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Speaker : Prof. Fuat Celik

*Department of Chemical and Biochemical Engineering
Rutgers, The State University of New Jersey, Piscataway, NJ*

***Bridging the Gap: Heterogeneous Catalysis by
Homogeneous Catalysts***

Graduate Student Speaker: Lina Lee

*Department of Chemical and Biomolecular Engineering, University of
Delaware*

***Theoretical study of ethylene hydroformylation on
atomically dispersed Rh/Al₂O₃ catalysts: Reaction
mechanism and influence of ReO_x promoters***

Meeting Schedule:

6:30 PM: Networking Time
7:00 PM: Opening Remarks
7:05 PM: Student Speaker
7:20 PM: Main Speaker

Meeting Fees:

Free to CCP Members

Meeting Etiquette:

Please remember to mute your
microphone and arrive early to
solve any technical issues.

Webinar Registration:

Please register online by
Wednesday, March 24th using
this [LINK](#) or notify Arrangements
Chair [Jian Chang \(CJ\)](#).

**A webinar meeting invite will be
provided on March 24th to all
those who register.**

Membership:

Dues for the 2020-21 season will
be \$25 (\$5 for the local chapter
and \$20 for the national club).
Dues for students, post-docs and
retirees will be \$10 (\$5 for local
club and \$5 for national club).
Use this [LINK](#) for membership
registration.

Catalysis Club of Philadelphia

Webinar: 6:30pm EST, Thursday, March 25th, 2021

Webinar link shared after registration

Bridging the Gap: Heterogeneous Catalysis by Homogeneous Catalysts

Prof. Fuat Celik

Department of Chemical and Biochemical Engineering

Rutgers, The State University of New Jersey, Piscataway, NJ

Abstract:

Homogeneous and organometallic catalysts play an important role in a limited number of industrial processes, including methanol carbonylation and hydroformylation. In these examples, the high activity and selectivity of the catalysts outweigh the complexities associated with large-scale homogeneous catalysis. Molecular catalysts are otherwise limited by the requirement of a compatible solvent, separation of the homogeneous catalyst from solution containing reactants and products, low thermal stability and recyclability, and high sensitivity to environmental conditions such as exposure to air and water. Proposed schemes to support or anchor organometallic catalysts have had mixed results, and typically decompose to form metal particles or leach from the support.

Our lab has successfully anchored pincer-ligated iridium complexes to high surface silica via surface condensation reaction, forming a covalent bond between the catalyst and the support. In this way, we have isolated iridium atoms on the surface with high accessibility for reaction, avoiding a common drawback when using nanoparticles of very precious metals. We have demonstrated that these catalysts are effective for continuous butane dehydrogenation in the gas-phase in a heterogeneous catalytic reactor, with no loss of activity with time on stream at temperatures up to 340 °C, at least 100 °C higher in temperature than observed in the liquid phase. Infrared and x-ray absorption spectroscopy confirm that the molecular structure of the catalyst is retained under these high temperatures, and electron microscopy reveals immobilized catalysts that are freely rotating around the anchoring bond. Mechanistic studies show that the catalytic behavior is nearly identical to that observed in the liquid phase, indicating that a truly heterogeneous organometallic catalyst has been achieved.

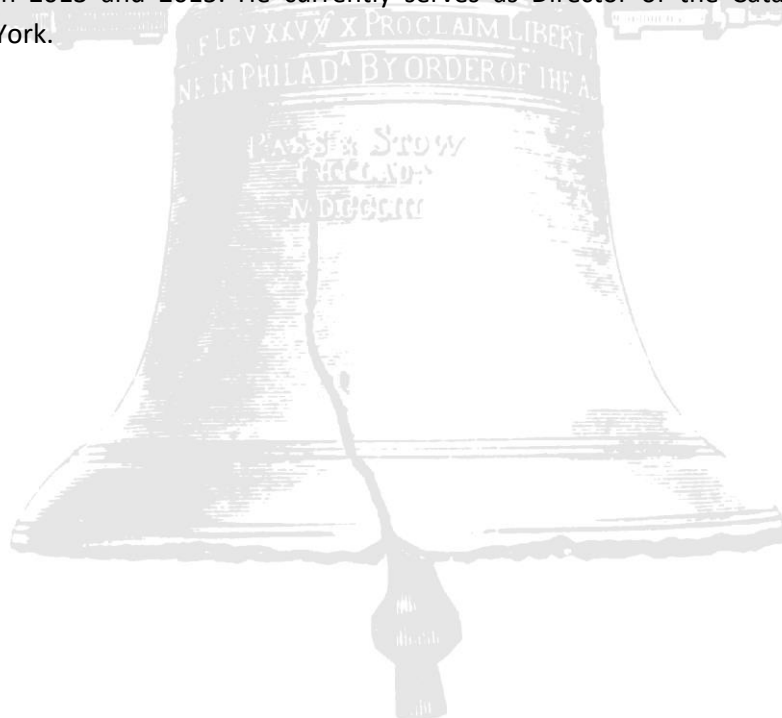
However, there is a major difference observed in the supported catalyst. NMR and infrared spectroscopy indicate the formation of a carbonyl ligand attached to iridium at temperatures above 200 °C. The role of CO is complex. While CO is typically a catalyst poison, in this system CO has another role. It helps prevent the iridium metal from interacting with the surface of the support. Such interactions lead to catalyst deactivation and eventual decomposition. At higher temperatures above 340 °C, this protective CO ligand was lost, deactivation ensued.

