O 8: Metal Substrates I: Adsorption and Reactivity

Time: Monday 10:30–13:00 Location: H25

O 8.1 Mon 10:30 H25

Interaction of AuZn surfaces with oxygen species and formation of ZnO_x on Au(111) — •Konstantin M. Schüttler, Albert K. Engstfeld, Joachim Bansmann, and R. Jürgen Behm — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

Au/ZnO is a highly active catalyst for the synthesis of "Green Methanol" from CO_2 and H_2, where the latter should stem from renewable sources [1]. Industrially, Cu/ZnO is used for MeOH synthesis, where under reaction conditions ZnO at the perimeter of the Cu nanoparticles is partly reduced, forming bimetallic CuZn sites [2]. For Au/ZnO catalysts, AuZn formation would be similarly plausible.

In order to gain more insight into the formation, structural, electronic and chemical properties of AuZn sites, bimetallic Zn/Au(111) model catalyst surfaces were studied under UHV conditions. We investigated the interaction of Zn surface atoms with oxygen by exposing various AuZn nanostructures to molecular and atomic oxygen. Furthermore we illustrate the thermal stability of the newly formed nanostructures. Second, we explored the formation of ZnO_x/Au(111) ($0 \leq x \leq 1$) and studied the species formed depending on the oxidation conditions. Consequences of these findings on our understanding of realistic Au/ZnO catalysts are discussed.

[1] Y. Hartadi et al., ChemSusChem 8 (2015), 456

[2] S. Kuld et al., Angew. Chem. Int. Ed. 53 (2014), 5941

O 8.2 Mon 10:45 H25

Ground state structure for 0.5 ML oxygen on Rh(100) — Tilman Kisslinger[1], Margareta Wagner[2], Michael Schmid[2], Ulrike Diebold[2], •M. Alexander Schneider[1], and Lutz Hammer[1] — [1]Ls. f. Festkörperphysik, Univ. Erlangen — [2]Inst. f. Angewandte Physik, TU Wien

The structure of 0.5 ML oxygen on Rh(100) was so far reported by experiment [1] and theory [2] to be a (2×2)-2O supercell where O sits on threefold hollow sites of the clockwise-anticlockwise reconstructed Rh(100). Newly taken LEED-IV data at first sight confirm this model with a quite low Pendry R-factor of R = 0.12. However, like in [1] the model fails to explain extinctions of diffraction spots in the LEED pattern and it also disagrees with DFT calculations that predict a 12 pm buckling between surface Rh atoms. Allowing for positional disorder of oxygen within the (2×2)-2O cell improves the fit of our LEED-IV data taken at 100 K and restores the symmetry elements. By STM at room temperature a (2×2) periodicity is found while at 77 K and 4 K the system is well-ordered with c(4×4)-4O surface cell. Applying DFT to a model with alternate occupation of threefold hollow sites by oxygen atoms reproduces the experimental STM image and shows that the c(4×4)-4O is energetically more favourable than the (2×2)-2O by 4 meV per oxygen atom. Furthermore, the new model describes the LEED-IV data with R = 0.08 even better, i.e. the structural elements of the c(4×4)-4O are locally present also at 100 K. [1] A. Baraldi et al., PRL **82**, 4874 (1999) [2] D. Alfè et al., Surf. Sci. **410**, 151 (1998)

O 8.3 Mon 11:00 H25

Oxidation of Transition-Metal Surfaces at Realistic Temperature and Pressure Conditions — •Zhong-Kang Han[1], Ray Miyazaki[2], Somayeh Faraji[1], Santiago Rigamoni[3], Maria Troppenz[3], Claudia Draxl[3,1], Jun-ya Hasegawa[2], Sergey V. Levchenko[4,1,5], and Matthias Scheffler[1] — [1]Fritz-Haber-Institut der MPG, Berlin, DE — [2]Hokkaido University, Sapporo, JP — [3]Humboldt–Universität zu Berlin, Berlin, DE — [4]Skolkovo Innovation Center, Moscow, RU — [5]NUST MISIS, Moscow, RU

Oxidation of metal surfaces is a ubiquitous phenomenon, but its thermodynamics is still not fully understood. Using the all-electron FHI-aims code, we perform a systematic DFT study (comparing various xc approximations) for the adsorption of atomic oxygen at (111) and (110) surfaces of Au, Pt, Ni, Pd and Cu, and the Pd- or Pt-alloyed Cu(111) and (110) surfaces. The finite-temperature thermodynamics is evaluated using a cluster expansion. At low coverages (<25%) O atoms are predicted to adsorb randomly at the short-bridge sites of elemental metal (110) surfaces, and they form a $c(2 \times 2)$ pattern when the coverage increases, until a new $c(2 \times \sqrt{2})$ pattern forms with top and hollow sites occupied. Quite differently, at (111) surfaces a variety of ordered adsorbed O phases is found, with a mixed occupation of the fcc and hcp hollow sites. The structures of adsorbed O at the alloyed surfaces exhibit a larger variety of patterns depending on coverage, with Pd/Pt segregating to the surface at low O chemical potentials (i.e., higher temperatures and/or lower O_2 pressures), while increasing the chemical potential induces Cu segregation.

