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INVESTIGATING DOPED MESOPOROUS ZSM-5 FOR CASCADE CATALYSIS

Introduction

With the recent innovations and progress in the nanotechnology industry, a family of microporous catalysts and adsorbents known as zeolites were developed in the mid 20th century. Zeolites have a wide-range of applications in energy utilization, so scientists have been carrying out research on this material with a focus on solving the world's global warming and energy crisis.

One Zeolite--commonly referred to as Zeolite Socony Mobil-5 (ZSM-5) has shown a significant promise especially regarding potential applications in the petrochemical industry. The petrochemical industry is a major contributor towards the emission of greenhouse gases which cause global warming. The petrochemical industry also suffers from inefficient energy consumption in processes such as fractional distillation, hydrocracking etc. Scientists have carried out extensive research on zeolites' application in post combustion CO₂ capture to reduce the emission of CO₂ and, in turn, reduce the effects of global warming. Similarly, scientists have also considered altering the acidity and basicity of the ZSM-5 to increase its catalytic efficiency for other industrial applications. Currently, the petrochemical Industry resorts to energetically intensive and inefficient processes to convert larger hydrocarbons to lighter, more valuable hydrocarbons and using ZSM-5 is a huge step towards solving this crisis.

This study plans on addressing this energy crisis by analyzing the catalytic efficiency of the ZSM-5 in carbon-carbon bond forming/breaking reactions like the aldol condensation reaction and the one-pot deacetylation Knoevenagel cascade reaction. In this research, I will start by varying the acidity of the ZSM-5 by synthesizing various forms of the ZSM-5 and substituting silica atoms for heteroatoms like Tin, Aluminum and Boron. The acid sites act as the catalyst for the first step of the Knoevenagel reaction I will then introduce mesopores into the ZSM-5s through a mesopore forming agent known as Dimethyloctadecyl[3-(trimethoxysilyl)propyl] ammonium chloride (TPOAC). The mesopores will serve to allow grafting of a fixed amount of organo-silanes on the surface of the ZSM-5. The fixed amount of organo-silanes in turn serves as a basic functional group and ensures the basicity of each ZSM-5 is roughly equal. The basic sites act as the catalyst for the second step of the Knoevenagel reaction. The bi-functional catalyst (acidic and basic) will be analyzed using X-ray diffraction and Thermogravimetric analysis to ensure the desired structural goal is achieved. Subsequently, the various bi-functional catalytic ZSM-5s will be analyzed for their respective catalytic efficiency in the one-pot deacetylation Knoevenagel cascade reaction with the non-catalyzed

reaction serving as a control experiment. The results of each experiment will be analyzed using gas chromatography and the catalytic efficiency will be determined through the measured conversion of each reactant. I hypothesize that the Tin, Aluminum, Boron and All-Silica ZSM-5s will have a decreasing order of acidity and in turn a decreasing order of catalytic efficiency in the cascade reaction. This is because the density functional theory suggests the level of acidity to be in that order and the first step of the cascade reaction is the rate determining step and is also acid-catalyzed.

Conclusively, the results from this research could highlight the catalytic efficiency of the ZSM-5 and highlight its effectiveness in solving the world's energy crisis. With the current move towards sustainable energy and energy efficiency globally, it is imperative that the Petrochemical Industry solves its energy crisis, to not be left behind in the energy race

Literature Review

Zeolites are microporous silica-based materials that are used commercially as adsorbents and catalysts. They have the potential to solve two primary issues facing the petrochemical industry; global warming and energetically expensive cracking processes. The specific zeolite focused on in this research is known as *Zeolite Socony Mobil-5 (ZSM-5)*. It has the advantage of being stable under high temperatures and pressures, which are usually the conditions of cracking processes [1]. Therefore, ZSM-5 is favored over other types of zeolites in the Petrochemical Industry.

Many carbon-carbon bond breaking reactions used in the petrochemical industry are acid-catalyzed. Thus, tuning the acidity of the ZSM-5 would serve as a very effective way to create a high-functional catalyst specific to a certain reaction. For a long time, scientists have debated whether the heteroatom composition, density or concentration influenced the ZSM-5's acidity. In a study performed by Jones et al, the effects of heteroatoms (Aluminum, Gallium, Boron and Iron) on the acidity of the ZSM-5 were investigated [3]. The effects of composition, location and concentration of the heteroatoms on the acidity of the ZSM-5 were also investigated and the results represented a huge progress for the nanotechnology industry. Through density functional theory estimates of acid strengths, Jones and his team could show that heteroatoms composition, not density/concentration, influences the acid strength of the ZSM-5 zeolite. The results also showed that Aluminum, Gallium, Iron and Boron had effects on the acidity of the MFI zeolite in a decreasing order. These results allow for petrochemical industries to fine tune the acidity of the zeolite to meet certain specifications for a carbon-carbon bond breaking chemical reaction.

