

College of Engineering | Department of Chemical & Biomolecular Engineering

CENTER FOR CATALYTIC SCIENCE & TECHNOLOGY



Presenting our

2016 RESEARCH REVIEW

October 5 - 6, 2016

Clayton Hall Conference Center

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SCHEDULE OF EVENTS

WEDNESDAY, OCTOBER 5, 2016

2:45 PM	REGISTRATION
3:00 PM	Opening Remarks by Dr. Raul Lobo Director, Center for Catalytic Science & Technology Claire D. LeClaire Professor of Chemical Engineering
3:05 PM	Eric Bloch , Assistant Professor of Chemistry & Biochemistry <i>"Small Molecule Activation with Metal-Organic Polyhedra"</i>
3:30 PM	Stephanie Velardo <i>"CO₂ Reduction Using 3D Printed Flow Electrolysis"</i>
3:50 PM	Jared Nash <i>"Effect of pH on the activity of hydrogen oxidation reaction/hydrogen evolution reaction over PtRu bimetallic catalysts"</i>
4:10 PM	Yun Zhao <i>"Chlorine Recovery by Gasous HCl Electrolysis with Iron Redox Assisted Cathode"</i>
4:30 PM	Wesley Luc <i>"Ultra-thin Electrocatalysts for Carbon Dioxide Reduction"</i>
4:50 PM	Reception / Poster Session
6:00 PM	Conclude for the day

THURSDAY, OCTOBER 6, 2016

8:00 AM	REGISTRATION
8:30 AM	OPENING REMARKS / INTRODUCTION BY DR. RAUL LOBO

SESSION I

8:40 AM	Raul Lobo , Claire D. LeClaire Professor of Chemical Engineering <i>"Catalysis Innovation for Valorization of C1 molecules"</i>
9:10 AM	Ali Mehdad <i>"Ethane Aromatization on Zinc Containing Zeolites"</i>
9:40 AM	Huibo Sheng <i>"Iron-promotion of Cu/SiO₂ catalyst for furfural hydrodeoxygenation"</i>

SCHEDULE OF EVENTS

CONTINUE

10:10 AM **Edward Schreiner**
"High-pressure Conversion of C₅-C₇ Alkanes for Aircraft Endothermic Cooling"

10:40 AM **BREAK / POSTER SESSION**

SESSION II

11:30 AM **Srimoyee Dasgupta**
"Copper(I)-Catalyzed Enantioselective Alkynylation of Oxocarbenium and Iminium Ions to set Diaryl Tetrasubstituted Stereocenters"

11:50 AM **Erisa Saraci**
"Cross metathesis of unsaturated carboxylic acids to terephthalic acid precursors"

12:10 PM **Kelsey Cobb**
"Stereospecific Nickel-Catalyzed Suzuki Cross Couplings of Allylic Carboxylates to Set Quaternary Stereocenters"

12:30 PM **LUNCH**

SESSION III

1:45 PM **Basudeb Saha**, Associate Director of Research, Catalysis Center for Energy Innovation
"Towards sustainable catalytic oxidation for dicarboxylic acid"

2:15 PM **Maura Koehle**
"Production of para-methylstyrene and para-divinylbenzene from furanic compounds"

2:35 PM **Matt Gilkey**
"Metal-Free Production of Adipic Acid via Hydrogenolysis of Bio-mass-Derived Tetrahydrofuran-2,5-Dicarboxylic Acid in Organic Acid Solvents"

2:55 PM **Efterpi Vasileiadou**
"Lewis acid catalyzed formaldehyde-olefin condensation: a valuable route for C-C formation"

3:15 PM **CLOSING REMARKS BY DR. LOBO**

3:30 PM **CONFERENCE CONCLUDES**

RESEARCH REVIEW PRESENTATION



CO₂ Reduction Using 3D Printed Flow Electrolysis

Stephanie M. Velardo
Advisor: Joel Rosenthal

The development of inexpensive electrolyzer platforms capable of efficient and rapid reduction of CO₂ to CO provide a route to solar fuel production when driven by renewable electricity generated from a PV assembly. Our laboratory has developed a bismuth-carbon monoxide evolving catalyst (Bi-CMEC) using an electrodeposition strategy. This Bi-CMEC catalyst promotes the conversion of CO₂ to CO at rates and selectivities comparable to those historically observed for precious metals such as silver and gold. In an effort to improve the scalability of the Bi-CMEC platform we have developed a streamlined method by which solutions of Bi³⁺ salts may be drop cast onto large two-dimensional electrode supports. These modified electrodes have been utilized in conjunction with 3D-printed flow cell assemblies to enable the large scale production of CO. This new CO₂ electrolyzer may be directly integrated with PV assemblies to drive to production of CO using solar energy and serves to underscore the feasibility of rapid solar fuel generation.

Effect of pH on the activity of hydrogen oxidation reaction/hydrogen evolution reaction over PtRu bimetallic catalysts

Jared Nash

Advisor: Bingjun Xu, Yushan Yan

Hydrogen proton exchange membrane fuel cell (PEMFC) powered automobiles have become commercially available, but are still too expensive. Hydroxide exchange membrane fuel cells (HEMFCs) offer the possibility of cheaper non-precious metal catalysts. However, the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) are significantly slower in base than in acid for Pt, Pd, Ir, and Rh¹⁻⁴. PtRu shows higher HOR/HER activity than Pt^{5, 6}, so understanding the mechanism of the HOR/HER on PtRu is key to developing non-precious metal catalysts for HEMFCs. Using the rotating disk electrode, bimetallic PtRu showed a minimum in the HOR/HER activity, pH relationship, not seen on monometallic catalysts. The hydrogen binding energy and the hydroxide binding energy measured from the hydrogen underpotential desorption peak and the CO stripping peak, respectively, did not change significantly with pH. Leaching Ru from the catalyst, it was found that the HOR/HER activity of PtRu remains approximately constant while the Ru content is reduced. Only after a significant amount of Ru has been removed does the activity change. The charge transfer coefficient, α , decreases with the Ru content going from 0.8 to 0.5. Fitting the kinetic data with the dual pathway model⁷ shows that below pH 11, the Heyrovsky and Volmer reaction barriers are comparable and above pH 11, the Volmer step becomes rate determining. It is proposed that Ru can align more oxygen species on the surface giving water a more favorable orientation for the Volmer step to proceed, which results in an increase in activity.

References:

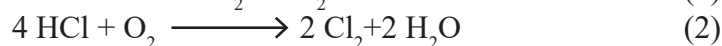
1. Sheng, W., et al., *Nature communications* **2015**, 6.
2. Zheng, J., et al., *Science Advances* **2016**, 2 (3).
3. Durst, J., et al., *J Electrochem Soc* **2015**, 162 (1), F190-F203.
4. Sheng, W., et al., *J Electrochem Soc* **2010**, 157 (11), B1529.
5. Wang, Y., et al., *Energy Environ. Sci.* **2014**, 8 (1), 177-181.
6. Wang, J. X., et al., *Scientific Reports* **2015**, 5, 12220.
7. Elbert, K., et al., *ACS Catal* **2015**, 6764-6772.

