

O 40: Heterogeneous Catalysis: Experiment

Time: Tuesday 14:00–16:00

Location: S053

O 40.1 Tue 14:00 S053

Bimetallic redox interactions in model Pt-Sn-CeO₂ catalysts for fuel cell applications — ●A. NEITZEL¹, Y. LYKHACH¹, N. TSUD², T. SKÁLA², M. VOROKHTA², K. C. PRINCE³, V. MATOLÍN², and J. LIBUDA¹ — ¹FAU Erlangen-Nürnberg, Germany — ²Charles University in Prague, Czech Republic — ³Elettra-Sincrotrone Trieste, Italy

We investigated bimetallic Pt-Sn interactions as a function of the oxidation state of Pt and Sn in model Pt-Sn-CeO₂ catalysts by synchrotron radiation photoelectron spectroscopy and resonant photoemission spectroscopy. The corresponding experiments involved model Sn-CeO₂ and Pt-CeO₂ mixed oxide films prepared on a stoichiometric CeO₂(111) buffer layer on Cu(111). Both systems are characterized by excellent stabilities of Sn²⁺ and Pt²⁺ upon annealing to 700 K in UHV. We found that deposition of metallic Sn⁰ on Pt-CeO₂ films initially leads to formation of Pt-Sn-CeO₂ mixed oxides. At larger amounts of Sn⁰, we observed conversion of Pt²⁺ to new species which we assign to small Pt or PtO_x particles. The following annealing of the deposit to 700 K in UHV leads to complete reduction of Pt²⁺ but does not yield Pt-Sn alloy nanoparticles. Stepwise deposition of Pt on Sn-CeO₂ films yields Pt-Sn alloy nanoparticles at the expense of Sn²⁺. Subsequent annealing of the deposit in UHV to 750 K promotes further Pt-Sn alloy formation. The surface composition of Pt-Sn-CeO₂ catalysts was probed by CO adsorption at 110 K. We found that CO adsorption at atop sites on the Pt-Sn nanoparticles is inhibited due to thermally promoted alloying.

O 40.2 Tue 14:15 S053

Physical and chemical properties of Au nanoparticles on CeO₂ supports in the CO oxidation reaction — ●JOACHIM BANSMANN¹, GABRIELA KUCEROVA¹, AYMAN ABD EL-MOEMEN², ALI ABDEL-MAGEED¹, and R. JÜRGEN BEHM¹ — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Chemistry Department, Suez Canal University, Ismailia, Egypt

Au nanoparticles (NPs) on metal oxide surfaces are interesting catalysts in the CO oxidation and water-gas shift (WGS) reaction. Here, we will focus on the influence of different oxidic and reductive pre-treatments of Au/CeO₂ catalysts on the size and the oxidation state of the Au NPs using ex-situ characterization techniques (XRD and XPS) as well as in-situ methods such as XANES/EXAFS and diffuse IR spectroscopy (DRIFTS). Reductive pre-treatments in CO generally lead to smaller metallic particles, whereas the presence of oxidic species results in slightly larger and partially oxidic Au NPs.

Moreover, using these in-situ spectroscopy techniques, we followed the changes in the Au particle size and chemical state in the CO oxidation reaction after the different pre-treatments. Sintering/Ostwald ripening process affect the catalytic activity by lowering the surface area of Au which contributes to a decreasing reactivity. Additionally, DRIFTS measurements offer insight into adsorption sites of CO on Au NPs and the formation of carbonates and formates, which often block active site in the CO oxidation reaction.

O 40.3 Tue 14:30 S053

Surface oxide on Pt(111) as the active phase for NO and CO oxidation — ●MATTHIJS VAN SPRONSEN¹, JOOST FRENKEN¹, and IRENE GROOT² — ¹Huygens-Kamerlingh Onnes Laboratory, Leiden University, Leiden, The Netherlands — ²Gorlaeus Laboratories, Leiden Institute of Chemistry, Leiden University, Leiden, The Netherlands

Pt find its main application in the automotive industry as a catalytic converter. As catalyst, Pt transforms harmful exhaust gases to more environment-friendly components. Technical catalysts are complex and is often obscuring fundamental processes. Therefore, model catalysts are frequently used. The simplest model catalyst is the close-packed (111) surface. Even though this model catalyst has been studied for over 45 years, the main questions remain unsolved. How does Pt oxidize? What is the atomic structures of the oxide(s)? And are the structures stable under chemical reaction conditions?

We studied the oxidation of Pt(111) with the ReactorSTM, which is an STM integrated with a small flow reactor. It allows to study the atomic structure of surfaces under chemical reaction conditions (high p & T).

This resulted in the observation of two novel structures, which were identified as single-layer thick surface oxides. The first one consisted of triangles forming spoked wheels, while the second one was a lifted-row oxide. Both structures were also observed under NO oxidation reaction conditions. These oxides contain weakly-bound oxygen atoms, which should be very reactive.

