O 3 Oberflächenreaktionen I

Zeit: Freitag 10:45–13:00 Raum: TU EB420

O 3.1 Fr 10:45 TU EB420

Investigation of Au/TiO_2 model catalysts prepared from micellar stabilized gold particles — •S. Kielbassa[1], F. Weigl[2], A. Ethirajan[2], H.G. Boyen[2], P. Ziemann[2] und R.J. Behm[1] — [1]Abt. Oberflächenchemie und Katalyse, Universität Ulm, 89069 Ulm — [2]Abt. Festkörperphysik, Universität Ulm, 89069 Ulm

Metal oxide supported Au catalysts have attracted considerable interest over the last years because of their high activity for low-temperature oxidation and hydrogenation reactions. For studying particle size and transport effects, we prepared model systems with a narrow distribution for particle sizes and particle separations by depositing Au loaded diblock copolymer micelles onto atomically smooth TiO_2 (110) rutile substrates. Removing of the polymer shells in an oxygen plasma leads to a hexagonal arrangement of Au particles. The stability of these model systems in typical activation and reaction atmospheres/temperatures as well as their activity for CO oxidation under high pressure conditions was investigated for different particle sizes and seperations. Consequences on the reaction mechanism are discussed.

O 3.2 Fr 11:00 TU EB420

Catalytic properties of UHV-prepared Au/TiO_2-model systems at elevated pressures up to 100 mbar — •Thomas Diemant, Zhong Zhao, Hubert Rauscher, and R. J. Behm — Abt. Oberfächenchemie und Katalyse, Universität Ulm, 89069 Ulm

Oxide supported Au catalysts have found increasing interest because of their high activity for various oxidation and reduction reactions. For model studies under realistic reaction conditions we performed in-situ IR spectrocopy (PEM-IRAS) and rate measurements for CO oxidation on structurally (STM) [1] and chemically (XPS, CO-TPD) well-defined model catalysts, prepared by Au deposition on thin TiO_2 films at pressures up to 100 mbar. Results for various Au particle sizes, temperatures, and partial pressures are presented and discussed in comparison with data obtained on real catalysts. Consequences for the reaction mechanism are derived.

[1] Zhong Zhao et al., DPG-Frühjahrstagung AKF Oberflächenphysik, Berlin (2005)

O 3.3 Fr 11:15 TU EB420

Reduction of the Surface Oxide Layer on Rh(111) by CO and H_2 — •Jan Klikovits[1], Michael Schmid[1], Edvin Lundgren[2], Jasper N. Andersen[2], Lukas Köhler[3], Georg Kresse[3], and Peter Varga[1] — [1]Institut für Allgemeine Physik, TU Wien, A-1040 Wien, Austria — [2]Department of Synchrotron Radiation Research, Lund University, Box 118, S-221 00, Sweden — [3]Inst. f. Materialphysik, Universität Wien, A-1090 Wien, Austria

We have studied the surface oxide on Rh(111) and its reduction by CO and H_2. The structure of the surface oxide has already been solved [1]. Reducing the oxide by CO requires temperatures of about 100 °C. Essentially all CO adsorbs at reduced areas, thus the reduction rate increases while the amount of oxide decreases at the surface. STM images show that the reduction starts at step edges and islands. A (2 x 2) superstructure is observed in the reduced areas. We argue that the CO molecules are immobilized by a oxygen superstructure which is in thermodynamic equilibrium with the oxide. The reduction of the surface oxide by H_2 was observed in-situ by STM. It starts already at room temperature, almost exclusively in stepped areas. We can also initiate the reduction process by deliberately creating defects with the STM tip allowing us to examine the reduction kinetics in detail. At low H_2 pressures or small reduced areas the reduction rate is limited by the hydrogen adsorption on the reduced area. For large reduced areas the reduction rate is limited by the processes at the border of the reduced area.

[1]: J. Gustafson et al., Phys. Rev. Lett 92, 126102, (2004).