Chlorine Recovery by Gaseous HCl Electrolysis with Iron Redox Assisted Cathode

Yun Zhao

Advisor: Yushan Yan

Chlorine is used to synthesize numerous consumer products and useful intermediates.^[1] Chlorination of alkanes or aromatics is a substitution reaction with hydrogen, for which only half of the chlorine atoms are actually used to produce chloro-organics, the other half being lost as waste HCl gas or recovered as low-value HCl aqueous solution. Today, the global by-production of HCl totals 9.3 million tons per year, when only the synthesis of polyurethane, chloromethane, and polycarbonate is considered. At present, only 15% of this HCl by-product is recycled, leaving an unrealized Cl₂ regeneration market of \$2.4 billion per year (based on the current price of Cl₂: \$315/ton).^[2] Currently, the dominant commercial processes today are electrochemical because of the simple modular design and milder operating conditions electrolyzers offer.^[3] Typical processes feed waste aqueous HCl solution to the anode and utilize a hydrogen evolution (HEC, Equation 1) or oxygen depolarization (ODC, Equation 2) cathode, generating hydrogen or water, respectively, in addition to Cl₂.



Despite the increasing demand for Cl₂, current HCl recycling technologies are not economical enough to deploy into more of this multi-billion-dollar market. Herein, we propose an iron reduction cathode (IRC) based gaseous HCl electrolyzer system to regenerate chlorine from waste hydrogen chloride at low temperature. At the anode, HCl gas is oxidized to generate chlorine and protons, at the cathode, Fe³⁺ is electrochemically reduced to form Fe²⁺. Subsequently, Fe²⁺ is chemically oxidized to Fe³⁺ by oxygen in a reactor external to the electrolytic cell. Regeneration Fe²⁺ is recycled to the electrolyzer. Due to high standard potential (p° , 0.77 V_{SHE}) and fast kinetics (exchange current density, i_0 , of $\sim 10^{-2}$ A/cm² on glassy carbon, no catalyst was required),^[4] IRC offers substantial benefits over alternative commercial HEC and ODC cathodes. Taking advantage of IRC, a much lower cell voltage is achieved: 0.67 V vs. 1.16 V (with ODC) and 1.22 V (HEC) at a typical current density of 4 kA/cm². Compared to the commercial HEC or ODC-based HCl electrolysis processes, it will save 45–50% of energy consumption approximately. Moreover, without the need for a precious metal cathode catalyst and a costly thick membrane, the capital cost can be reduced by 40%–50% (IRC: \$2,640/m² vs. HEC: \$4,339/m² and ODC: \$5,034/m², estimated with 4 kA/m² and current materials prices).

[1] J. Perez-Ramirez, C. Mondelli, T. Schmidt, et al, *Energy & Environmental Science*, 2011, **4**, 4786.

[2] ThyssenKrupp, *HCl electrolysis brochure*.

[3] I. G. Martinez, T. Vidaković-Koch, R. Kuwertz, et al, *Electrochimica Acta*, 2014, **123**, 387.

[4] Y. H. Wen, H. M. Zhang, P. Qian, et al, *Electrochimica Acta*, 2006, **51**, 3769.

Ultra-thin Electrocatalysts for Carbon Dioxide Reduction

Wesley Luc
Advisor: Dr. Feng Jiao

Converting greenhouse gas carbon dioxide (CO_2) to value-added chemicals is an appealing approach to tackle CO_2 emission challenges. The chemical transformation of CO_2 requires a suitable catalyst that can lower the activation energy barrier, thus minimizing the energy penalty associated with the CO_2 reduction reaction. First-row transition metals are potential candidates as catalysts for electrochemical CO_2 reduction; however, their high oxygen affinity makes them easy to be oxidized, which could, in turn, strongly affect the catalytic properties of metal-based catalysts. In this work, we propose a new strategy to synthesize ultra-thin electrocatalysts using a core-shell nanoarchitecture that contains a bimetallic core responsible for high electronic conductivity and an ultra-thin partially oxidized shell responsible for catalytic CO_2 conversion. This concept was demonstrated by a series of core-shell electrocatalysts with a Ag-Sn bimetallic core and a partially oxidized SnO_x shell. At an optimal SnO_x shell thickness of ~ 1.7 nm, the catalyst exhibited a high formate Faradaic efficiency of $\sim 80\%$ and a formate partial current density of ~ 16 mA cm^{-2} at -0.9 V vs. RHE, a remarkable performance in comparison to state-of-art formate-selective CO_2 reduction catalysts.

Ethane Aromatization on Zinc Containing Zeolites

Ali Mehdad
Advisor: Raul F. Lobo

Benzene, toluene and xylenes (BTX) are produced by naphtha reforming, a process in which naphtha represents about 80% of BTX production cost (1). The current oversupply of ethane makes ethane a relatively inexpensive feedstock, compared to naphtha (2), for the production of aromatics. Different metals have been investigated for aromatization of light alkanes and among them Zn and Ga incorporated into aluminosilicate zeolites have showed the best results. These two metals show good dehydrogenation activity without catalyzing hydrogenolysis (3).

Conversion of ethane on zinc containing zeolites has been investigated at 500 °C and atmospheric pressure. Initial tests indicate that H⁺/ZSM-5 and a zinc-containing small-pore zeolite (Zn/chabazite, SiO₂/Al₂O₃=6) do not catalyze the aromatization reaction; zinc-containing large-pore zeolite (Zn/BEA, SiO₂/Al₂O₃=25) has lower reaction rates as compared to that of zinc-containing medium-pore ZSM-5 zeolites (Zn/ZSM-5, SiO₂/Al₂O₃ = 23).

Zn/ZSM-5 showed different reaction rates and selectivity for conversion of ethane or ethylene depending on the amount of zinc, preparation technique and SiO₂/Al₂O₃ of the zeolite. If ethane is the feed, ethylene or aromatics product selectivity will be predominant and if ethylene is the feed, ethane or aromatics product selectivity will be predominant. Zinc sites are necessary for ethane activation and increasing the amount of zinc in the sample increases overall reaction rate. At SiO₂/Al₂O₃=23, samples prepared by ion exchange can contain up to 2.5%w/w of zinc. These samples showed lower deactivation rates and higher selectivity towards ethylene than aromatics, as compared to samples containing 5%w/w Zn/ZSM-5 prepared by incipient wetness impregnation (IWI). Diffuse-reflectance UV-vis spectra show that conventional oven drying of Zn/ZSM-5 (prepared by IWI) will form larger ZnO clusters as compared to the freeze-dried sample.

Lewis sites (cationic zinc sites) and Brønsted acid sites (BAS) both can catalyze the oligomerization of ethylene. Zinc sites in the ZSM-5 are also responsible for the dehydrogenation of naphthenic intermediates. Samples with higher concentrations of BAS, deactivate faster, and carbon deposition inside the zeolite pores is identified as the main source of deactivation. Small ZnO clusters can catalyze the dehydrogenation, but not the aromatization, as Zn/silicalite-1 was active for ethane dehydrogenation to ethylene, while it showed low reaction rates for conversion of ethylene.

References

1. Guisnet M, Gnep NS, Alario F. Aromatization of short chain alkanes on zeolite catalysts. *Applied Catalysis A: General*. 1992;89(1):1-30.
2. Short-Term Energy Outlook. US Energy Information Administration. 2016.
3. Hagen A, Roessner F. Ethane to Aromatic Hydrocarbons: Past, Present, Future. *Catalysis Reviews*. 2000;42(4):403-37.

