The Catalysis Club of Philadelphia

(In Person) Thursday, September 21st, 2023

Brandywine Plaza Hotel
630 Naamans Road, Claymont, DE 19703

Ab initio and machine learning models to infer catalytic reaction mechanisms

Speaker: Prof. Srinivas Rangarajan

Lehigh University

Investigation of Crystallization of LTA Zeolite Catalyst Using Raman Spectra

Student Speaker: Song Luo

University of Delaware

Meeting Agenda:

Social Hour ..... 5:30 PM
Dinner ..... 6:30 PM
Meeting ..... 7:30 PM

Meeting Registration:

Members: $45.00
Non-Members: $55.00
Stud. & Retired Members: $35.00

Please register online for this In-person meeting by ***Thursday, September 7th*** at CCP website.

Meal Selection (Included):

Please make one selection for your dinner (included in registration) when you sign-up for the meeting from the following options:

1. Entrée 1 — Baked Flounder
2. Entrée 2 — 6 oz Grilled Fillet
3. Entrée 3 — Vegan: Grilled Vegetables
4. Entrée 4 — Vegetarian: Pasta Dish

Membership Registration:

Membership dues for CCP 2023-24 meeting 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 the local club and $5 for the national club). Please sign-up membership (Link) for more benefits on meeting registrations and net-working events!

Please contact our Treasurer Steve Hardwick (sjh.wilm.de@gmail.com) or Chair Angela Zheng (angela.zheng@matthey.com) if you need any assistance.

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September 21st, 2023

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Prof. Srinivas Rangarajan

Ab initio and machine learning models to infer catalytic reaction mechanisms

Department of Chemical & Biomolecular Engineering, Lehigh University

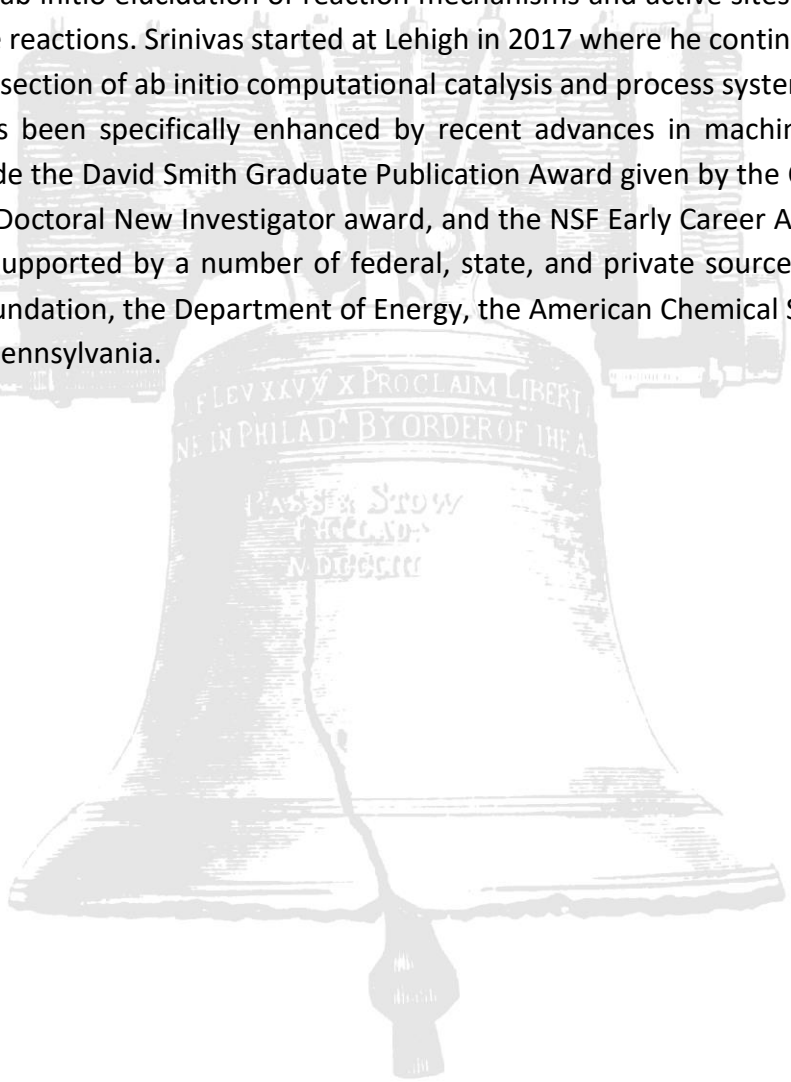
Abstract: Mechanistic models of heterogeneous catalytic systems enable addressing questions pertaining to the active sites and reaction mechanism, i.e., where and how the reaction proceeds on a catalyst. These insights further allow for designing new catalytic formulations and ultimately designing new processes. In this context, we employ ab initio techniques and experimental data to build mechanistic microkinetic models of the reaction system; we also apply machine learning approaches to learn kinetic and thermodynamic properties that allow us to model and infer the reaction mechanisms.

