

O 109: Heterogeneous Catalysis on Metal Oxides

Time: Thursday 15:00–17:30

Location: TRE Phy

O 109.1 Thu 15:00 TRE Phy

Photoinduced CO Oxidation on N-doped TiO₂ — ●HELENA GLEISSNER¹, MICHAEL WAGSTAFFE¹, HESHMAT NOEI¹, and ANDREAS STIERLE^{1,2} — ¹DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — ²Fachbereich Physik, Universität Hamburg

Modification of the electronic structure in TiO₂ is a crucial factor for developing more efficient and visible light sensitive photocatalysts [1]. We studied the effect of nitrogen doping on the photoactivity of the rutile (110) and anatase (101) surfaces for the CO oxidation to CO₂ under UV illumination. Rutile (110) and anatase (101) single crystals were doped with nitrogen via ion implantation and their surfaces were characterized using low energy electron diffraction (LEED). The low energy electron diffraction patterns of the doped surfaces reveal no reconstruction. The nitrogen incorporation and CO oxidation were examined by X-ray Photoelectron Spectroscopy (XPS). The CO oxidation was performed at 97 K under UV illumination of 365 nm and the O 1s and C 1s core levels were measured to monitor CO and CO₂ species. On rutile (110), the CO oxidation rate was slightly enhanced compared to the undoped surface, while on anatase (110) the inhibition of the reaction increased with the dopant concentration.

References

[1] Ulrike Diebold, *The surface science of titanium dioxide*, U. Surf. Sci. Rep. 48, 53-229 (2003).

O 109.2 Thu 15:15 TRE Phy

Adsorption of O₂ on the rutile TiO₂(110) surface revisited by nc-AFM — ●IGOR SOKOLOVIĆ¹, MICHELE RETICCIOLI², MARTIN ČALKOVSKÝ¹, MARGARETA WAGNER¹, MICHAEL SCHMID¹, CESARE FRANCHINI², ULRIKE DIEBOLD¹, and MARTIN SETVIN¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²Center for Computational Materials Science, Faculty of Physics, University of Vienna, Vienna, Austria

Rutile TiO₂(110) surface is extensively studied and it is considered a model transition-metal oxide surface [1]. The adsorption of molecular O₂ has been long investigated with various techniques [2], but still even the basic adsorption configurations remain unclear. In this research, we used non-contact atomic force microscopy (nc-AFM) to directly observe the adsorption configurations of molecular O₂ dosed at low sample temperatures. We demonstrate that an oxygen-terminated AFM tip provides excellent lateral resolution, and that it does not perturb the adsorbates. Using density functional theory (DFT) we simulated the observed adsorption configurations and determined the charge state of the adsorbed molecules, which is 2- (peroxo) in all cases. We performed experiments of thermal annealing, charge injection/removal, and ultraviolet light irradiation of the O₂ covered surface. By directly observing the reactants of such experiments, we explain that the rich behavior of O₂ on this surface stems from the differences in the types of the adsorbed molecules, thus answering several long-standing questions. [1] U. Diebold, *Surface science reports* 48, 53 (2003). [2] J. T. Yates Jr, *Surface Science* 603, 1605 (2009).

O 109.3 Thu 15:30 TRE Phy

Computational Scheme for Preparing Realistic Structural Models of Amorphous Metal Oxide Surfaces — ●HANNAH SCHLOTT and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg
Surfaces of metal oxides are often amorphous. The variation in the local environment of the surface sites, which gives rise to a distribution of their chemical and electronic properties, is not captured by using single crystal surface structure models in atomistic simulations. For studying the interaction of real metal oxide surfaces with a liquid or gas phase surrounding, it is therefore of great interest to have a computational scheme for generating amorphous surface structures with accurate and realistic distributions of atomic coordinations and bonding environments. Here we propose a new technique which allows the direct preparation of amorphous surface structures by the melt–quench technique without requiring to cleave amorphous bulk structures. The method also allows a seamless incorporation of other species such as hydroxyl groups into the amorphous surfaces. Using Car-Parrinello molecular dynamics (CPMD) we prepared amorphous ZnO, TiO₂ and Al₂O₃ bulk and surface structures. The reliability of our approach will be demonstrated by a detailed analysis of their structural features such

as radial and angular distribution functions, coordination numbers and binding motifs.