Iron-promotion of Cu/SiO₂ catalyst for furfural hydrodeoxygenation

Huibo Sheng
Advisor: Raul F. Lobo

Selective hydrogenation of biomass-derived compounds is often necessary for the valorization of compounds such as this form of renewable carbon is oxidized relative to the most important commodity organic chemicals such as ethylene, methanol, etc. A catalyst that is inexpensive, stable and selective is desired to accomplish such hydrogenations. As a derivative of lignocellulose,^[1] furfural is a platform chemical that can be upgraded to a variety of valuable organic chemicals and biofuels.^[2] Several cellulosic ethanol plants have been opened in the Midwest of the USA with 30-million gallon ethanol annual production capacity,^[3] and since C5 sugar streams are not ideal for fermentation, these could be used instead for the preparation of furfural. The hydrodeoxygenation (HDO) of furfural is a promising process to remove ‘excess’ oxygen and increase energy density and stability. The product, 2-methylfuran, for example, is an excellent biofuel candidate or additive. The challenge of this process is the stable hydrogenation of the side carbonyl group only, leaving the furan ring untouched.

Silica supported copper is a mild hydrogenation catalyst that is selective for the hydrogenation of the carbonyl group of furfural to furfuryl alcohol. We have found that iron-containing Cu-based catalyst show much higher reactivity and very high selectivity towards 2-methylfuran (85%+). It is of interest to understand the structural and chemical effects of the iron promotion (0.15% w/w) over the Cu catalyst (1% Cu w/w) and characterize the species responsible for the high hydrogenation performance. Our investigations indicate that after the catalyst is pre-treated in hydrogen, copper is fully reduced while iron is only partially reduced (a mixture of Fe^{III} and Fe^{II} is observed). An in situ DRIFT study suggests that Fe^{II} species are present on the catalyst surface, as indicated by the adsorption of NO.^[4]

1. G. W. Huber, S. Iborra, A. Corma, *Chemical Reviews* 2006, 106, 4044-4098.
2. J.-P. Lange, E. van der Heide, J. van Buijtenen, R. Price, *ChemSuschem* 2012, 5, 150-166.
3. U. S. Energy Information Administration (EIA), Vol. 2016, <http://www.eia.gov/todayinenergy/detail.cfm?id=17851#>, 2014.
4. H. Sheng, R. F. Lobo, *Chemcatchem*, 2016 (accepted).

High-pressure Conversion of C₅-C₇ Alkanes for Aircraft Endothermic Cooling

Edward P. Schreiner
Advisor: Raul F. Lobo

Practical use of hypersonic planes (> Mach 5) has been hindered by overheating of aircraft engine and electronic components, caused by high fuel combustion rates and air friction¹. Current military aircraft can use jet fuel as a heat sink, but future hypersonic aircraft will exceed the cooling capacity of the fuel^{2,3}. Cooling capacity can be increased through use of so-called endothermic fuels, which remove thermal energy produced by the aircraft through endothermic chemical reactions^{4,5}. Cracking reactions are endothermic and the solid acid zeolite, H-[Al]ZSM-5, was chosen to catalyze these reactions as it is known to yield light olefins with high selectivity in fluidized catalytic cracking units⁶. It was found, however, that secondary bimolecular reactions on H-[Al]ZSM-5 controlled product distribution and reduced reaction endothermicity⁷. Subsequently, supported molybdenum carbide catalysts were investigated as they can react with numerous hydrocarbons producing olefins⁸.

A number of pure and supported molybdenum carbides were investigated for the dehydrogenation of *n*-pentane. Two samples provided the highest reactivity and selectivity toward pentenes: Mo/H-[B]ZSM-5 (zeolite support) and Mo/Al₂O₃. These two catalysts exhibited an induction period, with the highest reaction rates observed 1.5 h after the start of the reaction. This increase in reactivity indicates that the most active form of the catalyst was formed in the reactor by interaction with the reactant. Slow deactivation was observed over the 5 h on stream investigated, but unlike the other catalysts tested, the selectivity of the dehydrogenation product from the zeolite support did not change with time on stream. Dehydrogenation of *n*-hexane and *n*-heptane were also tested on the most active catalysts.

The Mo/H-[B]ZSM-5 catalyst showed the highest conversion of all the catalysts investigated, while maintaining the same high selectivity towards the dehydrogenation product as Mo/Al₂O₃. Furthermore, by using H-[B]ZSM-5, the undesirable secondary bimolecular reactions observed in acidic H-[Al]ZSM-5, which include oligomerization and dehydrocyclization reactions, were suppressed, preserving the desired olefinic product and increasing reaction endothermicity.

1. Lander, H., Nixon, A.C. (1971) *Journal of Aircraft* 8: 200-207.
2. Widegren, J.A., Bruno, T.J. (2009) *Energy Fuels* 23: 5523-5528.
3. Chung H.S., Chen, C.S.H., Kremer, R.A., Boulton, J.R. (1999) *Energy Fuels* 13: 641-649.
4. Gascoin, N., Abraham, G., Gillard, P. (2010) *J Analytical and Applied Pyrolysis* 89: 294-306.
5. Kim, J., Hyeon, D.H., Park, S.H., Chun, B.H., Jeong, B.H., Han, J.S., Kim, S.H. (2014) *Catalysis Today* 232: 63-68.
6. Corma, A. (1995) *Chem. Rev.* 95: 559-614.
7. Schreiner, E., Teketel, S., Lobo, R. (2015) *New Journal of Chemistry*. 40: 4245-4251.
8. Solymosi, F., Nemeth, R., Ovari, L., and Egri, L. (2000) *J. of Catalysis* 195: 316-325.

Copper(I)-Catalyzed Enantioselective Alkynylation of Oxocarbenium and Iminium Ions to set Diaryl Tetrasubstituted Stereocenters

Srimoyee Dasgupta
Advisor: Mary P. Watson

The primary focus of our research group is to develop new synthetic methodologies that utilize the power of transition metal catalysis. Transition metal catalysis has transformed the field of synthetic organic chemistry by enabling new and highly efficient reactions with exceptional control over regio- and enantioselectivity. Most transition metal catalysis relies heavily on neutral electrophiles, but we envisioned that it could also be efficiently used with cationic electrophiles to solve significant, long-standing challenges in organic synthesis. In particular, few methods are available for enantioselective additions to cyclic ketoxocarbenium and ketiminium ions to form diaryl, *tetrasubstituted* stereocenters. Harnessing our success in developing a copper-catalyzed addition of terminal alkynes to oxocarbenium ions to deliver isochromans with *tertiary* stereocenters,¹ we have now developed a highly enantioselective, copper(I)/PyBox-catalyzed addition of terminal alkynes to isochroman ketals to set diaryl-substituted quaternary stereocenters.² The success of this transformation relies on identification of a Cu/PyBox catalyst capable of distinguishing two aryl substituents on the forming stereocenter, which differ predominantly in their freedom of rotation and by their relationship to the oxygen substituents (alkyl vs lone pair). This highly challenging transformation enables the efficient conversion of readily available, racemic ketals to high-value, enantioenriched isochroman products, presumably via prochiral oxocarbenium ion intermediates. Reaction optimization, scope of both the ketal and alkyne, and elaboration of products will be presented.

We were also able to use this potent copper(I)/PyBox catalyst to develop an enantioselective, copper(I)-catalyzed alkynylation of ketiminium ion intermediates to deliver tetrahydroisoquinolines with tetrasubstituted α -stereocenters in high yields and enantioselectivities. Select substrate scope and elaboration of products in this method will also be presented.

