

## O 39: Heterogeneous Catalysis

Time: Tuesday 18:15–21:00

Location: Poster A

O 39.1 Tue 18:15 Poster A

**High-resolution X-ray photoelectron spectroscopy investigations of the reaction of  $C_2H_4$  and  $C_6H_6$  on carbide-modified Mo(110)** — •UDO BAUER, CHRISTOPH GLEICHWEIT, OLIVER HÖFERT, CHRISTIAN PAPP, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Carbide-modified molybdenum surfaces have been proposed as noble metal-free catalysts for a variety of reactions, among them the dehydrogenation of hydrocarbons. The modification of Mo surfaces by carbon changes their reactivity towards the behavior of Pt-group metals. Herein, we study and compare the adsorption and reaction of ethylene and benzene on both a thin and a thick carbide layer on Mo(110) in-situ using synchrotron based high-resolution X-ray photoelectron spectroscopy (HR-XPS). Near edge X-ray absorption fine structure (NEXAFS) measurements are used for the identification of the adsorption geometry of the intact molecules and their reaction intermediates, whereas complementary temperature programmed desorption (TPD) experiments revealed the hydrogen evolution on both surfaces. The reaction pathway of all systems was followed by temperature programmed HR-XPS, which enabled us to determine intermediate species during reaction. When comparing the data of both thin and thick carbide overlayers, we only found minor differences concerning the reactivity towards ethylene and benzene. The work was supported by the Cluster of Excellence 'Engineering of Advanced Materials' of the University Erlangen-Nürnberg.

O 39.2 Tue 18:15 Poster A

**Adsorption and Diffusion of Oxygen in Silver** — •REGINA WYRWICH, HENDRIK SCHLOMBERG, CHRISTIAN MAAK, FLORIAN ROTT, LARS BULTHAUPT, LINH NGUYEN THUY, and JOOST WINTTERLIN — Ludwig-Maximilians-Universität, München, Germany

The heterogeneously catalyzed selective oxidation of ethylene over silver is a large scale industrial process. Many studies have investigated the oxygen adsorption on silver surfaces to identify the active species for this reaction. A central issue has been the question about a possible role of oxygen atoms on subsurface positions or dissolved in the bulk. We report about a study in which we have investigated exchange processes between surface and bulk oxygen. A home-built reactor system has been used to load polycrystalline silver foils or an Ag(111) single crystal with oxygen at pressures of up to 800 mbar. The sample was then analyzed by TDS. In addition, an UHV apparatus equipped with XPS and LEED was used to investigate the sample surface after loading with oxygen. Depending on the loading parameters, two oxygen species were detected and selectively prepared, the so-called 'electrophilic oxygen' with a desorption temperature of 720 K and an XPS O 1s binding energy of 530.2 eV and the so-called 'O-gamma' with a desorption temperature of >870 K and an XPS O 1s binding energy of 529.3 eV. The species could be located at the surface (electrophilic oxygen) and in the bulk (O-gamma). It was found that the two species do not grow independently from one another, but that the formation of the 530.2 eV-species depends on the amount of O-gamma present.

O 39.3 Tue 18:15 Poster A

**Zn segregation and AuZn alloy formation on Au/ZnO(000 $\bar{1}$ ) model catalysts in methanol synthesis gases ( $H_2/CO_2$ )** — •JAN MARTIN, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institut of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

For methanol (MeOH) synthesis, Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> is the main catalyst in industrial applications. Although used since the 1960s, many investigations are performed on a fundamental understanding of the reaction. It was recently found, that metallic Zn species are present in the reaction and of importance in MeOH synthesis [1]. Au/ZnO catalysts, which are currently investigated in this reaction, showed a superior selectivity compared to Cu/ZnO at comparable reactions rates.

Here, we will focus on Au/ZnO(000 $\bar{1}$ ) model catalysts and especially on the possible presence of metallic Zn species during MeOH synthesis. For this purpose, we monitored the development of the  $L_3M_{45}M_{45}$  Auger peak, which is sensitive to changes in the Zn oxidation state, upon exposure to  $H_2/CO_2$  gas mixtures (MeOH synthesis gas). Different from Cu/ZnO catalysts, where a clear relation was observed be-

tween metallic Zn species, the presence of Cu and reaction conditions, already the evaporation of Au onto ZnO(000 $\bar{1}$ ) under UHV conditions leads to a chemical modification of the ZnO surface. Exposure to MeOH synthesis gas (200-500mbar at 240°C) also affects the chemical state of the ZnO(000 $\bar{1}$ ) surface. Experimental results are presented for different preparations and MeOH synthesis conditions.

[1] S. Kuld et al., *Angew. Chem.* 126 (2014) 6051

O 39.4 Tue 18:15 Poster A

**The formox process: catalytic oxidation of methanol to formaldehyde** — •MARCOS RELLÁN and NÚRIA LÓPEZ — Institute of Chemical Research of Catalonia (ICIQ), Av. Països Catalans 16, 43007 Tarragona, Spain

Methanol is an important source to the production of formaldehyde, one of the most important industrial and research chemicals of the world. Comprehension of this process is the first step to understand the catalytic oxidation of heavy molecular weight alcohols. Selectivity is the next frontier in research of new catalytic processes and Density Functional Theory (DFT) has become an essential tool to understand and control catalytic activity and selectivity. In this work, we have performed a DFT study of oxidation mechanism of methanol in MoO<sub>2</sub> and MoO<sub>3</sub> (formox process) to explain the experimental selectivity.