O 109.4 Thu 15:45 TRE Phy

Poisoning by Hydroxylation: Photoreforming of Primary Alcohols on Rutile Titania — ●MARTIN TSCHURL, CARLA COURTOIS, MORITZ EDER, CONSTANTIN WALENTA, and UELI HEIZ — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Some years ago, we reported the catalyst poisoning during the photoreaction of ethanol on a titania(110) single crystal in an ultra-high vacuum atmosphere. In this work, we now focus on the origins of this peculiar reaction property. The comparison of different alcohols enables a closer look into the reaction mechanism, in order to determine the decisive factors for the inhibition of the reaction. For this purpose all steps of the reaction sequence, the alcohol adsorption, the migration of photon-generated charges, the photochemical reaction and the desorption of the oxidized products, are discussed to finally reveal the reason for the poisoning.

O 109.5 Thu 16:00 TRE Phy

Photocatalytic Conversion of Tertiary Alcohols on Rutile Titania — ●CARLA COURTOIS, MORITZ EDER, KORDULA SCHNABL, CONSTANTIN WALENTA, MARTIN TSCHURL, and UELI HEIZ — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

While tertiary alcohols are usually inert towards oxidation, photocatalysis of tertiary alcohols on a bare single crystal rutile titania show new and unexpected reaction pathways. Tertiary alcohols are selectively photo-oxidized on titania at room temperature by a C-C bond cleavage leading to a ketone and the respective alkane. Studies under highly defined vacuum conditions allow elucidating the reaction mechanism and the impact of adding a metal co-catalyst on the product spectrum.

O 109.6 Thu 16:15 TRE Phy

Sum frequency spectroscopy on the surface of semiconductors — ●DENISE FRANZISKA BULLERT, ANUPAM BERA, and ECKART HASSELBRINK — Universität Duisburg-Essen, Universitätsstr. 5, 45117 Essen, Germany

Titanium dioxide (TiO₂) is a versatile material with important applications in environmental purification. Therefore it gained much attention over the last decades. Recently the understanding of adsorbed organic molecules on TiO₂ has made much progress. But little is known about catalytic processes under near-ambient conditions. With a home-made compact cell and the application of sum frequency generation vibrational spectroscopy (SFG-VS) it was possible to address this problem for the first step of a catalytic process. SFG-VS is a powerful method to investigate the chemical identity and structure of adsorbates. Vibrational spectra of adsorbed short-chained alcohols such as methanol (MeOH), ethanol (EtOH) and isopropanol (iPrOH) could be recorded under room temperature and low vacuum conditions. For MeOH and EtOH it was revealed that the molecular species as well as dissociated species are present. In contrast for iPrOH the related spectra show only the molecular species on the surface of the catalyst. The next promising step would be to follow the reaction pathway of catalytically transferred short-chained alcohols under near-ambient conditions. Those kind of studies are also covered by applying SFG-VS because it allows for in-situ spectroscopy.

O 109.7 Thu 16:30 TRE Phy

Low-dimensional projections of high-dimensional kinetic phase diagrams — ●SINA DORTAJ and SEBASTIAN MATERA — Faculty of Mathematics and Computer Science, Freie Universität Berlin

Microkinetic models of heterogeneous catalysis depend on often dozens of kinetic parameters, each showing some degree of uncertainty. This high dimensional parameter space complicates the interpretation phase behaviour if we, ideally, want to take the uncertainty of these parameters into account. Using a first-principles kinetic Monte Carlo model for the CO oxidation on RuO₂(110), we demonstrate how methods from classification can be used to obtain low-dimensional projections

of the original high-dimensional phase diagram on the whole parameter space. For the problem at hand, we find that the original 22-dimensional space can efficiently be mapped onto only two effective dimensions. This then allows for a global picture of the phase behaviour.