We are currently investigating how the chiral copper/Pybox catalyst imparts enantioselectivity in these reactions. Initial mechanistic experiments elucidating the structure of the active catalyst as a dicopper acetylide species and further reactions inspired by these methods will also be discussed.

1. (a) Maity, P.; Srinivas, H. D.; Watson, M. P. *J. Am. Chem. Soc.* **2011**, *133*, 17142; (b) Srinivas, H. D.; Maity, P.; Yap, G. P. A.; Watson, M. P. *J. Org. Chem.* **2015**, *80*, 4003.
2. Dasgupta, S.; Rivas, T.; Watson, M. P. *Angew. Chem. Int. Ed.* **2015**, *54*, 14154.

Cross metathesis of unsaturated carboxylic acids to terephthalic acid precursors

Erisa Saraçi
Advisor: Raul F. Lobo

Terephthalic acid is essential for the preparation of a variety of polyester fibers and is largely produced via the catalytic oxidation of petroleum-derived p-xylene [1]. The ongoing exchange of naphtha crackers with shale gas crackers is causing a shortage in some aromatics species, such as p-xylene [2]. As a consequence, alternative and sustainable routes to produce terephthalic acid from biomass derivatives, e.g. bio-sourced sorbates [3], are highly desirable. In the last decade, Ru-catalyzed olefin metathesis, and in particularly cross-metathesis, has become an important tool for the formation of carbon-carbon bonds and the formation of valuable organic molecules [4].

We have investigated the ruthenium-catalyzed cross metathesis of sorbates with acrylates to form diester muconates. In a subsequent step, the reaction between alkyl muconates and ethylene affords the aromatization to dialkyl terephthalate. The effect of alkyl substituents and solvents was investigated over various organometallic ruthenium-based catalysts to increase conversion and selectivity towards the alkyl muconates. Conversions of up to 35% and 20% yields were achieved within the first hour of reaction with very low amounts (0.5 mol.%) of ruthenium-based catalyst containing a N-heterocyclic carbene (NHC) ligand. The conversion and yield can be increased by augmenting the catalyst amount. If a solvent was used, the cross metathesis products were formed in higher yields with the use of more polar solvents, i.e. CH₂Cl₂. To develop a greener process, the acrylate reactant was used in excess with no other solvent added. By using reactants (sorbates and acrylates) with smaller alkyl substituents the yield of cross metathesis products was favored, and ultimately the diester muconate precipitated in an easily recoverable solid form. Upon further development, this route for obtaining di-ester muconates, may provide a sustainable alternative for producing biomass derived precursors to polyethylene terephthalate (PET) and other valuable polyesters.

References

1. Rogério A. F. Tomás, João C. M. Bordado, and João F. P. Gomes. *Chem. Rev.* 113 (2013) 7421
2. C. Luke Williams, Chun-Chih Chang, Phuong Do, Nima Nikbin, Stavros Caratzoulas, Dionisios G. Vlachos, Raul F. Lobo, Wei Fan, and Paul J. Dauenhauer. *ACS Catal.* 2 (2012) 935
3. Sandrine Bérard, Christophe Vallée, and Damien Delcroix. *Ind. Eng. Chem. Res.* 54 (2015) 7164
4. Georgios C. Vougioukalakis, and Robert H. Grubbs. *Chem. Rev.* 110 (2010) 1746

Stereospecific Nickel-Catalyzed Suzuki Cross Couplings of Allylic Carboxylates to Set Quaternary Stereocenters

Kelsey M. Cobb
Advisor: Mary P. Watson

Asymmetric preparation of quaternary stereocenters remains an important goal and longstanding challenge in organic chemistry. Enantioselective or enantiospecific substitution of allylic electrophiles offers entry to the preparation of enantioenriched quaternary stereocenters. Allylic electrophiles have previously been utilized to prepare quaternary stereocenters, but these reactions typically rely on harsh air-sensitive nucleophiles such as Grignards or zinc reagents, and/or are limited to the formation of terminal alkenes or to specific substitution requirements. Our group has previously developed stereospecific Suzuki-Miyaura arylations of benzylic and allylic electrophiles to deliver products with tertiary stereocenters. We envisioned that this strategy may also enable the asymmetric synthesis of quaternary stereocenters. Our substrates are derived from allylic alcohols, which are ideal candidates for enantiospecific reactions due to their easy accessibility in high enantiopurity. In addition, our coupling partners are aryl boroxines, which are functional group tolerant and allow for a broad substrate scope. We will report our efforts to develop the allylic arylation to set quaternary stereocenters via Suzuki-Miyaura cross-couplings. Optimization, scope, and mechanistic understanding of this reaction will be presented.

Towards sustainable catalytic oxidation for dicarboxylic acid

Basudeb Saha

Catalysis Center for Energy Innovation, University of Delaware, Newark, DE 19716

Catalytic oxidation plays a critical role in the production of high volume commodity chemicals that are used for the manufacture of thousands of household consumable goods. One example is purified terephthalic acid (PTA), representing more than 100 billion pounds annual production by aerobic oxidation of para-xylene (pX) in acetic acid by homogeneous bromide containing catalyst. This oxidation process is corrosive and generates environmentally hazardous methyl bromide. Thus, an overarching goal is the development of oxidation processes that can be operated in water without utilizing hazardous chemicals. However, immiscibility of pX in water poses a barrier to this effort.

Recently, heterogeneous catalyzed aerobic oxidation of renewable substrates such as 5-hydroxymethylfurfural (HMF) and glucose to the corresponding dicarboxylic acids in water has been emerged as an effective alternate strategy. While significant technological advancement has been achieved in HMF oxidation over the past years enabling >95% 2,5-furandicarboxylic acid (FDCA) yield, efficient oxidation of glucose to glucaric acid has been proven to be a challenge due to slow and difficult oxidation of gluconic acid, an intermediate oxidation product of glucose.

We studied aerobic oxidation of glucose to glucaric acid using activated carbon, SiO₂ and Al₂O₃ supported Pt catalysts in water.¹ Through systematic optimization of the reaction conditions in a wide range of pH, O₂ pressure, temperatures and glucose to Pt molar ratio, we achieved a maximum 74% glucaric acid yield with Pt/C at initial pH of 7.2, which is the highest reported yield of glucaric acid to date. C–C bond scission of glucaric acid in basic pH results in low carbon chain carboxylic acids. Higher temperatures and higher Pt loadings cause degradation of glucaric acid, resulting in lower yields. Recyclability and characterization studies reveal that the catalyst is stable after five cycles with no sign of Pt leaching into the solution.

