O 6: Catalysis

Time: Monday 10:30–13:15 — Location: MA 043

O 6.1 Mon 10:30 MA 043

Support Effect in Oxide Catalysis: Methanol Oxidation on Vanadia/Ceria — Thomas Kropp, •Joachim Paier, and Joachim Sauer — Institut für Chemie, Humboldt-Universität zu Berlin, Unter den Linden 6, 10099 Berlin, Germany

We present a detailed mechanistic description of the methanol oxidation to formaldehyde at the $VO_x/CeO_2(111)$ catalytic system employing the DFT+U approach as well as hybrid functionals to assess selected results. Compared to clean ceria (and depending on the pathway), depositing VO_2 on the surface does not affect significantly intrinsic barriers (1.3 eV) in the rate-determining H-transfer. It rather substantially increases the adsorption energy, which in turn leads to negative apparent barriers. The previously discussed pseudo vacancy, a structural feature of VO_x-decorated ceria, appears to be a favorable adsorption site for the methanol. Its dissociative adsorption at this very site, which is created by a oxygen spillover process from the support to the catalyst, was found to be as exothermic (-1.9 eV) as its adsorption at vanadium, i.e. insertion into the V-O_{surf} bond, since both processes heal the aforementioned pseudo vacancy. Besides the above mentioned ease in transferring electrons from V $3d$ states to Ce $4f$ states, the pseudo vacancy is inherently related to surface morphology and represents another cooperative effect between catalyst and surface. Both, a highly exothermic adsorption step as well as a lowering of the activation energy in the rate-determining step explain the higher activity of $VO_x/CeO_2(111)$ compared to an inert SiO_2 support.

O 6.2 Mon 10:45 MA 043

Travelling Vanadium Oxide Islands in a Catalytic Reaction — •Bernhard von Boehn, Martin Hesse, and Ronald Imbihl — Institut für Physikalische Chemie und Elektrochemie, Leibniz-Universität Hannover, Callinstr. 3–3a, D-30167 Hannover, Germany

Upon evaporation of a submonolayer coverage of vanadium in O_2 onto a Rh(111) surface one obtains well ordered two-dimensional V-oxide islands which we use as model catalysts for the partial oxidation of methanol to formaldehyde [1]. With photoemission electron microscopy we observe that under reaction conditions in the 10^{-4} mbar range the initially homogeneous VO_x film ($\theta_V = 0.2$) transforms upon heating at 560 °C into a quasi-stationary macroscopic concentration pattern. This pattern consists of equidistant parallel stripes of VO_x surrounded by nearly bare metal surface. Above 700 °C the stripe pattern changes into a spot pattern of circular VO_x islands with 20–200 μm diameter. Due to attractive interactions the islands approach each other with a velocity up to a few μm/s depending on distance. The islands coalesce, afterwards their shape becomes rapidly circular again indicating a high line tension at the island boundaries. The islands only move under reaction conditions. A mechanism is proposed which is based on the chemical equilibrium of polymerization of individual VO_x clusters into macroscopic VOx islands. Since the poly-/depolymerisation equilibrium is controlled by oxygen coverage, oxygen gradients surrounding the VO_x islands under reaction conditions can cause the movement.

[1] J. Schoiswohl, S. Surnev, and F. P. Netzer, Topics in Catalysis **36** (2005) 91.

Invited Talk O 6.3 Mon 11:00 MA 043

CO oxidation over a Pt/Fe$_3$O$_4$ model catalyst: Watching Mars van Krevelen at work — •Gareth Parkinson — Institute of Applied Physics, TU Vienna, Vienna Austria

The nature of the active oxygen species during CO oxidation over supported metal catalysts is a long-standing and controversial issue. When metal oxides are utilized as the support, lattice O ions provide an additional pathway to CO_2 formation via the so-called Mars-van Krevelen (MvK) mechanism. Here, we provide direct evidence of an active MvK process during CO oxidation over a Pt/Fe$_3$O$_4$ model catalyst. Atomically resolved scanning tunneling microscopy images reveal etching of the Fe$_3$O$_4$ support in the vicinity of Pt clusters following exposure to CO at 280 °C, with subsequent re-growth upon exposure to O_2. The experimental data suggest CO oxidation is autocatalytic; extraction of the first O atom is most difficult energetically. The addition of H_2 to the gas mixture accelerates the reaction because a similar, more efficient, MvK process roughens the surface through the formation of water.

