Structure of Zn^{2+} at rutile TiO_2 (110)-aqueous solution interface

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Recent studies of the adsorption of mono-, di- and trivalent cations to the rutile (110)-water interface established that Zn^{2+} ions adsorb in a manner that is distinct from all other ions studied [1]. In particular, it was observed that Zn^{2+} adsorbs in two distinct sites: primarily above the surface bridging oxygen (BO) sites, and with a smaller amount bridging between terminal oxygen (TO) sites. To understand these observations, we have undertaken a more in-depth investigation of Zn^{2+}-rutile interactions, its partitioning between the two surface sites, and the surface Zn^{2+} coordination environment.

Bragg XSW measurements of rutile (110) in $[Zn^{2+}] = 10^{-5}$ mol/kg solution at pH 6 and 8, using the model independent XSW imaging method, reveal the site distribution of adsorbed Zn^{2+} ions projected into rutile unit cell. Quantitative refined Zn^{2+} positions and the fractional occupations at each position are then achieved with XSW triangulation. Polarized EXAFS measurements in $[Zn^{2+}] = 10^{-5}$ mol/kg solution at pH 8 with X-ray polarization along the rutile [110], [-110], and [001] crystallographic directions reveal the local Zn-O coordination of the adsorbed Zn^{2+}. The results are compared to density functional theory (DFT) calculations of 4- and 6-fold coordinated Zn at rutile (110) –water interface, and the results are discussed in the context of bond valence model.

Reference

[1] Zhang et al. (2004) *Langmuir* **20**(12), 4954-4969.