O 84: Poster Focus Session: Structure and Chemistry of Metal-Oxide Surfaces

Time: Wednesday 18:15–20:30 Location: Poster A

O 84.1 Wed 18:15 Poster A

Adsorption of O_2 on Rutile (110) surface studied by Atomically-resolved AFM/STM — •Igor Sokolovic, Martin Calkovsky, Michael Schmid, Ulrike Diebold, and Martin Setvin — TU Wien, Institute of Applied Physics, Wiedner Hauptstr. 8-10/134, 1040 Vienna, Austria

The Rutile TiO_2 (110) surface is a well-studied surface, which makes it an excellent model system for testing new methods. O_2 adsorption on this surface has been studied by many techniques [1] - [4], yet there are still controversies even about the basic O_2 adsorption configurations. This contribution will show that a combined non-contact qPlus atomic force microscopy (AFM) and scanning tunneling microscopy (STM) setup provides a powerful tool for direct imaging and manipulating the adsorbed molecules. The AFM allows for completely non-intrusive measurements, showing three distinct molecularly adsorbed O_2 species. Applying sample bias results in dissociation, desorption or configuration change of the adsorbed molecules. The role of sample and dosing temperature is discussed. The adsorbates are also investigated with Kelvin probe spectroscopy and force spectroscopy. The effect of electrons and holes induced by ultraviolet light irradiation is investigated for the various adsorbed species.

References: [1] Diebold, U. Surface science reports 48.5 (2003): 53-229. [2] Du, Y., et al. The Journal of Physical Chemistry C 112.7 (2008): 2649-2653. [3] Petrik, N.G., et al. The Journal of Physical Chemistry Letters 1.12 (2010): 1758-1762. [4] Henderson, M.A., et al. The Journal of Physical Chemistry B 103.25 (1999): 5328-5337.

O 84.2 Wed 18:15 Poster A

Roughening prevention in reactive ion beam figuring of aluminium mirror surfaces — •Jens Bauer, Melanie Ulitschka, Frank Frost, and Thomas Arnold — Leibniz-Institut für Oberflächenmodifizierung, Permoserstraße 15, D-04318 Leipzig, Germany

Mirror optics for short-wavelength imaging applications demand superior optical surface properties, i.e. a high figure accuracy down to the atomic level as well as a low surface micro-roughness below 1 nm rms. Up to now it is not possible to meet those requirements by direct machining of optical Al surfaces made from technical alloy materials as AL6061 or AL905. Conventional machining technologies fail, since the surface roughness increases drastically as a result of structural, crystallographic and chemical matrix irregularities. Recently has been shown, that ultra-precision machining by reactive ion beams can be a promising approach for surface figuring without considerable increase of the surface roughness. Based on process investigations by WLI, AFM, and TOF-SIMS and supplemented by Monte Carlo simulations a phenomenological model is suggested. In particular, the usage of O_2 or N_2 containing process gas induces the formation of a homogeneous and temporally stable surface oxide or nidride layer, respectively. This layer results from a quasi-stationary equilibrium between ion implantation and sputter erosion due to the impact of the energetic reactive ions. The surface layer acts as an etching front moderating the inhomogeneous structural conditions of the aluminium bulk material. As a result, by use of reactive ion beams the surface roughness can now be preserved in its initial state during ultra-precision figure correction.

O 84.3 Wed 18:15 Poster A

Electronic and reactive properties of alloyed Au_xPd_y nanoparticles on TiO_2 supports — •Xiaojuan Yu, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344, Eggenstein-Leopoldshafen, Germany.

PdAu bimetallic catalysts have been shown to display enhanced catalytic activities and selectivities compared with their monometallic counterparts in a variety of reactions. However, the nature of the improved catalytic performance of alloyed PdAu nanoparticles (NPs) is still under debate. Here we present the results of a thorough study on various monometallic and bimetallic Au_xPd_y-TiO_2 nanoparticles (x:y = 1:0, 7:3, 1:1, 3:7, 0:1) using primarily ultrahigh vacuum IR spectroscopy (UHV-FTIRS) in conjunction with photoelectron spectroscopy (XPS). The different surface sites of monometallic and bimetallic Au-Pd NPs supported on TiO_2 powders were identified by UHV-FTIRS using CO as a probe molecule. For monometallic Au and Pd NPs, the positively charged $Au^{\delta+}$ and Pd^{2+} were detected as majority of species, while for bimetallic AuPd NPs, Au^0, atop Pd^0 and bridge Pd^0become the dominating species. The strong electronic interaction between Au and Pd in the alloyed AuPd NPs was demonstrated based on the XPS results and the frequency shift of the corresponding CO bands. The catalysis experiments revealed that the Au_3Pd_7-TiO_2 sample exhibits the highest activity for CO oxidation. This was attributed to the activation of molecular oxygen at the enriched Pd species.

