

## O 45: Heterogeneous catalysis

Time: Thursday 10:30–13:00

Location: SCH A215

O 45.1 Thu 10:30 SCH A215

**Interaction of CO<sub>2</sub> and CH<sub>4</sub> with MgO/CeO<sub>2</sub>/Cu(111) and Pt/CeO<sub>2</sub>/Cu(111) model catalyst surfaces** — ●YAROSLAVA LYKHACH, THORSTEN STAUDT, MICHAEL P. A. LORENZ, REGINE STREBER, ANDREAS BAYER, HANS-PETER STEINRÜCK, and JÖRG LIBUDA — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058 Erlangen

We have studied the interaction of CO<sub>2</sub> and CH<sub>4</sub> with CeO<sub>2</sub> based model catalyst. Toward this aim, we employ epitaxially grown CeO<sub>2</sub> films on Cu(111) as well-ordered model supports [1]. Morphology and growth of the deposited films were characterized by means of STM and LEED. The CeO<sub>2</sub>/Cu(111) substrates were modified by deposition of MgO or Pt. The reaction behaviour of CO<sub>2</sub> on MgO/CeO<sub>2</sub>/Cu(111) was investigated by XPS. The interaction of CH<sub>4</sub> was studied on CeO<sub>2</sub>/Cu(111) and Pt/CeO<sub>2</sub>/Cu(111) in supersonic beam assisted experiments. Different carbonaceous species formed on the surfaces were monitored by XPS as a function of exposure, sample temperature and MgO or Pt particle sizes. Upon stepwise annealing removal of carbon is observed. While the Pt particles are recovered, significant reduction of CeO<sub>2</sub> substrate is observed at temperatures significantly lower than for clean Pt/CeO<sub>2</sub>/Cu(111). This indicates active participation of CeO<sub>2</sub> in removal of carbonaceous species via reverse-spillover of oxygen from the CeO<sub>2</sub> support to Pt.

[1] V. Matolin et al., *Thin Solid Films* 516 (2008) 6120-6124.

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**Studies on the substrate mediated vibrational excitation of CO/Si(100) by means of SFG spectroscopy** — XU HAN, KRISTIAN LASS, ●THORSTEN BALGAR, and ECKART HASSELBRINK — Universität Duisburg-Essen, Fachbereich Chemie, 45117 Essen, Germany

Vibrational excitations of adsorbates play an important role in chemical reaction dynamics. In the past decade CO on solid surfaces was chosen as adequate model system for studying vibrational relaxation dynamics [1 - 3]. Our work is focused on the energy dissipation of vibrationally excited CO adsorbed on a silicon surface by means of IR/Vis sum frequency generation (SFG) spectroscopy [4, 5]. Here we present studies on substrate mediated excitation of vibrational modes of CO on Si(100) induced by UV radiation. We suppose the observation of highly excited internal stretch vibrations of CO caused by hot electrons generated within the silicon substrate.

[1] A. Tadjeddine, A. Le Rille, O. Pluchery, F. Vidal, W.Q. Zheng, A. Peremans, *Phys. Status Solidi A* 175 (1999) 89 [2] H. Ueba, *Prog. Surf. Sci.* 55 (1997) 115 [3] M. Buck, M. Himmelhaus, *J. Vac. Sci. Technol. A* 19 (2001) 2717 [4] K. Lass, X. Han, E. Hasselbrink, *J. Chem. Phys.* 123 (2005) 051102 [5] K. Lass, X. Han, E. Hasselbrink, *Surf. Sci.* 600 (2006) 4275

O 45.3 Thu 11:00 SCH A215

**From electrons to reactive flow: Coupling first-principles kinetic Monte Carlo with continuum level simulations** — ●SEBASTIAN MATERA and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin

First-principles kinetic Monte Carlo (kMC) simulations have evolved into an important tool in the modeling of heterogeneous catalytic processes. The success of the approach relies on the accurate treatment of two central aspects for the reactive surface chemistry: A first-principles description of the involved elementary processes and an evaluation of their statistical interplay that fully accounts for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface. Particularly for technologically more relevant environments, i.e. ambient pressures and elevated temperatures with concomitant higher product formation rates, a third aspect in form of the heat and mass flow in the system becomes increasingly important. We investigate these effects by coupling first-principles kMC simulations self-consistently with continuum level simulations for the gas and solid phase transport, considering a stagnation point flow geometry as a model for recent *in situ* measurements over single-crystal model catalysts. Applying our method to the CO oxidation over RuO<sub>2</sub>(110) [1], we demonstrate how the build-up of temperature and pressure gradients over the active surface influence the observed catalytic activity and surface composition.

[1] K. Reuter and M. Scheffler, *Phys. Rev. B* 73, 045433 (2006).