O 8.4 Mon 11:15 H25

Modeling the formation and reactivity of surface oxide islands on metal surfaces — •Albert Bruix and Karsten Reuter — Technical University of Munich (Germany)

The surfaces of many transition metals are oxidized under ambient conditions or at increased oxygen pressures, which has strong implications for corrosion and catalysis. Stable O-enriched states resulting from oxidation may consist of the metal surface with high concentration of adsorbed O atoms, the corresponding metal-oxide, or something in between. The latter include surface oxides, i.e. ultrathin oxide layers formed on the surface of the metal.

A quantitative atomistic modeling of oxidation reactions catalyzed on such transition metals therefore requires an understanding of the chemical properties and formation mechanisms of the oxidized surfaces. In this work, PdO(101) surface oxide islands on the Pd(100) surface are studied by means of Density-Functional Theory calculations. We first establish a thermodynamic model for the formation and growth of surface oxide islands, focusing on the stability of different island edge types. We then use a multi-lattice microkinetic modeling approach to investigate the role of the metal and surface oxide phases, and how their coexistence under different operation conditions affects catalytic performance. Our approach also allows probing the relevance of sites at the interface between the two phases and the effect of phase transitions on the overall reactivity.

O 8.5 Mon 11:30 H25

The effect of temperature in plasmon driven reactions — •Wouter Koopman[1], Radwan Sarhan[1,2], Ferenc Liebig[3], Jan Pudell[1], Marc Herog[1], Matthias Rössle[4], Thomas Schmid[2,5], Sebastian Schmitt[4], Felix Stete[1,2], Clemens Schmitt[6], Joachim Koetz[3], and Matias Bargheer[1,4] — [1]Institute of Physics and Astronomy, University of Potsdam — [2]School of Analytical Sciences Adlershof, Humboldt-Universität zu Berlin — [3]Institute of Chemistry, University of Potsdam — [4]Helmholtz Zentrum Berlin — [5]Federal Institute for Materials Research and Testing, Berlin — [6]Max Planck Institute of Colloids and Interfaces, Potsdam

Metal nanoparticles form potent nanoreactors, driven by the optical generation of energetic electrons and nanoscale heat. The relative influence of these two factors on nanoscale chemistry is strongly debated. We investigate the temperature dependence of the dimerization of 4-NTP into DMAB adsorbed on goldnanoflowers.Static X-ray diffraction and Raman thermometry indicate a temperature increase of the nanoparticles in the order of 150K. A much higher temperature of the DMAB molecules, around 500K, is regarded as sign of vibrational activation of the molecules by electron injection. The role of the electron injection is corroborated by the observation of an intensity threshold for the photo-driven reaction. On the other hand, a comparison between measurements of the reaction kinetics at different temperatures and different intensities indicate, that an increased reaction rate at higher light intensities could be rooted in a higher temperatures of the particles.

O 8.6 Mon 11:45 H25

Real-space observation of far- and near-field-induced photolysis of molecular oxygen on a Ag(110) surface by visible light — •Chenfang Lin[1] and Takashi Kumagai[1,2] — [1]Department of Physical Chemistry, Fritz-Haber Institute of the Max-Planck Society, Faradayweg 4-6, 14195 Berlin, Germany — [2]JST-PRESTO, 4-1-8 Honcho, Kawaguchi, Saitama 332-0012, Japan

Dissociation of molecular oxygen is an important elementary process in heterogeneous catalysis. Recently, it has been demonstrated that photo-induced dissociation of molecular oxygen can be significantly enhanced using plasmonic Ag nanoparticles and occurs even by visible light via excitation of surface plasmons [1,2]. Here we report the direct observation of oxygen photolysis at low coverages (0.01 monolayer) by far- and near-field excitation in the visible range by using a combination of an STM and a wavelength-tunable laser. It is found that the cross section for the far-field excitation (about 10^{-19} cm^2) can be largely enhanced in a plasmonic STM junction with an Ag or Au tip. We also demonstrate that the wavelength dependence of the oxygen photolysis can be tuned by nanoscale fabrication of an STM tip with focused ion beam milling. Our approach provides a unique opportunity to investigate the optimal nanostructures for plasmonic catalysts.