O 84.4 Wed 18:15 Poster A

IRRAS studies of CO adsorption on well-defined iron oxide surfaces — •Ludger Schöttner, Alexei Nefedov, Chengwu Yang, Stefan Heissler, Yuemin Wang, and Christof Wöll — Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76344 Eggenstein-Leopoldshafen

The interaction between CO and iron oxide (Fe_2O_3, hematite, and Fe_3O_4, magnetite) surfaces is of great interest because of its applications in heterogeneous catalysis and industrial processes such as carbothermic iron ore reduction. In addition, CO is the simplest heteronuclear diatomic molecule and is widely used in infrared spectroscopy (IR) to probe the local structure of catalyst surfaces. In this work the adsorption of CO on various iron oxide monocrystalline surfaces was studied using polarization-dependent IR reflection absorption spectroscopy (IRRAS). Based on the IRRAS results, it was established that the stoichiometric surface of $Fe_2O_3(0001)$ is terminated with Fe^{3+}, as observed for the $Fe_3O_4(001)$ surface. On the $Fe_3O_4(111)$ surface two vibrational CO bands were detected which correspond to Fe^{3+} and Fe^{2+} species, respectively. It was found that after reduction the hematite (0001) surface is converted to the more stable magnetite (111) structure. Moreover, the magnetite (111) facets were identified as a primary topology on the reconstructed $Fe_3O_4(110)$ surface.

O 84.5 Wed 18:15 Poster A

Chemical Reactivity of Amorphous Oxide Surfaces — •Hannah Schlott and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

Theoretical studies on the chemical reactivity of surfaces have been performed almost exclusively for crystalline model surface structures. When it comes to oxides, however, surfaces are typically amorphous and are covered by residuals from the environment, in particular OH groups from contact with water or protective ligand shells in the case of nanoparticles. Using Car-Parrinello Molecular Dynamics (CPMD) we first prepared amorphous ZnO and TiO_2 surface structures and subsequently studied their chemical reactivity by exposing them to a variety of small molecules, in particular, water and small organic molecules. The amorphous structures were generated by melt-quench simulations starting from randomly positioned metal and oxygen atoms in a supercell. The volume of the supercell was adjusted such that the experimental density of ZnO and TiO_2 was reproduced. A special new technique was developed that allows to create amorphous surface structures in a direct way without the need to cleave amorphous bulk configurations. First results for the interaction of water and acetic acid with the amorphous surfaces will be shown and will be compared to their behavior on the crystalline counterparts.

O 84.6 Wed 18:15 Poster A

Adsorption of catechol-derivatives on ZnO surfaces — •Tobias Müller and Bernd Meyer — Interdisciplinary Center for Molecular Materials and Computer-Chemistry-Center, FAU Erlangen-Nürnberg

The physical and chemical properties of ZnO nanoparticles can be tuned by suitable ligand shells. Catechols are promising linker units since they are able to displace acetate ions from the ZnO surfaces which have remained from the wet-chemical ZnO nanoparticle synthesis. To obtain further insights into the competition of the binding strength of different linker groups on ZnO we have studied the adsorption structure and energy of three catechol derivatives (phenyl rings with one, two or three OH groups) and of acetate using density functional theory (DFT). The crystalline, nonpolar $ZnO(10\bar{1}0)$ wurtzite termination and three different amorphous model ZnO surface structures were considered. Particular attention was given to the investigation of different adsorption sites. The amorphous surfaces show a few highly reactive surface sites, but most other sites are less reactive than the crystalline surface. For the crystalline termination also the effect of higher surface coverages was investigated by increasing the surface coverage to 0.5, 0.75 and 1 monolayer. A thermodynamic analysis, which includes experimental temperature and pressure conditions via a chemical potential, shows that the saturation coverage is about 0.5 monolayers for all three catechol derivatives. Finally, the results are compared to experimental findings.