In another study by Shirazi et al., the effects of changes in the Si/Al ratio (ranging from 10-50) of ZSM-5 zeolites synthesized using the same organic template (tetrapropylammonium bromide (TPA-Br)) were investigated [4]. The samples were characterized using XRD, FT-IR, SEM and EDX techniques. The results from the XRD showed all samples to give the characteristic ZSM-5 X-ray diffraction pattern, as such altering the Si/Al ratio does not fundamentally alter the ZSM-5 zeolite. However, the SEM results showed that ZSM-5's synthesized with different Si/Al ratios had different morphologies and particle sizes. The general trend was that the average crystal size of the ZSM-5 increased as the Si/Al ratio increased. Results also showed that decrease in Si/Al ratio also decreased the surface area of the ZSM-5. Finally, the results also showed that decrease in Si/Al ratio led to increase in total acidity of the ZSM-5 zeolite. However, both studies by Dr. Jones and Dr.L. Shirazi failed to investigate how the basicity of the ZSM-5 can be altered. Aside from acid-catalyzed carbon-carbon chemical

reactions, base-catalyzed carbon-carbon chemical reactions are also prominent in the petrochemical Industry. Thus, the ability to tune the acidity and basicity of the ZSM-5 simultaneously would prove very useful.

In another study by Brunelli et al, the effects of grafting Organo-Silanes on SBA-15 which contains acid sites analogous to those present in ZSM-5 [2]. This study successfully showed that creating a bi-functional catalyst with the ZSM-5 is feasible. Bi-functional catalysts are superior because both the acid and basic functional groups are immobilized on the ZSM-5 silica support. The study took it a step further and investigated how changing the alkyl chain length (C_1 - C_5) on the organo-silane affected the co-operative interaction of the bi-functional catalyst between the organo-silane (basic group) and the silanol sites (acidic group). The results showed the alkyl chain length strongly affects the catalytic and adsorptive cooperativity for carbon-carbon bond forming/breaking reactions and CO_2 capture respectively. The catalytic co-cooperativity increases with the linker length from methyl (C_1) up to propyl (C_3). However, from propyl (C_3) to pentyl (C_5), no additional cooperativity was observed. Similar trends were also observed for the adsorptive co-cooperativity.

Aside from acidity and basicity, it's also important to understand how the physical properties of the ZSM-5 changes under different conditions during its synthesis. In another study by Sang et al., the differences in ZSM-5's synthesized using different templates (organic and inorganic) or no template at all were analyzed [5]. The authors analyzed the morphology, pore sizes, Silica/Aluminum ratio, surface areas and catalytic efficiencies in a *n*-Hexane cracking reaction of the various ZSM-5 samples. The samples were characterized using XRD, SEM, XRF, NH_3 -TPD and BET- surface area measurement. The results showed that it was easier to synthesize ZSM-5 using an organic template compared to using an inorganic template or no template at all. They also showed that Silica/Aluminum ratio and surface area was smallest for the ZSM-5's synthesized with ethanol was the template. The sample synthesized without a template was found to have the fewest strong acid sites but was the most effective in the *n*-Hexane cracking reaction. This paper shows how, with the same synthesis conditions, varying the template alters the properties of the ZSM-5. Thus, varying the template for the ZSM-5 can produce several ZSM-5's with different properties to meet specific needs or applications.

However, all these studies failed to investigate specifically how all these factors interplay and affect the overall catalytic efficiency of the ZSM-5 in common carbon-carbon bond breaking reactions used in the petrochemical Industry. They also failed to evaluate the catalytic efficiency of the hybrid bi-functional ZSM-5 catalyst (that is containing both the acidic and basic groups) and acid-base cooperativity in cascade reactions.

The current study plans to fill this gap of knowledge left by previous studies by synthesizing various forms of the bi-functional hybrid ZSM-5, tuning its acidity and investigating its catalytic efficiency in a cascade reaction known as the “One-Pot Deacetylation Knoevenagel” reaction. The structural properties and morphology of the hybrid ZSM-5 synthesized in this study will be analyzed using X-ray diffraction and Thermogravimetric Analysis. The results from these experiments will be compared to the expected results of a hybrid ZSM-5 for accuracy. The catalytic efficiency of the bifunctional ZSM-5 will be evaluated using gas chromatography and compared to the non-catalyzed reaction as control. The performance of each catalyst will also be evaluated to determine the effects of acidity on the catalytic efficiency in this cascade reaction. This study will provide a better understanding of the bi-functional hybrid ZSM-5 catalyst and how the acidic and basic functional groups interplay and affect its catalytic efficiency. This study will potentially positively contribute to solving the energy crisis plaguing the petrochemical industry’s cracking processes.