O 3.4 Fr 11:30 TU EB420

Hydrogen Transfer Reaction on the Surface of an Oxide catalyst — •Daniela Crihan, Marcus Knapp, and Herbert Over — Phys.Chem.Institut, Justus Liebig Univ. Giessen, D-35392 Giessen

RuO_2(110) exposes two kinds of active surface species (acidic and basic centers) which govern the interaction of the gas phase in contact with the catalysts surface. Here we will elucidate the cooperative interplay of these two active surface sites for a simple model reaction, namely the water formation over RuO_2(110) catalysts when supplying hydrogen and oxygen from the gas phase. The bridging O atoms harvest the hydrogen from the gas phase, while the on-top O atoms picks up those adsorbed hydrogen atoms from the bridging O atoms to form water. This mechanism of hydrogen transfer is mediated by a strong hydrogen bond. Hydrogen transfer is expected to play a vital role for the whole class of catalyzed hydrogenation and dehydrogenation reactions of hydrocarbons over RuO_2(110).

O 3.5 Fr 11:45 TU EB420

Interaction of Hydrogen with RuO_2(110) Surfaces — •Yuemin Wang[1,2], Jinhai Wang[2], Chaoyang Fan[2], Karl Jacobi[2], and Gerhard Ertl[2] — [1]Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum — [2]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin

The adsorption and reaction of hydrogen on the stoichiometric and oxygen-rich RuO_2(110) surfaces - the latter exposing a weakly bound atomic oxygen species (O-cus) on-top of the unsaturated Ru atom (Ru-cus) - was studied using high-resolution electron energy-loss spectroscopy (HREELS) and thermal desorption spectroscopy (TDS). On the stoichiometric RuO_2(110) surface two hydrogen adsorption states are identified at 85 K [1]: Molecular hydrogen at Ru-cus and dissociated hydrogen forming a dihydride with O-bridge, the other unsaturated surface oxygen besides O-cus. The dihydride is transformed into monohydride by release of hydrogen at 350 K. On oxygen-rich RuO_2(110) surfaces hydrogen reacts with O-cus forming H_2O-cus. This species undergoes desorption instead of dissociation with heating to higher temperatures. The reaction mechanisms of hydrogen with O-bridge and O-cus are derived.

[1] Wang, J.; Fan, C. Y.; Sun, Q.; Reuter, K.; Jacobi, K.; Scheffler, M.; Ertl, G. Angew. Chem. Internat. Edition 2003, 42, 2151.

O 3.6 Fr 12:00 TU EB420

Interaction of supported Pd nanoparticles with H, O and C — •Günther Rupprechter, Matthias Morkel, Marta Borasio, and Hans-Joachim Freund — Fritz-Haber-Institut, Faradayweg 4-6, 14195 Berlin

Vibrational sum frequency generation (SFG) spectroscopy, thermal desorption spectroscopy (TDS) and photoelectron spectroscopy (XPS) were utilized to examine the interaction of Al_2O_3 supported Pd nanoparticles with hydrogen, oxygen and methanol. Experiments were performed both under ultrahigh vacuum (UHV) as well as mbar pressure. The Pd nanoparticles had a mean size of 5 nm and exhibited mostly (111) facets.

Pd-hydride formation was observed to proceed predominantly via minority sites on Pd nanoparticles, i.e. defects and (100) faces. Explosive hydrogen desorption through a CO overlayer originates from the confinement of dissolved hydrogen within the limited nanoparticle volume. The oxidation of Pd nanoparticles under UHV and mbar pressure also seems to be strongly influenced by defects. Carbonaceous deposits that appear during methanol decomposition and oxidation are located both in surface and subsurface positions. A possible involvement of CH_x species in the oxidation reaction is discussed.

