



Chemical Engineering Spring 2023 Seminar Series

Organic Species, Alloys, and Support Identity Control the Transformation of H_2 , O_2 , and H_2O over Metal Nanoparticles



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4:15-5:00pm
4:00pm Reception

Direct reactions of H_2 and O_2 show promise for producing H_2O_2 , an environmentally benign oxidant used for bleaching, disinfection, and selective oxidations. Understanding how catalytic surfaces convert H_2 and O_2 can improve yields of H_2O_2 formation while guiding the design of materials for other redox reactions involving H-atom transfer. Herein, we examine the role of solvent molecules, alloy structures, metal-support interfaces, and surface redox mediators during transformations of H-H, O-O, and O-H bonds at the solid-liquid interface of noble metal nanoparticles. A combination of DFT calculations, in situ spectroscopy (XAS, FTIR), isotopic analysis, and kinetic measurements as a function of reactant activities and electrochemical potential suggest H_2O_2 forms by solvent-mediated proton-electron transfer paths resembling electrochemical oxygen reduction and hydrogen oxidation. Catalytic surfaces that present low barriers of hydrogen oxidation (Pd, Pt) increase reaction rates, while high barriers of O-O dissociation improve H_2O_2 selectivity. Consequently, alloying Pd or Pt with elements like Au, S, or H can create isolated sites of Pd or Pt that stabilize O-O bonds and favor H_2O_2 formation. Conversely, metal-support interfaces consisting of reducible metal-oxides (Au-La₂O₃) favor the cleavage of O-O bonds, while more acidic metal-support interfaces (Au-SiO₂) improve selectivity to H_2O_2 . Surface-bound redox mediators with carbonylic functions (CH_2O^* , quinones) introduce paths that improve rates and selectivities of H_2O_2 formation relative to clean Pd surfaces. Furthermore, this work informs the design of catalytic structures that heterolytically activate H_2 and O_2 with broad applications in hydrogenation and oxidation reactions at solid-liquid interfaces.

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