O 58: Surface chemical reactions II

Time: Wednesday 15:00–17:30 Location: H42

O 58.1 Wed 15:00 H42

Photoinduced substrate-mediated N_2O reduction on MgO/Ag(001) surfaces — •Harald Kirsch[1], Philipp Giese[1], Christian Frischkorn[1,2], and Martin Wolf[1,2] — [1]Institut für Experimentalphysik, FU Berlin, Arnimallee 14, 14195 Berlin — [2]Fritz-Haber-Institut, Abt. Physikalische Chemie, Faradayweg 4-6, 14195 Berlin

We investigate the photochemistry of N_2O on in-situ prepeared thin MgO films, grown on an Ag(001) crystal. Structure and growth of the MgO films were characterized by means of LEED and Auger spectroscopy. Our goal is to study if defects are responsible for the photoinduced decomposition of N_2O and the subsequent creation of reactive O^- sites. After irradiation with a KrF laser (248 nm), we observe an increasing N_2 signal together with a decrease of the N_2O mass in postirradiation thermal desorption spectra. From the increase of the N_2 signal with photon dose we determine a crossection of 3×10^{-18} cm^2. We propose a mechanism where UV photons create electron-hole pairs at defect sites, which are responsible for the reaction. After several cycles of UV induced N_2O reduction without subsequent annealing, the observed N_2 formation is dramatically reduced, which we interpret as a passivation of the reactive sites via occupation with oxygen.

O 58.2 Wed 15:15 H42

Single-molecule synthesis and characterization of metal ligand complexes by low-temperature STM — •Ingmar Swart[1,2], Peter Liljeroth[2,3], Sami Paavilainen[4], Jascha Repp[1,3], and Gerhard Meyer[3] — [1]Institute of Experimental and Applied Physics, University of Regensburg, 93040 Regensburg, Germany — [2]Condensed Matter and Interfaces, Debye Institute for Nanomaterials Science, PO Box 80000, 3508 TA Utrecht, the Netherlands. — [3]IBM Research - Zurich, 8803 Rüschlikon, Switzerland — [4]Institute of Physics, Tampere University of Technology, 33720 Tampere, Finland

The use of ultrathin insulating films facilitates the study of the unperturbed electronic structure of molecules by STM. This opens up the possibility of using the STM as a single-molecule laboratory where the molecules are both synthesized and electronically characterized in-situ.

Here, we present the STM-based synthesis of metal-ligand complexes, starting from individual metal atoms (iron and nickel) and organic molecules (dicyanoanthracene, DCA) deposited on an ultrathin insulating film. Lateral manipulation is used to form linear M(DCA)2 complexes. We directly visualize the frontier molecular orbitals by STM orbital imaging and characterize their spatial symmetries. In addition, we show how their order can be controlled by changing the nature of the metal atom. This is the first example of a synthesis and electronic characterization of a metal-ligand coordination complex on an ultrathin insulating film.

O 58.3 Wed 15:30 H42

Oxidation of CO over RuO_2(110): a Reflection-Absorption IR Spectroscopy study — •Attila Farkas, Georg Christoph Mellau, and Herbert Over — Physikalisch-Chemisches Institut, Justus-Liebig-Universitaet Giessen, Germany

Kinetic Monte Carlo (kMC) simulations [1,2] of heterogeneously catalyzed reactions present a powerful potential for unraveling the reaction mechanism at molecular level. The spatial distribution of the reactants at the catalyst surface can be computed even for pressures which fall outside the scope of standard ultra-high vacuum (UHV) experimental methods.

Reflection-Absorption IR Spectroscopy (RAIRS) has been used to study the oxidation of CO over the model catalyst RuO_2(110), under experimental conditions entailing a variation by four orders of magnitude in the reactant pressure (from 10^{-7} to 10^{-3} mbar) [3]. A careful analysis of high pressure RAIRS spectra has led to a rather complete picture of the steady state at the catalyst surface under reaction conditions at 350 K. While an elementary kMC approach of the type of Ref. [1] has been found satisfactory in accounting for the experimental results, more elaborated first principles (ab initio) kMC tretments [3] have failed to do so. The sources of discrepancy between experiment and first principles theory will be critically discussed.

