

O 9: Surface Chemical Reactions and Heterogeneous Catalysis I

Time: Monday 10:30–13:00

Location: PHY C 213

O 9.1 Mon 10:30 PHY C 213

In-situ investigation of the growth and oxidation of Mo₂C/Mo(100) using high-resolution X-ray photoelectron spectroscopy — ●UDO BAUER, CHRISTOPH GLEICHWALD, CHRISTIAN PAPP, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Molybdenum carbide has been proposed as a noble metal free catalyst for a variety of reactions. We used our supersonic molecular beam setup to carburize a Mo(100) single crystal. Ethylene adsorption at 900 K and subsequent oxidation of the carburized system at 1200 K were followed in-situ in the C 1s and Mo 3d core levels by fast X-ray photoelectron spectroscopy (XPS) performed at the synchrotron facility BESSY II. We observed three different species in the C 1s core level during the C₂H₄ deposition. Starting with the growth of a precursor carbide, surface and bulk carbide species arise and saturate after an exposure of 1200 L. Subsequent annealing to 1300 K removed excess carbon, resulting in the desired Mo₂C stoichiometry. Oxidation of the molybdenum carbide revealed a very fast diffusion of bulk carbon to the surface, refilling empty sites occurring due to CO desorption.

O 9.2 Mon 10:45 PHY C 213

Etching of Graphene on Ir(111) with Molecular Oxygen — ●ULRIKE A. SCHRÖDER¹, ELIN GRÄNÄS², TIMM GERBER¹, MOHAMMAD A. ARMAN², KARINA SCHULTE³, JAN KNUDSEN^{2,3}, JESPER N. ANDERSEN^{2,3}, and THOMAS MICHELY¹ — ¹Universität zu Köln, II. Physikalisches Institut, Germany — ²Lund University, Division of Synchrotron Radiation Research, Sweden — ³Lund University, MAX IV Laboratory, Sweden

Although oxidation of carbon has been studied for decades, it remains unclear how oxygen attacks and oxidizes closed and submonolayer graphene on the atomic scale level. We provide new insights by using the well-defined system graphene on Ir(111) and exposing it to molecular oxygen.

Using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and thermal desorption spectroscopy (TDS), we find that etching is a thermally activated process and depends on temperature and Gr morphology. For submonolayer Gr films, etching sets in at 550 K. The molecular oxygen dissociates on the free Ir(111) surface. Real time STM measurements reveal that oxygen then attacks Gr via the edges. Free edges are preferentially etched, compared to Gr bound to Ir steps. Perfectly closed Gr films are remarkably stable against oxygen etching, which only starts above 700 K. At this temperature, 5-7 defects stemming from the Gr growth process act as dissociation sites for the O₂ molecules. At higher etching temperatures, large hexagonal etch holes are visible in the STM: Zigzag edges are more stable against etching than armchair edges.

O 9.3 Mon 11:00 PHY C 213

From qualitative to atomistic: First-principles kinetic modeling of Pd surface oxide reduction by CO — ●MAX J HOFFMANN and KARSTEN REUTER — TU München, Germany

Obtaining detailed atomistic insight into oxide formation and reduction at metal surfaces is a key step to understand and ultimately engineer the function of these surfaces in a multitude of applications, not least in oxidation catalysis. On the modeling side, the analysis of kinetic measurements in terms of reaction rate laws is traditionally employed to extract qualitative information. First-principles calculations, on the other hand, describe the microscopic processes underlying the actual phase transition. First-principles microkinetic models offer the prospect to join these two strands and subject atomistic models to scrutiny against measured kinetic data. We illustrate this approach with first-principles kinetic Monte Carlo (1p-kMC) simulations of the reduction of a ($\sqrt{5} \times \sqrt{5}$)R27° surface oxide on Pd(100) in a CO atmosphere, and reference against kinetic data derived from X-ray photoelectron spectroscopy [1]. In full agreement with the experimental rate law analysis our atomistic simulations demonstrate that the reduction process can not occur via a homogeneous decomposition of the oxide phase. We overcome prevalent limitations to lattice-based 1p-kMC through a novel multi-lattice approach and present a mechanistic model that includes the full transformation from oxide to metal. This model fully rationalizes the measured data and proves that under the

investigated gas-phase conditions the reduction is a phase-boundary controlled process. [1] V.R. Fernandes *et al.*, Surf. Sci. (in press).