Some experimental studies concluded that MoO<sub>3</sub> can give a good yield and selectivity to formaldehyde under aerobic conditions. In the contrast, MoO<sub>2</sub> give a poor relationship between yield and selectivity in the same conditions. In anaerobic conditions the selectivity of MoO<sub>3</sub> to formaldehyde also is poor. We have found that the electronic structure stoichiometry controls activity and selectivity, and Mo-sites can be fine tuned to provide best yields.

O 39.5 Tue 18:15 Poster A

**Methanol Adsorption and Reaction on SmO<sub>x</sub>/Pt(111) Systems Studied by TPD and IRRAS** — •JIN-HAO JHANG<sup>1</sup>, ANDREAS SCHAEFER<sup>1</sup>, JASON F. WEAVER<sup>2</sup>, and MARCUS BÄUMER<sup>1</sup> — <sup>1</sup>Institute of Applied and Physical Chemistry, Center for Environmental Research and Sustainable Technology, University of Bremen, Germany — <sup>2</sup>Department of Chemical Engineering, University of Florida, USA

Samaria (SmO<sub>x</sub>) as one of rare earth oxides has been considered as a promising oxide catalyst as it shows, for instance, high selectivity in the oxidative coupling of methane (OCM). Whereas other rare earth oxides such as ceria have been studied intensively, detailed investigations of the surface chemistry of SmO<sub>x</sub> are still lacking. Here we used methanol (MeOH) as a smart probe molecule by means of temperature programmed desorption (TPD) and infrared reflection-absorption spectroscopy (IRRAS) to study the surface chemistry of SmO<sub>x</sub> thin films which were grown on a Pt(111) substrate. TPD results show that CO and H<sub>2</sub> are main products of the MeOH reaction on SmO<sub>x</sub>/Pt(111). Moreover, a cooperative effect by SmO<sub>x</sub> and the Pt substrate is only observed on the non-fully covered SmO<sub>x</sub>/Pt(111). Surprisingly CO<sub>2</sub> as an unexpected product is also found, and a measurable amount of hydrogen is missing. IRRAS results confirm the existence of methoxy and formate species during MeOH decomposition on SmO<sub>x</sub>/Pt(111) which indicates the domination of the dehydrogenation process. Additionally, monitoring the shift of the C-O stretch frequency provides information about the adsorption sites of methoxy on SmO<sub>x</sub> surfaces.

O 39.6 Tue 18:15 Poster A

**Heterogeneous Catalysis Driven by Piezoelectric and Pyroelectric Materials** — •MAXIMILIAN SONNTAG, MATEO UREÑA DE VIVANCO, BIANCA STÖRR, ERIK MEHNER, JULIANE HANZIG, TILMANN LEISEGANG, and DIRK C. MEYER — TU Bergakademie Freiberg, Institut für Experimentelle Physik, Leipziger Straße 23, 09596 Freiberg

Approximately 90% of all chemical processes are based on heterogeneous catalysis.<sup>1</sup> Conventional catalysis is often limited to high temperatures like for ammonia synthesis in order to activate the catalyst. Nevertheless, the use of low temperature waste heat or vibrations can also enhance catalytic reactions. Pyroelectric materials can generate charges by converting heat, whereas piezoelectric materials can generate charges from vibrations. These coupling phenomena provide electrical charges for the redox reactions (piezocatalysis<sup>2</sup> and pyrocatalysis<sup>3</sup>).

Utilizing LiNbO<sub>3</sub>, we present catalytic decolorization of organic and

inorganic indicators. Oxidation of indigo carmine and reduction of permanganate take place in aquatic solution under ultrasonic vibration. Results show that several radical species may be formed in water during mechanical stimulation.

[1] J. A. Dumesic, G. W. Huber, M. Boudart, *Handbook of Heterogeneous Catalysis*, Vol. 1, 2nd ed., **2008**, p.1. [2] K.-S. Hong, H. Xu, H. Konishi, X. Li, *J. Phys. Chem. Lett.* **2010**, *1*, 997 and *J. Phys. Chem. C* **2012**, *116*, 13045; M. B. Starr, X. Wang, *Sci. Rep.* **2013**, *3*, Art. 2160. [3] E. Gutmann, A. Benke, K. Gerth, H. Böttcher, E. Mehner, C. Klein, U. Krause-Buchholz, U. Bergmann, W. Pompe, D. C. Meyer, *J. Phys. Chem. C* **2012**, *119*, 5383.

O 39.7 Tue 18:15 Poster A

**Suggestion to simulate energy dissipation via electron hole-pair – vibrational coupling using ab initio fitted TD-tight binding** — MICHAEL GROTEMEYER and •PEHLKE ECKHARD — Institut für Theoretische Physik und Astrophysik, Universität Kiel, Germany

The ab initio molecular dynamics simulation of electronically non-adiabatic effects during the interaction (scattering or sticking) of atoms and molecules with solid surfaces using time-dependent density functional theory is computationally extremely expensive, even if simple Ehrenfest dynamics is assumed for the motion of the nuclei. This makes the required statistical averaging over initial conditions of the incoming particles impractical. For strong electron hole-pair – vibrational coupling between molecules and a metal surface, when most of the initial vibrational energy is dissipated during the incoming part of the trajectory (i.e. before reflection at the surface) an approximate approach appears to be feasible. The energy transfer into electron hole-pair excitations is estimated from the integration of a simple time-dependent 3D tight-binding hamiltonian with parameters adapted to ab initio data. In the TB model also distinctly thicker slabs than usually applied in density functional computations can be used, which alleviates the effects of finite bath size in case the simulation time corresponds to several vibrational periods of the molecular vibration. Aspects of this approach will be discussed.