

O 100: Metal Substrates: Adsorption and Reactivity

Time: Friday 10:30–13:00

Location: MA 043

O 100.1 Fri 10:30 MA 043

Following “hot” adatoms wherever they go: QM/Me with multiple embedding regions — ●VANESSA JANE BUKAS¹, JÖRG MEYER², and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Universiteit Leiden, The Netherlands

Exothermic surface chemical reactions may easily release several electron volts of energy. This challenges first-principles based dynamical simulations to account for adequate energy dissipation channels. Focusing on phononic dissipation we recently presented a novel embedding scheme for metallic substrates (QM/Me [1]), in which energy dissipation out of a quantum-mechanically described reaction zone occurs into a computationally undemanding, yet reliably described extended bath. In the application to oxygen dissociation over Pd(100) this predicted translationally “hot” dissociation fragments as a consequence of nonimmediate energy transfer to the metal surface. Here, we advance this approach to include the concurrent treatment of multiple reaction zones centered around individual fragments and dynamically following their motion. This suppresses unphysical interactions between reaction partners through periodic images, allows to use smaller supercells, and most importantly enables the application to chemical reactions for which the lateral direction of “hot” translational motion is not clear *a priori*. We demonstrate this new functionality by comparing oxygen dissociation at Pd(111) to the previously studied Pd(100). [1] J. Meyer and K. Reuter, *Angew. Chem. Int. Ed.*, **53**, 4721 (2014).

O 100.2 Fri 10:45 MA 043

Oxygen dissociation and recombination on Au/Ag(110) thin film alloys — ●MARTIN SCHMID¹, JOSHUA E. KLOBAS², and CYNTHIA M. FRIEND² — ¹Fachbereich Chemie, Philipps Universität Marburg — ²Dpt. of Chemistry and Chemical Biology, Harvard University, Cambridge MA, USA

In order to gain insight into the fundamental processes on complex bimetallic catalysts, such as nanoporous gold or bimetallic AuAg nanoparticles, O₂ dissociation and recombination on Au/Ag(110) thin film alloys of various compositions were studied with Temperature-Programmed Desorption (TPD). An increasing gold content of the thin film alloys is associated with a linear decrease of the maximum oxygen uptake of the surfaces; the oxygen uptake is completely quenched at gold concentrations higher than 50%. A closer analysis of the TPD signals shows that there is no transfer of oxygen adatoms between Au and Ag sites and that the oxygen chemistry is, in general, dominated by the Ag sites on the alloy surfaces. Apart from passivating the surface against oxygen uptake, gold also leads to a reduction of the recombination temperature of oxygen adatoms by ~20 K. These results indicate that there are at least two neighboring Ag atoms required to dissociate oxygen and demonstrate that gold efficiently lowers the amount of adsorbed oxygen and facilitates recombination and release of the remaining oxygen adatoms. The results provide a lower limit for the size of active groups of Ag atoms and show that the bond strength between surface and oxygen adatoms is influenced by the local Au:Ag stoichiometry.

O 100.3 Fri 11:00 MA 043

Interaction of CO with bimetallic Pt_xAg_{1-x}/Pt(111) surface alloys — ●KONSTANTIN M. SCHÜTTLER, THOMAS DIEMANT, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

From recent studies, it is known that supported PtAg nanoparticles show enhanced (electro-) catalytic properties compared to pure Pt nanoparticles. In order to understand their chemical properties and to correlate them with their atomic structure, structurally well-defined Pt_xAg_{1-x}/Pt(111) surface alloys, whose structure had been characterized by STM in our institute, were chosen as model system. The interaction of CO as probe molecule with these surface alloys was investigated by temperature-programmed desorption (TPD) and infrared spectroscopy (IRRAS) under UHV conditions.

TPD measurements show a modification of the chemical properties of both components in the surface alloy. For CO adsorbed on Pt sites, the trailing edge first shifts to higher temperature with increasing Ag content, indicating a stabilization of adsorbed CO. At higher Ag content in the surface alloy, an additional desorption feature appears at higher temperature, which is attributed to CO adsorption on smaller

Pt ensembles surrounded by Ag atoms. Additionally, a small desorption feature appeared at very low temperature for all surface alloys after CO saturation. This desorption feature is attributed to CO adsorption on Ag defect sites.

O 100.4 Fri 11:15 MA 043

IRRAS Investigation of Carbon Monoxide Adsorption on Pristine and Roughened Au(111) — ●JAN PISCHEL and AN-NEMARIE PUCCI — Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, D-69120 Heidelberg

The behavior of gold nanoparticles which are used, e.g., in surface enhanced spectroscopies [1] or heterogeneous catalysis [2], often critically depends on the properties of their surface.

