

O 28 Surface reactions II

Time: Tuesday 15:45–18:30

Room: WIL C207

O 28.1 Tue 15:45 WIL C207

CO-Oxidation measurements on Au/TiO₂ model catalysts — ●S. KIELBASSA¹, J. BANSMANN¹, F. WEIGL², H.G. BOYEN², P. ZIEMANN², and R.J. BEHM¹ — ¹Dept. of Surface Chemistry and Catalysis, University of Ulm — ²Dept. of Solid State Physics, University of Ulm

Model catalysts with tuneable particle size and distance parameters on flat surfaces open new opportunities for studying the influence of particle sizes and separations on the catalytic activity. However, the overall small active surface, approximately 1:500th of 1mg of a comparable powder catalyst, results in a very low total product conversion which is difficult to detect, especially in higher pressure regimes (1atm). Our model catalysts consist of Au particles with defined particle sizes (1-5nm) and separations (30-100nm) prepared by a micellar approach on flat TiO₂(110) single crystal surfaces. For the catalytic measurements, we use a novel design of a reactor with a very small volume (0.003ml) and constant gas-flow (0.0005ml) to detect the oxidation of CO. The reactor is situated in the load-lock of a UHV-chamber, which gives us the opportunity to characterize the samples in-situ with AFM and XPS without moving them through air. Results of the influence of particle sizes and separations on the activity are discussed.

O 28.2 Tue 16:00 WIL C207

Adsorption and Oxidation of CO on Au/TiO₂ model catalysts — ●THOMAS DIEMANT¹, ZHONG ZHAO¹, JOACHIM BANSMANN¹, HUBERT RAUSCHER², and R. J. BEHM¹ — ¹Abt. Oberflächenchemie und Katalyse, Universität Ulm, D-89069 Ulm — ²Institute for Health and Consumer Protection, European Commission, Joint Research Centre, I-21020 Ispra

Metal oxide supported gold catalysts have attracted considerable attention in the last years because of their surprising activity in a number of reactions such as the low temperature CO oxidation. We have studied the interaction of both pure CO and reactive CO/O₂ gas mixtures with planar Au/TiO₂ model catalysts at gas pressures up to 100 mbar and the activity of the model systems for CO oxidation in simultaneous kinetic and in-situ IR measurements (PM-IRAS). The possible evolution of additional surface species (carbonates, formates), which has been observed on real catalysts under similar conditions, was monitored. The results of this work will be compared with results from real catalysts, consequences for the reaction mechanism will be discussed.

O 28.3 Tue 16:15 WIL C207

Analysis of the compensation effect observed in first-principles kinetic Monte Carlo simulations of heterogeneous catalysis — ●HAKIM MESKINE, KARSTEN REUTER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany

First-principles kinetic Monte Carlo (kMC) simulations for heterogeneous catalysis provide quantitative microscopic insight into the steady-state catalytic activity, fully accounting for the correlations, fluctuations and spatial distributions of the chemicals at the catalyst surface [1]. Density-functional theory is employed to accurately obtain the energetics of the manifold of relevant processes, while a correct statistical mechanics treatment of their interplay is taken care of by the kMC algorithm. In the application of this approach to the CO oxidation at a RuO₂(110) model catalyst, we compute the composition and structure of the surface in reactive environments ranging from ultra-high vacuum to technologically relevant conditions with pressures of the order of atmospheres and elevated temperatures. The catalytic activity is narrowly peaked in environments, where the surface kinetics builds a disordered and dynamic adsorbate composition at the surface. Our analysis shows that the strong process interplay makes this resulting optimum mix at the catalyst surface highly adaptive.

[1] K. Reuter, D. Frenkel, and M. Scheffler, Phys. Rev. Lett. **93**, 116105 (2004).

O 28.4 Tue 16:30 WIL C207

Hot electron mediated associative desorption of hydrogen from Ru(001): insights from theory and experiment — ●STEFFEN WAGNER¹, CHRISTIAN FRISCHKORN¹, MARTIN WOLF¹, MATS PERSSON², and ALAN C. LUNTZ³ — ¹Freie Universität Berlin — ²Chalmers University of Technology, Göteborg — ³Dansk Fysik Institut Odense

Hot electron mediated associative desorption of hydrogen from a hydrogen covered Ru(001) surface was investigated both experimentally and theoretically. The hot electron distribution created by femtosecond-laser irradiation was proven to mediate H₂ desorption [1]. The desorbing hydrogen molecules were investigated regarding isotope effects, fluence dependence and energy transfer to the different molecular degrees of freedom [1, 2]. For the latter, different energy content in the different degrees of freedom was found. Those experimental findings are compared with the outcome of two-dimensional trajectory calculation, which take into account the electron mediated activation of the adsorbate via electronic friction. The friction coefficients are obtained from DFT calculations. This concept has been proven to be successful for the consideration of non-adiabatic effects in activated associative desorption and vibrational damping of adsorbed molecules [3,4]. Thus, we are able to give a microscopic description of the experimental observations.

