Final Technical Report

Award no.: DE-FG02-06ER15794

Title: Tandem and Bimetallic Catalysts for Oxidative Dehydrogenation of Light Hydrocarbon with Renewable Feedstock

Objectives. An estimated 490 million metric tons of lignocellulosic biomass is available annually from U.S. agriculture and forestry. With continuing concerns over greenhouse gas emission, the development of efficient catalytic processes for conversion of biomass derived compounds is an important area of research. Since carbohydrates and polyols are rich in oxygen, approximately one oxygen atom per carbon, removal of hydroxyl groups via deoxygenation is needed. The necessary hydrogen required for hydrodeoxygenation (HDO) would either come from reforming biomass itself or from steam reforming of natural gas. Both processes contribute to global CO_2 emission. The hope is that eventually renewable sources such as wind and solar for hydrogen production will become more viable and economic in the future. In the meantime, unconventional natural gas production in North America has boomed. As a result, light hydrocarbons present an opportunity when coupled with biomass derived oxygenates to generate valuable products from both streams without co-production of carbon dioxide. This concept is the focus of our current funding period. The objective of the project requires coupling two different types of catalysis, HDO and dehydrogenation. Our hypothesis was formulated around our success in establishing oxorhenium catalysts for polyol HDO reactions and known literature precedence for the use of iridium hydrides in alkane dehydrogenation. To examine our hypothesis we set out to investigate the reaction chemistry of binuclear complexes of oxorhenium and iridium hydride.

The specific goals of the project were defined as follows:

1. Investigate the reaction between pincer iridium hydride and oxorhenium complexes. Establish the kinetics and reaction mechanism for this novel organometallic transformation.

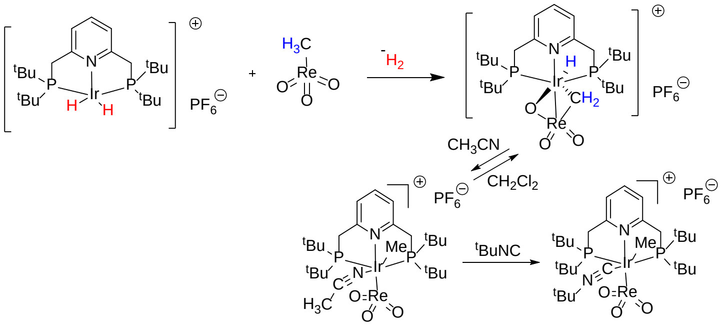
2. Evaluate if reactive iridium hydride and oxorhenium complexes can be combined in tandem to affect oxidative dehydrogenation of alkanes such as pentane with biomass derived polyols such as glycerol.

3. Prepare and study heterobimetallic Re-Ir complexes for oxidative dehydrogenation of alkanes with polyols. These binuclear complexes would improve the kinetics by transforming the key reaction between iridium hydride and oxorhenium from bimolecular (second-order kinetics) to unimolecular (first-order kinetics).

4. Synthesize Re and Re-Ir nanoparticles as heterogeneous catalysts for oxidative dehydrogenation of pentane with glycerol.

Accomplishments under the current grant period. The PNP pincer iridium dihydride reacts with MTO (methyltrioxorhenium) via novel C-H activation to yield a methylidene bridged Re-Ir bimetallic complex (Scheme 1). In the presence of a coordinating ligand or a solvent such as CH_3CN or ^{t}BuNC, the net result is methyl transfer to Ir and formation of the Re-Ir metal-metal bond. Both bimetallic Re-Ir complexes have been fully characterized in solution by NMR and in the solid state by single-crystal X-ray diffraction. The ability of these bimetallic complexes to catalyze oxidative dehydrogenation (ODH) of octane with glycerol was investigated. Alkane dehydrogenation requires conditions of ca. 200 °C, which proved to fragment the binuclear complexes resulting in low turnover numbers of 3-5.

We have pivoted our investigation to the more robust PCP pincer complexes that are known to withstand the required temperatures. However, the reaction with MTO yielded CH_4 followed by formation of an iridium hydride ligated by ReO_4^-. The use of this oxygen bridged Ir-O-Re bimetallic as catalyst for cyclooctane ODH was demonstrated; however, the turnover numbers remained low and in the range of ca. 5 turnovers. Mechanistic studies revealed the catalyst's deactivation mechanism. As the diol is deoxygenated some aldehyde side product is formed and iridium PCP reacts with the aldehyde byproduct to make (PCP)Ir(CO), which is inactive for alkane dehydrogenation. Understanding how to eliminate aldehyde formation as a byproduct is currently under investigation.



Scheme 1. Reactions of MTO and pincer PNP iridium dihydride. All Ir-Re complexes were characterized structurally by X-ray diffraction.

Heterogeneous binuclear Ir-Re nanoparticles have been synthesized and characterized by X-ray powder diffraction, TEM, and elemental analysis. These catalysts are being tested for ODH of octane under batch as well as continuous plug flow reactor conditions.

Opportunities for training. Three graduate researchers have been trained in synthesis, kinetics, spectroscopy and catalysis through this project. They have participated in group meetings and presented their results at ACS national meetings. One of the students had the opportunity to work closely with the facilities at Argonne National Laboratory to acquire X-ray data on our catalysts under in situ conditions. In addition to presenting research results, the students work closely with the PI to write manuscripts for publication. They also meet with seminar speakers as part of our professional development so they can receive suggestions and input on their research project from an external point of view. In the Abu-Omar research group safety practices and training are a top priority. Researchers are required to do safety training and updates on safety procedures and practices are given weekly at group meetings. Furthermore, online safety refresher is required of all researchers in the group on annual basis.

Products. The following publications resulted from research activities under the current funding period:

(1) "Catalytic Transformations with Oxorhenium and Chromium Complexes for Deoxygenation of Diols and Selective Reduction of Dioxygen." Shuo Liu, Ph.D. 2015.

(2) "Homogeneous and Heterogeneous Rhenium Catalysts for Sustainable Transformations of Polyols, Alcohols, and Amines." Jing Yi, Ph.D. 2015.

(3) "Activation of Methyltrioxorhenium by Pincer Iridium Hydride to Give Agile Ir-Re Bimetallic Compounds" *Organometallics*. **2014**, *33*, 5089-5092.

(4) "Concurrent Stabilization of π-Acceptor and π-Donor Ligands in Aromatized and Dearomatized Pincer [(PNN)Re(CO)(O)2] Complexes" *Angew. Chem. Int. Ed.* **2014**, *53*, 8320-8322.

(5) “Mechanism of Isomerization and Methyl Migration in Heterobimetallic Rhenium-Iridium Complexes: Experimental and DFT Study” *Organometallics*, **2016**, *35*, 605-611.

(6) “Mechanism of Me-Re Bond Addition to Platinum(II) and Dioxygen Activation by the Resulting Pt-Re Bimetallic Center.” Submitted for publication.

(7) “Reduction of Carbon Dioxide to Methanol Catalyzed by Oxorhenium Pincer Complex.” Manuscript in preparation.