O 3.7 Fr 12:15 TU EB420

Surface Diffusion and Fluctuations on Catalyst Nanoparticles — •Mathias Laurin[1], Viktor Johánek[1], Ann W. Grant[2], Bengt Kasemo[2], Jörg Libuda[1], and Hans-Joachim Freund[1] — [1]Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4–6, 14195 Berlin, Germany — [2]Department of Applied Physics, Chalmers University of Technology, 41296, Göteborg, Sweden

The CO oxidation and oxygen diffusion kinetics are investigated using molecular beam methods under ultrahigh vacuum (UHV). We employ oxide supported Pd nanoparticles prepared by physical vapor deposition (PVD) and electron beam lithography (EBL) covering a large range of particle sizes (1–500 nm).

The angular resolved distribution of CO_2 depends on the reaction conditions and particle size. In combination with the experiments, microkinetic simulations give information on the mobility of the adsorbed species under reaction conditions and on the local reaction rates on the particle surface.

A macroscopic bistability of the reaction is observed at low temperatures on the big particles. It is however quenched on small nanoparticles.

This is attributed to fluctuation induced transitions, accelerated in the presence of defect sites.

O 3.8 Fr 12:30 TU EB420

In-situ high resolution XPS study of the CO oxidation on Pt(355) — •Barbara Tränkenschuh, Thomas Fuhrmann, Christian Papp, Daniel Kiessling, Reinhard Denecke, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

The oxidation of CO on the stepped Pt(355)=[5(111)x(111)] surface was studied by in-situ high resolution XPS experiments at BESSY II. The different species and adsorption sites (O, CO on-top/bridge) on steps and terraces are clearly distinguishable in O 1s or C 1s spectra. In the experiments first an oxygen layer was prepared using a procedure, which leads to a p(2x2)-O-LEED pattern on Pt(111). On Pt(355), however, no ordered adsorbate structure was observed. Therefore, the coverages of the reactants (O, CO) were estimated by comparing the XPS intensities with those observed on Pt(111) [1]. CO was dosed by a supersonic molecular beam, which allows to vary the CO pressure on the sample. The oxidation was studied as a function of reaction temperature and CO pressure on the sample by recording time-dependent O 1s and C 1s intensities. Measurable reaction rates on Pt(355) are observed at much lower temperatures than on Pt(111) (200 vs. 270 K, respectively) [1]. The reaction product CO_2 was additionally detected by mass spectrometry. Supported by the DFG (STE 620/4-2).

[1] M. Kinne et al., J.Chem. Phys. 120 (2004) 7113.

O 3.9 Fr 12:45 TU EB420

Messungen an einer YSZ/Pt-Gasreferenzzelle zur elektrochemischen Promotion katalytischer Reaktionen — •Tobias Neubrand[1], Sebastian Günther[2] und Ronald Imbihl[1] — [1]Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstraße 3-3a, 30167 Hannover — [2]LMU München, Department Chemie, Butenandstr.11 E, 81377 München

Während elektrochemischen Pumpens ändert sich bei Festelektrolyt/ Metall-Systemen die Austrittsarbeit des Metalls. Es wurde eine 1:1 Beziehung zwischen Austrittsarbeitsänderung und eingestellter Spannung postuliert, die aber nur teilweise durch Messergebnisse bestätigt werden konnte. Zur Klärung dieser Frage wurde eine gasdichte elektrochemische Zelle für den Einsatz im UHV aufgebaut, bei der auf einem YSZ-Festkörperelektrolyten die Elektroden durch Aufsintern einer Pt-Paste aufgebracht wurden. Ein fester Sauerstoff-Referenzdruck verhindert das Verschieben des Referenzpotentials durch Anreduktion von YSZ. An dieser Zelle konnten Ratenmessungen der katalytischen CO-Oxidation an Pt mit Messungen der Austrittsarbeit korreliert werden, die integral über eine Kelvin-Sonde und lokal über Photoelektronenemissionsmikroskopie (PEEM) bestimmt wurden. Die verschiedenen Beiträge zu Kelvinsondenmessungen der Austrittsarbeit konnten damit identifiziert werden: Ein elektrostatischer durch Aufladung der Elektroden und ein ëchter", der durch SSpillover"von O-Ionen von YSZ zur Pt-Oberfläche zustande kommt.