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Phenol Deoxygenation over Hydrotreating Catalysts

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PHENOL DEOXYGENATION OVER HYDROTREATING CATALYSTS

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HONORS THESIS REPORT

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ABSTRACT

Phenol deoxygenation has been investigated as a model reaction for the deoxygenation of fatty acid methyl esters in biodiesel. Hydrodeoxygenated biodiesel is a drop-in fuel for petroleum diesel, and is a premium diesel with a high cetane number. As the first step in this research, two molybdenum catalysts were prepared, characterized and tested in a small-scale reactor. These catalysts were found to produce small amounts of benzene and cyclohexanol in the product stream, and confirmed the activity of the catalyst. A commercial cobalt molybdenum catalyst (Harshaw HT-400) was also tested and benzene, cyclohexanol, and cyclohexane were identified as products. Future work aims to synthesize catalysts to produce a high yield of cyclohexane. Once the conditions are optimized, we will do tests with biodiesel.

There exists a significant interest in developing fuels that are renewable, more environmentally friendly to produce, and will aid in powering our growing world. Biodiesel is just one of many biofuels that offers promise in this area. Since fatty acid methyl esters are found in diesel, they are of interest. By deoxygenating fatty acid methyl esters, a higher energy density fuel can be produced. [1] Additionally, deoxygenated biodiesel can be used as a drop in fuel, and can be mixed with diesel fuel and used without any engine changes. This mixture of biodiesel and petroleum diesel has lower emissions and is more sustainable than pure petroleum diesel. Deoxygenating diesel also increases the cetane number of the fuel. [2]

For deoxygenation reactions, phenol can be used as a model compound for fatty acid methyl esters. By investigating catalysts for phenol deoxygenation reactions, the reactor system can be optimized prior to testing catalysts on fatty acid methyl esters. Cobalt molybdenum catalysts are widely used in petroleum hydrotreating processes and in the hydrodesulphurization of diesel fuels.[3] Therefore, it is suggested that molybdenum catalysts will be effective for the deoxygenation of phenol.

The literature has suggested that the deoxygenation of phenol can take place through two different reaction mechanisms, shown below in Figure 1.[4]
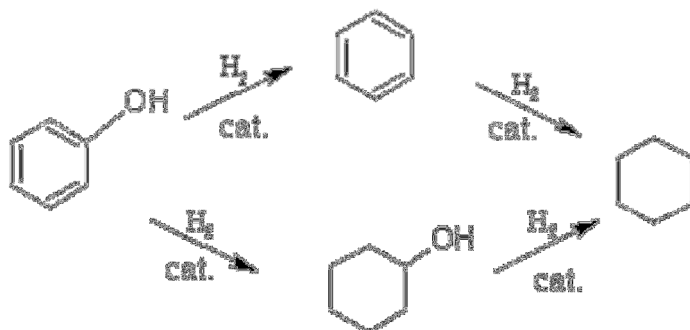

Figure 1. Proposed reaction mechanism

Phenol can be deoxygenated to form benzene and then saturated to form cyclohexane. It also can be saturated first to form cyclohexanol, and then deoxygenated to form cyclohexane. The desired product of this reaction is cyclohexane.

The goals of this experiment are to prepare and test molybdenum catalysts on the deoxygenation of phenol.

MATERIALS AND METHODS

CATALYST PREPARATION

Molybdenum on gamma alumina spheres (Davison Chemical) and Y-zeolite (Sigma Aldrich) supports were prepared. The pore volume of the supports was measured using a Micromeritics ASAP 2020 Surface Area and Porosity Analyzer. A molybdic acid in water solution was prepared with a volume equal to the pore volume of the sample. The concentration of molybdic acid in solution was selected to result in a 15 wt% molybdenum loading. Ammonia was added until the molybdic acid was fully dissolved. The molybdenum solution was added to the support and well mixed.

The catalyst sample was calcined under O_2 for 4 hours at 590 °C. A heating rate of 15 °C/min was used in the Thermo Scientific Lindberg Blue M Tube Furnace.

