

**Catalytic Hydrodeoxygenation and Dehydration of Bioderived
Oxygenates to Renewable Hydrocarbon Building Block
Molecules: Enabling Renewable Carbon Fiber**

A Dissertation Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

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May 2017

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DEDICATION

I would like to thank my parents, Nina and Bruce Lepore, for always supporting me and encouraging me to push past the stop sign. For showing me the meaning of hard work and sacrifice. This wouldn't have been possible without your belief in me.

ACKNOWLEDGEMENTS

I would like to thank the Bredesen Center and ORNL for my continued education and the opportunity to carry out this research. The funding for this work came from a grant from DOE- Bioenergy Technologies Office (BETO) to Drs. Narula and Davison. Also, thank you to Dr. Choi for helpful discussions and continued encouragement. A special thanks to Dr. Li for helping to build our laboratory's capabilities and for providing advice throughout this process. Thanks to Larry Allard for performing the STEM imaging and Gou-Shio for performing *in-situ* DRIFTS. I would also like to thank my doctoral committee Dr. Narula, Dr. Davison, Dr. Laursen and Dr. Naskar for taking time to review this work. Lastly, I want to acknowledge the support of great friends and family who have helped me over the years. A special thanks to J.B. Sherrod and N.M. Lepore for helping during the editing process.

ABSTRACT

It is our goal to develop inexpensive catalytic pathways that can effectively remove oxygen from bio-derived carboxylic acids and alcohols under mild reaction conditions to produce propene which can be converted to renewable carbon fibers. Carboxylic acid hydrodeoxygenation and alcohol dehydration are necessary for successfully producing propene from bio-mass derived precursors and are also broadly relevant to bio-oil upgrading. This body of research adds to the understanding of both known and novel catalyst materials and develops and optimizes pathways for valorizing oxygenates. Dehydration and hydrodeoxygenation catalysts were examined under both batch and continuous flow operation. Product selectivity and reactant conversion with respect to temperature and space velocity were measured. The most promising catalysts were evaluated in durability studies, <100 hours and found to be stable. The results, described in this thesis, facilitate renewable carbon fiber processes from bio-mass and provide input for techno-economic analysis performed by the National Renewable Energy Laboratory. In addition, these results further advance our understanding of possible heterogeneous transformations relevant to valorizing bio-derived molecules.

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CHAPTER ONE INTRODUCTION AND GENERAL INFORMATION

Background

This dissertation explores inexpensive catalytic routes for the transformation of bio-derived oxygenates to hydrocarbon building blocks. Specifically, we studied propionic and acetic acid hydrodeoxygenation, acetone hydrogenation, and 1-propanol dehydration as catalytic processes to synthesize propene for manufacturing renewable carbon fibers. Initial catalyst screening was done using pure oxygenate feeds. The most promising catalysts were subjected to conditions that extend beyond ideal test operation. This included durability and water sensitivity research.

Carbon fiber production is currently based on propene derived from petroleum. Propene is reacted with ammonia to obtain acrylonitrile (ACN). The ACN is polymerized to polyacrylonitrile (PAN), spun, and pyrolyzed into carbon fiber.⁴ Developing economical bio-chemical strategies to produce renewable propene could make carbon fiber markets independent of petroleum. The work described in this dissertation is done under an ongoing renewable carbon fiber consortium, led by the National Renewable Energy Lab., in partnership with Oak Ridge National Lab. and Johnson Matthey. One of the synthetic strategies being pursued involves sugar conversion to propionic acid which can be catalytically deoxygenated in two steps to propene. Ketonization of acetic acid to acetone followed by hydrogenation and dehydration to propene is an alternative approach. The upstream acid production and separation is being conducted at NREL and the downstream production of renewable carbon fiber from PAN is planned for ORNL's carbon fiber facility. Our work focuses on addressing the technoeconomic challenges of removing oxygen from bio-derived chemicals to produce propene in high yield.

The development of heterogeneous catalysts has enabled global production of fuels and chemicals essential to billions of people. As the population grows and resources become more limited, renewable resources must be developed through technological innovations and industrial scale implementation. This is one of the greatest challenges of our time. To this end, grown biomaterials have the potential to be a source for commodity chemicals. Over many years, extensive effort has been devoted to developing the

technology to convert biomass into fuels and chemicals. However, competing economically with petroleum derived chemicals remains difficult. Ethanol produced from corn cellulose has been the primary exception.⁵ It owes its success largely to the combined efforts of policy and technology; however, competition with edible biomass is a chief point of contention which may be resolved as feedstocks move beyond cellulose.⁶ Evolving to lignocellulosic ethanol will require creative and innovative research. We must learn from previous studies, and we must be conscientious of the additional technical, economic and political challenges associated with turning biomass into useful chemicals.

The three primary pathways to convert lignocellulosic biomass into chemicals are gasification, pyrolysis, and hydrolysis as outlined in Figure 1. Note: All tables and figures are located in the appendix. Gasification is a process in which biomass is converted into syngas or synthesis gas (CO and H_2).⁷ Syngas can then be upgraded to alkanes, methanol, or H_2 via Fischer-Tropsch Synthesis (FT) or water-gas shift reaction (WGSR).² or fermentation⁸. However, biomass gasification is more suitable for small scale operations.⁹ Pyrolysis, the second pathway, can convert biomass into a complex mixture of oxygenates which need to be upgraded into a petroleum substitute.¹⁰ Techno-economic challenges must be resolved for this path to be commercially viable.¹¹ The third pathway, hydrolysis of lignocellulosic biomass, affords aqueous sugars and lignin.¹² It is possible to ferment these aqueous sugars into alcohols with known or genetically-modified microbes. The resulting alcohols can be used after purification or can be catalytically upgraded to hydrocarbons.¹³ For each of these pathways, catalysts are required for successful implementation. Most of these pathways have been demonstrated successfully at the laboratory scale.¹⁴

Carbon fiber composites are highly desirable due to their high strength to weight ratio. Widespread implementation of carbon fiber composites in vehicles would significantly improve gas mileage by reducing vehicle weight. As discussed previously, acrylonitrile (CAN), the building block of carbon fiber, is traditionally made via propene ammoxidation. Propene is primarily produced via petroleum catalytic cracking. The major challenges with petroleum-derived carbon fiber are: 1) propene price volatility which

accounts for ~50% of ACN's cost, and 2) the energy intensive nature of the process which leads to carbon fiber costs >\$10/lb.¹⁵ Considering this, a sustainable, cost effective technology to produce renewable carbon fiber will be highly desirable especially if it alleviates propene price volatility.

The NREL led consortium's objective is to produce high yields of propene from biomass under mild operating conditions with inexpensive, durable catalysts. The details of the reactant conversion, desired product selectivity, purity, catalysts durability, as well as the temperature and pressure of the reaction will be the metrics to evaluate the viability of renewable carbon fiber. The five potential pathways to produce bio-ACN are shown in Scheme 1-5 with the following intermediates: polyhydroxybutyrate (PHB), isopropanol (IPA), 3-hydroxypropionic acid (3-HPA), propionic acid (PA), and Acetone (ACE).

The last catalytic pathways in Scheme 4 and 5 are the focus of this dissertation. A more general scheme for the overall reaction network of interest, beginning with a carboxylic acid, is shown in Scheme 6. This scheme illustrates the predominant reactions relevant to upgrading bio-derived carboxylic acids to aldehydes, esters, alcohols, ethers, alkenes, and alkanes (Reactions 1-6, respectively). This is a simplified reaction diagram which does not include all possible products or all the sequential reactions which can occur under reaction conditions. We calculated the Gibbs free energy of each of the 6 reactions as a function of temperature (Figure 2). Negative ΔG_{rxn} values indicate that the forward reaction is favorable. From these preliminary calculations, we conclude that all of the forward reactions are favorable except acid hydrogenation at low temperatures (<200 °C) and that ether formation becomes more unfavorable with increasing temperature. This information helps provide context for the reactions relevant to this body of work.

This thesis is organized into three main sections. The first section focuses on hydrodeoxygenation (which includes steps 1, 3 and 6), and the second section focuses on dehydration (which includes steps 2, 3, and 4). Each of the chapters in sections 1 and 2 includes additional details on the generally accepted reaction mechanisms; the state of the art catalysts (and conditions used in the transformations); the technoeconomic challenges

that need to be addressed; and our approach to address these issues. Section 3 of the thesis describes methods employed in this work.

Hydrodeoxygenation of carbonyl compounds has received extensive attention due to its wide applications.¹⁶⁻²⁴ Carbonyl compounds such as acids, esters, aldehyde, acid anhydrides, ketones and lactones are ubiquitous in biological streams. Through hydrodeoxygenation, they can be converted into a wide variety of alcohols which are used in cosmetics, detergents, pharmaceuticals and textiles.²⁵ We present a summary of catalytic hydrogenation for a number of carboxylic acids in Table 1. Considering that most of the hydrogenation catalysts are based on precious metals, there are two possible approaches to developing inexpensive catalysts. The first being non-precious metal hydrogenation catalysts (i.e., carbides), and the second being single atom precious metal catalysts (which have ideal dispersion). Both are rapidly emerging as highly active, relatively low cost catalysts. Our work investigates both approaches.

The first step in carboxylic acid hydrodeoxygenation is the combined process of adding hydrogen and removing water to form an aldehyde. However, carboxylic acids are one of the most difficult carbonyl groups to hydrogenate; the order of difficulty is as follows: acid chlorides > aldehydes, ketones > anhydrides > esters > carboxylic acids > amides.²⁶ Catalytic acid hydrogenation is challenging due to the low electrophilicity and polarizability of the COOH group.²⁴ Homogeneous techniques have proven to be highly effective; however, the catalysts are often expensive and difficult to separate from solution after reaction is complete, limiting their industrial application.²⁷⁻²⁸ Heterogeneous catalysts, on the other hand, are better suited for industrial application; however these catalysts generally require harsher reaction conditions (typically >200°C and pressures >300 psi). Effective catalysts must serve two necessary functions: activate the carbonyl and dissociate hydrogen. The metal site accomplishes the hydrogen splitting. The support absorbs the acid and activates the carbonyl.²⁹

Hydrogenation of carboxylic acids is thought to occur via nucleophilic attack of the α -carbon with a hydride ion. As the carbon chain length increases, it becomes more difficult to hydrogenate the COOH group due to the alkyl chain's electron donating nature.

Hydrogenation is more favorable with electron withdrawing groups adjacent to the carbonyl. It has also been shown that bifunctional catalysts greatly improve acid conversion and alcohol yield (see Table 1, entries 6-8).³⁰ The reaction temperature has been proven to dramatically affect acid hydrodeoxygenation. At lower temperatures acid conversion is low, while at higher temperatures alcohol selectivity suffers due to the ease of alcohol dehydration.²⁴ High hydrogen pressure promotes acid conversions.²⁴ Recent DFT calculations emphasize the importance of solvent effects on liquid phase hydrodeoxygenation.¹⁶ Polar solvents such as water can increase the turn over frequencies by a factor of 30 as compared with non-polar solvents.²²

We have successfully employed carbides for propionic and acetic acid hydrodeoxygenation [Chapter 2], as well as acetone hydrogenation over single atom catalysts [Chapter 3]. Most acid hydrodeoxygenation studies have employed supported precious metals such as Pt, Pd, Ru, and Rh [Table 1]. In addition to hydrodeoxygenation, these catalysts also tend to be active towards decarboxylation.³¹ Molybdenum carbide catalysts provide an alternative to supported precious metal catalysts and have been shown to have high performance in reactions such as the hydrodeoxygenation of propanal.²¹ In our work, we investigated bulk metal doped Mo₂C catalysts in the hydrodeoxygenation of propionic and acetic acid. We evaluated the catalysts performance with respect to temperature and time on stream (TOS). The results show that it is possible to preform acid HDO under mild reaction conditions. Furthermore, Ca-Mo₂C shows superior selectivity towards acetic acid ketonization to acetone. These results show that the pathway presented in Scheme 5 may be a viable option for renewable carbon fiber production.

Single metal atoms on acidic supports have been proposed to bridge the gap between heterogenous and homogeneous catalysts and have been shown to be highly active for hydrogenation reactions.³² Considering that single atom catalysts are isoelectronic with their organometallic counterparts, we reasoned that the reaction pathways might, on such catalysts, have more in common with homogeneous catalysts than heterogeneous ones. Homogeneous hydrogenation is thought to proceed via oxidative addition, insertion, and then reductive elimination either via mononuclear or binuclear pathways.³³ First, hydrogen

is added to a metal center (oxidative addition). Second, the C-O or C-C double bond inserts between the M-H bond resulting in the first hydrogen transfer. The successive hydrogen transfer in mononuclear pathways completes the hydrogenation, and the reduced species leaves the metal ready to accept another hydrogen molecule. Heterogeneous catalysis, on the other hand, follows a Langmuir-Hinshelwood mechanism in which both the organic species and the hydrogen adsorb onto the metal particle's surface.³⁴ After the hydrogen dissociates, it migrates until it reaches the adsorbed organic species. This stepwise reaction can lead to both C-C bond formation as well as cleavage yielding non-selective product distribution.

The hydrogenation mechanism of an unsaturated C-C bond is not well understood due to the ambiguity in characterizing the active site. It is well-known that a surface metal atom interacts with the alkene and hydrogen; but, intermediates such as a π -complex, σ -bond, π -allyl complex can also be formed.³⁵ It remains unclear if adjacent metal particles participate.³⁶ We focus on single atom catalysts containing Ru, Rh, Pt, and Pd supported on Al₂O₃. The metals in these catalysts are excellent hydrogenation catalysts as nanoparticles or organometallic species. Reported research on hydrogenation reactions over SACs is limited.^{32, 37-40} We reasoned that low metal loading ~0.1% will not only conserve precious metals but will lead to catalysis under milder reaction conditions especially if the reaction pathways are similar to homogenous catalysts.

The second section describes our work on alcohol dehydration. The focus of this section is on dehydration of bio-derived alcohols to ethers and alkenes (reaction steps 4 and 5 in Scheme 4). We also discuss esterification as it relates to dehydration (step 2 in Scheme 5). Alcohol dehydration catalysts, found in recent literature, are summarized in Table 2. The main requirement for alcohol dehydration is catalyst acidity.⁴¹ Both Lewis⁴² and Brønsted acid⁴³ sites have shown dehydration activity. There are many inorganic oxides which have been studied for their alcohol dehydration abilities. These include: amorphous silica-alumina, aluminum phosphates, zeolites, heteropoly acids and sulfated metal oxides.⁴⁴ Enhanced conversion and selectivity can be achieved by tailoring the strength and nature of the acid sites to fit the reaction.

Unlike aqueous acids, measuring the acidity of solid materials is not trivial. There is a great deal of heterogeneity on the surface of solid acids. Thus, not all acid sites are created equal; just because an acid site exists does not mean that it is catalytically active. Over the years, many methods have been used to correlate acid strength and catalytic acidity. Titrating with base molecules seems to have led to the most meaningful results. This includes techniques such as NH_3 and pyridine temperature programmed desorption (TPD).⁴⁵ Dehydration of alcohols, such as 2-propanol, is another method that has been used to evaluate catalyst acidity.⁴⁶⁻⁴⁹ Needless to say, there is a plethora of information available on alcohol dehydration over solid acid catalysts. We predominantly focused on 1-propanol dehydration over metal exchanged zeolites [Chapter 4] and gamma-alumina [Chapter 5]. Catalytic activity and durability are presented in these chapters, and our results on the mechanistic aspects of 1-propanol dehydration over zeolites and γ -alumina are covered in Chapter 6.

In summary, we have optimized existing and developed new catalysts to create renewable propene from bio-derived oxygenates. We present the effects of reaction temperature and space velocity on product selectivity and reactant conversion. These results have led to optimization of reaction conditions for high selectivity of the desired product. In addition, we investigated catalyst durability studies, catalysts synthesis and characterization. Finally, we explored the dehydration mechanism using in-situ spectroscopy and deuterium labeled reactants.

Section I Acid Hydrodeoxygenation

CHAPTER TWO CARBOXYLIC ACID CONVERSION OVER DOPED MOLYBDENUM CARBIDES

Abstract

Developing an inexpensive catalyst that can effectively remove oxygen from biomass-derived compounds under mild conditions is particularly desirable. In this work, we investigated carboxylic acid transformations over molybdenum carbide catalysts. The focus was on understanding activity, selectivity, and stability trends as a function of metal dopant type and reaction temperature via laboratory flow reactor studies. Catalysts were characterized before and after the reactor evaluation to assist data interpretation. Metal-doped molybdenum carbides are versatile catalysts in carboxylic acid conversion. They were active towards acetic and propionic acid hydrodeoxygenation under atmospheric pressure and moderate temperatures (<500 °C). Selectivity towards ketonization was generally favored at elevated temperatures while aldehyde production was favored at lower temperatures. Overall acid conversion improved with temperature. We also find that calcium doped Mo₂C offers high activity and selectivity towards ketonization of acetic acid to acetone (96% yield at 450 °C). Potential loss in activity was observed over the 4 hour experiments. Our results show that doped Mo₂C are inexpensive materials for valorizing bio-derived acids.

Introduction

Organic acids are frequently found as byproducts in fermentation streams. For example, acetic acid is simply formed via the oxidation of ethanol by Acetic Acid Bacteria (AAB).⁵⁰ Carboxylic acids such as acetic and propionic acid are commonly found in pyrolysis bio-oil as well.⁵¹ However, these acids are of low value and present challenges in overall biomass conversion processes. For instance, small carboxylic acids in bio-oils can act as homogeneous acid catalysts promoting condensation of reactive other reactive species with resultant degradation in oil quality during long-term storage or high temperature upgrading. Hydrodeoxygenation of acids usually requires precious metals, high temperatures, and high hydrogen pressures.³⁰ For example, optimal conversion of oleic acid with high alcohol

yield (79%) over a Ru-Sn catalyst was achieved at 250 °C and ~830 psig.⁵² An industrially proven method over copper chromite requires even more severe conditions (280 °C and 4,350 psig) to upgrade fatty acids to alcohols.⁵³ Therefore, it is desirable to develop inexpensive catalysts that are capable of performing carboxylic acid hydrodeoxygenation under mild conditions. Interstitial carbides are robust materials which have catalytic properties similar to precious metals due to their electronic structure. However, precious metals have a greater tendency towards decarbonylation (DCO) over hydrodeoxygenation, and tend to fully saturate double bonds via hydrogenation. Carbides, on the other hand, have been shown to be more selective towards HDO than DCO as well as have superior stability under upgrading conditions.^{18, 21, 54} By being less active towards C-C bond scission the hydrocarbons produced typically have greater molecular weight and value.¹⁹ Furthermore, generating CO₂ not only reduces the carbon efficiency but it is also not ideal from a greenhouse gas perspective. We have explored the HDO of acetic and propionic over metal doped bulk Mo₂C.

Experimental

Materials

The propionic acid (Sigma-Aldrich, $\geq 99.5\%$), acetic acid (Sigma-Aldrich, $> 99\%$), CH₄ (Airgas, 99.99%), and H₂ (Airgas, 99.999%) were used as received.

Catalyst Synthesis and Characterization

The bulk Mo₂C catalysts used in this chapter were synthesized via a temperature-programmed carburization (TPC) described previously.⁵⁵ To study the effects of metal doping on molybdenum carbide properties, metal doped MoO₃ precursors were prepared before carburization. The precursors were prepared via a gelation method.⁵⁶ In brief, MoO₃ powder (Alfa Aesar) was suspended in an aqueous solution of sodium alginate. The oxide slurry was dropped into an aqueous solution of a metal chloride (CaCl₂ or NiCl₂). The Na⁺ ions in the alginate binder exchanged with the divalent metal ions (e.g., one Ca²⁺ ion for two Na⁺ ions) causing the alginate polymer molecules to cross-link. This process created a

rigid MoO₃ bead. For preparation of the three catalysts used in this study, Ni–Mo₂C (Ni doping), Ca–Mo₂C (Ca-doping), Mo₂C (un-doped), their respective oxide precursors were soaked for 2 h in 10, 2, 0 wt% metal chloride solutions.

The precipitated oxide beads were separated from solution, rinsed, dried, and heat-treated to 600 °C for 2 h in air. Alginate was removed by calcining the particle leaving behind the doped MoO₃ beads. Carburizing the metal-doped MoO₃ beads was accomplished via the TPC method in a tubular quartz reactor of ~2.5 cm internal diameter. During carburization, the oxygen is removed from molybdenum in the form of water and carbon monoxide leaving behind Mo₂C. The carburizing gas consisted of 15% CH₄ and 85% H₂ (flow rate: 104 sccm per gram of precursor), the sample temperature was raised from room temperature to 700 °C at 1 °C/min and held for 1 h. After cooling to room temperature, the synthesized carbides were passivated in a 1% O₂/N₂ flow for 12 h.⁵⁷

The morphology of carbides was analyzed via N₂ sorption using a Quantachrome Autosorb-1. The samples were outgassed for 24 h at 400 °C prior to analysis. The total pore volume was measured at (p/p₀=0.99) using Barrett-Joyner-Halenda (BJH) method. The pore size distribution was found using 19 point adsorption and 19 point desorption isotherms. The surface area was calculated from adsorption points with p/p₀ < 0.35 per Brunauer-Emmett-Teller (BET) method.

Catalysts Testing

Acid hydrodeoxygenation experiments were conducted using a bench-top flow through reactor system, as describe in the Methods chapter. The product selectivity and reactant conversion were measured as a function of temperature and time on stream (TOS). These experiments were run under atmospheric pressure. In a typical test, 400 mg of catalyst was packed in a 1 cm I.D. quartz tube. After loading the catalyst, the bed was heated to 500 °C at a rate of 5 °C/min under 45 sccm helium. At 500 °C, 5 sccm H₂ was added to the helium stream. The pretreatment was continued for 2 hours before cooling the reactor to 250 °C at a rate of ~10°C/min. The carboxylic acid was introduced into the reactor by redirecting H₂-He gas through a bubbler/saturator with an average flow of 0.15 ml/h affording an effective

space velocity of 0.37 h^{-1} WHSV (acid basis). The exit vapor was analyzed by directly injecting to either the GC-FID for product quantification or GC-MS for product identification. After the 1st injection, the reactor temperature was increased and allowed to equilibrate for an hour. This was again repeated and after the third injection the reactor was cooled to the initial temperature. Another sample was taken after an hour of equilibration. The fourth injection was meant to assess the stability of the material over the 4 hours of operation. For more details on the reactor, please see the Chapter 7.

Results and Discussion

Catalyst Characterization

Previous work has shown that the Mo_2C synthesis method can have a dramatic effect on the physical and chemical properties of the catalyst.⁵⁸ The surface properties of the carbide catalysts both before and after reaction are summarized in Table 3. Metal doping had a significant effect on the surface area of the resulting catalyst. The fresh catalysts, the un-doped, Ni-doped and Ca-doped had BET surface areas of 23.5, 15.7, and 9.55 m^2/g , respectively. The addition of calcium had the greatest impact on surface area. It is believed that calcium slows the carburization process which leads to greater sintering, thus lowering the surface area.⁵⁹ The total pore volume followed a similar trend. However, the average pore radius followed an inverse relation. The surface areas, post acetic acid hydrogenation, remained relatively unchanged. This suggests that the catalyst's morphology was not greatly altered under our reaction conditions.

Propionic Acid Hydrodeoxygenation

Propionic acid conversion and product selectivity was dependent on reaction temperature for all three Mo_2C catalysts [Figures 3-5]. Un-doped Mo_2C had three main products, C3 hydrocarbons (propane and propene), C2 hydrocarbons (ethane and ethylene), and propanal. At 250 °C, propanal was the major product (55% selectivity) indicating that hydrogenation was the dominant reaction pathway. The presence of C3 species were also significant at 35% selectivity. The propene could have come from dehydration of 1-

propanol produced by propanal hydrogenation. It is known that Mo₂C surface can possess acidic sites due to the presence of surface oxygen.⁶⁰ 1-Propanol, however, was not detected throughout the experiment. This suggests that either 1-propanol dehydration was very fast (i.e., consumed as soon as it formed) or propene was produced by direct hydrogenolysis of the aldehyde carbonyl group. C₂ products, on the other hand, were negligible. This suggests that cracking is not a predominant occurrence under these conditions. As the reaction temperature increased from 250 to 350 °C, the selectivity shifted away from propanal to C₃ species. The olefin selectivity is the alkene selectivity over the sum of the alkane and alkene species. Thus, propene was ~ 80% of the C₃ product, indicating that the catalyst had moderate activity toward double bond hydrogenation. A similar trend was observed with C₂ species. Increasing the reaction temperature to 450 °C drove the selectivity towards C₂ species with ethylene as the major fraction. One possible explanation for this transition is that C-C bond cleavage of propene molecules became a dominant reaction pathway at high temperatures. However, considering the limited CH₄ formation, its reactivity towards C-C bond cleavage was relatively modest compared to precious metal catalysts which would have produced predominantly CH₄ gas at this temperature. Reducing the temperature back down to 250 °C revealed that the catalyst's activity had significantly changed over the experiment, evidenced by the meager acid conversion (~5%).

Nickel-doped Mo₂C was subjected to a slightly different reaction temperature scheme which is as follows: 350 → 250 → 450 → 350 °C. As in the case of Un-doped Mo₂C, propanal was the major product. However, selectivity patterns as a function of temperature presented some substantial differences. For example, while the nickel doped catalyst exhibited a dramatic increase in 3-pentanone at 450 °C as compared with the un-doped catalysts (25 vs. 2.5% selectivity). Interestingly, the 3-pentanone selectivity was much higher at 350 °C at the end of the experiment than it was in the beginning (15 vs. 1.5%). On the other hand, the C₃ selectivity decreased from 30 to 3% over the course of the experiment. The olefin selectivity appears unchanged. This suggests that as the catalyst becomes less active towards acid hydrogenation and dehydration, the ketonization activity

improves. Further investigation into the catalyst acidity and the mode of deactivation is necessary to understand the phenomena behind this mechanistic shift.

The Ca-doped Mo₂C was also subjected to a temperature scheme that differed from the un-doped carbide. The reaction temperature scheme was as follows: 250 → 350 → 450 → 500 °C. After sampling the product stream at 500 °C the reaction was continued overnight, at this temperature, to assess the catalyst's stability. The behavior of the calcium doped Mo₂C was remarkably different from the un-doped or the nickel doped catalysts. At 250 °C, the catalyst was relatively inactive (acid conversion ~ 10%). However, increasing the reaction temperature improved acid conversion monotonously. At low temperatures, propanal was again highly favored but at elevated temperatures 3-pentanone was dominant. The C3 and C2 hydrocarbons remain minor byproducts over the entire temperature range. At 500 °C, 3-pentanone selectivity was 62% and propionic acid conversion was 96%. The reaction was continued at this temperature for 12 h at which point the 3-pentanone selectivity increased to 83% but the acid conversion had dropped to 45%. Therefore, the deactivation of Ca-Mo₂C was mainly accompanied by loss in its hydrogenation function while maintaining its ketonization ability.

In view of our results of propionic acid hydrodeoxygenation over metal carbides, we reasoned that acetic acid could go through ketonization to form acetone over metal carbides as well. Hydrogenation of acetone can lead to 2-propanol which can subsequently be dehydrated to propene. With this in view, we explored hydrodeoxygenation of acetic acid over the same metal carbide catalysts and the results are described in the following paragraphs.

