SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
FINAL REPORT

SCHOLAR NAME:	David Hale
FACULTY ADVISOR:	Dr. Jason Hicks
PROJECT PERIOD:	Fall 2021/Spring 2022
PROJECT TITLE:	Catalyst Screening for the Plasma-Assisted Synthesis of Liquid Chemicals from Ethane
CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):	(X) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear ( ) Smart Storage and Distribution ( ) Transformation Solar (X) Sustainable Bio/Fossil Fuels ( ) Transformative Wind

MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

RESEARCH GOALS	ACTUAL PERFORMANCE AND ACCOMPLISHMENTS	% OF GOAL COMPLETED
Study non-catalytic shale gas feed to understand ethane activation	Ran mixed feed in plasma reactor, varying ethane composition, temperature, and power. The products of the reactions were analyzed using GC-MS, gas chromatography, and other methods	90%
Testing the effects of silica to alumina ratio in zeolite catalysis	Ran similar experiments at a fixed temperature (400°C), and power (10W), varying the silica to alumina ratio in the zeolites. This altered the production of various compounds.	40%
Test different metals and metal loadings in catalysis and activation of ethane	Tested using one specific metal loading, but focused primarily on silica to alumina ratio	10%

RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

CATEGORY	INFORMATION
EXTERNAL PROPOSALS SUBMITTED	
EXTERNAL AWARDS RECEIVED	
JOURNAL ARTICLES IN PROCESS OR PUBLISHED	
BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH	
PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH	
AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT	
INTERNAL COLLABORATIONS FOSTERED	
EXTERNAL COLLABORATIONS FOSTERED	
WEBSITE(S) FEATURING RESEARCH PROJECT	
OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups)	

RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

This experience was an excellent opportunity for me to explore the ins and outs of research. I found that the process of going to group meetings, listening to presentations, etc. was as helpful as the research itself in informing my goals beyond graduation. In a particular way, I found the interconnectedness of the chemical engineering department at Notre Dame to reveal a lot about research. The goal of research is to solve problems to make positive change, and I observed professionals and graduate students helping one another achieve that goal on various scales.

My research exceeded my expectations at the beginning of my Slatt fellowship. My PI Dr. Hicks, my graduate student mentor Deanna, and everyone else I worked with were very helpful towards my research. I learned a lot from each of them about the chemistry we were working with, and the process of research itself. The scope of my research changed throughout the course of the semester, and in retrospect I view that as a great example of how adaptable research must be. The only constraint that could be improved upon is simply the number of hours I was able to work. A lot of the experiments needed to be started in the morning to finish running in the early afternoon, so my class schedule made this difficult. In the summer this would not have been an issue, but in the future aligning my classes and the project I am on would be helpful to improve efficiency.

I look forward to engaging in similar research opportunities in the future. I have gained a lot of insight into my own desires in research and hope to use the information I have gained to participate in more meaningful experiences like this.

FINAL WRITTEN REPORT

Shale gas flaring accounts for an annual loss of upwards of 140 billion m^3 of natural gas. While natural gas can be used for heating and electricity, the search for alternative uses is growing, and processes are being developed for upgrading to more valuable gas and liquid products. This project is part of a recent push to find sustainable methods of using light hydrocarbon gases more effectively.

In general, C-H single bonds and N-N triple bonds are stable, requiring high reaction temperatures and pressures to realize reactions. Non-thermal plasma catalysis is low temperature and pressure alternative to traditional catalytic carbon and nitrogen coupling. Taking advantage of non-equilibrium conditions between energetic electrons and the gas in a reactor, shale gas components can be converted to liquid products in a nitrogen-rich plasma environment. This project focused on ethane, the second most abundant component of shale gas, and the zeolite ZSM-5 as shown in Figure 1 below.
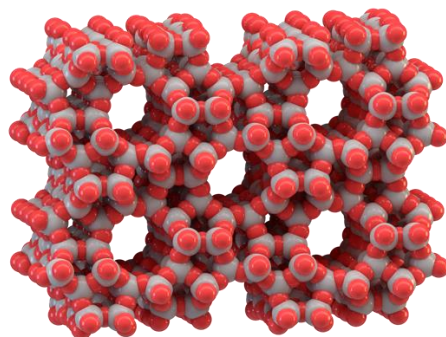

Figure 1. ZSM-5 catalyst structure

ZSM-5 is made up of silicon, aluminum, and oxygen atoms. For each aluminum atom substituted for a silicon atom in this matrix, a negative charge is balanced by a hydrogen ion creating a Brønsted acid site where aromatization readily occurs. After studying non-catalytic reaction conditions, the focus of this project shifted to studying the effect of altering the silica to alumina ratio.

