

## O 28: Heterogeneous catalysis II

Time: Tuesday 10:30–13:15

Location: MA 042

O 28.1 Tue 10:30 MA 042

**Ethylene Oxide Formation over Ag: Investigation of the "electrophilic" Oxygen on Ag(111)** — •SEBASTIAN BÖCKLEIN<sup>1</sup>, MIGUEL A. NIÑO<sup>2</sup>, TEVFIK O. MENTES<sup>2</sup>, ANDREA LOCATELLI<sup>2</sup>, SEBASTIAN GÜNTHER<sup>3</sup>, and JOOST WINTERLIN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Germany — <sup>2</sup>Sincrotrone Trieste S.C.p.A., Trieste, Italy — <sup>3</sup>Technische Universität München, Germany

The understanding of the ethylene oxide formation crucially depends on the active oxygen species on the Ag catalyst. We have used x-ray photoelectron spectroscopy (XPS), temperature-programmed desorption and reaction (TPD and TPR), low-energy electron- as well as photo electron emission microscopy (LEEM / XPEEM) and scanning tunneling microscopy (STM) to identify and characterize O species on Ag(111). In addition to the (4×4)O phase (O 1s BE 528.3 eV) assigned to "nucleophilic" oxygen, the "electrophilic" oxygen (most likely the active species for the partial oxidation) was prepared under UHV conditions applying a special treatment using NO<sub>2</sub>. The latter phase has previously only been prepared by extremely high O<sub>2</sub> exposures. XPS reveals two species (O 1s BE 530.2 and 530.7 eV). STM and LEED show a (7×√3)rect structure, which is connected with a massive change of the surface morphology. STM and TPR experiments show that this phase reacts with ethylene to give ethylene oxide. In situ STM experiments, performed under reaction conditions in the mbar regime, show structures and surface morphology changes that had before been observed in UHV experiments.

O 28.2 Tue 10:45 MA 042

**CO adsorption and oxidation study on different types of Au clusters on C/W(110)** — •MAGDALENA BACHMANN, NORBERT MEMMEL, and ERMINALD BERTEL — Institute of Physical Chemistry, University of Innsbruck, Austria

In the last years gold nanoparticles on oxidic supports have gained great attention due to their catalytic activity for oxidation reactions. Despite 20 years of research, it is not clear if this unexpected behavior originates either from support effects (charge transfer etc.) or from intrinsic properties of the clusters (quantum size effect, number of low coordinated atoms etc.). We introduce two different carburized W(110) substrates for the growth of gold nanoclusters: On R(15×12)C/W(110) regularly spaced nanodot arrays with a cluster size of  $\approx 7$  atoms are formed, whereas on R(15×3)C/W(110) larger particles of bilayer height are fabricated. The catalytic properties of both systems are studied; CO combustion is chosen as a well-explored test reaction. As TPD measurements clearly indicate, CO is adsorbed on both types of clusters as well as on extended gold islands on the bare W(110) substrate. Although in-situ STM investigations on the influence of oxygen on the clusters suggest dissociation (which is regarded as the most crucial step), TPR experiments do not indicate the formation of CO<sub>2</sub>. Probable reasons for these observations are discussed as well as the position of our findings within the field of research.

O 28.3 Tue 11:00 MA 042

**Computational screening approach to redox-active metal-organic frameworks** — •JELENA JELIC<sup>1</sup>, DMYTRO DENYSENKO<sup>2</sup>, DIRK VOLKMER<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München (Germany) — <sup>2</sup>Universität Augsburg (Germany)

Metal-organic frameworks (MOFs) have been suggested for a wide range of applications including gas storage, gas separation and drug delivery. For catalytic applications, MOFs possessing highly accessible, redox active metal centers are particularly interesting. The highly robust and modular MFU-4l structural family offers such sites, with MFU-4l in particular featuring catalytically appealing large pore apertures [1]. We perform large-scale density-functional theory calculations to support the successful postsynthetic metal ion exchange to Co-based MFU-4l [2]. With the compound exhibiting promising reversible gas-phase oxidation properties, we computationally screen for other coordinatively unsaturated metal centers or ligands that yield equally redox-active frameworks.

[1] S. Biswas *et al.*, Dalton Trans. 6487 (2009).