Acetic Acid Hydrodeoxygenation

Hydrodeoxygenation of acetic acid was carried out over un-doped, Ni-, and Ca-Mo₂C. Product selectivity and acid conversion as a function of reaction temperature are summarized in Figures 6-8. Each reaction in this series was subjected to the same temperature sequence which was as follows: 250 → 350 → 450 → 250 °C. The only

exception to this was Ca-Mo₂C's final temperature was 350 °C because sampling at 250 °C would not have yielded useful data due to low conversion.

The un-doped catalyst produced mainly ethanal at 250 °C and the conversion was low (~20%). As the reaction temperature increased to 350 and 450 °C the conversion improved. However, selectivity towards methane became dominant (45% at 450 °C) indicating increased contribution from the DCO pathway. Acetone, the ketonization product, was being produced over the un-doped carbide; however, the yield was only ~15% at 450 °C. The final injection at 250 °C revealed a significant drop in catalyst activity.

Ni-doped Mo₂C had superior selectivity for the aldehyde product at low temperatures. This was consistent with the results seen from propionic acid hydrodeoxygenation. At higher temperatures methane and acetone became major products and the ethanal selectivity was diminished similarly to the un-doped Mo₂C. Returning to the lower temperature again revealed that catalyst deactivation had occurred to this catalyst also. Acetone selectivity was yet again enhanced in the catalyst's less active state. Acetic acid conversion decreased from 15 to ~1% between the two 250 °C measurements. In other words, Ni-Mo₂C deactivated with resultant selectivity changes. It appears that active sites responsible for acid hydrogenation were negatively affected possibly to the benefit of ketonization pathway. As described in Catalyst Characterization, the surface area and porosity of this catalyst did not experience any significant changes. Hydrogen activation property of carbides is known to suffer with surface oxygen accumulation, while oxygen-modified carbide surfaces present acid properties.²⁰ The observed deactivation could therefore be related to surface oxygen accumulation with TOS and temperature.⁶⁰

Ca-doped Mo₂C provided the highest acetone selectivity. At 450 °C quantitative conversion was achieved with 94% selectivity towards the ketone. At lower temperatures ethanal selectivity was dominant. Little selectivity towards light gases including methane was observed. Furthermore, the C₂ and C₃ products detected were purely alkene as shown in the olefin selectivity [Figure 8]. This suggests that Ca-Mo₂C was less active in reactions involved H₂ activation such as acid hydrogenation, alkene hydrogenation, and hydrogenolysis. This property may arise from its "basic" nature. In one study looking at

the decomposition of 2-propanol over Mo_2C , acetone selectivity was greatly enhanced by NH_3 poisoning.^{49, 61} This suggests that apparent basicity of the catalyst's surface may control selectivity.^{49, 61} It has also been shown that both acid and basic sites exist on Mo_2C and modification of these sites can have a profound effect on reactivity.⁴⁹ Based on our preliminary results, Ca- Mo_2C was more stable than un-doped and Ni-doped Mo_2C catalysts. Despite the fact that the former was run for 12 h at 500 °C, it retained significant activity, whereas the un-doped and Ni-doped catalysts lost most of their activity after just 4 h TOS (250-450 °C). This observation strongly suggests that the ketonization active sites (e.g., basic sites) are more stable than those responsible for hydrogen-activating sites (e.g., metallic sites). Further investigation is necessary to better understand the reasons that control the product distribution. With a more detailed understanding, a better catalyst may be designed.

Propene production from acetic acid may be accomplished via acetone hydrogenation to isopropanol followed by isopropanol dehydration. This provides yet another pathway to produce renewable propene. The hydrogenation of acetone will be explored more deeply in the proceeding chapter. Dehydration of 2-propanol is trivial in comparison to 1-propanol due to the enhanced stability of its transition state.⁶² Therefore, the dehydration research conducted over zeolites and γ -alumina is directly transferable to this potential pathway.

Conclusion and Future Work

In conclusion, we have shown that un-doped Mo_2C is active towards both acetic and propionic acid hydrodeoxygenation under atmospheric pressure. Additionally, we found that doping the MoO_3 precursor prior to carburization can have dramatic effects on the physical characteristics as well as the reactivity of the resulting carbides. Ni- Mo_2C was found to be more active towards alkene hydrogenation than the other catalysts. Ca was found to exhibit superior selectivity towards the aldehyde at lower temperatures and for the ketone at higher temperatures. Overall, the reactivity trends observed on a given catalyst type was consistent between acetic and propionic acids. Mo_2C catalysts were shown to possess distinct catalytic properties compared to conventional precious metal or

metal oxide catalysts. Thus, Mo₂C catalysts are promising for deoxygenation of bio-derived compounds with possibility of tailoring product selectivity via metal doping. Further catalyst characterization would be useful to understand the deactivation pathways, which could provide insight into the nature of the various active sites. This information would aid in designing the physical and chemical properties of these materials to achieve greater conversions, enhanced selectivity and extended durability.

CHAPTER THREE HYDROGENATION OVER ATOMICALLY DISPERSED PRECIOUS METALS SUPPORTED ON ALUMINA

Abstract

The exceptional activity of single atom catalysts (SACs) for a variety of reactions has been documented in recent years. We initiated the work with acetone hydrogenation as a model compound and then evaluated propyl propionate, propionic acid and other carbonyl compounds including ethyl acetate, propanal, glycolaldehyde, diacetone alcohol, and hydroxy acetone. All SACs showed acetone hydrogenation resulting in the formation of both isopropanol and methyl isobutyl ketone. The acetone hydrogenation rate of ~ 86 mol/min·g at 150 °C with 0.1% Ru on alumina is about five times that on Raney Nickel (~ 0.0015 mol/min·g at 40 °C). STEM imaging of the catalysts, post acetone hydrodeoxygenation, show the presence of ~ 2 nm particles on all catalysts except Ru on γ -alumina which remained predominantly single atoms. The SACs were found to be inactive towards propionic acid or propyl propionate hydrogenation under our reaction conditions. Hydroxy acetone was observed to favor bimolecular cyclization to form maple-lactone in the presence of Ru and Rh SACs with no selectivity towards the diol product. The hydrodeoxygenation of propanal over Ru SAC led to aldol condensation to form 2-methyl-2-pentenal, with propionic acid as a minor byproduct. These preliminary results show that SACs are active towards hydrogenation of ketones but extensive work is needed to determine the optimum catalyst(s) and conditions to carry out hydrogenation of propionic acid over SACs.

Introduction

As discussed in the previous chapter, the hydrodeoxygenation of bio-derived species generally needs to be carried out at relatively low-temperatures to avoid side reactions which lead to reduced yields and undesirable products. The moderate operating condition requires homogenous catalysts which are uneconomical since spent catalysts cannot be easily recovered. Our results clearly show that doped Mo_2C are promising catalysts for vapor phase upgrading. The high ketonization activity displayed by Ca- Mo_2C presents a path towards upgrading bioderived acids over a robust catalyst. Ketones are

more stable products and as shown in this chapter can be further upgraded via liquid phase single atom catalysis (SAC).

Simple synthetic routes and availability of aberration corrected electron microscope to directly image SACs have made it possible to explore their reactivity.⁶³⁻⁶⁶ In general SACs have been shown to be highly active towards CO and NO oxidation,⁶⁷⁻⁶⁹ water gas shift reactions,⁷⁰⁻⁷⁴ methanol reforming,⁷⁵ electro-catalysis,⁷⁶⁻⁷⁸ and photo-catalysis.⁷⁹⁻⁸⁰ Although there are only a few examples of hydrogenation reactions over SACs,^{37-39, 81} the moderate reaction conditions suggest that SACs might be able to substitute homogenous catalysts in some cases. SACs are attractive because they offer high atom efficiency, are anchored on a recoverable support, and can have unique selectivity.

Isolated single atoms exist fully exposed to their environment and bonded to support. Being unobstructed allows for substrate-metal-support interactions. This leads to greater atom efficiency and provides unique reaction selectivity as compared to agglomerated metal particles. By improving the atom efficiency of the precious metal, the catalysts' cost can be minimized which is highly desirable. This inherent property alone makes SACs worthy of further investigation. However, they have additional properties that explicate their gained attention.

It has been observed that single metals behave differently than typical supported precious metal catalysts. For example, the hydrogenation of benzaldehyde over Pd1/TiO₂ can be accomplished at room temperature while Pd/C is an ineffective catalyst.⁸¹ Also, 1,3-butadienes can be selectively hydrogenated to butenes over Pd1/graphene or Pt1/Cu under mild conditions.^{37, 39} Similarly, homogeneous catalyst SACs can offer unique reactivity and selectivity compared even with nanoparticles. The hydrogenation of acetylene over Pd1/Cu is possible at low conversion (10-20%) and moderate ethylene selectivity (30%).³⁸ Furthermore, magnetite supported palladium single atoms are reported to be ineffective for alkene hydrogenation.⁸² However, highly selective and efficient 1-hexyne conversion to 1-hexene is possible over [Pd]mpg-C₃N₄.³² The hydrogenation of succinic acid to γ -butyrolactone over atomically dispersed Pd catalyst has been reported but there is some

uncertainty on the activity of single atoms since the catalyst is a mix of single atoms and nanoparticles.⁴⁰

Other than the report on succinic acid, SAC catalyzed hydrodeoxygenation reactions have not been reported. With this in view, we choose to investigate the hydrodeoxygenation activity of SACs on γ -alumina. We selected acetone, propanal, propyl propionate, glycol aldehyde, ethyl acetate and propionic acid as compounds as potential carbon fiber precursors. The transition metals, Pd, Ru, Pt, and Rh were picked base on their predetermined affinity towards hydrodeoxygenation chemistry.^{1, 83-86} Alumina has proven to be a suitable support for synthesizing SACs via wet impregnation methods.⁶⁸⁻⁶⁹ The unique selectivity and enhanced reactivity of SACs can greatly depend on the solvent,²² the operating conditions and the support material.^{66, 72} These experiments were predominantly run with pure reagents as to limit solvent effects. The operating conditions were designed to simulate bio-oil upgrading conditions to assess catalyst activity and stability.

Experimental

Catalysts Synthesis and Characterization

For this work, the Pt1/ θ -Al₂O₃ samples were prepared and characterized as reported previously.⁶⁸ The samples of Pd1/ γ -Al₂O₃ were prepared by the method described by Datye et al.⁸⁷ The Rh1/ γ -Al₂O₃ was prepared from Rh(OOCCH₃)₃ by impregnation and subsequent calcination.⁸⁸ The samples of Ru1/ γ -Al₂O₃ were prepared employing Ru(CH₃COCH₂COCH₃)₂ solution in chloroform to impregnate γ -Al₂O₃ and subsequent calcination. Both γ - and θ -Al₂O₃ were prepared by a sol-gel process as reported in literature.⁸⁹ The surface properties of catalysts are summarized in Table 1. High-angle annular dark-field (HAADF) scanning transmission electron microscope (STEM) with a hexapole aberration-corrector (ACEM), was used to observe the single metal atoms, as well as, nanoparticles on the support. Elemental analysis by energy-dispersive x-ray spectroscopy (EDS) was employed to qualify the metals present on the aggregate's surface.

Catalyst testing

Oxygenates were selected to investigate SACs potential ability to upgrade bioderived compounds to carbon fiber precursors. As mentioned earlier, to avoid complicating solvent effects initial experiments were run in pure reagents. The batch experiments were run using a 600 ml Parr reactor. Typically, 200 mg of catalyst was loaded into the stainless steam bomb and then 50 ml of reagent was added to the vessel. After adding the pure reagent, the reactor was sealed and purged four times with 250 psi H₂ under stirring. This was done to remove oxygen from the system. The reactor was then charged to 885 psig. After reaching the desired pressure, heating began at a rate of 5 °C/min. Until reaching the desired reaction temperature. The reaction time began as soon as the heating started. At 150 °C the vessel pressure reached ~1175 psig. After the desired run time, the reaction was immediately quenched with a 5-liter beaker of water. Most of the experiments presented in this chapter were run for 2 hours. After cooling to room temperature, the pressure was released and the product collected. The catalyst was removed from solution via centrifuge. The resulting solution was injected manually into GC-MS and FID for analysis.

Results and Discussion

Catalyst Characterization

The metal loading of the single atom catalysts and the surface area of the SACs and their supports are presented in Table 4. Generally, the surface area of the catalyst slightly decreased after metal loading; however, the changes were small. As expected the γ -alumina (214 m²/g) has a higher surface area than θ -alumina (127 m²/g).

Typically, SACs are characterized by atomic imaging microscopy which allows for direct observation of single atoms. The extended X-ray absorption fine structure (EXAFS) and X-ray absorption near edge structure (XANES) techniques have been employed to obtain information of metal atom bonding. For example, absence of M-M bond supports lack of metal nanoparticles. The number of M-O bonds provide information on the oxidation state of metal. Standard powder diffraction techniques are ineffective in

discerning the structure of SACs as they are too small to exhibit diffraction peaks. In our work, we have relied primarily on electron microscopy to ascertain that our fresh catalyst are single atoms and to monitor changes in SACs after exposure to operating conditions. The characterization of Pt and Pd SACs has been described previously.^{64, 68-69} The Images of the Ru and Rh SACs on alumina are shown in Figure 9. To make the single atom clearly visible they have been circled.

Acetone Hydrodeoxygenation

We selected acetone to begin our work on hydrodeoxygenation. Successfully reducing this simple ketone to isopropanol would enable one strategy to produce renewable propene as illustrated in Scheme 5, Chapter 1. Acetone also served as a bio-oil model compound which gave insight into the capabilities for supported SACs. All SACs were capable of acetone and diacetone alcohol hydrogenation. The production of diacetone alcohol is believed to occur through the aldol condensation of acetone [Scheme 7]. Completing the aldol condensation to methyl isobutyl ketone (MIBK) requires proton donation. No MIBK was found in the presence of the un-doped support. While the presence of metal supported on alumina produced both isopropanol and methyl isobutyl ketone at remarkable rates. The site normalized rates of reaction for the three products MIBK, DDA and IPA are shown in Table 5. Davison et al. reported the initial rate of acetone hydrogenation to be ~ 0.0015 mol/min·g at 40 °C employing a Raney Nickel catalyst.⁹⁰ In our study, we show acetone hydrogenation at a rate of ~ 86 mol/min·g at 150 °C with 0.1% Ru on alumina, an almost 5 orders of magnitude rate enhancement. The rates of the competing reactions are unequally sensitive to temperature as shown in the Arrhenius plot for acetone HDO over Pt/ θ -alumina [Figure 10]. We find that the apparent activation energies are 2.809×10^4 and 5.191×10^4 kJ/mol and the pre-exponential factor are 2.915×10^3 and 1.045×10^6 s⁻¹ for IPA and MIBK, respectively. With this, the overall reaction selectivity as a function of temperature can be predicted, as shown in Figure 11. By decreasing the reaction temperature, we can achieve greater IPA selectivity. As the temperature increases the rates become equivalent. However above 200 °C the rate of

MIBK becomes greater than the rate of IPA production. Therefore, by increasing the temperature, a greater MIBK selectivity can be achieved.

Imaging the catalysts post acetone hydrodeoxygenation, evidences the presence of ~2 nm nanometer particles on all catalysts except Ru on γ -alumina which remains unchanged (Figures 12-15). Figure 12 shows Pd on γ -alumina, the presence of highly dispersed nanoparticles is clearly evident on the aggregate's surface. Nanoparticles of Rh on γ -alumina [Figure 13], are present but are neither as pronounced nor as populous on the surface as compared with the Pd sample. Pt/ θ -alumina nanoparticles [Figure 14], on the other hand, are more similar to those seen on Pd/ γ -alumina. Most of the nanoparticles observed were in the 1-3 nm range. Interestingly, no nanoparticles were found when examining Ru on γ -alumina [Figure 15]. While no single atoms were discovered directly due to issues with the electron microscope, the presence of Ru on the surface of the aggregate was apparent by EDS [Figure 16]. Figure 17 shows the EDS spectra for the aggregate, which explicates ruthenium's incidence. These results suggest that Pt, Pd, Rh single atoms are either inactive and become active as they sinter or they are active but agglomeration is concurrent with catalytic activity. This led us to prepare Ru nanoparticles and compare their activity with Ru single particles.

The Ru nanoparticles with a higher loading of Ru was prepared on γ -alumina (1%) and diluted with alumina to keep the total Ru constant. All reaction conditions were kept constant. Interestingly, the conversion and selectivity were almost identical to the original 0.1% trial. This was a surprising result which points to a few different explanations: 1) the 1% sample has a very similar dispersion to the 0.1% catalyst; 2) the ruthenium can "leach" from the surface and react in solution. Leaching and agglomeration has been previously reported for gold.⁷¹ Further investigation is necessary to determine the state of Ru post-reaction. Furthermore, the presence of nanoparticles on the other catalysts does not dismiss the presence of single atoms. However, by their presence we must take into consideration the activity and selectivity contributions of dispersed nanoparticles. These results provide further insight into the unique challenges and opportunities for SACs hydrodeoxygenation.

Carboxylic Acid Hydrogenation

Propionic acid hydrodeoxygenation was an additional strategy towards renewable propene production [Chapter 1, Scheme 4]. However, the pure acid dissolved the catalysts and no hydrodeoxygenation products were detected. Future work should explore supports that are stable in the presence of concentrated carboxylic acids. Another possible hydrodeoxygenation strategy is to first perform esterification of the acid with an alcohol. The strong carboxylic acid reagent is avoided by creating an ester.

Hydrodeoxygenation of Esters, Aldehydes, and α -Hydroxyketones

The hydrodeoxygenation of other carbonyl compounds were also explored. These include ethyl acetate, propyl propionate, hydroxy acetone, propanal, and glycolaldehyde. We find that the SACs are not active towards ethyl acetate or propyl propionate hydrogenation under our reaction conditions. Hydroxy acetone was found to favor bimolecular cyclization to form maple-lactone in the presence of Ru and Rh SACs with no selectivity towards the diol product. The hydrodeoxygenation of propanal over Ru SAC favored aldol condensation product to form 2-methyl-2-pentenal, with propionic acid as a minor byproduct. Surprisingly, propanol formation was not detected. The reaction mechanism for the aldol condensation of propanal to 2-methyl-2-pentenal is presented in Scheme 8. Interestingly, the product remains β,γ -unsaturated which may be a product of steric hindrance. Furthermore, there is a possibility for two diastereoisomer products, E and Z. Insight into the reaction mechanism may be gained by elucidating any preference for a certain handedness. However, it is likely that a mixture of both E and Z isomers form. At this point it remains unclear if there is any selectivity preference or if single atoms alone are responsible for 2-methyl-2-pentenal production.

Conclusion and Future Work

While homogenous organometallic catalysis has been shown to be more effective for carboxylic acid hydrodeoxygenation than heterogeneous catalysis, heterogeneous catalysts are easier to recover leading to cheaper more practical operation. By improving the dispersion on the supports surface, we can greatly improve the catalysts efficiency. In

recent literature nanoparticles of precious metals have been shown to out-perform their larger particle counterparts. This enhanced activity is mainly attributed to their improved metal dispersion. The ultimate limit of metal dispersion is single atom catalyst. These novel heterogeneous catalysts have been shown to possess superior performance. These materials not only have unique activity but may offer a cost-effective solution for bio-oil hydrodeoxygenation.^{68-69, 91} We find that Ru1/ γ -alumina is highly active towards acetone hydrogenation to isopropanol as well as the hydrogenation of diacetone alcohol to MIBK. By tuning the reaction temperature the selectivity can be controlled. The catalysts investigated in this chapter were not able to perform carboxylic acid hydrodeoxygenation due to the instability of the alumina support. Therefore, it is necessary to develop alternative support materials that are durable in strongly acidic media to create SACs better suited for bio-oil HDO. Mono-atomically dispersed precious metals may play a key role in the future of catalyst technology and with further research, novel reactivity and selectivity may be achieved.

Section II Alcohol Dehydration

CHAPTER FOUR ALCOHOL DEHYDRATION OVER METAL EXCHANGED ZEOLITES

This Chapter includes work previously published.

Lepore, A. W.; Li, Z.; Davison, B. H.; Foo, G. S.; Wu, Z.; Narula, C. K., Catalytic Dehydration of Biomass Derived 1-Propanol to Propene over M-ZSM-5 (M=H, V, Cu, or Zn). *Industrial & Engineering Chemistry Research* **2017**.

Andrew Lepore's contributions to this work include designing and conducting the experiments, collecting, processing, and interpreting the results, as well as, drafting the manuscript for publication.

Abstract

As discussed in the introduction, the conversion of 1-propanol is an integral step in the preparation of green carbon fibers. To this end, we report catalytic production of propene, a building-block molecule, from 1-propanol. Zeolite catalysts are quite versatile and can produce propene at or below 230 °C with high selectivity. Increasing the reaction temperature above 230 °C shifts product selectivity towards C4+ hydrocarbons. Metal incorporation in zeolites have significant impact on the operating condition for optimal 1-propanol dehydration. For example, Cu-ZSM-5 was found to exhibit a broader temperature range for high propene selectivity and could function at higher 1-propanol space velocities than H-ZSM-5.

Introduction

The successful deployment of renewable industrial chemicals includes biomass derived ethanol in fuel⁹² and ethylene⁹³⁻⁹⁴, a polymer precursor, from the dehydration of bio-ethanol. Propene, typically produced as a petroleum processing byproduct, has experienced a recent drop in supply due to the increased availability of lighter crude oil. This reduced production has led to an anticipated propene supply gap for markets such as polypropylene and acrylonitrile.⁹⁵ Thus, there is a surge in research on developing alternate “on-purpose” strategies for propene production. Propanol dehydration of bio-derived propanol is one imaginable approach that employs renewable resources. It is possible to

produce 1-propanol or 2-propanol depending on the microbe's metabolic pathways.⁹⁶⁻⁹⁹ While technology to produce higher alcohols from biomass via fermentation is awaiting deployment, gasification¹⁰⁰ to produce higher alcohols via syn-gas is already commercial.¹⁰¹ Bio-mass derived 1- and 2-propanol mixtures can also be produced from glycerol.¹⁰² These biomass derived alcohols can be dehydrated to a variety of valuable alkenes.^{41, 62} At present, giga tons of fossil oil derived propene is employed in producing materials such as ABS plastic and carbon fiber.⁹⁵ Anticipating large scale production of 1-propanol from renewable biomass sources, we are exploring a scalable process for vapor phase alcohol dehydration over ZSM-5 catalysts.

For 1-propanol dehydration to become commercial, optimum reaction conditions (temperature and space velocity) for high propene selectivity, impact of water on 1-propanol conversion, catalyst durability are necessary. Here, we present our results on metal exchanged zeolites as catalysts for 1-propanol dehydration. The conversion of 1-propanol over H-ZSM-5 has been reported to depend on the Si:Al ratio¹⁰³, however, several articles show that the Si:Al ratio alone does not influence activity and zeolite structure should be considered.¹⁰⁴⁻¹⁰⁷

We chose to optimize the reaction conditions for commercially available NH₄-ZSM-5 Si:Al ratio (23) for industrial scale production. For metal exchange, we selected V, Cu and Zn; V and Zn are known to block Brønsted sites¹⁰⁸⁻¹⁰⁹ while Cu is known to occupy cationic sites.¹¹⁰⁻¹¹¹ We find that M-ZSM-5 (H, V, Cu, Zn) can selectively dehydrate 1-propanol at ~230 °C but does experience deactivation due to coking over time. Furthermore, increasing temperature or decreasing space velocity resulted in increased C₄⁺ production. The formation of C₄⁺ under such moderate conditions suggested that more complex reactions are taking place simultaneous to 1-propanol dehydration. In view of this, we carried out experiments with 1-propan(ol-D) (CH₃CH₂CH₂OD) and diffuse reflectance infra-red spectroscopic studies (DRIFTS) to further investigate the reaction networks of alcohol dehydration which will be discussed in Chapter 4.

Experimental

Catalysts Synthesis and Characterization

NH₄-ZSM-5 (SiO₂/Al₂O₃ molar ratio: 23, surface area: 425 m²/g), zeolites were purchased from Zeolyst International. 1-propanol ($\geq 99.9\%$), 1-propan(ol-D) (99%), deuterium oxide (99.9 atom % D), propylene ($\geq 99.9\%$), V(III)Cl₃ (97%) and Zn(NO₃)₂ ($\geq 99.9\%$) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification. H-ZSM-5 was obtained by calcination in air at 500 °C for 4 h. Aqueous ion exchange method was used to prepare M-ZSM-5 (Cu, V, Zn) by literature procedures.¹¹²⁻¹¹³ Catalysts were sieved to 125-250 μm (120-80 mesh) before use. Elemental analyses were performed by Galbraith Incorporated, Knoxville, TN, United States. BET surface area measurements were carried out on a Quantachrome Autosorb-1 instrument. Powder X-ray diffraction (XRD) scans were performed on the Panalytical X'pert diffractometer from 5 to 80° 2 θ in 30 minute scans using CuK α radiation (45 kV, 40 mA, $\lambda=1.5406 \text{ \AA}$).

1-Propanol Dehydration

All 1-propanol dehydration experiments were performed in a packed bed reactor with 200 mg of catalyst. The catalytic bed was held at a fixed position with quartz wool in a vertical tubular quartz reactor (tube diameter: 1 cm). The outlet was at atmospheric pressure. Pretreatment included heating the bed to the temperature of interest (200-450 °C) under a 45 sccm helium purge for 1 h. Then 1-propanol (100% or mixed with deionized water) was introduced to the inlet gas line via syringe pump to achieve the desired WHSV. For the 50 wt% aq. 1-propanol studies the total flow was increased to achieve the desired WHSV based on 1-propanol. The products were carried directly through heated and insulated lines to an Agilent 6850 gas chromatograph mass spectrometer (GC-MS) or an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID) and thermal conductivity detector (GC-TCD). A PLOT-Q capillary column was used in all gas chromatographs. Nitrogen (5 sccm) was used as an internal standard to insure consistency among injections. Helium was flown at 45 sccm as the carrier gas. All experiments

(including catalyst syntheses) were carried out twice to ensure reproducibility. All results displayed in this chapter are the average of at least two parallel data points excluding the durability studies. 1-propanol conversion and product selectivities were determined by integrating the FID spectra peak area. The selectivity of a particular product was calculated by dividing the moles of that product by the total moles of hydrocarbons produced. Propene yield is determined by the molar selectivity of the product multiplied by the conversion of the reactant, 1-propanol.

Results and Discussion

Catalyst Characterization

The surface properties of zeolite catalysts used in this study are summarized in Table 6. The BET surface area and pore size of H-ZSM-5 are 344 m²/g and 21.4 Å, respectively which do not change significantly post metal exchange. The size of the pore opening is important because the kinetic diameter of 1-propanol (4.56 Å) is close to the largest size molecule that can freely enter the channels. Any significant decrease in pore diameter could block 1-propanol from entering the pores. The X-ray powder diffraction of H-ZSM-5 and metal-exchanged M-ZSM-5 is shown in Figure 18. There are no diffraction peaks assignable to metal oxides. The diffraction peaks from ZSM-5 framework are identical for all samples, suggesting that ZSM-5's framework remains intact after metal exchange.

1-Propanol Dehydration over M-ZSM-5

The dehydration reactions were first carried out between 200-300 °C at a weight hourly space velocity (WHSV) of 1.6 h⁻¹ at atmospheric pressure [Figure 19] and propene yield was monitored. Here, the yield is determined by the molar selectivity of the product multiplied by the conversion of 1-propanol.

