

## O 15: Heterogeneous catalysis I

Time: Monday 16:00–19:00

Location: MA 042

O 15.1 Mon 16:00 MA 042

**Flow Reactor Investigations of the Ethylene Epoxide Oxide Formation over Ag(111)** — ●REGINA WYRWICH<sup>1</sup>, SEBASTIAN BÖCKLEIN<sup>1</sup>, SEBASTIAN GÜNTHER<sup>2</sup>, and JOOST WINTTERLIN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität, München, Germany — <sup>2</sup>Technische Universität München, Germany

The partial oxidation of ethylene to form ethylene epoxide (EtO) over Ag catalysts is a large scale catalytic process in chemical industry. Although intensive studies have been performed in the last decades the mechanism of the reaction is still not clear. Surface science experiments are hardly possible because of the extremely low reaction probability of the ethylene molecules, an example of the "pressure gap" problem. To overcome this problem we used a specially designed flow reactor in which experiments on single crystals up to atmospheric pressure could be realized. Product gas analysis was performed by quadrupole mass spectrometry (QMS). Because of the low reaction probability the QMS data are strongly affected by errors and cross sensitivities, but we show that by a careful analysis EtO formation on a Ag(111) single crystal surface can be unambiguously detected. An initial annealing step to 600 °C reproducibly led to an active state of the sample. Quantitative data on the pressure, temperature and gas composition dependence of the activity and selectivity were obtained. Indications of a participation of oxygen atoms in the near-surface bulk of the Ag sample were found. We also report on experiments in which Ag samples were promoted by Cs, an important component of the industrial EtO catalyst.

O 15.2 Mon 16:15 MA 042

**Oxygen dissociation on pristine and doped CaO films** — ●YI CUI, NIKLAS NILIUS, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Dissociation of O<sub>2</sub> is often the initial step for oxidation reactions on supported metal catalysts. As the dissociation cross section is low on the surface of many wide-gap oxides, we have tried to improve the performance by inserting impurity ions that act as electron donors. For this purpose, Mo-doped CaO films have been prepared and analyzed with respect to their O<sub>2</sub> adsorption behavior, using scanning tunneling microscopy. Whereas at room temperature, both the pristine and doped films spontaneously dissociate oxygen, intact O<sub>2</sub> molecules are detected on pristine CaO upon exposure at 100 K. These molecules can be split in a controlled manner by electron injection from the STM tip. On the doped films, on the other hand, oxygen dissociation takes place at any temperature, suggesting that a spontaneous electron transfer from the Mo dopants into the anti-bonding oxygen orbitals triggers the decay of the molecule.

O 15.3 Mon 16:30 MA 042

**CO oxidation reaction on mesoporous Au/TiO<sub>2</sub> model catalysts - a kinetic and spectroscopic study** — ●MATTHIAS ROOS<sup>1</sup>, DOMINIQUE BÖCKING<sup>2</sup>, KWABENA OFFEH GYIMAH<sup>1</sup>, GABRIELA KUCEROVA<sup>1</sup>, JOACHIM BANSMANN<sup>1</sup>, NICOLA HÜSING<sup>2,3</sup>, and R. JÜRGEN BEHM<sup>1</sup> — <sup>1</sup>Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — <sup>2</sup>Institute of Inorganic Chemistry II, Ulm University, D-89069 Ulm, Germany — <sup>3</sup>Materials Chemistry, Paris-Lodron University, A-5020 Salzburg, Austria

Ultrathin mesoporous Au/TiO<sub>2</sub> layers of about 150 nm thickness, can be considered as a close-to-realistic model system for realistic Au/TiO<sub>2</sub> catalysts. Their catalytic properties towards the CO oxidation reaction were studied using two different types of reactors, which have been developed for kinetic measurements on low surface area model catalysts. A locally resolving and differentially pumped mass spectrometer was used to determine reaction parameters like reaction orders and the activation energy of the samples [1,2]. In order to measure absolute reaction rates, a micro flow tube reactor was developed, based on the design by K. Wong et al. [3], which was optimized for the CO oxidation on mesoporous Au/TiO<sub>2</sub> film samples. Furthermore, infra red spectroscopic measurements were performed to investigate the accumulation of stable carbon based species on the sample surface, such as surface carbonates, as potential origin for the observed deactivation.

