pi$ -complexation mechanism the cations can form the usual  $\sigma$  bonds with their empty s-orbitals and, in addition, their d-orbitals can backdonate electron density to the antibonding  $\pi$ -orbitals ( $\pi^*$ ) of the sulfur rings.<sup>49</sup> In a recent article, Li and coworkers use conceptual density functional theory as evidence to support the mechanism of sulfur adsorption via  $\pi$ -complexation.<sup>60</sup> Yang and coworkers also reported that Ni<sup>2+</sup> is capable of bonding via  $\pi$ -complexation, however, Cu<sup>+</sup> shows a higher bond energy in bonding with thiophene, making Cu(I)Y a superior adsorbent than Ni(II)Y.<sup>25,37</sup> For the present work, this may enable Cu(I)Y to remove more sulfur compounds than Ni(II)Y in IFO380 and JP8.

The design of adsorbents that selectively adsorb sulfur compounds through  $\pi$ complexation has the undesired effect of allowing other non-sulfur aromatic compounds, also capable of bonding via  $\pi$ -complexation, to compete for the active sites on Cu(I)Y or Ni(II)Y. Therefore, it is necessary to show that competitive adsorption of non-sulfur compounds does not render Cu(I)Y and Ni(II)Y ineffective. Yang investigated this using Cu(I)Y and binary model fuel of thiophene (T), benzothiophene (BT), dibenzothiophene (DBT), or benzene in n-octane. The adsorption isotherms shows the Cu(I)Y adsorption capacity in the following order: DBT > BT > T > Benzene. However, a ternary mixture of DBT, BT, or T in 20wt% benzene and 80wt% n-octane significantly reduced the sulfur removal capacity of each sulfur compound by 75-80%.<sup>61</sup> This drastic reduction in sulfur removal led other researchers to approach sulfur removal via direct sulfur-metal interaction.

#### 1.4.4.3 Direct Sulfur-Metal (S-M) Interaction

Ma and coworkers explored the two coordination geometries where thiophene coordinates directly with the metal through sulfur–metal interaction,  $\eta^{1}S$  or S– $\mu$ 3 bonding.<sup>29,54</sup> Theoretical calculations were performed via computational analysis that show the highest occupied molecular orbital (HOMO) of thiophene, benzothiophene and dibenzothiophene is located on the sulfur atom, whereas the HOMO of alkyl benzenes and naphthalene on the conjugated six-member ring.<sup>29</sup> The results found by Ma and coworkers suggest that it may be possible to achieve selective adsorption by interaction

of sulfur atom with certain metal species through the direct interaction of HOMO on sulfur with lowest unoccupied molecular orbital (LUMO) on metal species.

Whether the metal species and sulfur compound bond via direct S-M interaction or  $\pi$ -complexation is directly related to the specific metal ion used.<sup>54</sup> These adsorption mechanisms were investigated by Velu and coworkers using a model fuel containing thiophene, tetrahydrothiophene (a sulfur compound without  $\pi$  system), each containing about 270 ppmww of sulfur, benzene (non-sulfur aromatic), and 1,5-hexadiene (nonsulfur olefin).<sup>54</sup> The metal ions used were Ag<sup>+</sup>, which is known for its capability to bond via  $\pi$ -complexation, and Ce<sup>4+</sup> which is unlikely to bond via  $\pi$ -complexation due to its high polarizability and would rely on direct S-M interaction. It was found that Ag(I)Y forms  $\pi$ -complexes with benzene, 1,5-hexadiene, and thiophene, and that the  $\pi$ complexes with 1,5-hexadiene are the strongest. Ce(IV)Y showed much higher selectivity for the adsorption of thiophene and tetrahydrothiophene as compared to the adsorption of benzene and 1,5-hexadiene. Therefore, synthesizing metal ion exchanged zeolites that adsorb sulfur compounds via direct sulfur-metal interaction are more effective than those that rely of  $\pi$ -complexes due to the improved selectivity over competing aromatic compounds.<sup>54</sup> However, Velu and coworkers do not address the effect of steric hindrance in refractory compounds such as 4,6-dimethyl-benzothiophene in direct S-M interaction.

# 1.4.4.4 Adsorption via Combined $\pi$ -complexation and Direct Sulfur-Metal (S-M) Interaction

Recently, other investigators have focused on designing sorbents intended to adsorb thiophenic compounds via combined  $\pi$ -complexation and direct sulfur-metal (S-M) interaction, utilizing the  $\eta^4$ , S- $\mu$ 2 and  $\eta^4$ , S- $\mu$ 3 coordination geometries.<sup>32,44,62,63</sup>This is achieved through the synthesis of bi-metallic zeolite Y, were one metal forms  $\pi$ complexes with sulfur compounds and the other metal bonds via direct S-M interaction. Wang and coworkers explored Ni(II)Y, Ce(IV)Y, and Ni(II)Ce(IV)Y through a ternary mixture of 5wt% toluene in n-octane with 500mg/L of dibenzothiophene. The removal of sulfur increased in the following order: Ni(II)Y < Ce(IV)Y < Ni(II)Ce(IV)Y, with adsorption capacities of 5.4, 6.6 and 7.8mg/g, respectively. Wang and coworkers do not provide a decisive explanation for the enhanced sulfur removal, but propose that it is due to the synergistic interaction between Ni<sup>2+</sup> and Ce<sup>4+</sup>.<sup>63</sup> Song and coworkers performed similar work to Wang and coworkers using Ag(I)Y, Ce(IV)Y and Ag(I)Ce(IV)Y as well as Cu(I)Y, Ce(IV)Y, and Cu(I)Ce(IV)Y on model fuels.<sup>32,44,62</sup> Song and coworkers also report that the bimetallic zeolite Y has improved selectivity and sulfur removal capacity in model fuels that included competing compounds, namely cyclohexene and toluene.<sup>32,44</sup> Again, a sound explanation as to why the sulfur removal was improved was not provided. Neither groups tested their adsorbents on real fuels or model fuels containing refractory compounds. It is therefore uncertain whether or not bimetallic zeolite Y further advances selective adsorptive desulfurization.

1.5 Adsorbent Characterization via Hydrogen Temperature Programmed Reduction

As discussed in Section 1.4.4.2, the oxidation state of copper ions within copper exchanged zeolite Y determines the type of mechanism by which sulfur containing compound are adsorbed. Therefore, the determination and quantification of copper ions by oxidation state is very useful. A common characterization method used in literature is hydrogen temperature programmed reduction,  $H_2 - TPR$ .<sup>42,45,47,49,64–69</sup>

In H<sub>2</sub>-TPR, a gas flow of typically 5-10wt% H<sub>2</sub> balanced by an inert passes over a sample of CuY. The gas flow then passes through a cold trap, designed to allow any water vapor to condense. Finally, the gas flow enters a thermal conductivity detector (TCD), which also has a separate flow of reference gas that runs directly from the hydrogen in inert cylinder. The TCD continuously measures the amount of energy needed to maintain a certain temperature, typically 100°C. The measurement from the reference gas is subtracted from the gas flow that has passed over the sample of CuY. If no hydrogen is consumed by the CuY, the difference between the two readings is zero, and a stable baseline is achieved. The temperature of the CuY is slowly increased. At certain temperatures, the copper species absorb the hydrogen from the inlet gas flow and are subsequently reduced according to the following well known equations:

 $2Cu^{2+} + H_2 \rightarrow 2Cu^+ + 2H^+$  $2Cu^+ + H_2 \rightarrow 2Cu^0 + 2H^+$  $CuO + H_2 \rightarrow Cu^0 + H_2O$ 

The removal of hydrogen from the gas flow causes its thermal conductivity to decrease, while the thermal conductivity of the reference gas remains constant. The difference between the two thermal conductivities is recorded as a peak. From this data, it is possible to determine the location of  $Cu^{2+}$  within the zeolite structure and quantify the copper species that exist in each oxidation state.<sup>42,45,67</sup>

#### 1.6 Research Objectives

For this thesis, I chose to investigate selective adsorption desulfurization of IFO380 and JP-8 with a focus on copper or nickel loaded zeolite Y. Desulfurization experiments with sodium zeolite Y are included as controls. In the case of IFO380, selective adsorption desulfurization experiments have not been reported in literature. Therefore, this work will serve as an exploratory study to examine if it is possible to successfully remove sulfur using metal loaded zeolites. This work is detailed in Chapter 2 of this thesis. Chapter 3 of this thesis seeks to build upon the success shown by Gupta and coworkers in which sequential batch reactor desulfurization experiments show an improved sulfur adsorption in JP-8.<sup>70</sup> Chapter 4 of this thesis shows a thorough investigation as to the in situ and ex situ reduction with varying temperatures and gases as well as varying hold times at maximum temperature and the subsequent effect on  $H_2 - TPR$  analysis. A more in depth discussion of the  $H_2 - TPR$  analysis technique can be found in Chapter 4. A summary of conclusions and a discussion of future work are included as Chapter 5.

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Adsorptive Removal of Sulfur Containing Compounds from Intermediate Fuel Oil 380

# 2.1 Introduction

Maritime transport is essential to the world's economy as over 90% of the world's trade is carried by sea.<sup>1</sup> Maritime shipping is regulated by an international governing body called the International Maritime Organization (IMO). One function of the IMO is to generate maritime pollution regulations, or MARPOL regulations, which govern all shipboard generated waste, including air emissions. MARPOL defines sensitive emission control areas (ECAs) in certain waters of North America and Northern Europe.<sup>2</sup> As of January 1<sup>st</sup>, 2015, the maximum allowable total sulfur amount in marine fuel for a vessel transiting outside of an ECA is 35,000ppmww. Before entering an ECA, the vessel must switch to fuel with no more than 1,000ppmww of total sulfur. On January 1<sup>st</sup>, 2020, the total allowable sulfur for outside an ECA will reduce to 5,000ppmww.<sup>2</sup>

The predominant type of marine fuel used by the world's fleet is heavy fuel oil (HFO), otherwise known as Bunker-C or fuel oil number 6.<sup>3,4</sup> Several different cuts of crude oil combine to produce HFO, including, atmospheric gas oil, light gas oil, and heavy gas oil. Once produced, the HFO undergoes very little processing before being used as fuel. Figure 2.1 is a simplified schematic of the atmospheric and vacuum distillation process that yields HFO.<sup>5</sup>



Figure 2.1. Simplified schematic of refinery process for HFO. Schematic shows that HFO is a blend of multiple fractions of crude oil.<sup>5</sup> The composition and sulfur content of HFO is largely dependent on its parent crude oil and predominant fractions.