The conversion of 1-propanol over all zeolites is highly sensitive to temperature. The optimum temperature for propanol conversion over H-ZSM-5 is 230 °C furnishing ~97% propene. H-ZSM-5 also has a greater propensity to produce C₄+ hydrocarbons as compared

to Cu-ZSM-5 at temperatures above 220 °C [Figure 20 and 21]. A sharp decrease in propene yield is observed above 230 °C for H-ZSM-5. Vanadium incorporation did not dramatically improve the propene selectivity or temperature window while zinc slightly increased the optimum temperature (to 245 °C) for 1-propanol conversion to propene [Figure 19]. The Cu-ZSM-5, on the other hand, showed enhanced propene selectivity over a broader temperature range.

The conversion of 1-propanol becomes quantitative at 225 °C for Cu-ZSM-5 with propene yield above 99% [Figure 21]. Increasing the reaction temperature above 240 °C promoted C4+ formation while concurrently suppressing propene yield. At temperatures above 220 °C, alcohol conversion is quantitative with high propene selectivity between 220 and 235 °C.

The impact of space velocity on 1-propanol conversion and selectivity for Cu-ZSM-5 can be seen in Figure 22. For Cu-ZSM-5 at WHSV below 1.6 h⁻¹, 1-propanol conversion is quantitative and the product stream contains no oxygenates. While at WHSV below 0.6 h⁻¹ the product stream contains ~10% C4+ hydrocarbons. At increased space velocities, above WHSV of 3.2 h⁻¹, di-propyl ether and other oxygenate are co-produced.

The behavior of Zn-ZSM-5 is nearly identical to that of Cu-ZSM-5 at 1.6 h⁻¹ WHSV, however, there is dramatic increase in C4+ production (~50% at 0.3 h⁻¹ WHSV) as the alcohol feed rate slows [Figure 23]. These results were quite unexpected since a simple dehydration pathway would not predict C4+ formation at low temperatures. Clearly, a more complex pathway(s) for 1-propanol conversion are operational under our experimental conditions. The mechanistic pathways are discussed in Chapter 4.

Since fermentation derived alcohols require multi-step purification, we carried out experiments with aqueous 1-propanol to determine if a partially purified stream can be employed instead of pure 1-propanol. The impact of water was monitored by first increasing the water concentration and the total flow to maintain a 1-propanol WHSV of 1.6 h⁻¹. In a second set of experiments, the concentration of water was increased while maintaining the total liquid flow rate at 0.4 ml/h and 230 °C over Cu-ZSM-5. When the total WHSV of 1-propanol is kept constant at 1.6 h⁻¹ but the water concentration is

increased, there was no significant impact observed for 1-propanol conversion or propene selectivity for feed concentrations between 50-100 wt% aqueous 1-propanol [Figure 24]. On the other hand, when the total flow rate is kept constant (0.4 ml/h), the effective 1-propanol WHSV decreases with increased water concentration [Figure 25]. For example, the effective WHSV of 20 wt% 1-propanol is $\sim 0.3 \text{ h}^{-1}$ and the product stream is comparable to that obtained with pure 1-propanol at WHSV of 0.3 h^{-1} . This suggests that water does not have a significant impact on the product stream under our reaction conditions.

The durability of the most promising catalysts, Cu-ZSM-5, was investigated by operating the dehydration reaction with pure 1-propanol at the optimum temperature (230°C). The product stream was monitored as a function of time on stream (TOS) at a WHSV of 2.4 h^{-1} [Figure 26]. A higher flow rate was chosen to accelerate the aging process. Alcohol conversion tended to decrease gradually over 7 h while propene selectivity remained consistent with slight improvements. Coking of Cu-ZSM-5 may explain the loss in conversion and may also play a role in the dehydration enhancing the reaction selectivity. Decoking of the catalyst was performed at 520°C overnight with 20 sccm air flow. Alcohol conversion and propene selectivity recovered after the first regeneration, and continued to decrease as a function of time on stream. The catalyst appears to be extremely sensitive to decoking conditions and even a slight variation lead to catalyst failure. Further investigation is needed into ideal decoking protocols for the effects of long term operation.

Conclusion

In conclusion, we find that 1-propanol dehydration occurs at moderate temperatures over M-ZSM-5. The operating temperature and WHSV range for high propene selectivity and conversion is relatively narrow for M-ZSM-5. If the reaction is run near the upper limit of 2.4 h^{-1} WHSV for optimal propene yield; M-ZSM-5 requires decoking after ~ 7 hours, as shown in the durability study. Temperatures above 240°C favored C4+ hydrocarbons while temperatures below 220°C showed dipropyl ether formation and incomplete 1-propanol conversion.

CHAPTER FIVE ALCOHOL DEHYDARTION OVER GAMMA ALUMINA

Abstract

The facilitation of renewable chemicals relies on high yielding chemical transformations. We report the catalytic production of propene, a commodity chemical, over an inexpensive heterogeneous catalyst. Industrially relevant catalysts such as γ -alumina offer a simple yet effective material for 1-propanol dehydration selectively to propene. The dehydration of 1-propanol was quantitative over γ -alumina with high selectivity to propene at temperatures above 320 °C and below 6 h⁻¹ WHSV. Water had negligible effect on product selectivity under short term evaluations. Future research is needed to focus on the limits of alumina's durability in terms of temperature, water, space velocity, and time on stream.

Introduction

As discussed previously, the anticipated propene supply shortages¹ necessitate the development of commercially viable approaches to produce propene for products such as polypropylene and acrylonitrile. In the preceding chapter, we investigated zeolites as a potential catalyst for 1-propanol dehydration. Among the metal exchanged zeolites, Cu-ZSM-5 was found to be the most commercially promising catalyst. However, it is advantageous to develop catalysts that can produce propylene in high yield over a broader set of operating conditions. Common catalyst support materials may offer these advantages.

The focus of this chapter is on establishing the optimal operating conditions for a prolific solid acid catalyst, γ -alumina. Information about the optimum reaction conditions (temperature and space velocity) for high propene selectivity, impact of water on 1-propanol conversion, catalyst durability, and reaction mechanism is needed. Here, we present our studies optimizing the reaction conditions for γ -alumina. While zeolites are active in a narrow temperature and space velocity range, we find that they are effective at ~100 °C lower temperature than metal oxides. A detailed technoeconomic analysis (outside the scope of this work) is needed to down-select the catalyst.

There are many inorganic oxides which have been studied for their alcohol dehydration abilities. These include: amorphous silica-alumina¹¹⁴, transitional alumina⁴², zeolites¹¹⁵, heteropoly acids⁴⁴ and niobium phosphate.⁴¹ Enhanced conversion and selectivity can be achieved by tailoring the strength and nature of the acid sites to fit the reaction. Furthermore, 2-propanol has been used as a probe molecule to measure catalyst acidity.^{62, 116-117} While many studies have focused on 2-propanol and there only a few examples of 1-propanol dehydration.^{44, 118-119} Previous literature on 1-propanol conversion over metal oxides ZrO₂,¹¹⁹ X13 molecular sieves,¹²⁰ and heteropoly acids.⁴⁴ This work aims to optimize the reaction condition for 1-propanol dehydration over γ -alumina.

Experimental

Catalysts Synthesis and Characterization

1-propanol ($\geq 99.9\%$) was purchased from Sigma-Aldrich. Aluminum oxide, γ -alumina 99% (surface area: 186 m²/g) was purchased from Alfa Aesar. All chemicals were used as received without further purification. Catalysts were sieved to 125-250 μm (120-80 mesh) before use.

Dehydration of 1-Propanol over γ -alumina and silica-zirconia

Dehydration reactions were carried out with 200 mg of catalyst in a quartz tube (1 cm ID) reactor contained within a tube furnace. Alcohol conversion and product selectivity were used to assess the catalysts performance. The effects of reaction temperature, reactant flow rate, and water composition were evaluated. For more information on the reactor or its operation please see Chapter 6.

Hydrothermal catalyst aging

The hydrothermal aging of γ -alumina was carried out under conditions that was anticipated to decrease its performance as a dehydration catalyst. Catalytic dehydration ability was measured as a function of reaction temperature before and after the aging protocol. The hydrothermal aging process is as follows: heating the catalysts to 700 °C at

a rate of 5 °C/min and then holding for 12 h under 5 sccm water vapor in 45 sccm helium. The catalyst was then cooled and tested for its alcohol dehydration ability using a temperature sweep. This provides data which show that drop in performance is an indication of catalyst failure.

Results and Discussion

Dehydration of 1-Propanol over γ -alumina

The dehydration of 1-propanol over alumina at 250 °C has been reported previously to produce propene in low yields (~28%).¹¹⁸ In our experiments, 1-propanol conversion was 45% at 250 °C and 1.6 h⁻¹ WHSV [Figure 27]. The product stream contained almost 85% propene, with di-propyl ether as the major byproduct. Lowering the reaction temperature resulted in lower alcohol conversion but greater selectivity towards the bimolecular dehydration product, dipropyl ether. Increasing the temperature led to increased 1-propanol conversion which became quantitative at 350 °C with 100% propene selectivity. No C4+ selectivity was observed under our reaction conditions.

The effect of alcohol flow rate on conversion and selectivity at 350 °C, is shown in Figure 28. Below 6 h⁻¹ WHSV, the reaction is highly selective toward propene. However, as the flow rate increases above 6 h⁻¹ WHSV, the alcohol conversion drops linearly with WHSV. This decrease in 1-propanol conversion can be attributed to exceeding the diffusion limitations of the reaction.¹²¹ At the space velocity of 25 h⁻¹, C4+ species in low yield (<3%) were observed probably due to oligomerization. Bimolecular dehydration was not observed at this temperature in the range of space velocities examined. This suggest that unimolecular dehydration is much more favorable than bimolecular dehydration at elevated temperatures.

The reaction was monitored over a 33-hour period to assess its short-term stability. The propene selectivity and 1-propanol conversion remain unchanged over time [Figure 29]. In this particular experiment, the feed composition was 50 wt% water. Water was included in the feed stream to confirm how the catalyst would respond to a “real” bio-derived fermentation broth. The catalyst appeared to be very stable under this short-term

test with idyllic conversion and product selectivity. The effect of water's inhibitory role on alcohol dehydration has been well established.¹²² However, it is also well established that the strong Lewis acid Al^{3+} sites, liable for alcohol dehydration, are occupied by hydroxyl groups at lower temperatures.¹²² Fortunately, as the reaction temperature increases, the hydroxyl groups are less bound to this active sites and can be easily accessed by alcohol species.¹²³ Therefore, we do not see such inhibitory phenomena.

Hydrothermal catalyst aging

The decrease in the performance of a catalyst can occur if its reactive sites are blocked (e.g. coking) or its structure undergoes changes under operating conditions over time. Coking of the catalysts surface is a common reversible mode of deactivation. By decoking the surface (combustion in air) the catalyst can be regenerated.¹²⁴ Since γ -alumina did not exhibit any change in catalyst performance after TON of 33 h, we decided to carry out accelerated hydrothermal aging to obtain a catalyst whose structural integrity has been compromised and can be expected to exhibit decreased performance. We carried out hydrothermal aging of γ -alumina under conditions commonly used to test emission treatment catalysts which are subjected to harsher environments than our catalytic reaction conditions.

The catalyst's ability to selectively dehydrate 1-propanol as a function of reaction temperature before and after hydrothermal aging is presented in Figures 30 and 31, respectively. Post aging, γ -alumina is less selective towards propene production. The catalyst appears to have an increased tendency towards bimolecular dehydration (hence the increased production of oxygenates such as diplopy ether). At 240 °C the propene selectivity has dropped 20% post hydrothermal aging. Furthermore, alcohol conversion is significantly reduced after aging. At 350 °C the once quantitative conversion has been suppressed to ~70%. The apparent drop in conversion and selectivity indicates partial deactivation of the γ -alumina under hydrothermal conditions. This is further evidence by the drop-in surface area from 186 to 94.3 m^2/g . It known that surface area and acidity are inversely related.¹²⁵ This aging process can be slowed by adding lanthanum.¹²⁶

Furthermore, it has been reported that the phase transformation begins in the bulk phase; rearrangement on the surface requires longer time and higher temperatures.¹²³ Regardless, γ -alumina is an inexpensive material and can be replaced once 1-propanol conversion begins to decrease.

Conclusion

In conclusion, γ -alumina exhibited higher propene selectivity over a greater range of operating conditions than metal exchanged zeolites, presented in Chapter 2. However, they require ~ 100 °C higher reaction temperatures to reach quantitative alcohol conversion. Water had little effect on product selectivity under short term evaluations. Future research on the limits of alumina's durability in terms of temperature, water, space velocity, and time on stream is necessary. A detailed technoeconomic evaluation is needed to determine which catalysts Cu-ZSM-5 or γ -alumina would provide the best process economics.

**CHAPTER SIX MECHANISTIC INVESTIGATION OF 1-
PROPANOL DEHYDRATION OVER GAMMA ALUMINA AND
METAL EXCHANGED ZSM-5**

This Chapter includes work previously published.

Lepore, A. W.; Li, Z.; Davison, B. H.; Foo, G. S.; Wu, Z.; Narula, C. K., Catalytic Dehydration of Biomass Derived 1-Propanol to Propene over M-ZSM-5 (M=H, V, Cu, or Zn). *Industrial & Engineering Chemistry Research* 2017.

Andrew Lepore's contributions to this work include designing and conducting the experiments, collecting processing and interpreting the results, as well as, drafting the manuscript for publication.

Abstract

The catalytic dehydration of 1-propanol to propene, as described in Chapter 4 & 5, is quite facile. Metal exchanged zeolites can produce propene at or below 230 °C with high yield, >95%. However, the optimal operating conditions for zeolite catalysts are highly sensitive to temperature. By increasing the reaction temperature above 230 °C the product selectivity began favoring C4+ hydrocarbons as was discussed in Chapter 4. Cu-ZSM-5 was found to exhibit a broader temperature and space velocity range for high propene yield compared with the other metal exchanged ZSM-5 catalysts tested. Based on NH₃-TPD measurements, the change in selectivity is caused by attenuation of strong acid sites [Figure 32]. A series of experiments with 1-propan(ol-D) over zeolites and alumina showed deuterium incorporation in the hydrocarbon product stream. Diffuse reflectance infrared spectroscopy of 1-propanol and 1-propan(ol-D) over Cu-ZSM-5 in combination with deuterium labeling experiments suggest that deuterium incorporation occurs in two steps. First step is dehydration which is followed by propene interaction with the partially deuterated catalyst surface. Furthermore, the hydrocarbon pool type pathway is most likely for the formation of C4+ hydrocarbons over zeolites.

Introduction

Alcohol conversion over zeolites has been extensively studied over the past century.^{8,17-43} Previous mechanistic studies suggest that 1-propanol dehydration over metal oxides initiates via physisorption or chemisorption on zeolites leading to a direct

interaction of 1-propanol's hydroxyl group with Brønsted acid sites.^{43, 127-128} Lewis acid sites were shown to have no significant effect on alcohol e.g. isobutanol¹¹⁵ and methanol¹²⁹ dehydration rates. The alcohol dehydration over γ -alumina has also been a subject of several publications.^{44-47,48-56} Early works reported the rate of alcohol dehydration over γ -alumina to increase as follows: butyl, propyl, isobutyl, ethyl, isopropyl, and secbutyl.⁵⁵ The intra-molecular dehydration of 1-propanol then proceeds via an E1 or E2 type mechanism. Inter-molecular S_N1 or S_N2 type mechanisms have also been proposed for alcohol dehydration.⁴³

Alcohol dehydration and hydrocarbon upgrading over zeolites have also been extensively researched.^{44-52, 57-63} For example, the dehydration pathway of 1-propanol on H-ZSM-5 in the presence of water was recently investigated by Zhi et al.²⁹ They found water and excess alcohol are both able to stabilize adsorbed 1-propanol leading to higher activation barriers and entropy gains which depress dehydration rates. They also suggest that, unlike γ -alumina, the rate limiting step is the C-O bond cleavage.⁶⁴⁻⁷² Mechanistic studies suggest that 1-propanol dehydration initiates via direct interaction of the hydroxyl group with the Brønsted acid site.²²⁻²⁷ Lewis acid sites were shown to have no significant effect on isobutanol³⁰ and methanol³⁸ dehydration rates.

In contrast to ZSM-5, recent work by Bhan et al., demonstrates Lewis acid sites to be primarily responsible for alcohol dehydration over γ -alumina.⁴² Like zeolite chemistry, they suggest that water can inhibit dehydration. Furthermore, dehydration rate retardation was not due to competitive inhibition but stable complex formation. They propose the stable compound consists of one water and two alcohol molecules. The observed kinetic isotope effect for alcohol dehydration indicates the C _{β} -H bond cleavage is involved in the rate determining step which is proportional to the stability of the carbocation-like transition state. This is also in agreement with isopropanol's relatively fast rate of dehydration.⁴⁴⁻⁴⁷ Kinetic studies are typically performed at low conversion to avoid mass transfer limitations. However, this work was run under conditions relevant to industrial application and therefore provides supplementary insight into primary alcohol dehydration over heterogeneous catalysts.

In our work on optimization of 1-propanol dehydration, discussed in Chapters 4 and 5, we noticed that C₄+ hydrocarbons also formed along with propene depending on the WHSV and reaction temperature. The formation of C₄+ products under such moderate conditions suggested additional reactions accompanying 1-propanol dehydration. In our efforts to gain insights into concurrent pathways that produce C₄+ hydrocarbons, we carried out dehydration experiments with 1-propan(ol-D) (CH₃CH₂CH₂OD) over both Zn-ZSM-5 and alumina. Previous work on the conversion of C₂H₅OD over ZSM-5 zeolites showed that C₃+ formation takes place via the hydrocarbon pool mechanism.¹¹² We reasoned that if C₄+ does not contain deuterium, it must be a consequence of propene. Otherwise, the hydrocarbon pool mechanism must be operating concurrently. However, we were surprised to find deuterium in all products including propene. Diffuse reflectance infra-red spectroscopic studies (DRIFTS), on the other hand, suggest that dehydration occurs via 1-propoxy adsorbed species and that C₄+ molecules likely result from a hydrocarbon pool type pathway operating under the reaction conditions. Our attempts to correlate 1-propanol conversion with acid sites are also presented.

Experimental

Catalysts Synthesis and Characterization

For zeolite and γ -alumina catalysts information see Chapters 4 and 5, respectively. 1-propanol ($\geq 99.9\%$), 1-propan(ol-D) (99%), deuterium oxide (99.9 atom % D), propene ($\geq 99.9\%$), V(III)Cl₃ (97%) and Zn(NO₃)₂ ($\geq 99.9\%$) were purchased from Sigma-Aldrich. All chemicals were used as received without further purification.

NH₃ Temperature Programed Desorption

NH₃-TPD measurements were made to evaluate the acidic nature of the catalysts using a Quantachrome AUTOSORB-1. The procedure was as follows: degas 200 mg of catalyst at 500 °C for 1 h, and then cool to 50 °C before flowing NH₃ gas over catalyst for 1 h, followed by heating to 110 °C and purging with Helium for 1 h to remove loosely held

NH₃. The TPD signal was monitored with a Mass Spectrometer as a function of temperature as the catalyst was heated to 650 °C at 10 °C/min.

Dehydration of 1-propan(ol-D) and D₂O

All 1-propanol dehydration experiments were performed in a packed bed reactor with 200 mg of catalyst. The catalytic bed was held at a fixed position with quartz wool in a vertical tubular quartz reactor (tube diameter: 1 cm). The outlet was at atmospheric pressure. Pretreatment included heating the bed to the temperature of interest (200-450 °C) under a 45 sccm helium purge for 1 h. Deuterium experiments were conducted with either 1-propan(ol-D) or pure propene with D₂O. The reagents were carried through heated and insulated lines through the catalyst bed and to an Agilent 6850 gas chromatograph mass spectrometer (GC-MS) or an Agilent 6850 gas chromatograph with a flame ionization detector (GC-FID) and thermal conductivity detector (GC-TCD). A PLOT-Q capillary column was used in all gas chromatographs. Helium was flown at 45 sccm as the carrier gas.

In-situ DRIFTS of 1-propanol dehydration over H- and Cu-ZSM-5

In-situ diffuse reflectance Fourier transform infrared spectroscopy (DRIFTS) measurements were performed on a Nicolet Nexus 670 spectrometer equipped with a mercury cadmium telluride (MCT) detector cooled by liquid nitrogen, and an in situ chamber (HC-900, Pike Technologies) with capability to heat samples to 900 °C. Each spectrum was collected with 32 scans at a resolution of 4 cm⁻¹. The exiting stream was analyzed by an online quadrupole mass spectrometer (QMS) (OmniStar GSD-301 O₂, Pfeiffer Vacuum). For the adsorption of 1-propanol or 1-propan(ol-D), each sample was heated to 300 °C under 50 sccm of helium for 1 h. After cooling down to 25 °C, a background spectrum was collected. A pulse of 1-propanol or 1-propan(ol-D) was introduced into the DRIFTS cell and purged with helium for 10 min before a spectrum was collected. For in situ reaction experiments, each sample was pretreated in helium (50 sccm) for 1 h at 300 °C. A background spectrum was collected at 300, 240, 220, and 200 °C. Subsequently, 1-propanol or 1-propan(ol-D) was introduced into the DRIFTS cell using a

syringe pump (Chemyx Nexus 3000) at a rate of 0.03 ml/h. During this period, a spectrum was collected every minute for 1 h. The sample was heated at 220, 240 and 260 °C for 1 h, and a spectrum was also collected every minute.

Results and Discussion

NH₃ Temperature Programed Desorption

The metal exchanged zeolites tested were examined with NH₃ temperature programed desorption to better understand how metal incorporation modified the catalyst's acidity and correlate catalyst acidity with catalytic activity. Both H-ZSM-5 and V-ZSM-5 exhibit two broad peaks in their NH₃-TPD profile centered at 240 and 470 °C, Figure 32. The 240 °C peak is ascribed to physisorbed NH₃ or ammonium species.¹³⁰ The desorption peak at 470 °C is attributed to NH₃ absorbed on Brønsted acid sites.¹³¹ It is important to note that NH₃ indiscriminately adsorbs to both Lewis and Brønsted acid sites and therefore strong Lewis acid sites created by metal incorporation are difficult to quantify with this method.¹³² After Cu exchange, the 240 °C peak decreases in intensity and 440 °C peak radically decreases in intensity. The NH₃-TPD of Zn-ZSM-5 exhibits a dramatically decreased 240 and 470 °C peaks but a new broad peak at 310 °C is observed which is attributed to strong Lewis acidity produced by the replacement of Brønsted acid protons with metal (Zn and Cu).^{108, 133} Figure 33 shows the NH₃-TPD profile for γ -alumina which is less intense and has a broader “low” temperature peak which is consistent with its relatively weaker acidity as compared with ZSM-5. The NH₃-TPD of M-ZSM-5 suggests that the attenuation of strong Brønsted acid sites hinders C₄+ hydrocarbon formation. Therefore, ion exchange with Cu helped favor propene selectivity at slightly elevated temperatures and over a broader range of space velocities.

1-Propan(ol-D) Dehydration over Metal Exchanged ZSM-5

The dehydration reactions employing 1-propan(ol-D) over Zn-ZSM-5 leads to ~50% C₄+ at 0.3 h⁻¹ WHSV. As discussed in the preceding section, we did not expect to see deuterium incorporation in the product stream under 1-propanol dehydration

conditions. The hydrocarbon pool pathway, on the other hand, would lead to deuterium in the C4+ product stream as outlined in Scheme 9.

1-propan(ol-D) was reacted over a fresh Zn-ZSM-5 (23) at 230 °C and 0.3 h⁻¹ WHSV. To our surprise, the C4+ hydrocarbons from the reaction showed deuterium incorporation in all products. In addition, we also observed deuterium incorporation into propene with 48% (M+1) and 10% (M+2) ion peaks. Increasing the WHSV to 3.2 h⁻¹ leads to incomplete 1-propan(ol-D) conversion and the product stream shows the presence of dipropyl ether and propanal. However, most of the 1-propanol in the product stream does not contain deuterium, suggesting 1-propanol(ol-D) has undergone surface exchange. Dipropyl ether shows a 14% (M+1) ion peak and propanal shows 52% (M+1) and 5% (M+2) ion peaks, further supporting deuterium surface exchange. Propene generated at this space velocity still shows deuterium incorporation with 49% (M+1) and 18% (M+2) ion peaks. It is likely that deuterium incorporation occurs after propene is formed either by HDO addition-elimination to propene or via exchange with deuterated hydroxyl groups on the catalyst's surface.

Reacting propene with D₂O in a 1:1 stoichiometry over Zn-ZSM-5 (23) at 230 °C, WHSV of 0.3 h⁻¹ shows all the propene in the product stream to be propene-1-D, suggesting that either of these pathways are likely after propene is formed. Furthermore, it is likely that C4+ hydrocarbons are formed either via propene-1-D oligomerization or hydrocarbon pool pathway. Thus, studies with 1-propan(ol-D) did suggest interaction of propene with catalyst surface but did not clarify the pathway for C4+ formation.

1-Propan(ol-D) Dehydration over γ -Alumina

Since 1-propanol dehydration on γ -alumina is proposed to occur via an E1 or E2 type pathway, we expected no deuterium incorporation in propene. But, we carried out 1-propan(ol-D) over alumina, because the reaction is less complicated since hydrocarbon pool type pathways cannot occur on alumina. We reasoned that we should be able to strengthen our argument of propene interaction with deuterium exchanged alumina surface.

It is generally accepted that between 25 and 33% of the Al ions in γ -alumina have tetrahedral geometry, while the remainder are octahedral. Its structure closely resembles a ccp (cubic close packed) typical of spinel structures, which have an AB_2O_4 stoichiometry, (B^{3+}) and (A^{2+}) cations. Al is considered to only take on an (3+) oxidation state; therefore, non-traditional geometries and positions are required to balance the structures overall charge. These irregularities manifest in interstitial occupancy, vacancies, and highly distorted tetrahedral geometries. The surface is thought to have Lewis acid sites originating from Al^{3+} ions with unsaturated coordination: (e.g. a pentacoordinated Al^{3+} in octahedral geometry with one open coordination position). There are however different types of Lewis acid sites with high, medium, and low acid strength observed on the surface. Unsaturated tricoordinated Al yields the strongest acid sites. The number of acid sites is directly proportional to the surface area. Aluminum oxide anions also exist on the surface and provide basic sites. The proximity of both acidic and basic sites on the surface have been found to be advantageous for reactions such as alcohol dehydration. For example, γ -alumina has been used to dehydrate ethanol to ethylene.⁶⁹ Recent investigations by Bhan and Kang show that there are two distinct pools of sites on alumina surface which have different tendencies toward ether and alkene production for dehydration of ethanol (Bhan 2016).⁴⁷ Long chain alcohols (C_4+) over γ -alumina lead to alkenes exclusively while short chain alcohols have been shown to form a mixture of alkenes and ethers.¹³⁴

The dehydration of 1-propanol over alumina has been proposed to occur via E1 or E2 type pathways with competing reactions of ether formation via S_N1 or S_N2 type pathways. DTF studies by Vlachos et al. and Lauron-Pernot et al. have shown that ethanol dehydration favours an E2 elimination type mechanism on the pentacoordinated (100) Al_2O_3 surface.^{49,70,76} Similarly, Bhan et al. concludes, C_β -H bond cleavage as the rate determining step in the unimolecular dehydration of 1-propanol and discusses the inhibitory nature of irreversibly absorbed water.^{44-46,77} Lamier et al. calculated activation enthalpies of an E2 mechanism for propene and a S_N2 mechanism for isopropyl ether on Al_V Lewis acid sites of (100) termination, which agree with experimental values.⁵⁴

The product stream from the reaction of 1-propan(ol-D) over γ -alumina at a WHSV of 1.6 h⁻¹ and 350 °C showed deuterium incorporation into propene with 38% (M+1) and 8% (M+2) ion peaks. In a subsequent experiment with pure propene and D₂O at 350 °C, deuterium incorporation was also found in propene with ~50% (M+1) and ~25% (M+2) ion peaks. These results suggest that 1-propan(ol-D) or D₂O exchange with the catalyst surface hydroxy groups and propene undergoes proton exchange with -OD/-OH groups on the surface of alumina.