While scanning tunneling microscopy as a well-suited method to explore the morphology of gold surfaces has already abundantly been applied [e.g. 3], we use infrared reflection absorption spectroscopy (IRRAS) in combination with CO adsorbed at cryogenic temperatures to probe the chemical properties of available sites at the surface. In this context, we present the first IRRAS investigation of CO adsorption on single crystalline Au(111) under ultra-high vacuum conditions. The interaction between CO and the flat surface is shown to differ significantly from that between CO and other types of gold surfaces known from literature. To make the connection, we introduced surface roughness in a well-defined manner by cold-depositing submonolayer amounts of gold onto the surface at 30K. Adsorption of CO on these rough surfaces is shown to result in the IR-response known from literature. A gradual transition between these two limiting cases can be realized by successively annealing the rough substrates.

[1] Neubrech, F. and A. Pucci, *IEEE J. Select. Topics Quant. Electronics* 19(3):4600809, 2013. [2] Haruta, M., *Gold Bulletin* 37(1–2):27, 2004. [3] Rai, A. et al., *Surf. Sci.* 625:97, 2014.

O 100.5 Fri 11:30 MA 043

Following PtAg/Pt(111) surface alloy formation by CO adsorption — ●THOMAS DIEMANT, KONSTANTIN M. SCHÜTTLER, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The influence of the structure of a bimetallic surface on the chemical and catalytic properties is of high interest to further the understanding of the working principles of bimetallic catalysts. In this context, the growth of Ag films on a Pt(111) substrate at room temperature, the formation of PtAg/Pt(111) surface alloys by annealing to higher temperature (up to 900 K) and the consequences of surface alloy formation on the CO adsorption properties were studied by a combination of XPS, TPD and IR spectroscopy (IRRAS) measurements using CO as probe molecule in the two latter methods. Previous STM studies by Röder et al.^[1] and in our institute had revealed a change of the atom distribution from extended Ag overlayer islands on the Pt(111) substrate directly after deposition at RT to disperse PtAg surface alloys.

The modification of the electronic properties of the components in the bimetallic surface layer upon alloy formation, which starts at 600 K, is resolved in XPS by a shift of the Ag(3d) peak to lower binding energy. The CO adsorption also starts to change drastically after heating to this temperature. New features in the CO TPD spectra (extra peak at higher desorption temperature) and in the IRRAS (2025 cm⁻¹) occur, which we attribute to the formation of isolated Pt sites surrounded by Ag atoms.

[1] Röder et al., *Phys. Rev. Lett.* 71 (1993) 2086.

O 100.6 Fri 11:45 MA 043

An ab initio study on the oxidation of Mg-Zn alloys and the MgZn₂ intermetallic compound — ●SU-TING CHENG, MIRA TODOROVA, and JÖRG NEUGEBAUER — Max-Panck-Institut für Eisenforschung GmbH, Düsseldorf, Germany

A first step towards protecting iron from corrosion is galvanization, i.e. coating the iron surface with Zn. Recent experimental investigations have revealed [1], that addition of Mg can significantly improve the corrosion properties of Zn: the loss of weight during electrolysis of the intermetallic compound MgZn₂ was reduced by 1/3 compared to results for pure Zn [2]. This seems astonishing in view of the high affinity of Mg to oxidise, which we relate to the appearance of attractive in-

teractions arising between electronegative adsorbates on the Mg(0001) surface [3]. Using density functional theory calculations we investigate clean and oxygen covered Mg-Zn and MgZn₂ surfaces and find the formation of a rather compact surface oxide. We will discuss our results in the context of corrosion protection.

[1] R. Hausbrand, M. Stratmann, and M. Rohwerder, *Corrosion Science* 51 2107 (2009)

[2] E. Diler, S. Rioual, B. Lescop, D. Thierry, and B. Rouvellou, *Corrosion Science* 65 178 (2012).

[3] S.-T. Cheng, M. Todorova, C. Freysoldt, and J. Neugebauer, *Phys. Rev. Lett.*, 113, 136102 (2014).

O 100.7 Fri 12:00 MA 043

Correlation between adsorption and strain: a first-principles study of the H/Ir(111) system — ●ANJA MICHL and STEFAN MÜLLER — Hamburg University of Technology, Institute of Advanced Ceramics, Denickestr. 15, D-21073 Hamburg

The interaction of hydrogen with Iridium surfaces is relevant for a wide range of catalytic reactions. Straining the catalysts surface has an impact on adsorption energies and energy barriers and thus can be used to tune the catalytic activity.