Additionally, the CO ligand could be generated from either ethylene and HCl ligated complexes under reaction conditions. The protective effect of the CO ligand also extends to handling: it is air-stable and can be safely handled under ambient conditions, so the catalyst can be handled similarly to other heterogeneous catalyst powders.

Speaker's Biography:



Fuat E. Celik is Associate Professor and Graduate Program Director of Chemical and Biochemical Engineering at Rutgers, The State University of New Jersey. Research in his group involves experimental and computational (DFT) investigation of the relationship between the nanoscale structure and composition of a catalyst and its macroscopic performance, with applications focused on renewable and alternative energy. He holds his B.S.E. (2002) and M.Eng. (2003) degrees from Princeton University, and his Ph.D. from the University of California, Berkeley (2010), all in Chemical Engineering. From 2003 to 2004, he worked at the Princeton Environmental Institute, Princeton University as a Research Assistant building technoeconomic models of biomass and coal conversion systems producing renewable and alternative fuels and electricity. His Ph.D. experimental work with Alexis T. Bell was on acid-catalyzed carbonylation over zeolites and heteropoly acids, for which he was awarded a patent. From 2010 to 2012, he worked on computational investigation of binary metal alloys with Manos Mavrikakis at the University of Wisconsin-Madison as Postdoctoral Research Assistant. He has been awarded the A. Walter Tyson Assistant Professorship in 2014 and the Rutgers School of Engineering Teaching Excellence Award in 2013 and 2015. He currently serves as Director of the Catalysis Society of Metropolitan New York.



Theoretical study of ethylene hydroformylation on atomically dispersed Rh/Al₂O₃ catalysts: Reaction mechanism and influence of ReO_x promoters

Lina Lee

Department of Chemical and Biomolecular Engineering, University of Delaware

Abstract:

Hydroformylation is an important industrial process for synthesis of aldehydes from olefins and synthesis gas.¹ It is performed homogeneously over Rh or Co complexes, a process that is cost-intensive due to recycling and loss of catalyst through leaching.¹ An approach to mitigate these drawbacks and maximize metal efficiency is to utilize atomically dispersed Rh atoms on supported oxides.² Recent work has demonstrated that singly dispersed Rh atoms supported on ReO_x-modified γ -Al₂O₃ can enhance selectivity for ethylene hydroformylation to propanal, whereas Rh atoms on pristine γ -Al₂O₃ selectively catalyze hydrogenation to ethane.³ The enhanced selectivity and activity of the ReO_x-modified γ -Al₂O₃ surface has been attributed to weaker binding of CO to the Rh atoms, manifesting itself in blue-shifted CO stretching vibrations relative to those of Rh-CO complexes on unmodified γ -Al₂O₃. It has been hypothesized that Rh atoms vicinal to ReO_x particles are more cationic.

Here we first characterize the electronic properties of Rh atoms on γ -Al₂O₃ and ReO_x-modified γ -Al₂O₃ surfaces. We explore numerous binding sites, compute IR spectra and compare to the experimentally observed blue-shift in the CO spectra. By analyzing the electron density and the density of states, we conclude that there is indeed less Rh to CO π -back-donation in the presence of ReO_x. Furthermore, we perform mechanistic studies and microkinetic analysis of an extensive reaction network to gain insights into the enhanced selectivity of Rh atoms on ReO_x-modified γ -Al₂O₃ surfaces for ethylene hydroformylation. We reproduce experimental selectivity trends and kinetic parameters and reveal that selectivity to hydroformylation is due to an interplay between coordination geometry and electronic structure

References:

1. Franke R. et al. *Chem. Rev.*, doi. 10.1021/cr3001803 (2012).
2. Amsler J. et al. *J. Am. Chem. Soc.*, doi. 10.1021/jacs.9b12171 (2020).
3. Ro I. et al. *ACS Catal.*, doi. 10.1021/acscatal.9b02111 (2019).

Speaker Biography:

Lina is a third-year Ph.D. student at the University of Delaware working with Prof. Dion Vlachos. Lina received her Bachelor's of Science degree from the University of Texas at Austin in Chemical Engineering and worked in the offshore industry as a Process Design Engineer for 3 years before starting the Ph.D. program. In between, she obtained a Master's degree in Energy at Texas A&M University, which allowed her to explore various aspects of the energy sector. Her education and professional experience working in the oil and gas industry propelled her to pursue a career in green energy, which brought her to catalyst research at University of Delaware. Her current research interests lie in investigating single-atom catalysts for selective chemistries, such as hydroformylation or hydrodeoxygenation reaction, which are ineffective and hence not practiced on pristine metal or metal-oxide catalysts.