In-situ DRIFTS of 1-propanol dehydration over H- and Cu-ZSM-5

The experiments with 1-propan(ol-D) dehydration, described in the preceding sections, suggested that dehydration on both zeolites and alumina occurs via E1 or E2 type mechanisms as suggested in the literature. The deuterium incorporation in propene is most likely due to propene interaction with deuterium exchanged catalyst surfaces. The C₄+ formation over zeolites could occur either via a hydrocarbon pool type pathway or propene upgrading. In order to find support for a hydrocarbon pool type pathway, operating concurrently, we carried out dehydration pathways on ZSM-5 *in situ* spectroscopy experiments on 1-propanol dehydration over ZSM-5 catalysts.

The exposure of Cu-ZSM-5 to 1-propanol and 1-propan(ol-D) results is almost identical FTIR spectrum at 25 °C [Figure 34]. After exposure to both alcohols, the perturbed bands at 3742, 3665, and 3623 cm⁻¹ in hydroxy region are visible. The perturbation is likely due to 1-propanol adsorption on -Si-(OH)-Al- surface. The bands at 3742 and 3623 cm⁻¹ are due to silanol groups and hydroxyl groups associated with Al atoms in zeolites.¹³² In addition, bands for ν OD D-ZSM-5 at 2758, 2700 and 2667 cm⁻¹,¹³² and ν OD of 1-propan(ol-D) at ~2500 cm⁻¹ are not observed. The δ OH band, generally present in gaseous 1-propanol at 1270 cm⁻¹, is also not observed when 1-propanol is adsorbed on Cu-ZSM-5. As such, we do not assign this band to δ OH of 1-propanol. Likely, this band represents ν C-O-C linkages, as the peak is not downshifted in the presence of deuterium. The absence of ν OD band suggests that 1-propan(ol-D) exchanges with hydroxy groups on the catalyst's surface even at 25 °C, or it adsorbs dissociatively. The ν CH₃ and ν CH₂ bands

are seen at 2969, 2940, and 2882 cm^{-1} .¹³⁵ The δCH_2 and $\nu\text{C-C}$ absorptions are observed at 1169 and 888 cm^{-1} , respectively.¹³⁵ The $\nu\text{C-O-M}$ bands are seen in metal iso-propoxide at $\sim 1161 \text{ cm}^{-1}$.¹³⁶ It is likely that the δCH_2 band at 1161 cm^{-1} has a component of $\nu\text{C-O-M}$ where M is either framework silicon or aluminum. The band at 944 cm^{-1} is also perturbed indicating interaction of 1-propanol with $\nu\text{Si-O}^-$ and highly strained or broken siloxane bridge surface defects¹³² due to extra-lattice oxygen incorporated during synthesis. This perturbation is not seen in the FTIR spectra of 1-propanol flow over H-ZSM-5 surface since H-ZSM-5 does not contain such a defect [Figure 34].

The FTIR spectra for the *in-situ* reaction of 1-propanol over Cu-ZSM-5 in the DRIFTS reactor at 200-260 °C is shown in Figure 35. The spectral evolutions show that νOH , νCH_3 and νCH_2 bands remain essentially unchanged. Among the new bands seen at 3302, 3230, and 3117 cm^{-1} , the band at 3117 can be assigned to propene since propene peaks on Cu-ZSM-5 have been reported to be at 3100, 2967, and 2931 cm^{-1} .¹³⁷ A weak peak at $\sim 1551 \text{ cm}^{-1}$ is also observed at 200 °C which becomes a shoulder to a new band at 1509 cm^{-1} at 220 °C and above. The peaks at 1560 and 1510 cm^{-1} have been observed previously for alcohol adsorption on H-ZSM-5 [Figure 36] and have been assigned to O-C-O, surface aromatic structures, and electron deficient C=C bonds.¹³⁸ Adsorbed propene has previously been shown to exhibit a band at 1547 cm^{-1} which diminishes as the temperature increases.¹³⁷ The band at $\sim 1510 \text{ cm}^{-1}$ has been attributed to hydrocarbon pool species. This implies that the small amounts of C4+ hydrocarbons produced along with propene at $\sim 200 \text{ °C}$ results from the hydrocarbon pool mechanism.

The FTIR spectra of 1-propan(ol-D) over Cu-ZSM-5 at 200-260 °C are identical to those of 1-propanol over Cu-ZSM-5. Since the adsorption of 1-propanol at room temperature suggests deuterium loss from 1-propan(ol-D), it is likely that deuterium incorporation in propene occurs via exchange with deuterium on zeolitic deuterioxy groups. Deuterium incorporation into C4+ species, is likely due to hydrocarbon pool pathways since previous work has not shown evidence of propene oligomerization in DRIFTS even at 400 °C.¹³⁷

Conclusion

Our results show that 1-propanol dehydration over ZSM-5 zeolites or alumina occur via an E1 or an E2 type mechanism. The experiments with 1-propanol (and propene + D₂O) suggest that deuterium incorporation in propene occurs via interaction with the catalyst's surface which becomes deuterated by interaction with HDO or D₂O. The *in-situ* spectroscopy of 1-propanol over ZSM-5 supports the formation of C₄+ hydrocarbons via the hydrocarbon pool mechanism.

Section III Methods & Conclusions

CHAPTER SEVEN METHOD FOR STUDYING IN-LINE PACKED BED REACTORS

Abstract

The vapor phase experiments described in Chapters 2, 4, 5 and 6 required the development of a home-built bench scale continuous flow reactor system. This chapter describes in detail the experimental setup and analytical approach used to conduct the catalysis experiments. The first section will discuss the reactor setup. The second section will describe the methods used to calibrate reactants and products. The third section will present a python code used to process GC-FID chromatograph data. This chapter is meant to aid those devolving in-line bench-top continuous flow systems.

Introduction

Continuous flow bench-top reactors are useful tools for catalyst development. Being on a small scale, allows for relatively inexpensive operation. Packed bed reactors (PBR) are prolific to heterogeneous catalysts because they offer simple steady state operation. Therefore, with in-line analysis the effects of temperature, space velocity and durability can be easily measured with an on-line instrument such as a gas chromatograph - mass spectrometer (GC-MS). However, by running on a small scale the products cannot simply be collected and analyzed. Because collection would require substantial time over which subtle changes in selectivity and conversion would be lost. Furthermore, the wide range in boiling points of the product would make accurate quantification extremely difficult. Accurately operating an in-line vapor phase analytical system does come with its own set of challenges and careful consideration is required. The reactor system described herein was built in-house and required many revisions to obtain accurate and reproducible data. The reactor and analytical procedure is described in following paragraphs

Packed Bed Reactors

The rate of reaction (r_1) for PBRs can be described by equation 1 where the change in moles of reactant of feed $F_{1,\text{mol}}$ is directly related to the mass of the catalyst (W). It is important to note that moles cannot be measured directly but molar concentration can be measured using detectors such as flame ionization detectors (FID), thermal conductivity

detectors (TCD) and mass spectrometers (MS), provided a reliable calibration curve has been established. Flame ionization detection is the preferred method for analyzing hydrocarbon species.¹³⁹ The method works by ionizing the species in a flame. The flame temperature is ~2000 °C and is created by combusting hydrogen and air. As the sample is sprayed into the flame the species fragment into ions which can be detected. This method is preferred because of its reliability and linearity although some species such as CO₂ are not visible by this method.¹⁴⁰ Another popular method of detection is TCD. This method measures the thermal conductivity of the gas as it passes through the detector. This method is extremely sensitive and offers a reliable way of measuring most vapor phase products. Mass spectrometry which is best known for its ability to identify chemical species can also be used for quantification. This method also deconstructs molecules into ions similar to FID using a plasma in a high vacuum. By reconstructing the molecular fragments the original species can be identified. Unfortunately, the response of a species can greatly depend on its composition and change with time and therefore this method is not ideal for quantification purposes. No matter the detector used the quantification can only be as good as the calibration.

$$\text{Eq.1} \quad \frac{dF_{1,mol}}{dW} = r_1'$$

Calibration

Calibrating the detector is an essential step when trying to quantify product selectivity and reactant conversion. This requires flowing a known concentration, generally in the expected concentration range of the product stream, of a species through the system. A curve relating the peak area to the concentration of that species can thus be plotted. This can be used to directly quantify the species concentration in the product stream.¹⁴¹ In our system, we used a calibration mixture of alkenes and alkanes supplied by Air Liquide. The details of the standard are as follows: 6% ethane, 3% propane, 3% propene, 0.1% isobutane, 1% isobutene, 2% 2-butene in N₂. Using this gas mixture and helium as a diluent and two mass flow controllers the concentration of each species was controlled. It is important to

note that a bubble flow meter was used measure the exact flow rate out of each mass flow controller. This was done to avoid errors that can arise from the mass flow controllers. The calibration curves for ethylene and propene are presented in Figures 37. The other light gases were not included for simplicity; however, all linear curves had R^2 values > 0.999 . It is also important to keep the transfer lines heated as they would be during catalyst testing. This is critical when establishing a calibration curve for reactants which are liquids under standard conditions.

Loading the catalyst

The packed catalysts bed was assembled employing a 1 cm diameter quartz tube. Dimples in tube's wall were used to fix the catalysts bed but also to center the thermal couple axially. Quartz wool was used on each end of the catalyst bed to support the powder and maintain a well-defined bed. Figure 38 illustrates the catalysts assembly. To prevent channeling, it is essential to ensure the catalysts is well packed. To accomplish this the tube was repeatedly tapped to shake the particles into a tight arrangement. It is also important not to pack the bed too tightly, to prevent a large pressure drop across the catalyst.

Continuous Flow Bench-Top Reactor

The alcohol dehydration and the acid hydrodeoxygenation reactions were carried using the continuous flow reactor. An illustration of the reactor setup is presented in Figure 39. During the experiments helium was used as the carrier gas and N_2 was used as an internal standard. The total carrier gas flow was maintained at 50 sccm for most experiments. Space velocity as used in this work is defined as the flow of the reactant in ml/h multiplied by the reactant's density under standard conditions over the weight of the catalyst, as shown in equation 2.

$$\text{Eq. 2} \quad WHSV = \frac{\text{Flow rate reagent} \times \text{density of reagent}}{\text{Mass of catalyst}} = \frac{\left[\frac{\text{ml}}{\text{h}}\right] \times \left[\frac{\text{g}}{\text{ml}}\right]}{[\text{g}]} = h^{-1}$$

Reactants were delivered via either a syringe pump or a saturator. A syringe pump offers simple to measure delivery; however, accurate syringe pumps are costly and may

not be accurate at low flowrate. Saturators or bubblers provide a steady delivery of even difficult to vaporize compounds but delivery must be calculated based on temperature, pressure and flow of the carrier gas. Therefore, changes in any of these variables over time will lead to drifts in the effective feed rate. Using the saturator requires the concentration of the reagent to be calculated. This can be accomplished using the Antoine Equation (Eq. 3).

$\phi_{1,v}^*$ = molar fraction

$F_{1,v}^*$ = flow rate of the vapor [sccm]

F_C = flow rate of the carrier gas [sccm]

T_{bub} = Bubbler Temperature [Kelvin]

P_{Tot} = Total pressure [bar]

$P_{1,v}^*$ = Saturated vapor pressure [bar]

A, B, C = Antione equation parameters

Acetic Acid: A 4.68206, B 1642.54, C -39.764 valid for temperatures between 290.26-391.01 K.¹⁴²

$$(Eq. 3) \quad P_{1,v}^* = 10^{\left(A - \frac{B}{C + T_{bub}}\right)}$$

$$(Eq. 4) \quad \phi_{1,v}^* = \frac{P_{1,v}^*}{P_{Tot}} = \frac{F_{1,v}^*}{F_{1,v}^* + F_C}$$

$$(Eq. 5) \quad F_{1,v}^* = \frac{\phi_{1,v}^* \cdot F_C}{(1 - \phi_{1,v}^*)}$$

$$(Eq. 6) \quad F_{1,v}^* = \frac{\frac{P_{1,v}^*}{P_{Tot}} \cdot F_C}{\left(1 - \frac{P_{1,v}^*}{P_{Tot}}\right)}$$

$$(Eq. 7) \quad F_{1,v}^* = \frac{F_C}{\left(\frac{P_{Tot}}{P_{1,v}^*} - 1\right)}$$

Python Code for Processing chromatograph data

This code is meant to aid in developing reliable and quick quantification of chromatographic data. The code relies on peak elution time to “signature” compounds. To use this code, it is important to download the 4.1.0 version of python, as well as, openpyxl for the code to interface with Microsoft Office. The code presented below was used to process the acetic acid HDO data. The script works by calling a file name, performing the

following operations, and then writing a new file (with the name you assign to it at the end of the code). It is also important to have your raw data organized in columns which include peak number, elution time, and peak area. If using a saturator, the Antoine parameters can be entered, as well as, the bubbler temperature and the total gas flow. These values can be saved within the script. If using a syringe pump to deliver the reactant, the flow rate can also be entered directly without having the script calculate it. The product library can be modified to fit the product distribution for the specific process.

CHAPTER EIGHT SUMMARY & FUTURE RESEARCH

Creating alternative synthetic pathways for petroleum-derived commodity chemicals provides future generations the flexibility to generate consumer products when traditional strategies are no longer viable. Carbon fiber is and will continue to be a valuable composite material. Enabling renewable carbon fiber is an important piece in establishing the bio-economy. The catalytic transformation described herein shed light on two strategies used to produce propene, a building block molecule for a variety of polymers from bio-derived precursors. The development of novel catalysts for HDO as well as the practical and fundamental insight gained through this work will surely extend beyond the production of renewable carbon fiber and help direct future research efforts.

In the first part of this thesis, we describe our work on carboxylic acid HDO to produce alcohols that can be subsequently converted to propene. Our aim was to develop robust, inexpensive, and high-performance catalysts that operate under moderate conditions. Experiments with doped-Mo₂C catalysts revealed that these materials were quite active towards reducing carboxylic acids under mild operating conditions. Metal doping had significant effects on both the physical and chemical properties of the resulting carbide catalyst. Further characterization of these materials, such as acidity/basicity measurements and *in-situ* spectroscopic studies, would provide valuable information about the reaction dynamics taking place on the catalyst's surface. This understanding is critical in developing tailored carbide materials.

In Chapter 3, we summarize our efforts employing supported SACs. We found these novel catalysts to be remarkably active towards ketone hydrogenation. We showed that reducing the reaction temperature, leads to higher isopropanol selectivity while reducing selectivity towards the aldol condensation product. Unfortunately, the SACs were not suitable for HDO of pure propionic acid due to support instability. Future research should focus on SACs that are stable under carboxylic acid HDO conditions. This includes developing SACs on more robust supports such as TiO₂. As well as developing co-doping strategies that prevent the formation of rafts and nanoparticles.

The second part to the dissertation focused on alcohol dehydration. More specifically, it focused on the dehydration of 1-propanol to propene over γ -alumina and

zeolites. We find that ZSM-5 is quite capable of producing propene at nearly quantitative yields. However, this high productivity is contingent upon a narrow set of operating conditions due to the plethora of chemical pathways operational within zeolites. We found that that ZSM-5's reactivity can be greatly altered by introducing metals. Of the metals exchanged, copper had the most profound effects. With its incorporation, the operating window for high propene yield was extended. This included broadening the temperature range and drastically improving propene yield at higher space velocities. An alternative catalyst, γ -alumina, was also investigated and found to produce propene in high yields as long as the reaction temperature was sufficient (~ 100 °C higher than zeolites) and the flow rate did not exceed the system's mass transfer limitations.

In Chapter 6, we explored the dehydration reaction mechanisms. Dehydration occurs primarily through an E1 type pathway under our reaction conditions. Furthermore, hydrogen bound to the catalyst's surface can actively exchange with molecules present in the vapor phase. The hydrocarbon pool mechanism concurrently operates within ZSM-5. The pool mechanism becomes dominant at higher temperatures and lower space velocities, leading to the production of C₄+ hydrocarbons. Further work to develop this process should include long-term durability studies and de-coking optimization to completely restore catalytic activity over many cycles. Also, more research is needed to improve our understanding of metal-zeolite interactions and how they can be tuned to afford a desired outcome. This has and will continue to be a fruitful endeavor.

Finally, we offered a detailed description of the packed bed reactor system used in much of this research. The Python code presented in the appendix may be modified and used by future researchers to develop automated quantification of their chromatographic data. Having the capabilities to evaluate heterogeneous catalysts will enable future research.

In summary, we have developed new catalysts and catalytic pathways to prepare propene for renewable carbon fiber production. Much of the work presented in the previous chapters was conducted over the past three years. Our results provide practical information about the chemical transformations relevant to upgrading bio-derived precursors into

valuable commodity chemicals. These results are necessary for developing techno-economic analyses which may encourage commercial production of renewable chemicals.

The development of heterogeneous catalysts has enabled global production of fuels and chemicals essential to life as we know it. As the population grows and resources become more limited, renewable resources must be established through technological innovations and industrial scale implementation. This is one of the greatest challenges of our time. To this end, grown biomaterials have the potential to be a source for commodity chemicals.

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APPENDIX

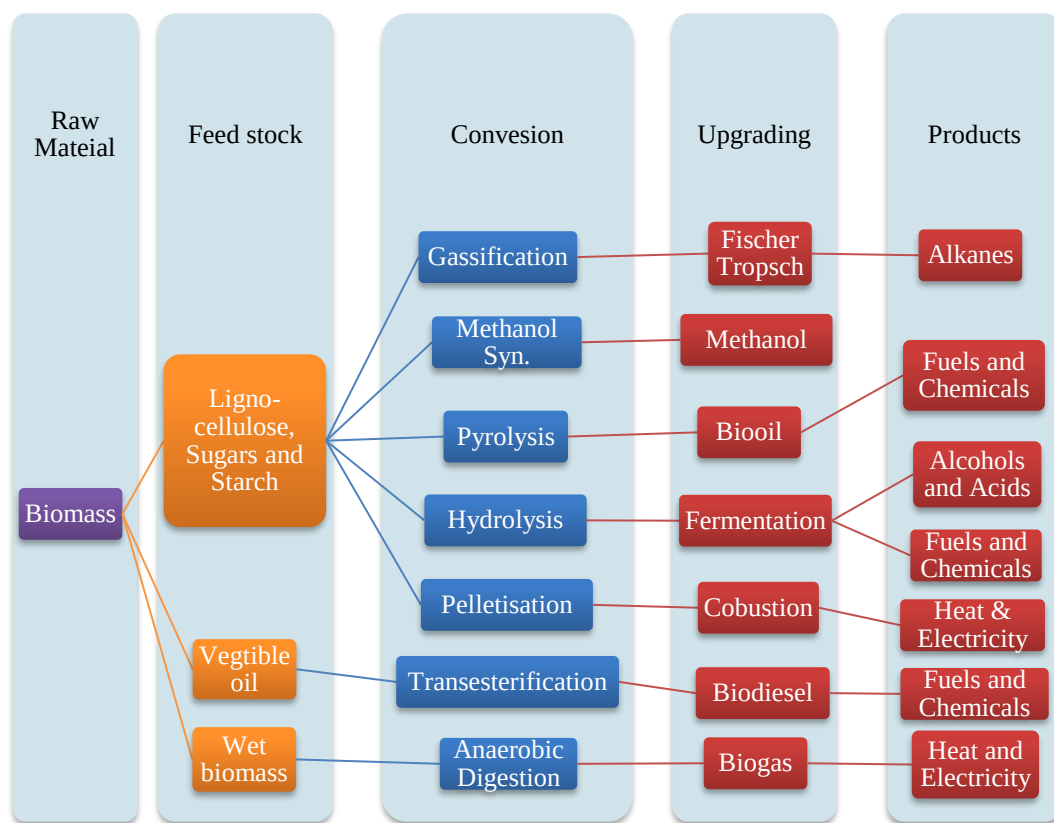
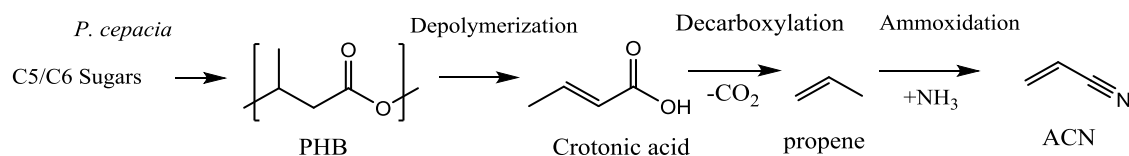
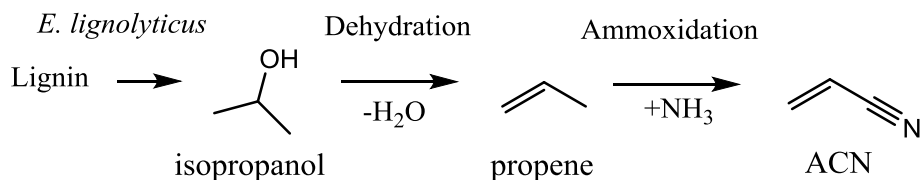


Figure 1. An overview of the pathways to create commodity chemicals from biomass .¹⁻²

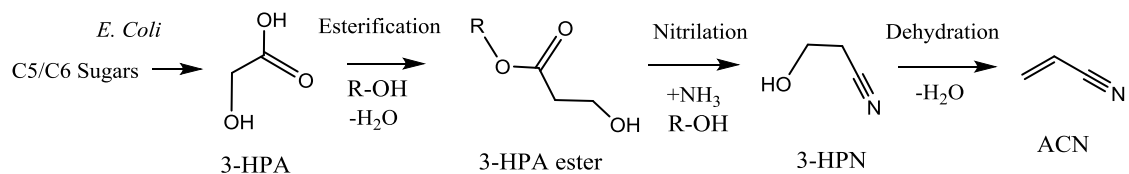
Scheme 1. Sugar to PHB: C5/C6 hydrolyzates can be converted to PHB in wild-type strains of *P. cepacia* and isolated from the cells via filtration-pH swing-bleaching.



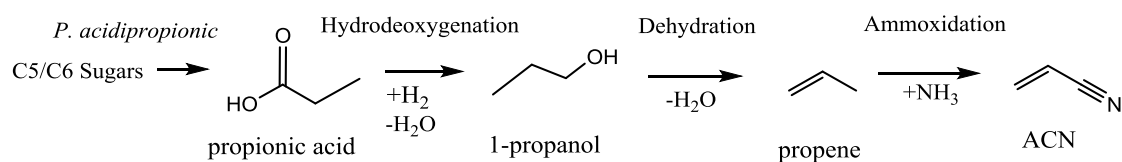
Scheme 2. Lignin to IPA followed by dehydration and ammoxidation to ACN. IPA from C6 sugars has been engineered into *Escherichia coli* 2 and *Candida utilis*.¹⁴³



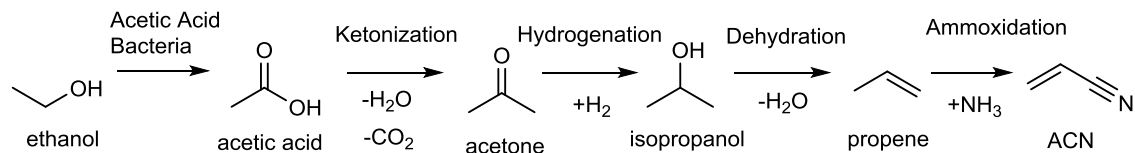
Scheme 3. Sugars to 3-HPA, followed by esterification, nitrilation, and dehydration to produce ACN.



Scheme 4. C5/C6 sugars to PA followed by hydrodeoxygenation to 1-propanol, dehydration to propene, and ammoxidation to ACN.



Scheme 5. Ethanol to acetic acid followed by ketonization to acetone, hydrogenation to isopropanol, dehydration to propene, ammoxidation to ACN.



Scheme 6. General reaction network for upgrading bioderived acids.

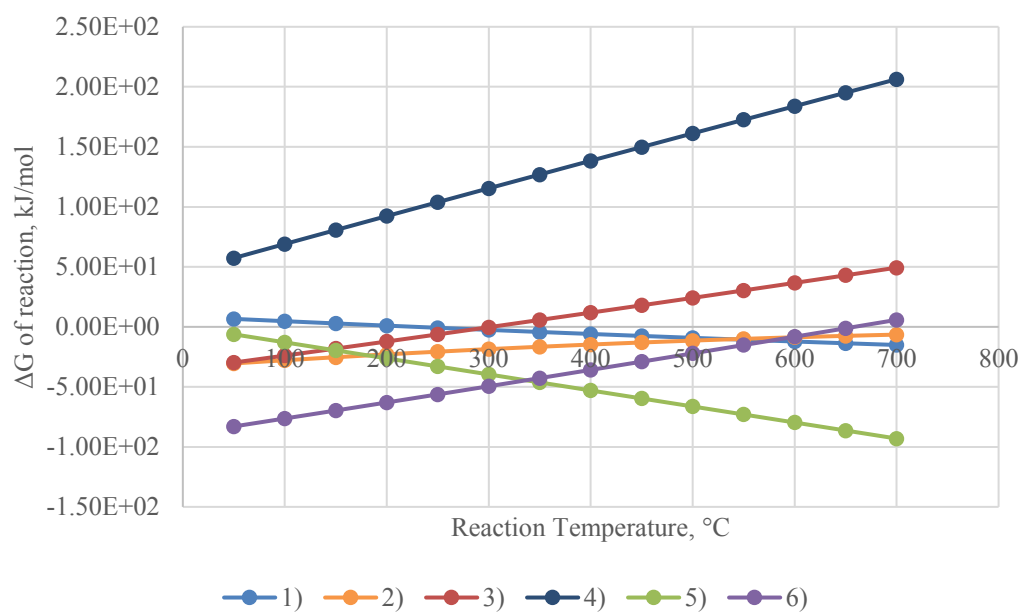
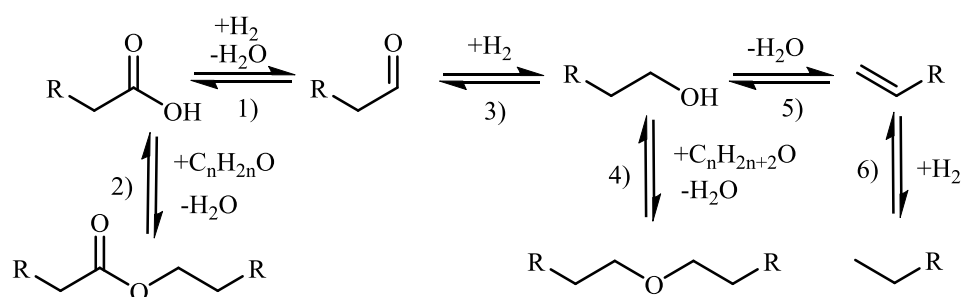


Figure 2. Gibbs energy of reaction for the network of reactions in Scheme 5 regression coefficients were found in literature.³

Table 1. Hydrodeoxygenation of various carboxylic acids using respective catalysts under cited conditions.

