

EILERS GRADUATE STUDENT FELLOWSHIP FINAL REPORT

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| EILERS FELLOW: | Yolanda Bonita |
| FACULTY ADVISOR: | Jason C. Hicks |
| REPORT PERIOD: | January 2018 – December 2018 |
| PROJECT TITLE: | Bimetallic phosphide catalysts for biomass upgrading |
| CONNECTION TO ND ENERGY'S RESEARCH AREAS (CHECK ALL THAT APPLY): | <input type="checkbox"/> Energy Conversion and Efficiency <input type="checkbox"/> Sustainable and Secure Nuclear <input type="checkbox"/> Smart Storage and Distribution <input type="checkbox"/> Transformation Solar <input checked="" type="checkbox"/> Sustainable Bio/Fossil Fuels <input type="checkbox"/> Transformative Wind |

MAJOR GOALS AND ACCOMPLISHMENTS:

List your major research goals and provide a brief description of your accomplishments (1-2 sentences). Indicate the percentage completed for each goal. Please use a separate sheet to share additional details, technical results, charts, and graphics.

| MAJOR RESEARCH GOALS | ACTUAL PERFORMANCE AND ACCOMPLISHMENTS | % OF GOAL COMPLETED |
|---|--|---------------------|
| Discover new bimetallic phosphides (i.e. RuMoP) | Bimetallic RuMoP was successfully synthesized and characterized with various techniques such as XRD, ICP, SEM, TEM, XPS, XANES, N ₂ physisorption, CO pulse chemisorption, pyridine FTIR | 100 |
| Apply material for biomass upgrading such as furfural hydrogenation | Bimetallic RuMoP was applied for furfural hydrogenation, which is an example of biomass upgrading reactions. The study explores the benefit of using bimetallic phosphides, the effect of ratio of the metals, and solvent effect during reactions. The work is currently under revision in ACS Catalysis. | 95 |
| Show bimetallic effect and superiority of bimetallic phosphides | | |
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RESEARCH OUTPUT:

Please provide detailed information below regarding any output resulting from your research project.

| CATEGORY | INFORMATION |
|---------------------------|--|
| EXTERNAL PROPOSALS | (Sponsor, Project Title, PIs, Submission Date, Proposal Amount) |
| EXTERNAL AWARDS | (Sponsor, Project Title, PIs, Award Date, Award Amount) <ol style="list-style-type: none"> Johnson Matthey Student Award from International Precious Metal Institute Project title: Award date: June 2018 Award amount: \$5,000 + \$2,000 travel award Description: this award is given from company sponsors to 7 selected students whose research is of significance in the utilization of precious metal. Student Travel Award from Catalysis and Reaction Engineering (CRE) Division from American Institute of Chemical Engineers (AIChE) Project title: Catalytic Hydrogenation of Furfural over RuMoP: Probing Bimetallic and Compositional Effects on Catalyst Performance Award date: October 2018 Award amount: \$400 Description: this award is given to 20 students in CRE division to cover some travel cost associated with the AIChE conference |
| JOURNAL ARTICLES | (Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) <ol style="list-style-type: none"> Bonita, Y., Jain, V., Geng, F., O'Connell, T. P., Wilson, W. N., Rai, N., and Hicks, J.C.* Direct Synthesis of Furfuryl Alcohol from Furfural: Catalytic Performance of Monometallic and Bimetallic Mo and Ru Phosphides. <i>ACS Catal.</i> 2019 In review |

