TRANSITION METAL MEDIATED TRANSFORMATIONS OF SMALL MOLECULES

Final Report
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Keywords: Catalysis, Transition metals, Polymerization, Biomass, Green chemistry, Carbon dioxide.

ABSTRACT

DE-FG02-84ER13295 Ayusman Sen

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Total Budget: $480,000; **Period:** 8/1/1984 - 8/31/2016

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Catalysis at metal centers is of great scientific, as well as practical, importance because of the high efficiency, high specificity, and low energy demands often associated with such systems. The two major themes of our research are (a) the design of metal-based systems for the synthesis of novel classes of polymers and (b) the identification of new metal-catalyzed systems for the conversion of biomass to fuels and chemicals, and related "green" chemical processes.

In the past three years, work was performed on several aspects of organotransition metal chemistry and catalysis. These include (a) the study of steric and electronic effects in ethene/norbornene copolymerization by neutral salicylaldiminato-ligated palladium(II) catalysts and (b) rhodium-catalyzed conversion of biomass to fuels and chemicals. In addition, we have designed of new materials to reversibly sense and capture carbon dioxide. We are also addressing key questions concerning the steps involved in these transformations.

The achievement of a fundamental understanding of all aspects of catalysis is an important goal. The Technology Vision 2020 report also cites the importance of developing new catalysts for customizing polymer properties. Our previous DOE-BES sponsored work on palladium-catalyzed norbornene polymerization systems led to several patents and Pennsylvania State University licensed the technology to Promerus, Inc. (www.promerus.com/) who is commercializing several polymeric materials based on such catalytic processes. There is also great interest in identifying new technical approaches to the efficient, catalytic conversion of biomass to fuels and chemicals. Again, Pennsylvania State University has obtained a patent on our biomass conversion procedures and is negotiating possible licensing of the technology to interested commercial entities.

Keywords: Catalysis, Transition metals, Polymerization, Biomass, Green chemistry, Carbon dioxide.

PROGRESS REPORT

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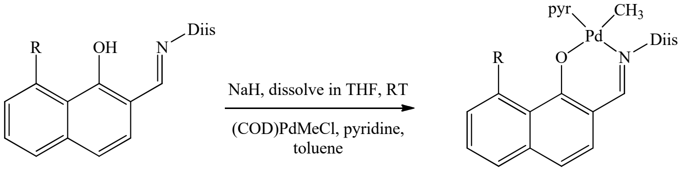
The major themes of the our research in the current grant period are (a) the design of metal-catalyzed systems for the synthesis of novel classes of polymers, and (b) the identification of new metal-mediated systems for the conversion of biomass to fuels and chemicals. In addition, we are studying new materials to sense and capture carbon dioxide. Below we summarize our most significant recent results. Details of these and other work performed during this grant period can be found in the publications.

Steric and Electronic Effects in Ethene/Norbornene Copolymerization by Neutral Salicylaldiminato-Ligated Palladium(II) Catalysts.[6] Late transition metal catalysts have been researched extensively for both homo- and co-polymerization of polar monomers. We have examined the effects of naphthoxyimine ligands, with different C8 functional groups, on the polymerization activity of the corresponding palladium(II) complex. Our group has previously studied Pd(II) catalysts extensively because of their ability to tolerate polar functional groups in monomers.[3]