The catalysts are shown in Figure 2 below, with the Mo-gamma-alumina on the left and the Mo-Y-zeolite on the right.
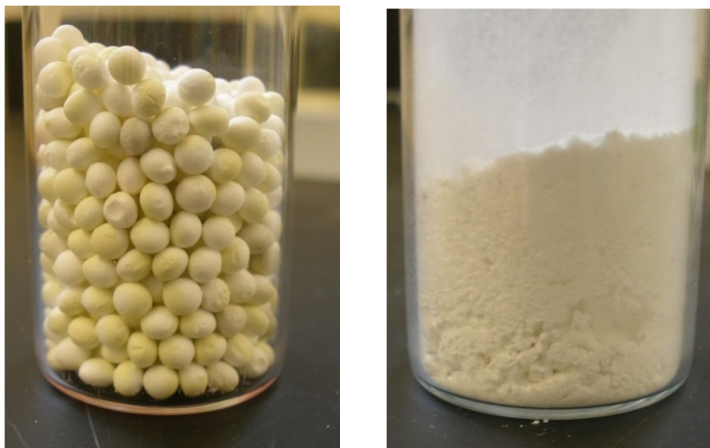

Figure 2. Prepared Mo-gamma alumina (left) and Mo-Y-zeolite (right)

After the catalyst was cooled, it was re-analyzed in the Micromeritics Analyzer to determine the final surface area of the catalyst.

REACTOR SYSTEM

Each catalyst was tested in a small scale packed bed reactor. The catalysts were reduced in hydrogen at 300 °C for 1 hour.

Hydrogen was fed through the bubbler containing 10 vol% phenol in decalin for 10 minutes and then the outlet of the bubbler was sampled and tested in a Hewlett Packard 5890A Gas Chromatograph with a 3396 Series II Integrator.

The flow rate of hydrogen was calibrated by running hydrogen through the bubbler at varied flow rates. The flow rate with the highest GC area count of phenol, corresponding to the highest concentration of phenol in the reactor feed stream, was used in the reactions. Figure 3 below shows the flow rates tested. A rate of 30 mL/min was determined to be the optimal hydrogen flow rate.
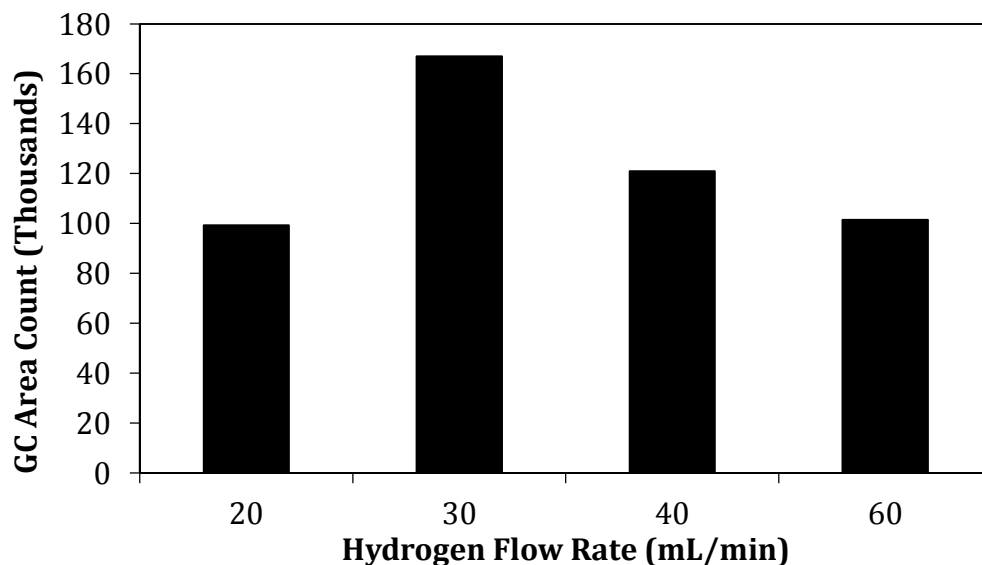

Figure 3. Calibration of hydrogen flow rate through bubbler

The bubbler outlet was then connected to the reactor. This reactant stream contained phenol and decalin in the vapor phase, carried by hydrogen gas, as shown in Figure 4 below.
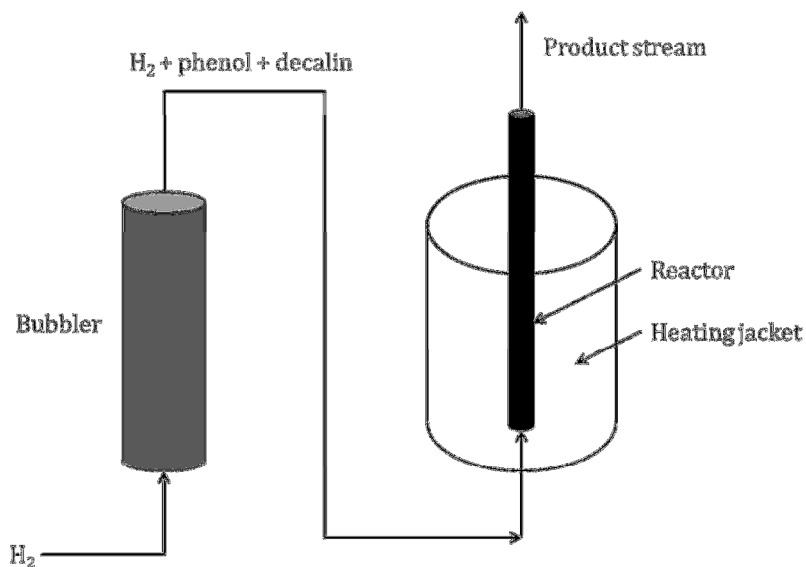

