

Behavior of Oscillation Modes during Alcohol Adsorption on Rutile TiO₂ (110)

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The surface chemistry of titanium oxides is of crucial interest for many applications ranging from medical implants over dye pigments to catalysts. In the most cases the oxide surface is contaminated by strongly bonded hydrocarbons [1,2] because of the exposition to the ambient air. These contaminants are a mixture of different volatile organic compounds (VOCs) containing small alcohols. Because of the large dwell period of methanol and ethanol [3], these alcohols are assumed to be a major part of the contaminate layer. We present a study of the adsorption mechanism of methanol on Rutile TiO₂ (110) with Car Parinello Molecular Dynamics (CPMD) and Ultra high vacuum – Infrared Reflection Absorption Spectroscopy.

A single methanol molecule was simulated in a vacuum phase over a defective free r-TiO₂ (110) surface. During the first free dynamic simulation the molecule freely moved to the surface, which we assume as the initial step of adsorption. During this period different molecular oscillations were monitored. To decrease the time of adsorption, a fictitious velocity was added to the molecule movement. This fictitious momentum little changed the elongation in the hetero atom bonds, but not the frequency of the stretching vibration. After adsorption the oscillation frequencies of the OH and CO are decreased by 50 – 70 cm⁻¹ and 70 – 80 cm⁻¹. This shift might be explained by a change of the chemical environment and the coordination of the alcohol at the surface.

Unfortunately, studies on oxide single crystals are extremely scarce due to the fact that the sensitivity of reflection IR-spectroscopy for molecular adsorbates is two orders of magnitude lower for oxides than for metal single crystals. Only recently it became possible to overcome these technical problems by employing a novel, advanced spectrometer [4].

Methanol and ethanol were deposited at room temperature and at low temperature (around 130 K) on the surface in analysis chamber and the IR spectra were taken directly.

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