

## O 24: Catalysis: Structural Effects

Time: Tuesday 10:30–13:15

Location: MA 144

O 24.1 Tue 10:30 MA 144

**Theoretical and in-situ studies for the dissociation of water on an active Ni/CeO<sub>2</sub> catalyst: Importance of strong metal-support interactions for the cleavage of O–H bonds** — ●M. V. GANDUGLIA-PIROVANO<sup>1</sup>, D. LÓPEZ-DURÁN<sup>1,2</sup>, J. CARRASCO<sup>1,2</sup>, Z. LIU<sup>3</sup>, S. D. SENANAYAKE<sup>3</sup>, T. DUCHOŇ<sup>4</sup>, V. MATOLÍN<sup>4</sup>, and J. A. RODRIGUEZ<sup>3</sup> — <sup>1</sup>Inst. de Catálisis y Petroleoquímica, CSIC, Spain — <sup>2</sup>CIC Energigune, Álava, Spain — <sup>3</sup>Brookhaven Natl. Lab., N.Y., U.S. — <sup>4</sup>Faculty of Math. and Phys., Charles Univ., Praha, Czech Rep.

Water dissociation is crucial in numerous heterogeneous catalytic reactions on oxide-supported transition-metal catalysts. Here, supported by a combination of density-functional theory and experimental results, we elucidate the effect of the support on O–H bond cleavage activity for nickel/ceria systems. Ambient-pressure O1s photoemission spectra at low Ni loadings on CeO<sub>2</sub>(111) reveal a substantially larger amount of OH groups as compared to the bare oxide support. Our computed activation energy barriers for water dissociation show an enhanced reactivity of Ni adatoms on CeO<sub>2</sub>(111) compared with larger Ni particles and extended Ni(111) surfaces. At the origin of this support effect is the ability of ceria to stabilize oxidized Ni<sup>2+</sup> reactive species by accommodating electrons in localized *f*-states. The fast dissociation of water on Ni/CeO<sub>2</sub> has a dramatic effect on the activity and stability of this system as a catalyst for the water-gas shift reaction [1,2].

[1] J. Carrasco et al., *J. Phys. Chem. C*, 117, 8241 (2013).

[2] J. Carrasco et al., *Angew. Chem.* (2015), DOI: 10.1002/anie.201410697R2.

O 24.2 Tue 10:45 MA 144

**Alumina model supports on NiAl(110) studied by High-Pressure STM** — ●RIK MOM<sup>1</sup>, JOOST FRENKEN<sup>2</sup>, and IRENE GROOT<sup>1</sup> — <sup>1</sup>Huygens-Kamerlingh Onnes Laboratory, Leiden, The Netherlands — <sup>2</sup>ARCNL, Amsterdam, The Netherlands

Modern research on the atomic- and molecular-scale working mechanisms of industrial catalysis increasingly involves efforts to extend the use of traditional surface science characterization tools to high pressures and to increase the complexity of the investigated model catalysts.

In order to mimic the alumina that is often used to support catalytic nanoparticles, ultrathin alumina films have been developed on single crystal metal surfaces. Because of its high degree of crystallinity and good conductivity, the Al<sub>2</sub>O<sub>3</sub>/NiAl(110) system has received particular interest[1].

Here, we investigate the stability of this thin-film support under high pressures, e.g. 1 bar, of various gasses. We used high-pressure STM[2] to follow the structural evolution of the film and post-mortem XPS to inspect the end result. Our observations show that alumina films on NiAl(110) are stable under 1 bar of H<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>S. Under millibar levels of H<sub>2</sub>O, film growth occurs in defective areas, gradually expanding these over the surface. Experiments using thicker alumina films with the same level of crystallinity show that film thickness has little effect on the reactivity towards water. [1] G.H. Simon et al., *J. Phys.: Condens. Matter* 24, 084007 (2012) [2] C.T. Herbschleb et al., *Rev. Sci.Instr.* 85, 083703 (2014)

O 24.3 Tue 11:00 MA 144

**Tuning Excitability by Alloying: The System Rh(111)/Ni/O<sub>2</sub>+H<sub>2</sub>** — ●TIM SMOLINSKY, MATHIAS HOMANN, FLORIAN LOVIS, and RONALD IMBIHL — Institut für Physikalische Chemie und Elektrochemie, Leibniz Universität Hannover, Germany

Catalytic oxidation of hydrogen on Rh(111) is a bistable system but through alloying with nickel the system becomes excitable [1]. Varying the nickel coverage from zero up to several monolayers we studied chemical wave patterns and adsorbate-induced Ni segregation in the 10<sup>-6</sup> and 10<sup>-5</sup> mbar range at temperatures between 323 K and 773 K with photo electron emission microscopy (PEEM). The surface was characterized with Auger Electron Spectroscopy (AES) and Low Energy Electron Diffraction (LEED). Already small Ni coverages lead to excitable behavior and at high Ni coverages 3D-NiO particles start to nucleate on the surface. Nickel is apparently highly mobile in the top layers of the crystal. Shape, velocity and wavelength of the pulses

depend on the nickel coverage. A bifurcation diagram showing the dependence of the system behavior on the nickel coverage was constructed.