[1] Denzler et al, Phys. Rev. Lett. 91, 226102 (2003) [2] Wagner et al, Phys. Rev. B 72, 205404 (2005); [3] Luntz, Persson, J.Chem. Phys. 123, 074704 (2005) [4] Persson, Hellsing, Phys. Rev. Lett. 49, 662 (1982)

O 28.5 Tue 16:45 WIL C207

Ammonia oxidation on Pt single crystal surfaces in an intermediary pressure range up to 1 mbar — ●YINGFENG ZENG¹, SEBASTIAN GÜNTHER², LING ZHOU³, and RONALD IMBIHL¹ — ¹Institute for Physical Chemistry, Hannover University, Callinstr. 3-3a, D-30167 Hannover, Germany — ²LMU München, Department Chemie, Butenandstr. 11 E, D-81377 München, Germany — ³Division of Engineering and Applied Sciences, Harvard University, Pierce Hall, 29 Oxford St., Cambridge, MA 02138, USA

The kinetics of ammonia oxidation on Pt(443), Pt(533) and Pt(100), have been investigated under stationary reaction condition in the 10⁻⁴ to 10⁻² mbar range with low-energy electron diffraction (LEED), ellipsometry and rate measurement. Rate hysteresis in T-cycling occurs associated with structural modification of the Pt substrate is verified by LEED measurements with Pt(533) and Pt(443). Surprisingly, the occurrence of a hysteresis depends on the total pressure. For Pt(533) and Pt(443) we found a hysteresis at 10⁻³ mbar, but no hysteresis at P ≥ 10⁻² mbar, on Pt(443) hysteresis vanishes at P ≤ 10⁻⁴ mbar. On Pt(100) we found under all conditions a very broad hysteresis due to the phase transition of substrate from (1 × 1) to hex. The origin of the P-dependent hysteresis on Pt(443) and Pt(533) is discussed in terms of reversible and irreversible structural changes of the Pt surfaces.

O 28.6 Tue 17:00 WIL C207

Methanol steam reforming on Zn/Pd(111) — ●REINHARD DENECHE, ERCAN ÜNVEREN, ARMIN REINDL, HEIKO WUSTMANN, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

Hydrogen as energy source for mobile applications can be obtained by steam reforming of methanol over Pd/ZnO catalysts. On other supported Pd catalysts, the addition of Zn increases the selectivity and the rate of hydrogen formation [1].

In order to prepare the active PdZn alloy, 3 or 6 ML Zn are deposited on Pd(111) at 300 K and alloyed at 500 to 600 K. The adsorption of methanol and consequently the reaction with water at different temperatures are investigated in-situ in a pressure range from ultra-high-vacuum up to 0.3 mbar by "high-pressure" X-ray photoelectron spectroscopy [2]. For methanol adsorption, CH_xO (x=0-3) and CH₃OH species are found on the catalyst surface. In contrast to Pd(111), nearly no dissociation to CH_x was observed, suggesting different reaction pathways. Co-adsorption of methanol and water leads to reduced intensity of the CH_xO (x=0-3) species, signalling a reaction process. Gas phase analysis complements these results. Supported by DFG (SPP 1091).

[1] N. Iwasa et al., J. Chem. Eng. Japan 37 (2004) 286

[2] J. Pantförder et al., Rev. Sci. Instrum. 76 (2005) 014102

O 28.7 Tue 17:15 WIL C207

Adsorption and Reaction of Methanol on Partially Oxidized Pd Model Catalysts — •BJÖRN BRANDT¹, TOBIAS SCHALOW¹, SWETLANA SCHAUERMANN¹, JÖRG LIBUDA², and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany — ²Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstrasse 3, 91058 Erlangen, Germany

The chemical state of metal nanoparticles under oxidizing reaction conditions and its influence on the reactivity is a subject of enduring discussion for many catalytic systems. On transition metal surfaces, a variety of different oxygen species has been reported, whose role in reaction kinetics is poorly understood. In this study we present first results on the interaction of methanol with well-defined Pd/Fe₃O₄ model catalysts, applying molecular beam methods combined with TR-IRAS. Previously, we have shown that oxidation of iron oxide supported Pd particles above 500 K results in the formation of Pd oxides, located primarily at the particle/support interface. We probe the reactivity of partially oxidized and pristine metallic Pd nanoparticles for methanol decomposition and oxidation. On the pristine Fe₃O₄ support, the formation of stable methoxy species was observed up to 350 K. On Pd particles, methanol decomposition undergoes two competing reaction pathways, resulting in formation of CO and carbonaceous species. The influence of Pd particle oxidation on the two decomposition pathways was studied by transient and steady-state experiments, combined with TR-IRAS.

