

The role of acidic α -hydrogen in the redox (photo)chemistry at titania

Besides oxygen defects mobile Ti^{3+} -defects may be formed in TiO_2 so that TiO_2 -bulk crystals may be self doped with higher concentrations of Ti^{3+} [1]. Accordingly the partly reduced system Ti(III)/Ti(IV) in Titania is an interesting redox pair in heterogeneous catalysis. When adsorbing O_2 at Rutile- $\text{TiO}_2(110)$, reactive species are formed at the surface. Depending on the density of Ti^{3+} -defects and the adsorption temperature the formation of superoxide species $\text{O}_2^{\delta-}$ or $\text{O}_{ad}^{\delta-}$ -atoms may be observed. They partially oxidize Ti^{3+} close to the surface to TiO_2 -islands at temperatures above 360 K and fully above 410 K when bulk Ti^{3+} species diffuse towards the surface [2]. The high affinity of titanium ions towards oxygen also causes activation of oxygen containing organic molecules [3]. Mechanistic studies showed that oxidation and reduction path ways of benzaldehyde and acetone adsorbed at Rutile- $\text{TiO}_2(110)$ probably depend on the presence of α -CH-Atoms in the neighborhood of the keto-group. The C-C coupling reaction of benzaldehyde with subsequent formation of stilbene under reductive conditions is for example depending on the concentration of bulk Ti^{3+} defects [4]. This reaction path is quenched in the presence of coadsorbed oxygen. On the other hand first experiments indicate that the oxidation of acetone containing an α -H in contrast to benzaldehyde not only results in the formation of an intermediate diolate but also undergoes a C-C coupling to a β -hydroxyketone intermediate and OH_{ad} with coadsorbed $\text{O}_{ad}^{\delta-}$. This is apparent from polarisation depending Fourier-Transform-Infrared-Reflection-Absorption-Spectroscopy (FT-IRRAS) [5] and would correspond to an aldol-like equivalent surface reaction, in other words a steering of heterogeneous catalysed redox reactions via acidic hydrogen. The aim of the project is to elucidate this in more detail for thermal and photochemical reactions of ketones, aldehydes and amines with and without coadsorption of oxygen and water at single crystalline Rutile- $\text{TiO}_2(110)$ and surfaces modified with cocatalysts as a function of the density of Ti^{3+} -defects. Methods like FT-IRRAS, thermal desorption spectroscopy (TDS), x-ray photoelectron spectroscopy (XPS) and low energy electron diffraction (LEED) will be used under ultra high vacuum conditions.

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