

Elucidating the bimodal acid-base behavior of the water-silica interface from first principles

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Understanding the acid-base behavior of silica surfaces is critical for many nanoscience and bio-nano interface applications. Silanol groups (SiOH) on silica surfaces exhibit two acidity constants—one as acidic as vinegar—but their structural basis remains controversial. The atomic details of the more acidic silanol site govern not just the overall surface charge density at near neutral solution pH, but also how ions and bio-molecules interact with and bind to silica immersed in water. Using ab initio molecular dynamics simulations and multiple representative crystalline silica surfaces, we determine the deprotonation free energies of silanol groups with different structural motifs. We show that previously proposed motifs related to chemical connectivity or inter-silanol hydrogen bonds do not yield high acidity. Instead, a plausible candidate for pKa=4.5 silanol groups may be found in locally strained or defected regions with sparse silanol coverage. In the process, irreversible ring-opening reactions of strained silica trimer rings in contact with liquid water are observed.

Sulfidation of silver nanoparticles

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The focus of this study is on understanding the behavior of coated Ag nanoparticles (Np) under varying environmental conditions (Eh, pH, different solution components and concentrations). A significant effort has been made to characterize corrosion product formation prior to solubility measurements and reactivity studies and in particular the sulfidation process, which is the most likely corrosion phenomenon that might happen in the environment.

Therefore, three sizes of Ag Np coated with PVP (polyvinyl pyrrolidone) were produced using the polyol process (7 ± 1 nm; 25 ± 4 nm and 55 ± 9 nm). The Ag NP samples were reacted with a Na₂S solution with different concentrations so the sulfidation process could be studied step-wise for each particle size. Corrosion products were characterized (SEM, XPS, XRD, surface charge, etc.) after 24 hours of reaction

Based on SEM results, we infer that the sulfidation process is the result of dissolution-precipitation. Moreover, we found that: (i) acanthite (Ag₂S) is formed as a corrosion product; (ii) Ag Np aggregation increased with sulfidation rate; (iii) pH_{PZC} increases with the sulfidation rate; and (iv) the solubility of corroded, sulfidated Ag Np appears to be lower than that of fresh Ag Np.

These results are important to consider in predicting the behavior of Ag Np in natural ecosystems. The aggregation caused by sulfidation may seriously limit their transport in porous media such as soils. Modification of the surface charge during the sulfidation process may have an important impact on electrostatic interactions between the Ag Np and charged phases in soils such as natural organic matter. Finally, the observed decrease in solubility of Ag Np after sulfidation may strongly impact the toxicity of silver since it is well known that Ag⁺ has a greater toxicity than metallic Ag. Sulfidation of Ag Np may limit their transport and toxicity in soils.