O 40.4 Tue 14:45 S053

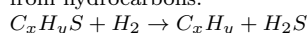
CO and D₂O chemistry on continuous and discontinuous samaria thin films on Pt(111) — JIN-HAO JHANG¹, ●SIMONA KEIL¹, ANDREAS SCHAEFER², VOLKMAR ZIELASEK¹, and MARCUS BÄUMER¹ — ¹Institute of Applied and Physical Chemistry, University of Bremen, Germany — ²Division of Synchrotron Radiation Research, Lund University, Sweden

The water-gas shift (WGS) reaction is among the most relevant for sustainable chemistry and energy conversion. Exemplarily for mixed metal – rare earth oxide WGS catalysts, the chemistry of CO and D₂O, individually adsorbed or co-adsorbed, on epitaxial thin films and islands of samaria on Pt(111) was studied by temperature programmed desorption spectroscopy in ultra-high vacuum. The comparative study indicates that Sm₂O₃ islands provide lattice oxygen at their perimeter for oxidation of CO adsorbed on adjacent Pt area. However, the reduced SmO_x islands are not fully reoxidized by subsequent exposure to D₂O. Upon CO and D₂O coadsorption, interaction between CO and OD species at the perimeter of SmO_x islands promotes D₂ formation but does not yield CO₂ as product. The study demonstrates the relevance of structural details at interface sites between metal and oxide for chemical reactions.

O 40.5 Tue 15:00 S053

High-pressure scanning tunneling microscopy during hydrodesulfurization catalysis — ●RIK V. MOM¹, JOOST W.M. FRENKEN^{1,2}, and IRENE M.N. GROOT³ — ¹Huygens-Kamerlingh Onnes Laboratory, Niels Bohrweg 2, Leiden, The Netherlands — ²Advanced Research Center for Nanolithography, Science Park 104, Amsterdam, The Netherlands — ³Gorlaeus Laboratories, Einsteinweg 55, Leiden, The Netherlands

Many catalysts show reversible physical and chemical changes during operation. To capture these changes, *in situ* studies at elevated temperatures and pressures are essential. Using a home-built high-pressure scanning tunneling microscope we have studied reversible changes during the desulfurization reaction, in which sulfur is removed from hydrocarbons.



To mimic the industrial catalyst, MoS₂ nanoparticles were deposited on Au(111). We have studied the surface dynamics of this model catalyst during the conversion of CH₃SH to CH₄ in 1 bar of various CH₃SH/H₂ mixtures at temperatures up to 250°C. From our observations, it is clear that the atomic arrangement of the active sites depends on the gas environment. We show that the sulfur coverage of the active sites during catalysis is higher than expected from DFT equilibrium calculations [1]. We show that this can be explained by kinetic effects based on the high-energy barriers involved in the reaction.

[1] Lauritsen et al., Journal of Catalysis 221 (2004) 510-522

O 40.6 Tue 15:15 S053

In situ probing of structural changes in hydrogen activation over ceria/Ru inverse model catalysts — ●JAN INGO FLEGE¹, JAN HÖCKER¹, T. ONUR MENTES², ALESSANDRO SALA², ANDREA LOCATELLI², THOMAS SCHMIDT¹, SANJAYA D. SENANAYAKE³, and JENS FALTA¹ — ¹Institute of Solid State Physics, University of Bremen, Bremen, Germany — ²Sincrotrone Elettra, Trieste, Italy — ³Chemistry Department, Brookhaven National Lab, United States

Ceria is a highly versatile oxide and used in many catalytic applications today; however, its structure-function relation and true active nature in chemical redox reactions are still not well understood. An important example is the interaction of ceria with molecular hydrogen, which is an integral part of the hydrogenation process that produces methanol from CO₂. Here, employing a powerful combination of electron spectromicroscopy with synchrotron radiation, low-energy electron microscopy (LEEM), and micro-illumination diffraction anal-

ysis, we follow *in situ* the complex structural transformations of a well-defined ceria/Ru(0001) model catalyst system when exposed to a reactive H₂ environment [1]. We demonstrate that the transition from CeO₂ to crystalline Ce₂O₃ occurs through a mixture of transient, ordered cerium oxide phases whose average size is on the order of just a few nanometers. Furthermore, these crystalline surface phases are shown to exhibit characteristic intensity-voltage curves in low-energy electron microscopy, which allow their spatial distribution to be imaged in real space directly.

[1] J. Höcker *et al.*, Adv. Mater. Interfaces, in press (2015).

O 40.7 Tue 15:30 S053

Yet another view on catalysts: probing surface roughness with nm-scale sensitivity using visible light —

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We have developed a flow reactor with an optical window which allows us to measure the reflectivity of a catalytically active sample using a 625nm light source. We will show that we can relate the reflectivity to surface roughness, even if the correlation length of the roughness is much smaller than the wavelength of the light. We will show that

using this technique we can follow the roughening/smoothing of a Pd(100) surface in space and time during switches between the oxidized and metallic state. We conclude that this easy yet powerful technique provides complementary information to more local probes such as STM and SXRD.

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***In-situ* temperature measurement using chemoelectronic nanodiodes** — •JAN PHILIPP MEYBURG, DETLEF DIESING, and ECKART HASSELBRINK — Fakultät für Chemie, Universität Duisburg-Essen, Essen, Germany

Chemoelectronic nanodiodes based on metal–insulator–metal thin film structures allow the detection of hot charge carriers that are excited in the course of surface reactions. In this context, the Pt-catalyzed oxidation of carbon monoxide is studied on a Pt–Ta₂O₃–Ta nanodiode. In order to activate this surface reaction locally the nanodiode is heated while the sample holder is held at a constant temperature below 80 K. Thus, a temperature gradient results and an accurate *in-situ* temperature measurement is required. During a continuous variation of the potential between the Pt electrode and the Ta electrode a device current is recorded that exhibits a temperature dependence. Consequently, this current can be used in order to monitor the device temperature. Therewith, exclusively the temperature of the nanoscopic MIM volume is measurable during the reaction process.