First, the talk will discuss the basics of "ab initio microkinetic models" for catalytic systems. Second, I will show two recent examples from our group wherein microkinetic modeling, along with a host of allied tools, has allowed us to infer the mechanisms of catalytic reactions. In particular, I will discuss epoxidation of ethylene on silver catalysts where we used density functional theory (DFT) and microkinetic modeling, in conjunction with experiments, to show that the surface is oxidic under reaction conditions which enriches the plausible network of surface reactions than previously thought. I will also present our recent work on elucidating the effect of zeolite confinement on a prototypical Diels-Alder reaction via microkinetic modeling. Further, using a machine learned model, I will discuss which geometric factors of the adsorbate and zeolite influence the loss in entropy (and hence the degrees of freedom) and change in free energy upon adsorption of the reactant.

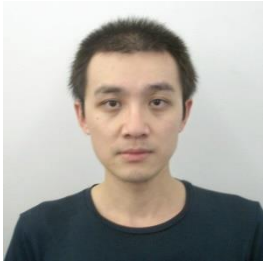
Finally, given the plethora of varied data that are becoming available in catalysis, I will present our group's vision of a data-driven modeling paradigm for catalysis.

Speaker Bio:

Dr. Srinivas Rangarajan is an Associate Professor and Dolores and William Schiesser faculty fellow in the Department of Chemical & Biomolecular Engineering at Lehigh University. He received his PhD at the University of Minnesota from 2008 – 2013 under the advisorship of Profs. Prodromos Daoutidis and Aditya Bhan, for developing techniques to study complex reaction networks. He then spent three years as a postdoc at the University of Wisconsin at Madison with Profs. Manos Mavrikakis and Christos Maravelias, moving on to problems on microkinetic modeling as well as ab initio elucidation of reaction mechanisms and active sites of a number of catalytic and surface reactions. Srinivas started at Lehigh in 2017 where he continues to carry out research at the intersection of ab initio computational catalysis and process systems engineering; this intersection has been specifically enhanced by recent advances in machine learning. His recent awards include the David Smith Graduate Publication Award given by the CAST division of the AIChE, ACS PRF Doctoral New Investigator award, and the NSF Early Career Award. Srinivas's research has been supported by a number of federal, state, and private sources, including the National Science Foundation, the Department of Energy, the American Chemical Society, and the Commonwealth of Pennsylvania.



Investigation of Crystallization of LTA Zeolite Catalyst Using Raman Spectra



Song Luo

Advisor: Prof. Dongxia Liu, University of Delaware

Understanding the formation mechanisms of nanoporous catalysts such as zeolites, which can open the door to tailoring materials for advanced applications in catalysis and separations, has remained a tantalizing challenge. Discovering how zeolites form is complicated by the fact that zeolite precursor structures fall into a nanoscale blind spot — too large for atomic-level and functional group structural analyses by methods like IR and NMR, and too disordered for X-ray diffraction — necessitating characterization methods sensitive to medium-range structures such as rings and larger building units. Raman spectroscopy has emerged as a powerful tool for probing medium-range structures in a variety of materials including disordered silica, zeolites, MOFs, and zeolite precursor solutions. However, despite significant research into the Raman spectra of zeolites, the detailed assignments of such Raman spectra are not completely understood, though it is often assumed that Raman bands can be assigned to individual ring structures. In this presentation, we report a systematic zeolite synthesis, spectroscopy, and periodic DFT study of several all-silica zeolites to determine the fundamental structural motifs that explain Raman spectral features. We have discovered from normal mode analysis that Raman peaks can be assigned to tricyclic bridges – three zeolite rings that share a common Si-O-Si bridge. A precise anti-correlation between Raman frequency and Si-O-Si angle has been determined. Raman study was performed on siliceous LTA synthesized in the presence of F-. It was discovered that F--filled double-4-ring (F-/D4R) and empty D4R exhibit distinct Raman features. The Raman band density of F-/D4R and empty D4R can be used to quantify the distribution of these two different D4R units in the final LTA zeolite and during the zeolite crystallization. Understanding the Raman signature of the F-/D4R units and difference between the F-/D4R and empty D4R opens an interesting new window for studying the roles of F- during zeolite formation, control nanopore hydrophobicity and design syntheses of zeolites with new structures and compositions.

Speaker Bio

Dr. Song Luo is a postdoctoral researcher in the Department of Chemical and Biomolecular Engineering at the University of Delaware. He earned a B.S. in Chemical Engineering and Technology from Sichuan University in 2012, and a PhD in Chemical Engineering from the University of Massachusetts-Amherst in 2022, where he worked with Prof. Wei Fan and Prof. Scott M. Auerbach to study zeolite crystallization mechanisms by integrating simulated and experimental Raman spectroscopy. Currently, in his postdoctoral period he is researching plastic waste decomposition using mesoporous zeolite catalysts with Prof. Dongxia Liu, to achieve a circular economy for plastics. As of

today, he has published 14 papers, including Journal of the American Chemical Society (as a cover paper), Chemistry of Materials, et al.