Reference

1. J. Lee, B. Saha and D. G. Vlachos, Green Chemistry, 2016.

Metal-Free Production of Adipic Acid via Hydrogenolysis of Biomass-Derived Tetrahydrofuran-2,5-Dicarboxylic Acid in Organic Acid Solvents

Matthew J. Gilkey

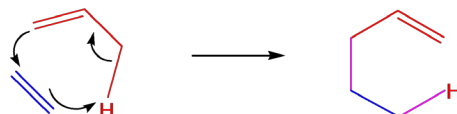
Advisors: Bingjun Xu and Dionisios G. Vlachos

Adipic acid (AA) is an essential precursor in the polymer industry, primarily for its use in the synthesis of Nylon-66. However, AA's current production method, which relies on the selective oxidation of petroleum-derived cyclohexane, contains several drawbacks including the emission of N_2O , a potent greenhouse gas. In effort to create a sustainable route to AA, significant research effort has been dedicated to develop pathways from biomass-derived platform chemicals through selective hydrodeoxygenation. Of particular interest is the hydrogenolytic ring opening of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) to AA. By reacting THFDCA in a mixture of hydriodic acid (HI) and molecular hydrogen in an organic acid solvent, an AA yield of up to 87% yield can be achieved in the absence of a metal catalyst. Through a combination of experimental and theoretical contributions, we reveal key mechanistic insights into the hydrogenolysis mechanism, noting that the nature of the solvent is critical in maintaining high ring opening activity. We have subsequently performed kinetic measurements to determined reaction orders of THFDCA, HI, and molecular hydrogen, where each component in the reaction mixture create an intricate recipe to synergistically remove C-O bonds in THFDCA to form AA.

Lewis acid catalyzed formaldehyde-olefin condensation: a valuable route for C-C formation

Efterpi (Efi) Vasileiadou
Advisor: Prof. Raul Lobo

New carbon-carbon bonds can be formed via the “ene” reaction, a pericyclic process between an alkene having an allylic hydrogen atom (an “ene”) and an electron-deficient multiple bond (an enophile) to form two sigma-bonds with transposition of the pi-bond [1] (see Scheme 1).



Scheme 1 Schematic Interaction in “ene” reaction

Prins reaction (Carbonyl-ene reaction) is an example of the “ene” reaction referring to condensation of formaldehyde with olefins [2]. The commercial availability of lower olefins, especially those formed by on-purpose methods from their corresponding alkanes (C3 and C4), coupled with the versatility of formaldehyde as a one-carbon electrophile make this reaction potentially important. Prins condensation can form unsaturated alcohols, diols, alkyl dioxanes, pyran skeleton compounds and dienes. The reaction is an acid catalyzed addition of aldehydes to olefins and is traditionally catalyzed by homogeneous mineral acids such as sulphuric acid or homogeneous Lewis acids like SnCl_4 , BF_3 and ZnCl_2 [3].

We have investigated solid Lewis acid catalysis for the reaction. Initially, acidic zeolite Beta catalysts have been synthesized and evaluated in the condensation of formaldehyde propylene. Specifically, framework Sn-, Zr-beta, and Zn-Beta—the last prepared by ion exchange— were prepared and characterized. The catalytic activity was tested by autoclaving formaldehyde and propylene using an appropriate solvent at a temperature range of 120–180°C.

We have found that Zn-Beta is the most active catalyst for this reaction. Different reaction pathways are followed producing valuable products. The product spectra can be divided into two categories; compounds with four carbon atoms (3-buten-1-ol and 1,3-butadiene) and compounds having five carbon atoms (1,3-Dioxane, 4-methyl-, tetrahydro-4H-pyran-4-ol and 3,6-dihydro-2H-pyran). The dominant reaction route in the presence of Zn-Beta when reacting formaldehyde with propylene is 3,6-dihydro-2H-pyran; a five carbon product formed via Prins cyclization-sequential reaction of formaldehyde with 3-buten-1-ol. Aiming to induce shape selectivity and minimize the routes forming five carbon compounds we synthesized and tested a series of different pore size Zn-exchanged zeolites. Our purpose was to drive the reaction towards 3-buten-1-ol which upon dehydration forms 1,3-butadiene; an important chemical used in the production of synthetic rubber. Zn-ZSM-5 showed very promising results as 3-buten-1-ol is selectively (60% selectivity) formed, while the extent to five carbon products considerably decreased. The reaction between formaldehyde and isobutene was also studied in the presence of Zn-ZSM-5. In this case the target product is 3-methyl-3-buten-1-ol which dehydrates to isoprene; the synthetic monomer of natural rubber. The catalyst was highly selective achieving up to 92% selectivity. Most importantly, we also formed isoprene in one-step showing great potential of this process.

[1] M. Yamanaka and K. Mikami, *Helvetica Chimica Acta*, 85 (2002) 4264

[2] P. C. Bloys van Treslong Prins, *Chem. Weekbl.* 1919, 1510

[3] D. R. Adams and S. P. Bhatnagar, *Synthesis* 10 (1977) 661

POSTER PRESENTATIONS



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Reverse Water-Gas Shift Iron Catalyst Derived from Fe_3O_4

Chen-Yu Chou
Advisor: Raul F. Lobo

CO_2 is the most widely known global warming gas. Conversions of CO_2 to fuels and chemicals offer opportunities to mitigate the increasing CO_2 buildup. Hydrogenation of CO_2 , particularly reverse water-gas shift (RWGS) reaction, to intermediate chemicals or fuels such as CO is a feasible and valuable process with this regard [1]. One of the major challenges is that the conventional Cu-ZnO catalyst is temperature-sensitive while high temperature in endothermic RWGS reaction is preferable[2,3].

In this work, unsupported iron oxides, specifically magnetite (Fe_3O_4), were used as a catalyst for the RWGS reaction at temperatures between 723 K and 773 K. This catalyst exhibited fast catalytic CO formation rate ($35.1 \text{ mmol h}^{-1} \text{ g}^{-1}$), high turnover frequency ($2.33 \times 10^6 \text{ s}^{-1}$), high CO selectivity (>99%), and high stability. Reaction rates over Fe_3O_4 catalyst displayed a strong dependence on H_2 partial pressure (reaction order of 0.79) and a weaker dependence on CO_2 partial pressure (reaction order of 0.33) under equimolar flow of both reactants. X-ray powder diffraction patterns and XPS spectra reveal that the bulk structure of the post-reaction sample was mostly metallic Fe and Fe_3C while the surface contained Fe^{2+} , Fe^{3+} , metallic Fe, and Fe_3C . The activity test on pure Fe_3C (iron carbide) suggests that Fe_3C may not be the major active sites. Gas-switching experiments (CO_2 or H_2) indicated that a redox mechanism is the predominant reaction pathway, but the inverse kinetic isotope effect suggested a secondary pathway for CO formation, which is probably the so-called associative mechanism. Potential reaction mechanisms for this reaction were analyzed.

- [1] W. Wang, S. Wang, X. Ma, J. Gong, Recent advances in catalytic hydrogenation of carbon dioxide, *Chem Soc Rev.* 40 (2011) 3703–3727.
- [2] J.A. Loiland, M.J. Wulfers, N.S. Marinkovic, R.F. Lobo, $\text{Fe}/\gamma\text{-Al}_2\text{O}_3$ and $\text{Fe-K}/\gamma\text{-Al}_2\text{O}_3$ as reverse water-gas shift catalysts, *Catal. Sci. Technol.* 6 (2016) 5267-5279.
- [3] D.H. Kim, S.W. Han, H.S. Yoon, Y.D. Kim, Reverse water gas shift reaction catalyzed by Fe nanoparticles with high catalytic activity and stability, *J. Ind. Eng. Chem.* 23 (2014) 67–71.