[1] F. Lovis, T. Smolinsky, A. Locatelli, M. Á. Niño and R. Imbihl, *J. Phys. Chem. C* 116 (2012) 4083-4090.

O 24.4 Tue 11:15 MA 144

**Near-ambient pressure XPS investigation of the oxidation of liquid Gallium and Platinum-Gallium alloys** — ●MATHIAS GRABAU<sup>1</sup>, SANDRA KRICK-CALDERÓN<sup>1</sup>, FLORIAN RIETZLER<sup>1</sup>, FLORIAN MAIER<sup>1</sup>, NICOLA TACCARDI<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and CHRISTIAN PAPP<sup>1</sup> — <sup>1</sup>Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — <sup>2</sup>Lehrstuhl für Chemische Reaktionstechnik, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

The oxidation of the liquid samples of gallium and gallium based platinum alloys (2 and 5 wt% Pt) by molecular oxygen at temperatures between 300 and 550 K was examined using near ambient pressure XPS. Gallium oxide films of different thickness were prepared on the surface of the liquid samples under isothermal and isobaric conditions; the growth was monitored in situ. The thickness of the prepared oxide films increased to up to 30 Å with rising temperature and O<sub>2</sub> pressure. The gallium oxide films were found to be stable in UHV up to temperatures just below 740 K. Enrichment of metallic platinum in the grown gallium oxide films was found for the examined alloys. The enrichment of platinum in the oxide films was found to be independent of the composition of the alloy, the film thickness, and the temperature and pressure during growth of the oxide films.

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O 24.5 Tue 11:30 MA 144

**H<sub>2</sub> activation on Pt-CeO<sub>2</sub> mixed oxides for fuel cell applications** — ●ARMIN NEITZEL<sup>1</sup>, YAROSLAVA LYKHACH<sup>1</sup>, TOMAS SKÁLA<sup>2</sup>, NATALIYA TSUD<sup>2</sup>, MYKHAILO VOROKHTA<sup>2</sup>, KEVIN CHARLES PRINCE<sup>3</sup>, VLADIMIR MATOLÍN<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Charles University in Prague, Czech Republic — <sup>3</sup>Elettra-Sincrotrone Trieste, Italy

We investigated H<sub>2</sub> activation on Pt-CeO<sub>2</sub> mixed oxides as a function of Pt content by means of synchrotron radiation photoelectron spectroscopy and resonant photoemission spectroscopy. Pt-CeO<sub>2</sub> mixed oxides were prepared by co-deposition of metallic Pt and Ce in oxygen atmosphere on well-ordered CeO<sub>2</sub>(111) buffer layers on Cu(111) at 110 K. Mixed oxides contain Pt<sup>2+</sup>, Pt<sup>4+</sup>, Ce<sup>4+</sup> and fractions of Ce<sup>3+</sup> ions. Pt<sup>2+</sup> ions are stabilized at (100) nanofacets at the surface of nanostructured CeO<sub>2</sub> films. Thermal stability of nanostructured Pt-CeO<sub>2</sub> mixed oxides depends strongly on the Pt concentration. Annealing to 700 K in UHV leads to partial reduction of Pt<sup>2+</sup> ions to metallic Pt particles once their number exceeds that of the (100) sites. H<sub>2</sub> dissociation occurs only in presence of metallic Pt<sup>0</sup> on the Pt-CeO<sub>2</sub> substrates. Below 300 K, H<sub>2</sub> activation yields hydroxyl groups which prevent hydrogen spillover from Pt to the substrate. Above 350 K, reduction of Pt<sup>2+</sup> is accompanied by formation of oxygen vacancies due to the reaction of hydrogen with oxygen provided by the reverse oxygen spillover from the substrate to the Pt particles.