	Acid	Catalyst	Temp., °C	Pressure, psi	Time, h	Conv., %	Selectivity, %			Ref.
							Hydro- carbon	Ester	Alcohol	
1	decanoic ^a	Re ₂ O ₇ /OsO ₄	100	1,470	6.6	94.4	8.2	1.4	84.9	
2	decanoic ^b	Re ₂ O ₇ /OsO ₄	110	735	7.5	94.4	12.7	3.1	79.6	144
3	decanoic ^b	Re ₂ O ₇ /OsO ₄	120	367	8.5	91.5	17.1	4.8	71.9	
4	oleic	Re/Sn	250	812	17	88.4			84.8	52
5	hexanoic	Ru- Triphos	195	725	16	50			98	145
6	pentadecanoic	5%Rh/ Al ₂ O ₃	170	1,470	16	-	-	-	15 ^z	30
7	pentadecanoic	Mo(CO) ₆	170	1,470	16	-	-	-	0 ^z	30
8	pentadecanoic	5%Rh/Al ₂ O ₃ Mo(CO) ₆	150	1,470	16	-	-	-	98 ^z	30
9	lactic	Cu/SiO ₂	200	104	Cont.	100			90.8 ^c	146
10	propanoic	Ru-Pt/ AlOOH	180	725	6	41.7	-	1.9	98.1	85
11	propanoic	1.0Ru/C	150	928	Cont.	40.4	73	-	25.7	23
12	propanoic	1.0Ru/ZrO ₂	180	928	Cont.	47.0	54.7	-	43.2	23
13	propanoic	1.0Ru/ Al ₂ O ₃	190	928	Cont.	47.9	11.5	-	85.1	23
14	propanoic	1.0Ru/ Al ₂ O ₃	200	928	Cont.	32.8	8.9 ^y	-	90.3 ^x	23
15	propanoic	4.0Ru/ Al ₂ O ₃	200	928	Cont.	37.1	10.5 ^y	-	82.7 ^x	23
16	propanoic	6.0Ru/ Al ₂ O ₃	200	928	Cont.	34.9	16.6 ^y	-	73.6 ^x	23
17	octanoic	36In ₂ O ₃ / 14Cu zeolite-P	380	304	Cont.	86	13	-	64	147

Table 2. Literature reports on the conversion and selectivity of the dehydration of 1-propanol to propene at various conditions and with different catalysts. a) 10 wt% aqueous b) 50 wt% aqueous 1-propanol, c) with co-feed of H₂, d) by difference, e) needs verification.

Catalyst	Conversion (%)	Selectivity (%)			Temp. (°C)	WHSV (h ⁻¹)	TOS (h)	Reference
		Propene	C4+	Propyl Ether				
HZSM-5-30	99	>99	Trace	Trace	250	1.0	2.0	
HZSM-5-60	96	99	1	Trace	250	1.0	2.0	
HZSM-5-100	91	96	4	Trace	250	1.0	2.0	
HZSM-5-200	78	91	9	Trace	250	1.0	2.0	
SAPO-34	35	82	-	18	250	1.0	2.0	118
MCM-41	27	78	-	22	250	1.0	2.0	
Al ₂ O ₃	42	66	-	34	250	1.0	2.0	
HZSM-5-30 ^a	99	99	Trace	Trace	250	1.0	2.0	
HZSM-5-30 ⁿ	99	99	Trace	Trace	250	1.0	2.0	
WC ^c	85	>95	Trace	Trace	380	4.0	2.0	148
AM-11	45	100	Trace	Trace	250	2.0	1.0	149
H-ZSM5-30	99	55	45 ^d	Trace	240	1.6	3.0	
H-ZSM5-23	99	72	28 ^d	Trace	240	1.6	3.0	This Work
V-ZSM5-23	99 ^e	92	8 ^d	Trace	240	1.6	3.0	

Table 3. Surface properties of Mo₂C catalysts.

Catalyst	Loading, %	Surface Area, m ² /g	Total Pore Volume, cm ³ /g	Average Pore Size, Å
Mo ₂ C	-	18.6	0.1062	119.1
Ni-Mo ₂ C	T.B.D	18.3	0.0779	85.2
Ca-Mo ₂ C	T.B.D	9.55	0.0375	78.5
Mo ₂ C*	-	23.7	0.0869	73.5
Ni-Mo ₂ C*	T.B.D	17.2	0.0701	81.4
Ca-Mo ₂ C*	T.B.D	7.14	0.0346	97.0

*Post reaction with Acetic Acid

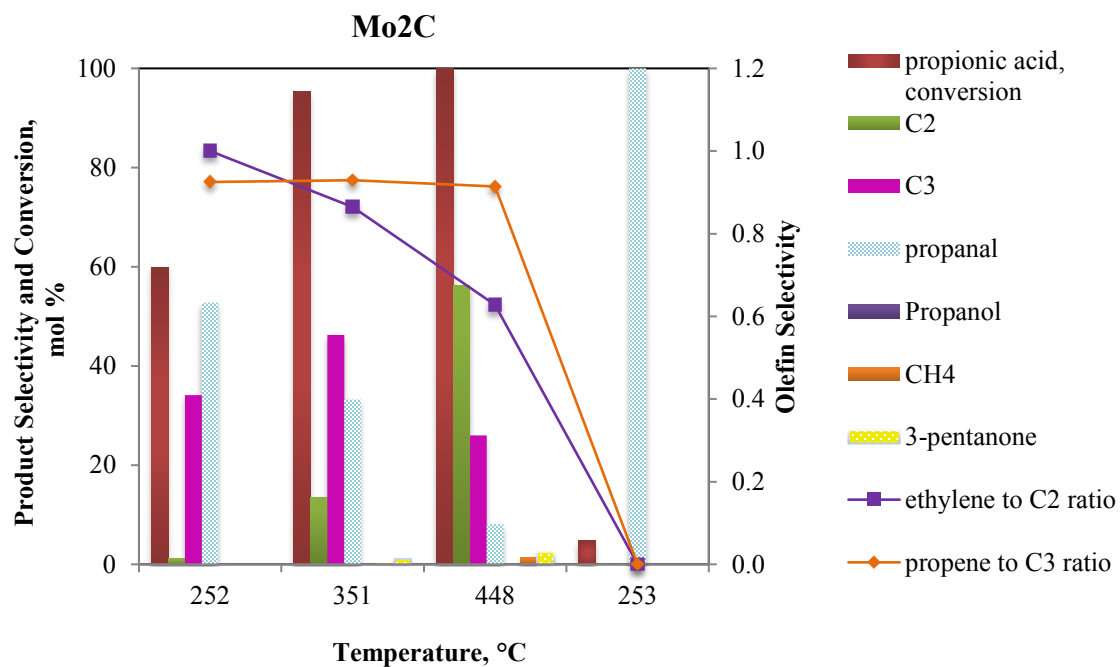


Figure 3. Propionic acid conversion and product selectivity over Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h.

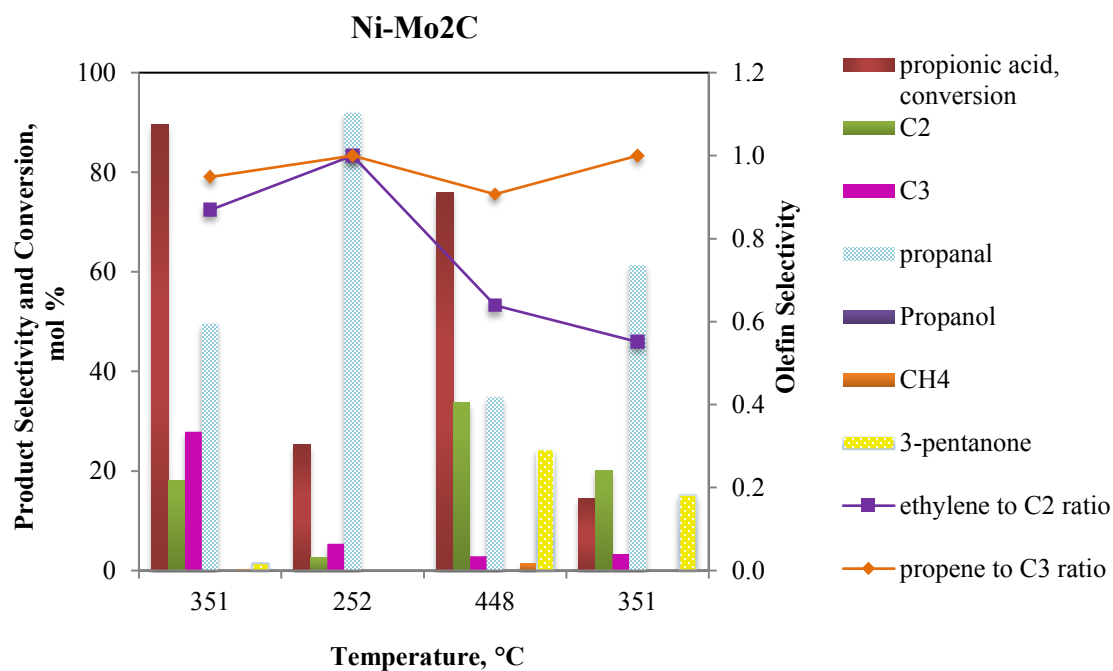


Figure 4. Propionic acid conversion and product selectivity over Ni-Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h.

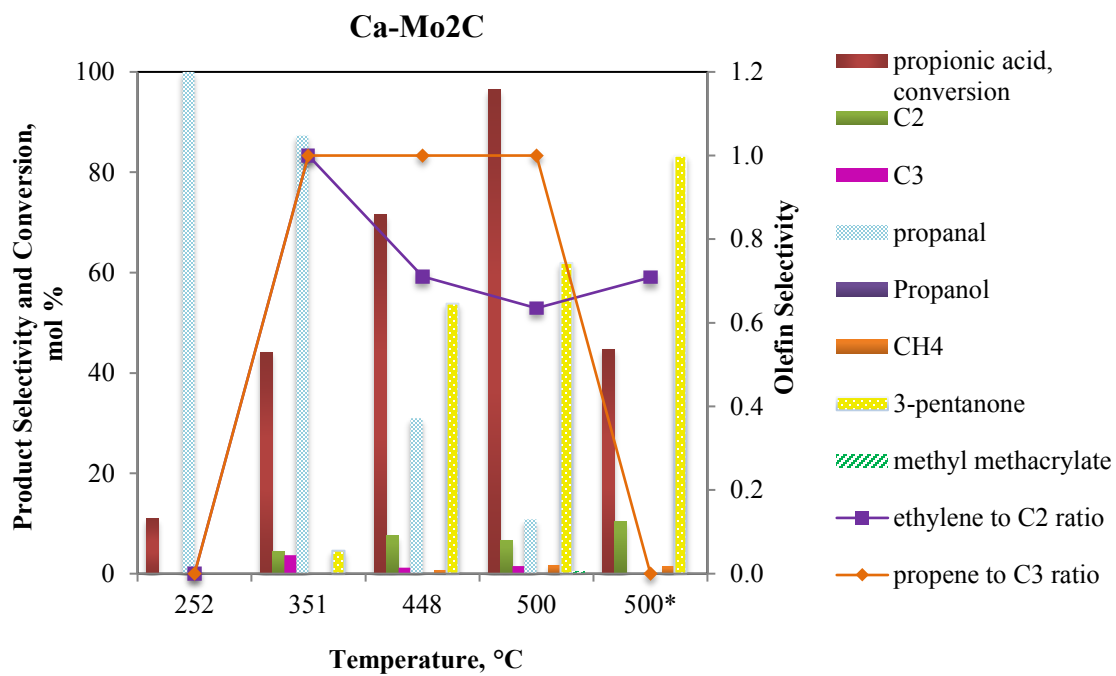


Figure 5. Propionic acid conversion and product selectivity over Ca-Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h. *The final injection was taken after running the reaction overnight 12 h.

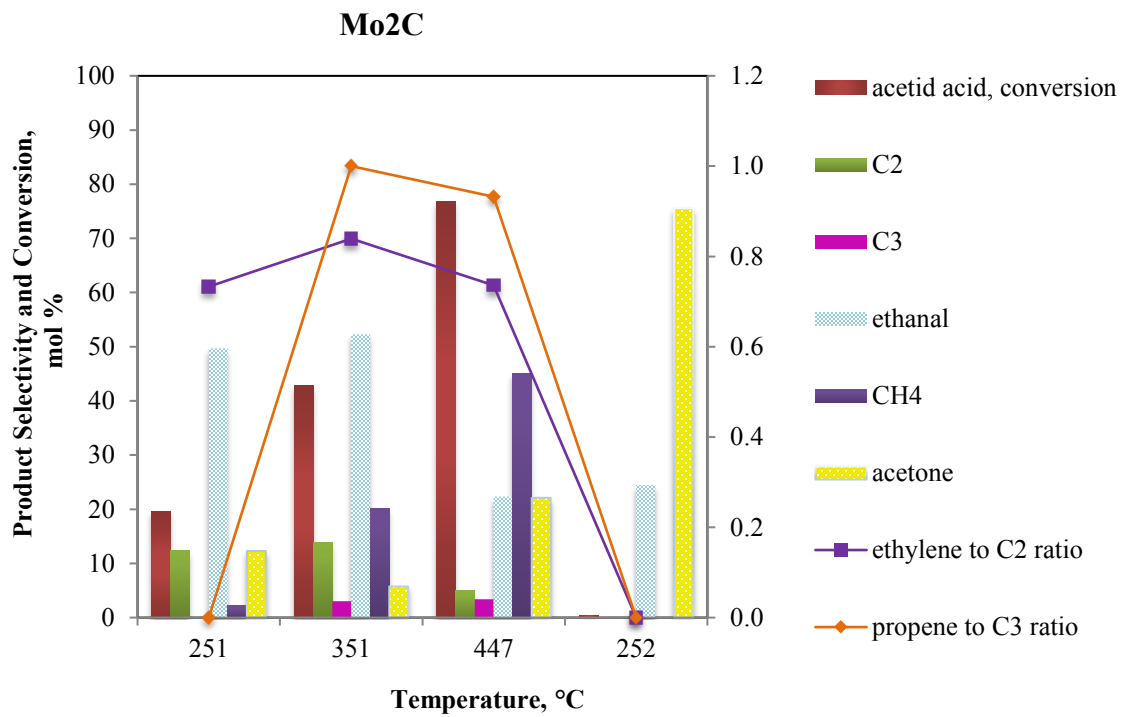


Figure 6. Acetic acid conversion and product selectivity over un-doped Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h.

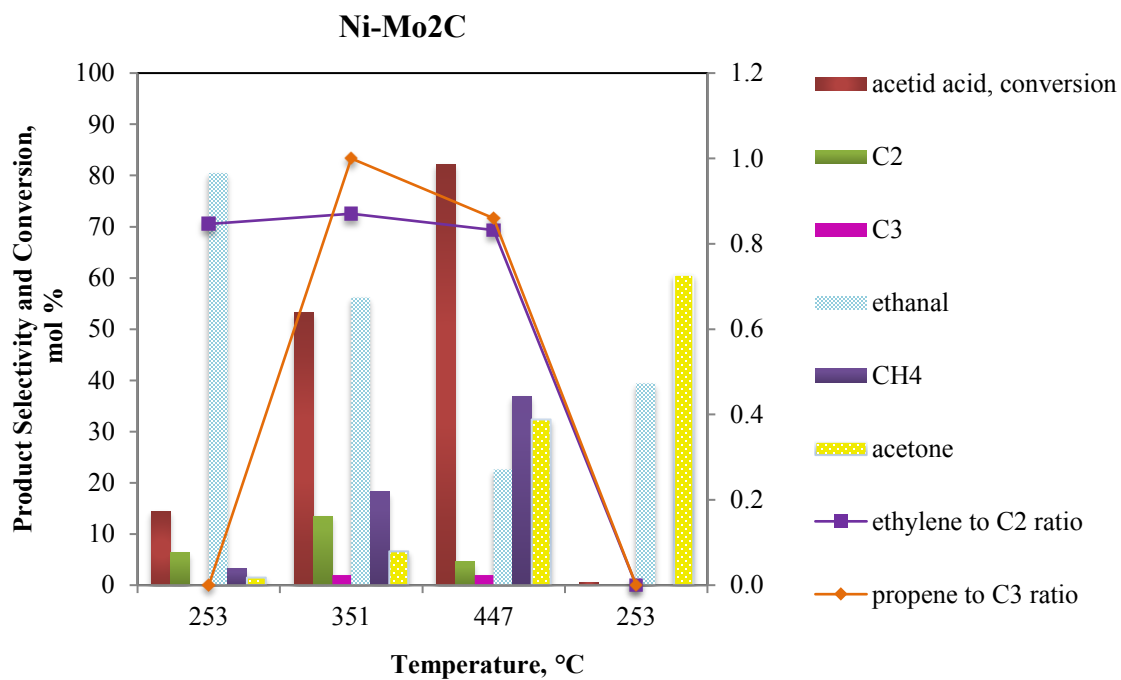


Figure 7. Acetic acid conversion and product selectivity over Ni-Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h.

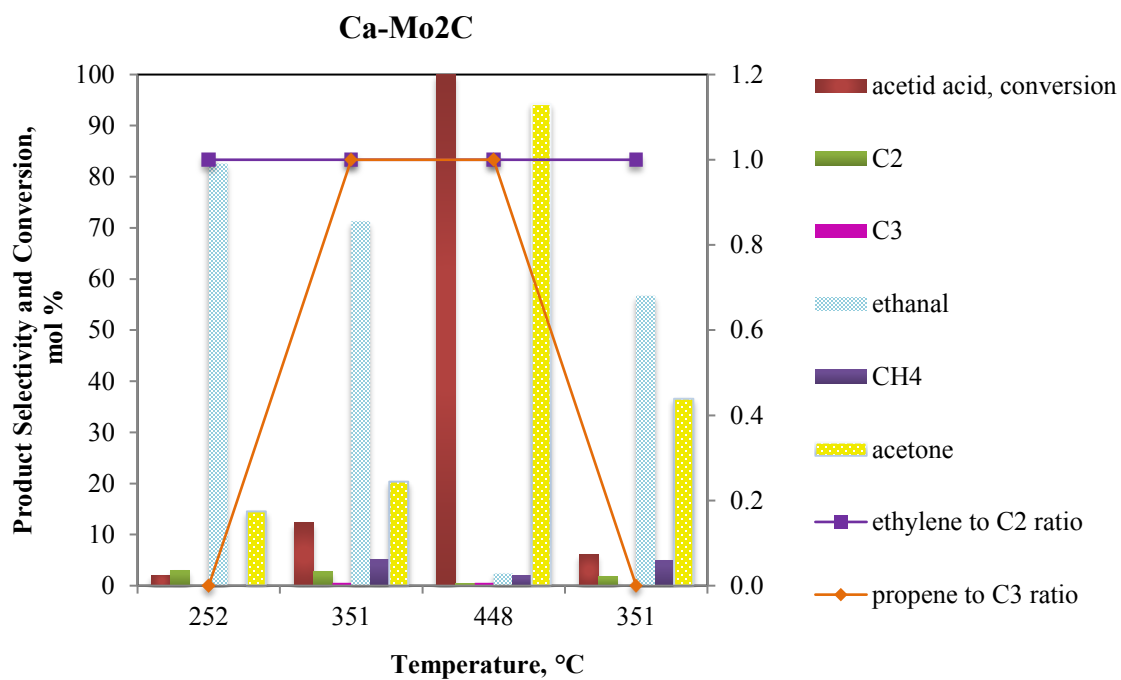


Figure 8. Acetic acid conversion and product selectivity over Ca-Mo₂C run over 4 h TOS. Pretreatment 2 h 10% H₂ 500 °C 2 h.

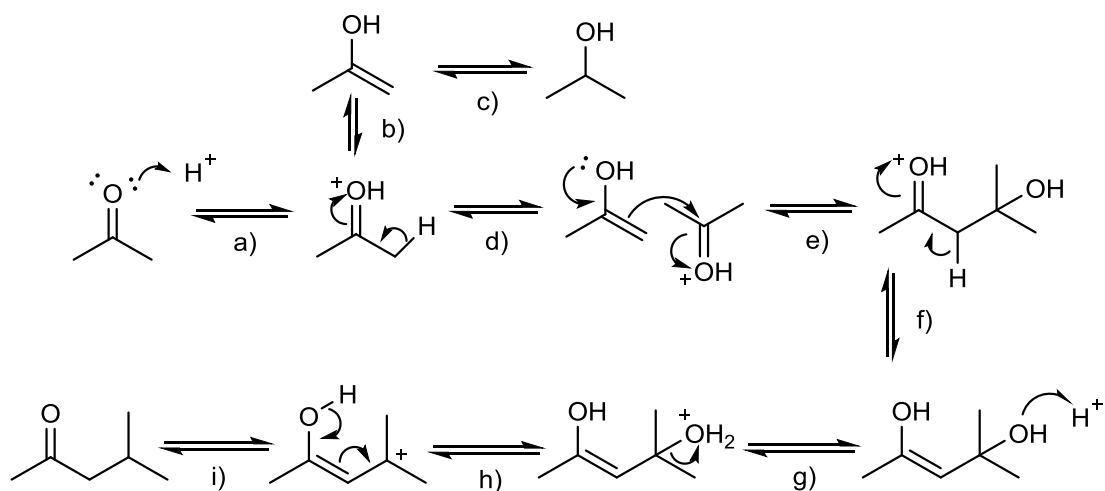
Table 4. Surface properties of single atom catalysts.

Catalyst	Loading, %	Surface Area, m ² /g
Ru/ γ -Al ₂ O ₃	0.10	196.4
Ru/ γ -Al ₂ O ₃	1.0%	193.7
Pt/ θ -Al ₂ O ₃	0.10	104.8
Rh/ γ -Al ₂ O ₃	0.10	189.0
Pd/ γ -Al ₂ O ₃	0.17	-
θ -Al ₂ O ₃	n.a.	127.0
γ -Al ₂ O ₃	n.a.	214.2

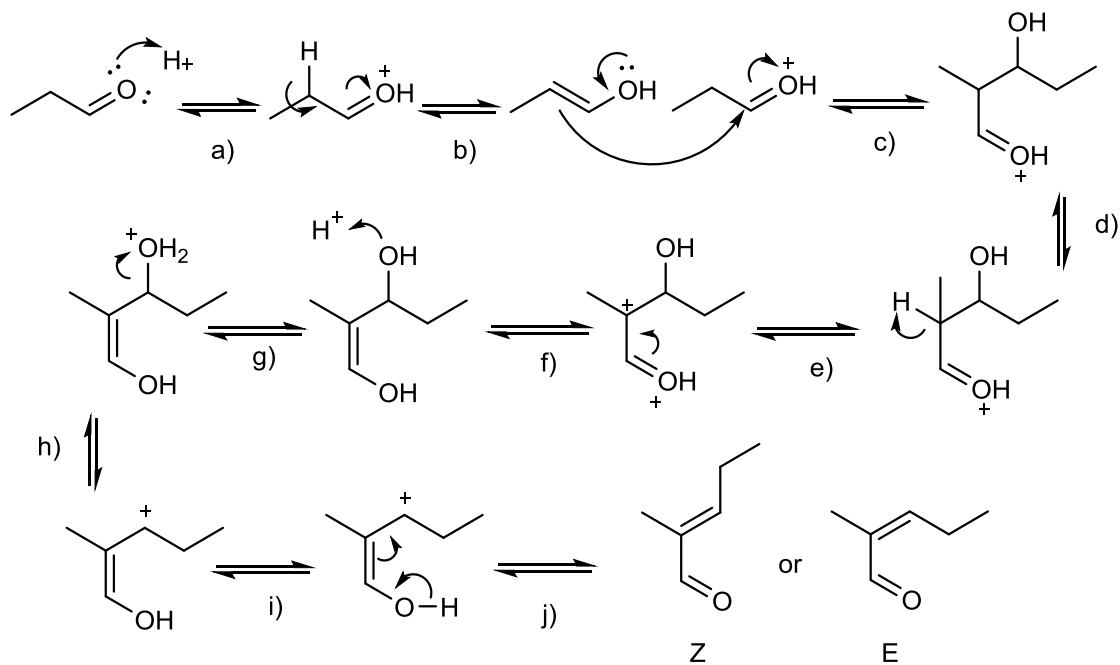
Table 5. Turnover frequencies for single atom catalysts and their bare alumina support materials for isopropanol (IPA), methyl isobutyl ketone (MIBK) and diacetone alcohol (DDA). Reactions at 150 °C for 2 h under 1175 psig H₂.

Catalyst	TOF, mol/g·s			Selectivity, mol/mol		Conversion, %
	IPA	MIBK	DDA	IPA	MIBK	
Ru/ γ -Al ₂ O ₃	1.03	1.30	3.15E-02	44.26	55.74	4.94
Pt/ θ -Al ₂ O ₃	0.99	0.41	n.a.	70.89	29.11	5.04
Rh/ γ -Al ₂ O ₃	0.25	1.98	n.a.	11.19	88.81	4.71
Pd/ γ -Al ₂ O ₃	0.69	0.58	n.a.	54.25	45.75	2.70
θ -Al ₂ O ₃	3.54E-03	1.66E-03	3.39E-02	68.12	31.88	0.11
γ -Al ₂ O ₃	1.68E-03	5.01E-04	2.33E-02	76.99	23.01	0.05

Scheme 7. Acetone hydrogenation reaction mechanism.



Scheme 8. Propanal aldol condensation reaction mechanism.



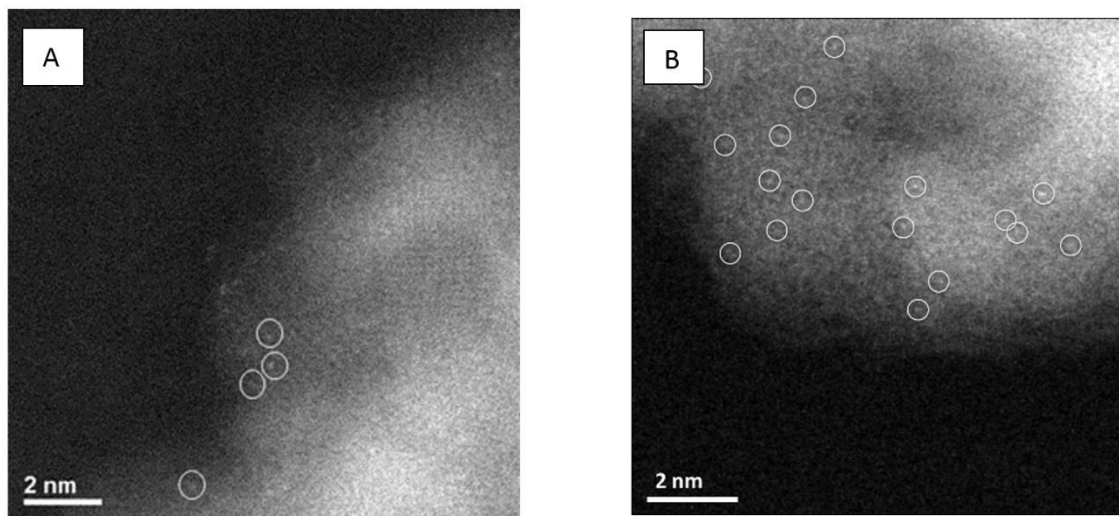


Figure 9. AC-STEM HAADF-STEM images of A) Rh1/ γ -Al₂O₃ and B) Ru1/ γ -Al₂O₃ prior to reaction.