Copper(I)-Catalyzed Enantioselective Alkynylation of Oxocarbenium and Iminium Ions to set Diaryl Tetrasubstituted Stereocenters

Srimoyee Dasgupta
Advisor: Mary P. Watson

The primary focus of our research group is to develop new synthetic methodologies that utilize the power of transition metal catalysis. Transition metal catalysis has transformed the field of synthetic organic chemistry by enabling new and highly efficient reactions with exceptional control over regio- and enantioselectivity. Most transition metal catalysis relies heavily on neutral electrophiles, but we envisioned that it could also be efficiently used with cationic electrophiles to solve significant, long-standing challenges in organic synthesis. In particular, few methods are available for enantioselective additions to cyclic ketoxocarbenium and ketiminium ions to form diaryl, *tetrasubstituted* stereocenters. Harnessing our success in developing a copper-catalyzed addition of terminal alkynes to oxocarbenium ions to deliver isochromans with *tertiary* stereocenters,¹ we have now developed a highly enantioselective, copper(I)/PyBox-catalyzed addition of terminal alkynes to isochroman ketals to set diaryl-substituted quaternary stereocenters.² The success of this transformation relies on identification of a Cu/PyBox catalyst capable of distinguishing two aryl substituents on the forming stereocenter, which differ predominantly in their freedom of rotation and by their relationship to the oxygen substituents (alkyl vs lone pair). This highly challenging transformation enables the efficient conversion of readily available, racemic ketals to high-value, enantioenriched isochroman products, presumably via prochiral oxocarbenium ion intermediates. Reaction optimization, scope of both the ketal and alkyne, and elaboration of products will be presented.

We were also able to use this potent copper(I)/PyBox catalyst to develop an enantioselective, copper(I)-catalyzed alkynylation of ketiminium ion intermediates to deliver tetrahydroisoquinolines with tetrasubstituted α -stereocenters in high yields and enantioselectivities. Select substrate scope and elaboration of products in this method will also be presented.

We are currently investigating how the chiral copper/Pybox catalyst imparts enantioselectivity in these reactions. Initial mechanistic experiments elucidating the structure of the active catalyst as a dicopper acetylide species and further reactions inspired by these methods will also be discussed.

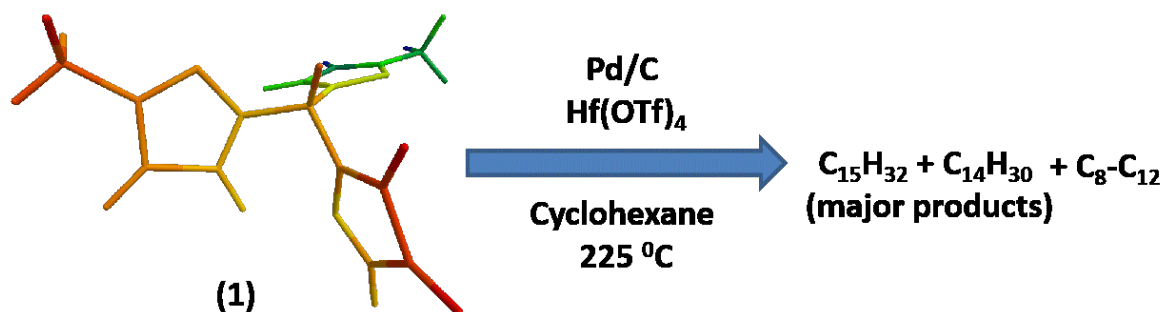
1. (a) Maity, P.; Srinivas, H. D.; Watson, M. P. *J. Am. Chem. Soc.* **2011**, *133*, 17142; (b) Srinivas, H. D.; Maity, P.; Yap, G. P. A.; Watson, M. P. *J. Org. Chem.* **2015**, *80*, 4003.
2. Dasgupta, S.; Rivas, T.; Watson, M. P. *Angew. Chem. Int. Ed.* **2015**, *54*, 14154.

Hydrodeoxygenation of Long-Carbon Trifurylmethane into Jet Fuels with Pd/C-Hf(OTf)₄

Dr. Saikat Dutta

Advisor: Prof. Basudeb Saha, Prof. Dionisios G. Vlachos

Beyond fossil-based hydrocarbons such as heavy oil, shale gas, and oil sands that protect global fossil fuel production, constituted development of renewable alternatives to petrochemicals production not only reduces dependence on finite crude oil but also take us one-step ahead for an energy secure future.¹ To overcome logistic problems of replacing fuel infrastructures that is already in place, accessing linear and branched alkanes for transportation fuel from biomass-derived molecules will be desired strategy.² Controlled removal of oxygen-containing functional groups from these biomass-derived molecules using common reagents and catalysts offer alkanes in good yields and high selectivity.³ Catalytic defunctionalization of oxygen groups by reducing C-O bonds to C-H bonds known as hydrodeoxygenation (HDO) which increases energy density of the resulting molecule by reducing oxygen contents. Here, we describe the catalytic HDO of a long carbon trifurylmethane (C₁₅) derivative (1) using palladium on carbon (Pd/C) as catalyst in combination with hafnium triflate (Hf(OTf)₄) in cyclohexane which offers C15 and C14 alkanes as major products (Scheme 1). We reveal the roles of Pd nanoparticles on carbon support and Hf(OTf)₄ for the HDO of (1). Time profile of obtained products and intermediates and additional experimental results suggests the reaction progresses via rapid hydrogenation of (1) to a saturated furan derivative which then transformed to alkane products via ring-opening-oxygen removal event.



Scheme 1. HDO of trifurylmethane (1)

References:

1. Murray *et al.* *Nature* **2012**, 481, 433.
2. King *et al.* *ACS Catal.* **2015**, 5, 1223.
3. Sutton *et al.* *Nature Chem.* **2013**, 5, 428.

Heterogeneous Catalytic Route towards Succinic Acid from Biorenewable Tartaric Acid

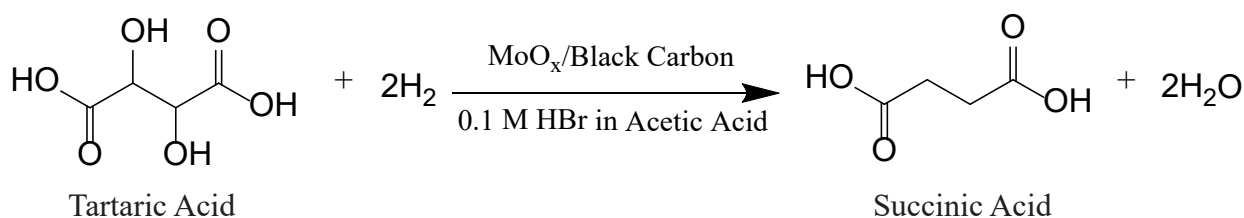
Jiayi Fu

Advisor: Dionisios G. Vlachos

Succinic acid (C₄H₆O₄), a 4-C dicarboxylic acid, is recognized by DOE as one of the top value-added platform chemicals that can be derived from biomass.¹ It can replace malic acid and malic anhydride to produce valuable commodities chemicals, such as tetrahydrofuran, γ -butyrolactone and 1,4-butanediol.² In industry, the production of succinic acid relies on fossil fuels, which brings negative impacts on environment and energy security.³ Fermentation has been proposed as a renewable alternative with a better environmental footprint, yet the process is not economically complete due to the high purification cost.^{2,4}

Here, we propose a heterogeneous catalytic route to succinic acid using tartaric acid (C₄H₆O₆) as the substrate. Tartaric acid occurs naturally in grapes and can be recovered from the waste of winery industry.⁵ In this study, we show that in a mixture of hydrobromic acid and acetic acid partially reduced molybdenum oxide is an effective hydrodeoxygenation (HDO) catalyst that can selectively cleave the C-O bonds at C2 and C3 positions of tartaric acid. Currently, the best yield is 67% at 170 °C under 40 bar of hydrogen. A time evolution study as well as controlled experiments using intermediate species and products as reactants provide insights into the reaction pathways and mechanism, which can guide in depth understanding and efficient process design.

