DEVELOPMENT OF AN IDEAL HYDROTREATING CATALYST FOR THE CONVERSION OF PHOSPHOLIPIDS TO BIOFUELS

Tracy J. Benson^{1*}, Michael S. Miquez¹, William E Holmes², W. Todd French², and Rafael Hernandez²

¹Dan F. Smith Department of Chemical Engineering, Lamar University, Beaumont, TX 77713

²Dave C Swalm School of Chemical Engineering, Mississippi State University, Mississippi State, MS 39762

Summary

This work covers the elucidation of the reaction pathways and the reaction site mechanism(s) for the conversion of phospholipids into transportation fuels using hydrotreating catalysts. Broadening the knowledge of heteroatoms, such as phosphorus, on solid acid catalysts allows for a more diverse spectrum of usable lipids as motor fuels. Current biodiesel processes are not robust enough to handle the more complicated lipids found in feedstocks derived from microorganisms such as algae, yeasts, or bacteria. By reacting phospholipids on hydrotreating catalysts and then through surface characterization of the catalyst, these mechanisms can then be investigated and an appropriate catalyst identified.

Keywords

Reaction Pathway Analysis, Rational Design of Catalysts, Alternate Energy

Introduction

Due to increased volatility in the petroleum market, environmental concerns, and the need for independence of foreign oils, renewable fuels has become a topic of increasingly importance in recent years. Biodiesel, a mixture of fatty acid methyl esters, has been used as a motor fuel over the last decade but is limited to highly refined and degummed feedstocks.¹ Current research has identified the use of lipids for the production of green via heterogeneous catalytic cracking fuels and hydrotreating conversion technologies.²⁻⁶ These green fuels, which are comprised of the same types of compounds as petroleum diesel fuels, could be produced from a wide variety of plant, animal, and microbial lipid sources and could replace significant amounts of petroleum-based fuels. This type of processing would be a more robust conversion technique than that of biodiesel. The lipid feedstocks would be comprised mainly of free fatty acids, acylglycerols, and phospholipids.

Inasmuch, traditional petroleum refining using hydrotreating with transition metals embedded on Al_2O_3 catalysts have had difficulties in cracking compounds which contain inorganic species, such as phosphorus. However, combinations of Ni-Mo have shown to have better success over Co-Mo in terms of poisoning of the catalyst.

Methods and Materials

This study focuses on the cracking and hydrotreating of phospholipid model compounds (Fig. 1), namely phosphatidylglycerol, phosphatidylethanolamine, phosphatic acid, and phosphatidylcholine, on petroleumtype catalysts. A pulsed-type micro-reactor was used to investigate reaction products and reactant/surface interactions during the production of renewable fuels. The catalysts chosen for this study were both cracking and hydrotreating catalysts to identify reaction pathways. The hydrotreating catalysts, Co-Mo and Ni-Mo on Al_2O_3 solid acid catalysts, had been sulfided for increased heteroatom removal and reactions were carried out in the presence of hydrogen.

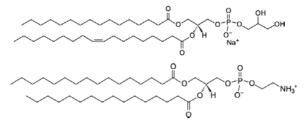


Fig. 1. Chemical structure of phosphatidylglycerol (top) and phosphatidylethanolamine (bottom)

In an attempt to identify the reaction site mechanism of phosphorus on the catalyst surface, thermogravimetric analysis, photoacustic FTIR, SEM equipped with energy dispersive x-ray (EDX), and XRF were used on unreacted and post-reacted catalysts.

Results

Cracking reactions using ZSM-5 showed the formation of fatty acids and aromatic compounds, while saturated hydrocarbons were the main products of the hydrotreating reactions (Fig. 2). The initial step in the hydrotreating reactions was the saturation of any double bonds found within the fatty acid chains. Also, decarbonylation, and not decarboxylation, was the dominant mechanism towards deoxygenation. Additional, reaction products and pathways will be shown.

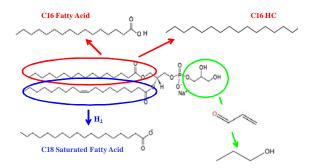


Fig. 2. Proposed reaction pathway for the hydrotreating of phosphatidylglycerol showing that hydrogenation of double bonds occurs before cracking from the phospholipid head group.

Preliminary thermo-gravimetric results suggest that phospholipids are comparable to acylglycerides in regards to catalyst coking, which is ~14% higher than that of a sweet petroleum crude. SEM-EDX shows the build up of phosphorus on the catalyst, which may have a negative effect on the catalyst after repeated reaction/regeneration cycles. This work, therefore, will be used to develop an ideal hydrotreating catalyst that can withstand, and even utilize, phosphorus as part of the catalytic activity.

References

(1) Ma, F. and Hanna, M.A. Biodiesel Production: A Review. *Bioresource Technology* 1999, 70,1.

(2) Idem, R.O., Katikaneni, S.P.R., Bakhshi, N.N. Catalytic conversion of canola oil to fuels and chemicals: roles of catalyst, acidity, basicity, and shape selectivity on product distribution, *Fuel Processing Tech.* 1997, 51, 101.
(3) Katikaneni, S.P.R., Adjaye, J.D., and Bakhshi, N.N. (1997) Conversion of Canola Oil to Various Hydrocarbons

Over Pt/HZSM-5 Bifunctional Catalyst, *Canadian Journal* of Chemical Engineering 1997, 75, 391.

(4) Ooi, Y.S., Zakaria, R., Mohamed, A.R., and Bhatia, S. Catalytic Conversion of Fatty Acids Mixture to Liquid Fuel and Chemicals Over Composite Microporous/ Mesoporous Catalysts, *Energy and Fuels* 2005, 19, 736 – 743.

(5)Benson, T., Hernandez, R., French, T., Alley, E., and Holmes, W. Reactions of Fatty Acids in Superacid Media: Identification of Equilibrium Products, *J. Mol. Catal. A: Chem.* 2007, 274, 173.

(6) Benson, T., Hernandez, R., French, T., Alley, E., and Holmes, W. Elucidation of the Catalytic Cracking

Pathway for Unsaturated Mono-, Di-, and

Triacylglycerides on Solid Acid Catalysts. J. Molec. Catal. A: Chem. 2009, 303, 117