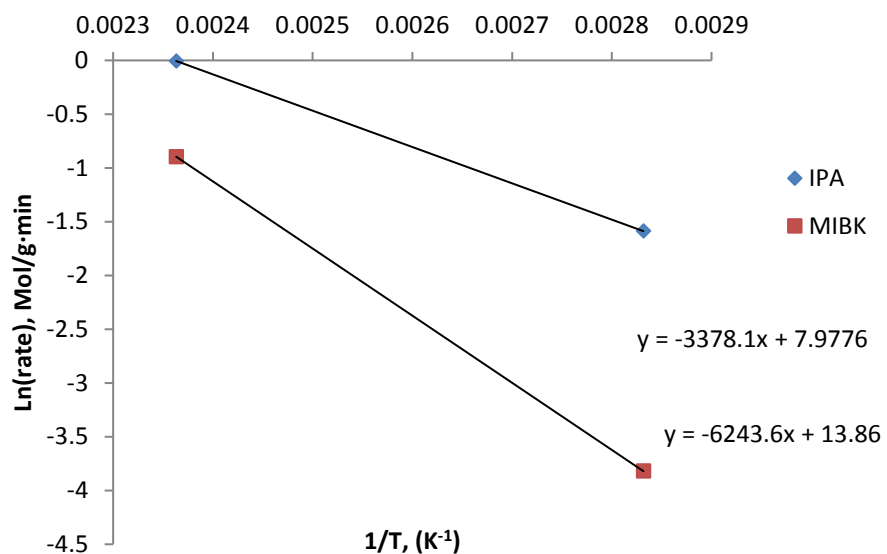


Figure 10. Arrhenius plot for Pt on θ -alumina for isopropanol (IPA) and methyl isobutyl ketone (MIBK).

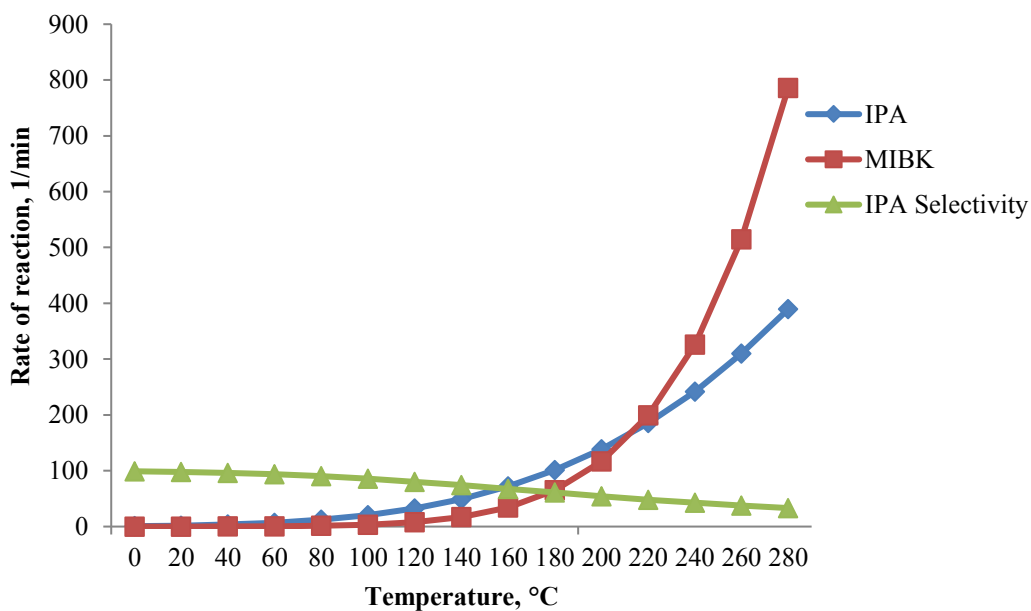


Figure 11. Predicted rates of reaction for isopropanol (IPA) and methyl isobutyl ketone (MIBK) and IPA selectivity as a function of temperature using the constants derived from the Arrhenius plot.

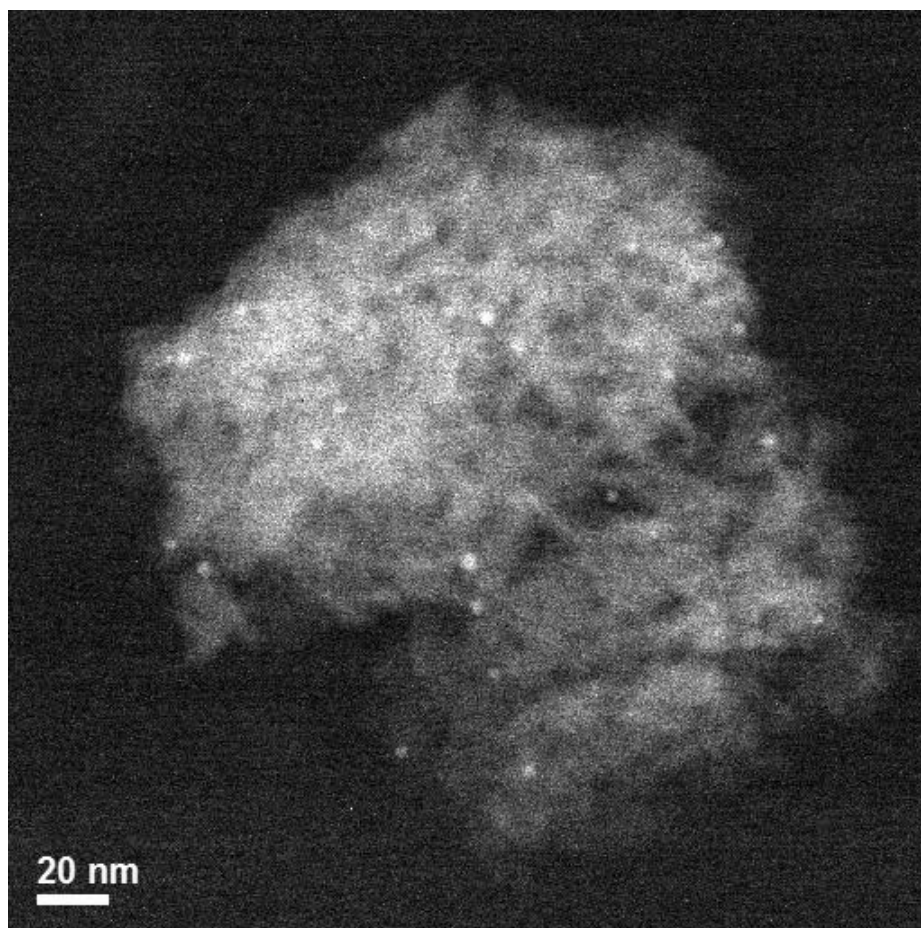


Figure 12. ACEM HAADF-STEM image of Pd on alumina post acetone hydrogenation at 150 °C, 2 h.

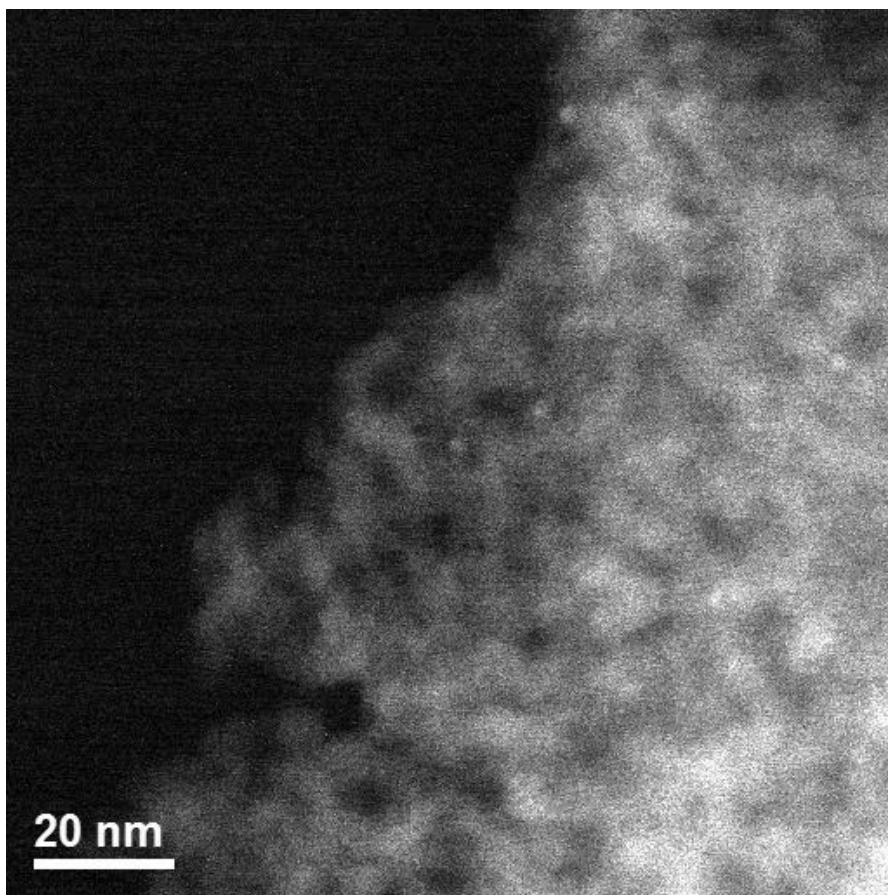


Figure 13. ACEM HAADF-STEM image of Rh on alumina post acetone hydrogenation at 150 °C, 2 h.

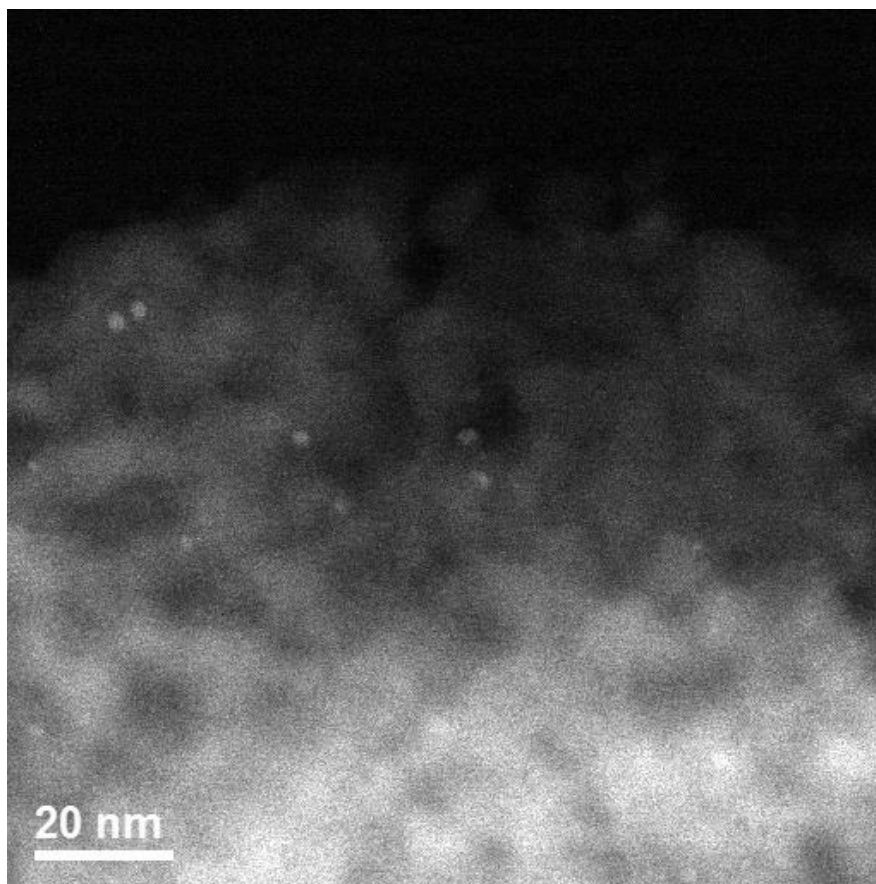


Figure 14. ACEM HAADF-STEM image of Pt on alumina post acetone hydrogenation at 150 °C, 2 h.

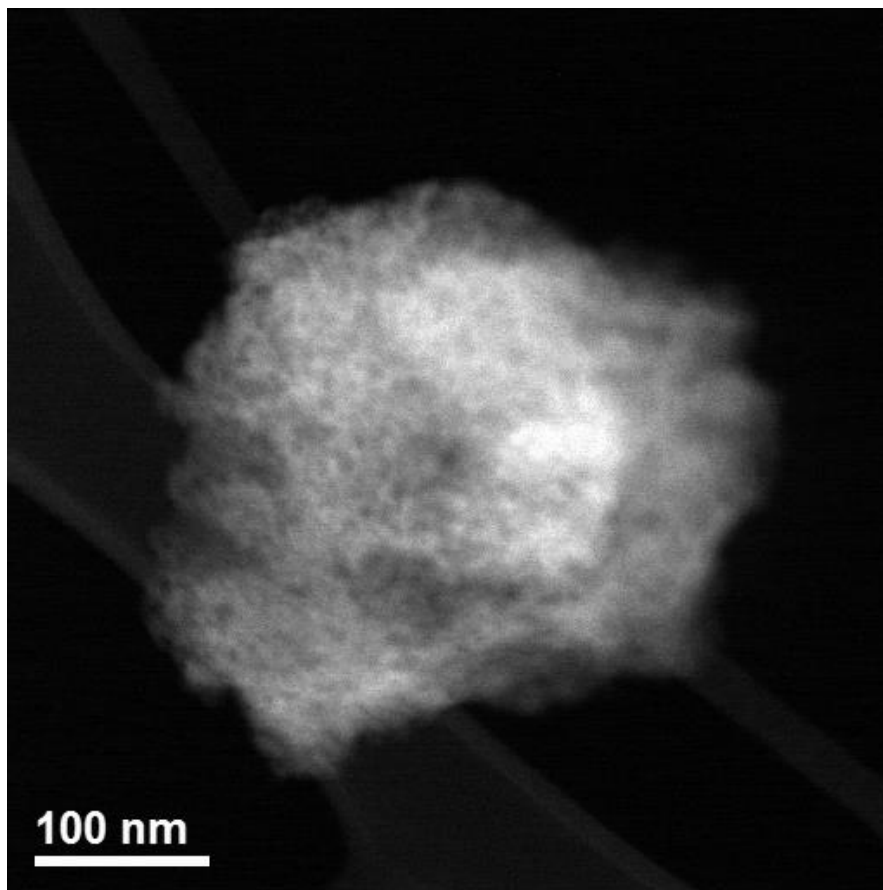


Figure 15. ACEM HAADF-STEM image of Ru on alumina post acetone hydrogenation at 150 °C, 2 h.

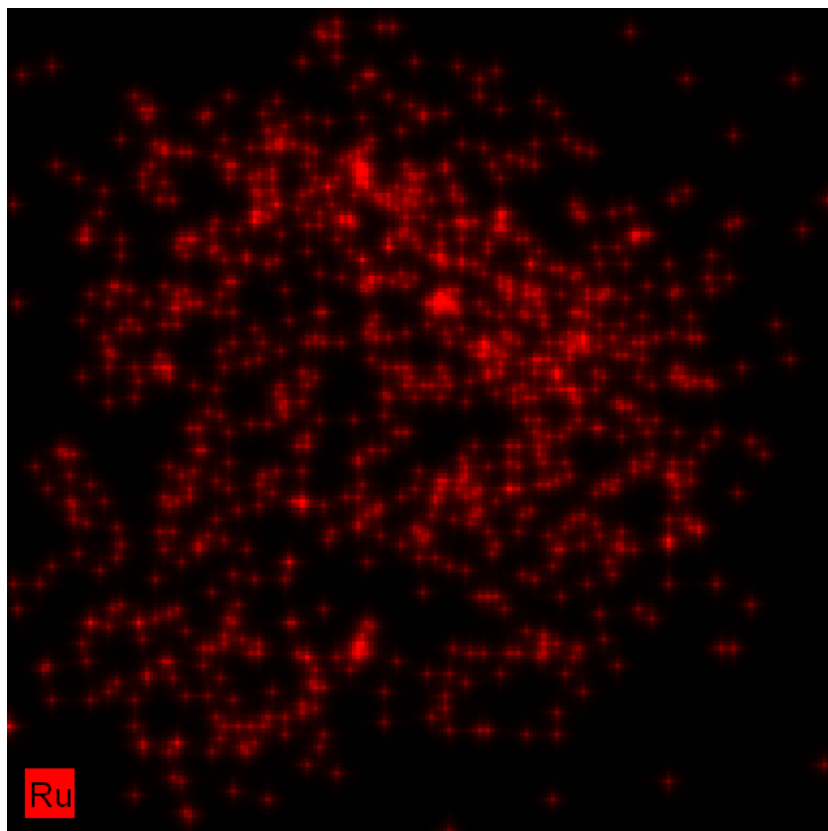


Figure 16. Elemental analysis by energy-dispersive x-ray spectroscopy (EDS) image of Ru on alumina post acetone hydrogenation at 150 °C, 2 h.

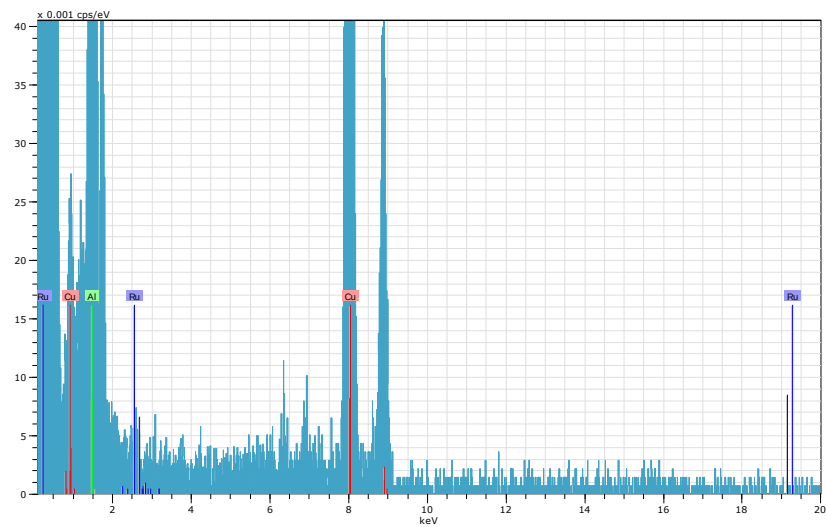


Figure 17. Elemental analysis by energy-dispersive x-ray spectroscopy (EDS) of aggregate.

Table 6. Surface properties of the M-ZSM-5 catalysts tested.

Zeolite	M (%)	BET (m²g⁻¹)	Pore Volume (cc/g)
H-ZSM-5	-	344	0.19
Cu-ZSM-5	2.76	335.0	0.199
V-ZSM-5	0.73	344.0	0.208
Zn-ZSM-5	3.1	342.1	0.201

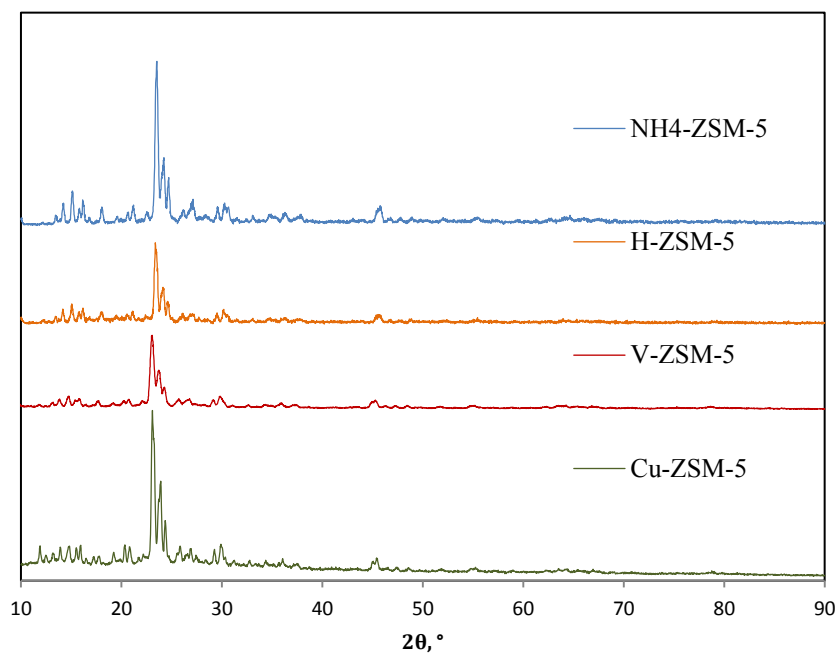


Figure 18. X-Ray Powder Diffraction Patterns of M-ZSM-5.

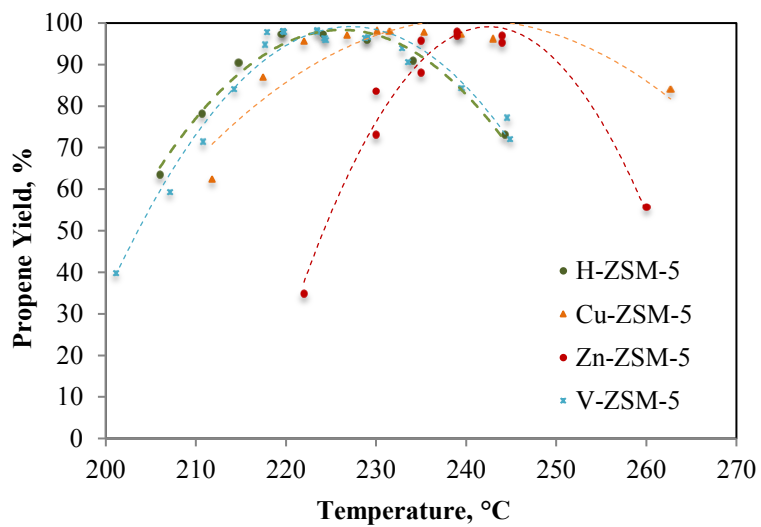


Figure 19. Propene yield as a function of catalyst temperature at 1-propanol WHSV of 1.6 h⁻¹.

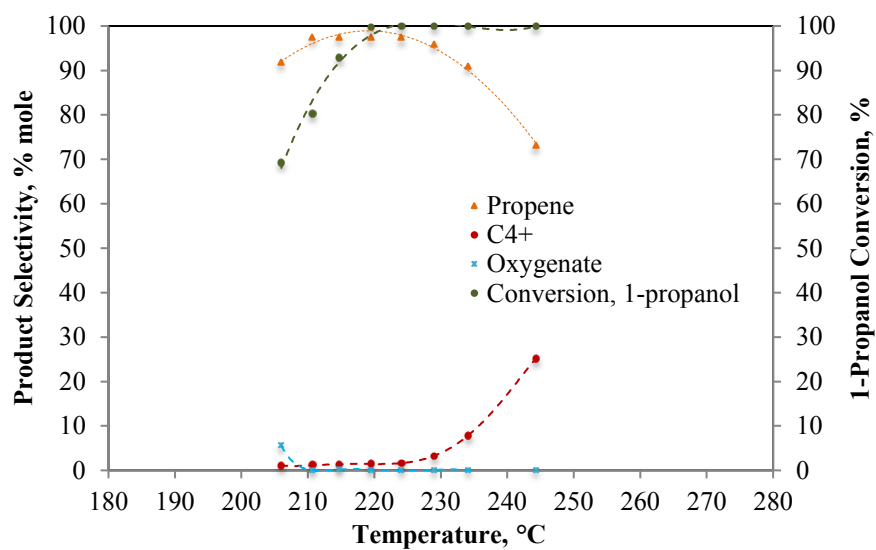


Figure 20. 1-Propanol conversion and product selectivity as a function of temperature at WHSV of 1.6 h⁻¹ over H-ZSM-5.

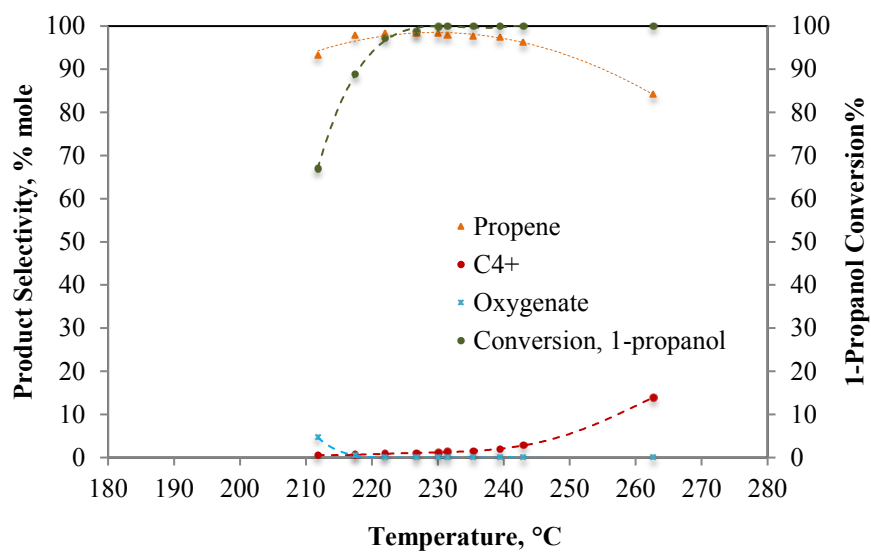


Figure 21. 1-Propanol conversion and product molar selectivity as a function of temperature at WHSV of 1.6 h^{-1} at 230°C over Cu-ZSM-5.

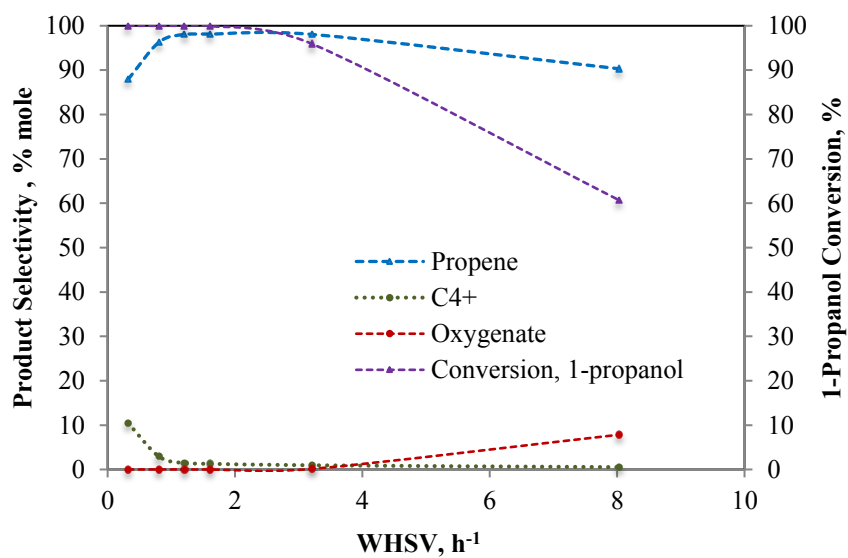


Figure 22. 1-Propanol conversion and product molar selectivity as a function of WHSV at 230°C over Cu-ZSM-5.