Methods and Materials

Synthesis of Hierarchical ZSM-5 Zeolites

In this study, various types of ZSM-5 Zeolites were synthesized by changing the heteroatom. As a form of control, the Silicon: Heteroatom mole ratio was kept fixed at 250:1. The general procedure used in this study for synthesizing the ZSM-5 zeolite is as outlined below.

First, 80 mL of deionized water was measured and poured into a 250-mL beaker. 0.47 g of Sodium Hydroxide (NaOH) was then added to the beaker. The equivalent amount of the heteroatom source, following the 250:1 molar ratio, was then added to the mixture in the 250 mL Beaker. For Boron, the source was Borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and 0.009 g of Borax was used for this experiment. For Aluminum, the source was Sodium Aluminate (NaAlO_2) and 0.008 g was used for this experiment. For Tin, Tin(IV)Chloride Pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$) was the source and 0.034 g of this source was used for this experiment. For the control sample, All-Silica ZSM-5, no heteroatom source was used. After introducing the heteroatom source to the mixture, 1.66 g of Tetrapropyl Ammonium Bromide (TPABr) was added to the mixture in the 250-mL beaker and this mixture was stirred continuously for 10 minutes for proper mixing.

Subsequently, 5.08 g of the Silica source, TetraEthylorthoSilicate (TEOS), was added to a 100-mL beaker along with 2.55 g of the mesopore forming agent, Dimethyl Octadecyl [3-trimethoxysilyl]propyl] Ammonium Chloride (TPOAC). After the mixture in the 250-mL beaker was continuously stirred for 10 minutes, The TEOS/TPOAC mixture was then added to it dropwise using a pipette. The subsequent reaction mixture was then stirred continuously for 3 hours.

The reaction mixture was then added to a Teflon-coated stainless-steel autoclave and put in a rotating oven to react at 150°C for 5 days. The precipitated product was then filtered by suction and washed with 1 L of deionized water. The filtered product was then dried in an oven at 110°C for 24 hours. The dried product was then calcined in a calcination oven at 550°C for 12 hours.

The synthesized ZSM-5 then undergoes a cation exchange treatment. First, 35 ml of a 1M aqueous Ammonium Nitrate solution was added to a round bottom flask with 0.125 g of the ZSM-5. The solution was then mixed and stirred at 80 °C for 4 hour before being filtered. These steps are repeated 2 more times before the filtered product is re-calcined in a calcination oven at 550 °C for 6 hours.

X-ray diffraction (XRD) was used to study the bulk crystal structure of each synthesized ZSM-5 to ensure that we have synthesized the desired material.

Grafting AminoPropyl Trimethyl Silane (APTMS)

Aside from synthesizing Hierarchical ZSM-5's, Bi-functional ZSM-5s were also synthesized by grafting AminoPropyl Trimethyl Silane (APTMS) onto the mesopores of the ZSM-5's. The target was to graft 0.002 mole of APTMS per gram of ZSM-5. The general procedure used in this study for grafting APTMS is as outlined below.

First, 500 mg of ZSM-5 sample was added to a 50-mL round bottom flask along with 25 mL of Toluene and 0.001 mL of deionized water. 0.179 g of APTMS was then added to the mixture and stirred at 80 °C for 24 hours. The product was then filtered and washed several times with 200 mL each of Toluene, Hexane, and Methanol. The filtered product was then dried under vacuum at 60°C for 24 hours. Thermogravimetric Analysis (TGA) was used to determine the material's organic content and confirm the target of 0.002 mole of APTMS per gram of ZSM-5.

Analyzing catalytic efficiency in the One-pot Deacetylation Knoevenagel Cascade reaction

In this study, one-pot deacetylation Knoevenagel reaction was used to analyze the catalytic efficiency of the ZSM-5 zeolites that were synthesized. The catalytic efficiency of both the APTMS and Non-APTMS forms of all the various types of ZSM-5s (Tin, Aluminum, Boron and All-Silica) were analyzed. The non-catalyzed reaction served as a control for this experiment. The general procedure for this experiment is outlined below.

A stock solution was prepared in a graduate cylinder using 20 mL of Ethyl Cyanoacetate and 1 mL of Benzaldehyde dimethyl acetal. 10 mL of the stock solution is used and added to a round bottom flask along with 79 mg of the ZSM-5. The reaction mixture is continuously stirred and reacted at 80°C. Samples of the reaction mixture were taken at several time intervals and analyzed using Gas chromatography. The results of the analysis were then compared to the control experiment to determine the catalytic efficiency of the ZSM-5s.