We use density functional theory (DFT) to study the energetics of hydrogen adsorption on Ir(111). Vibrational frequencies are determined to account for zero-point energy corrections. The most favorable adsorption configurations are identified by using the DFT data to construct a cluster-expansion Hamiltonian, which enables an exhaustive scan of the configuration space. We find that top site adsorption is preferred over the whole coverage range from 0 to 1 ML. At low coverage the distance between adsorbed hydrogen atoms is maximized, while at higher coverage ground states exhibit hydrogen covered stripes of varying width. However, the ordering tendencies of the system are not very pronounced, with energy differences less than 30 meV per 1×1 surface site. Biaxial strain in the surface plane is applied to energetically favorable configurations in order to reveal strain-induced changes in the energetic hierarchy and to determine the coupling strength between adsorption energies and strain.

O 100.8 Fri 12:15 MA 043

Metalocene adsorption and customization on copper — ●NICOLAS BACHELLIER¹, MAIDER ORMAZA¹, PAULA ABUFAGER², ROBERTO ROBLES², MARTIN VÉROT³, TANGUI LE BAHERS³, MARIE-LAURE BOCQUET³, NICOLAS LORENTE², and LAURENT LIMOT¹ — ¹IPCMS, Université de Strasbourg, UMR CNRS 7504, 67034 Strasbourg, France — ²ICN2, Campus UAB, 08193 Bellaterra, Spain — ³ENS Lyon, Université Claude Bernard, CNRS, 69007 Lyon, France

Organometallic molecules offer promising perspectives for improving spintronic devices. Metalloenes wires, in particular ferrocene wires (FeCp₂, Cp=C₅H₅), have been predicted to produce currents with a spin polarization close to 100%. The design and conception of such wires is however hampered by the little and often contradictory knowledge we have concerning the molecule-substrate and molecule-molecule interaction of ferrocene.

By means of low-temperature STM and DFT calculations, we show how associatively adsorbed ferrocene self-assembles on copper surfaces

adopting a configuration that is independent of the surface orientation. The stability of the two-dimensional structure is ensured by a combination of vertical and horizontal-lying molecules relative to the surface. We also show that a subsequent exposure of the molecular layer to single magnetic cobalt atoms leads to the formation of up-standing Co-FeCp₂ molecules that exhibit the Kondo effect. Through a tip-assisted manipulation, we show that the newly formed molecule consists of ferrocene adsorbed on top of cobalt.

O 100.9 Fri 12:30 MA 043

The adsorption and recognition of carborane thiols molecules on the Au(111) surface — ●JAN BERGER¹, MARTIN ŠVEC¹, PINGO MUTOMBO¹, TOMÁŠ BAŠE², WOJCIECH KAMIŃSKI³, and PAVEL JELÍNEK¹ — ¹Institute of Physics, Academy of Sciences of the Czech Republic, Cukrovarnická 10, CZ-16200, Prague, Czech Republic — ²Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Husinec-Rez, c.p. 1001, Czech Republic — ³Institute of Experimental Physics, University of Wrocław, plac Maksa Borna 9, 50-204 Wrocław, Poland

We present simultaneous qPlus AFM/STM measurements of carborane molecules functionalized by thiol groups (1,2-(HS)2-1,2-C₂B₁₀H₁₀) deposited on Au (111) surface. The morphology of different adsorption configurations of molecules on Au (111), depending on surface coverage, was characterized. At low coverage, carboranes adopt a mobile triangle configuration with one molecule up, two molecules down.

Using *df(z)/I(z)* local spectroscopy we revealed, that two different molecule configuration show distinct transport and mechanical properties. Thus we attribute this observation to different binding mechanism to the substrate. Molecules tend to create multi-domain islands at higher coverage. The STM/AFM experimental findings are complemented - and supported - by state-of-the-art DFT calculations.

O 100.10 Fri 12:45 MA 043

Carbene-based self-assembly of diamondoids on metal surfaces — ●BIBEK ADHIKARI¹, SHENG MENG², and MARIA FYTA¹ — ¹Institute for Computational Physics, Stuttgart, Germany — ²Institute of Physics, Chinese Academy of Sciences, Beijing, China

N-hetero-cyclic carbenes (NHC)s are emerging as the alternative class of molecules to thiol based self-assembled monolayers (SAMs). A gold-sulfur bond is weaker compared to the carbon-gold, which makes the carbene-based self-assembled monolayers much more stable in harsh environmental conditions. The NHCs bind easily to metal surfaces. By attaching diamondoids to the opposite end of these NHCs, we prepare very stable self-assembled monolayers of diamondoids on metal substrates such as gold and silver. Diamondoids are diamond-like cage structures with hydrogen terminations and have excellent electron-emission properties. These have potential applications as field-emission display devices. In this work, we perform quantum mechanical simulations under the frame work of density functional theory (DFT) to reveal the electronic properties of the carbene-based diamondoid SAMs. We focus on the binding possibility, stability and the adsorption sites of these newly formed monolayers on Au/Ag surfaces. We next turn to the investigation of their optical and emission properties in view of their nanotechnological applications.