O 24.6 Tue 11:45 MA 144

**Microkinetics of the Deacon process over RuO<sub>2</sub>(110): Rate-determining steps and diffusion limitations** — ●ZHEN YAO, FARNAZ SOTOODEH, and KARSTEN REUTER — Technische Universität München

Cl<sub>2</sub> is widely used in many chemical industries which produce HCl as byproduct. For a sustainable operation recycling HCl back to high purity Cl<sub>2</sub> is therefore mandatory. In the corresponding oxidative Deacon process (4HCl + O<sub>2</sub> → 2 Cl<sub>2</sub> + 2H<sub>2</sub>O) RuO<sub>2</sub> shows unique activities. Ultimately aiming for cheaper substitutes comprising earth-abundant metals, an atomic-scale understanding of what makes up for the special performance of RuO<sub>2</sub> represents a first step.

We contribute to this endeavor by analyzing the Deacon reaction network on a RuO<sub>2</sub>(110) model catalyst with microkinetic simulations. Specific targets are the role of the trench-like surface geometry of RuO<sub>2</sub>(110), as well as the identification of the rate-limiting steps under

varying operation conditions. For this we compare different mean-field and kinetic Monte Carlo models, and employ both first-principles and empirically determined rate constants.

O 24.7 Tue 12:00 MA 144

**Comparison of mean-field and kinetic Monte Carlo microkinetic models of CO methanation on Rh(211): Influence of lateral interactions between adsorbates** — •MIE ANDERSEN<sup>1</sup>, ANDREW J. MEDFORD<sup>2,3</sup>, THOMAS BLIGAARD<sup>2,3</sup>, JENS K. NØRSKOV<sup>2,3</sup>, and KARSTEN REUTER<sup>1,2,3</sup> — <sup>1</sup>Theoretical Chemistry, Technische Universität München, Germany — <sup>2</sup>SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, CA, USA — <sup>3</sup>Department of Chemical Engineering, Stanford University, CA, USA

In heterogeneous catalysis microkinetic modeling is often carried out in the mean-field approximation (MFA), which assumes a rapid mixing of the adsorbates and leads to a uniform distribution of all atomic and molecular species on the surface. Here, we loosen some of the underlying assumptions inherent in the MFA by moving to a full kinetic Monte Carlo (KMC) description of relevant surface processes such as adsorption, diffusion, reaction, and desorption. Using CO methanation on Rh(211) as a test case and energetic input from density functional theory calculations, we compare the predicted coverages and turnover-frequencies between mean-field and KMC microkinetic models. Further, we discuss simple first-order models for lateral interactions between adsorbates [1], where the statistically correct description of fluctuations and correlations in the coverage and binding sites of adsorbates in KMC is expected to outperform the MFA.

[1] Journal of Catalysis 307, 275-282 (2013)

O 24.8 Tue 12:15 MA 144

**Stabilization of CH<sub>2</sub> on Ru(0001) by hydrogen co-adsorption** — •XUNHUA ZHAO<sup>1</sup>, HARALD KIRSCH<sup>1</sup>, ZEFENG REN<sup>1,2</sup>, R. KRAMER CAMPEN<sup>1</sup>, SERGEY V. LEVCHENKO<sup>1</sup>, MARTIN WOLF<sup>1</sup>, and MATTHIAS SCHEFFLER<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der MPG, Berlin, DE — <sup>2</sup>Present address: Peking University, Beijing, CN

Based on indirect experimental evidence, CH<sub>2</sub> was proposed as a building block for hydrocarbon chain growth on the Ru(0001) surface during the Fischer-Tropsch process. However, previous calculations agreed that CH<sub>2</sub> is not stable on Ru(0001) at the reaction conditions, and should quickly convert into CH. Employing density-functional theory, we show that this disagreement can be reconciled if coadsorbed hydrogen is present on the surface. All possible CH<sub>x</sub>+H<sub>y</sub> configurations with adsorbates at hollow sites are calculated. CH<sub>x</sub> dissociation barriers are obtained using the string method. We further demonstrate, by calculating the surface phase diagram for one-carbon species on Ru(0001) as a function of H<sub>2</sub> chemical potential, that the stabilization of CH<sub>2</sub> by co-adsorbed hydrogen requires non-equilibrium conditions. The calculated barrier for the CH<sub>2</sub> dissociation in the presence of hydrogen is significantly increased, and is close to the one recently measured by vibrational sum-frequency generation spectroscopy [1]. Our results also explain why CH<sub>2</sub> was not observed when C or CH are hydrogenated on Ru(0001) [2], although it is observed after methane decomposition.—[1] H. Kirsch, X. Zhao, Z. Ren, S. V. Levchenko, M. Wolf, and R. K. Campen, *J. Catal.* **320**, 89 (2014); [2] T. K. Shimizu *et al.*, *J. Chem. Phys.* **129**, 244103 (2008).