[1] M. Roos et al., *J. Chem. Phys.* 133, **2010**, 94504.

[2] M. Roos et al., *Beilstein J. Nanotechnol.* 2, **2011**, 593.

[3] K. Wong et al., *Faraday Discuss.* 105, **1996**, 237.

O 15.4 Mon 16:45 MA 042

**Chemical-to-electric energy conversion in reactions of oxygen and hydrogen molecules on Pt surface.** — ●LEVGEN NEDRY-GAILOV, JAN PHILIPP MEYBURG, ECKART HASSELBRINK, and DETLEF DIESING — Fakultät für Chemie, Universität Duisburg-Essen, D-45117 Essen, Germany

A number of scientific and technological challenges motivate the study of energy transfer to the electronic degrees of freedom in the course of exothermic chemical reactions on catalyst surfaces. However, the energy flow in the single steps of a reaction is incompletely understood. In the present study, we use planar metal-oxide-semiconductor (MOS) Pt-SiO<sub>2</sub>-*n*-Si diodes for the detection of electronic excitations associated with the reactive interaction of hydrogen and oxygen molecules on Pt surfaces. We show experimental results for the chemically induced currents in the mentioned diodes while the Pt top electrode is exposed to H<sub>2</sub>, O<sub>2</sub> and hydrogen–oxygen mixture in different molar ratios. Experiments were carried out for initial temperature of the diodes ranging from 298 to 500 K. Chemical heating of the diodes up to 900 K was observed for pressures of 10 mbar. The mechanisms of chemically induced currents generated and detected in our MOS diodes are discussed.

O 15.5 Mon 17:00 MA 042

**Chemical Waves and Rate Oscillations in the H<sub>2</sub> + O<sub>2</sub> Reaction on a Bimetallic Rh(111)/Ni Catalyst** — ●TIM SMOLINSKY<sup>1</sup>, FLORIAN LOVIS<sup>1</sup>, ANDREA LOCATELLI<sup>2</sup>, MIGUEL NIÑO<sup>2,3</sup>, and RONALD IMBIHL<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3-3a, D-30167 Hannover, Germany — <sup>2</sup>Sincrotrone Trieste, S.C.p.A., S.S. 14, km 163.5 in Area Science Park, 34012 Basovizza, Trieste, Italy — <sup>3</sup>Instituto Madrileño de Estudios Avanzados IMDEA Nanociencia, Cantoblanco 28049, Madrid, Spain

The H<sub>2</sub> + O<sub>2</sub> reaction on a Rh(111) surface alloyed with Ni was studied in the 10<sup>-6</sup> - 10<sup>-4</sup> mbar range using photoemission electron microscopy (PEEM), low energy electron microscopy (LEEM) and its spectroscopic variant (SPELEEM) as main analytical methods. The Rh(111)/Ni surface was prepared by decomposing Ni(CO)<sub>4</sub> on the Rh(111) surface resulting in an alloy with about 25% Ni in the topmost layers. The original bistable system Rh(111)/O<sub>2</sub> + H<sub>2</sub> is transformed into an excitable system through the addition of Ni. Chemical wave patterns involving target patterns, pulse trains and rotating spirals can be observed. These spatiotemporal patterns were accompanied by rate oscillations observed with mass-spectrometry. Under reaction conditions three-dimensional NiO particles form on the surface ranging from less than 1 μm up to 50 μm in size. The size of these particles depends on the total pressure. A preliminary excitation/oscillation mechanism is proposed based on the reversible segregation of Ni to the surface thus modifying the catalytic properties of the Rh/Ni surface.