O 45.4 Thu 11:15 SCH A215

**XPS, TDS and STM Characterization of Carbonate Species and O- $\alpha$  on Ag(111)** — ●R. REICHEL, S. BÖCKLEIN, S. GÜNTHER, and J. WINTTERLIN — Ludwig-Maximilians-Universität, 81377 München, Germany

The interaction between Ag surfaces and oxygen is extremely complex and characterized by several different oxygen species. For this reason there is no general agreement about the role of these species in the Ag-catalyzed ethylene epoxidation. Carbonate is one of the species, and it is formed on silver at high pressures. Another one is atomic oxygen on reconstructed Ag surfaces, such as the (4×4)O reconstruction on Ag(111). An important role in recent reaction models is played by the so called O- $\alpha$ , O atoms on the non-reconstructed Ag surface.

Using XPS, TDS and STM we have investigated carbonate and other oxygen species on Ag(111). The species obtained sensitively depend on the preparation conditions, especially on very low impurities of CO<sub>x</sub>. Instead of the formation of O- $\alpha$  by exposure of Ag(111) to oxygen at room temperature we could identify three different species. Besides the (4×4)O we observed carbonate and CO<sub>2,ad</sub>. Those two can be distinguished in TDS and can be discriminated from the postulated O- $\alpha$  by XPS. Carbonate could be decomposed by heating to 475 K forming the (4×4)O. Thus it shows the behaviour of O- $\alpha$  described in literature, and the O- $\alpha$  species may have to be reinterpreted. CO<sub>2,ad</sub> however may be mistaken for carbonate. In STM we followed the decomposition of (4×4)O-patches under exposure of CO<sub>2</sub>, and CO<sub>2,ad</sub> is formed instead of carbonate.

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**Morphology of alloy catalysts in an oxidizing environment: Structure-sensitivity of ethylene epoxidation over Ag-Cu particles** — ●SIMONE PICCININ<sup>1</sup>, CATHERINE STAMPFL<sup>1</sup>, and MATTHIAS SCHEFFLER<sup>2</sup> — <sup>1</sup>University of Sydney, Sydney, Australia — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Ag-Cu alloys have been proposed as catalysts for ethylene epoxidation due to their superior selectivity compared to pure silver, the predominant catalyst for this reaction [1]. By means of density-functional theory and atomistic thermodynamics, we study the surface structure and morphology of Ag-Cu particles in thermodynamic equilibrium with an oxygen atmosphere. Contrary to the common assumption of the formation of a 2D surface alloy, we find that at temperatures and pressures of interest for practical applications the particles can display a variety of structures, including thin Cu-surface-oxides in coexistence with clean Ag. At variance with pure Ag in UHV, we find that under reactive conditions the (111) facet is not dominant. We identify different reaction pathways that will compete and/or synergetically interplay in the catalysis. In general, the reaction mechanism is structure-dependent and often the reaction does not proceed through the formation of stable intermediates, in contrast to clean Ag and the 2D alloy. Analyzing the competing reactions, we discuss how the addition of Cu improves the selectivity and stress the overall importance of accounting for the effect of ambient conditions.

[1] S. Linic et al. *J. Catal.* 224, 148 (2004)

O 45.6 Thu 11:45 SCH A215

**Carbon in palladium catalysts** — ●NICOLA SERIANI, FLORIAN MITTENDORFER, and GEORG KRESSE — University of Vienna, Austria

A carbon-rich film at the surface of a palladium catalyst is thought to be responsible for the high selectivity observed in partial hydrogenation reactions [1]. The exact nature of this phase is still unclear. We have employed density functional theory as implemented in VASP to investigate the Pd-C configuration space and the thermodynamic stability of possible phases. Bulk carbides, intercalated graphite, diamond-like phases and dissolved carbon have been considered. The calculated core level shifts and formation energies exclude the formation of a bulk carbide, as suggested in Ref. [1]. A more complex picture involving graphite and dissolved carbon arises from our calculations. The results shed light on the complex Pd-C interactions important for partial hydrogenation catalysis.

[1] D. Teschner et al., *Science* 320, 86 (2008).

O 45.7 Thu 12:00 SCH A215

**Bifunctional Nanostructured Model Catalysts: Metal/Oxide**

**Interaction Controls Initial NO<sub>x</sub> Storage Mechanism —**

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In order to get detailed insights into the underlying mechanism and microkinetics, we investigated the initial NO<sub>x</sub> uptake on a model nitrogen storage and reduction (NSR) catalyst. This model system is prepared under UHV conditions by co-deposition of noble metal particles (Pd) and Ba-containing oxide particles, representing the storage compound, onto an ordered alumina film on a NiAl(110) substrate.