[2] D. Denysenko *et al.*, Chem. Commun. (accepted).

O 28.4 Tue 11:15 MA 042

**Structure and reactivity of PdAg/Pd(111) surface alloys** —

•LUIS MANCERA and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm, Germany

Bimetallic surface structures often exhibit catalytic activities and selectivities higher than their pure components. Therefore there is a strong interest in understanding the factors leading to the properties of bimetallic catalysts. Surface alloys often serve as model systems for bimetallic catalysts. Very recently, a study of the structural and catalytic properties of PdAg/Pd(111) upon CO exposure was carried out using a combination of various UHV techniques, i.e. STM, TPD and HREELS [1]. This study showed that the activity of this system is mainly driven by ensemble effects, i.e. by the configuration of Pd adsorption sites. It was also found that the CO bonding strength is significantly reduced upon increasing the Ag concentration. In this contribution, we address the reactivity of bimetallic PdAg/Pd(111) surface alloys based on density functional theory (DFT) calculations. Since changes in the relative metal composition often lead to a non-linear variation of their catalytic properties, mainly due to the interplay of electronic ligand and geometrical effects, we investigate their dependence on the concentration and configuration of Ag atoms in the surface alloy. Furthermore, we also study trends in the CO adsorption energies as a function of CO coverage.

[1] Y. Ma, T. Diemant, J. Bansmann and R. J. Behm. Phys. Chem. Chem. Phys. **13**, 10741 (2011)

O 28.5 Tue 11:30 MA 042

**HR-EELS studies on zinc oxide powder samples** — •SEBASTIAN FREY, MARTIN KROLL, and ULRICH KÖHLER — Ruhr-Universität, Bochum, Deutschland

High resolution electron energy loss spectroscopy is a useful tool in heterogeneous catalysis as it provides information about vibration states of adsorbates. With this, not only the adsorbed species can be identified, but also their orientation can be determined. In methanol synthesis HR-EELS is successfully applied to doped oxide single crystals [1] while studies on oxide powders, which are more similar to real catalysts, rely on infrared spectroscopy (FTIRS, [2]) due to their low conductivity.

However, with a thoroughly preparation it is possible to sediment a thin powder layer on a gold plate substrate. This avoids the conductivity problem and enables HR-EELS studies also on powders. Results show a distinct signal of Fuchs-Kliwer phonons and their multiples decreasing during adsorption which is comparable to ZnO single crystal samples. Further measurements contain CO, CO<sub>2</sub>, Methanol and other gases.

[1] Y. Wang *et al.*, Angew. Chem. Int. Ed., **46**, 5624-5627 (2007)

[2] H. Noei *et al.*, Appl. Catalysis A, **391**, 31-35 (2011)

O 28.6 Tue 11:45 MA 042

**MgO on Mo(001) — Growth Study of a Model System for Heterogeneous Catalysis** — •STEFANIE STUCKENHOLZ, CHRISTIN BÜCHNER, LEONID LICHTENSTEIN, MARKUS HEYDE, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

The morphology and electronic structure of oxide surfaces play an important role in surface reactions and thus in heterogeneous catalysis [1]. Insight into reactivity influencing parameters at the atomic level can be gained by incorporating scanning probe techniques.

The main tool we use is a microscope combining frequency modulation dynamic force microscopy (FM-DFM) with scanning tunneling microscopy (STM) [2]. This custom-built instrumentation provides atomically resolved complementary information about the morphology and the electronic properties of local surface sites.

Following previous studies on thin MgO films [3] we want to use our versatile microscope to characterize the change in morphology and the electronic structure of the oxide surface with respect to the transition from a thin film to a bulk-system. In this study we use MgO on Mo(001) as a model system for catalysis. We will present findings which were made during the growth study of the model system.