O 15.6 Mon 17:15 MA 042

**First-principles kinetic Monte Carlo simulations of CO oxidation at Pd(100): Surface oxide or metal? Both!** — ●MAX J. HOFFMANN<sup>1</sup>, MATTHIAS SCHEFFLER<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>TU München, Germany — <sup>2</sup>Fritz-Haber-Institut, Berlin, Germany

CO oxidation at Palladium model catalysts is an evergreen in the quest to establish an atomic-scale understanding of heterogeneous catalytic processes and the relation between atomistic structure and catalytic activity. Notwithstanding and despite numerous experiments, the character of the active surface above Pd(100) under ambient reaction conditions remains heavily debated [1]. The pristine metal surface, a thin surface oxide layer, and bulk palladium oxide have each been suggested to be present and responsible for the catalytic activity.

Contributing to this we perform first-principles kinetic Monte Carlo (1p-kMC) simulations for each of these phases as a function of temperature and partial pressures. Next to obtaining their inherent catalytic activities at steady-state, we can use the determined surface coverages to infer on the stability ranges of the different phases. Intriguingly, this indicates an overlap of the stability regimes of pristine and oxidized Pd(100), which could be underlying the experimentally observed bistability switching between different reaction kinetics.[2]

[1] Gao et al., *J. Phys. Chem. C*, **114**, 6874 (2010).

[2] Frenken et al., *Topics Catal.* **36**, 43 (2005).

O 15.7 Mon 17:30 MA 042

**The electrochemical promotion of ethylene oxidation at bimetallic Pt-Ag/YSZ catalyst** — ●ARAFAT TOGHAN<sup>1</sup>, ROSA ARRIGO<sup>2</sup>, AXEL KNOP-GERICKE<sup>2</sup>, ROBERT SCHLÖGL<sup>2</sup>, and RONALD IMBIHL<sup>1</sup> — <sup>1</sup>Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstrasse 3-3a, D-30167 Hannover, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck Gesellschaft, Abteilung Anorganische Chemie, Faradayweg 4-6, D-14195 Berlin, Germany

The electrochemical promotion of the  $C_2H_4 + O_2$  reaction at bimetallic Pt/Ag catalyst interfaced to yttrium stabilized zirconia (YSZ) has been studied at high pressure (close to 1 mbar) using X-ray photoelectron spectroscopy (XPS) at BESSY as in situ method to identify the relevant surface species. Setting the working electrode at positive potential of 2V causes a relative rate increase in the  $CO_2$  production up to 120%; the electrocatalytic promotion effect (EPOC) is non-Faradaic ( $\Lambda = 2.18$ ). An EPOC effect is only observed at high  $p(C_2H_4)/p(O_2)$  ratios when a carbonaceous  $CH_x$  layers builds up inhibiting  $O_2$  adsorption. Only at low  $p(C_2H_4)$  the application of an electric potential causes a decrease in the carbon signal associated with a growth of the  $O_1s$  signal at 529.3 eV [1-2]. The latter species can be assigned to an electrochemically generated oxygen spillover species at Ag sites. [1] A. Toghan, L. M. Rösken, R. Imbihl, ChemPhysChem 2010, 11, 1452-1459. [2] A. Toghan, L. M. Rösken, R. Imbihl, Phys. Chem. Chem. Phys. 2010, 12, 9811-9815.

O 15.8 Mon 17:45 MA 042

**Interaction of  $H_2O$  with ceria and Pt/ceria model catalysts** — ●Y. LYKHACH<sup>1</sup>, G. N. VAYSSILOV<sup>2</sup>, M. HAPPEL<sup>1</sup>, N. TSUD<sup>3</sup>, H. A. ALEKSANDROV<sup>2</sup>, T. SKÁLA<sup>4</sup>, V. JOHÁNEK<sup>3</sup>, P. ST. PETKOV<sup>2</sup>, K. C. PRINCE<sup>4</sup>, V. MATOLÍN<sup>3</sup>, K. M. NEYMAN<sup>5,6</sup>, and J. LIBUDA<sup>1</sup> — <sup>1</sup>FAU Erlangen-Nürnberg, Germany — <sup>2</sup>University of Sofia, Bulgaria — <sup>3</sup>Charles University in Prague, Czech Republic — <sup>4</sup>Sincrotron Trieste, Italy — <sup>5</sup>Universitat de Barcelona, Spain — <sup>6</sup>ICREA, Barcelona, Spain