O 84.7 Wed 18:15 Poster A

Measuring the work function of ultrathin FeO(111) films on Ag(111) using STM — •Ying Wang, Visnja Babacic, and Mikolaj Lewandowski — NanoBioMedical Centre, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland

Ultrathin films constitute a new class of 2D materials which, due to finite size effects, exhibit unique physical and chemical properties not observed for the corresponding bulk materials. It was experimentally and theoretically shown that ultrathin FeO(111) films grown on Pt(111) exhibit superior catalytic activity in the CO oxidation reaction as compared to clean Pt(111) [J. Catal 266 (2009) 359; Angew. Chem. Int. Ed. 49 (2010) 4418]. This enhanced activity was found to be related, among other factors, to the work function of the FeO(111)/Pt(111) system. We used scanning tunneling microscopy (STM) operating in dI/dz spectroscopy mode to measure the work function of ultrathin FeO(111) films grown on Ag(111). The results are compared to those obtained for FeO(111) on Pt(111).

Acknowledgment: The "Multifunctional ultrathin Fe(x)O(y), Fe(x)S(y) and Fe(x)N(y) films with unique electronic, catalytic and magnetic properties" project is carried out within the First TEAM programme of the Foundation for Polish Science (project number First TEAM/2016-2/14) co-financed by the European Union under the European Regional Development Fund.

O 84.8 Wed 18:15 Poster A

FeO(111) islands on Ru(0001): A potential catalyst for the CO oxidation reaction — •Natalia Michalak[1,2], Zygmunt Milosz[1], Stefan Jurga[1], and Mikolaj Lewandowski[1] — [1]NanoBioMedical Centre, Adam Mickiewicz University, Umultowska 85, 61-614 Poznan, Poland — [2]Institute of Molecular Physics, Polish Academy of Sciences, M. Smoluchowskiego 17, 60-179 Poznan, Poland

Oxide films epitaxially grown on metal single crystal surfaces are widely used as model catalysts that allow deeper understanding of processes that occur on the surfaces of bulk oxide catalysts. We studied ultrathin FeO(111) islands epitaxially grown on Ru(0001) by room temperature iron deposition and post-oxidation in molecular oxygen. Such preparation leads to the formation of well-dispersed and well-ordered FeO(111) islands the size of which can be tuned by additional UHV annealing. Scanning tunneling microscopy (STM) operating in dI/dV mapping mode revealed the presence of potentially catalytically-active coordinatively unsaturated ferrous sites (CUFs) at the perimeter of the FeO islands and within the islands. The results indicate that FeO(111)/Ru(0001) can be a promising catalytic system for the CO oxidation reaction. Acknowledgement: This work was financially supported by the National Science Centre of Poland (PRELUDIUM project No. 2016/21/N/ST4/00302).

O 84.9 Wed 18:15 Poster A

Ordered and disordered surface vacancies on a ceria film surface — •Reinhard Olbrich[1], Gustavo E. Murgida[2,3], Valeria Ferrari[2,3], Clemens Barth[4], Ana M. Llois[2,3], Michael Reichling[1], and M. Veronica Ganduglia-Pirovano[5] — [1]Fachbereich Physik, Universität Osnabrück, Barbarastr. 7, 49076 Osnabrück, Germany — [2]Departamento de Física de la Materia Condensada, GIyA, CAC-CNEA, 1650 San Martín, Buenos Aires, Argentina — [3]Consejo Nacional de Investigaciones Científicas y Técnicas - CONICET, C1033AAJ, Buenos Aires, Argentina — [4]Aix-Marseille University, CNRS, CINaM UMR 7325, 13288 Marseille, France — [5]Instituto de Catálisis y Petroleoquímica, Consejo Superior de Investigaciones Científicas- CSIC, 28049 Madrid, Spain

Obtaining information about the defect structure of cerium oxide surfaces is of paramount importance in catalytic applications relying on the high oxygen storage capacity (OSC) of ceria.

We reveal surface vacancies on a 180 nm thick ceria film that arise from annealing in an ultra-high vacuum (UHV) environment at various temperatures up to 1100K by direct imaging with a non-contact atomic force microscope (NC-AFM). The oxygen vacancies can be separated in regularly arranged vacancies in form of surface reconstructions representing reduction stages ranging from CeO_2 to Ce_2O_3 and in vacancies appearing at disordered surface positions. We found that the disordered surface vacancies rearrange to some extend over time while the ordered vacancies are stable.