In the non-catalytic experiments, gas products flowed directly to a gas chromatograph equipped with FID, TCD, and PID. Measuring the gas products throughout the experiment, the conversion of reactants can be tracked. This analysis also gives insight to the production of olefins, aromatics, and ammonia gas. The tunable parameters in this experiment are power, gas composition (varying ethane and nitrogen), and temperature. Power refers to the amount of energy deposited into the system. There is an inner electrode inside the reactor, and one outer electrode on the outside of the reactor. The plasma discharges in the gap between them, and this is where most of the chemistry takes place. Typical power for a reaction is on the order of 10W.

The gas composition affects the selectivity and yields of both the gas and liquid products. Most often, a low ethane fraction (<50%) is chosen for best results. Lastly, the temperature plays a large role in activating the bulk gas; at lower temperatures, the reactions are plasma-driven, but at higher temperatures some conversion of product is thermal-driven.

The data shown in Figure 2 below was taken from a non-catalytic experiment at 10W, 200°C, varying the ethane fraction and monitoring the liquid components using GC-MS.
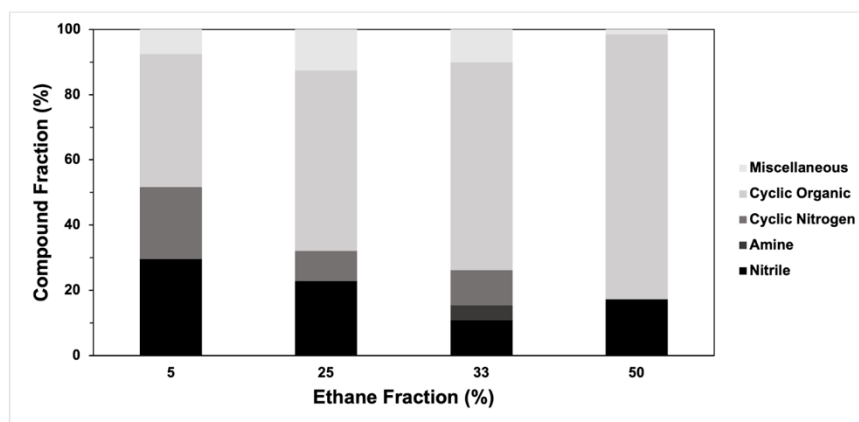

Figure 2. Liquid product types at varying ethane feed compositions (200°C, 10W)

This data shows the types of components detected in GC-MS. While in some cases specific components can be identified, in general at such low compositions and selectivity only functional groups can be identified with confidence. It is still helpful to understand at what compositions certain reactions take place. For example, at 5% and 25% ethane in an excess of nitrogen, 20-30% of the liquid products are nitrogen-containing aromatics, which are valuable products that can be produced from this reaction. Thus, in the next stage of the project (running catalytic experiments), low ethane compositions were used.

Results were taken from a series of catalytic experiments, monitoring the production of aromatics like benzene and toluene as a benchmark for production. Informed by the results of the non-catalytic experiment, a 400°C reaction with 25% ethane feed was run. Figure 3 below shows the production and selectivity of these products.
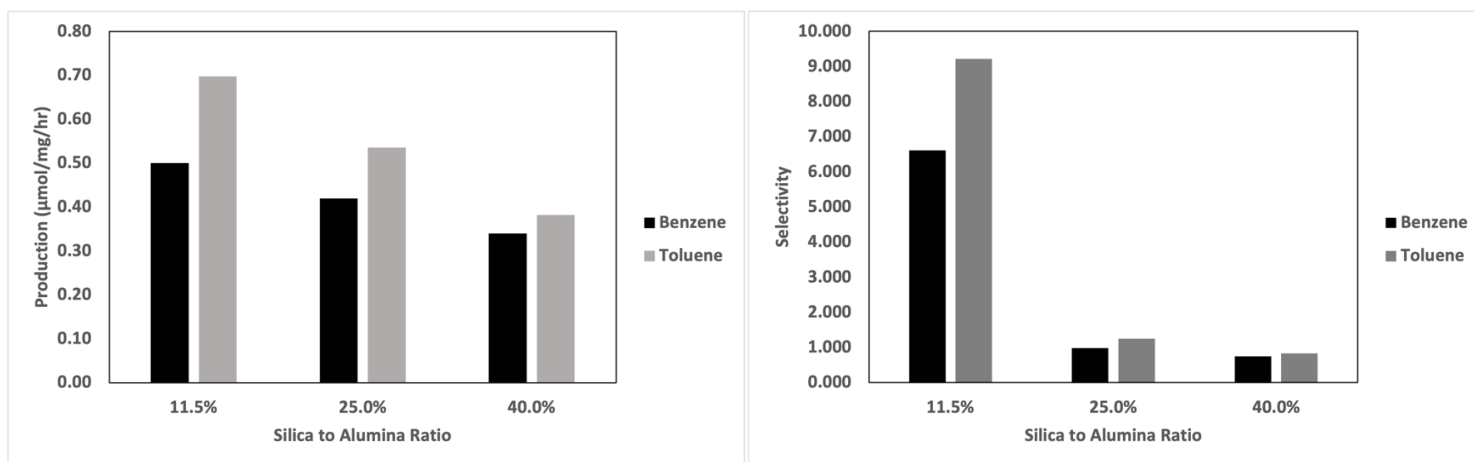