O 28.8 Tue 17:30 WIL C207

Formation and Activity of Partially Oxidized Pd Nanoparticles — •TOBIAS SCHALOW¹, BJÖRN BRANDT¹, MATHIAS LAURIN¹, SEBASTIEN GUIMOND¹, HELMUT KUHNLEBECK¹, DAVID E. STARR¹, SHAMIL K. SHAIKHUTDINOV¹, SWETLANA SCHAUERMANN¹, JÖRG LIBUDA², and HANS-JOACHIM FREUND¹ — ¹Fritz-Haber-Institut der Max-Planck-Gesellschaft, Department of Chemical Physics, Faradayweg 4-6, 14195 Berlin, Germany — ²Friedrich-Alexander-Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Egerlandstrasse 3, 91058 Erlangen, Germany

The formation and reactivity of different oxygen species formed on iron-oxide supported Pd nanoparticles are studied by combining well-defined model catalysts, molecular beam experiments and various surface science techniques. It is shown that at temperatures above 500 K, large amounts of oxygen can be stored in form of a thin Pd oxide layer at the particle support interface, which can be reversibly accumulated and depleted. The formation of this interface oxide layer, however, shows a strong particle size dependence: While for small particles the oxygen storage capacity is limited by the amount of metal available, for large particles strong kinetic hindrances and a limited amount of accessible interface sites inhibit the oxygen storage process. Consequently, a pronounced maximum in oxygen storage capacity is found for particles of about 7 nm in diameter. Furthermore it is demonstrated how the formation and reduction of this interface oxide layer affects the activity of the catalyst towards CO oxidation under reaction conditions.

O 28.9 Tue 17:45 WIL C207

On the oxidation and reduction of Co nanoparticles on thin aluminum oxide films — •TOBIAS NOWITZKI¹, THOMAS RISSE², VOLKMAR ZIELASEK¹, and MARCUS BÄUMER¹ — ¹Institut für Angewandte und Physikalische Chemie, Universität Bremen, Leobener Str. NW II, 28359 Bremen — ²Abteilung Chemische Physik, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin

Cobalt is used as a catalyst for the hydration of carbon monoxide, the so called Fischer-Tropsch process. As a model catalyst for this reaction, Co nanoparticles on thin aluminum oxide films have been studied in ultrahigh vacuum (UHV) with respect to their oxidation and reduction behaviour. The Co particles were prepared in UHV by physical vapor deposition on a thin aluminum oxide film grown on a NiAl(110) single crystal. X-ray photoelectron (XP) and thermal desorption (TD) spectroscopy data show that Co particles are entirely oxidized at room temperature. After heating to temperatures > 500 K, XPS shows mostly metallic Co, indicating reduction, while TDS shows a mixture of metallic and oxidic components, revealing the existence of a thin surface oxide. Our results indicate that the surface oxide formation depends on particle size. We also find that carbon monoxide can dissociate on metallic particles, which is interesting for the Fischer-Tropsch reaction. In the XP spectra, the oxidic component of the Al 2p substrate signal is increased after heating in presence of the Co particles. Obviously, the aluminum

oxide film gets thicker during this procedure, enhancing its thermal stability.

O 28.10 Tue 18:00 WIL C207

EPOXIDATION OF ETHYLENE ON SILVER STUDIED BY HIGH-PRESSURE STM — •R. REICHELTL, M. RÖSSLER, S. GÜNTHER, and J. WINTTERLIN — Ludwig-Maximilians-Universität, Department Chemie, 81377 München, Germany

Using an improved high pressure scanning tunneling microscope (STM) we have investigated the epoxidation of ethylene on silver surfaces. The setup consists of a high-pressure cell (up to 1 bar) housing the STM that is attached to an ultra-high vacuum chamber and to a gas analysis system containing a mass spectrometer. In the STM cell catalytic reactions can be performed under pressure and temperature conditions close to those of industrial catalytic processes, both in batch and flow mode. In the UHV chamber single crystal surfaces are prepared under clean surface-science conditions, and standard surface science techniques are used for post-reaction analysis of the sample surface. It has been achieved to detect a reaction to give ethylene oxide at pressures of approximately 1 mbar and at temperatures around 500 K. Atomic resolution was obtained on an Ag(111) surface under epoxidation conditions. Several different surface structures were observed, suggesting that more than one species of oxygen is involved in this reaction.

O 28.11 Tue 18:15 WIL C207

SCANNING TUNNELING MICROSCOPY INVESTIGATIONS OF THE STRUCTURAL BASIS FOR CATALYST DEACTIVATION — •S. MARCHINI, S. GÜNTHER, and J. WINTTERLIN — Ludwig-Maximilians-Universität, Department Chemie, 81377 München, Germany

Deactivation and poisoning is an essential phenomenon in industrial catalysis. A poison can influence both the activity and the selectivity of the catalyst chemically, by modifying the electronic properties of the surface, or physically, by altering the geometry or blocking the active sites of the catalyst. We here present a scanning tunneling microscopy investigation of the formation of a graphitic layer on the Ru(0001) surface. Prolonged annealing of the sample causes carbon segregation from the bulk of the crystal and the formation of a superstructure whose coverage increases up to saturation upon increasing the heating temperature to 1400K. LEED measurements show that the structure is incommensurate (~12.5x12.5) and rotationally aligned to the surface. STM images exhibit a Moiré pattern with a periodicity of 28Å and whose structure could be atomically resolved. The system exhibits an interesting spectroscopic behavior: images taken with different tunneling voltages show strong changes in the way the structure appears, revealing the presence of a composite surface electronic structure.