The interaction of  $H_2O$  with ceria-based catalysts plays an important role in hydrogen production via reforming. Still, we are lacking detailed understanding of the water surface chemistry on pure and metal-loaded ceria. We have performed a comprehensive investigation of water adsorption and dissociation on stoichiometric  $CeO_2(111)$ , partially reduced  $CeO_2 - x$ , and Pt/ $CeO_2(111)$  films on Cu(111), combining high resolution photoelectron spectroscopy (HR-PES), resonant PES, infrared absorption spectroscopy (IRAS), and density functional theory (DFT). Identification of OH-derived spectral signatures and chemisorbed water on ceria turned out to be difficult, both in HR-PES or IRAS. Despite strong signals from OH/ $H_2O$  in O 1s core level spectra upon annealing to 500 K, no corresponding vibrational bands were detected on both  $CeO_2$  and  $CeO_2 - x$  films above 200 K. DFT suggest that these experimental findings result from strong hydrogen bond between OH and neighboring oxygen anions and strong bending of OH group. Dissociation and spillover on Pt/ $CeO_2(111)$  is monitored by RPES via the Ce oxidation state as a function of temperature.

O 15.9 Mon 18:00 MA 042

**When atomic-scale resolution is not enough: Spatial effects in *in-situ* model catalyst studies** — ●SEBASTIAN MATERA<sup>1,2</sup> and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>TU München — <sup>2</sup>Fritz-Haber-Institut der MPG

A central goal in *in-situ* studies of defined model catalysts has been to obtain (at best) equally resolved spectro- or microscopic information as has been established in UHV surface science. With this focus possible heat and mass transport limitations in the ambient environments have not received much attention. We investigate such effects with our newly developed first-principles based multi-scale modeling approach integrating kinetic Monte Carlo simulations into a fluid dynamical treatment [1]. We consider two limiting cases for flow geometries in modern *in-situ* reaction chambers: i) the gas approaches the single crystal from the side, ii) the flow direction is perpendicular to the surface. Using the CO oxidation at  $RuO_2(110)$  as a showcase we obtain a strong coupling between surface chemistry and mass, heat and momentum transfer. This generates substantial variation in gas-phase pressures and temperature between the inlet and the catalyst surface. In particular for case i) we obtain large lateral changes in surface composition across the catalyst surface. This prevents the aspired direct relation between measured activity and defined catalyst structure, and therewith underscores the importance of carefully designed reactor geometries in *in-situ* studies. [1] S. Matera and K. Reuter, Catal. Lett.

133, 156 (2009); Phys. Rev. B 82, 085446 (2010).

O 15.10 Mon 18:15 MA 042

**Dynamic distribution patterns of ultrathin VOx films on Rh(111) during the  $O_2 + CH_3OH$  reaction.** — ●MARTIN HESSE and RONALD IMBIHL — Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3a, 30167 Hannover, Germany

Vanadium oxides play an important role as catalysts in partial oxidation of hydrocarbons. As a model system for VOx based catalysts we studied the behavior of ultrathin VOx films on a Rh(111) surface in the  $O_2 + CH_3OH$  reaction. VOx catalyzes the production of formaldehyde. The reaction was investigated in the 10-4 - 10-5 mbar range with photoemission electron microscopy (PEEM) as a spatial resolving method. We observed that at  $T > 600^\circ C$  the distribution of VOx on Rh(111) is no longer homogeneous but a stationary macroscopic concentration pattern developed consisting of parallel stripes of VOx surrounded by bare Rh(111) surface. In analogy to the patterns formed in the  $O_2 + H_2$  reaction on Rh(111)/VOx we interpret the patterns as being due to reactive phase separation[1]. The dependence of the rate of formaldehyde production on the distribution pattern of vanadium oxide on Rh(111) was studied.