[1] L. Giordano, *et al.*, Acc. Chem. Res. **44**, 1244 (2011)

[2] M. Heyde, *et al.*, Appl. Phys. Lett. **89**, 263107 (2006)

[3] T. König, *et al.*, J. Am. Chem. Soc. **131**, 17544 (2009)

O 28.7 Tue 12:00 MA 042

**ZnO micro- and nanostructures for photocatalytic applications** — INGO PAULOWICZ, YOGENDRA KUMAR MISHRA, SEBASTIAN WILLE, and •RAINER ADELUNG — Institute for Materials Science, Functional Nanomaterials, University of Kiel, Kaiserstr. 2, D-24143 Kiel, Germany

Photocatalysis has demonstrated great potential in degrading organic pollutants and thus is a promising mechanism in environmental and medical cleaning applications.

We present results on ZnO micro- and nanostructures which were produced employing two variants of a novel synthesis route.

ZnO microstructures were synthesized using a batch process, called the Flame Transport Synthesis (FTS, patent pending, DE 10 2010 012 385.4). The resulting powder can be formed into various shapes like tetrapods or core spike particles. Density as well as porosity can be tuned over a wide range by applying a post synthesis sintering step, underlining the possibility for upscaling.

ZnO nanostructures were synthesized using a modification of the FTS, which allows a continuous and ultra-rapid fabrication process, in which ZnO structures are produced from Zn in less than 20 ms.

Both systems were evaluated using a test-dye (methylene blue) and showed high conversion rates, where the nanostructured ZnO samples were about 20 times more efficient than their micro structured counterparts. First experiments with waste water were conducted.

O 28.8 Tue 12:15 MA 042

**Oxidation of Platinum Nanoparticles on Gallium Nitride Surfaces: the effect of semiconductor doping on nanoparticle reactivity** — •SUSANNE SCHÄFER<sup>1</sup>, SONJA A. WYRZGOL<sup>2</sup>, MICHAEL HÄVECKER<sup>3</sup>, AXEL KNOP-GERICKE<sup>3</sup>, JOHANNES A. LERCHER<sup>2</sup>, IAN D. SHARP<sup>1,4</sup>, and MARTIN STUTZMANN<sup>1,2</sup> — <sup>1</sup>WSI, Technische Universität München, Am Coulombwall 4, 85748 Garching — <sup>2</sup>Catalysis Research Center, Technische Universität München, Garching — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — <sup>4</sup>Joint Center for Artificial Photosynthesis, LBNL, Berkeley, USA

Platinum nanoparticles supported on p- and n-type GaN are investigated as novel hybrid systems for the electronic control of catalytic activity. In-situ oxidation and reduction were studied with high pressure XPS. The experiments revealed that the underlying wide bandgap semiconductor has a large influence on the surface properties and reactivity of supported nanoparticles. For as-deposited Pt cuboctahedra supported on n-type GaN, a higher fraction of oxidized surface atoms was observed compared to cuboctahedral particles supported on p-type GaN. Under an oxygen atmosphere, immediate oxidation was recorded for nanoparticles on n-type GaN, whereas little oxidation was found for nanoparticles on p-type GaN. Together, these results indicate that changes of the Pt chemical activity under X-ray irradiation are dependent on the type of GaN doping. The strong nanoparticle-support interaction is consistent with charge transfer of X-ray photogenerated free carriers at the GaN/Pt interface and suggests that GaN is a promising support material for photocatalysis and catalysis on demand.

O 28.9 Tue 12:30 MA 042

**Composition-dependent size and shape changes of Pt-Rh alloy nanoparticles on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) during CO oxidation reactions** — •UTA HEJRAL<sup>1</sup>, PATRICK MÜLLER<sup>1</sup>, OLIVIER BALMES<sup>2</sup>, DIEGO PONTONI<sup>2</sup>, and ANDREAS STIERLE<sup>1</sup> — <sup>1</sup>University of Siegen, 57068 Siegen, Germany — <sup>2</sup>European Synchrotron Radiation Facility, 38043 Grenoble, France

Pt-Rh nanoparticles are widely used in chemical industry and in automotive exhaust control where they catalyze the oxidation of CO among other reactions. Major attention has in recent years been paid to the study of alloy nanoparticles with the aim to identify systems that allow to control the catalyst selectivity and to enhance its activity and lifetime [1]. Sintering is regarded as one of the major causes of cat-

alyst deactivation and it is of utmost scientific and economic interest to find ways to prevent it. Here we present concentration-dependent size and shape changes of epitaxial Pt-Rh alloy nanoparticles on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates observed in-situ during CO oxidation at near atmospheric pressures. The experiments were performed in a flow-reactor at the high energy beamline ID15A (ESRF, E=78.8 keV) by means of grazing incidence x-ray diffraction, x-ray reflectivity measurements and in-situ mass-spectrometry [2]. During the experiments the O<sub>2</sub> pressure ranged between 0 and 14 mbar while the temperature and CO pressure were kept at 550 K and 20 mbar, respectively. Our results demonstrate that a higher Rh concentration reduces sintering significantly.

