

Abstract template:

Title

Comparative Study of Acetic Acid, Methanol, and Water Adsorbed on Anatase TiO₂ Probed by Sum-Frequency Generation Spectroscopy

Reference

J. Am. Chem. Soc. **2005**, *127*, 9736-9744

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Abstract

Sum frequency generation (SFG) vibrational spectroscopy is used to investigate the surface adsorption of three probe molecules: acetic acid, methanol, and water on a film composed of nanoscale anatase TiO₂ particles. On the TiO₂ surface, only one adsorption mode, chemisorption, is observed for acetic acid. This is evidenced by one sharp SFG peak in the C-H region, which is stable with time and robust both to evacuation and to the addition of water. A Langmuir constant of $(9.21 (\pm 0.71) \times 10^3)$ is determined from the adsorption isotherm. In the case of methanol adsorption, however, there are two adsorption modes, molecular physisorption and dissociative chemisorption. The corresponding SFG signals are stable with time but diminished with addition of water. Changes in the SFG features for methanol and for the methoxy species with addition of water and subsequent evacuation provide the first experimental proof of reversible hydroxylation and dehydroxylation at the TiO₂ surface. For water adsorption, only one mode, physisorption, is observed on the hydroxylated TiO₂ surface. The water adlayer is mobile, as is evidenced by variation of the water H-bonded SFG signal with time. Competitive adsorption among the three molecular probes is clearly resolved by in situ SFG measurements. The adsorption strength follows the order acetic acid (strongest), methanol, water (weakest). The adsorption order as well as the difference in response of methanol versus acetic acid adsorption to addition of water has direct implications for understanding TiO₂ photocatalysis as well as the surface modifications involved in TiO₂ photoelectrochemical solar cells and processes in TiO₂ nanomaterial synthesis and assembly.