[1] F. Lovis et. al, J. Phys. Chem. C 115, 2011, 19141

O 15.11 Mon 18:30 MA 042

**Structural Investigation of the  $(7 \times \sqrt{3})$  rect Oxygen Phase on Ag(111)** — ●MARTIN EHRENSPERGER<sup>1</sup>, MIGUEL A. NIÑO<sup>2</sup>, TEVFIK O. MENTEŞ<sup>2</sup>, ANDREA LOCATELLI<sup>2</sup>, SEBASTIAN BÖCKLEIN<sup>1</sup>, WOLFGANG MORITZ<sup>1</sup>, SEBASTIAN GÜNTHER<sup>3</sup>, and JOOST WINTTERLIN<sup>1</sup> — <sup>1</sup>Ludwig-Maximilians-Universität München, Germany — <sup>2</sup>Sincrotrone Trieste S.C.p.A., Italy — <sup>3</sup>Technische Universität München, Germany

We have investigated the structure of the  $(7 \times \sqrt{3})$  rect oxygen phase on the Ag(111) surface by means of a low-energy electron diffraction (LEED)- $I/V$  analysis. Further techniques were scanning tunneling microscopy, x-ray photoelectron spectroscopy (XPS), and low-energy electron microscopy. Three rotational domains are observed on a completely covered substrate surface. The symmetry is  $Pm$  with a mirror plane parallel to the  $\langle 112 \rangle$  substrate directions. According to XPS the structure contains about one monolayer of an oxygen species that is closely related to the so-called "electrophilic" oxygen. Following the literature this oxygen species is the active species for the partial oxidation of ethylene to give ethylene oxide over Ag catalysts. Structures were tested containing adsorbed O atoms on the unchanged Ag(111) surface, possible reconstructions of the surface, surface oxide type structures and structures derived from bulk silver oxides. Relative integral intensities suggest a thickness of at least two layers of Ag atoms. All models deduced from variations of known structures of the entire Ag-O system or comparable surface oxygen systems of other metals can be excluded.

O 15.12 Mon 18:45 MA 042

**From atoms to eddies: a novel general approach to chemical reaction engineering** — ●MATTEO MAESTRI<sup>1,2</sup>, ALBERTO CUOCI<sup>1</sup>, SEBASTIAN MATERA<sup>2</sup>, and KARSTEN REUTER<sup>2</sup> — <sup>1</sup>Politecnico di Milano, Italy — <sup>2</sup>TU München, Germany

The identification of the dominant reaction mechanism is a center piece in the quest towards an atomic-scale understanding of a catalytic process. Inherently, this mechanism is a multiscale property and its identification requires efficient and general tools that properly integrate a detailed (first-principles) description of the surface catalytic chemistry and the macroscale flow structures in the reactor. To this end we recently introduced the new solver CatalyticFOAM [1]. By exploiting the operator splitting technique, it allows for the solution of Navier-Stokes equations even for complex reacting flow profiles at surfaces. Here, we now extend its functionality to also explicitly account for site heterogeneity and the detailed surface chemical distributions in the microkinetic description of the surface reactivity. Relying on the assumption of a quasi-instantaneous adaption of the reactive chemistry to changes in the fluid properties above the surface [2] allows us to efficiently integrate corresponding kinetic Monte Carlo based microkinetics through an interpolation technique. We demonstrate our approach using the CO oxidation on  $RuO_2(110)$  for different reactor configurations and fluid dynamics conditions. [1] M. Maestri and A. Cuoci, CatalyticFOAM, www.catalyticfoam.polimi.it; [2] S. Matera and K. Reuter, Phys. Rev. B 82, 085446 (2010).