O 9.4 Mon 11:15 PHY C 213

Cu/ZnO nanocatalysts in response to environmental conditions: Surface morphology, electronic structure, redox state and CO₂ activation — LUIS MARTÍNEZ-SUÁREZ¹, ●JOHANNES FRENZEL¹, BERND MEYER^{1,2}, and DOMINK MARX¹ — ¹Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany — ²ICMM and CCC, Uni Erlangen-Nürnberg, 91052 Erlangen, Germany

By performing extensive DFT calculations in combination with a thermodynamic formalism we establish an atomistic understanding of gas phase-induced changes of surface morphology, redox properties and reactivity of ZnO supported Cu nanocatalyst [1] which shows strong metal-support interactions (SMSI) [2-7]. Being subject to electronic charge transfer processes across the metal-support interface [7,8] we explore surface stabilization and site dependent redox state of both catalyst components in response to the redox properties of the surrounding gas phase. Further, *ab initio* molecular dynamics unveils the vital nature of the deposited metal which, besides reduced Zn in the ZnO support, enhances CO₂ activation over Cu.

[1] Martínez-Suárez, L., Frenzel, J., Meyer, B., and Marx, D., PRL **110**, 086108 (2013) [2] Tauster, S. J., Fung, S. C., Baker, R. T. K., and Horsley, J. A., Science **211**, 1121 (1981). [3] Clausen, B. S., *et al.*, Top. Catal. **1**, 367-376 (1994). [4] Wagner, J. B., *et al.*, J. Phys. Chem. B **107**, 7753 (2003). [5] Wilmer, H., and Hinrichsen, O., Catal. Lett. **82**, 117-122 (2002). [6] Behrens, M., *et al.*, Science **336**, 893 (2012). [7] Frost, J. C., Nature (London) **334**, 577 (1998) [8] Liao, F., *et al.* Angew. Chem. Int. Ed. **51**, 5832 (2012).

O 9.5 Mon 11:30 PHY C 213

Complex surface structure determination through first-principles global geometry optimization: c(2 × 2)-RuO₂(100) — ●TONGYU WANG, DENNIS PALAGIN, SASKIA STEGMAIER, and KARSTEN REUTER — Technische Universität München, Germany

"Ruthenium" catalysts exhibit a remarkable change of CO oxidation activity with reactant pressure [1]. Current understanding rationalizes the high activity at near-ambient conditions with a change of oxidation state. The enigmatic deactivation observed under oxidizing conditions is in turn assigned to a microfaceting of (otherwise highly active) RuO₂(110) facets into an inactive c(2 × 2)-RuO₂(100) phase [2]. A detailed structural model of the latter phase would be an important step towards understanding (and possibly suppressing) the deactivation mechanism. Yet, despite detailed experimental characterization, such a model could not be established to date. To this end, we perform density-functional theory based global geometry optimization using a basin hopping approach. Combined within *ab initio* thermodynamics we assess the relative stabilities of the obtained structural candidates and discuss their properties in light of the existing experimental data. [1] H. Over, Chem. Rev. **112**, 3356 (2012); [2] J. Assmann *et al.*, Angew. Chem. Int. Ed. **44**, 917 (2005).