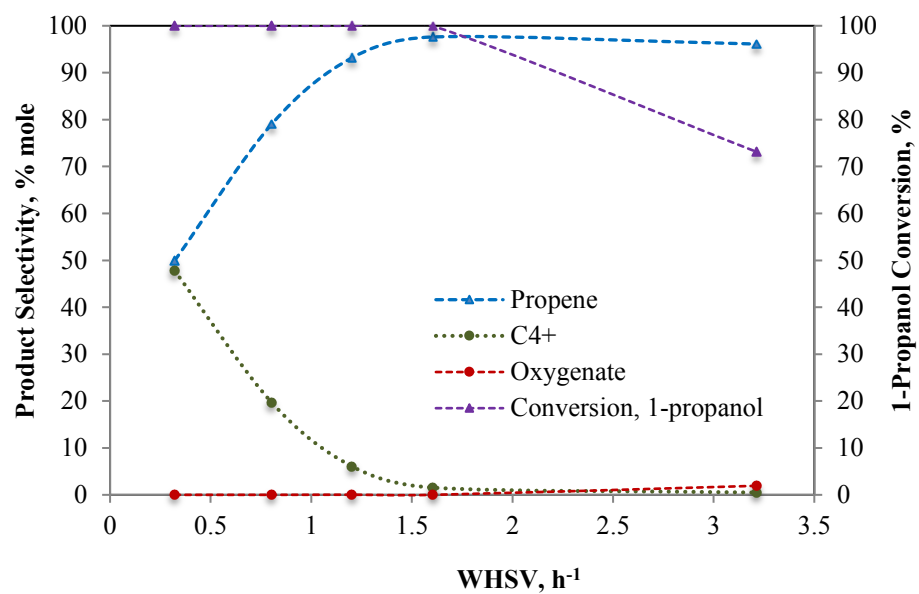


Figure 23. 1-propanol conversion and product selectivity over Zn-ZSM-5 as a function of WHSV (h^{-1}) at 230 °C.

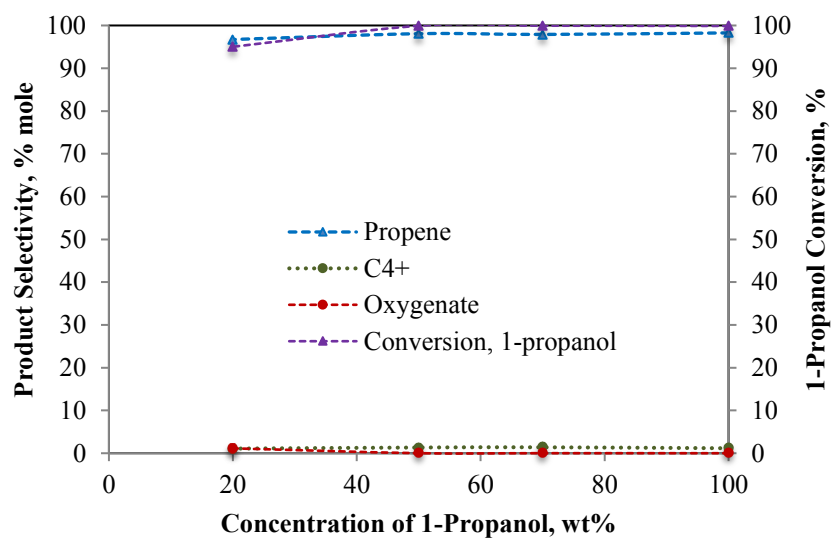


Figure 24. Impact of water on 1-propanol conversion and product molar selectivity at 230 °C and constant effective 1-propanol WHSV, (1.6 h^{-1}) over Cu-ZSM-5.

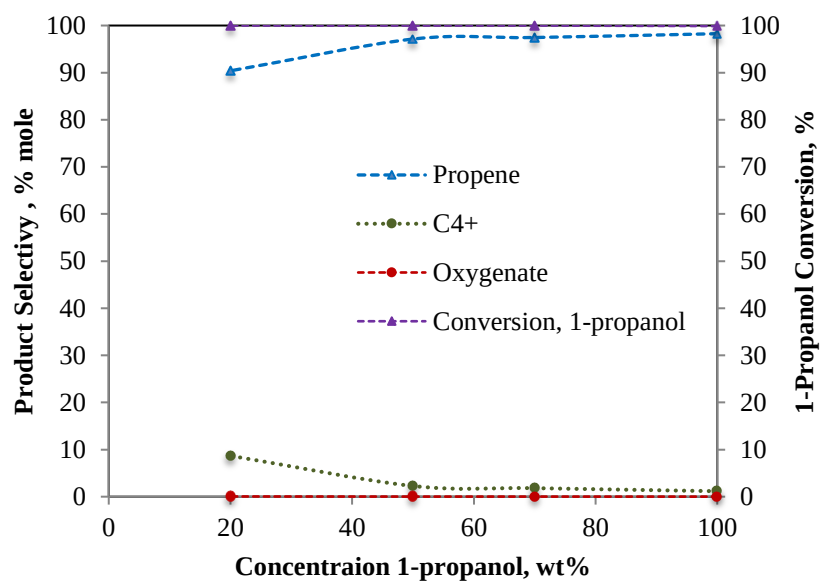


Figure 25. Impact of water on 1-propanol conversion and product molar selectivity at 230 °C and constant total flow 0.4 ml/h over Cu-ZSM-5.

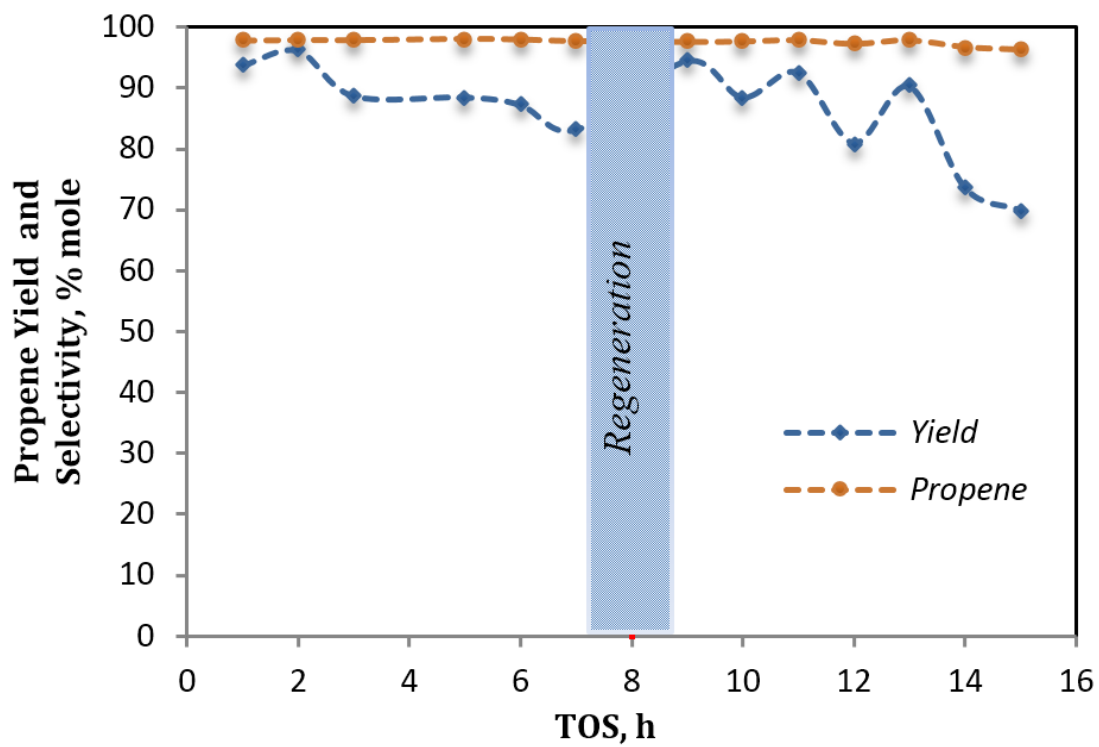


Figure 26. Propene yield and selectivity as a function of time on stream over Cu- ZSM-5. Reactions were carried out at ~ 230 °C with an effective 1-propanol WHSV of 2.4 h^{-1} at atmospheric pressure. Catalyst was regenerated after 7 h TOS.

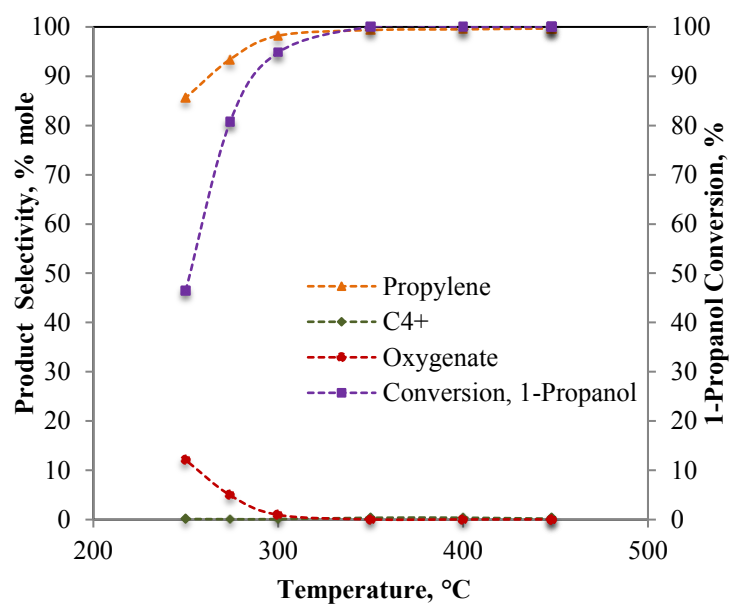


Figure 27. Product molar selectivity and 1-propanol conversion as a function of temperature at WHSV = 1.6 h^{-1} over $\gamma\text{-Al}_2\text{O}_3$.

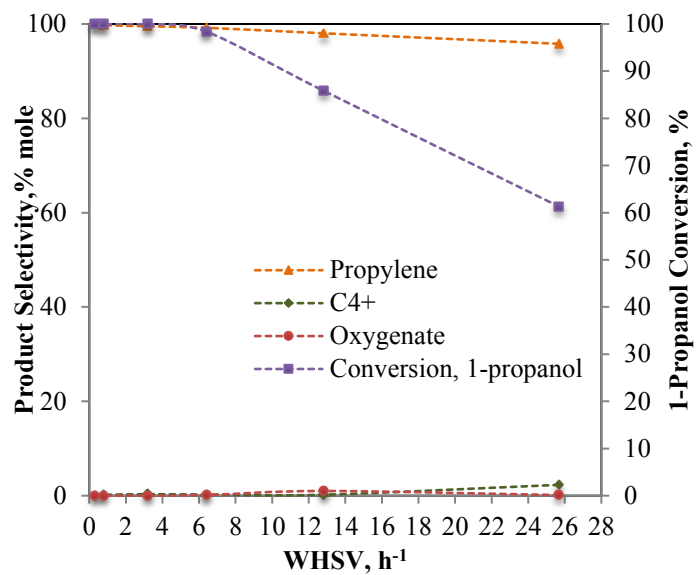


Figure 28. Product molar selectivity and 1-propanol conversion as a function of WHSV at 350 °C over γ - Al_2O_3 .

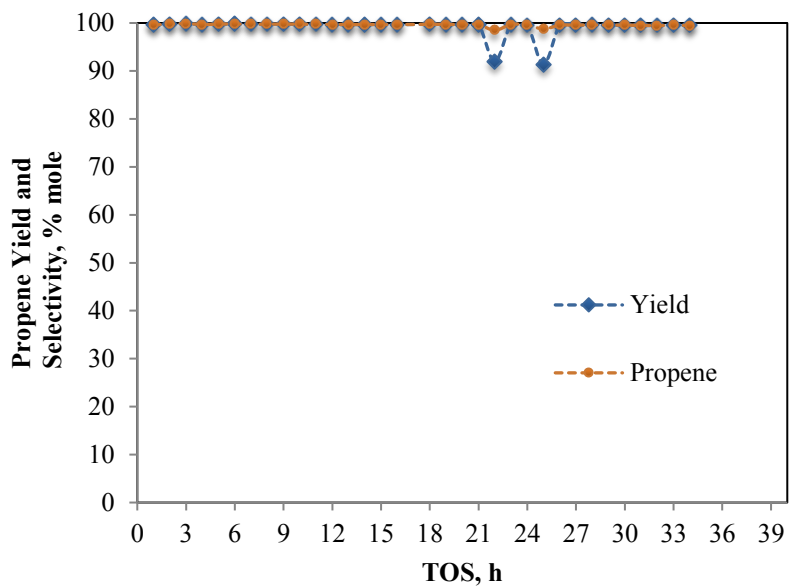


Figure 29. Conversion of 50 wt% aqueous 1-propanol over γ -alumina as a function of time on stream at 350 °C and an effective WHSV of 1.6 h⁻¹ based on 1-propanol.

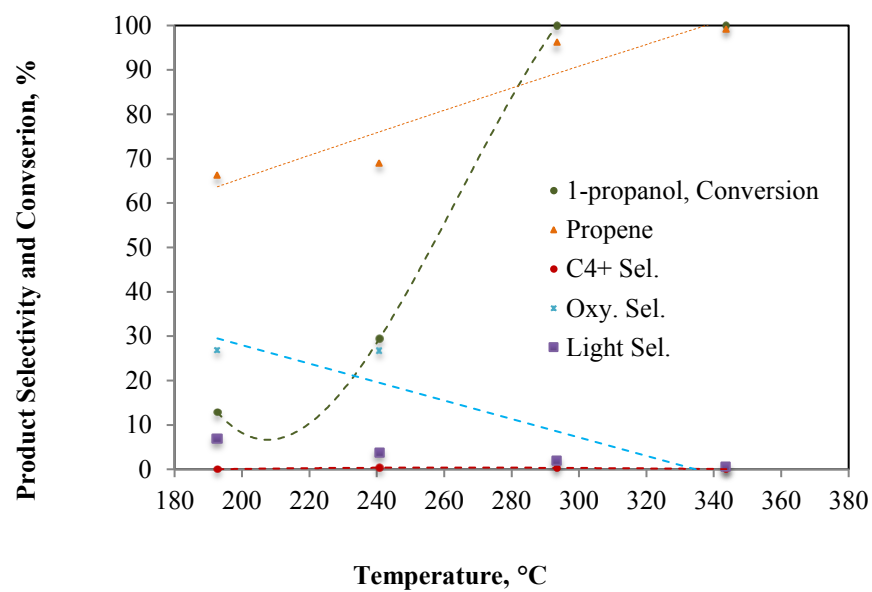


Figure 30. Product selectivity and 1-propanol conversion over γ -alumina as a function of temperature under 1.6 h^{-1} WHSV prior to hydrothermal aging.

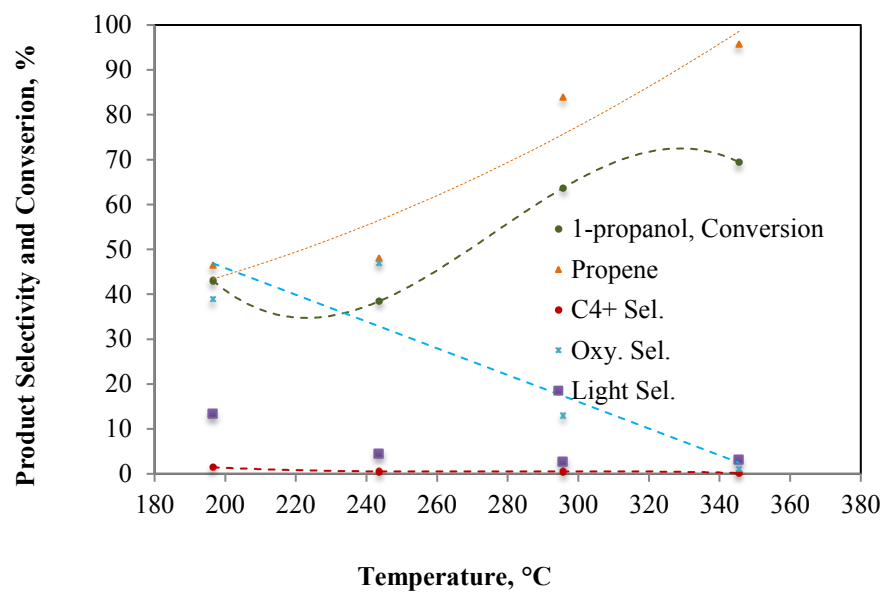


Figure 31. Product selectivity and 1-propanol conversion over γ -alumina as a function of temperature under 1.6 h^{-1} WHSV, after hydrothermal aging.

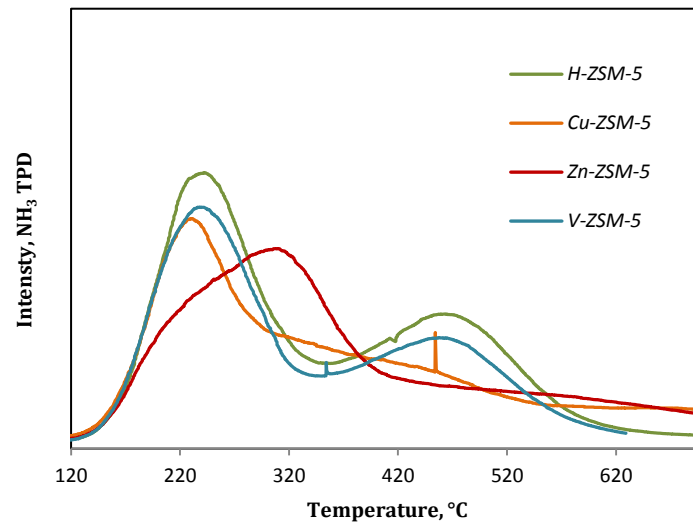


Figure 32. NH₃-TPD profiles for M-ZSM-5.

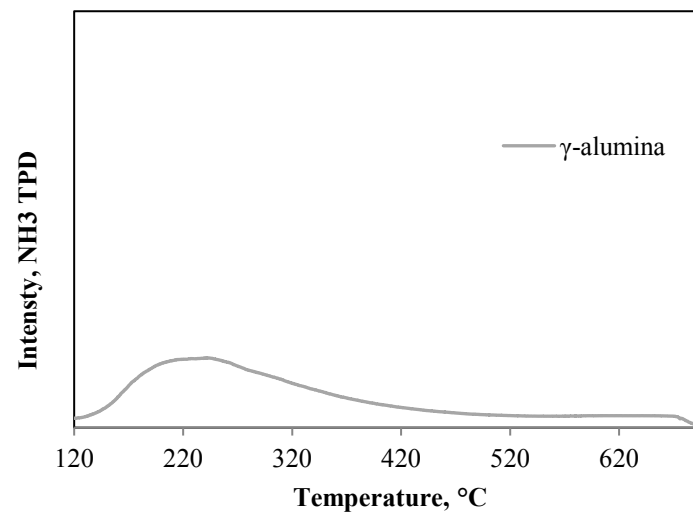
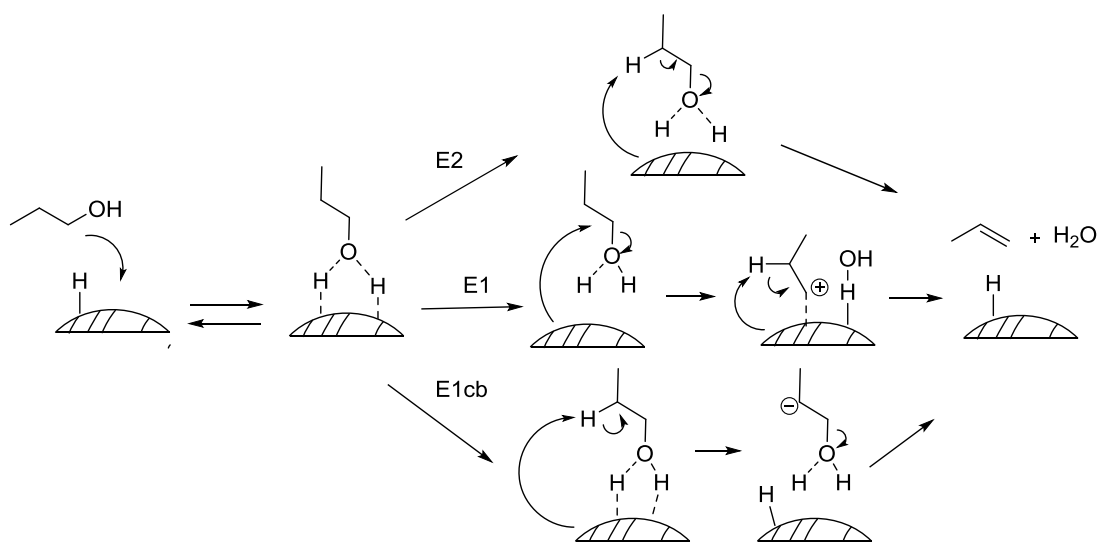


Figure 33. NH₃-TPD profiles for γ -alumina.



Scheme 9. 1-Propanol dehydration pathways.

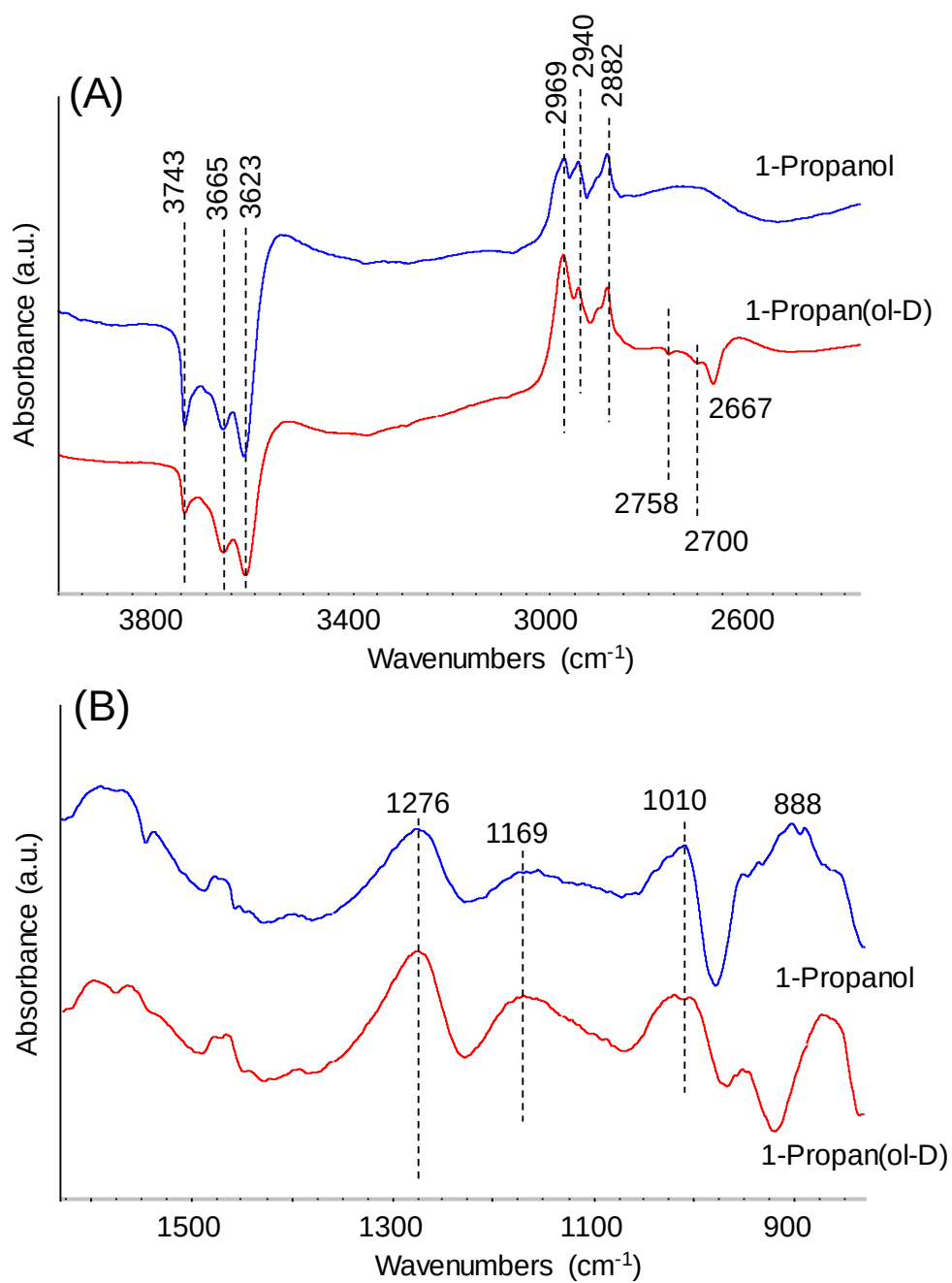


Figure 34. FTIR spectra of 1-propanol and 1-propan(ol-D) adsorbed on Cu-ZSM-5 at 25 °C.

(A) 4000 cm⁻¹ to 2500 cm⁻¹, (B) 1600 cm⁻¹ to 800 cm⁻¹.

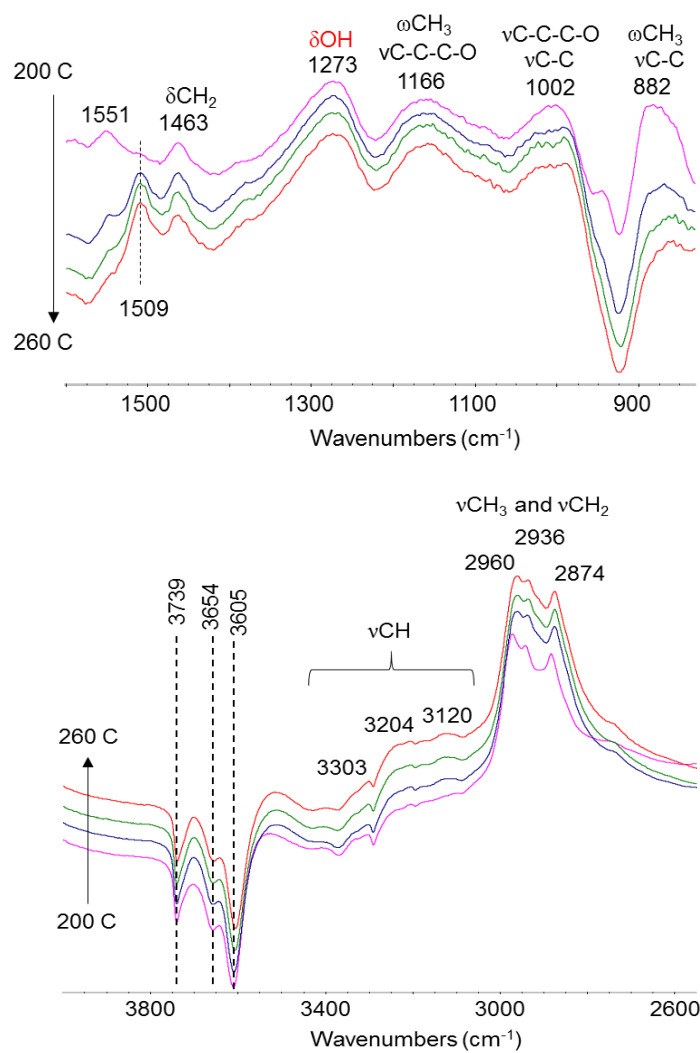


Figure 35. FTIR spectra for the *in-situ* reaction of 1-propanol over Cu-ZSM-5 at 200, 220, 240, and 260 °C. Reaction conditions: 0.03 ml/h of 1-propanol, 16 mg of catalyst.