Figure 4. Reactor schematic

The reactor was kept at 300 °C throughout the experiment. The hydrogen, phenol, and decalin stream was fed through the catalyst bed for 1 hour and samples of the product stream were taken after 10, 30 and 60 minutes. The product samples were analyzed using gas chromatography.

RESULTS AND DISCUSSION

CATALYST CHARACTERIZATION

The pore volume of the catalyst supports was measured prior to impregnation. The results are shown in Table 1.

Table 1. Support pore volume

	Gamma Alumina Spheres	Y-zeolite powder
Pore Volume (cm³/g)	0.723075	0.307854

The gamma alumina spheres have more than twice as large of a pore volume per mass as the y-zeolite support. This is related to the density of each support since the y-zeolite powder is much more dense than the gamma alumina spheres.

Once loaded with molybdenum, the BET surface area of the catalysts was measured. Since surface area corresponds to the number of active sites, surface area is an important consideration for catalyst activity. The BET analysis applies the Langmuir isotherm to multilayer adsorption. Table 2 below shows the BET surface area for each of the tested catalysts.

Table 2. BET surface area of tested catalysts

	Harshaw HT-400 Hydrotreating Catalyst	Mo on Gamma Alumina (Davison Chemical)	Mo on Y-zeolite (Sigma)
BET surface area (m^2/g)	227	206	111

The commercial Harshaw catalyst had the highest surface area overall. Of the two prepared catalysts, the molybdenum gamma alumina catalyst had the highest surface area of 206 m^2/g. The molybdenum on Y-zeolite catalyst had the lowest surface area of 111 m^2/g. From these results, it is expected that the greatest activity will be on the catalyst with

the largest surface area, the Harshaw Hydrotreating catalyst. The least activity is expected to be on the catalyst with the smallest surface area, the Y-zeolite catalyst.

REACTION RESULTS

The product distribution over time was observed for each of the catalysts. For the reaction over the Harshaw HT-400 catalyst, all three expected products were observed. Figure 5, below, shows the change in production composition for samples taken after 10 and 30 minutes.
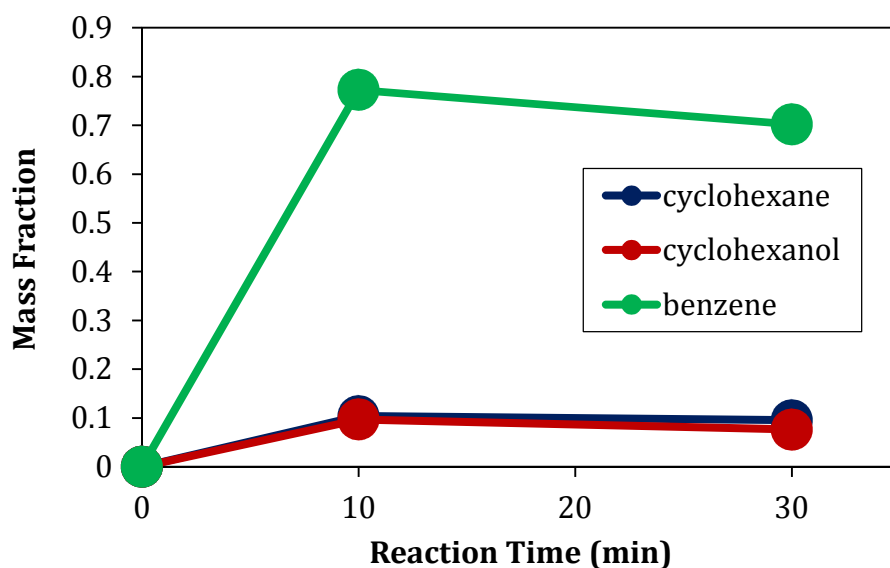

Figure 5. Harshaw HT-400 catalyst products over a 30 minute reaction

A large amount of benzene was produced, with the sample after 10 minutes containing around 80 wt% benzene and the sample after 30 minutes containing around 70 wt% benzene. Both cyclohexanol and cyclohexane were also found in the product stream, at about 10 wt% each.

