The Reaction Specificity of Nano Particles in Solution

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Iron-based metallic and oxide nanoparticles have been shown to have enhanced reactivity towards a variety of chemical species, including chlorinated hydrocarbons and reducible oxyanions, which frequently contaminate ground water at DOE and other government and industrial sites. Possibly of greater importance is the ability of these nanoparticles to select specific reaction pathways, potentially facilitating the formation of more environmentally acceptable reaction products. Since iron-based nanoparticles are oxidized by the surrounding water and the contaminant species, the ability of the particle surface and protective coatings to mediate or control the relative reaction rates has a major impact on the reactions that take place and the ultimate productive lifetime of the particles. It is useful to understand the impact of particle evolution or diagenesis on the reaction properties as a function of time. *The objective of this project is to develop a fundamental understanding of the mechanism(s) responsible for the overall particle reactivity and reaction selectivity of iron-based metallic, bimetallic, and oxide nanoparticles.* To achieve this objective the project is organized around three major tasks: 1) synthesis (using solution and vacuum synthesis methods) and characterization of well-defined nanoparticles, 2) measurements of particle reactivity in solution or vacuum environments, and 3) theory and modeling efforts to rationalize particle structure and reactivity. Results to date show that the nature of the nanoparticle coating can make a factor of four or more difference in the production of toxic versus non-toxic products during reduction of carbon tetrachloride [Nurmi et. al. Env. Sci & Tech. 39 (2005) 1221-1230]. Measurements of particles at different stages of reaction with pure or contaminant-bearing water show that the processes that control contaminant degradation evolve with time. A major focus of the current research is on the nature of the particle changes with time and the impact on reaction pathways. Particle and surface characterization techniques include high-resolution transmission electron microscopy, x-ray photoelectron spectroscopy, electron paramagnetic resonance spectroscopy, and synchrotron-based x-ray absorption spectroscopy (bulk and microscopic). Theoretical and model system studies are designed to unravel molecular-level contaminant dissociation and the impact of the oxide on the process. A self-consistent self-interaction-corrected density functional theory is being applied to the understand charge transport in oxide shells.

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