1. R.M. Ziff, E. Gulari, Y. Barshad, Phys. Rev. Lett., 56, 2553 (1986)
2. K. Reuter, M. Scheffler, Phys. Rev. B, 73, 045433, (2006)
3. A. Farkas, G.Ch. Mellau, H. Over, J. Phys. Chem. C,113, 14341-14355, (2009)

O 58.4 Wed 15:45 H42

High pressure XPS on supported planar model and powder Au/TiO_2 catalysts in the presence of reactive gases — •Joachim Bansmann[1], Yvonne Denkwitz[1], Stefan Kielbassa[1], Birgit Schumacher[1], R. Jürgen Behm[1], Peter Schnörch[2], Elaine Vass[2], Michael Hävecker[2], Axel Knop-Gericke[2], and Robert Schlögl[2] — [1]Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm — [2]Dept. Inorganic Chemistry, Fritz-Haber-Institut, D-14195 Berlin

The interaction of pre-conditioned, planar Au/TiO_2(110) model and dispersed Au/TiO_2 catalysts with O_2, CO and CO/O_2 atmospheres at sub-millibar pressures was investigated by in-situ X-ray photoelectron spectroscopy at BESSY. Measurements in different reaction atmospheres showed that Au is present as metallic Au nanoparticles on both types of catalysts. There was no evidence for positively charged $Au^{\delta+}$ species, neither during nor after exposure to the respective atmospheres. The TiO_2(110) substrate, on the other hand, changed its chemical, electronic and electric properties during these treatments, which results in variable shift of the substrate-related binding energy of the valence band and the Ti(2p) core levels. Whereas a detailed analysis in the case of powder catalysts was largely limited by severe charging effects, we could follow the chemically-induced variations in the electronic states of the planar Au/TiO_2(110) model catalysts.

O 58.5 Wed 16:00 H42

Electronic valence band structure of V_2O_5 — •Torsten Stemmler, Eric Meyer, and Recardo Manzke — Institut für Physik, Humboldt-Universität zu Berlin, Newtonstr. 15, 12489 Berlin

We present high-resolution ARPES measurements of V_2O_5 single crystals carried out with synchrotron radiation and He I resonance lamp. The obtained experimentally band structure in k parallel is compared with calculations, e.g.[1] and [2]. The aging behavior of different bands with time is studied. The degradation of the surface due to the high reactivity is discussed referring to the previous reported experimental work, e.g. [3] and [4].

[1] A.Chakrabarti et al., Phys. Rev. B59, 10583 (1999)
[2] V.Eyert et al., Phys. Rev. B57, 12727 (1998)
[3] S.Shin, Phys. Rev. B41, 4993 (1990)
[4] Q.Wu, Chem. Phys. Let. 430, 309 (2006)

O 58.6 Wed 16:15 H42

Reactions of Methanol on pseudomorphic Cu/Ru(0001) and O/Cu/Ru(0001) — •Pawel Gazdzicki and Peter Jakob — Fachbereich Physik, Philipps-Universität Marburg, 35032 Marburg, Germany

The adsorption and reactions of methanol on pseudomorphic Cu/Ru(0001) and oxygen precovered Cu/Ru(0001) surfaces have been studied in UHV by IRAS and TDS. In contrast to the clean Cu(111) surface (reversible adsorption), a variety of reaction intermediates have been observed on the laterally expanded Cu/Ru(0001) monolayer. The reaction scheme with perpendicularly oriented methoxy (CH_3O) as the most prominent species proceeds very similar to Ru(0001). Interestingly, the Cu monolayer enhances the stability range of methoxy (with respect to decay into CO + 3H) considerably, which is attributed to a lower hydrogen binding energy on Cu/Ru(0001) as compared to Ru(0001).

Inspired by the possibility to enhance the reactivity of Cu(111) by the coadsorption of oxygen, the methanol decomposition has been investigated for Cu/Ru(0001) with preadsorbed oxygen as well. In fact, a completely new reaction pathway could be identified, with the methoxy species being present at 200-350 K and getting oxidized to produce formate (HCOO), as identified by characteristic bands in IRAS in the temperature range 380-460 K. As the dominant desorption product CO_2 is detected, which is in contrast to the non-oxidized surfaces which predominantly produce CO and H_2.

O 58.7 Wed 16:30 H42

Interaction of methanol with the O-terminated ZnO(000-1) surface — •Lanying Jin, Hengshan Qiu, and Yuemin Wang — Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, 44801

Bochum, Germany

Zinc oxide has attracted much research interest due to its particular electronic, optical and catalytic properties [1]. In catalysis, Cu/ZnO is the standard heterogeneous catalyst for the industrial methanol synthesis and its stream reforming. Therefore, studies of the interaction of methanol with ZnO are of fundamental importance in understanding the relevant catalytic processes on the atomic scale. In this work, the adsorption of methanol on O-ZnO(000-1) was studied by high resolution electron energy loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). The clean, adsorbate-free O-ZnO(000-1) surface is electrostatically unstable and exhibits a (1x3) reconstruction with the presence of abundance of oxygen vacancies. It was found that exposing ZnO(000-1) to methanol at room temperature leads to the dissociative adsorption forming methoxy species at oxygen vacancies. After heating to higher temperatures the adsorbed methoxy species undergo further decomposition at 590 and 660 K releasing CH_2O, H_2, CO, and CO_2. The formation of formate species, which has been observed in methanol oxidation over ZnO powder samples, could be clearly ruled out based on the present results on ZnO(000-1). [1] Ch. Wöll, Prog, Surf. Sci. 82(2007) 55.

