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Interfacial chemistry of lanthanides under nano-scale confinement

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We assessed the reactivity of spatially-confined silica-water interfaces using trivalent lanthanides. The ionic radii of lanthanides decrease with increasing atomic number, while the hydration energy increases across the series. We use these systematic variations to quantify how nano-scale confinement affects the kinetics and energetics of adsorption, overall uptake, and coordination environment. We use synthetic mesoporous silicas with 4 nm and 8 nm pore diameters (SBA-15), and non-porous amorphous silica. These substrates were reacted in single adsorbate and in competitive adsorption experiments. The energetics of adsorption on non-porous and porous silica is quantified using flow-microcalorimetry. The local coordination environment for neodymium (Nd), terbium (Tb) and lutetium (Lu) is quantified using synchrotron-based X-ray absorption spectroscopy. The adsorption capacity increases with decreasing ionic radius in both competitive and single adsorbate experiments on non-porous and porous silicas; however, non-porous silica surface is more selective towards heavier lanthanides. On porous silicas, the uptake capacity for heavier lanthanides is independent of pore size. Lighter lanthanides (Nd and Tb) have a higher uptake on SBA-15 with 4 nm pores, compared to SBA-15 with 8 nm pores. To assess the degree of hydrolysis of lanthanide ions at the interface, we used *ab initio* molecular dynamics (AIMD) simulations for europium (Eu) and Lu on the surface of β-cristobalite. The preliminary results indicate inner-sphere adsorption, with each lanthanide hydrolyzing one water molecule upon adsorption onto cristobalite surface.

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