Adsorption of oxalic acid on rutile surfaces

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Interactions between molecules and solid metal-oxides surfaces play crucial role in many scientific applications. Rutile surfaces are known for their photocatalytic applications, whereas oxalic acid is used in the cleaning and dishwashing products, paints and coatings, and also as surface active agent.

The adsorption of oxalate on rutile was evaluated using macroscopic pH titrations, performed from 10 to 150°C in NaCl media. Oxalate increases the development of proton charge curves; moreover, oxalate adsorption is enhanced at elevated temperature. At all temperatures, adsorption of oxalate commences at pH above the pH_{znpc} value. All experimental results were rationalized using a CD-MUSIC model combination.

From the molecular point of view, oxalic acid $(COOH)_2$ and its deprotonated forms, i.e. hydrogenoxalate (bioxalate) $HOOCCOO^-$ and oxalate $(COO^-)_2$ ions represent the only molecules with a direct bond between two carboxylic carbons. We have optimized the classical molecular dynamics parameters of these molecules to match our AIMD data. Applying the scaled charges and modified vdW parameters according to the Electronic continuum correction (ECC) was found to significantly improve the model performance.

Our models of nonhydroxylated and hydroxylated (110) rutile surfaces were extended to a charge density +0.2 C/m^2, allowing to study the adsorption in the range of pH values between 2 and 12.

The molecular level description of the surface interactions is provided by molecular dynamics simulations yielding adsorbed amount, binding patterns and role of pH. Inner-sphere vs. outer-sphere binding motifs will be discussed and compared with information inferred from published ATR-FTIR spectra.

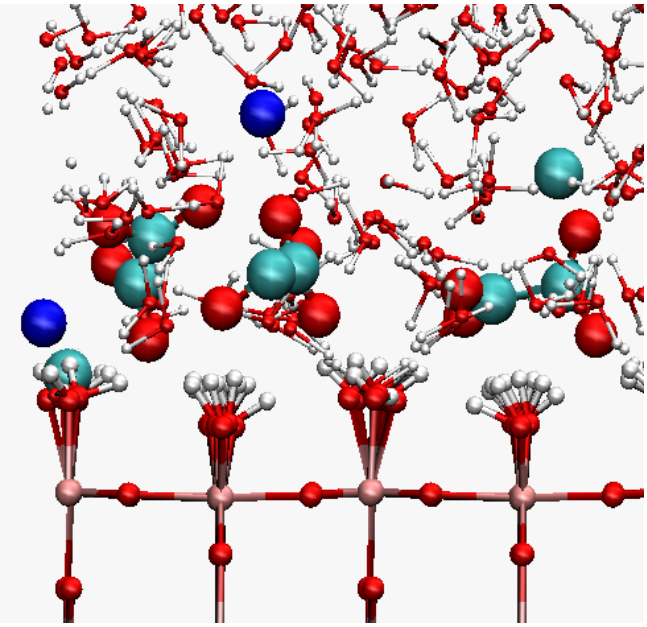

Figure 1: Snapshot of oxalate and bioxalate ions interacting with positively charged (110) rutile surface (+0.2 C/m^2).