223e Adsorption of Water in Polyoxoniobate Materials. a Molecular Simulation Investigation

James P. Larentzos, François Bonhomme, May Nyman, and Edward J. Maginn

Polyoxometalates have gained a tremendous amount of attention in recent studies due to their strong binding capabilities and their high stability in acidic conditions. Recently, the polyoxoniobate class of materials have been synthesized, which are especially attractive due to their stability in alkaline conditions, thus making them potentially useful as high-capacity ion exchangers for nuclear waste remediation. Various forms have been synthesized and characterized through single-crystal and powder x-ray diffraction experiments. Although single-crystal x-ray diffraction provides concrete evidence of cation and water locations, powder diffraction can have difficulty in distinguishing between cations and water molecules, especially in instances where they have high mobility and similar scattering lengths.

Molecular simulations can be an extremely powerful tool when used in conjunction with experiments, having the advantage that the positions of cations and water molecules can be unambiguously assigned to crystallographic sites. In this work, an intermolecular force field is developed to describe the nature of the interactions between the cations, water molecules and the polyoxoniobate framework. The electronic structure is computed through density functional theory simulations and extended to classical, force-field based simulations. Molecular dynamics simulations are conducted to assign cation and water locations and also to provide insight into cation stability located in each crystallographic site. In addition, the adsorption behavior of water is investigated through grand canonical Monte Carlo simulations. The water loading in the potassium polyoxoniobate agrees remarkably well with structural refinement estimates obtained through single-crystal x-ray diffraction experiments as well as TGA experiments. Agreement of the sodium analogue is obtained only with TGA experiments, thus demonstrating the apparent limitation of powder diffraction to correctly determine water loading and highlighting the potential of molecular simulations as a tool to provide fundamental, molecular-level insight to any material of interest.