pyr: pyridine, diis: 2,6-diisopropylphenyl

Ligand A: R = H
Ligand B: R = OH
Ligand C: R = OCH_3

Catalyst A: R = H
Catalyst B: R = OH
Catalyst C: R = OCH_3

Figure 1. *Naphthoxyimine ligands 1-3 used to synthesize Catalyst A-C.*

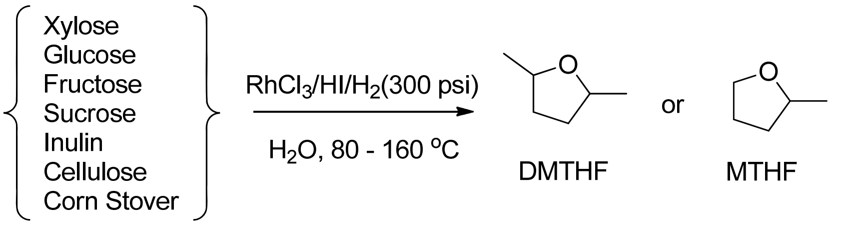
Three palladium(II) catalysts, ligated with naphthoxyimine ligands, were synthesized, structurally characterized, and used to copolymerize ethene with norbornene derivatives (see Fig. 1).[6] Results show that modification of the functional group on the 8-carbon of the naphthol ligand can significantly influence polymer composition and structure. The three functional groups on the 8-carbon studied were: -H (Catalyst **A**), -OH (Catalyst **B**), and –OCH_3 (Catalyst **C**). Catalyst **B** significantly outperforms both **A** and **C** in production of ethene-norbornene copolymer. **B** yields over twice the amount of NB/E copolymer that **A** produces, and nearly five times as much as **C** under the same conditions. Both **A** and **B** are capable producing appreciable amounts of ethene/5-norbornene-*tert*-butyl-2-carboxylate copolymers which contain over 30% of functionalized norbornene. **C**, in contrast to both **A** and **B**, is incapable of copolymerizing functionalized norbornene with ethene.

One Step Catalytic Transformation of Cellulosic Biomass to 2,5-Dimethyltetrahydrofuran (DMTHF) for Liquid Fuel.[2,10] The production of liquid fuel directly from biomass is of great current interest, given the diminishing reserves of fossil fuels such as coal, oil, and natural gas – the current commercial sources of fuels.[7] We are attempting to develop a commercially viable, high yield process for the conversion of carbohydrates to the target liquid fuel 2,5-

dimethyltetrahydrofuran (DMTHF). Carbohydrates, such as mono and polysaccharides and cellulose, typically constitute 50-80% of plant biomass.

Our experimental results obtained to date clearly demonstrate that it is possible to convert, *in one step*, a wide range of biomass derived carbohydrates and raw cellulosic biomass, the most abundant plant biomass, into liquid fuel (Scheme 1).[1,2] DMTHF, our initial fuel target, removes most oxygen atoms but keeps all the carbon and hydrogen content from the biomass, which preserves the highest energy content among all the liquid fuel candidates (such as ethanol). Compared to ethanol, the most common biomass-derived fuel, DMTHF possesses higher energy density (31.8 MJ/L), lower solubility in water (immiscible), and higher boiling point (90-92°C), and can be incorporated directly into the existing transportation infrastructure.

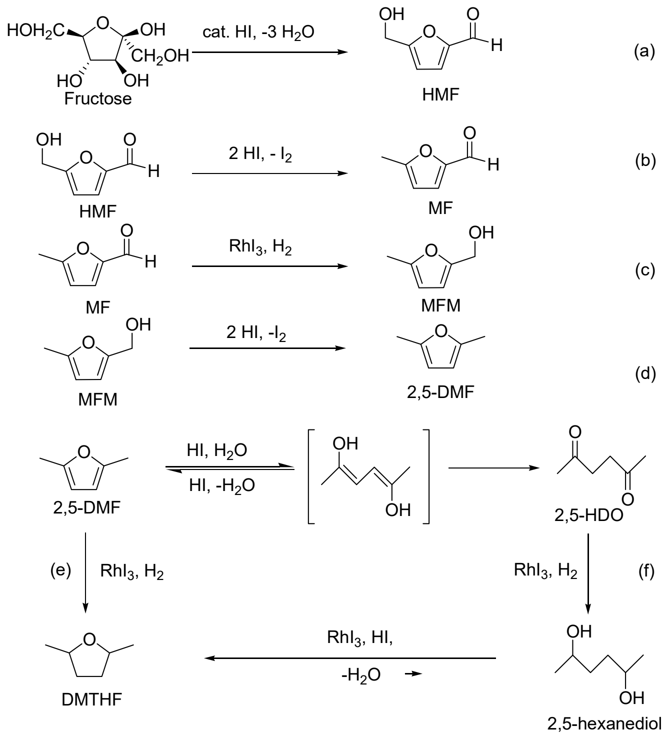
Scheme 1. *One step transformation of carbohydrates and cellulosic biomass to tetrahydrofuran derivatives.*[2]



