

O 86: Heterogeneous catalysis I

Time: Thursday 16:30–19:30

Location: WIL B122

O 86.1 Thu 16:30 WIL B122

First-Principles kinetic Monte Carlo Simulations of Ammonia Oxidation at RuO₂(110): Selectivity vs. semi-local DFT — ●CLAUDIA MANGOLD¹ and KARSTEN REUTER^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Technische Universität München

Reaching a detailed mechanistic understanding of high selectivity in surface catalytic processes is one of the central goals in present-day catalysis research. The Surface Science approach to this problem focuses on the investigation of well-defined model systems that reduce the complexity but still capture the relevant aspects. In this respect, the almost 100% selectivity reported in detailed experiments for the oxidation of NH₃ to NO at RuO₂(110) [1] presents an ideal benchmark for a quantitative theoretical analysis. To this end we perform detailed kinetic Monte Carlo simulations based on kinetic parameters derived from density-functional theory (DFT). The obtained turnover frequency for molecular nitrogen is in rather good agreement with the experimental data. However, even with an extended set of elementary processes we are not able to reproduce the experimental findings for the production of NO and therewith the selectivity. The central quantities that decisively determine the latter are the binding energy of NO and the N diffusion barrier. Suspecting the approximate energetics obtained with the employed semi-local DFT functional as reason for the discrepancy, we recalculate the kinetic parameters with different functionals and discuss the resulting effects in the kMC simulations.

[1] Y. Wang *et al.*, *J. Phys. Chem. B* 109 (2005) 7883.

O 86.2 Thu 16:45 WIL B122

Au/TiO₂(110) model catalysts on stoichiometric supports: Size dependence of the Au nanoparticles and activation energy in the CO oxidation reaction — ●MENHILD EYRICH, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany

Since the late 1980s numerous studies on Au nanoparticles on metal oxide supports were carried out. Due to the low conductivity of fully oxidized TiO₂(110) supports which hinders many surface science based methods such as STM, most investigations were carried out on reduced TiO₂(110) supports. The catalytic activity of planar Au/TiO₂(110) model catalysts depends, in analogy to the respective powder catalysts, strongly on the size of the Au nanoparticles and on the pretreatment of the catalyst or the catalyst support. Here, we report the experimental results from a study on fully oxidized planar Au/TiO₂ model catalysts with fully oxidized TiO₂(110) support materials performed at different Au coverages (i.e., different particle size) and different temperatures. The strong influence of the size of the Au nanoparticles on the catalytic activity was studied at different temperatures showing a less pronounced size dependence (but very high activity) at low temperatures (around room temperature). Then, the activation energy was determined for different particle sizes, in the size regime of the high catalytic activity (small Au nanoparticles) and for larger Au nanoparticles. The results will be compared to results for other (reduced) Au/TiO₂ model and for powder catalysts.

O 86.3 Thu 17:00 WIL B122

Role of Pt in SO₂ storage over ceria-based traps — MARKUS HAPPEL¹, ●YAROSLAVA LYKHACH¹, NATALIA TSUD², TOMÁŠ SKÁLA³, KEVIN C. PRINCE³, VLADIMÍR MATOLÍN², and JÖRG LIBUDA¹ — ¹Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, D-91058 Erlangen — ²Department of Plasma and Surface Science, Charles University, CZ-18000 Prague 8 — ³Sincrotrone Trieste, I-34012 Basovizza-Trieste

CeO₂ based materials are efficient SO_x traps that can be used in combination with three-way catalytic converters and NO_x storage and reduction catalysts. Pt significantly enhances the SO_x storage capability. However, the mechanism of this enhancement is not fully clear. In order to explore the role of Pt, we have studied the adsorption of SO₂ on single-crystal-based stoichiometric and reduced ceria films and on Pt/CeO₂(111) model catalysts. Reaction and decomposition of SO₂ were investigated by means of synchrotron radiation and resonant PES. We found that SO₃ is the major product of SO₂ reaction on the surfaces of both, stoichiometric and reduced ceria. On stoichiometric ceria, SO₃ decomposition occurs by desorption of SO₂. In contrast,

we detect progressive decomposition of SO₃ to SO_x and S species on reduced ceria. This leads to partial reoxidation of ceria and formation of sulfides. On Pt/CeO₂, formation of SO₃ on the ceria surface is accompanied by partial decomposition of SO₂ to atomic sulfur on the Pt surface. Further decomposition of SO₃ proceeds via spillover of SO_x species to Pt followed by decomposition to atomic sulfur. Spillover of atomic sulfur from Pt to CeO₂ results in formation of cerium sulfides.