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| | 2. Bonita, Y., Miller, H. E., O'Connell, T.P, Hicks, J. C.* Revealing the Hydrogenation Performance of RuMo Phosphide For Chemoselective Reduction of Functionalized Aromatic Hydrocarbons. <i>Ind. Eng. Chem. Res.</i> 2019 Submitted |
| BOOKS AND CHAPTERS | (Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) |
| PUBLIC PRESENTATIONS, SEMINARS, LECTURES | (Event, Presentation Title, Presentation Date, Location) <ol style="list-style-type: none"> 1. International Precious Metal Institute Presentation title: Catalytic Applications of Bimetallic Noble Metal Phosphides for Biomass Upgrading Presentation date: June 2018 Location: San Antonio, TX 2. American Institute of Chemical Engineers Presentation title: Catalytic Hydrogenation of Furfural over RuMoP: Probing Bimetallic and Compositional Effects on Catalyst Performance Presentation date: November 2018 Location: Pittsburgh, PA 3. Chemical and Biomolecular Engineering Department Seminar Presentation title: Catalytic Hydrogenation of Furfural over RuMoP: Probing Bimetallic and Compositional Effects on Catalyst Performance Presentation date: December 2018 Location: Notre Dame, IN |
| AWARDS, PRIZES, RECOGNITIONS | (Purpose, Title, Date Received) <ol style="list-style-type: none"> 1. Best Poster Award at the Chemical and Biomolecular Engineering Research Symposium Poster title: Catalytic Hydrogenation of Furfural Over RuMoP: A Model Reaction to Probe Bimetallic and Compositional Effects Date received: 09/2018 2. Student Travel Award from Catalysis and Reaction Engineering Division in American Institute of Chemical Engineers (AIChE) Presentation title: Catalytic Hydrogenation of Furfural over RuMoP: Probing Bimetallic and Compositional Effects on Catalyst Performance Date received: 10/2018 3. Student Travel Award from Graduate Student Union Date received: 10/2018 4. Graduate Teaching Assistant Award from Kaneb Center Date received: 05/2018 |
| INTERNAL COLLABORATIONS FOSTERED | (Collaborator Name, Organization, Purpose of Affiliation) |
| EXTERNAL COLLABORATIONS FOSTERED | (Collaborator Name, Organization, Purpose of Affiliation) <ol style="list-style-type: none"> 1. Neeraj Rai research group Affiliation: Dave C. Swalm School of Chemical Engineering, Mississippi State University Purpose: Theory/computational collaborator to complement our experimental work |
| WEBSITE(S) FEATURING RESEARCH PROJECT | (URL) |
| OTHER PRODUCTS AND SERVICES (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups) | (Please describe each item in detail) <ol style="list-style-type: none"> 1. Expanding Your Horizon (Outreach) Date: April 2018 |
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MAJOR GOALS AND ACCOMPLISHMENTS

Project 1: Identifying bimetallic and composition effect in $Ru_xMo_{2-x}P$ for furfural hydrogenation

The objective of this work is to identify the bimetallic effect in $Ru_xMo_{2-x}P$ as well as the ratio effect of Ru:Mo. To address this goal, furfural hydrogenation is used as a probe reaction. Furfural can be derived from the hemicellulose part of biomass and 60% of it is converted to furfuryl alcohol that is a useful intermediate chemical in dyes, fragrances, and lubricants industry. The challenge of this transformation is the current commercial catalyst, copper chromite, deactivates. Moreover, the disposal of chromite catalyst is toxic to the environment. Therefore, there is a need for a new catalyst with comparable performance.

Monometallic phosphides (MoP, Mo_3P , RuP, Ru_2P) and bimetallic phosphides $Ru_xMo_{2-x}P$ ($x = 0.8, 1.0, \text{ and } 1.2$) were synthesized with temperature programmed reduction method. The materials were characterized using various characterization methods such as powder x-ray diffraction (XRD), inductively coupled plasma – optical emission spectroscopy (ICP-OES), CO-pulse chemisorption, N_2 physisorption for surface area, and x-ray photoelectron spectroscopy (XPS).