[1] J.Y. Park et al., Nano Lett. 8 673 (2008)

[2] R. v. Rijn et al., Rev. Sci. Instr. 81 014101 (2010)

O 28.10 Tue 12:45 MA 042

**Concentration dependent oxidation of Pd-Rh alloy nanoparticles on MgAl<sub>2</sub>O<sub>4</sub>(001)** — •PATRICK MÜLLER<sup>1</sup>, UTA HEJRAL<sup>1</sup>, UTA RÜTT<sup>2</sup>, and ANDREAS STIERLE<sup>1</sup> — <sup>1</sup>University of Siegen, Walter-Flex-Str. 3, 57068 Siegen, Germany — <sup>2</sup>Deutsches Elektronen-Synchrotron (DESY), Notkestraße 85, 22607 Hamburg, Germany

Noble metal alloy nanoparticles play an eminent role in heterogeneous catalysis, especially as catalyst in automotive exhaust control (CO oxidation, NO<sub>x</sub> reduction). Understanding oxidation and reduction behavior of Pd-Rh alloy nanoparticles on the nanoscale is of great importance for improving their functionality [1]. To this end we prepared a combinatorial sample containing five stripes of epitaxial alloy nanoparticles of varying Pd-Rh concentrations on an MgAl<sub>2</sub>O<sub>4</sub>(001) support.

We present concentration-dependent size and shape changes of epitaxial Pd-Rh alloy nanoparticles as well as bulk oxide formation observed in-situ during oxidation. The experiments were carried out in a high pressure compatible UHV chamber at the high energy materials science beamline P07 at DESY in the temperature range between 570 K and 670 K and at oxygen pressures from UHV up to 0.1mbar. We employed grazing incidence x-ray reciprocal space mapping using a 2D detector and complementary x-ray reflectivity at an energy of 85 keV [2]. Our results demonstrate a strong influence of the nanoparticles composition on the oxidation behavior.

[1] F. Tao, et al., Science Vol. 322, 1164170 (2008)

[2] P. Nolte, et al., Phys. Rev. B 77, 115444 (2008)

O 28.11 Tue 13:00 MA 042

**Cu clusters on ZnO: Atomistic Insights into Strong Metal-Support Interaction** — •LUIS MARTINEZ SUAREZ<sup>1</sup>, JOHANNES FRENZEL<sup>1</sup>, BERND MEYER<sup>2</sup>, and DOMINIK MARX<sup>1</sup> — <sup>1</sup>Ruhr-Universität Bochum, Theoretical Chemistry, Bochum, Germany — <sup>2</sup>Interdisziplinäres Centrum für Molekulare Materialien (ICMM) and ComputerChemieCentrum (CCC), Department Chemie und Pharmazie, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany

The morphology of nanodispersed Cu on ZnO surfaces, used as a catalyst for the industrial synthesis of methanol, directly depends on the interplay of chemical and physical processes of the environment.[1] In the present study, the underlying complex phase diagram of a ZnO-supported copper cluster exposed to wide ranges of H<sub>2</sub> and O<sub>2</sub> pressures is generated in the first place by *ab initio* thermodynamics. After having identified the relevant mechanisms of surface stabilization and Cu cluster morphology, i. e. hydrogen adsorption, oxygen vacancy formation and the experimentally observed[1] brass formation, insights into the strong metal-support interaction are obtained based on exploring the electronic structure of the catalyst under high temperature and reducing gas phase conditions of the industrial process. Furthermore, the response of the support and metal nanoparticle upon surface chemical reactions are probed by studying such processes with H<sub>2</sub> and CO<sub>2</sub>, which are the key reactants.

[1] J.-D. Grunwaldt et al., J. Catal., 194, (2000) 452