O 9.6 Mon 11:45 PHY C 213

From macro to micro: Kinetics of HCl oxidation on RuO₂(110) — ●FARNAZ SOTOODEH¹, PATRICK GÜTLEIN¹, IRENE M. N. GROOT², JOOST W. M. FRENKEN², and KARSTEN REUTER¹ — ¹TU München, Germany — ²Leiden University, Netherlands

A large portion of Cl₂ is used in industries that produce HCl as a waste byproduct [1]. The catalytic conversion of waste HCl back to high purity Cl₂ through oxidation (Deacon process) is thus highly desirable. However, the current process is expensive since it requires the precious metal Ruthenium. As this process is important to most industries, even small improvements in its efficiency will have a global economic and environmental impact by extending catalyst life time and stability. Therefore, designing an active and stable catalyst in the sustainable Cl₂ production is extremely valuable. Optimizing the catalyst activity under often "harsh" industrial implementations, requires an in-depth understanding of reaction kinetics over a wide range of operating conditions. Here, macrokinetic models including power-law and Langmuir-Hinshelwood are applied to measured activities. On the way towards microkinetics, the Langmuir-Hinshelwood kinetics is scrutinized closely by looking at elementary steps on RuO₂(110) surface,

with reaction barriers and binding energies of surface species calculated using DFT. The adaptability of the examined models are compared to available ones [2] where the model parameters were estimated by fitting to a restricted range of operating conditions.

[1] H. Y. Pan *et al.*, *Ind. Eng. Chem. Res.* **33**, 2996 (1994).

[2] D. Teschner *et al.*, *J. Catal.* **285**, 273 (2012).

O 9.7 Mon 12:00 PHY C 213

Simulation of Ni/CeO₂ surfaces for CO₂ catalysis — ●KONSTANZE HAHN¹ and JÜRIG HUTTER² — ¹University of Cagliari, Monserrato, Italy — ²University of Zurich, Zurich, Switzerland

Combined metal-metal oxide systems are important materials for numerous technological applications such as microelectronics, photovoltaics, gas sensors and in particular in oxide-supported metal catalysts. Deposition of small metal particles on metal oxides such as Al₂O₃, CeO₂ and TiO₂ has led to enhanced catalytic activity, for example, for the water gas shift reaction or CO oxidation. Metal oxide supported materials are also promising catalysts for hydrocarbon production from CO₂, a reaction process interesting for alternative energy production since it provides high energy density fuel from CO₂ which is omnipresent in our environment. In fact, CeO₂-supported Ni particles have proven to be promising materials for the activation of methanation of CO₂. Here, density functional theory within the Gaussian and plane waves formalism has been used for the simulation of Ni cluster formation on CeO₂(111) surfaces. Stabilization of Ni particles has been observed with increasing cluster size up to ten atoms. It has been found that O diffusion from the subsurface layer of CeO₂(111) to the surface layer is facilitated in the presence of Ni particles on the surface. Furthermore, the adsorption and dissociation of CO₂ has been investigated on clean CeO₂(111), on non-supported Ni clusters in the gas phase and on the Ni/CeO₂(111) system. This study gives fundamental insight into the metal-metal oxide interactions and its function for CO₂ catalysis.

O 9.8 Mon 12:15 PHY C 213

Combining High-Resolution Scanning Probe Microscopy Studies with Reactivity Experiments — ●STEFANIE STUCKENHOLZ, CHRISTIN BÜCHNER, HENDRIK RONNEBURG, GERO THIELSCH, MARKUS HEYDE, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

We use thin metal supported MgO films as a model system to understand the correlation between morphology, electronic structure and reactivity of heterogeneous catalysts on the atomic scale.

For investigation of our samples we operate a scanning tunnelling microscope (STM) and noncontact atomic force microscope (nc-AFM). With the dual mode microscope we study the sample morphology and perform spectroscopic measurements, such as field emission resonance (FER) and Kelvin probe force microscopy (KPFM). The influence of a thin MgO film on the Mo(001) local work function, as well as differences between pristine terrace sites and line defect sites will be discussed.