Figure 3. Production (left) and selectivity (right) of benzene and toluene at 400°C and 25% ethane feed

These experiments show a clear trend when varying the silica to alumina ratio. In all three experiments, toluene had a greater selectivity and production. This is interesting, because it suggests that if benzene is an intermediate to toluene, the rate of the conversion from the former to the latter must be greater than the rate of production of benzene. Due to the high reactivity of a plasma, the existence of additional intermediates is possible. These experiments also showed a variety of products with higher carbon numbers (C5+), but it is unclear what their exact chemical structure is.

Varying the silica to alumina ratio shows that there is less production of these aromatics at greater silica to alumina ratios in the range studied. It is important to note that at even lower silica to alumina ratios, the production may decrease as well. For the experiments run, a silica to alumina ratio of 11.5 had the best reaction conditions based on highest production of aromatics and selectivity. The selectivity at 11.5 a large increase compared to ratios of 25 and 40.

Another factor to consider in catalyst characterization and screening is affinity for coking. Coke is an unwanted byproduct of any reaction, as it slows the reaction rate over time, clogs the catalyst, and wastes reactants to unusable solids. When it comes to adding metal ions to the catalyst, coke production often increases especially in active metal loadings like platinum. The same experiment conditions as described in Figure 3 above were used to assess coke production as a function of increasing silica to

alumina ratio. Looking at the carbon balance, there is not a 100% balance from the known amount of carbon in the system from ethane and the amount out through products (and unreacted ethane). Using this metric and unbalanced carbon goes towards coking, the amount of coke produced was analyzed. The results are shown in Figure 4 below.
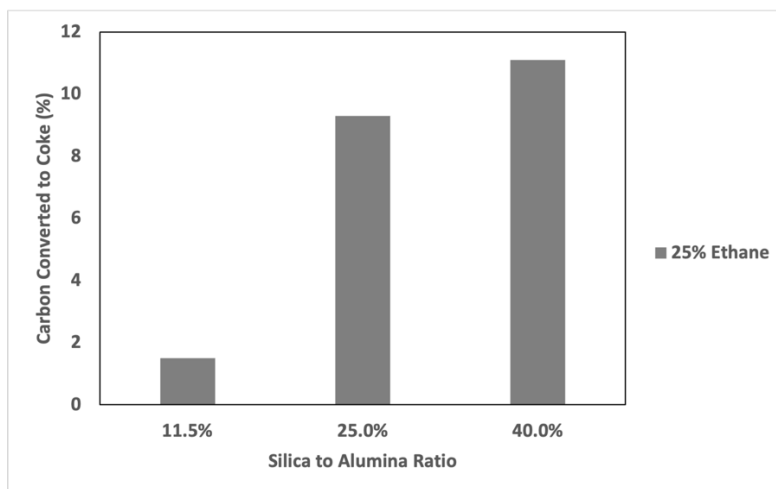

Figure 4. Coke production as a function of increasing silica to alumina ratio

These results show that coking increases with higher silica to alumina ratios. Each of these results are used holistically to determine the best silica to alumina ratio to use. In future experiments, it would be helpful to look at these same results over a broader range of silica to alumina ratios, as well as varying the ethane feed composition. Introducing new factors increases complexity, so the optimal conditions for non-catalytic experiments may differ from those with ZSM-5 present.

The next phase of this project, which I was unable to complete this semester, is focused on loading the catalyst with metals. I was able to complete this using two different methods, ion exchange (IE) and incipient wetness impregnation (IWI). Both methods are a way to load catalyst with metals, such as Molybdenum, Nickel, or Platinum. Using metal salt precursors in aqueous solution, IWI acts to mix directly into the catalyst. This process can be performed using many different metals and can be controlled by metal salt concentration. IE allows metals such as Nickel (2+) to exchange with hydrogen atoms in the ZSM-5 catalyst, replacing Brønsted acid sites with a metal site. This leads to better metal dispersion of the catalyst. Comparing these methods of synthesizing heterogeneous catalysts is one way to improve upon this study.