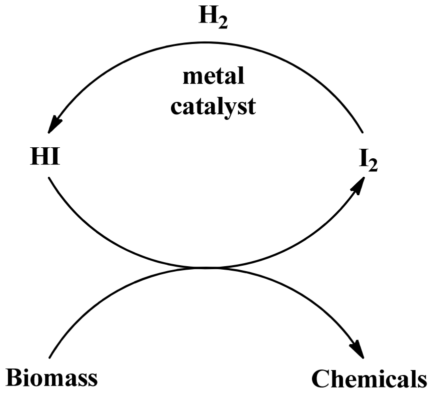
We have examined in some detail the respective roles of HI and RhX_3/H_2 in the conversion of carbohydrates to DMTHF.[2] HI serves to hydrolyze complex carbohydrates to fructose and glucose and then acts as a dehydration agent in converting these to 5-hydroxymethylfurfural (HMF). HI also acts as a reducing reagent to convert HMF to 5-methylfurfural (MF) by reducing conjugated carbinols and generates iodine as a byproduct. It also enables the hydration of 2,5-dimethylfuran (DMF) to 2,5-hexanedione (HDO), an important intermediate on route to DMTHF. The RhX_3 catalyzes the conversion of iodine back to HI with hydrogen. The Rh catalyst is also necessary for the hydrogenation of the unsaturated C=C and C=O bonds of the intermediates which lead to the final product DMTHF. The overall series of reactions is shown in Scheme 2. The exact identity of the Rh catalyst under the reaction conditions could not be determined, but RhI_3 was been established as the catalyst precursor.

Role of HI in selective transformation of biomass.[1,10] Hydroiodic acid (HI) is a required reagent for the one step transformation of carbohydrates to DMTHF. Substituting HI with either HCl or H_2SO_4 does not lead to the desired products in any significant yields. Thus, it was critically important to understand the role of HI in this biomass conversion process. HI is a highly selective reducing reagent for a wide variety of substrates. Its application has hitherto been limited by iodine (I_2) formation and the difficulty in reconverting I_2 back to HI in situ. We have now discovered a procedure for the facile conversion of I_2 to HI by metal-catalyzed hydrogenation in the presence of water.[1]

The fact that (a) HI is a strong reducing agent and (b) I_2 can be readily reconverted back to HI in the presence of water, has allowed us to efficiently convert a number of carbohydrate derivatives to useful chemicals *without involving a metal catalyst in the actual biomass reduction step* (Scheme 3).[1] This is important because it avoids the search for an appropriate metal catalyst that is tolerant of the specific reaction conditions. We first illustrated our approach with two important transformations: (a) fructose to 5-methyl furfural and (b) glycerol to 2-iodopropane.[1]

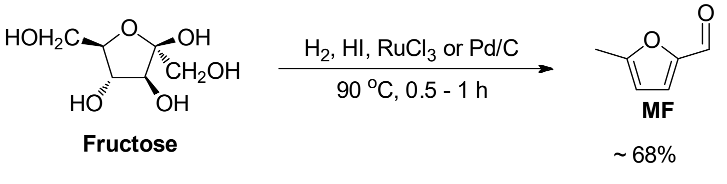


Scheme 2. *Proposed reaction mechanism for the conversion of fructose to DMTHF.*[2]



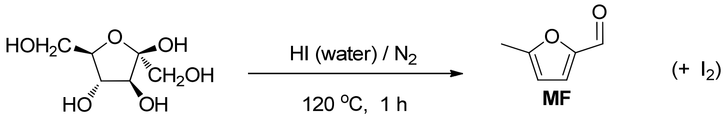
Scheme 3. *HI/I*$_2$*-mediated selective transformation of biomass.*[1]

Synthesis of 5-methylfurfural from carbohydrates. We have developed a method to convert biomass-derived carbohydrates directly to MF in 2 h or less with relatively high yield using a biphasic reaction system (Scheme 4).[1]



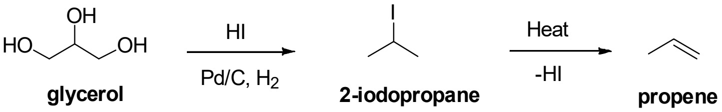
Scheme 4. *Direct catalytic synthesis of 5-methylfurfural from fructose.*[1]

The actual conversion of fructose to MF does not need either H_2 or a metal catalyst; only a slightly lower yield of MF can be obtained with HI alone (Scheme 5).[1] This is the first example of MF formation from fructose without the use of a metal catalyst. Thus, the metal/hydrogen combination (Scheme 3) serves to convert iodine back to HI in situ, while HI functions as dehydration and reducing reagent to convert fructose to MF.[1] As a control experiment, reaction involving fructose with only metal catalyst (Pd/C)/H_2 and no HI was performed under the same reaction conditions and np fructose conversion was observed.