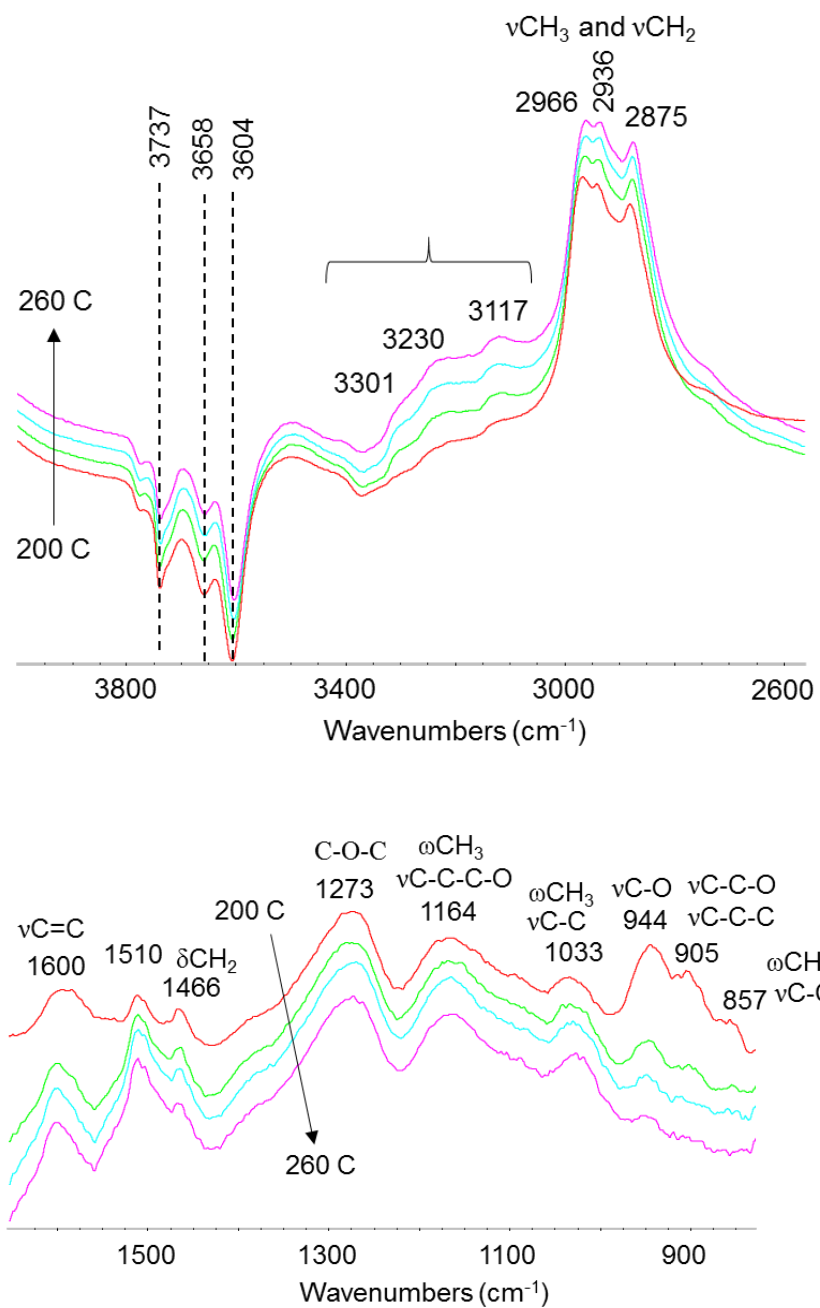


Figure 36. FTIR spectra of 1-propanol over H-ZSM-5 at 200, 220, 240, and 260 °C. Reaction condition: 0.5 $\mu\text{l}/\text{min}$ of 1-propanol, 16 mg of catalyst.

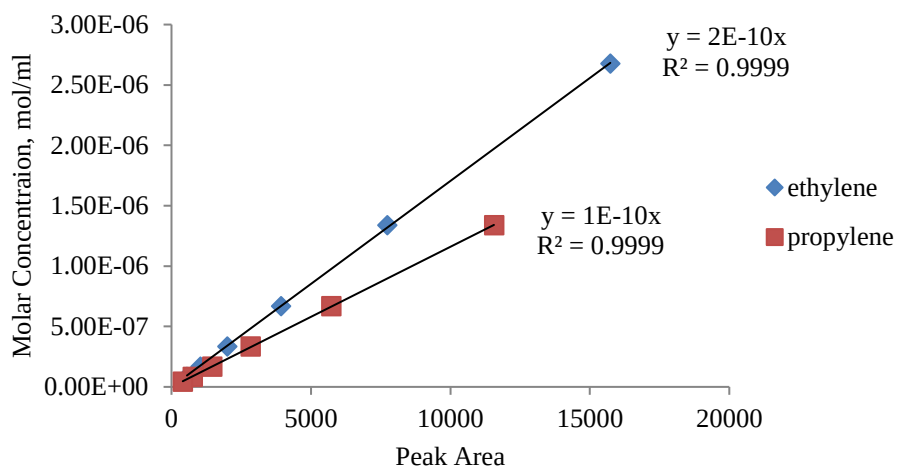


Figure 37. GC-FID calibration curves for ethene and propene.

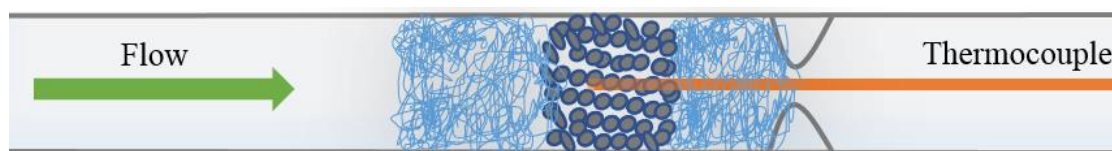


Figure 38. Packed bed reactor tube loaded with catalyst sandwiched between quartz wool.

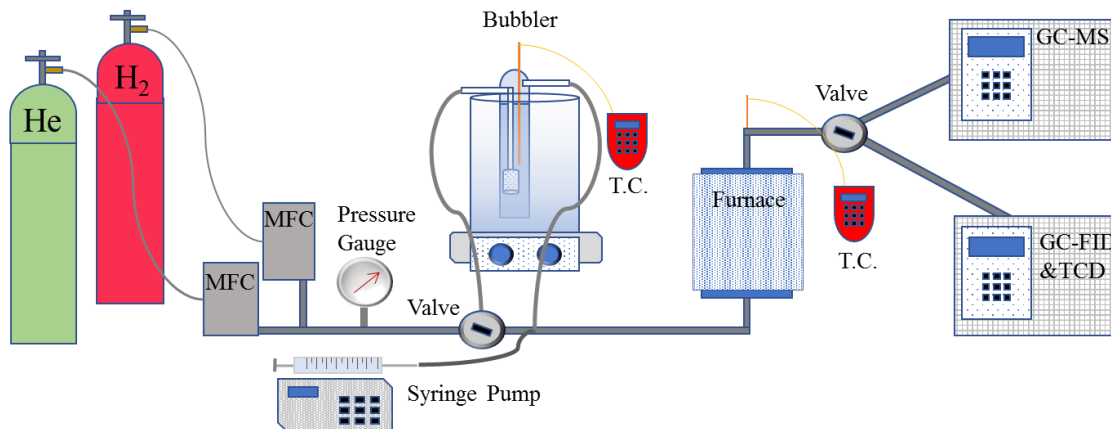


Figure 39. Packed bed bench-top reactor system.

Python Code for Processing chromatograph data

```
import openpyxl,sys
wb = openpyxl.load_workbook('file_name.xlsx')
sheet = wb.get_active_sheet()
target = sheet.get_highest_row()

print(sys.argv)
#*****Catalyst
information*****
tgf=50 #total gas flow H2+He sccm
masscat= 0.4 #mass of the catalysts in grams
tcat = 350.8
hour = 4 #time on stream in h
Tbub=26.3 #bubler temperature, Celcius
Preactor=3.8 # measured gauge pressure, psig
#*****Species
Library*****
time=0
for i in range(1, target+1, 1):
```

```

time = sheet.cell(row=i, column=2).value
if time < 3.0:
    sheet.cell(row = i, column=4).value = 'Methane'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2 #need a better number for this
    sheet.cell(row = i, column=6).value = 16.04
    sheet.cell(row = i, column=11).value = 1
elif time < 4.2:
    sheet.cell(row = i, column=4).value = 'ethylene'
    sheet.cell(row = i, column=5).value = 1.7051E-10
    sheet.cell(row = i, column=6).value = 28
    sheet.cell(row = i, column=11).value = 2
elif time < 4.8:
    sheet.cell(row = i, column=4).value = 'ethane'
    sheet.cell(row = i, column=5).value = 1.7051E-10
    sheet.cell(row = i, column=6).value = 30
    sheet.cell(row = i, column=11).value = 2
elif time < 8.65:
    sheet.cell(row = i, column=4).value = 'propene'
    sheet.cell(row = i, column=5).value = 1.16001E-10
    sheet.cell(row = i, column=6).value = 42
    sheet.cell(row = i, column=11).value = 3
elif time < 8.9:
    sheet.cell(row = i, column=4).value = 'propane'
    sheet.cell(row = i, column=5).value = 1.15199E-10
    sheet.cell(row = i, column=6).value = 44
    sheet.cell(row = i, column=11).value = 3
elif time < 9.3:
    sheet.cell(row = i, column=4).value = 'cyclopropane'
    sheet.cell(row = i, column=5).value = 1.15199E-10
    sheet.cell(row = i, column=6).value = 42
    sheet.cell(row = i, column=11).value = 3
elif time < 11.8:
    sheet.cell(row = i, column=4).value = 'ethanal'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2 #based on ECN estimates
    sheet.cell(row = i, column=6).value = 44.05

```

```

    sheet.cell(row = i, column=11).value = 2
elif time < 12.1:
    sheet.cell(row = i, column=4).value = '2-butene'
    sheet.cell(row = i, column=5).value = 8.75229E-11
    sheet.cell(row = i, column=6).value = 56
    sheet.cell(row = i, column=11).value = 4
elif time < 12.4:
    sheet.cell(row = i, column=4).value = 'butane'
    sheet.cell(row = i, column=5).value = 8.75229E-11
    sheet.cell(row = i, column=6).value = 56
    sheet.cell(row = i, column=11).value = 4
elif time < 12.6:
    sheet.cell(row = i, column=4).value = 'isobutene'
    sheet.cell(row = i, column=5).value = 8.79487E-11
    sheet.cell(row = i, column=6).value = 56
    sheet.cell(row = i, column=11).value = 4
#elif time < 14.5:
#    sheet.cell(row = i, column=4).value = 'propanal'
#    sheet.cell(row = i, column=5).value = 1.7051E-10*2/2
#    sheet.cell(row = i, column=6).value = 58
#    sheet.cell(row = i, column=11).value = 3
elif time < 15.5:
    sheet.cell(row = i, column=4).value = 'acetone'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2/2
    sheet.cell(row = i, column=6).value = 58.08
    sheet.cell(row = i, column=11).value = 3
elif time < 16.04:
    sheet.cell(row = i, column=4).value = '1-Propanol'
    sheet.cell(row = i, column=5).value = 1.15199E-10 #need to adjust this number!!!
    sheet.cell(row = i, column=6).value = 60
    sheet.cell(row = i, column=11).value = 3
elif time < 17.1:
    sheet.cell(row = i, column=4).value = '2-butanone'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2/3
    sheet.cell(row = i, column=6).value = 72.11

```

```

    sheet.cell(row = i, column=11).value = 4
elif time < 17.81:
    sheet.cell(row = i, column=4).value = 'Acetic Acid'
    sheet.cell(row = i, column=5).value = 2.15624E-10
    sheet.cell(row = i, column=6).value = 60.05
    sheet.cell(row = i, column=11).value = 2
# elif time < 17.8:
#     sheet.cell(row = i, column=4).value = 'C6'
#     sheet.cell(row = i, column=5).value = 6.97306E-11*3/6
#     sheet.cell(row = i, column=6).value = 86
#     sheet.cell(row = i, column=11).value = 6
# elif time < 18:
#     sheet.cell(row = i, column=4).value = 'Benzene'
#     sheet.cell(row = i, column=5).value = 6.97306E-11*3/6
#     sheet.cell(row = i, column=6).value = 78
#     sheet.cell(row = i, column=11).value = 6
# elif time < 19.1:
#     sheet.cell(row = i, column=4).value = 'C7'
#     sheet.cell(row = i, column=5).value = 6.97306E-11*3/7
#     sheet.cell(row = i, column=6).value = 98
#     sheet.cell(row = i, column=11).value = 7
elif time < 18.9:
    sheet.cell(row = i, column=4).value = 'methyl methacrylate'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2/1.8 #0.95 is added due to the olefinic
species see Willis et al.
    sheet.cell(row = i, column=6).value = 100
    sheet.cell(row = i, column=11).value = 5
elif time < 19.5:
    sheet.cell(row = i, column=4).value = '3-pentanone'
    sheet.cell(row = i, column=5).value = 1.7051E-10*2/4 #1.15199E-10*3/5
    sheet.cell(row = i, column=6).value = 86.13
    sheet.cell(row = i, column=11).value = 5
elif time < 19.55:
    sheet.cell(row = i, column=4).value = 'dipropyl ether'
    sheet.cell(row = i, column=5).value = 1.15199E-10*3/5

```

```

sheet.cell(row = i, column=6).value = 102
sheet.cell(row = i, column=11).value = 6

elif time < 26:
    sheet.cell(row = i, column=4).value = 'C8'
    sheet.cell(row = i, column=5).value = 1.15199E-10*3/8
    sheet.cell(row = i, column=6).value = 112
    sheet.cell(row = i, column=11).value = 8
# the multiplication code: area*(mols/area)= moles of each in column 7
for i in range(1, target+1, 1):
    sheet.cell(row = i, column=7).value = sheet.cell(row = i, column=3).value*sheet.cell(row = i,
column=5).value
# moles*(g/moles)= mass of each product in column 8
for i in range(1, target+1, 1):
    sheet.cell(row = i, column=8).value = sheet.cell(row = i, column=6).value*sheet.cell(row = i,
column=7).value
# moles of product*carbon number = moles of carbon in column 12
for i in range(1, target+1, 1):
    sheet.cell(row = i, column=12).value = sheet.cell(row = i, column=7).value*sheet.cell(row = i,
column=11).value
#total all masses out not including acetic acid
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 17.3:
        num = sheet.cell(row = i, column = 8).value
        sum = sum + num
    elif time < 17.81:
        num = 0
        sum = sum + num
    elif time < 30:
        num = sheet.cell(row = i, column = 8).value
        sum = sum + num
sheet.cell(row = target+1, column=8).value = sum

```

```
MTP = sheet.cell(row = target+1, column=8).value
```

```
#code for calculation mass percent of the product stream
```

```
for i in range(1, target+1, 1):
```

```
    time = sheet.cell(row=i, column=2).value
```

```
    if time < 17.3:
```

```
        sheet.cell(row = i, column=9).value = sheet.cell(row = i, column=8).value/MTP*100
```

```
    elif time < 17.81:
```

```
        sheet.cell(row = i, column=9).value = 0
```

```
    elif time < 30:
```

```
        sheet.cell(row = i, column=9).value = sheet.cell(row = i, column=8).value/MTP*100
```

```
# adding all moles in column 7 not including Propionic acid
```

```
sum = 0
```

```
time = 0
```

```
for i in range(1, target+1, 1):
```

```
    time = sheet.cell(row=i, column=2).value
```

```
    if time < 17.3:
```

```
        num = sheet.cell(row = i, column = 7).value
```

```
        sum = sum + num
```

```
    elif time < 17.81:
```

```
        num = 0
```

```
        sum = sum + num
```

```
    elif time < 30:
```

```
        num = sheet.cell(row = i, column = 7).value
```

```
        sum = sum + num
```

```
sheet.cell(row = target+1, column=7).value = sum
```

```
MoTP = sheet.cell(row = target+1, column=7).value
```

```
#total all moles of carbon includeing reactant
```

```
sum = 0
```

```
time = 0
```

```
for i in range(1, target+1, 1):
```

```
    time = sheet.cell(row=i, column=2).value
```

```
    if time < 30:
```

```

    num = sheet.cell(row = i, column = 12).value
    sum = sum + num
sheet.cell(row = target+1, column=12).value = sum
MoTC = sheet.cell(row = target+1, column=12).value

#code for calculation molar percent of the product stream
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 17.3:
        sheet.cell(row = i, column=10).value = sheet.cell(row = i, column=7).value/MoTP*100
    elif time < 17.81:
        sheet.cell(row = i, column=10).value = 0
    elif time < 30:
        sheet.cell(row = i, column=10).value = sheet.cell(row = i, column=7).value/MoTP*100

#code for finding methane selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 3.0:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoCH4 = sum
#code for finding ethylene selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 3.5:
        num = 0
        sum = sum + num
    elif time < 4.2:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num

```

```

MoEthylene = sum
#code for finding ethane selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 4.2:
        num = 0
        sum = sum + num
    elif time < 4.8:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoEthane = sum
#code for finding PE selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 8:
        num = 0
        sum = sum + num
    elif time < 8.65:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
    elif time < 25:
        num = 0
        sum = sum + num
MoPE = sum
#code for finding c3 gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 4.8:
        num = 0

```

```

    sum = sum + num
elif time < 9.3:
    num = sheet.cell(row = i, column = 7).value
    sum = sum + num
MoC3 = sum
#code for finding c4 gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 9.3:
        num = 0
        sum = sum + num
    elif time < 12.2:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoC4 = sum
#code for finding ethanal gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 11:
        num = 0
        sum = sum + num
    elif time < 11.8:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoEthanal = sum
#code for finding c5 gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 14.0: #need to fix this in other codes!!!

```

```

    num = 0
    sum = sum + num
elif time < 14.2:
    num = sheet.cell(row = i, column = 7).value
    sum = sum + num
MoC5 = sum
#code for finding moles of Propanal
#sum = 0
#time = 0
#for i in range(1, target+1, 1):
#    time = sheet.cell(row=i, column=2).value
#    if time <12.6:
#        num = 0
#        sum = sum + num
#    elif time < 14.5:
#        num = sheet.cell(row = i, column = 7).value
#        sum = sum + num
#MoPA = sum
#code for finding acetone gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 14.2:
        num = 0
        sum = sum + num
    elif time < 15.5:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoAcetone = sum
#code for finding c6 gas selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value

```

```

if time < 16.5:
    num = 0
    sum = sum + num
elif time < 18:
    num = sheet.cell(row = i, column = 7).value
    sum = sum + num
MoC6 = sum
#code for finding c7 selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 18:
        num = 0
        sum = sum + num
    elif time < 19.1:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoC7 = sum
#code for finding moles of 1-PO unreacted
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time <15.5:
        num = 0
        sum = sum + num
    elif time < 16.04:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoPO = sum
#code for finding moles of butanone
sum = 0
time = 0
for i in range(1, target+1, 1):

```

```

time = sheet.cell(row=i, column=2).value
if time <16.04:
    num = 0
    sum = sum + num
elif time < 17.1:
    num = sheet.cell(row = i, column = 7).value
    sum = sum + num
MoButanone = sum
#code for finding 3MMA
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 17.81:
        num = 0
        sum = sum + num
    elif time < 18.9:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoMMA = sum
#code for finding 3-pentanone selectivity
sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 19.1:
        num = 0
        sum = sum + num
    elif time < 19.37:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
Mo3pentanone = sum
#code for finding moles of dipropyl ether
sum = 0
time = 0

```

```

for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 19.37:
        num = 0
        sum = sum + num
    elif time < 19.55:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoDPE = sum

```

#code for finding moles of Acetic Acid

```

sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 17.1:
        num = 0
        sum = sum + num
    elif time < 17.81:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoAA = sum

```

#code for finding c8

```

sum = 0
time = 0
for i in range(1, target+1, 1):
    time = sheet.cell(row=i, column=2).value
    if time < 22:
        num = 0
        sum = sum + num
    elif time < 26.2:
        num = sheet.cell(row = i, column = 7).value
        sum = sum + num
MoC8 = sum

```

#Arenius Parameters

A = 4.68206

B= 1642.54

C= -39.764

Molarvolume=22.414 #L/mol assumption ideal gas

MW=60.05 #mol/g acetic acid

density = 1.05 #g/ml acetic acid

Pv=10((A-B/(C+(Tbub+273.15)))) #saturadted vapor pressure as a funcion of Bubler
temperature, bar**

**F1v = tgf/((Preactor+14.5)*0.0689476/Pv-1) #sccm assume 1) atm pressure is 14.5 mmhg and 2) the
total gas flow =50 sccm**

flowrate=F1v*60*MW/Molarvolume/density/1000 #ml/h

MoAAin=F1v/Molarvolume/tgf/1000 #mole of reactant per ml of gas

#code for mass balance

sheet.cell(row = target +2, column = 1).value = ('Mass Bal.')

massbal = ((MTP+MoAA*MW)/(MoAAin*MW))*100

sheet.cell(row = target+3, column=1).value = massbal

#code for carbon balance

sheet.cell(row = target +2, column = 2).value = ('Carbon Bal.')

carbonbal = (1+(MoTC-MoAAin*2)/(MoAAin*2))*100

sheet.cell(row = target+3, column=2).value = carbonbal

#code for WHSV space velocity

sheet.cell(row = target +2, column = 3).value = ('WHSV h-1')

**sheet.cell(row = target +3, column = 3).value = (flowrate*density)/masscat #WHSV mass flow rate
of reactant over mass of catalyst**

sheet.cell(row = target +2, column = 4).value = ('Temperature, C')

sheet.cell(row = target +3, column = 4).value = tcat

sheet.cell(row = target +2, column = 5).value = ('Time, h')

sheet.cell(row = target +3, column = 5).value = hour

```

#code for the conversion based on theoretical feed based on mole of reactant and measured moles
out
sheet.cell(row = target +2, column = 6).value = ('acetic acid, conversion')
sheet.cell(row = target +3, column = 6).value = ((1-MoAA*MW/(MTP+MoAA*MW))*100) #code
for the conversion based on the estimated feed
sheet.cell(row = target +4, column = 6).value = (1-(MoAA/MoAAin))*100#conversion if mass
balance =100

#sheet.cell(row = target +2, column = 4).value = ('Conversion')
#sheet.cell(row = target+3, column=4).value = (1-
(MoProA/(molescarbonin/3)))*100#flowrate*0.99/74.08))*100

sheet.cell(row = target +1, column = 9).value = ('mass sel.')
sheet.cell(row = target +1, column = 10).value = ('molar sel.')

sheet.cell(row = target +2, column = 7).value = ('C2')
sheet.cell(row = target +3, column = 7).value = (MoEthylene+MoEthane)/MoTP*100
sheet.cell(row = target +2, column = 8).value = ('ethylene to C2 ratio')
MoC2 = MoEthylene+MoEthane
if MoC2 == 0:
    sheet.cell(row = target +3, column = 8).value = 0
if MoC2 > 0:
    sheet.cell(row = target +3, column = 8).value = (MoEthylene)/(MoEthane+MoEthylene)

sheet.cell(row = target +2, column = 9).value = ('C3')
sheet.cell(row = target +3, column = 9).value = MoC3/MoTP*100
sheet.cell(row = target +2, column = 10).value = ('propene to C3 ratio')
if MoC3 == 0:
    sheet.cell(row = target +3, column = 10).value = 0
if MoC3 > 0:
    sheet.cell(row = target +3, column = 10).value = (MoPE)/(MoC3)

sheet.cell(row = target +2, column = 11).value = ('propanal')
#sheet.cell(row = target +3, column = 11).value = (MoPA)/MoTP*100
sheet.cell(row = target +2, column = 12).value = ('Propanol')

```

```

sheet.cell(row = target +3, column = 12).value = (MoPO)/MoTP*100
sheet.cell(row = target +2, column = 13).value = ('CH4')
sheet.cell(row = target +3, column = 13).value = (MoCH4)/MoTP*100
sheet.cell(row = target +2, column = 14).value = ('Ethanal')
sheet.cell(row = target +3, column = 14).value = (MoEthanal)/MoTP*100
sheet.cell(row = target +2, column = 15).value = ('acetone')
sheet.cell(row = target +3, column = 15).value = (MoAcetone)/MoTP*100
sheet.cell(row = target +2, column = 16).value = ('methyl methacrylate')
sheet.cell(row = target +3, column = 16).value = (MoMMA)/MoTP*100
print(MTP)
print (MoAA)
print(((1-MoAA*60/(MTP+MoAA*60))*100)

wb.save('file_name_results.xlsx')

```

Publications & Presentations

Publications

Li, Z., Lepore, A. W., Davison, B.H., Narula, C. K. *Catalytic Conversion of Biomass Derived Ethanol to Liquid Hydrocarbon Blend-Stock: Effect of Light Gas Recirculation*, Energy & Fuels, DOI. 10.1021/acs.energyfuels.6b02562.

Lepore, A. W.; Li, Z.; Davison, B. H.; Foo, G. S.; Wu, Z.; Narula, C. K., Catalytic Dehydration of Biomass Derived 1-Propanol to Propene over M-ZSM-5 (M=H, V, Cu, or Zn). *Industrial & Engineering Chemistry Research* **2017**.

Lepore, A.W., Ashworth, A. J., Connaster, R. M., Kim, P., Labbé, N., Allen, F. *Red Mud as an In Situ Pyrolysis Catalyst: Its Ability and its Concurrent Remediation*. Energy & Fuels (manuscript in preparation)

Li, Z. Lepore, A. W. Salazar, M. F., Davison, B. H., Narula, C. K. *Selective Catalytic Conversion of Biomass Derived Ethanol to BTX on Ga-ZSM-5: Role of Exchanged Ga*. ACS Catalysis (manuscript in preparation)

Presentations

Lepore, A.W., Ashworth, A. J., Connaster, R. M., Kim, P., Labbé, N., Allen, F. Red Mud as an *In Situ* Pyrolysis Catalyst: Its Ability and its Concurrent Remediation. *Symposium on thermal and Catalytic Sciences for Biofuels and Biobased Products*, November 1-4, 2016.

Lepore, A.W., Ashworth, A. J., Connaster, R. M., Kim, P., Labbé, N., Allen, F. Red Mud as an *In Situ* Pyrolysis Catalyst: Its Ability and its Concurrent Remediation. *Frontiers in Biorefining: Chemicals and Products from Renewable Carbon*, November 8-11, 2016.

Li, Z., Lepore, A. W., Connaster, R. M., Choi, J. Hydroprocessing of Biomass Derived Oxygenates Using Molybdenum Carbides. *Symposium on thermal and Catalytic Sciences for Biofuels and Biobased Products*, November 1-4, 2016

VITA

Andrew hails from Pelham, New Hampshire. He attended Pelham Memorial Middle School and Bishop Guertin High School. He began his undergraduate education at St. Lawrence University as a chemistry major. His Sophomore year he conducted biosensor research through a NSF-REU grant at Auburn University with Dr. Jeffrey Fergus. The following summer was spent at St. Lawrence University funded by a Stradling fellowship under Dr. Larry French. He worked to add beta-thujone to the list of chiral reagents available to the art of synthetic organic chemistry. His fourth and fifth years of college were spent at Columbia University majoring in chemical engineering. While there he researched carbon sequestration and mineralization funded by a DOE-ARPA-E grant under Dr. Ah-Hyung (Alissa) Park. He then moved to Tennessee to pursue his doctorate degree through the Interdisciplinary Bredesen Center. Andrew researched heterogeneous catalysis for the synthesis of liquid fuels and valuable feedstock chemicals under Dr. Chaitanya Narula. He also conducted experiments on *in-situ* catalytic pyrolysis. His chief ambition is finding suitable pathways to close the carbon loop.