

O 40: Semiconductor substrates: Adsorption

Time: Tuesday 15:15–15:45

Location: MA 005

O 40.1 Tue 15:15 MA 005

Defect density dependence of partial oxidation and deoxygenation reactions of small organic compounds on rutile TiO_2 (110) surfaces — •LARS MOHRHUSEN, MILENA OSMIĆ, and KATHARINA AL-SHAMERY — Carl von Ossietzky University of Oldenburg, Institute of Chemistry, D-26129 Oldenburg, Germany

Though titanium dioxide is among the most interesting (photo-) catalyst materials, many structural details of the occurring thermic and photo-stimulated reactions remain unclear. For our mechanistic studies under ultra-high vacuum (UHV) conditions we use a rutile TiO_2 (110) single crystal surface to investigate the adsorption and reaction of small organic molecules such as methanol or methylamine with respect to the defect density.

Defect states like bridging oxygen vacancies as well as Ti^{+III} interstitials can easily be introduced to this material via argon ion sputtering and subsequent annealing in UHV. Around 300 K the Ti^{+III} interstitials start to be mobile and can diffuse towards the surface. We shall present our latest results illustrating the importance of such diffusive bulk defects for thermal reactions of organic molecules such as deoxygenation C-C coupling reactions or partial oxidation in different temperature regimes for alcohols in comparison to amines. Furthermore, we demonstrate the importance of different oxygen species present at the surface for these reactions, using low energy electron diffraction (LEED), temperature programmed desorption spectroscopy (TPD)

and in addition Fourier-transformation polarized infrared reflection-absorption spectroscopy (FT-IRRAS).

O 40.2 Tue 15:30 MA 005

Predicting the surface phase diagram of redox-active adsorbates on semiconductor surfaces: The case of ZnO — •MATTI HELLSTRÖM and JÖRG BEHLER — Universität Göttingen, Institut für Physikalische Chemie, Theoretische Chemie, Tammanstr. 6, 37077 Göttingen

We propose an efficient method for calculating surface phase diagrams for redox-active adsorbates on semiconductors, that we apply to the important example of proton (H^+) and hydride (H^-) adsorbates on a ZnO surface [1]. We identify the leading cause for the coverage dependence of the adsorption energies to be the filling and depletion of the disperse substrate conduction band. From only four DFT calculations, coupled with an analysis of the substrate electronic band structure and changes in the electrostatic potential within the substrate upon adsorption, we derive a phenomenological model that well describes the coverage-dependent adsorption energies. We expect that such models can be applied to a wide range of semiconductor substrates and redox-active adsorbates.

[1]. M. Hellström, J. Behler. *Phys. Chem. Chem. Phys.* **19** (2017) 28731