Using a combination of vibrational spectroscopy (IRAS), molecular-beam methods (MB) and scanning tunnelling microscopy (STM), we were able to show that the reaction mechanism is critically controlled by the metal-oxide interaction between the active noble metal particles and the NO<sub>x</sub> storage compound [1][2]. We suggest that a reverse spillover of activated oxygen species from the NO<sub>x</sub> storage compound to the noble metal is facilitated by the strong interaction between both components. A partial oxidation of the metal particles and a simultaneous stabilization of surface nitrite intermediates are a consequence of this process. [1] A. Desikusumastuti et al., ChemPhysChem 9 (2008), 2191-2197 [2] A. Desikusumastuti et al., Surf. Sci. Lett. in press

O 45.8 Thu 12:15 SCH A215

**Infrared spectroscopic studies of syngas adsorption on ZnO nanoparticles —**

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Zinc oxide is an important material with a wide range of applications in catalysis. Presently, the most prominent application of ZnO is industrial methanol synthesis from syngas (CO<sub>2</sub>/CO/H<sub>2</sub>) over Cu/ZnO catalysts. The study of syngas adsorption on ZnO surfaces is of fundamental importance in understanding the microscopic processes occurring in methanol synthesis. In this work, the interaction of CO and CO<sub>2</sub> with ZnO nanoparticles has been studied by ultra-high vacuum Fourier-transform infrared spectroscopy (UHV-FTIRS) together with diffuse reflectance IR spectroscopy (DRIFTS). Based on the corresponding HREELS data obtained from single-crystal surfaces, the IR results on ZnO powder samples can be understood on the atomic level. Exposing ZnO to CO<sub>2</sub> leads to the formation of a number of carbonate species on different facets. For CO adsorption on clean ZnO powder one dominant band is observed at 2189 cm<sup>-1</sup> and assigned to CO bound to Zn sites on ZnO(10-10). Furthermore, the FTIRS data demonstrated that the binding energy of CO is dramatically increased when ZnO is pre-modified by CO<sub>2</sub>. This unexpected effect results from the formation of tridentate carbonate species on the nonpolar (10-10) surfaces, which increase the Lewis acidity of neighboring Zn<sup>2+</sup> cations.

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**Reactivity of Hydrogen Related Reactions of Platinum Nanoparticles on Graphite —**

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A present challenge in electrocatalysis is to identify novel, highly active catalysts. Former experimental investigations of the systems Pd/Au(111) [1,2] and Pt/Au(111) [3,4] show that with decreasing amount of the catalyst material the specific catalytic activity increases considerably with respect to hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER). In order to improve the understanding of such an enhanced catalytic activity, hydrogen based reactions were investigated for platinum supported on HOPG (highly oriented pyrolytic graphite). For that purpose, the HOPG surface was structured with nanoparticles of platinum using electrochemical pulse techniques. First results on the catalytic activity of Pt/HOPG regarding HOR and HER are presented and compared to the results of the bimetallic systems Pd/Au(111) and Pt/Au(111).

[1] Kibler, L. A. ChemPhysChem 7 (2006) 985 [2] Pandelov, S.; Stimming, U. Electrochimica Acta 2007, 52, 5548 [3] Wolfschmidt, H.; Buřar, R.; Stimming, U. J. Phys. Condens. Matter, 2008, 20/37, 374127 [4] Wolfschmidt, H.; Buřar, R.; Stimming, U. submitted for publication

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**Similarities and Differences of the Reactivity of Pt/Au(111) and Pd/Au(111) towards HER/HOR, ORR and MOR —**

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Nanoparticles and nanostructures often show a different behavior compared to the bulk material. Especially in the field of catalysis high reactivity and low amounts of catalyst are required. Thereby, well known noble metal catalysts such as Pt and Pd were electrochemically deposited onto inert Au(111) supports. These nanostructured model surfaces allow investigating the effects of particle dispersion, particle size and the influence of the substrate material. The following reactions were investigated: I.) hydrogen evolution reaction (HER), II.) hydrogen oxidation reaction (HOR), III.) oxygen reduction reaction (ORR) and IV.) methanol oxidation reaction (MOR). Electrochemical methods such as pulse techniques and cyclic voltammetry were used to determine the electrocatalytic properties. The morphology of the model electrodes and the amount of noble metal was obtained with EC-STM. It was found that with decreasing amount of Pd and Pt deposited onto Au(111) the specific activity towards hydrogen related reactions increases by up to three orders of magnitude. In contrast to the strong enhancement for the hydrogen reactions the ORR shows an increasing electrocatalytic activity with increasing amount of noble metal as one would expect. The specific reactivity of Pt on Au(111) for the MOR seems to behave also in an expected way.