The chemistry of oxide-water interfaces: a comprehensive account from first-principles simulation studies

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Abstract

Aqueous chemistry at TiO_2 surfaces is of practical and fundamental interest. Materials based on TiO_2 are finding novel use in a host of technologies. Moreover, since TiO_2 is the archetypal metal oxide and water a favorite probe the system has become a prototype for understanding metal-oxide surface chemistry. This is crucial basic science in numerous fields including sensors, catalysis, electrochemistry, batteries and fuel cells, active coatings, corrosion and photochemical applications such as solar cells [1,2]. The theory of systems in the vacuum regime (adsorbates at low coverages) is developing rapidly but first-principles studies of proper oxide-solution interfaces are in their infancy. Indeed, even the theory in vacuum surface science has many gaps that need bridging on route to oxide-solution studies.

Here we discuss our recent work in three areas: improving the theory of low-coverage water adsorption [3]; the chemistry of small molecules at clean and defective TiO_2 surfaces; and the formation and properties of the oxide-water interface. This work relies heavily on first-principles molecular dynamics. We make special efforts to compare with experiment where the latter is available [4], and we will present analyses and predictions of vibrational spectra and temperature programmed desorption measurements. Some of the topics covered will be the details of coverage-dependent adsoption mechanisms, the properties of water chains on the (110) surface (as illustrated in Figure 1) and the reaction of SO_2 and H_2S on clean and defective surfaces (Figure 2). The former present several novel and interesting features because protons become mobile within the structures.

References
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Figure 1. Schematic illustrations of an adsorption process of a third molecule on a fully-hydrated surface. For the hydrated surface, ions are depicted as large open circles (oxygen), small open circles (hydrogen) and filled circles (titanium). For clarity, however, the third molecule is depicted as smaller filled circles. The third molecule is initially positioned above a terminal oxygen. A small arrow is drawn to indicate the proton transfer.

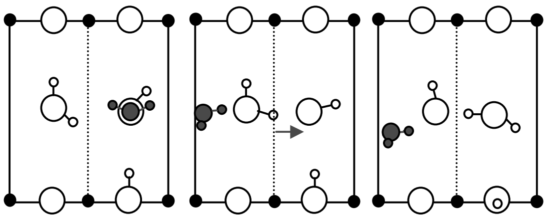
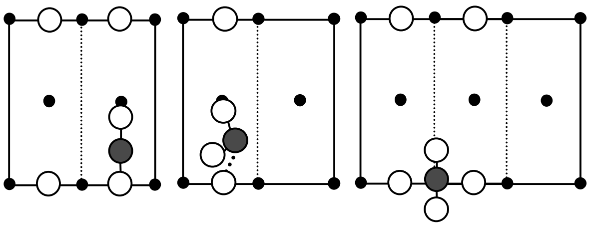


Figure 2. Adsorption structures of SO_2 on defective TiO_2 surfaces. Ions are depicted the same way as that in Fig. 1. Three typical adsorption structures are identified, in which: (a) the SO_2 adsorbs strongly on the defect site with an O sitting on the oxygen vacancy and another O binding to a 5*f* Ti; (b) an O of the molecule bonds to a 5*f* Ti and the S bonds to a bridging O, forming a SO_3-like structure; and (c) the SO_4-like structure formed in a larger unit cell.



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