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Book of Abstracts

A quantum chemical and X-ray absorption spectroscopy investigation of arsenic and nickel sorption mechanism on Mn-oxides

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Mn-oxides are important reactive mineral surfaces in terms of heavy metal sorption and redox processes in natural environments. Many spectroscopy techniques such as X-ray absorption spectroscopy (XAS) and Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy have been employed in probing Mn-oxide reaction mechanisms. Meanwhile, computational chemistry is emerging as another power tool for investigations of interfacial reaction mechanisms at a molecular scale. In this study, we combined quantum chemical calculations and XAFS spectroscopy including X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) spectroscopy to elucidate As(III) oxidation /sorption and Ni(II) sorption mechanisms on Mn-oxides. Specifically, we compared the As(III) oxidizing reactivity of Mn(III) and Mn(IV) in birnessite (layered MnO₂) and Ni(II) sorption preferences on birnessite edge sites. Adsorption reaction energies and adsorption geometries were predicted using edge-sharing dioctahedral Mn(III/IV) clusters using density functional theory calculations implemented in Gaussian 03. Theoretical XANES simulations were conducted based on the predicted sorption geometries to compare with experimental XANES.

Results of quantum chemical calculations show that Mn(III) sites are less reactive in terms of As(III) oxidation due to their lower affinity for As(III) adsorption, higher potential to be blocked by As(V) complexes, and slower electron transfer rates with adsorbed As(III). Results from this study offer an explanation regarding the experimental observations of Mn(III) accumulation on Mn-oxides during As(III) oxidation. Quantum chemical calculations predicted that the tridentate-edge (TE) sharing adsorption mode is more stable than double-corner sharing (DC) adsorption on the edge sites of triclinic birnessite, which is consistent with EXAFS results.

Keywords: quantum chemical calculations, XAFS, XANES, Mn-oxides, arsenic, nickel