The catalytic properties of two molybdenum phosphides (MoP and Mo_3P) and two ruthenium phosphides (RuP and Ru_2P) were evaluated for furfural hydrogenation in a batch reactor using a first order kinetics. MoP showed remarkable selectivity (99%) towards furfuryl alcohol at 15% conversion, while Mo_3P was found to be inactive at 100°C and 600 psig H_2 . At the same conversion, RuP and Ru_2P also showed high selectivity to furfuryl alcohol of 98% and 96% respectively. However, at higher conversion, the selectivity dropped for RuP and Ru_2P , while MoP maintained a selectivity of 99%. Moreover, a bimetallic RuMoP catalyst was synthesized to compare to the monometallic compositions. A bimetallic effect was observed with RuMoP, as the pseudo-first order reaction rate constant for furfural hydrogenation to furfuryl alcohol, k_1 , was 5x higher than MoP, RuP, and Ru_2P while maintaining the high selectivity (99%) at 15% conversion. Additional compositions of $Ru_xMo_{2-x}P$ ($0.8 < x < 1.2$) were also synthesized and provided evidence that Ru rich compositions positively influence the reaction rate, but not the selectivity. Rate constants for the subsequent cascade reactions of furfuryl alcohol hydrogenation to methyl furan (k_2) and tetrahydrofurfuryl alcohol (k_3) were quantified. The ratio of the furfuryl alcohol production rate compared to other products (k_1/k_2+k_3) followed the trend of RuMoP > $Ru_{1.2}Mo_{0.8}P$ > MoP > $Ru_{0.8}Mo_{1.2}P$ > RuP > Ru_2P . Diffuse reflectance infrared fourier transform spectroscopy (DRIFTS) was used to examine the configuration of adsorbed furfural on the synthesized catalysts, but the results were inconclusive and no correlation could be found with the selectivity due to the IR inactive surface modes possible with furfural adsorption. However, gas phase density functional theory calculations were also performed for furfural adsorption on the surface of the bimetallic catalysts, $Ru_xMo_{2-x}P$ ($0.8 < x < 1.2$), which suggested the $x = 1$ material had the most favorable furfural adsorption energy. Experimentally, we also observed that the solvent greatly influenced both the conversion and selectivity, where isopropanol provided the highest selectivities to furfuryl alcohol. Finally, recycling experiments showed a 12% decrease in k_1 after 3 cycles without any regeneration, but the activity could be fully recovered through a re-reduction step.

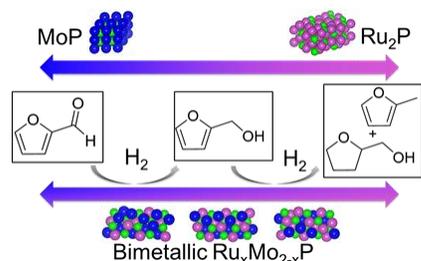


Figure 1. Catalytic result of furfural hydrogenation with monometallic and bimetallic $Ru_xMo_{2-x}P$

Project 2: Effect of aromatics with electron withdrawing groups and electron donating groups on hydrogenation reactions using RuMoP

Bimetallic RuMoP catalyst is a promising catalyst for low temperature liquid phase hydrogenation reactions. Based on our previous results, RuMoP hydrogenates phenol to cyclohexanol and furfural to furfuryl alcohol. The result is interesting because in the phenol case, the hydrogenation occurs on the aromatic ring, while on furfural case, the hydrogenation occurs on the aldehyde. This observation motivates further study on hydrogenation reactions using RuMoP to determine the factor dictating the catalytic results.

This work explores the hydrogenation capability of RuMoP for functionalized aromatic compounds to understand how these functional groups can compete in the same system and to gain insight to the active site of RuMoP. High selectivity (99%) can be achieved for the reduction of electron withdrawing functionalities such as nitrobenzene, benzaldehyde, and benzophenone with RuMoP to yield aniline, benzyl alcohol, and benzyhydrol respectively. On the other hand, aromatic with electron donating groups such as phenol, anisole and toluene show high ring hydrogenation selectivity (99%) to form cyclohexanol, methoxycyclohexane, and methyl cyclohexane respectively although the reaction was slow. Pyridine adsorption studied with diffuse reflectance infrared spectra (DRIFTS) indicates the dominant presence of electron deficient site, Lewis acid, that could be responsible for the selectively hydrogenating part of the substrates that is electron rich. Additional DRIFTS study on nitrobenzene and anisole adsorption shows features from $-NO_2$ adsorption from nitrobenzene and ring adsorption mode from anisole, which agrees to the observed reaction results.

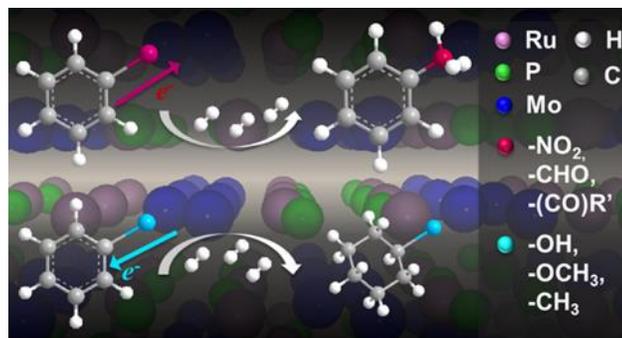


Figure 2. Reduction of electron withdrawing group and electron donating group