Results & Discussion

After carrying out several experiments and carefully analyzing the results from each one, I was able to make the following conclusions about the various ZSM-5 catalysts I synthesized. The APTMS hierarchical ZSM-5 produced the target product, Ethyl trans-alpha-cyanocinnamate, whereas the non-APTMS hierarchical ZSM-5 did not. This was as expected because since the second step of the cascade reaction is base-catalyzed, the non-APTMS hierarchical ZSM-5 shouldn't be able to produce the target product due to the absence of the basic amine functional group.

Step one of the cascade reaction was also confirmed to be the rate determining step. This was confirmed by carrying out the overall reaction and subsequently carrying out the second step of the reaction separately. In the latter, the benzaldehyde reagent was completely reacted in one hour using both Tin and Aluminum APTMS ZSM-5 as catalysts. However, in the overall reaction the Benzaldehyde dimethyl acetal reagent didn't completely react in the 24-hour mark using the same catalysts. This confirms the first step of the cascade reaction as the slow or rate-determining step.

Finally, I confirmed the order of decreasing acidity to be as follows: Tin ZSM-5, Aluminum ZSM-5, Boron ZSM-5 and All Silica ZSM-5. This was achieved by evaluating the yield of Benzaldehyde from the first step using the Non-APTMS forms of these zeolites. Using the non-APTMS forms of these zeolites reduces the possibility of the second step of the reaction occurring. This allows me to get an accurate representation of the acidity of the zeolites from the yield of Benzaldehyde derived from the first step of the reaction, which is acid-catalyzed.

References

1. R. J. Argauer, M. D. Kensington, G. R. Landolt, and N. J. Audubon., "Crystalline Zeolite ZSM-5 and Method of Preparing the Same," US Patent no. 3702886, Mobil Co., (1972).
2. Brunelli et al., "Tuning cooperativity by controlling the linker length of silica-supported amines in catalysis and CO₂ capture." Journal of American Chemical Society (2012).
3. Jones, Iglesia, et al., "Acid strength and solvation in catalysis by MFI zeolites and effects of the identity, concentration and location of framework heteroatoms." Journal of Catalysis 213 (2014).
4. L. Shirazi, E. Jamshidi, and M.R. Ghasemi., "The effect of Si/Al Ratio of ZSM-5 Zeolite on its morphology, acidity and crystal size". Crystal Research and Technology (2008).
5. Sh. Sang, F. Chang, Zh. Liu, Ch. He, Y. He, and L. Xu, Catal. Today 93-95, 729 (2004).

Work Plan

Spring 2016, Summer 2016 and Spring 2017 semesters

Low Target (Achieved):

Scientific Reading: Read all scientific journals recommended by research advisor by Jan 2016.

Experiment #1: Synthesized hierarchical All Silica ZSM-5 by Jan 2016.

PURA Application: Applied for PURA for the summer 2016 semester by Feb 2016.

Experiment #2: Synthesized hierarchical Boron ZSM-5 by Feb 2016.

Experiment #3: Synthesized hierarchical Aluminum & Tin ZSM-5 by March 2016.

Ideal Target (Achieved):

Experiment #1: Grafted (3-AminoPropyl) TriMethyl Silane (APTMS) on all synthesized ZSM-5 by April 2016.

Data Analysis #1: Confirmed Loading of APTMS on all synthesized ZSM-5 using ThermoGravimetric Analysis (TGA) by April 2016.

Experiment #2: Synthesized Non-Mesoporous All Silica, Boron, Tin & Aluminum ZSM-5 by April 2016.

High Target 1 (Achieved):

PURA Acceptance: Accepted PURA for summer 2016 semester and commenced summer research project by May 2016.

Experiments: Performed multiple reactions using the various forms of synthesized ZSM-5 in the “One-Pot Deacetylation Knoevenagel” cascade reaction by July 2016.

Data Analysis: Data retrieval and analysis from the various experiments completed by July 2016.

Presentation: Present results from research to research group by Aug 2016.

High Target 2 (Not yet Achieved):

Return to research group to continue research project by Jan 2017.

Interesting results from summer project initiating additional experiments to be designed and carried out by March 2017.

Repeat experiments for data accuracy and retrieve publishable data by April 2017.

Publish scientific article based on research project under the advice of my research mentors Dr. Ryan Lively and Dr. Simon Pang by April 2017.

Present research at the UROP spring research symposium by April 2017.

Graduate with Bachelors' of Science degree in Chemical and Biomolecular Engineering with research designation by May 2017.