V.G.13 Sub Nanometer Sized Clusters for Heterogeneous Catalysis

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Program Scope

Providing sustainable sources of energy, chemicals, and materials is one of the most important long-term issues facing society. Catalysis plays a central role in creating sustainable sources of energy through efficient transformations of hydrocarbon resources. Our quality of life depends on myriad products that involve a catalytic step at some point in their manufacture. It is widely accepted that chemical catalysis is a major economic driver in both the U.S. and world economies, with estimates as high as ~35% of the world's gross domestic product arising via catalytic processes. Due to this significant commercial impact, there is a heavy demand for rare and expensive transition metals whose pricing and availability is at risk due to increasing geopolitical pressures. As our resource base shifts to alternate energy sources such as natural gas or biomass, there will be a need to develop new catalysts for converting these materials. Our project focuses on sub-nanometer (nm) clusters, of size <30 atoms, which provide unusual reactivity and selectivity for catalytic reactions. The objective of our project is to improve methods to tailor surfaces of high surface area supports to anchor platinum group metals (PGM). Heterogeneous catalysis using nanoparticles of PGMs is highly developed, but the science of using ionic forms of these metals as heterogeneous catalysts is still in its infancy. New methods only recently available allow us to study these atomically dispersed metals. Catalysis using single isolated atoms provides the highest atom efficiency for conducting catalytic reactions. As we learn how to obtain desired catalytic properties in these tailored catalysts, we will develop a fundamental understanding of how catalyst activity and selectivity can be improved. This understanding will allow us to create more selective and energy efficient processes for catalytic transformations. The atomically dispersed catalysts developed here will be ideally suited for reactions of interest to the DOE as described in the "Basic Research Needs: Catalysis for Energy" report. Atomically dispersed PGMs tend to coarsen and form sub-nm clusters. Stabilizing these structures under industrial operating conditions is a challenge. The proposed research will help advance the science of anchoring single metal atoms and sub-nm clusters on high surface area supports.

FY 2016 Highlights

Our FY 2016 accomplishment includes the fundamental understanding of the roles of tin (Sn) in stabilizing and re-dispersing Pt and elucidation of the roles of sub-nm sized palladium (Pd) in the promotion of activity and stability of iron (Fe)-based catalysts.

Alumina-supported Pt is one of the major industrial catalysts for light alkane dehydrogenation. This catalyst loses activity during reaction, with coke formation often considered as the reason for deactivation. As we recently demonstrated, the amount and nature of carbon deposits do not directly correlate with the loss of activity. Rather, it is the transformation of sub-nm Pt species into larger Pt nanoparticles that appears to be responsible for the loss of catalytic activity. Surprisingly, a portion of the Sn remains atomically dispersed on the alumina surface in the spent catalyst and helps in the redispersion of the Pt. In the absence of Sn on the alumina support, the larger Pt nanoparticles formed during the reaction are not redispersed during oxidative regeneration. It is known that Sn is added as a promoter in the industrial catalyst to help in achieving high propene selectivity and to minimize coke formation. We have shown that an important role of Sn is to help in the regeneration of Pt, by providing nucleation sites on the alumina surface. Aberration-corrected scanning transmission electron microscopy helps to provide unique insights into the operating characteristics of an industrially important catalyst by demonstrating the role of promoter elements, such as Sn, in the oxidative regeneration of Pt on γ-Al_2O_3.

Hydrodeoxygenation (HDO) of phenolic compounds is an important model reaction in understanding the fundamental and application of catalysis in lignin-based biofuel production. Recently, Fe has emerged as a promising catalyst for HDO of phenolics, due to its low cost and high selectivity in C-O bond cleavage. However, Fe's low HDO activity and poor stability under HDO conditions has limited its application. We have recently developed an efficient approach to promote Fe's activity and stability without altering its unique selectivity in HDO of phenolics, by doping noble metals such as Pd onto the Fe catalyst surface.

A series of noble metal doped Fe catalysts were tested in HDO of m-cresol. Noble metals remarkably promoted Fe's activity and stability, while maintaining Fe's high C-O bond cleavage selectivity. The Pd-on-Fe nanostructure with sub-nm Pd clusters on a reduced Fe surface in a Pd-Fe catalyst was evidenced by high resolution scanning transmission electron microscopy and pseudo in situ X-ray photoelectron spectroscopy (XPS). A direct C-O bond cleavage mechanism, in which m-cresol decomposes on Fe surface into C_7H_7* and OH* species and the formed species further reacts with H atoms to form toluene and water, respectively, was proposed based on density function theory calculation and kinetic modeling. Kinetic modeling and in situ ambient pressure XPS results suggested that the Fe catalyst surface is dominated by OH* species, which ultimately lead to a deactivation of the Fe catalyst. Addition of Pd to Fe significantly changes its kinetics by creating new sites for H_2 activation and new reaction pathways via reaction between H activated on Pd sites and C_7H_7* and OH* on Fe sites, as suggested by kinetic modeling. As a result, the surface of Pd-Fe is no longer dominated by OH*, and catalyst deactivation by water-induced oxidation is thus avoided.