O 86.4 Thu 17:15 WIL B122

Size and Shape Changes of Pt Nanoparticles on α-Al₂O₃(0001) during CO Oxidation Reactions — ●UTA HEJRAL¹, RICHARD VAN RIJN^{2,3}, SANDER ROOBOL², WILLEM ONDERWAATER², OLIVIER BALMES³, HELENA ISERN³, ROBERTO FELICI³, JOOST FRENKEN², and ANDREAS STIERLE¹ — ¹University of Siegen, Walter-Flex-Str. 3, D-57072 Siegen, Germany — ²Kamerlingh Onnes Laboratory, Leiden University, RA Leiden 2300, The Netherlands — ³ESRF, Grenoble F-38043, France

Pt nanoparticles on aluminum oxide supports are widely used in heterogeneous catalysis and are applied successfully in reactions like the oxidation of hydrocarbons or CO. In order to achieve better catalyst efficiency, lifetime and selectivity it is important to understand catalytic processes on an atomic basis: the particle structure but also the interfacial region between particle and substrate is considered to be crucial for the catalytic properties.

To this end Pt nanoparticles were epitaxially grown on α-Al₂O₃(0001) substrates by means of physical vapour deposition at a substrate temperature of 500 °C. The particle size, shape and interfacial registry were studied in-situ during CO oxidation reactions (T=300 °C, pO₂=10 mbar, pCO=10 mbar) by surface x-ray diffraction and x-ray reflectivity. The measurements were carried out at the ESRF ID03 beamline in a dedicated flow reactor supporting conditions from UHV to ambient pressures [1]. The x-ray investigations were completed by complementary atomic force microscopy studies.

[1] R. van Rijn, *et al.*, *Rev. Sci. Instr.*, **81** (2010) 014101

O 86.5 Thu 17:30 WIL B122

Non-equilibrium surface pattern formation during catalytic reactions with nanoscale resolution — ●JEAN-SABIN MCEWEN¹, PIERRE GASPARD¹, THIERRY VISART DE BOCARMÉ², and NORBERT KRUSE² — ¹Center for Nonlinear Phenomena and Complex Systems, Université Libre de Bruxelles, Campus Plaine CP 231, 1050 Bruxelles, Belgium — ²Chemical Physics of Materials, Université Libre de Bruxelles, Campus Plaine CP 243, 1050 Bruxelles, Belgium

Despite the large progress made in the recent years to provide a sound understanding of the oscillatory behavior of various catalytic surface reactions, there still are a number of questions apparently unsolved. One of these open questions concerns the gap between the choice of catalyst in surface science studies and those used in heterogeneous catalysis. Indeed, in surface science, oriented single crystals are mainly used while multi-faceted metal particles are present in catalysis. A field emitter tip on the other hand can be regarded as a good approximation of a nanometer-sized metal particle. Stunningly, a field emitter tip is also large enough to allow the emergence of regular oscillations from the molecular fluctuations. This is the case when a rhodium nanosized crystal is exposed to hydrogen and oxygen. Here, we show that the observed nonequilibrium oscillatory patterns find their origin in the different catalytic properties of all of the nanofacets that are simultaneously exposed at the tip's surface. These results suggest that the underlying surface anisotropy, rather than a standard reaction-diffusion mechanism, plays a major role in determining the self-organizational behavior of multifaceted nanostructured surfaces.