It is common for bunkering facilities to blend HFO on site with distillate fuel prior to bunkering a marine vessel. This blended fuel is called Intermediate Fuel Oil (IFO), with the most common blend being 98% HFO and 2% distillate. This blend is called IFO380, due to its viscosity at 40°C being 380cp. The total sulfur content of IFO380 commonly ranges from 10,000 – 35,000ppmw and is largely dependent on the parent crude oil and specific fractions used during the distillation process to produce the HFO.<sup>6</sup> In order to meet more stringent sulfur regulations within ECAs, marine vessels switched to a distillate fuel called Marine Gas Oil (MGO) due to the non-availability of IFO380 with

<1,000pppmw total sulfur. This fuel change is undesirable for marine operators as distillate fuel prices are significantly higher than IFO380. However, currently an economically viable desulfurization method capable of reducing the total sulfur content in IFO380 to less than 1,000ppmw for use inside ECAs does not exist.

There are two primary approaches for sulfur removal from fuel, pretreatment during the refining process and posttreatment. The most common desulfurization method used during pretreatment fuel processing at refineries is hydrodesulfurization (HDS). HDS has been widely researched over the last few decades.<sup>7-12</sup> However, HDS is inefficient at removing refractory sulfur compounds, which are predominant in HFO. As such, many alternative methods for posttreatment desulfurization have been studied, biodesulfurization<sup>13–16</sup>, oxidative desulfurization<sup>17–19</sup>, includina and extractive desulfurization<sup>20-22</sup>. One challenge with implementing a shipboard alternative desulfurization method is the amount of sulfur that would need to be removed per transit. Bialystocki and coworkers developed a method for determining fuel efficiency using a 200m long case ship, and determined that while traveling 15 knots, the vessel consumed approximately 35 metric tons of fuel a day.<sup>23</sup> Assuming the reduction of 3.5wt% of total sulfur to 0.1wt%, this much fuel translates to the removal of nearly 1,200 kg of sulfur per day.

To date there has been no study published on adsorptive removal of sulfur containing compounds from HFO or IFO380. The objective of this study is to investigate the effectiveness of adsorptive removal of sulfur containing compounds from IFO380.

#### 2.2 Experimental

### 2.2.1 Adsorbent Preparation

Sodium zeolite Y (NaY, Si/AI = 2.55, Surface area =  $700m^2/g$ ) was purchased from Alfa Aesar, lot Y16B006. The general formula for the as purchased NaY is as follows:

Copper (II) nitrate ( $Cu(NO_3)_2$ ) and nickel (II) nitrate ( $Ni(NO_3)_2$ ) were purchased from Alfa Aesar, lots X14B033 and 10181075 respectively.

Liquid phase ion exchange (LPIE) was utilized to synthesize Cu(II)Y and Ni(II)Y. The synthesis was performed in 0.35M aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> or Ni(NO<sub>3</sub>)<sub>2</sub> and de-ionized water.<sup>24</sup> The amount of NaY used during LPIE corresponded to five-fold excess of Na<sup>+</sup> to Cu<sup>2+</sup> or Ni<sup>2+</sup>, respectively, assuming that two sodium ions would be replaced by one transition metal ion.<sup>25,26</sup> LPIE was conducted at ambient conditions and continuous stirring for 24 hours. After exchange, the zeolite suspension was vacuum filtered, washed with de-ionized water, and vacuum filtered again. The exchanged zeolite was then dried on a hot plate at 150°C for 15-20 minutes and broken up into a powder. The exchanged zeolite powder was then placed in an oven at 105°C for 24 hours. Immediately prior to desulfurization, the Cu(II)Y or Ni(II)Y was activated in a tube furnace under helium gas with a flow rate of 5cm<sup>3</sup>/min for 8 hours at 450°C.<sup>24</sup> During activation, the exchanged zeolites are dehydrated, ions migrate within the framework of the zeolite, and in the case of Cu(II)Y, there is partial reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>.

# 2.2.2 IFO380

IFO 380 was obtained via Bomin Bunkers, LLC from Pelican Island Storage Terminal – Shore tank 100-3, located in Galveston, TX. The total sulfur amount was measured by Texas OilTech Labs in Houston, Texas, using x-ray fluorescence (XRF) in accordance with ASTM D4294, and found to be 2.67wt% or 26,700ppmw ± 3%.<sup>27</sup> The viscosity was measured using an Anton Paar SVM 3000 viscometer and found to be 2159.3cp at 30°C. Gas chromatography with mass spectrometry (GC-MS), using an Agilent Technologies 7890B, was used to analyze the carbon distribution of IFO380. Prior to GC-MS analysis, the IFO380 was diluted to 25wt% IFO380 in toluene. The results, including the most probable hydrocarbon compound for each major peak, are shown in Figure 2.1.



Figure2.2: GC-MS data for 25wt% IFO380 in toluene. GCMS data was obtained by Dr. Sivaram Pradhan.

As can be seen in Figure 2.1, the carbon number distribution ranges from  $C_{12}$  to  $C_{44}$ , with  $C_{20}$  being the most prevalent.

# 2.2.3 Batch Experimentation Procedure

Batch experiments were performed in a 125mL autoclave with a PTFE liner, manufactured by Parr Instrument Company, LLC. The experimental procedures developed by Gupta and coworkers were utilized.<sup>24</sup> Each batch consisted of 27mL of

IFO380 and 0.74g of activated adsorbent. Experiments were performed at 176°C for 3 hours, followed by 45 minutes of cooling with oven fan to return to near ambient conditions. Upon completion of cooling, the autoclaves were removed from the oven and opened in a fume hood. The adsorbent – fuel mixture was then separated by vacuum filtration, using  $0.2 - 0.25 \mu m$  pore size filter paper, with the spent adsorbent and treated IFO380 retained in separate vials. However, the viscosity of IFO380 did not allow for vacuum filtration as the fuel was unable to pass though the filter paper. Therefore, in order to perform batch experiments in this manner, it was necessary to find a suitable solvent to dilute the IFO380.

### 2.1.4 IFO380 Dilutions

In order to perform batch experimentation and vacuum filtration as described, it was necessary to dilute the IFO 380 to 5wt% in solvent. Five different solvents were surveyed: n-heptane, dimethylformamide, dichloromethane, toluene, and cyclohexane, described below in Table 2.1.

	Chemical Formula	Boiling Point (°C)	Density (kg/m <sup>3</sup> )
n- heptane	C <sub>7</sub> H <sub>16</sub>	98	684
Dimethylformamide	C <sub>3</sub> H <sub>7</sub> NO	153	944
Dichloromethane	CH <sub>2</sub> Cl <sub>2</sub>	39.6	1330
Toluene	C <sub>6</sub> H <sub>5</sub> CH <sub>3</sub>	110.6	867
Cyclohexane	C <sub>6</sub> H <sub>12</sub>	80.74	779

Table 2.1. Description of solvents used to dilute IFO380.<sup>28</sup>

### 2.3 Results and Discussion

### 2.3.1 Adsorbent Characterization

Bulk metal loading of the exchanged zeolite was conducted using inductively coupled plasma (ICP) analysis and found to be 8.2% copper in CuY and 7.2% nickel in NiY.<sup>24</sup> Thermal gravimetric analysis (TGA) was performed on CuY, and it was found to desorb 24.7% of its mass in water.<sup>29</sup> Thus, the general formulas for the hydrated exchanged zeolites are as follows:

BET surface area of the NaY, CuY, and NiY was found to be 650, 623, 596 m<sup>2</sup>/g, respectively, indicating the surface area is similar before and after ion exchange.<sup>24</sup>

### 2.3.2 Choosing the Most Suitable Solvent

For the purposes of conducting batch experimentation and vacuum filtration, a suitable solvent is one that reduces the viscosity of the IFO380 without causing separation of the fuel or visible precipitation of any solids. The n-heptane dilution resulted in the immediate precipitation of solids and separation of heavier carbon compounds from the fuel during vacuum filtration. The dimethyformamide dilution also immediately resulted in the precipitation of solids, and the emulsification of heavier carbon compounds. Furthermore, the lighter hydrocarbon compounds that did not emulsify turned from IFO380's characteristic dark brown color to a brownish green. On the contrary, dichloromethane, toluene, and cyclohexane were initially found to be suitable solvents.

experiments, to determine which dilution would best allow for adsorptive removal of sulfur containing compounds. In order to assess how the diluted IFO380 performed during desulfurization, batch experiments were conducted without adsorbent and with activated CuY. The results are summarized below in Table 2.2.

Solvent	Adsorbent	Mass prior to experiment (g)	Mass after filtration (g)	Mass Loss (%)
Toluene	None	24.0	19.4	19.2
	CuY	24.0	14.8	38.3
Dichloromethane	None	32.9	17.0	48.3
	CuY	29.3	0.8	97.3
Cyclohexane	None	21.2	6.3	70.3
	CuY	21.3	6.5	69.5

Table 2.2. Summary of mass balance before and after batch experiments with 5wt% IFO380 in toluene, dichloromethane, or cyclohexane.

The dilution with dichloromethane resulted in significant mass loss before the addition of adsorbent. It was visually observed that the vast majority of the mass loss occurred due to evaporation during vacuum filtration. This is most likely attributable to the solvent's low boiling point. The addition of activated CuY to dilution with dichloromethane allowed for significantly greater mass loss as compared to the experiment without adsorbent. The resulting 0.8 grams of filtrate was a very thick residue, indicating little of the dichloromethane remained after treatment with CuY. These results suggest a possible reaction between the adsorbent and the diluted fuel that is undesirable. On the contrary, the addition of adsorbent to the dilution with

cyclohexane did not result in additional mass loss. However, upon filtration, it was noted that significant solid deposits remained on the filtration paper. This suggests that the IFO380 is separating due to the addition of this solvent, which is also undesirable. The dilution with toluene resulted in acceptable mass loss during experimentation and filtration, with no visual signs of fuel separation or solid deposits. Therefore, toluene was found to be a suitable solvent and was selected for further investigation via desulfurization experiments using additional adsorbents.