[1] Phillip Christopher, Hongliang Xin and Suljo Linic, Nature Chemistry 3, 467-472 (2011)

[2] Phillip Christopher, Hongliang Xin, Andiappan Marimuthu and Suljo Linic, Nature Materials 11, 1044-1050 (2012)

O 8.7 Mon 12:00 H25

Colliding Molecules at Selected Impact Parameters — •Kelvin Anggara, Lydie Leung, Matthew Timm, Zhixin Hu, and John Polanyi — Department of Chemistry and Institute of Optical Sciences, University of Toronto, 80 St. George Street, Toronto M5S 3H6, Canada

The dynamics for bimolecular reaction has been elucidated by crossing two molecular beams in the gas-phase under single-collision conditions. The results however have inevitably been averaged over impact parameters - the collision 'miss-distance' - ranging from zero to infinity, obscuring the effect of this important parameter on reaction dynamics. We show that this averaging can be avoided by a aiming a highly-collimated 'projectile' molecule towards a fixed 'target' molecule, with both adsorbed at a surface. Using an electron from the tip of a Scanning Tunnelling Microscope (STM), a single chemisorbed CF_3 on Cu(110) at 4.6 K can be reacted to give a recoiling CF_2 radical that is collimated to a lateral spread of only ±1°. Previous work from this lab has shown that this collimation effect is due to the interaction of the CF_2 with the underlying Cu-row which acts as an atomic guide to give a directed CF_2 'surface-molecular-beam'. Here we have aimed the CF_2 beam at a chemisorbed vinyl ($CHCH_2$) with three impact parameters (-4.0, -0.4, and +3.2 Å), giving insights into the dynamics of carbon chain growth on the metal surface. The scattering experiment presented here has the potential to be aimed at any target that can be detected by STM on a surface, thereby providing a means to explore the dynamics in a wide range of surface reactions.

O 8.8 Mon 12:15 H25

Development of Descriptors for the Prediction of Adsorption Energies on Transition Metal Catalysts and their Alloys — •Martin Deimel, Karsten Reuter, and Mie Andersen — Theoretical Chemistry, Technical University of Munich, Germany

The construction of microkinetic models for catalytic processes requires the knowledge of both adsorption energies of the different species and reaction barriers. In the pursuit of discovering new catalysts with improved activity and selectivity, computational screening renders the explicit calculation from first principles intractable. In order to reduce the computational effort, it is desirable to identify descriptors that allow for a cheap and accurate prediction of these quantities. In the present work we apply the recently developed compressed-sensing method Sure Independence Screening and Sparsifying Operator (SISSO) [1] to identify cheaper and more accurate descriptors for adsorption energies on transition metals (TMs) and their binary alloys [2]. These descriptors are constructed as non-linear functions of properties of the clean catalyst surface (primary features). The different metal atom composition of sites on surface alloys introduces an additional tunable parameter. In combination with distinct site preferences and coordination patterns of different adsorbates, this provides the opportunity to break the interdependence of adsorption energies imposed by scaling relations. Such interdependence is often viewed as one of the major limiting factors for identifying even better catalysts than we know today.

[1] R. Ouyang *et al.*, Phys. Rev. Materials **2**, 083802 (2018)

[2] M. Andersen *et al.*, submitted

Invited Talk O 8.9 Mon 12:30 H25

Deposition and properties of ultrathin films of organic radicals — •Maria Benedetta Casu — Institute of Physical and Theoretical Chemistry, University of Tübingen, Germany

In this work, we demonstrate that it is possible to evaporate and deposit organic radicals onto well-defined surfaces under controlled conditions, without degradation. Using soft X-ray spectroscopies, we investigate thin film processes, surfaces, and interfaces at the nanoscale of organic radicals deposited on metal and metal oxide surfaces. We find that organic radicals are physisorbed and keep their magnetic moment on inert and passivated surfaces, while defective sites such as oxygen vacancies or presence of OH groups lead to chemisorption of the organic radicals on the surface with quenching of their magnetic moment. Our work shows that the use of X-ray based techniques represents a powerful approach to reveal the mechanisms governing complex interfaces, such as radical/metal and radical/metal-oxide where it is important to describe both charge and spin behavior (spinterfaces). A deep understanding of stable radical/inorganic spinterfaces may open the way to use radicals in solid state devices, or as quantum bits with dedicated configurations, as proposed for other molecular quantum bits, and in spin-based electronics.