Scheme 1. Production of succinic acid from the HDO of tartaric acid.



- (1) Werpy, T. and Petersen, G. *Top Value Added Chemicals from Biomass*; **2004**.
- (2) Carlson, A.; Coggio, B.; Lau, K.; Mercogliano, C.; Millis, J. **2016**; pp 173–190.
- (3) Gallezot, P. *Chem. Soc. Rev.* **2012**, *41* (4), 1538.
- (4) Cheng, K. K.; Zhao, X. B.; Zeng, J.; Wu, R. C.; Xu, Y. Z.; Liu, D. H.; Zhang, J. A. *Appl. Microbiol. Biotechnol.* **2012**, *95* (4), 841–850.
- (5) Versari, A.; Castellari, M.; Spinabelli, U.; Galassi, S. *J. Chem. Technol. Biotechnol.* **2001**, *76* (5), 485–488.

Mechanistic Insights into the Ring Opening of Biomass-Derived Tetrahydrofuran-2,5-Dicarboxylic Acid to Adipic Acid

Matthew J. Gilkey

Advisors: Bingjun Xu and Dionisios G. Vlachos

Adipic acid (AA) is an essential precursor in the polymer industry, primarily for its use in the synthesis of Nylon-66. However, AA's current production method, which relies on the selective oxidation of petroleum-derived cyclohexane, contains several drawbacks including the emission of N_2O , a potent greenhouse gas. In effort to create a sustainable route to AA, significant research effort has been dedicated to develop pathways from biomass-derived platform chemicals through selective hydrodeoxygenation. Of particular interest is the hydrogenolytic ring opening of tetrahydrofuran-2,5-dicarboxylic acid (THFDCA) to AA. By reacting THFDCA in a mixture of hydriodic acid (HI) and molecular hydrogen in an organic acid solvent, an AA yield of up to 87% yield can be achieved in the absence of a metal catalyst. Through a combination of experimental and theoretical contributions, we reveal key mechanistic insights into the hydrogenolysis mechanism, noting that the nature of the solvent is critical in maintaining high ring opening activity. Due to the corrosive nature of HI and organic acids, however, the development of active, heterogeneous catalysts is desired to take the place of HI. Here, I will present our mechanistic understanding of HI-mediated ring opening and our ongoing work in designing solid materials for effective AA production.

Solvent Effects on Zeolites: Liquid Phase FTIR Extinction Coefficient Determination

Nicholas Gould
Advisor: Bingjun Xu

Fundamental understanding of solvent effects, including how solvent choice affects catalyst structure, catalyst acidity, and product distributions is still lacking. To provide insight, attenuated total reflection (ATR) Fourier transform infrared spectroscopy (FTIR) was used to study the in-situ interactions between solvent, substrate, and catalyst. Specifically, pyridine was used as a probe molecule to characterize the relative ease of protonation in commonly used solvents. This has been used to understand how solvent choice affects substrate protonation and activity in Brønsted acid catalyzed reactions.

However, the FTIR technique is limited by its inability to quantify adsorbed and bulk species. Quantitative FTIR requires integrated molar extinction coefficients (IMEC), or the amount of signal per mole of adsorbed or bulk species. A method has been established for vapor phase IMECs,¹ but liquid phase IMECs are still missing. A simple method is outlined for calculating extinction coefficients of pyridine adsorbed on zeolites in the liquid phase in an ATR cell. The same technique is also applicable to other substrates than pyridine. Liquid phase IMECs allow for future quantification of adsorbates in the liquid phase, improving the robustness of the ATR-FTIR technique, and opening the door to quantitative studies of how solvent choice affects substrate protonation by zeolites and other solid acids. The extinction coefficients for pyridine adsorbed on Brønsted and Lewis acid sites in water, ethanol, and acetonitrile were derived. The IMEC values are shown to be dependent on solvent choice, but independent of zeolite framework. These values will be used to quantify protonated pyridine in commonly used solvents. A Brønsted acid catalyzed dehydration reaction in these solvents will be used to correlate the protonation to activity. This

The ATR-FTIR technique also showed the probe molecule, pyridine, getting protonated on sodium faujasite (NaY) in the presence of liquid water.² This is an example of how ATR-FTIR detected a solvent induced modification of catalyst surface structure. The NaY was shown to be crucial to the production of protonated species in water and to the accumulation of pyridinium in its pores. This is an occurrence usually only associated with proton form zeolites, such as HY.

1. Emeis, C. A. *J. Catal.* 141, 347–354. 1993.
2. Gould, N. S.; Xu, B. *J. Catal.* 342, 193–202. 2016.

Group Contribution Method for Solvation Free Energy Estimation of Aliphatic Alcohols on Metal Surface

Geun Ho Gu

Advisor: Dionisios G. Vlachos

Catalytic renewable biomass conversion has been projected as the key technology by U.S. Department of Energy as it is the only renewable technology to produce carbon-based products. Concerning this issue, theoretical investigation has been shown in the past to provide useful insights into reaction mechanisms of catalytic cycles, and, furthermore, predict an efficient catalyst for a target process. However, these applications fall short for the biomass conversion study as the biomass feedstock is often in aqueous phase and the simulation of the solvent environment is expensive for quantum mechanical calculations.

In this contribution, we present a fast estimation method for solvation free energy of aliphatic alcohol adsorbates on metal surface. In this work, we compute the solvation free energy of 164 molecules and adsorbates using newly developed polarizable continuum method (PCM) for the simulation of solvation environment. Using experimental values, we validate that the PCM method is reliable (mean absolute error of 2.00 kcal/mol or 0.09 eV). Using the computed solvation free energy as a training set, we present a group contribution method for the solvated adsorbates on metal surface for the first time. Our model is reliable (max absolute error of 3.59 kcal/mol and mean absolute error of 0.54 kcal/mol) and reduces the expensive solvation quantum mechanical calculations time to less than an hour.

Reaction Pathways and Intermediates in Selective Ring Opening of Biomass-Derived Heterocyclic Compounds by Iridium

Dr. Glen R. Jenness
Advisor: Dionisios G. Vlachos

As the chemical economy gradually shifts from fossil fuels to renewable resources, it becomes important to develop technologies to upgrade renewable platform molecules to final products of industrial relevance. It has been shown the renewable heterocyclic molecules 5-hydroxymethylfurfural and furfural, can be produced in high yields by depolymerizing and dehydrating lignocellulosic biomass. These heterocyclics can undergo reduction of their side groups with a subsequent hydrogenolysis to produce liquid fuel additives and value added products for the chemical industry. Selective hydrogenolysis of these heterocyclic molecules at the C–O bond in the aromatic ring has been shown to be a viable route towards the production of long-chain hydrocarbons, alcohols, and polyols. The selective hydrogenolysis of furfural can result in the production of 1,5-pentanediol (1,5-PeD), a valuable precursor for the production of polyesters and polyurethanes, with current research showing iridium to have a high selectivity for this process.