O 58.8 Wed 16:45 H42

First-principles assessment of UBI-QEP derived rate constants for chemical kinetics — •Matteo Maestri[1,2] and Karsten Reuter[1,3] — [1]Fritz-Haber-Institut Berlin, Germany — [2]Politecnico di Milano, Italy — [3]TU München, Germany

An accurate description of the elementary steps involved in a catalytic process is the basis for a reliable microkinetic modeling of the surface chemistry. Though desirable, a first-principles calculation of the reaction parameters is presently unfeasible but for models involving a small number of reactions. For complex catalytic systems, semi-empirical approaches, such as the UBI-QEP method [1], are therefore often employed to estimate reaction barriers and coverage effects. While computationally less demanding, the accuracy of UBI-QEP is uncertain and one has to question whether the corresponding energetics are mere artifacts of the employed effective modeling. At this scope and using the water-gas shift reacting system on Rh(111) as a showcase, we perform a density-functional theory based assessment of the UBI-QEP derived rate constants for specific classes of reactions (namely, dissociation/recombination and disproportionation). This comprises in particular the explicit coverage dependence of the reaction barriers predicted within the UBI-QEP framework. In doing so we aim at an increased awareness of the limitations of UBI-QEP methodology and the demonstration of possible strategies to overcome them. [1] E. Shustorovich and H. Sellers, Surface Science Reports, 31 (1998) 5.

O 58.9 Wed 17:00 H42

Theoretical investigation of the mass-scaling of chemicurrents — •Matthias Timmer and Peter Kratzer — Faculty of Physics and Centre for Nanointegration (CeNIDE), University Duisburg-Essen, Lotharstr. 1, 47048 Duisburg, Germany

In recent years electronically nonadiabatic effects in adsorption on metal surfaces have been investigated. The chemicurrents detected by adsorption on a Schottky diode are of particular interest to our work. Utilizing our approach to calculate these currents [1], we investigate the electronic excitation spectra generated by adsorbates as function of their mass. Specifically, we study H isotopes on K(110) and Al(111) surfaces. From the insight gained in these calculations, we predict that the decay of the detectable current with increasing adsorbate mass should be weaker than expected from simple chemicurrent models used previously. We compare our predictions to recent experiments on Mg/Mg(0001) adsorption, and to calculations of this system.

[1] M. Timmer and P. Kratzer, Phys. Rev. B 79, 165407 (2009)

O 58.10 Wed 17:15 H42

Structure-Sensitivity in Catalytic Reactions on Ir(210) Surfaces — •Payam Kaghazchi[1], Wenhua Chen[2], and Timo Jacob[1] — [1]Universität Ulm, Albert-Einstein-Allee 47, D-89069 Ulm, Germany — [2]Rutgers University, NJ 08854, USA

The formation of facets on single-crystal surfaces provides a reproducible basis and model systems for studying catalytic reactions. In this context, recent experiments on the adsorption and decomposition of NO on O-covered planar and nano-faceted Ir(210) with variable facet sizes showed pronounced structure-sensitivity and an unexpectedly high reactivity for NO decomposition. Using density functional theory we studied the adsorption of NO, O, and (NO+O) on Ir(210), as well as on Ir(311) and Ir(110), the surfaces which are exposed after facet formation. In agreement with TPD and HREELS data, we find that NO adsorbs on atop sites of planar Ir(210) but on both bridge and atop sites of Ir(311) and (110) faces of faceted Ir(210) [1]. Coadsorption of O does not influence adsorption sites of NO but reduces the Ir–NO bond strength on Ir(210), Ir(110) and Ir(311). In contrast, coadsorption of NO (on O-covered Ir surfaces) indeed influences adsorption sites of O and reduces Ir-O bond strength on Ir(110) and Ir(311) significantly [2]. Our findings should be of importance for the development of Ir-based catalysts for NO decomposition under oxygen-rich conditions. [1] W. Chen, T. E. Madey, A. L. Stottlemyer, J. G. Chen, P. Kaghazchi, T. Jacob, *J. Phys. Chem. C*, **112**, 19113, (2008), [2] W. Chen a, A. L. Stottlemyer, J. G. Chen, P. Kaghazchi, T. Jacob, T. E. Madey, R. A. Bartynski, *Surf. Sci.*, **603**, 3136, (2009).