O 24.9 Tue 12:30 MA 144

**Controlling CH<sub>2</sub> dissociation on Ru(0001) through surface site blocking by adsorbed hydrogen** — •HARALD KIRSCH<sup>1</sup>, XUNHUA ZHAO<sup>1</sup>, SERGEY V. LEVCHENKO<sup>1</sup>, MARTIN WOLF<sup>1</sup>, ZEFENG REN<sup>2</sup>, and R. KRAMER CAMPEN<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin, Germany — <sup>2</sup>International Center for Quantum Materials and School of Physics, 100871 Beijing, China

Understanding the relative stability of CH<sub>x</sub> species on surfaces is nec-

essary for mechanistic description of such important catalytic chemistry as the Fischer-Tropsch synthesis or the steam reforming process of methane. Here we investigate the thermal stability of surface bound CH<sub>2</sub> radical on Ru(0001). We produce a CH<sub>2</sub> covered surface in UHV at low temperatures (< 250 K) by employing a supersonic molecular beam source for CH<sub>4</sub> dissociation and characterize CH<sub>2</sub> population using vibrational sum frequency spectroscopy (> 5 cm<sup>-1</sup> resolution). By this approach we experimentally quantify the barrier of the reaction CH<sub>2</sub>→CH+H via an Arrhenius analysis and find an activation energy of 65 ± 6 kJ/mol, which is > 4× higher than previous computational results [1]. Our density functional theory calculations show, that this disagreement can be reconciled if 3 coadsorbed H atoms per CH<sub>2</sub> are present in our experiment [2] and that such hydrogen coverages require non-equilibrium with respect to the overlying gas phase.

[1] I.M. Ciobica *et al.*, *J. Phys. Chem. B* **104**, 3364 (2000); [2] H. Kirsch, X. Zhao, Z. Ren, S. V. Levchenko, M. Wolf, and R. K. Campen, *J. Catal.* **320**, 89 (2014)

O 24.10 Tue 12:45 MA 144

**Dissociation of carbon monoxide on Co(0001) - an in situ scanning tunneling microscopy study at high pressures and high temperatures** — •BERNHARD BÖLLER, MARTIN EHRENSPERGER, and JOOST WINTTERLIN — Ludwig-Maximilians-Universität, Munich, Germany

The dissociation of carbon monoxide on Co surfaces is a key element in the discussion of the mechanism of the cobalt-catalyzed Fischer-Tropsch synthesis. We have investigated a Co(0001) single crystal at 493 K in CO pressures up to 0.85 mbar using high pressure scanning tunneling microscopy (STM). Ex situ photoelectron spectroscopy (XPS) was used to detect the resulting surface carbon. At CO pressures higher than 0.05 mbar XPS showed significant amounts of surface carbon, indicating dissociation of CO. Because of the high activity of the cobalt surface and the unavoidable presence of traces of contaminants at elevated pressures, extensive experiments were performed to exclude other sources than CO dissociation for the surface carbon. As the coverage of carbon increased, the in situ STM data showed the evolution of new surface features. Starting from local changes they finally covered most of the surface, forming a (5x5) superstructure. Most likely a carbon-induced surface reconstruction is involved in these processes. Additionally, after exceeding a certain coverage, surface carbide started to form. Simultaneous structure changes near the steps indicate transport processes of cobalt atoms.

O 24.11 Tue 13:00 MA 144

**In Situ Scanning Tunneling Microscopy of a Co(0001) Fischer-Tropsch model catalyst** — •MARTIN EHRENSPERGER, BERNHARD BÖLLER, and JOOST WINTTERLIN — Ludwig-Maximilians-Universität, Munich, Germany

The low temperature Fischer-Tropsch process produces long chain hydrocarbons over cobalt catalysts, starting from syngas, a mixture of hydrogen and carbon monoxide. Whereas the reaction mechanism has been intensively discussed, key questions about molecular processes and the structure of the catalyst surface remain unanswered. We have investigated a Co(0001) single crystal in 10 mbar of syngas at 493 K with in situ high temperature and high pressure scanning tunneling microscopy (STM). Methane was catalytically produced on the cobalt surface, as proven by quadrupole mass spectrometry. The STM data show a metallic surface. The surface was neither transformed into a surface oxide or carbide nor was it reconstructed. A reorganization of the surface morphology during reaction, as has often been postulated, was not observed under the applied experimental conditions. The STM images are in agreement with reversibly bound molecules that form a mobile mixed adsorbate layer on a flat metallic surface. Using ex situ x-ray photoelectron spectroscopy only low amounts of carbon and oxygen were detected.