CATALYSIS CLUB OF PHILADELPHIA

Promoting Catalytic Science and Technologies

The Catalysis Club of Philadelphia

Webinar: 7 PM, Thursday, March 24th, 2022

Zoom link shared after registration

Speaker: Prof. Alexander Orlov

Stony Brook University

Student Speaker: Sanjana Srinivas

Meeting Schedule:

6:30 PM EST: Welcome
7:00: Talk by Sanjana Srinivas
7:25: Talk by Prof. Orlov
8:30: Meeting adjourns

Meeting Fees:

Free to all who register

Meeting Etiquette:

Please remember to mute your microphone and arrive early to solve any technical issues. Camera sharing prior to the talks is encouraged.

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Online Registration – Please register online by Wednesday, March 23rd at http://catalysisclubphilly.org/webinar-registration/ or Arrangements Chair, hrenjing@seas.upenn.edu.

A Zoom meeting invite will be provided through the confirmation email. If you do not receive a confirmation email immediately after registration, please contact Renjing Huang, hrenjing@seas.upenn.edu.

Membership – Dues for the 2021-22 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).

Development of a New Generation of Stable, Tunable, and Catalytically Active Nanoparticles Produced By the in-Situ and Ex-Situ Synthesis Methods

Nanoparticles (NPs) are revolutionizing many areas of science and technology, often delivering unprecedented improvements to properties of the conventional materials. However, despite important advances in NPs synthesis and applications, numerous challenges remain. Development of alternative synthetic method capable of producing very uniform, extremely clean and very stable NPs is urgently needed. If successful, such method can potentially transform several areas of nanoscience, including environmental and energy related catalysis. Here we present the latest developments in demonstration of catalytically active NPs synthesis achieved by the helium nanodroplet isolation method. This alternative method of NPs fabrication and deposition produces narrowly distributed, clean, and remarkably stable NPs. The fabrication is achieved inside ultralow temperature, superfluid helium nanodroplets, which can be subsequently deposited onto any substrate. This technique is universal enough to be applied to nearly any element, while achieving high deposition rates for single element as well as composite core -shell NPs. In addition, our work also involves development of a new generation of doping-segregation method on nanoparticle synthesis. Here we studied behavior of dopants by various in-situ characterization techniques including environmental TEM, complemented by such in-situ techniques as XAFS, XRD and DRIFTS. More specifically, we investigated the effect of such conditions as reduction temperature on the size of nanoparticles. In collaboration with Prof. Chen group at Columbia we then applied this method to prepare very active and selective catalysts for CO_2 reduction by reverse water gas shifts reaction.

Biography

Dr. Alexander Orlov is a Professor of Materials Science and Chemical Engineering at State University of New York, Stony Brook, USA. He is also a faculty member of the Consortium for Interdisciplinary Environmental Research, an affiliate faculty of the Chemistry Department and the Institute for Advanced Computational Science at Stony Brook University. Dr. Orlov's principal research and teaching activities are in the development of novel materials for energy generation, structural applications and environmental protection. The majority of his research focuses on synthesis of novel catalytic nanomaterials and tuning their properties for environmental and energy related applications. Dr. Orlov was awarded the US National Science Foundation CAREER Award and the UK National Endowment for Science Technology and Arts CRUCIBLE award. He was also selected to the Fellowship of the UK Royal Society of Chemistry, the US National Academy of Engineering (NAE) Frontiers of Engineering (US), the EU-US (NAE) Frontiers of Engineering and was made Kavli Fellow in 2014 by the Kavli Foundation and the US National

Academy of Sciences. In 2016 Dr. Orlov was named Sigma Xi Distinguished Lecturer and was recognized by the State University of New York with Chancellor's Award of Excellence in Scholarship and Creative Activities. In addition to research awards, Dr. Orlov has received several teaching awards, including 2018 American Institute of Chemical Engineers (AIChE) SEF Education Award, 2017 American Chemical Society Award for Incorporating Sustainability into Chemistry Education and 2015 NAE Frontiers of Engineering Education selection. His commercialization efforts have been recognized by the R&D 100 Award, often referred to as the "Oscar of Innovation", and the 2021 AIChE Sustainable Engineering Forum Industrial Practice Award. Dr. Orlov serves on the editorial boards of Chemical Engineering Journal and Materials Letters. In addition, Dr. Orlov is Chair of the AIChE Environmental Division, immediate Past Chair of the American Institute of Chemical Engineers (AIChE) Research and New Technology Committee (RANTC) and Alternate Councilor of the American Chemical Society (ACS) Environmental Chemistry Division.

Spin-crossing in heterogeneous catalysis by atomically dispersed transition metals. An example: Ethane dehydrogenation by Co/SiO_2

Sanjana Srinivas

University of Delaware

Supported atomically dispersed metals and sub-nanometer metal clusters have been garnering attention on account of their efficient metal utilization and the high activity and selectivity they impart to several reactions. Of particular interest is the dehydrogenation (DH) of small alkanes to alkenes, as the latter are used in the synthesis of several commodity chemicals and the recent shale gas boom in the US has made dehydrogenation economically viable.

Common catalysts of the reaction are Pt-Sn alloys and alumina-supported chromium oxides, both of which have several shortcomings such as the high cost of Pt and the toxicity of Cr- based catalysts (Cr^{6+}). The burgeoning activity in replacing supported Pt-group metal atom/sub-nanometer cluster catalysts with earth abundant metals is driven by the lower biological toxicity and cost of the latter. Experimental reports have demonstrated that highly dispersed Co(II) on am-SiO_2, both as single sites and sub-nanometer CoO_x clusters, exhibit high activity and selectivity for alkenes (>95%), under oxidative and non-oxidative reaction conditions.[1-3]

Here, we use DFT calculations and microkinetic modelling to explore the theoretical efficiencies due to spin-crossing kinetics shown by Co and other earth abundant 3d metal catalysts, of varying nuclearity, for small alkane DH. We develop reaction mechanisms and rank them in kinetic importance using micro-kinetic analysis for single-site Co(II)/SiO_2 and di-nuclear Co(II)/SiO_2 active sites. Our microkinetic analysis shows that the reaction rate on the di-nuclear site is much higher than the rate on the mononuclear site and we explain this difference by comparing the π-donor strength of the ligands. We argue that the lower barriers associated with spin- crossing kinetics can be attributed to the flexibility of the am-SiO_2 substrate, which allows the Co(II) coordination to change from tetrahedral to square planar. Finally, we construct an ensemble of single- site models with varying degrees of distortion and calculate the Fukui indices to understand the implication of active site heterogeneity on the reaction barriers.

[1] Lee, S. *et al. Nature communications* **10**, (2019)
[2] Estes, D. P. *et al. Journal of the American Chemical Society* **138**, 14987-14997, (2016).
[3] Hu, B. *et al. Journal of Catalysis* **322**, 24-37, (2015).

Speaker Bio

Sanjana is a 3rd year PhD candidate in the Vlachos group at the University of Delaware, with broad interests in computational chemistry for the rational design of catalysts. Her current research in the Vlachos group focuses on the kinetics and dynamics of supported atomically dispersed transition metals for small alkane dehydrogenation. Prior to joining the University of Delaware, Sanjana completed her undergraduate studies in Chemical engineering at IIT Madras, India, where her research focused on fabricating dye sensitized solar cells and supercritical fluid deposition.