While the hydrogenolysis of cyclic compounds to long chain alcohols and polyols has been known for decades, the factors that control the selectivity remain either unknown or debated. It has long been thought the hydrogenolysis of aromatic cyclic compounds proceeds after saturation of the aromatic ring; however recent studies have shown that full ring saturation is not required. Furthermore, any aromatic ring side groups are capable of undergoing reduction and oxidation, and the impact of such reactions on the selectivity are unknown. In the current study, we combine density functional theory and high resolution electron energy loss spectroscopy (HREELS) to probe the hydrogenolysis of saturated and unsaturated heterocyclic molecules. The reduction of the aromatic ring side group in conjunction with the selective hydrogenation of the aromatic ring shifts the selectivity towards either terminal or secondary diols, with the selectivity being determined via the rearrangement of the electronic density of the aromatic π -system. Furthermore, there is a competition between the kinetics and thermodynamics governing the hydrogenolysis, indicating a strong temperature and time effect on the selectivity. Comparison of DFT and HREELS spectra allow for several key intermediates to be identified and characterized on the Ir(111). These insights may allow for the development of more efficient catalysts and processes that can render renewable chemicals commercial.

Metal/Metal Oxide Cooperativity for Selective C-O Bond Activation

Alexander V. Mironenko
Advisor: Dionisios G. Vlachos

Selective C-O bond scission is a key step for a variety of industrial processes ranging from Fischer-Tropsch synthesis to valorization of biomass. Recently discovered multifunctional metal/metal oxide catalysts (e.g., Rh/MoO_x, Ir/VO_x) exhibit unusual activity and selectivity for C-O bond hydrogenolysis at temperatures < 200°C. Here, we combine density functional theory calculations, electronic structure analysis and microkinetic modeling to develop comprehensive insights.

We describe a highly efficient mechanism of carbon-oxygen bond activation on metal/metal oxide multifunctional catalysts [1], which potentially reconciles the contradiction between low C-O bond scission activities, exposed by models and surface science experiments, and high experimentally observed reaction rates. We employ catalytic transfer hydrogenolysis chemistry of furfural to 2-methyl furan on a Ru/RuO₂ catalyst as an illustrative example due to its importance in the production of renewable fuels and chemicals. Unexpectedly, we discover an oxygen vacancy-mediated reverse Mars-van Krevelen-type radical mechanism that explains the high catalyst activity. Radical mechanisms are ubiquitous in various catalytic high temperature oxidations of, e.g. methane or propylene; yet, to our knowledge, this is the first study introducing the radical *reduction* mechanism in heterogeneous catalysis at low temperatures in the liquid phase. We describe electronic properties of both the catalyst and the key reaction intermediate that contribute to facile chemistry and overcome energy scalings. Finally, we find the mechanistic picture to be fully consistent with isotopic labeling experiments and kinetic studies. Given the importance of heterogeneous catalysis for tailored bond-breaking in energy production and storage, we believe that our discovered mechanism provides an important step toward development of low temperature processes catalyzed by surfaces.

References:

1. Mironenko, A.V.; Vlachos, D.G. *J. Am. Chem. Soc.*, **2016**, 138 (26), pp 8104–8113

Optimization of transition metal catalyst structure for the oxygen reduction reaction

Marcel Nunez

Advisor: Dionisios G. Vlachos

Descriptor-based models provide a powerful and exciting approach to catalyst screening by creating activity maps. These maps typically assume that the catalyst surface is uniform and the active site is known a priori. These assumptions fail for structure sensitive chemistries, such as the oxygen reduction reaction (ORR). We develop an approach which resolves the catalyst structure atomistically by identifying the active site and the density and spatial arrangement of such sites. Simultaneously, we estimate the surface energy in order to address catalyst stability. Activity and stability are optimized simultaneously using a multi-objective optimization methodology which exhaustively searches for suitable structures. In doing so, we predict the structure of the active site. We apply this methodology to the ORR on defected Pt(111), Pt(100), Au(111), and Au(100) surfaces. It is shown that defects increase the activity of each surface but by much less than would be predicted using the volcano plot. The benefit of producing sites of higher activity is offset by thermodynamic and geometric constraints, rationalizing why only a modest increase in activity is seen experimentally. In addition, we show that Pt and Au behave differently. Au activity is increased by lower-coordinated edge sites whereas Pt benefits from high-coordinated cavity sites. Our approach to finding the active site while imposing stability constraints has profound implications for catalyst design of structure sensitive reactions.

Catalytic Effects of Transition Metal Oxide Surfaces on Diels-Alder Cycloaddition between Furan and Methyl Acrylate: A DFT Study.

Taha Salavati-fard
Advisor: Douglas J Doren

Using density functional theory with periodic boundary conditions, we study the catalytic effects of oxide surfaces such as ZrO_2 and HfO_2 on Diels-Alder reaction between biomass-derived furan and methyl acrylate. The cycloadduct can be dehydrated later to produce methyl benzoic which is an important step toward benzoic acid production. The gas-phase and on-surface reaction mechanisms are studied in detail. The surface hydration effects on the reaction mechanism and energy profile are studied as well. Our calculations show that the transition metal oxide surfaces catalyze the reaction significantly through the interaction of metal sites with the electron-poor reactant (methyl acrylate). The calculations are interpreted by making use of electronic density of states and band structure of the catalyst.



Methane non-oxidative coupling to ethylene on Mo₂C/[B]ZSM-5

Huibo Sheng, Edward P. Schreiner, Weiqing Zheng
Advisor: Raul F. Lobo

Effective utilization of methane is of great interest and importance to the chemical industry because of the rapid growth of shale gas production and lower cost of this raw material.^[1] Due to the high chemical stability of methane, much effort has been devoted to convert methane to higher hydrocarbons, such as ethylene. Non-oxidative coupling of methane to ethylene is a promising alternative to generate a carbon stream that can be fed directly into the existing structure of the chemical industry. Here we report on a fundamental investigation of methane coupling on molybdenum carbide nanoparticles supported on non-acidic [B]ZSM-5.

Mo/H-[Al]ZSM-5 based catalysts are a well-studied group of materials for the methane dehydrogenative aromatization reaction.^[2] This reaction is thermodynamic limited with only 12% equilibrium conversion of methane at 700 °C. The accepted reaction mechanism involves a two steps process with ethylene as a key intermediate species. The second step, from ethylene to benzene, is an acid catalyzed reaction occurring on the zeolite acid sites.

In this work, boron is employed instead of aluminum in the zeolite framework, leading to a drastic reduction in the zeolite acidity. After calcination, mono and binuclear Mo oxide species were anchored onto the zeolite surface, as deduced from analysis of UV-vis spectra that yielded an energy band gap of ~4.1 eV.^[3] After carburization the catalyst show good selectivity towards ethylene (~90%).^[4]

- [1] T.V. Choudhary, E. Aksoylu, W.D. Goodman. *Cat. Rev.* 45(2003), 151-203.
- [2] L. Wang, L. Tao, M. Xie, G. Xu, J. Huang, Y. Xu. *Catal. Lett.*, 21(1993), 35-41.
- [3] R. S. Weber. *J. of Catal.* 151(1995): 470-474.
- [4] H. Sheng, E. P. Schreiner, W. Zheng, R. F. Lobo, 2016 (in preparation).

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