### 2.3.3 Desulfurization of 5wt% IFO380 in Toluene

Batch experiments were conducted with 5wt% IFO380 in toluene using no adsorbent, NaY, CuY, and NiY. Because of the total mass loss during experimentation and filtration, it was necessary to include the no adsorbent scenario as the initial baseline for total sulfur amounts. This is because total sulfur amount in parts per million is defined as follows:

$$\frac{\text{total mass of sulfur (g)}}{\text{total mass of IFO380 in Toluene (g)}}*10^6 = \frac{\text{total mass of sulfur (g)}}{(\text{total mass of sulfur + total mass of non-sulfur)(g)}}*10^6$$

Therefore, if mass is lost due to the nature of batch experimentation or vacuum filtration, the ppmw of total sulfur may differ from the pre-treated diluted IFO380 if the primary mass loss is due strictly to non-sulfur compounds. The results are summarized below in Table 2.3. All total sulfur results were obtained via Texas Oil Tech as described in Section 2.2.2. Table 2.3. Summary of desulfurization experiment results using 5wt% IFO380 in Toluene. All total sulfur analysis has an error of ±3%

Adsorbent	Total Sulfur Amount Post Treatment (ppmw)	Total Mass of Filtrate(g)	Total Mass of Sulfur (mg)	Reduction in Total Sulfur* (%)	Corresponding Total Sulfur Amount in IFO 380 (ppmw)
None	1290	19.4	25.1	n/a	26,700
NaY	1470	16.3	24.0	4.2 (1.5)	25,600
CuY	1490	14.8	22.1	11.8 (4.1)	23,500
NiY	1360	16.5	22.5	10.3 (3.5)	23,900

\*The number outside parenthesis refers to percentage of total sulfur removed. The number inside parenthesis refers to milligram sulfur removed per gram of activated adsorbent.

The results summarized in Table 2.3 show that despite an increase in total sulfur parts per million after treatment, the total mass of sulfur does decrease, indicating that sulfur containing compounds are being removed by each adsorbent. These results suggest that CuY and NiY remove similar amounts of total sulfur and that both are superior adsorbents than NaY. However, these results show significantly worse performance than similar adsorbents with distillate fuels.<sup>24,30–35</sup> To investigate the decreased performance in sulfur removal and mass loss of non-sulfur compounds, a study of model fuels was necessary.

# 2.3.4 Desulfurization of Model Fuel

Two model fuels were prepared: MF1 was dibenzothiophene (DBT) in toluene and MF2 is DBT in dodecane (Boiling Point: 216°C; Density: 750kg/m<sup>3</sup>)<sup>28</sup>. Batch experimentation

was repeated as in Section 2.3.2. The total sulfur amount was measured by Texas

OilTech as described in Section 2.2.2. The results are summarized in Table 2.4.

MF1 – DBT in Toluene									
Adsorbent	Total Sulfur Amount (ppmw)	Total Mass of Filtrate(g)	Total Mass of Sulfur (mg)	Reduction in Total Sulfur* (%)					
None	1950	19.2	37.5	n/a					
NaY	2030	16.2	33.0	12.0 (6.1)					
CuY	1840	16.2	30.0	20.0 (10.1)					
NiY	1780	16.9	30.1	19.7 (10.0)					
	MF2 – DBT in Dodecane								
None	1590	18.1	28.7	n/a					
NaY	670	17.1	11.4	60.2 (23.4)					
CuY	460	17.4	7.7	73.0 (28.3)					
NiY	690	16.9	11.7	59.0 (23.0)					

Table 2.4. Summary of desulfurization experiment results using model fuel. All total sulfur analysis has an error of  $\pm 3\%$ 

\*The number outside parenthesis refers to percentage of total sulfur removed. The number inside parenthesis refers to milligram sulfur removed per gram of activated adsorbent.

The results suggest that the sulfur removal in both MF1 and MF2 is improved over the diluted IFO380, with the sulfur removal in MF2 being the highest. Furthermore, the results suggest that the trend in sulfur removal between diluted IFO380 and MF1 is similar with CuY = NiY > NaY, while the sulfur removal in MF2 decreases in the following order CuY > NiY = NaY.

The decreased performance of MF1 as compared to MF2 is likely due in part to competitive adsorption of toluene. It is known from literature that aromatic hydrocarbon compounds, such as toluene, can compete for the active sites on metal loaded zeolite Y.<sup>36</sup> As discussed in detail in Section 1.4.4.1, this competition can be due to the similarity to which  $Cu^+$  or  $Ni^{2+}$  ions form  $\pi$ -complexes with the delocalized electrons in both aromatic sulfur and non-sulfur containing compounds. Chapter 4 of this thesis suggests that the activated CuY contains primarily Cu<sup>2+</sup> ions, which unlike Cu<sup>+</sup> do not have sufficient electron density in the d orbital to form  $\pi$  – complexes with the toluene.<sup>33,37,38</sup> Therefore, competitive adsorption of toluene via  $\pi$  – complexes likely accounts for the decreased performance of NiY in MF1 compared to MF2, but not CuY. However, aromatic compounds are known to bond to metal loaded zeolite Y via direct o bonds as well, albeit with lower energies of adsorption.<sup>39–41</sup> Therefore, it is likely that toluene competes for the active sites in CuY because of its overwhelming presence in the model fuel. Dodecane, however, is a saturate hydrocarbon compound and does not compete for active sites, thus allowing the adsorbent to more easily adsorb sulfur containing compounds. Direct comparison of the sulfur removal results from MF1 and MF2 indicate that the competitive adsorption of toluene likely is a contributing factor for the reduced removal of total sulfur in MF1 and thereby in part responsible for the low sulfur removal in 5wt% IFO380 in toluene.

While competitive adsorption of toluene is likely the cause of the decreased performance in sulfur removal, it is not likely the cause of the mass loss after desulfurization and filtration. The overall pore volume of zeolite Y is approximately 4,000Å<sup>3.42</sup> Assuming the entire volume of the adsorbent is occupied by toluene, the

maximum amount of toluene adsorbed is 0.12g, assuming density of toluene is 0.867g/mL. Thus adsorption of toluene cannot account for the entirety of the approximately 3g of mass loss in both the diluted IFO380 or MF1. The additional mass loss is therefore likely caused by increased evaporation of toluene during either batch experimentation or vacuum filtration due to its low boiling point as compared to dodecane.

Direct comparison of the sulfur removal results from MF1 and 5wt% IFO380 in toluene shows that copper and nickel loaded zeolite Y remove significantly more sulfur in MF1. Both fuels are comprised of a vast majority of toluene and thus the adsorbent is in a similarly competitive environment for sulfur removal. The difference between these two fuels is in their respective compositions, namely, MF1 is a binary mixture comprised of one sulfur and one non-sulfur aromatic compound whereas IFO380 is comprised of hundreds of possible sulfur and non-sulfur compounds as saturates, aromatics, resins, and asphaltenes. It was hypothesized that the reduced sulfur removal in diluted IFO380 was due to the presence of asphaltenes in the IFO380 blocking the zeolite pores and limiting accessibility to the active sites of the adsorbent. To test this hypothesis, it was necessary to extract the asphaltenes from the IFO380 and repeat the batch desulfurization experiments on the IFO380 maltenes diluted with toluene and n-heptane.

### 2.3.5 Extraction of Asphaltenes from IFO380

Asphaltenes were precipitated from IFO380 according to ASTM D2007-80.<sup>43</sup> IFO380 was diluted forty times in n-heptane in a 500mL round bottom flask and placed on a heating mantel at 135°C for 2 hours under continuous stirring. Upon completion, the diluted IFO380 was allowed to cool until reaching ambient temperature and then vacuum filtered as before. The extracted asphaltenes were placed in an oven at 95 °C overnight. The weight percentage of asphaltene was found to be 9.0  $\pm$ 0.5% of the IFO380. Total sulfur analysis of the asphaltenes was conducted by Texas OilTech as described in Section 2.2.2 and found to be 3810 ppmw  $\pm$  3% of total sulfur, approximately 14.3% of the total the total sulfur within IFO380.These results are consistent with what is found in literature for asphaltenes found within atmospheric and vacuum gas oil.<sup>44</sup>

The filtrated IFO380 maltenes and n-heptane mixture was poured into a 500mL round bottom flask and placed in an IKA RV 10 Rotary Evaporator for 2 hours using a mineral oil bath at 90 °C under continuous rotation at 135rpm. The remaining IFO380 maltenes were allowed to cool to ambient temperature. The total sulfur of the evaporated n-heptane was found to be below the 0.5ppmw quantification limit of the XRF analysis technique, suggesting that no lighter sulfur containing compounds were evaporated.

# 2.3.6 Desulfurization of IFO380 Maltenes

The 5 wt% dilution of IFO380 maltenes in toluene or n-heptane were made as in Section 2.1.4. Both dilutions were satisfactory, with no precipitations of solids or any other observed degradation of the fuel. Batch desulfurization experiments were conducted as before using no adsorbent, NaY, CuY, and NiY. It was observed that the desulfurization of diluted IFO 380 maltenes in n-heptane resulted in significant carbon residue on the inside of the PTFE liner. It was unknown whether or not this residue contained sulfur compounds or not. This suggests that n-heptane is not an appropriate solvent for IFO380 maltenes for batch desulfurization. Toluene remained to be an effective solvent as before. The desulfurization results for 5wt% IFO380 maltenes in toluene are shown below in Table 2.5.

Table 2.5.	Summary	of	desulfurization	experiment	results	using	IFO380	Maltenes	in
toluene. All	total sulfu	r ar	alysis has an e	rror of ±3%					

IFO380 Maltenes in Toluene									
Adsorbent	Total Sulfur Amount (ppmw)	Total Mass of Filtrate(g)	Total Mass of Sulfur (mg)	Reduction in Total Sulfur* (%)	Corresponding Total Sulfur Amount in IFO 380 (ppmw)				
None	1000	19.3	19.3	n/a	22,900				
NaY	960	18.6	17.9	7.4 (1.9)	20,900				
CuY	980	17.5	17.2	11.1 (2.9)	19,900				
NiY	1001	16.8	16.8	12.8 (3.4)	19,500				

\*The number outside parenthesis refers to percentage of total sulfur removed. The number inside parenthesis refers to milligram sulfur removed per gram of activated adsorbent.