Scheme 5. *Metal-Free Conversion of Fructose to MF.*[1]

Conversion of glycerol to propene via 2-iodopropene. The second example illustrating the role of HI as a reducing agent in biomass conversion involves the conversion of abundant biomass-derived glycerol to propene. The propene market is driven by the strong demand for polypropylene, which is one of the most important thermoplastic resins. Thus, the direct conversion of glycerol to propene is a very useful and attractive process. However, reports of selective propene production from glycerol are limited. Our procedure for the highly selective conversion of glycerol to propene is shown in Scheme 6.[1] Under optimal conditions, near complete conversion of glycerol to propene was observed.



Scheme 6. *HI-mediated Conversion of Glycerol to Propene.*[1]

The stoichiometric conversion of glycerol to 2-iodopropane using excess HI is represented by eq. 1. We were able to reduce the iodine byproduct back to HI in situ by using a metal catalyst (Pd/C, $RhCl_3$) and hydrogen in the presence of water. No I_2 formation was observed when the metal catalyst/H_2 combination was present.

$$\mathbf{HOCH_2CH(OH)CH_2OH + 5\,HI \longrightarrow CH_3CH(I)CH_3 + 3\,H_2O + 2\,I_2} \qquad \mathbf{(1)}$$

Novel Materials for the Reversible Capture and Sensing of Carbon Dioxide.[8] We have discovered a new class of absorbents for carbon dioxide, amino alcohols. They reversibly absorb carbon dioxide at ambient temperature. Carbon dioxide is released back by simply purging the material with air or nitrogen. By coupling the process with a standard pH indicator, the system acts as a sensitive and reversible carbon dioxide sensor with a visual color output (Fig. 2).[8] The detection of carbon dioxide in confined spaces is of great interest for food, beverage, health, as well as for mining, biotechnology, and chemical industries and our sensors can detect carbon dioxide down to 500 ppm levels. Solid state sensors can be readily fabricated by supporting the amino alcohol and the pH indicator on alumina. This colorimetric response is completely reversible and is not interfered by moisture, oxygen or trace CO_2, present in ambient air.

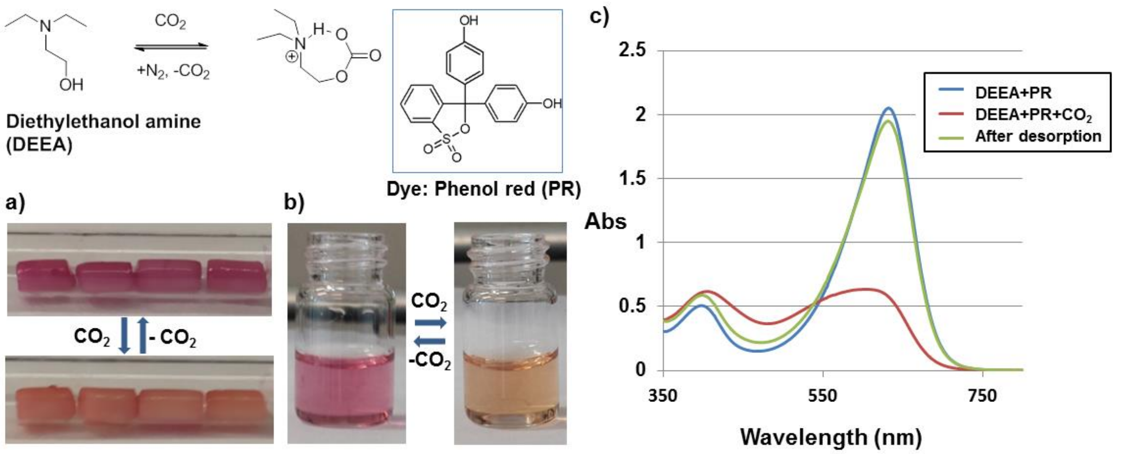


Figure 2. *The observed colorimetric responses to pure CO_2 at ambient temperature, using pH sensitive phenol red dye in diethylethanolamine (DEEA). a) Visual color change observed with alumina-supported DEEA-phenol red system, b) visual color change observed in DEEA-phenol red solution, c) changes observed in the UV-visible spectra of DEEA-phenol red solution after absorption of pure CO_2 and the subsequent CO_2 desorption by purging N_2 at ambient temperature.*[8]

Impact on Science and Technologies of Relevance to DOE

Catalytic polymer synthesis by metal compounds is of great scientific, as well as practical, importance. Indeed, several high-volume commercial polymers are only accessible through metal-mediated routes. Hence, the achievement of a fundamental understanding of all aspects of such reactions is an important goal. The Technology Vision 2020 report also cites the importance of developing new catalysts for customizing polymer properties. A major theme of our research is the design of new metal-based catalytic systems for the synthesis of novel classes of polymers. We have in the past and continue to develop and study metal-mediated polymerization systems that are of practical importance. Some of these have led to commercial products. Most recently, our work on palladium-catalyzed norbornene homopolymerization and norbornene/acrylate copolymerization led to several patents and Pennsylvania State University licensed the technology to Promerus, LLC (www.promerus.com/). The latter is in the process of commercializing several polymeric materials based on such catalytic processes.