O 6.4 Mon 11:30 MA 043

Spectromicroscopy of Dynamic Redistribution Patterns of V-Oxide on Rh(111) in Catalytic Methanol Oxidation — •Martin Hesse[1], Bernhard von Boehn[1], Tevfik Onur Mentes[2], Andrea Locatelli[2], and Ronald Imbihl[1] — [1]Institut für Physikalische Chemie und Elektrochemie, 30167 Hannover, Germany — [2]Sincrotrone Trieste, 34012 Basovizza, Italy

Upon partial oxidation of methanol to formaldehyde onto a Rh(111) surface with a submonolayer coverage of vanadium one observes a redistribution of the supported vanadium oxide catalyst. Under reaction conditions (10^{-6} mbar, >560°C) the initially homogeneous VO_x film transforms into a quasi-stationary concentration pattern[1]. Depending on the temperature we find two kinds of patterns, stripes and circular islands. These patterns are investigated with LEEM (low energy electron microscopy), microprobe-LEED (low energy electron diffraction) and microprobe-XPS (X-ray photoelectron spectroscopy). The interior of the VO_x islands contains a substructure with an inner boundary separating two regions. Remarkably, the highest V-concentration (θ_V =0.8MLE) connected with a Moire pattern in LEED is located at the inner boundary whereas left and right of the boundary the V concentration reaches only about half of this value. Transport processes of the reactants that feedback on the V distribution are apparently responsible for this substructure.

[1] F. Lovis and R. Imbihl, J. Phys. Chem. C 115 (2011) 19149-19157

O 6.5 Mon 11:45 MA 043

Surface oxide on Pt(111) as the active phase for NO and CO oxidation — •Matthijs A. van Spronsen, Joost W.M. Frenken, and Irene M.N. Groot — Huygens-Kamerlingh Onnes Laboratory, Leiden University, The Netherlands

Platinum finds its main application as a car catalyst to control the emission of exhaust gases. When the catalyst operates in excess oxygen, platinum catalyzes the oxidation of CO, NO, and remnant hydrocarbons. Despite platinum's wide use for catalytic oxidation, the active surface phase under oxygen-rich reaction conditions is still highly debated. Traditionally, it was believed that the bare metallic surface was the most reactive. But the recent development of new in situ surface science tools led to the discovery of phase transitions to states of higher activity for CO oxidation. The explaining models are ranging from a hyperactive oxygen-covered surface, surface oxide, or bulk oxide.

For the Pt(111) surface, the facet lowest in energy, it is also not clear what the relevant structure is under oxygen-rich reaction conditions. Both a surface oxide and a bulk α-PtO2 were found to be stable in different experiments. With the high-pressure, high-temperature ReactorSTM, we studied the oxidation of Pt(111) and found a stable surface oxide which assembles in a 'spoke wheel' superstructure at 1 bar O2 at 430 K. This surface oxide was also studied in both NO and CO oxidation under reaction conditions.

O 6.6 Mon 12:00 MA 043

First-principles based modeling of the transport reactivity coupling: Catalytic explosion and non-chemical oscillations — •Sandra Döpking[1,2], Karsten Reuter[1,3], and Sebastian Matera[1,2] — [1]Technische Universität München, Germany — [2]Freie Universität Berlin, Germany — [3]Stanford University, USA

Bridging the gap between ultra-high vacuum and realistic operation conditions is the goal of in-situ studies of defined model catalysts. In these near ambient environments a further level of complexity arises by the coupling of surface chemical reactions with macro-scale heat and mass transport. To investigate such effects, we revisit the CO oxidation on the RuO$_2$(110) in a stagnation flow reactor [1]. Differently to the previous studies, we now perform fully spatially and temporally resolved simulation employing our a first-principles based multi-scale modeling approach, which integrates kinetic Monte Carlo simulations into the Computational Fluid Dynamics code catalyticFOAM [2]. We find that, after changing the inlet composition, the surface experiences a rapid explosion-like heat up by several hundred Kelvin. Furthermore, depending on the diameter of the single crystal, the system may end up in an oscillating state. However, these oscillations are non-chemical, i. e. they originate from the thermo-convection driven by the temperature difference between inlet and surface. [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. Cuoci, and K. Reuter, ACS Catal. 4, 4081 (2014).

O 6.7   Mon 12:15   MA 043

A perturbative approach for quantifying mass transfer limitations in in-situ model catalyst studies — ●Sebastian Matera[1,2], Sara Blomberg[3], Max J. Hoffmann[1], Johan Zetterberg[3], Johan Gustafson[3], Edvin Lundgren[3], and Karsten Reuter[1,4] — [1]Technische Universität München, Germany — [2]Freie Universität Berlin, Germany — [3]Lund University, Sweden — [4]Stanford University, USA

