

Baddeleyite surface reactivity in aqueous media: A combined experimental and computational study

MOIRA K RIDLEY¹, FEIXIANG LIU¹ AND MICHAEL MACHESKY²

¹Texas Tech University

²Unaffiliated

Presenting Author: moira.ridley@ttu.edu

Zirconium dioxide materials have long been of interest to industry because of their thermal stability, and stability across oxidizing and reducing atmospheres. Zirconia is used as a catalyst support material and to catalyze hydrogenation and various carbon-containing reactions, including CO and CO₂ adsorption, and methanol synthesis. Application of ZrO₂ extends to solid oxide fuels cells and nuclear waste confinement. Most ZrO₂ applications occur in aqueous environments and rely on acid–base properties of the surface. Surface sites of ZrO₂ hydroxylate readily, even at ambient conditions. Despite significant use and numerous experimental studies, a description of the surface charging behavior of ZrO₂ in aqueous solutions, over a broad temperature range, is incomplete.

This work presents the surface charging behavior of ZrO₂ in NaCl media at 0.03 and 0.3 *m* ionic strength, from 10 to 250 °C. For the study, two potentiometric experimental titration approaches were used. At low temperatures, 10–50 °C, we used a combination glass electrode and autotitrator, whereas titrations from 50 to 250 °C used a hydrogen-electrode concentration cell. The ZrO₂ powder used for all titrations was baddeleyite (monoclinic–ZrO₂) from Tosoh Corporation, TZ Series. Experimental results showed that surface charge increases systematically with increasing temperature and ionic strength, as is typical for metal oxides. The pH_{znpc} values decrease almost linearly from 10 to 150 °C, then decrease slightly to 250 °C. We used surface complexation modeling, following the CD-MUSIC formalism, to interpret the titration data. The combination of potentiometric titrations and surface complexation modeling is routinely used to evaluate pH-dependent surface charging behavior. However, application of CD-MUSIC is most effective when constrained by molecular-scale information.

Thus, we performed molecular simulations focusing on the most stable (-111) ZrO₂ surface. Molecular-level detail for the ZrO₂–water interface was obtained from DFT-MD simulations, using the Vienna *ab initio* simulation package (VASP). The (-111) ZrO₂ surface is complex, with eight distinct surface functional groups (–OH, μ-OH, and μ₃-OH). Six surface sites may protonate/deprotonate and contribute to interfacial H-bonding. The interaction of water molecules with surface atoms and H-bonding were analyzed, with the results used to constrain the surface complexation models.