The results suggest that total sulfur removal decreases as follows: NiY = CuY > NaY, which is similar to 5wt% IFO380 diluted in toluene. The results also suggest that amount of total sulfur removed by each adsorbent in 5wt% IFO380 maltenes in toluene does not significantly differ than that removed in 5wt% IFO380 in toluene. Therefore, the extraction of asphaltenes from IFO380 does not allow for improved sulfur removal. This suggests that asphaltenes do not block the active sites of the zeolite. Therefore, the challenge of adsorptive removal of sulfur compounds from IFO380 is likely due to another reason. It is possible that another undesirable component that comprises IFO380, such as ash or heavy metals, is blocking the active sites of the zeolite, thereby not allowing for sulfur removal. Another possibility is that the IFO380 used in this work does not contain a significant amount of dibenzothiophenes or lighter, which can be removed by metal loaded zeolite Y. In this case, the IFO380 may be comprised primarily of refractory compounds such as 4-6 Dimethyl-dibenzothiophene and heavier, which are known to be challenging to remove.<sup>10,39,45–47</sup> The challenge of removing these compounds is likely exacerbated by diluting the IFO380 or IFO380 maltenes in toluene, resulting in an overall low reduction of total sulfur.

## 2.4 Conclusion

The effectiveness of adsorptive removal of sulfur containing compounds from IFO380 using metal loaded zeolite Y in a batch reactor was investigated. The results indicate that adsorptive desulfurization with metal loaded zeolite Y is capable of removing sulfur from IFO380. The high viscosity of IFO380 at room temperature did not allow for proper batch experimentation and vacuum filtration, therefore, it was necessary to dilute the IFO380 to 5wt% IFO380 in solvent. An acceptable solvent is one that successfully

diluted the IFO380 by reducing its viscosity without causing separation and has minimal mass loss during batch experimentation and vacuum filtration. Of the five dilution experiments, toluene was the only successful solvent.

Desulfurization batch experiments were performed with 5wt% IFO380 in toluene using NaY, CuY, and NiY. The results indicate that each adsorbent is capable of reducing the total amount of sulfur in the following decreasing order: CuY = NiY > NaY. While sulfur was removed from the IFO380, the amount of sulfur removal was significantly less than in jet propellant under similar conditions and the amount of mass loss was greater. This was investigated through the study of model fuels. It was determined that with each adsorbent, toluene competes with aromatic sulfur compounds, causing over 60% reduction in total sulfur removed as compared to model fuel with dodecane.

Model fuel with DBT and toluene showed significantly increased sulfur removal than diluted IFO380. It was hypothesized that this was due to asphaltenes compounds blocking the active sites of the zeolite. Thus, asphaltenes were extracted and desulfurization experiments were repeated using IFO380 maltenes diluted in toluene. However, the results show that the sulfur removal in diluted IFO380 and diluted IFO380 maltenes are similar. This suggests that the IFO380 used in this work does not contain a significant amount of dibenzothiophenes or lighter, and is comprised primarily of refractory compounds such as 4-6 Dimethyl-dibenzothiophene and heavier.

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Adsorptive Removal of Sulfur Containing Compounds from Jet Propellant 8

### 3.1 Introduction

The U.S. military desires to use solid-oxide fuel cells (SOFCs) for power generation. These fuel cells use hydrogen-rich synthesis gas, or syngas, which can be catalytically reformed from a transportation fuel, such as diesel, gasoline or jet propellant. The reforming catalysts are poisoned by sulfur compounds in the fuel. Therefore, for proper operation, it is essential that the transportation fuel chosen for use contains less than 1ppmw of total sulfur, preferably less than 0.1ppm.<sup>1,2</sup> The U.S. military is specifically interested in SOFC application using a jet fuel called Jet Propellant 8, or JP-8.<sup>3,4</sup>

As a military fuel, JP-8 is regulated by military specifications or MILSPECs, specifically MILSPEC  $83133E^5$ . It is a kerosene based turbine fuel with a complex mixture of hydrocarbons that also contains certain additives for corrosion inhibitor, static dissipater, biocides and anti-icing.<sup>5</sup> The composition of JP-8 is approximately 71 vol% paraffins, 19% alkylbenzenes, 6.2% napthalenes, and 3.5% olefins, with a carbon distribution of C<sub>6</sub>-C<sub>18</sub> centered round C<sub>12</sub>.<sup>6,7</sup> MILSPEC 83133E requires that fuel contain no more than 3000 ppmw of total sulfur. The predominant sulfur compound by weight is benzothiophene and its alkylated derivatives.<sup>6–8</sup>

There are two approaches for sulfur removal from fuel, pretreatment during the refining process and posttreatment. The most common desulfurization method used during pretreatment fuel processing at refineries is hydrodesulfurization (HDS). HDS has been widely researched over the last few decades.<sup>9–11</sup> However, HDS is inefficient

at removing refractory sulfur compounds, which is necessary to achieve ultra-deep desulfurization of JP-8 to less than 0.1ppmw. As such, many alternative methods for posttreatment desulfurization have been studied, including biodesulfurization<sup>12–15</sup>, oxidative desulfurization<sup>16–19</sup>, extractive desulfurization<sup>20–22</sup>, and adsorptive desulfurization.<sup>2,3,23–29</sup>

Recently, Gupta and coworkers developed an adsorptive desulfurization method using metal loaded zeolite Y that utilized sequential batch experiments using different adsorbents for different steps.<sup>30</sup> This method is a new approach to adsorptive desulfurization which hypothesizes that different metal cations have different affinities towards different sulfur containing compounds. The objective of this study is to build upon the work performed by Gupta and coworkers by performing additional sequential batch desulfurization experiments to determine the most promising sequence of adsorbents and gain a more fundamental understanding of why certain sequences are superior to others.

### 3.2 Experimental

### 3.2.1 Adsorbent Preparation

Sodium zeolite Y (NaY, Si/Al = 2.55, Surface area = 700m<sup>2</sup>/g) was purchased from Alfa Aesar, lot Y16B006. The general formula for the as purchased NaY is as follows:

Copper (II) nitrate ( $Cu(NO_3)_2$ ) and nickel (II) nitrate ( $Ni(NO_3)_2$ ) were purchased from Alfa Aesar, lots X14B033 and 10181075 respectively.

Liquid phase ion exchange (LPIE) was utilized to synthesize CuY and NiY. The synthesis was performed in 0.35M aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> or Ni(NO<sub>3</sub>)<sub>2</sub> and deionized water.<sup>30</sup> The amount of NaY used during LPIE corresponded to four-fold excess of Na<sup>+</sup> to Cu<sup>2+</sup> or Ni<sup>2+</sup>, respectively, assuming that two sodium ions would be replaced by one transition metal ion.<sup>31</sup> LPIE was conducted at ambient conditions and continuous stirring for 24 hours. After exchange, the zeolite suspension was vacuum filtered, washed with de-ionized water, and vacuum filtered again. The exchanged zeolite was then dried on a hot plate at 150°C for 15-20 minutes and broken up into a powder. The exchanged zeolite powder was then placed in an oven at 105°C for 24 hours. Immediately prior to desulfurization, the CuY or NiY was activated in a tube furnace under helium gas with a flow rate of 5cm<sup>3</sup>/min for 8 hours at 450°C.<sup>30</sup> During activation, the exchanged zeolites are dehydrated, ions migrate within the framework of the zeolite, and in the case of CuY, there is partial reduction of Cu<sup>2+</sup> to Cu<sup>+</sup>.<sup>31–34</sup>

# 3.2.2 JP-8

JP-8 was obtained via Synovision Solutions, LLC. The total sulfur amount of the untreated JP-8 was measured by Texas OilTech Labs in Houston, Texas, using energy dispersive X-ray fluorescence (XRF) in accordance with ASTM D4294, and found to be 1280ppmw  $\pm$  3%.<sup>35</sup> ASTM D4294 is a common total sulfur analysis technique for a wide range of hydrocarbons, such as, diesel, jet fuels, residuals, hydraulic oils, and crude

oils. The sample to be analyzed is placed in a beam emitted from an X-ray source. The resultant excited characteristic sulfur radiation is measured, and the accumulated count is compared with the counts from previously prepared calibration samples.<sup>35</sup>

### 3.2.3 Batch Experimentation Procedure

Batch experiments were performed in a 125mL autoclave with a PTFE liner, manufactured by Parr Instrument Company, LLC. The experimental procedures developed by Gupta and coworkers were utilized.<sup>30</sup> First step desulfurization experiments consisted of 27mL of JP-8 and 0.74g of activated adsorbent. Experiments were performed at 176°C (oven temperature) for 3 hours, followed by 45 minutes of cooling with oven fan to return to near ambient conditions. Upon completion of cooling, the autoclaves were removed from the oven and opened in a fume hood. The adsorbent – fuel mixture was then separated by vacuum filtration, using  $0.2 - 0.25 \mu m$  pore size filter paper, with the spent adsorbent and treated JP-8 retained in separate vials. Second step desulfurization experiments were performed using the treated JP-8 from the first step. Due to the nature of the experiments, mass of the fuel is lost during each step thereby reducing the amount of treated fuel. To maintain the ratio of 0.03 grams of activated adsorbent per milliliter of JP-8, second step desulfurization experiments were performed with 22mL of JP-8 and 0.6g of activated adsorbent.

### 3.3 Results and Discussion

### 3.3.1 Adsorbent Characterization

Bulk metal loading of the exchanged zeolite was conducted using inductively coupled plasma (ICP) analysis and found to be 8.2% copper in CuY and 7.2% nickel in NiY.<sup>30</sup> Thermal gravimetric analysis (TGA) was performed on CuY, and it was found to desorb 24.7% of its mass in water.<sup>36</sup> Thus, the general formulas for the hydrated exchanged zeolites are as follows:

BET surface area of the NaY, CuY, and NiY was found to be 650, 623, 596  $m^2/g$ , respectively, indicating the surface area is similar before and after ion exchange.<sup>30</sup>

# 3.3.2 First Step Desulfurization of JP-8 using Metal Loaded Zeolite Y

Batch experiments were conducted with JP-8 using CuY and NiY, with NaY used as the control. The results are summarized below in Tables 3.1.

Table	3.1	Summary	of	first	step	desulfurization	results	using	JP-8.	All	total	sulfur
analys	sis ha	as an error	of ±	£3%.								