To connect the findings of the dual mode microscope with reactivity studies we are setting up a new temperature programmed desorption (TPD) experiment. Here, desorption of gaseous species, e.g. CO from MgO surfaces, will be studied. This reaction serves as a model for the interaction of CO with an ionic surface.[1, 2] First results of the low

temperature TPD setup will be presented.

[1] R. Wichtendahl, *et al.*, *Phys. Status Solidi A* **173**, 93 (1999)

[2] M. Sterrer, *et al.*, *Surf. Sci.* **596**, 222 (2005)

O 9.9 Mon 12:30 PHY C 213

Near ambient pressure XPS investigation of the interaction of ethanol with Co/CeO₂(111) — ●SANDRA KRICK CALDERÓN¹, ÓVÁRI LÁSZLÓ², LYKHACH YAROSLAVA¹, LIBUDA JÖRG¹, ERDOHELYI ANDRAS³, PAPP CHRISTIAN¹, KISS JÁNOS^{2,3}, and STEINRÜCK HANSPETER¹ — ¹Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany — ²MTA-SZTE Reaction Kinetics and Surface Chemistry Research Group, H-6720 Szeged, Rerrich Béla tér 1, Hungary — ³Department of Physical Chemistry and Materials Science, University of Szeged, H-6720 Szeged, Aradi vértanúk tere 1, Hungary

The adsorption of ethanol on a CeO₂(111) surface and a Co/CeO₂(111) model catalyst was studied with near ambient XPS at pressures up to 1 mbar. The main species adsorbed on the surface was found to be ethoxide, formed by dissociative adsorption. Upon ethanol exposure on pristine ceria at 300 K a gradual reduction with increasing pressure was observed; reduction was even further enhanced by heating to 600 K at 0.1 mbar. This effect was attributed to increased diffusion of the Ce³⁺ centers or lattice oxygen at elevated temperatures. Partial reduction of the ceria layer upon Co deposition was observed. Ethanol strongly reduced the Co particles leaving almost solely metallic Co on the concurrently reduced CeO₂ surface at 600 K. While no coke formation occurred during reaction with the pristine CeO₂ layer, carbonaceous species were observed at 600 K on the Co/CeO₂ model catalyst.

O 9.10 Mon 12:45 PHY C 213

Imaging mass transfer limitations in in-situ model catalyst studies — ●SEBASTIAN MATERA¹, SARA BLOMBERG², MAX J. HOFFMANN¹, JOHAN ZETTERBERG², JOHAN GUSTAFSON², EDVIN LUNDGREN², and KARSTEN REUTER¹ — ¹Technische Universität München, Germany — ²Lund University, Sweden

A central goal in in-situ studies of defined model catalysts is to establish a correlation between surface micro-structure and observed reactivity. In corresponding near-ambient environments this observable reactivity may be intricately influenced by macroscale heat and mass transport limitations in the reactor. We investigate such effects with a first-principles based multi-scale modeling approach integrating kinetic Monte Carlo simulations into a fluid dynamical treatment [1]. Recent methodological advances [2] allow the full consideration of the experimental reactor geometry, which we illustrate with the application to recent Planar Laser Induced Fluorescence measurements [3] of CO oxidation at Pd(100). Experiment and theory consistently reveal strong mass transfer limitations under near-ambient operation conditions. Intriguingly, the detailed comparison of calculated and measured gas-phase concentration profiles offers an unprecedented route to draw conclusions on the prevalent surface phases and reaction pathways. [1] S. Matera and K. Reuter, *Catal. Lett.* **133**, 156 (2009); *Phys. Rev. B* **82**, 085446 (2010); *J. Catal.* **295**, 261 (2012). [2] S. Matera, M. Maestri, A. Couci, and K. Reuter, in preparation. [3] J. Zetterberg *et al.*, *Rev. Sci. Instrum.* **83**, 053104 (2012)