O 109.8 Thu 16:45 TRE Phy

Trends in Oxidation of Transition-Metal Surfaces at Realistic Temperature and Pressure Conditions — ●ZHONG-KANG HAN^{1,2}, SANTIAGO RIGAMONI³, MARIA TROPPEZ³, CLAUDIA DRAXL³, MATTHIAS SCHEFFLER², and SERGEY V. LEVCHENKO^{1,2} — ¹Skolkovo Institute of Science and Technology, Moscow, RU — ²Fritz-Haber-Institut der MPG, Berlin, DE — ³Humboldt Universität zu Berlin, Berlin, DE

Oxidation of transition-metal surfaces is a ubiquitous phenomenon, but its thermodynamics is still not fully understood. Using the all-electron FHI-aims code, we present a systematic DFT study (comparing various xc approximations) of the adsorption of oxygen at different elemental and alloyed metal surfaces. The effects of configurational entropy are evaluated by combining a cluster expansion (CE) model with Monte Carlo sampling and the Wang-Landau algorithm, as implemented in our python package CELL [1]. Configurational disorder for both alloy components and adsorbates within several atomic layers of the surface is explicitly taken into account. We show that long-range repulsive interactions between the negatively charged oxygen anions are essential to explain the stability of ordered structures of adsorbed O atoms at (110) and (111) surfaces of elemental metals. The stronger the repulsive interaction is, the higher is the temperature of order-disorder phase transitions. The structures of adsorbed O at the Pd- or Pt-alloyed Cu surfaces exhibit a larger variety of patterns depending on coverage, with Pd/Pt segregating to the surface at low oxygen coverages. 1. <http://sol.physik.hu-berlin.de/cell>

O 109.9 Thu 17:00 TRE Phy

Revisiting the high temperature oxidation of Ni₃Al(111) by in situ STM — ●TIM KRATKY¹, XINZHOU MA^{1,2}, and SEBASTIAN GÜNTHER¹ — ¹TUM, Dept. Chemie, Lichtenbergstr. 4, D-85748 Garching — ²Foshan University, Materials Science and Energy Engineering, CN-528000 Guangdong

The Ni₃Al(111) surface was characterized during oxidation within the

temperature range of 690-800 K by in situ scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and auger electron spectroscopy (AES). Surface aluminum oxide formation is observed. Above 790 K, the known ($\sqrt{67} \times \sqrt{67}$)R12.2° double layer oxide grows, which consists of two Al-O layers. Oxygen dosing at the lower temperature of 740±10 K leads to a single layer oxide showing a (7 × 7) moiré pattern. Surprisingly, when lowering the temperature below 720 K during oxygen exposure, a so far unknown bilayer oxide arises. At temperatures close to 720 K, the 2nd layer is ordered and a novel diffraction pattern with a (4√3 × 4√3)R30° unit cell is observed with its hexagonal O lattice aligned to the support. Below 700 K, the 2nd oxide layer is still formed on top of the single layer oxide but in a disordered state so that the LEED pattern of the single layer oxide with a (7 × 7) moiré unit cell is observed again. Thus, the confusing fact arises that the (7 × 7) LEED pattern may originate from both, a single- or a low temperature double layer oxide.

O 109.10 Thu 17:15 TRE Phy

X-ray standing waves reveal lack of OH-termination at hydroxylated ZnO(0001) surfaces — ●JENS NIEDERHAUSEN^{1,2}, ANTONI FRANCO-CAÑELLAS³, SIMON ERKER⁴, THORSTEN SCHULTZ^{1,2}, KATHARINA BROCH³, ALEXANDER HINDERHOFER³, STEFFEN DUHM⁵, PARDEEP K. THAKUR⁶, DAVID A. DUNCAN⁶, ALEXANDER GERLACH³, TIEN-LIN LEE⁶, OLIVER T. HOFMANN⁴, FRANK SCHREIBER³, and NORBERT KOCH^{1,2} — ¹Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Germany — ²Humboldt-Universität zu Berlin, Germany — ³Universität Tübingen, Germany — ⁴Graz University of Technology, Austria — ⁵Soochow University, China — ⁶Diamond Light Source, UK

The vertical adsorption distances of the planar conjugated organic molecule 3,4,9,10-perylenetetracarboxylicdiimide (PTCDI) on hydroxylated ZnO(0001), determined with the X-ray standing wave technique (XSW), are at variance with adsorption geometries simulated with density functional theory for surface-structure models that employ terminating hydroxyl groups (OH). In contrast, good agreement is found for PTCDI in direct contact with the topmost Zn layer. The consequential assignment of OH to subsurface sites is supported by additional XSW and energy scanned photoelectron diffraction data and calls for a reconsideration of the prevalent surface models with important implications for the understanding of ZnO(0001) surfaces.