Reaction chambers in in-situ studies of defined model catalysts often prohibit the disentangling of surface chemistry and gas phase transport by idealized reactor models. A full Computational Fluid Dynamics (CFD) treatment, however, is computationally extremely costly due to the stiff surface kinetics requiring very small times steps. We present a perturbative approach which decomposes the problem, such that the CFD can be performed with a low reactivity, non-stiff surface chemistry. The actual solution to the targeted problem, is then approximated in a post processing phase. In order to analyze recent Planar Laser Induced Fluorescence experiments [2] on the CO oxidation at Pd(100), we combine the perturbative approach with our first-principles based multi-scale modelling methodology integrating kinetic Monte Carlo simulations into CFD [1]. We find that a mixture of two different surface terminations explains the experiment the best, where the observed the reactivity stems from the minority termination. [1] S. Matera, M. Maestri, A. Cuoci, and K. Reuter, ACS Catal. 4, 4081 (2014). [2] J. Zetterberg et al., Rev. Sci. Instrum. 83, 053104 (2012)

O 6.8   Mon 12:30   MA 043

CO oxidation on TiO_2 nanotube-supported Pt particles at near ambient pressures — ●Sandra Krick Calderon[1], Mathias Grabau[1], Jeong Eun Yoo[2], Patrik Schmuki[2], Hans-Peter Steinrück[1], and Christian Papp[1] — [1]Physikalische Chemie II, University of Erlangen-Nürnberg, Egerlandstr. 3 — [2]Lehrstuhl für Korrosion und Oberflächentechnik, University of Erlangen-Nürnberg, Martensstraße 7, 91058 Erlangen, Germany

The CO oxidation reaction on two types of TiO_2 nanotube-supported Pt particle samples was examined by near-ambient pressure (NAP)-XPS and simultaneous online gas analyses. Both samples consist of vertical nanotubes (d=80, l=100 nm) decorated with platinum particles of different size. Temperature-programmed reaction experiments in continuous flow mode at a total pressure of 1 mbar and a CO:O_2 ratio of 1:4 were performed in the temperature range of 300 to 600 K. We compare these experiments to results obtained for the CO oxidation on a Pt(111) single crystal. The reaction onset temperatures were obtained by online gas analyses while the surface chemistry was investigated by XPS: we find a lower onset temperature on the nanoparticles with decreasing size and overall compared to Pt(111). Isothermal reactions were performed in-situ before at and above the onset temperatures, showing no adsorbed CO after reaction onset. Strong ageing of the samples with reaction time was observed resulting in changes of the reaction onset and CO conversion.

O 6.9   Mon 12:45   MA 043

Comparing facets: First-principles kinetic Monte Carlo simulations of CO oxidation at $RuO_2(111)$ — ●Tongyu Wang and Karsten Reuter — Technische Universität München, Germany

Systematic studies on polycrystalline powders are an appealing link between detailed surface science work on single crystals and the supported nanoparticles in real catalysis. Recent such work on RuO_2 powders points at a prominent role of the hitherto little studied apical facets for the long-term catalytic activity [1]. At near-ambient reaction conditions, particularly the {111} facet establishes a super-O-rich termination that features a singly-coordinated O_{cus} species, similar to the exhaustively studied (110) facet. In this context we establish a first-principles kinetic Monte Carlo model for CO oxidation at $RuO_2(111)$, rigorously using rate constants derived from density-functional theory. For stoichiometric and net-oxidizing feed our simulations predict a catalytic activity of this facet that is comparable to the one of $RuO_2(110)$. This indeed supports the relevance of this facet in understanding the catalytic activity of RuO_2 nanoparticles. [1] D. Rosenthal et al., Z. Phys. Chem. (Muenchen Ger.) **57**, 225 (2001); T. Wang, J. Jelic, D. Rosenthal, and K. Reuter, Chem. Cat. Chem. **5**, 3398 (2013).

O 6.10   Mon 13:00   MA 043

First Principles kinetic Monte Carlo simulations of competitive CO and NO Oxidation on Pd(100) — ●Juan Manuel Lorenzi[1], Sebastian Matera[1,2], and Karsten Reuter[1] — [1]Technische Universität München — [2]Freie Universität Berlin

Lean-burn automotive emissions are characterized by an increased NO_x content. A crucial step for the effective operation of NO_x storage reduction (NSR) catalysts is to oxidize excess NO into NO_2. In this context, interest shifts to understanding the oxidation properties of typically employed Pt-group catalysts under the simultaneous exposure to CO, NO and O_2. We assess this for the Pd(100) model catalyst surface with first-principles kinetic Monte Carlo (1p-kMC) simulations that are based on an extensive set of density-functional theory derived rate constants. For gas-phase conditions representative for the oxidative mode of NSR (600 K, 1 atm O_2, 10^{-3} atm NO) we obtain a NO oxidation activity of Pd(100) that is comparable to the one obtained previously for the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide on Pd(100) [1]. Intriguingly, already corresponding small amounts of NO in the gas-mixture lead to qualitative changes in the CO oxidation properties. Particularly for oxygen-rich feeds the O coverage is substantially reduced, suggesting an increased resistance against oxide formation. [1] J. Jelic, K. Reuter, and R. Meyer, Chem. Cat. Chem. 2, 658 (2010).