First Step Desulfurization Results							
Adsorbent	Total Sulfur Amount Post Treatment (ppmw)	Reduction inTotal Sulfur (%)	Total Sulfur Removed* (mg S / g adsorbent)				
NaY	1080	15.6	5.9				
CuY	680**	46.9	17.6 (0.42)				
NiY	980	23.4	8.8 (0.22)				

\*The number inside parenthesis refers to mmol sulfur removed per mmol of metal in the activated adsorbent.

\*\*Value was obtained by Gupta and coworkers.<sup>30</sup>

Both the copper and nickel loaded zeolites showed improved performance over the control NaY. The results suggest that CuY is a superior first step adsorbent than NiY. There are many factors that may contribute to the improved performance of one cation over another, including, the bonding mechanism by which the cation would bond to sulfur containing compounds, the effect of competing hydrocarbon compounds, and the location of the cation within the zeolite structure.

After activation, the adsorbents were exposed to ambient air for a short time to allow for preparation of batch reactor experiments. In the case of CuY, this exposure to ambient air causes fast re-oxidation of Cu<sup>+</sup> to Cu<sup>2+</sup>.<sup>23</sup> From the H<sub>2</sub> – TPR results discussed in Chapter 4 of this thesis, the predominant copper ion within the activated CuY after short exposure to ambient air is Cu<sup>2+</sup>. From literature it is known that unlike Cu<sup>+</sup>, Cu<sup>2+</sup> does not have sufficient electron density in its d-orbital to form  $\pi$  – complexes with compounds having delocalized electrons.<sup>23–25,27</sup> Therefore, similar to NaY, the primary bonding mechanism for CuY used under the conditions tested is likely to be

direct  $\sigma$  bonds.<sup>27</sup> Figure 3.1 below shows direct S-M bonding of Cu<sup>2+</sup> as well as  $\pi$  – complexation of Cu<sup>+</sup>.



Figure 3.1. On the left is the most stable molecular adsorption configuration of thiophene on a copper surface, indicating direct S-M bond is preferable. Figure from Wang et al.<sup>37</sup> On the right is Cu<sup>+</sup> bonding to thiophene via  $\pi$  – complexation. Figure from Hernandez – Maldonado et al.<sup>38</sup>

The bonding mechanism of NiY is likely similar to Cu<sup>+</sup>, as Ni<sup>2+</sup> is known to bond via  $\pi$  – complexation.<sup>7,23</sup>

The different bonding mechanisms of Cu<sup>2+</sup> and Ni<sup>2+</sup> can cause the two cations to interact differently with competing compounds, such as the aromatic, napthalenic, and olefinic compounds that are contained in JP-8 compound. These compounds compete for the active sites within the zeolite because they also characteristically have delocalized electrons that are capable of forming  $\pi$  – complexes. Wang and coworkers showed that the presence of aromatic non-sulfur compounds can reduce the sulfur removal by  $\pi$  – complexation adsorbents in model jet fuel up to 80%.<sup>39</sup> Velu and
coworkers showed that zeolites loaded with metals that form direct S-M bonds do not show competition for active sites and thus can selectively adsorb the sulfur containing compounds.<sup>7</sup> Therefore, because  $Cu^{2+}$  does not form  $\pi$  complexes, it is more capable of selectively adsorbing sulfur containing compounds via direct S-M bonds than Ni<sup>2+</sup>, resulting in the improved performance of CuY. The improved performance of CuY over NaY is not due to differing bonding mechanisms, but because CuY has a higher energy of adsorption with sulfur containing compounds than does NaY.<sup>27</sup>

The improved performance of CuY versus NiY can also be attributable to location of the Cu<sup>2+</sup> and Ni<sup>2+</sup> ions within the zeolite framework. The exchanged Cu<sup>2+</sup> ions are primarily located in the zeolite supercage and sodalite cavity, sites III and II, and II\* respectively.<sup>23</sup> During activation, these ions can migrate in the framework. From the H<sub>2</sub> – TPR analysis in Chapter 4 of this thesis, a majority of the Cu<sup>2+</sup> ions remain in the supercage, site III, of the zeolite. On the contrary, Ni<sup>2+</sup> ions are primarily located in the sodalite cavity or hexagonal prism of the zeolite structure, sites II, II\*, I, and I\* respectively.<sup>23,40</sup> The presence of the Cu<sup>2+</sup> ions in the supercage make the active sites more accessible to thiophenic compounds and contribute to the improved sulfur removal in JP-8.

#### 3.3.2 Second Step Desulfurization of JP-8 using Metal Loaded Zeolite Y

In order to determine the most effective two step sequence for sulfur adsorption, it was necessary to run desulfurization experiments with all nine two step combinations. The results are shown below in Table 3.2.

Table 3.2 Summary of second step desulfurization results using JP-8. All total sulfur analysis has an error of ±3%.

Second Step Desulfurization Results					
First Step Adsorbent	Second Step Adsorbent	Total Sulfur Amount Post Treatment (ppmw)	Reduction in Total Sulfur* (%)	Total Sulfur Removed** (mg S / g adsorbent)	
NaY	NaY	940	13.0 (26.6)	11.3	
	CuY	640	40.7 (50.0)	20.2 (0.48)	
	NiY	860	20.4 (32.8)	13.7 (0.35)	
	NaY	500	26.5 (60.9)	9.9	
CuY	CuY	370***	45.6 (71.1)	13.7 (0.33)	
	NiY	540	20.6 (57.8)	8.7 (0.22)	
	NaY	890	9.2 (30.5)	9.2	
NiY	CuY	550	43.9 (57.0)	19.2 (0.46)	
	NiY	790	19.4 (38.3)	12.2 (0.31)	

<sup>\*</sup>The number outside the parenthesis refers to the percentage of total sulfur removed by the second step, while the number inside refers to the total sulfur removed by the two-step series.

\*\*The number inside parenthesis refers to mmol sulfur removed per mmol metal in the activated adsorbent.

\*\*\*Value was obtained by Gupta and coworkers.<sup>30</sup>

The results suggest that the sequence of CuY - CuY was the most effective and the control sequence of NaY - NaY was the least effective for sulfur removal.

The two – step sequences that begin with NaY follow the similar order of sulfur removal as the one step, namely: NaY – CuY > NaY – NiY > NaY – NaY. This suggests that the same performance factors as discussed in section 3.3.1 remain valid. Specifically, after first step NaY, it is likely that sufficient aromatic and other competing

compounds remain in the fuel which reduce the effectiveness of NiY, while CuY remains capable of selectively adsorbing sulfur compounds. However, the data suggests that the second step sulfur removal of each NaY, CuY, and NiY is improved from the first step sulfur removal as follows: 5.9, 17.6, and 8.8 mg S / g adsorbent to 11.3, 20.2, and 13.7 mg S / g adsorbent, respectively. This improved performance can be attributable to one of two reasons. First, as previously mentioned, it is likely that the first step NaY removes a significant percentage of competing compounds which enables the second step material to be more effective. Secondly, it is possible that, while the ratio of adsorbent to fuel was maintained between steps, the reduced mass of adsorbent and volume of fuel decreases the diffusional limitations in the batch reactor set up and allows more sulfur compounds to come into contact with the adsorbent.

The two - step sequences that begin with CuY show dissimilarity with the other sequences, in that the order of sulfur removal is CuY - CuY > CuY - NaY = CuY - NiY. Again, the results suggest that CuY is the superior adsorbent regardless of its order in the sequence. However, the difference between second step NaY and NiY insignificant under the conditions tested. This occurrence is unique to this set of sequences. This similarity is likely rooted in the ability of CuY to selectively adsorb sulfur compounds, leaving the competing compounds in the treated fuel, thus decreasing the performance of both NaY and NiY. Furthermore, first step CuY, is likely removing the sulfur containing compounds with which it has the highest energy of adsorption, and thus the highest adsorbance capacity.<sup>39</sup> Therefore, after first step treatment by CuY, the treated fuel is likely a mixture of competing and non - competing hydrocarbon compounds and sulfur compounds with lower energies of adsorption. The results suggest that second

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step NaY and NiY are both unable to remove significant amounts of sulfur compounds in this environment. This unfavorable environment is likely the cause for the decrease in sulfur removal with CuY from 17.6 mg S / g adsorbent to 13.7 mg S / g adsorbent in the first and second step respectively.

The two – step sequence beginning with NiY agrees with the two – step sequence beginning with NaY, with the sulfur removal in the following order: NiY – CuY > NiY – NiY > NiY – NaY. Again, the sulfur removal of each second step adsorbent was improved from 5.9, 17.6, and 8.8 mg S / g adsorbent to 9.2, 19.2, and 12.2 mg S / g adsorbent, respectively. As such, the reasons that the order of sulfur removal remains similar and why the sulfur removal improves is likely similar to that discussed above for the two – step sequence beginning with NaY. This sequence does however show that the total sulfur removal in NiY – CuY is insignificantly different from CuY – NiY. This result further suggests that not only do Cu<sup>2+</sup> and Ni<sup>2+</sup> adsorb sulfur containing compounds via different mechanisms, but also that the order in which they are utilized in the two – step process is insignificant for the conditions studied here.

#### 3.4 Conclusions

The most effective adsorbent tested for the sulfur removal in JP 8 is copper loaded zeolite Y. CuY was found to be the superior adsorbent, regardless if it was used in the first or second step. It was hypothesized that CuY is likely the most effective adsorbent because the predominant copper species found in the activated adsorbent after exposure to air is Cu<sup>2+</sup>, which bonds to sulfur containing compounds via direct (S-M)

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interaction. This type of bonding mechanism enables the CuY to more selectively adsorb sulfur containing compounds over competing non – sulfur containing compounds, such as aromatics. The presence of competing compounds in JP – 8 is most likely the reason why NiY is less effective than CuY, as Ni<sup>2+</sup> is known to bond to sulfur containing compounds via  $\pi$  – complexation. As such, of the nine two – step sequences analyzed, the most effective four are as follows: CuY – CuY > CuY – NaY = CuY – NiY > NiY – NiY.

