Nanostructural Features that Govern Effective Oxidation Reactions in Liquid Phase with Gold-based Catalysts

Kimberly N. Heck, 1 Yiyuan Ben Yin, 1 Zhun Zhao, 1 Michael S. Wong 1,2,3,4,5,*

(1) Department of Chemical & Biomolecular Engineering
(2) Department of Chemistry
(3) Department of Civil & Environmental Engineering
(4) Department of Materials Science & NanoEngineering, Rice University, Houston, TX, USA
(5) Nanotechnology Enabled Water Treatment (NEWT) Center

Gold catalysts have long been studied for selective oxidation of organic compounds, thought to be due to their lower oxophilicity compared to other oxidation catalysts (e.g. Pt or Pd), but often suffer from low activity. To improve activity and prevent over oxidation, bimetallic catalysts which combine gold with a more active metal have been investigated. Through a combination of geometric and electronic effects, these catalysts have improved activity, selectivity and/or durability compared to their monometallic counterparts. To better understand structure-activity relationships in bimetallic catalysts, we use our metal-on-metal model catalytic materials with well characterized surface structures. For example, our Pd-on-Au NPs consist of a Au NP core decorated with submonolayer amounts of Pd atoms (Figure 1). By varying the amount of Pd added, we can create Pd surface structures ranging from isolated Pd monomers on the Au, to 2D islands, and even 3D ensembles. Recently, we used these NPs to study the selective oxidation of alcohols (glycerol 1,2 or functionalized glucose 3) to fine chemicals. While in both cases all bimetallics synthesized were more active and selective than monometallic analogs, we found that Pd-on-Au NPs with 80% surface coverage of Pd were the most active (Figure 1). The metal-on-metal catalysts were also remarkably selective to partially oxidized intermediates, possibly due to the decreased production of H₂O₂ byproduct. In situ X-ray absorption spectra suggests that Au exerts an electronic effect on Pd, stabilizing it from forming Pd-O which is less active and prone to deactivation. These studies offer valuable insights into the selective oxidation of alcohols in water.

Figure 1. Initial TOF vs Pd-on-Au NP surface coverage for glycerol oxidation. 0.2 g catalyst, 60 °C, 1000 rpm stirring rate, 107 mL, 0.1 M glycerol, 0.4 M NaOH, and 120 mL min⁻¹ O₂ flow. Schematic of model Pd-on-Au NP catalysts.

References

Corresponding author email: mswong@rice.edu