UCLA College | Physical Sciences Chemistry & Biochemistry

Chem 218: Student Exit Seminar

"Rewriting the Rules of Heterogeneous Catalysis for Supported Subnanometer Metal Cluster Catalysts"

By Borna Zandkarimi
Prof. Anastassia Alexandrova Group

We showed that the catalyst structure in the subnano regime should be viewed as an evolving statistical ensemble of many structures, undergoing continuous structural dynamics under reaction conditions, such as high temperatures and pressures, and changing adsorbates. This view reforms the accepted models and calls for a new theory and modeling approaches in catalysis, as well as revised design strategies. I will show how scaling relations, most typically used in catalysis literature break down in sub-nano regime. Next, as chemically distinct states of the catalyst (characterized by distinct reaction kinetics) get populated at rising temperatures, the Arrhenius plot might become nonlinear. Hence, I proposed a modification to the Arrhenius equation using an ensemble-average representation. Finally, while operando XANES spectroscopy is a highly valuable and frequently used tool for cluster catalyst characterization in reaction conditions, I showed that spectra interpretation requires a revision for the dynamic catalysts that operate as ensembles. Instead of using bulk standards, the more accurate spectral fit can be done by using calculated spectra of computed ensembles of supported clusters. The approach gives excellent fits and insight into the spectrum-composition-structure relation.

One example where this theory was applied to an experimentally studied system are silica and alumina-supported sub-nano Pt clusters nano-alloyed with Sn. Alloying suppresses both sintering and coking of Pt_n clusters on these supports in conditions of thermal dehydrogenation. The effect can be explained on the basis of quenching electronic spin in the entire thermal ensemble of Pt_n cluster catalysts, by which adding Sn closes most of the reaction paths toward deeper dehydrogenation.

Thursday, October 22nd, 2020
12:00 p.m. (PDT)

For questions, please contact: jzabala@chem.ucla.edu