Single Nanoparticle Surface Chemistry: Structure-Reactivity Relationships, Evolution During Reactions, and an Approach to Ultra-High Temperature Surface Chemistry.

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Abstract

Nanoparticles and materials composed of nanoparticles (NPs) are inherently heterogeneous, with variations in size, shape, and distributions of reactive sites. This talk will explore the kinetics for oxidative etching and growth reactions of *individual* carbon and silicon NPs, tracking changes in reactivity as the NP structure evolves under reaction conditions.

O_2 oxidation of carbon NPs varies significantly between NP from different feedstocks (graphitic, graphene oxide, diamond, carbon black, nano-onions), as might be expected. There are also order-of-magnitude variations of reactivity between different NPs from the same feedstock, reflecting variations in the distributions of under-coordinated surface sites. Furthermore, the reactivity of individual NPs evolves non-monotonically in time as the NPs etch, with rate fluctuations of up to 3 orders of magnitude. Eventually, all carbon NPs evolve to become nearly inert to O_2, signaling that the surface layer(s) have transformed to multiwall fullerene-like structures with no under-coordinated reactive sites.

For silicon (and SiO_x) NPs, we are able to study oxidation over a temperature range from 1200 to 2500 K, spanning the bulk melting points of both silicon and silica. Oxidative etching involves several interacting processes, including O_2 chemisorption, SiO desorption, silica nucleation and growth, and diffusion between the NP surface and core. Because each of these processes depend differently on temperature, the oxidation etching of silicon-based NPs can have quite complex time dependence. For example, at temperatures (e.g. 1200 K) well below the silicon melting point (T_{melt} = 1683 K), the etching mass loss rate is initially low, accelerating as etching progresses, but eventually dropping several orders of magnitude to ~zero as the NP surface grows a passivating silica layer. At temperatures closer to the melting point (e.g. 1500 K), the oxidative mass loss rate starts high and remains high as the NP loses 15 – 30% of its initial mass, then abruptly drops to near zero as the surface passivates. For temperatures above T_{melt}, the etch rate begins to decrease immediately upon O_2 exposure, but it never drops to zero, i.e., the NP surface never passivates.

One of the features of this method is that the upper temperature possible is limited only by the sublimation rate of the particle's material. Thus for Si, it is straightforward to examine temperatures well above T_{melt}. For ultra-high temperature ceramic materials, it is possible to study surface chemistry at temperatures to well above 3000 K. Oxidation of HfC (T_{melt} ≈ 4200 K), will be used to illustrate this capability.

Examples of carbon NP oxidation measured via single NP mass spectrometry. Top row: NP mass (in Da) vs. time at 1200 K under inert conditions (unshaded background) and oxidizing conditions (cyan background). Note initial fast oxidative etching, but with substantial fluctuations in the mass loss rate. Bottom row: Etching efficiencies (EE_{O2}) plotted vs. NP mass, showing how the etching reactivity varies as the NP etching and isomerizes under oxidizing conditions.