There is also great interest in identifying new technical approaches to producing chemicals and fuels from biomass. The U.S. Energy Independence and Security Act of 2007 (EISA), signed into law on December 19, 2007, is a comprehensive federal energy policy initiative aimed at reducing America's dependence on foreign oil and greenhouse gas emissions. The Act sets standards for vehicle efficiency and renewable fuel use, including target production volumes for specific renewable fuels such as cellulosic biofuel and biodiesel. It is evident that new technology is needed to improve the conversion of cellulosic feedstocks to biofuel in order to meet the renewable fuel standards. A recent DOE funding solicitation seeks applications "to develop new and innovative approaches for the conversion of biomass to advanced biofuels that are infrastructure compatible, essentially going beyond current technical pathways for producing hydrocarbons from biomass feedstocks." [Funding Opportunity Announcement Number: DE-FOA-0000123, http://www.grants.gov/search/search.do?mode=VIEW&oppId=48495].

Pennsylvania State University has obtained a patent on our biomass conversion procedures[10] and is negotiating possible licensing of the technology to interested commercial entities.

Refereed Publications Acknowledging DOE Grant: 2012-present

1. Yang, W.; Grochowski, M.; Sen, A. Selective Reduction of Biomass by Hydroiodic Acid and Its In Situ Regeneration from Iodine by Metal/Hydrogen. *ChemSusChem*, **2012**, *5*, 1218-1222..

2. Grochowski, M.; Yang, W.; Sen, A. Mechanistic Study of One Step Catalytic Conversion of Fructose to 2,5-Dimethyltetrahydrofuran. *Chem. Europ. J.,* **2012**, *18*, 12363-12371.

3. Nakamura, A.; Anselment, T. M. J.; Claverie, J.; Goodall, B.; Jordan, R. F.; Mecking, S.; Rieger, B.; Sen, A.; van Leewuen, P. W. N. M.; Nozaki, K. Ortho-Phosphonebenzenesulfonate: A Superb Ligand for Palladium-Catalyzed Coordination-Insertion Copolymerization of Polar Vinyl Monomers. *Acc. Chem. Res.*, **2013**, 46, 1438-1449.

4. Biltek, S. R.; Sen, A.; Pedicini, A. F.; Reber, A. C.; Khanna, S. N. Isolation and Structural Characterization of a Silver-Platinum Nanocluster, $Ag_4Pt_2(DMSA)_4$. *J. Phys. Chem. A*, **2014**, *118*, 8314-8319.

5. Liu, R.; Wong, F.; Duan, W. Synthesis and Characterization of Silver Halide Nanowires. *Polyhedron*, **2014**, *84*, 192-196.

6. Pong, F. Y.; Mandal, S.; Sen, A. Steric and Electronic Effects in Ethene/Norbornene Copolymerization by Neutral Salicylaldiminato-Ligated Palladium(II) Catalysts. *Organometallics*, **2014**, *33*, 7044–7051.

7. Chatterjee, C.; Pong, F.; Sen, A. Chemical Conversion Pathways for Carbohydrates. *Green Chemistry*, **2015**, *17*, 40-71.

8. Chatterjee, C.; Sen, A. Sensitive Colorimetric Sensors for Visual Detection of Carbon Dioxide. *J. Mater. Chem. A*, **2015**, *3*, 5642-5647.

9. Dey, K. K.; Pong, F. Y. Breffke, J.; Pavlick, R.; Pacheco, C.; Sen, A. Dynamic Coupling at the Ångström Scale. *Angew. Chem., Int. Ed.*, **2016**, *55*, 1113-1117.

10. Sen, A.; Yang, W. One-step Catalytic Conversion of Biomass-derived Carbohydrates to Liquid Fuels. *U. S. Patent,* 8,674,150 B2 (2014).