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Hydrogen - Temperature Programmed Reduction Studies of Copper Loaded Zeolite Y

# 4.1 Introduction

Copper loaded zeolite Y has been widely studied for a variety of applications, including, separations of olefins and paraffins, the selective reduction of nitrous oxide, the synthesis of dimethyl carbonate, and the selective adsorption of sulfur containing compounds from fuel.<sup>1-8</sup> The first group to use copper loaded zeolite Y for sulfur removal from fuel was Yang and coworkers.<sup>8</sup> The loaded copper species can exist within the zeolite structure as  $Cu^{2+}$ ,  $Cu^{+}$ ,  $Cu^{0}$ , or CuO, with the synthesis method and activation conditions dictating the relative percentages of each.<sup>3,5,6</sup> It is a common practice that copper species are loaded via ion exchange using copper nitrate as the precursor. After ion exchange, the resulting copper species primarily exists as Cu<sup>2+</sup> and are partially reduced to Cu<sup>+</sup> during activation at elevated temperature (50-600°C) under inert conditions.<sup>3,9</sup> The oxidation state of the copper species dictates the mechanism by which it selectively bonds to desired species during separation or adsorption applications. This is due Cu<sup>+</sup> having sufficient electron density in its d-orbital to form  $\pi$ complexes with targeted compounds such as olefins or thiophenic sulfur compounds with delocalized electrons.<sup>1,3,10</sup> Therefore, the reducibility of copper species has been of key importance and has been heavily researched.<sup>4–7,9,11–20</sup> Hydrogen – temperature programmed reduction  $(H_2 - TPR)$  is a common characterization method to show the presence and location of each species, as well as, allow for guantification.<sup>6,7,15,17,21,22</sup>

It is common in literature, to conduct  $H_2 - TPR$  under one condition to compare copper loaded zeolites synthesized by multiple methods with various metal loadings.<sup>6,7,17,23</sup> The objective of this study is to use  $H_2 - TPR$  to determine the location and relative quantity of each copper species found within copper loaded zeolite Y synthesized with one method and metal loading, but activated under various conditions.

#### 4.2 Experimental

# 4.2.1 Preparation of Copper Loaded Zeolite Y

Sodium zeolite Y (NaY, Si/AI = 2.55, Surface area =  $700m^2/g$ ) was purchased from Alfa Aesar, lot Y16B006. The general formula for the as purchased NaY is as follows:

Copper (II) nitrate  $(Cu(NO_3)_2)$  was purchased from Alfa Aesar, lots X14B033.

Liquid phase ion exchange (LPIE) was utilized to synthesize CuY. The synthesis was performed in 0.35M aqueous solution of Cu(NO<sub>3</sub>)<sub>2</sub> and de-ionized water.<sup>24</sup> The amount of NaY used during LPIE corresponded to four-fold excess of Na<sup>+</sup> to Cu<sup>2+</sup> assuming that two sodium ions would be replaced by one copper ion.<sup>3</sup> LPIE was conducted at ambient conditions and continuous stirring for 24 hours. After exchange, the zeolite suspension was vacuum filtered, washed with de-ionized water, and vacuum filtered again. The exchanged zeolite was then dried on a hot plate at 150°C for 15-20 minutes and broken up into a powder. The exchanged zeolite powder was then placed in an oven at 105°C for 24 hours. Immediately prior to performing H<sub>2</sub> - TPR, the CuY was activated under various conditions as described in the following sections.

#### 4.2.2 Reduction Mechanisms of Copper Loaded Zeolite Y

This study will discuss two methods for the reduction of copper species in CuY: reduction under inert gas and reduction under a reducing agent. The inert used was helium, and the reducing agent was a balance of hydrogen in inert gas.

Reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> under inert gas, often called autoreduction, has previously been investigated.<sup>15,17,21,22,25</sup> Two predominant autoreduction mechanisms have been proposed. Gentry and coworkers hypothesized the following mechanism:

 $H_2O + Cu^{2+} + ZO^- \rightarrow [Cu(OH)]^+ + ZOH$ 2[Cu(OH)]<sup>+</sup> → 2Cu<sup>+</sup> +  $H_2O + \frac{1}{2}O_2$ 

where the Z denotes zeolitic oxygen or hydroxyls.<sup>15</sup> This mechanism proposes that only  $Cu^{2+}$  ions located in the supercage, Site III, can reduce to  $Cu^{+}$ . This reduction is caused by zeolitic water and loosely bound extra lattice oxygens surrounding the framework  $Al^{3+}$  being dispelled at elevated temperatures. Using  $H_2 - TPR$ , Gentry and coworkers concluded that the maximum reduction of  $Cu^{2+}$  to  $Cu^{+}$  that can occur in inert gas is 50%, with the degree of reduction only being a function of maximum temperature and not of length of hold time at maximum temperature.

More recently, Larsen and coworkers proposed the following mechanism for the autoreduction of  $Cu^{2+}$  to  $Cu^{+}$ :

$$[Cu^{2+}OH^{-}]^{+} \leftrightarrow Cu^{+} + OH$$
$$[Cu^{2+}OH^{-}]^{+} + OH \leftrightarrow Cu^{2+}O^{-} + H_{2}O$$
$$2[Cu^{2+}OH^{-}]^{+} \leftrightarrow Cu^{+} + Cu^{2+}O^{-} + H_{2}O$$

which hypothesizes that copper ions are exchanged in the zeolite structure as copper hydroxide.<sup>25</sup> Reduction of Cu<sup>2+</sup> occurs due the hydroxyl radicals being dispelled at elevated temperatures. The byproducts of autoreduction in this method are CuO and water. Larsen and coworkers theorized that greater than 50% autoreduction of Cu<sup>2+</sup> ions is possible after long enough time. Using this mechanism, Gedeon and coworkers concluded via <sup>129</sup>Xe nuclear magnetic resonance (NMR) that they acheived 75% reduction after 12 hours at temperatures greater than 250°C, however, H<sub>2</sub> – TPR was not conducted to confirm this conclusion.<sup>9</sup>

The reduction of copper species using hydrogen gas as the reducing agent is commonly understood to occur under the proposed mechanisms:

$$Cu2+ + \frac{1}{2} H_2 \rightarrow Cu+ + H+$$
  

$$Cu+ + \frac{1}{2} H_2 \rightarrow Cu0 + H+$$
  

$$CuO + H_2 \rightarrow Cu0 + H_2O$$

where the reduction of  $Cu^{2+}$  to metallic copper occurs via a two step process, with  $Cu^{2+}$  to  $Cu^{+}$  occuring between 150 - 450°C and  $Cu^{+}$  to  $Cu^{0}$  occuring between 800 - 900°C. CuO is known to reduce to metallic copper via a one step process between 180 - 285°C.<sup>4-6,13,17</sup>

#### 4.2.3 Characterization of Copper Loaded Zeolite Y

Bulk metal loading of the exchanged zeolite was conducted using inductively coupled plasma (ICP) analysis and found to be 8.2% copper in CuY.<sup>24</sup> Thermal gravimetric analysis (TGA) was performed on the hydrated CuY, and it was found to

desorb 24.7% of its mass in water.<sup>26</sup> Thus, the general formula for the hydrated exchanged zeolite is as follows:

BET surface area of the NaY and CuY was found to be 650 and 623m<sup>2</sup>/g, respectively, indicating the surface area is similar before and after ion exchange.<sup>24</sup>

X-ray diffraction analysis was performed using a Rigaku D/Max (EAST) Ultima II Powder XRD 6s. The XRD patterns were acquired in the 2 $\theta$  range of 3-90°, with a step size of 0.02° and scan speed of 1.5s. H<sub>2</sub> – TPR analyses were conducted using a Micromeritics Autochem II equipped with a thermal conductivity detector (TCD). Each H<sub>2</sub> – TPR experiment was conducting using 50mg of CuY under 5cm<sup>3</sup>min<sup>-1</sup> flow of 10.125wt% H<sub>2</sub>/Ar, with a sample ramp rate of 10°C min<sup>-1</sup>. Prior to conducting XRD or H<sub>2</sub> – TPR, the CuY was activated at various conditions as shown in Table 4.1.

Ex Situ						
Condition	Activation Gas	Final Temperature				
1	Helium	150°C				
2	Helium	300°C				
3	Helium	450°C				
4	Helium	600°C				
5	50% H <sub>2</sub> /N <sub>2</sub>	150°C				
6	50% H <sub>2</sub> /N <sub>2</sub>	300°C				
7	7 50% H <sub>2</sub> /N <sub>2</sub>					
8	50% H <sub>2</sub> /N <sub>2</sub>	600°C				
In Situ						
1	Helium	150°C				
2	Helium	300°C				
3	Helium	450°C				
4	Helium	600°C				
5	10.125%H <sub>2</sub> / Ar	150°C				
6	10.125%H <sub>2</sub> / Ar	300°C				
7	10.125%H <sub>2</sub> / Ar	450°C				
8	10.125%H <sub>2</sub> / Ar	600°C				

Table 4.1. Summary of ex situ and in situ activation conditions prior to conducting  $H_2$  – TPR.

Ex situ activation was performed in a tube furnace with a ramp rate of  $10^{\circ}$ C/min and hold time of 4h at final temperature. Upon completion, the CuY was removed from the furnace and immediately loaded into the Autochem for analysis. In situ activation was performed in the Autochem directly preceding analysis by H<sub>2</sub> – TPR, and thus was not exposed to air. In situ activation was performed with various hold times at 450 °C in helium condition to investigate how time affects reduction percentage, as discussed in Section 4.3.3. The comparison of ex situ and in situ results would allow for investigation into the re-oxidation effects of CuY upon exposure to air.

#### 4.3 Results and Discussion

#### 4.3.1 X-ray Diffraction

During XRD analysis, the activated CuY was exposed to ambient conditions. As such, the XRD patterns reflect a re-oxidized, re-hydrated state. The XRD patterns were conducted after in situ reduction conditions and are shown below as Figure 4.1.





Figure 4.1 . XRD patterns of each of the eight activation conditions. Conditions 1 – 4 are under a flow of helium gas at 150°C, 300°C, 450°C, and 600°C respectively. Conditions

5 – 8 are under a flow of 50%  $H_2$  /  $N_2$  gas at 150°C, 300°C, 450°C, and 600°C respectively.

The XRD patterns show that the crystalline structure of the zeolite is maintained after each activation condition. The characteristic peaks for crystalline CuO of  $35.5^{\circ}$  and  $38.7^{\circ}$  were not found in any of the XRD patterns.<sup>6</sup> This suggests that crystalline CuO > 5nm does not exist in the zeolite, but does not eliminate the possibility of CuO <5nm.<sup>15</sup> Additionally, there was no evidence of crystalline metallic copper.