All three expected products were found in the product stream; this indicates that the suggested reaction pathways in Figure 1 holds true for this catalyst system. The large amount of benzene compared to cyclohexanol indicates that the pathway from phenol to benzene is favored at the experimental reaction conditions. Additionally, the large amount of benzene compared to cyclohexane indicates that benzene is very stable and an improved catalyst system needs to be developed to increase the selectivity towards cyclohexane.

The product yields for the molybdenum gamma alumina catalyst were much lower than for the commercial catalyst. There was 7 wt% benzene after 10 minutes and 12 wt% benzene after 30 minutes. After 60 minutes, the product stream sample contained no benzene. Around 5 wt% cyclohexanol was in the product stream at each sample time. No cyclohexane was produced and a much larger amount of solvent remained in the product stream at each sample time. The product compositions are shown below in Figure 6 below.
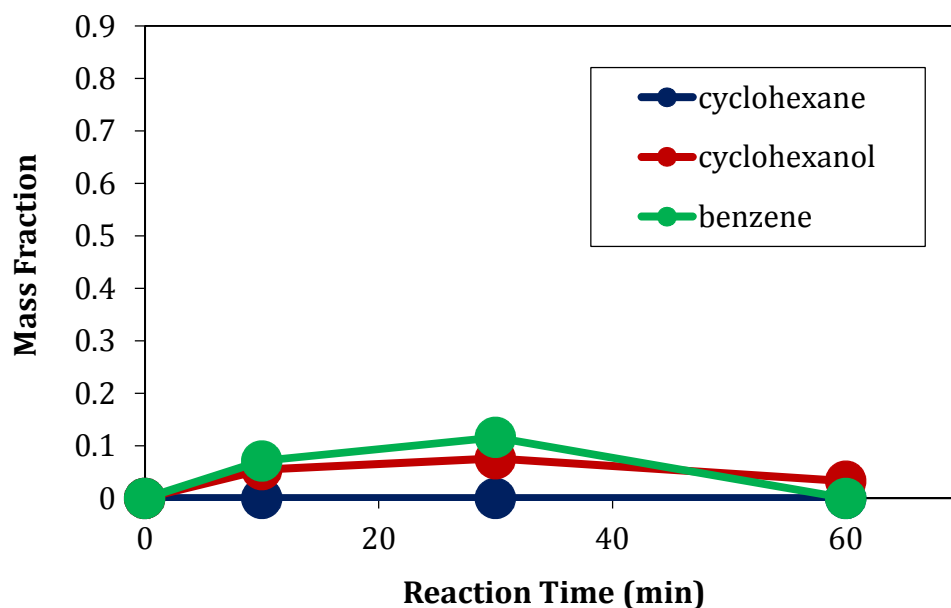

Figure 6. Product composition for the Mo-gamma-alumina catalyst

The spherical shape of the gamma alumina support may contribute to the low activity of the catalyst. The diameter of the catalyst pellets was almost as large as the reactor diameter, and therefore the catalyst bed was not tightly packed. This likely resulted in a large portion of the reactant stream flowing around the catalyst pellets, rather than through the catalyst, and subsequently lowered the activity.