O 86.6 Thu 17:45 WIL B122

Molecular-level understanding of the water-gas-shift reaction on Rh(111) — ●MATTEO MAESTRI^{1,3} and KARSTEN REUTER^{2,3} — ¹Politecnico di Milano, Italy — ²Technische Universität München, Germany — ³Fritz-Haber-Institut der MPG, Berlin, Germany

The identification of the reaction mechanism is the center piece for the atomic-scale understanding of a catalytic process and requires the kinetic assessment of all potential steps at the surface. At this level, processes of technological interest involve a large number of potential reactions and, due to the huge computational costs, are still largely

outside the capabilities of a full density-functional theory (DFT) analysis. To this end we propose a hierarchical approach for the identification of prevalent reaction mechanisms by efficiently combining DFT and semi-empirical methods [1]. The obtained computationally undemanding barrier estimates serve as initial approximate input for the identification of the prevalent paths that subsequently require refined kinetic parameters from explicit DFT calculations. As showcase we consider the water-gas-shift (WGS) and reverse reactions on Rh(111). Our results reveal that CO follows different chemical paths depending on the operating conditions. A carboxyl pathway is preferred for the consumption of CO, while its formation proceeds through the direct decomposition of carbon dioxide. These insights into the atomic-scale mechanism allow for a new understanding of the WGS system in full agreement with existing experimental evidence. [1] M.Maestri and K. Reuter, *Angew. Chemie Int. Ed.*, 2010, in press.

O 86.7 Thu 18:00 WIL B122

Structure and stability of CH₃OH/Pt(111) under potential control — ●TANGLAW ROMAN and AXEL GROSS — Institut für Theoretische Chemie, Universität Ulm, D-89069 Ulm

The attention that has been given to fuel cell technology has increased interest in understanding the catalytic oxidation of methanol. Despite all the past efforts on this topic, the exact nature of this reaction is still a subject of debate. While theoretical descriptions of methanol electrooxidation have provided meaningful inputs into the discussions, studies up until now have been performed primarily for the solid/vacuum interface, i.e., no electrolyte and no external fields or excess charges were present. In light of the need to more realistically model the electrooxidation reaction, in this study we examine the structure and stability of methanol, as well as reaction intermediates in the oxidation process on Pt electrodes, for varying electrode potentials, but in the absence of water as a first step. In our model, a Gaussian-shaped counter electrode is used to complement the charged surface. Techniques in estimating the electrode potential corresponding to a certain charge of the counter electrode and steps to more realistically model the electrochemical solid-liquid interface are discussed.

O 86.8 Thu 18:15 WIL B122

The interaction of adsorbates on a roughened Cu(111) surface examined with HREELS and work function measurements — HEINER MASLOSZ, ●OLAF SKIBBE, and ANNEMARIE PUCCI — Kirchhoff-Institut für Physik, Im Neuenheimer Feld 227, D-69120 Heidelberg

Rough and defect-rich surfaces play a key-role in heterogeneous catalysis as well as in surface enhancement effects (i.e. surface enhanced Raman scattering (SERS)). To contribute to a deeper understanding of the interactions at such surfaces, we performed vibrational spectroscopy (HREELS) and work function measurements of gases adsorbed on a Cu(111) surface which we roughened by evaporation of small amounts of copper at low temperatures. The examined gases are C₂H₄, O₂ and CO.

O 86.9 Thu 18:30 WIL B122

Investigation of the Ethylene Oxide Formation over Ag using ¹⁸O₂ — ●SEBASTIAN BÖCKLEIN, MANUEL JOAS, CHRISTINA HETTSTEDT, SEBASTIAN GÜNTHER, and JOOST WINTTERLIN — Ludwig-Maximilians-Universität, München, Germany

As part of an extensive surface science/catalysis project to investigate the reaction mechanism of the partial oxidation of ethylene to ethylene oxide (EtO) over Ag we have performed experiments in a model reactor. Experiments were performed with Ag-foils at pressures in the mbar range and by using ¹⁸O₂. The findings are in partial disagreement with the existing literature. The reaction probability to give EtO is extremely low, and proper product detection, and quantification are essential. In very careful experiments we have been able to unambiguously detect the product. By changing the reaction parameters we could also deactivate and reactivate the silver catalyst (by heating the catalyst up to 600°C in Ar) in a controlled way. There are strong hints of a bulk-dissolved oxygen species that desorbs during this procedure. Its role in the reaction was further investigated with ¹⁸O₂. Depending on whether ¹⁸O₂ was used in the high temperature/high pressure pretreatment with oxygen or in the reaction gas feed different isotope compositions were found in the EtO and in the total oxidation product (CO₂). The isotope used in the O₂ in the reaction feed is mainly found in the products but bulk-dissolved oxygen reacts too as well. The reaction is connected with transport processes of oxygen into and out of the Ag bulk. XPS investigations and sputter/heating experiments show large amounts of oxygen at the surface of the active Ag-foils.