# 4.3.2 H<sub>2</sub> – TPR Analysis after Ex Situ Activation

As shown in Figure 4.2 below, the H<sub>2</sub> – TPR results can be divided into two regions: the low temperature region (<450°C) and the high temperature region (>450°C). The low temperature region consists of two distinct peaks: Peak  $\alpha$  at 210°C and Peak  $\beta$  at 300°C. It is well known in literature that Peak  $\alpha$  corresponds to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> from the zeolite supercage.<sup>6,7,15</sup> Furthermore, CuO also reduces in the low temperature range between 180 - 285°C.<sup>5,6,13,16,27,28</sup> Peak  $\beta$  corresponds to the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> to Cu<sup>+</sup> in the smaller, sodalite cavities of the zeolite structure. If Cu<sup>2+</sup> ions are present in the hexagonal prism, a peak will appear at 450°C, corresponding to the reduction to Cu<sup>+</sup>.<sup>29</sup> The results shown in Figure 4.2 suggest there are no Cu<sup>2+</sup> ions present in the hexagonal prism. The high temperature region, peak  $\gamma$ , corresponds to the complete reduction of all Cu<sup>+</sup> to Cu<sup>0</sup>.



Temperature (°C)

Figure 4.2  $H_2$  – TPR results after ex situ activation.

The similarity of these peaks suggests that regardless of the activation conditions, the activated CuY re-oxides upon exposure to ambient air. Herman and coworkers developed the following mechanism to describe this fast re-oxidation:

$$\frac{1}{2}$$
O<sub>2</sub> + H<sub>2</sub>O +2Cu<sup>+</sup> → 2[Cu(OH)]<sup>+</sup>  
2[Cu(OH)]<sup>+</sup> + Z-OH → H<sub>2</sub>O + Cu<sup>2+</sup> + ZO<sup>-</sup>

in which Z denotes zeolitic oxygen or hydroxyls.<sup>16</sup> It is also known that Cu<sup>+</sup> is unstable in ambient air and can disproportionate to Cu<sup>2+</sup> and Cu<sup>0</sup>.<sup>30</sup> The hydrogen consumption corresponding to the ex situ H<sub>2</sub> – TPR peak areas is shown below as Table 4.2.

		High Temp		
Condition	Peak α	Peak β	Total	Peak γ
1	13.9 (0.47) <sup>a</sup>	2.7 (0.09)	16.6 (0.56)	14.4 (0.48)
2	12.0 (0.40)	3.7 (0.12)	15.9 (0.53)	15.6 (0.52)
3	10.2 ( 0.33)	3.8 (0.12)	14.1 (0.47)	14.9 (0.49)
4	9.9 (0.33)	3.2 (0.11)	13.2 (0.44)	15.7 (0.52)
5	8.7 (0.29)	3.1 (0.11)	11.9 (0.40)	14.7 (0.49)
6	4.3 (0.15)	3.2 (0.11)	7.4 (0.25)	15.4 (0.52)
7	5.3 (0.17)	2.7 (0.09)	8.0 (0.27)	15.2 (0.51)
8	3.2 (0.11)	1.2 (0.04)	4.3 (0.15)	14.4 (0.47)

Table 4.2 Hydrogen consumption after ex situ activation.

<sup>a</sup> The number outside the parenthesis is the volume of  $H_2$  consumed per gram of activated adsorbent (cm<sup>3</sup>/g). The number inside the parenthesis is the moles of  $H_2$  consumed per mole of Cu, assuming the ideal gas law with constant temperature of 100°C in the TCD. The hydrogen consumption error is ±3%.

The hydrogen consumption in the high temperature region remains constant throughout each of the eight conditions. The value of approximately 0.5 mol H<sub>2</sub>/mol Cu agreed with the theoretical value discussed in Section 4.2.2 for the complete reduction of Cu<sup>+</sup> to Cu<sup>0</sup>. The amount of reduced Cu<sup>2+</sup> species is determined by comparing this high temperature value to the total low temperature value. For condition 1, the value of the low temperature region is greater than the high temperature region, suggesting the presence of CuO < 5nm in the activated adsorbent.<sup>5</sup> Therefore, the results suggest that under ex situ conditions the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> in the zeolite supercage and the reduction of CuO to metallic copper both occur in a similar temperature range, rendering the two species indistinguishable. However, CuO is not known in literature to reduce in inert conditions or under reducing agent below 180°C.<sup>6,31</sup> Therefore, the downward trend in hydrogen consumption in the low temperature region from conditions 1 - 5 is likely attributable to the reduction of  $Cu^{2+}$  to  $Cu^{+}$ . The reduction only occurs in Peak  $\alpha$ , which suggests that only the Cu<sup>2+</sup> ions in the supercage are being reduced. This observation concurs with that of Gentry and coworkers.<sup>15</sup>

The likelihood of re-oxidation in ambient air is further noted by the observed color change in the activated adsorbent. Immediately after activation, prior to exposing the CuY to air, there was a noticeable color change in the CuY from its hydrated blue color to greenish blue at condition 1, green at conditions 2 - 4, pale green at conditions 5 - 6, and whitish purple at conditions 7 - 8. From literature, blue signifies hydrated Cu<sup>2+</sup>, green indicates dehydrated Cu<sup>2+</sup>, white indicates Cu<sup>+</sup>, and purple indicates the presence of metallic copper.<sup>7,16,25</sup> However, immediately after exposure to air, the color of activated adsorbent from conditions 1 - 6 returned to a blueish green and conditions

7 – 8 returned to a grayish color. These color changes upon exposure to oxygen and moisture in ambient air further suggest that  $Cu^+$  is re-oxidizing to  $Cu^{2+}$  and re-hydrating, and aid the explanation of H<sub>2</sub> – TPR peak similarity. Upon completion of H<sub>2</sub> – TPR the CuY turns a reddish brown, suggesting that all copper species have reduced to metallic copper, as shown below in Figure 4.3.



Figure 4.3. CuY before (left) and after (right)  $H_2 - TPR$  Analysis.

Because of the fast re-oxidation of copper species in CuY upon exposure to ambient air, any attempt to quantify the relative amount of each copper species would not accurately reflect the oxidation state that would occur directly after activation. The relative amount of copper species in each state is actively changing until placed in an atmosphere void of moisture or oxygen. The challenge of quantification is further exacerbated due to the aforementioned similarity in reduction range of supercage  $Cu^{2+}$ to  $Cu^+$  and CuO to  $Cu^0$ . Therefore, in order to properly investigate the effect of activation conditions of copper reducibility and perform accurate quantifications, it was necessary to perform in situ activation prior to  $H_2 - TPR$ .

# 4.3.3 H<sub>2</sub> – TPR Analysis after In Situ Activation

As discussed in Section 4.2.2, there is disagreement in literature as to the effect of reduction time in inert conditions to the reducibility of  $Cu^{2+}$  to  $Cu^{+,9,15,30}$  For this work, the effect of reduction time was investigated using in situ condition 3. The H<sub>2</sub> – TPR results are shown below as Figure 4.4.



Temperature (°C)

Figure 4.4  $H_2$  – TPR after in situ activation with varying hold times.

The similarity in peak shape and size suggests that the reducibility of  $Cu^{2+}$  to  $Cu^{+}$  is independent of time. This conclusion agrees with that of Gentry and coworkers.<sup>15</sup> The results also show peak  $\mu$  at 230°C, which likely corresponds to CuO < 5nm reducing to metallic copper.<sup>6,13</sup> The hydrogen consumption corresponding to these peaks is shown below in Table 4.3.

	Low Temperature				High Temperature
Condition	Peak α	Peak µ	Peak β	Total	Peak γ
30 min	6.0 (0.20) <sup>a</sup>	1.0 (0.04)	4.1 (0.13)	11.1 (0.37)	13.7 (0.45)
1 hr	5.4 (0.19)	1.2 (0.04)	4.6 (0.15)	11.2 (0.37)	13.1 (0.44)
2 hr	5.4 (0.18)	1.2 (0.04)	5.0 (0.17)	11.6 (0.39)	13.4 (0.44)
4 hr	5.4 (0.19)	1.2 (0.04)	5.1 (0.17)	11.7 (0.39)	13.3 (0.44)
10 hr	5.4 (0.19)	1.0 (0.04)	5.3 (0.17)	11.7 (0.39)	13.2 (0.44)

Table 4.3  $H_2$  – TPR after in situ activation with varying hold times.

<sup>a</sup> The number outside the parenthesis is the volume of  $H_2$  consumed per gram of activated adsorbent (cm<sup>3</sup>/g). The number inside the parenthesis is the moles of  $H_2$  consumed per mole of Cu, assuming the ideal gas law with constant temperature of 100°C in the TCD. The hydrogen consumption error is ±3%.

Due to the similarity in  $H_2$  – TPR results, a 30 minute hold time was utilized for

the following eight in situ activation conditions shown in Figure 4.5.



Temperature (°C)

Figure 4.5  $H_2$  – TPR analysis after in situ activation with a hold time of 30 minutes at maximum temperature.

The hydrogen consumption corresponding to the peaks in Figure 4.4 are shown

below as Table 4.4.

Table 4.4  $H_2$  – TPR after in situ activation with a constant hold time of 30 min at maximum temperature.

	Low Temperature				High Temperature
Condition	Peak α	Peak µ	Peak β	Total	Peak γ
1	12.3 (0.41) <sup>a</sup>	-	2.9 (0.09)	15.1 (0.51)	12.7 (0.43)
2	6.3 (0.21)	2.9 (0.08)	4.1 (0.13)	13.4 (0.44)	13.0 (0.43)
3	6.0 (0.20)	1.2 (0.04)	4.1 (0.13)	11.1 (0.37)	13.7 (0.45)
4	5.0 (0.17)	0.8 (0.03)	4.6 (0.15)	10.4 (0.35)	13.1 (0.44)
5	11.0 (0.37)	-	2.4 (0.08)	13.5 (0.45)	12.3 (0.41)
6					12.3 (0.41)
7					12.1 (0.40)
8					12.4 (0.41)

<sup>a</sup> The number outside the parenthesis is the volume of  $H_2$  consumed per gram of hydrated adsorbent (cm<sup>3</sup>/g). The number inside the parenthesis is the moles of  $H_2$  consumed per mole of Cu, assuming the ideal gas law with constant temperature of 100°C in the TCD. The hydrogen consumption error is ±3%.