The molybdenum Y-zeolite catalyst showed a product distribution and yield in between the commercial catalyst and the gamma alumina catalyst. A large fraction of benzene was observed in the product stream, similar to the commercial Harshaw catalyst. Like the gamma alumina catalyst, however, no cyclohexane was found in the product stream. Between 47 and 65 wt% benzene was produced at each sample time, and around 8 wt% cyclohexanol was observed at the 10 and 30 minute sample times. The sample taken after 1 hour found no cyclohexanol. A moderate amount of unreacted phenol was found to be present in the product stream at each sample time. The product distribution is shown below in Figure 7.
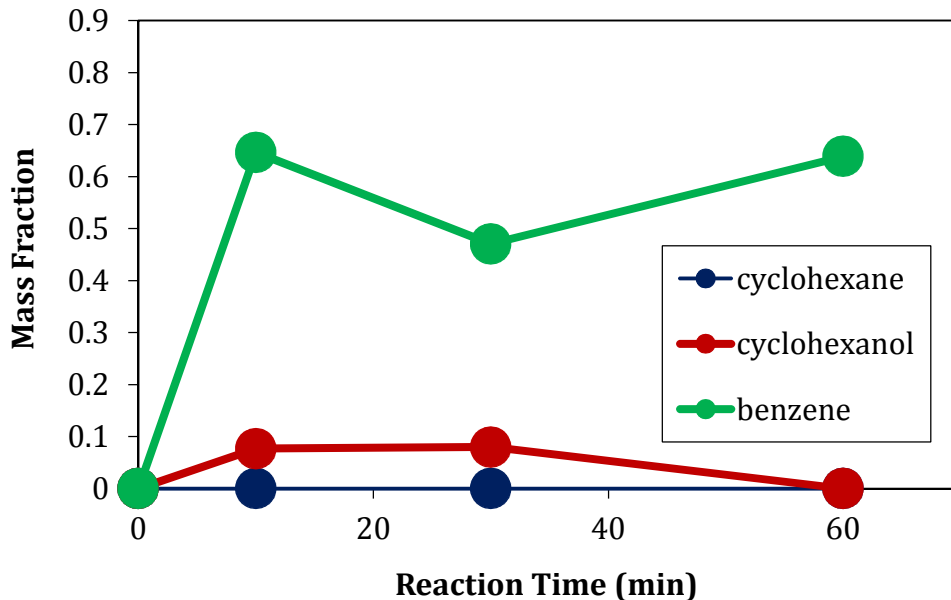
Figure 7. Product composition for the reaction over the Mo-Y-zeolite catalyst

The high production of benzene on the Y-zeolite catalyst may be in part due to the acid active sites on the zeolite. Zeolites are known to have catalytic activity, even without metal added. The deoxygenation of phenol to benzene is expected to be acid catalyzed, and therefore more benzene would be expected to be produced on a catalyst with acid sites.

As with the Mo-gamma alumina catalyst, the high stability of benzene and low yield of cyclohexanol inhibited the production of cyclohexane. Future work aims to overcome this challenge and produce cyclohexane with high yield and selectivity.

Another point of interest for this reaction is the deposit of coke on the catalyst surface. This may cause deactivation of the catalyst, if it were to be used for repeated reactions. Figure 8 below shows the commercial and gamma alumina catalysts after the reaction.

Figure 8. Spent catalyst

Although lower reaction temperatures are often used to reduce the formation of coke, optimization needs to be performed to determine the best conditions to increase product yields and decrease coke production.

CONCLUSIONS

This work found some activity for phenol deoxygenation on all three of the catalysts tested, the Harshaw HT-400 Hydrotreating catalyst, the prepared Mo-gamma-alumina catalyst, and the prepared Mo-Y-zeolite catalyst. The desired product, cyclohexane, was produced only on the Harshaw catalyst. Because of this, the prepared catalyst did not improve the deoxygenation of phenol over the commercial catalyst.

The Mo-gamma-alumina catalyst had the lowest activity, which is likely related to the shape and size of the catalyst particles. The spherical shape prevented a tightly packed bed in the reactor, and thus the contact time between the reactant stream and catalyst surface was reduced.

The Y-zeolite had the higher activity of the prepared molybdenum catalysts. This is likely due to the powder form, which allowed for a tightly packed bed. Additionally, the acid active sites known to be present on zeolites likely contributed to the activity of the reaction of phenol to benzene.

This work was successful in establishing a reaction procedure and confirming activity on all catalysts. Several areas for future work and improvement exist before moving on to the deoxygenation of fatty acid methyl esters.

FUTURE WORK

Future work on this project includes testing different reaction conditions and other catalyst preparation methods.

Reacting phenol at higher temperatures and/or pressures may increase the yields and selectivity to the desired product of cyclohexane.

Other catalyst preparation methods, such as incipient wetness, may improve the catalyst activity. By influencing the metal distribution on the catalyst surface, the selectivity may change from one pathway to another. Additionally, a more even distribution of active sites may improve the conversion of benzene to cyclohexane. Since the stability of benzene has been shown to be a challenge in the deoxygenation of phenol, a great interest exists in improving the conversion of benzene.

Once a catalyst system has been shown to be effective in the deoxygenation of phenol, the deoxygenation of fatty acid methyl esters will be tests.

Since the aromatic ring in phenol creates many challenges for the deoxygenation reaction, it may also be of interest to test other model compounds. Fatty acid methyl esters do not contain the aromatic ring, and so the saturation of that carbon ring is not of great interest. By testing non-cyclic model compounds, more comparable catalytic activity may be observed.

Several approaches for the improvement of this catalytic deoxygenation system exist with the end goal of deoxygenating fatty acid methyl esters.

ACKNOWLEDGEMENTS

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