O 86.10 Thu 18:45 WIL B122

Methane activation on palladium (-oxide) — ●ANDERS HELLMAN¹, ADRIANA TRINCHERO¹, HENRIK GRÖNBECK¹, JOHAN GUSTAFSON², EDVIN LUNDGREN², and JESPER ANDERSEN² — ¹Applied Physics and Competence Centre of Catalysis, Chalmers University of Technology, Göteborg, Sweden — ²Division of synchrotron radiation research, Lund University, Sweden

The transition state and the activation energy of methane dissociation on several palladium and palladium oxide facets together with known surface oxides phase is investigated by density-functional theory calculations. Depending on the phase of the palladium there is a correlation between the activation energy and the final energy of the CH₃+H product. The metal phase of palladium has a low activation energy, with a steep correlation to the final state. The palladium oxide and surface oxide have higher activation energies and a more moderate dependence on the final state. If the palladium oxide and surface oxide is reduced, i.e., a removal of an oxygen atom at the active site, another correlation appears that lie in between the metal and oxide phase.

Given the high activation energy of the two most stable palladium oxides, i.e., PdO(100) and PdO(101), the general belief that palladium oxide is a particularly active methane oxidation catalyst is challenged. Instead, our first-principles results suggest that the high activity of palladium can be explained by the appearances of high surface energy facets of the palladium oxide and/or as the occurrences of reduced palladium oxides as the temperature varies under the experiment.

O 86.11 Thu 19:00 WIL B122

Multi-lattice approach to first-principles kinetic Monte Carlo simulations: Application to catalytic CO oxidation at Pd(100) — ●MAX J. HOFFMANN^{1,2}, MATTHIAS SCHEFFLER¹, and KARSTEN REUTER^{1,2} — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — ²Technische Universität München

First-principles kinetic Monte Carlo (1p-kMC) simulations enable a quantitative microkinetic modeling of heterogeneous chemical reactions while accounting for the full spatial distributions at the surface. Application to reaction-induced surface morphological transitions is hitherto prevented by the inability to describe the system within prevalent fixed-lattice 1p-kMC and the excessive cost of off-lattice 1p-kMC variants.

To this end we develop a novel multi-lattice 1p-kMC approach and apply it as a case in point to the CO oxidation at Pd(100). In the catalytically active state this system is suspected to undergo transitions from the pristine metal surface to a PdO surface-oxide film. As a first step towards a comprehensive simulation we focus on the initial oxide destruction step induced by clustering of oxygen vacancies. First simulations confirm the stability of the oxide film at stoichiometric feed as predicted by preceding fixed-lattice 1p-kMC simulations [1]. [1] J. Rogal, K. Reuter, and M. Scheffler, *Phys. Rev. Lett.* **98**, 046101 (2007).

O 86.12 Thu 19:15 WIL B122

Pressure gap and electrode artefacts in the electrochemically induced oxygen spillover on Pt/YSZ electrodes — ●ARAFAT TOGHAN¹, LIZ RÖSKEN¹, MICHAEL HÄVECKER², AXEL KNOP-GERICKE², and RONALD IMBHL¹ — ¹Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3 - 3a, D-30167 Hannover, Germany — ²Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-14195 Berlin, Germany

Mechanistically, the electrochemical promotion of catalytic reactions (EPOC) on Pt/YSZ (yttrium stabilized zirconia) catalysts has been shown to be due to the spillover of oxygen from the solid electrolyte onto the Pt surface. This spillover has been studied on Pt/YSZ catalysts with photoemission electron microscope (PEEM) and with a differentially pumped x-ray photoelectron spectrometer (XPS) allowing to conduct in situ studies up to 1 mbar. PEEM revealed that upon electrochemical pumping not only the expected darkening of the Pt electrodes can be observed which is due to spillover oxygen but that also bright spots develop. These bright spots were attributed to metallic zirconium formed as electrically disconnected parts of the Pt electrode assume a negative potential thus causing a local reduction of zirconia. With XPS the main goal was to study whether a second special spillover species develops upon electrochemical pumping at high pressure which is different from chemisorbed oxygen. This special spillover species has been postulated by Vayenas et al. and was supposedly responsible for the non-Faradaic nature of EPOC. Up to now even at p= 0.2 mbar only chemisorbed oxygen was detected.