Similar to what was seen in ex situ activation, the value of the low temperature region in conditions 1 and 5 are greater than the high temperature region, suggesting the presence of CuO < 5nm in the activated adsorbent.<sup>5</sup> For these two conditions the results suggest that the reduction of CuO to metallic copper and the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> in the zeolite supercage both occur in a similar temperature range, rendering the

two species indistinguishable. However, conditions 2 - 4 show a third, distinguishable peak  $\mu$  that corresponds to the reduction of CuO < 5nm to metallic copper. This CuO could either be formed during adsorbent synthesis, or it is formed as a byproduct during reduction in inert atmosphere as in the mechanism hypothesized by Larsen and coworkers.<sup>25</sup> Due to the apparent evolution of the appearance and shape of this peak, as can be seen by comparison of conditions 1 - 4, the data suggests that the former is the most likely cause of peak µ. As the activation conditions become more severe, more  $Cu^{2+}$  in the supercage is reduced to  $Cu^{+}$ , therefore the area of peak  $\alpha$  is reduced. Additionally, as can be seen by the upward trend of peak  $\beta$ , Cu<sup>2+</sup> ions appear to be migrating inward from the supercage to the sodalite cavity. As peaks  $\alpha$  and  $\beta$  change size and shape, peak  $\mu$  becomes more distinct. This would explain why peak  $\mu$  is not visible after ex situ activation, as the re-oxidation of  $Cu^+$  to  $Cu^{2+}$  causes the area of peak  $\alpha$  to grow to such a degree as to cause overlapping in the two peaks. If CuO was being formed by the activation process, it would be expected that its corresponding peak would grow in area, not decrease slightly as a function of temperature. Similar to what was found after ex situ activation, the decrease in peak  $\alpha$  as activation conditions become more severe between conditions 1 - 4, suggests that only the Cu<sup>2+</sup> ions in the supercage are being reduced. This observation, along with CuO not being formed during reduction in inert conditions and the degree of reduction being independent of hold time at maximum temperature, all agree with the work of Gentry and coworkers.<sup>15</sup>

Comparison of peak  $\alpha$  of conditions 1 and 5 suggests that under condition 5 a small amount of Cu<sup>2+</sup> is reduced to Cu<sup>+</sup>. However, conditions 6 – 8 show that complete reduction of all Cu<sup>2+</sup> and CuO is achieved. This is consistent with literature that

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suggests complete reduction of  $Cu^{2+}$  to  $Cu^+$  occurs at 231°C under reducing agent and CuO to  $Cu^0$  is achieved at 285 °C.<sup>6,13,30</sup> The similarity of peak  $\gamma$  throughout all conditions suggests that no additional  $Cu^0$  is being formed from the  $Cu^{2+}$ . Therefore, the data suggests that no  $Cu^0$  is present in the adsorbent after in situ activation conditions 1 - 5, but  $Cu^0$  is present after conditions 6 - 8, proportional to the amount of CuO present. Quantification of all copper species is now possible, and is shown below in Table 4.5.

Condition	Supercage Cu <sup>2+</sup>	CuO	Sodalite Cavity Cu <sup>2+</sup>	Cu⁺	Cu <sup>0</sup>
1	66.0%	16.0%	18.0%	0%	0%
2	42.0%	16.0%	26.0%	16.0%	0%
3	40.0%	8.0%	26.0%	18.0%	8.0%
4	34.0%	6.0%	30.0%	20.0%	10%
5	59.2%	16.0%	16.3%	8.2%	0%
6	0%	0%	0%	84.0%	16.0%
7	0%	0%	0%	84.0%	16.0%
8	0%	0%	0%	84.0%	16.0%

Table 4.5 Quantification of copper species after in situ activation, represented as corresponding copper species over the total copper mass.

The relative percentages error is ±3%.

From Table 4.5, the greatest percentage of  $Cu^+$  species that exist after reduction in inert environment is 20%, which is reduced entirely from supercage  $Cu^{2+}$ . The greatest percentage of  $Cu^+$  species that exist after reduction under reducing agent is 84.0% which accounts for the total amount of  $Cu^{2+}$  that exist in the prepared adsorbent.

#### 4.4 Conclusions

This study investigated eight ex situ and eight in situ activation conditions on copper loaded zeolite Y prior to conducting  $H_2 - TPR$ . Through noted color changes and similarity in  $H_2 - TPR$  peaks, all eight ex situ activation conditions resulted in the fast re-oxidation of Cu<sup>+</sup> species to Cu<sup>2+</sup> upon exposure to ambient air. Therefore, quantification of copper species directly after these activation conditions was not possible and in situ activation conditions were necessary. In situ activation under helium gas at 450°C was chosen to investigate the effects of reduction time. Six reduction times from 30 min to 10 hours all yielded similar H<sub>2</sub> – TPR peaks and corresponding hydrogen consumptions. Therefore, it was concluded that the degree of reduction is independent of time, which concurs with Gentry and coworkers.<sup>15</sup>

The eight in situ activation conditions were conducted with a 30 min hold time at maximum temperature. Under conditions 1 and 5, it was noted that the hydrogen consumption in the low temperature region was greater than the high temperature region, signifying the presence of CuO < 5nm. It was concluded that this CuO was formed during of the ion exchange process and was not formed during activation. The amount of CuO slightly decreased through conditions 1 - 4 and completely reduced to Cu<sup>0</sup> under conditions 6 - 8. The remaining peak area in the low temperature region is a result of the reduction of Cu<sup>2+</sup> to Cu<sup>+</sup> with separate peaks corresponding to copper ions located in the supercage or sodalite cavity of the zeolite Y. It was concluded that only Cu<sup>2+</sup> ions located in the supercage reduce under inert gas, with a maximum of 20% reduction observed at 600°C. The results also suggest that a smaller percentage of the

 $Cu^{2+}$  in the supercage migrated inwards to the sodalite cavity, but remained unreduced, as temperature under helium gas increased. Furthermore, due to the similarity in H<sub>2</sub> – TPR peaks in the high temperature region throughout all eight in situ activation conditions, it was concluded that no additional  $Cu^{0}$  is being formed by the  $Cu^{2+}$ . These conclusions are also consistent with that of Gentry and coworkers.<sup>15</sup> It was concluded that complete reduction of all  $Cu^{2+}$  ions and CuO occurred under conditions 6 – 8, yielding the relative percentage of copper species to be 84%  $Cu^{+}$  and 16%  $Cu^{0}$ .

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# Future Work

This thesis has advanced the study of adsorptive removal of sulfur containing compounds from fuel. In particular, we have performed an exploratory study of the effectiveness of adsorptive desulfurization using metal loaded zeolite Y on Intermediate Fuel Oil 380, IFO380. Additionally, we have expanded the initial work of Gupta and coworkers in sequential batch desulfurization of Jet Propellant 8, JP – 8. Finally, hydrogen - temperature programmed reduction of copper loaded zeolite Y was thoroughly investigated to determine the reducibility of copper species under various activation conditions. However, continued research could lead to further advancements.

This thesis concluded that adsorptive desulfurization with metal loaded zeolite Y is capable of removing sulfur from IFO380. Further investigation is needed for sulfur speciation of IFO380 to ascertain the relative amounts of each sulfur compound that is contained in the fuel. Once the types of sulfur compounds that exist within IFO380 are better understood, it may be possible to develop new adsorbents, with increased pore size and improved active site accessibility, to allow for better sulfur removal. The adsorptive removal of IFO380 was limited due to the presence of asphaltenes within the fuel, which accounted for over 14wt% of the total sulfur. More work is needed in this area to understand the full extent of the effect of asphaltenes on the adsorptive sulfur removal from IFO380, and how detrimental their presence is on the advancement of this desulfurization method.

This thesis also concluded that the copper and nickel loaded zeolite Y used in sequential batch sulfur removal of JP – 8 bonded to sulfur containing compounds via differing mechanisms. This assertion was largely based on the total sulfur results of the treated fuel and extensive literature review. However, to fully justify this claim, much more work is needed to speciate the sulfur compounds contained in the JP8 before and after each step. This information would provide insight into the affinity of each metal cation to specific sulfur compounds. Furthermore, the effect of aromatic and other competing compounds was only discussed in terms of the total sulfur removal in real JP8. In order to show the effect of these competing compounds more definitively, a more extensive study using model fuels is necessary.

Much work has been done over the last decade to improve the selective catalytic reduction (SCR) of NO<sub>x</sub> to N<sub>2</sub> using Cu-SSZ-13.<sup>1–4</sup> This zeolite is an eight membered ring of silica to alumina (Si/Al >15) with pore diameter of 3.8Å<sup>1</sup>. This zeolite has enabled much higher selectivity towards N<sub>2</sub> over N<sub>2</sub>O as compared to other copper zeolites, such as Cu-ZSM5 and Cu-beta and shows improved hydrothermal stability in temperatures of up to 800°C.<sup>1–3</sup> The improved selectivity and thermal stability is thought to be in part due to the non-exchanged copper salt that remains in the zeolite structure after synthesis. When calcined, the copper salt becomes CuO which is both active for SCR and selective.<sup>1</sup> Figure 5.1 below shows the location of copper in the Cu-SSZ-13 framework.



Figure 5.1. Copper location in Cu-SSZ-13 framework. Figure from Fickel and Lobo.<sup>3</sup>

Cu-SSZ-13 has not been investigated for its effectiveness for the adsorptive removal of sulfur containing compounds within heavy fuels or JP - 8. The scientific community in this field generally seek out zeolites with comparatively large pore diameters, such as zeolite Y, to improve the accessibility of the sulfur species to the active sites.<sup>5</sup> The pore diameter of SSZ-13 is 3.8Å, significantly smaller than the 7.4Å diameter of zeolite Y. Therefore, Cu-SSZ-13 may show decreased performance as compared to CuY for the removal of two – ringed or more aromatic compounds, but may show improved selectivity for aliphatic sulfur species and single ringed thiophenes.

Finally, this thesis thoroughly investigated the temperature programmed reducibility of copper species in copper loaded zeolite Y. The results obtained after activation under inert gas agreed heavily with previous work performed in literature
using  $H_2 - TPR$ . However, significant disagreement exists in literature as a whole as to the maximum achievable reducibility of  $Cu^{2+}$  ions to  $Cu^+$  using other analysis techniques, namely electron paramagnetic resonance (EPR). More work is needed to investigate the reducibility of copper species in copper loaded zeolite Y using both techniques to investigate why the different analyses provide such widely differing results.

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