

Designing, Constructing, and Uniformly Accessing Arrays of Clusters of Atomically Precise Composition for Heterogeneous Catalysis of Chemical Reactions

Joseph T. Hupp

Dept. of Chemistry, Northwestern University, Evanston, IL 60093, U.S.A.

For many gas-phase chemical and condensed-phase electrochemical reactions, rate acceleration by heterogeneous catalysts is indispensable. Such catalysts often rely upon precious-metal components. Further, they often comprise non-uniform collections of active sites, i.e. sites presenting differing facets, geometries, and/or numbers of functional atoms, situated on non-uniform supports and residing in non-uniform chemical & physical environments. Non-uniformities can greatly complicate both characterization of catalyst structures and elucidation of catalysis mechanisms. The resulting uncertainties weaken links between theory and experiment, obscure structure/activity correlations, and impede exploitation of computational methods to design or discover superior catalysts. Desirable would be much more chemically & structurally ideal collections of heterogeneous catalysts.

This presentation focuses on the synthesis of uniformly supported and distributed arrays of catalytic clusters having atomically precise compositions. Array organization is based upon installing clusters into size-matched pores of crystalline metal-organic framework (MOF) materials. Notably, the employed MOFs are reasonably thermally stable (~580K in air) and chemically robust (e.g., retention of crystallinity & porosity following prolonged exposure to steam or corrosive media). Catalysts of most interest to us are: a) polyoxometalates (POMs), presented in gas-phase environments, and b) previously unknown polythiometalates (PTMs) that are functionally reminiscent of enzymes having competency for reduction reactions. Representative catalytic reactions are CO₂ to methanol; semi-hydrogenation of alkynes via H₂-derived, sulfur-vacancy-stabilized, metal hydrides; and electrochemical reduction of ¹⁵N₂ to ¹⁵NH₃ at ambient temp. and pressure, via the intermediacy of water-derived hydrides. DED (difference electron density) measurements inform about catalyst accessibility and about active-site steric & chemical environments. Detailed catalyst structural information is obtainable from *disordered* arrays by combining the results of computational modeling (Getman, Ohio State Univ.) and experimental pair-distribution function analysis of total-X-ray-scattering (Chapman, Stony Brook Univ.). Rxn. rates, orders, and product distributions; *operando* spectroscopy; and DFT modeling, provide information about catalytic mechanisms and inform design of new catalysts.