

## O 13: Heterogeneous Catalysis

Time: Monday 14:00–16:30

Location: HE 101

O 13.1 Mon 14:00 HE 101

**Geometry of silica supported vanadium oxide particles: theoretical core excitation spectra can provide new insight.** — ●MATTEO CAVALLERI and KLAUS HERMANN — Fritz-Haber-Institut der MPG, Berlin, Germany

The characterization of vanadia units in supported vanadium oxide catalysts is of paramount importance for an understanding of the reactive behavior of these materials.

Here we compare results from density-functional theory calculations on O 1s core excitations of small model particles with experimental data from Near-Edge X-ray Absorption Fine Structure (NEXAFS) measurements of well-known reference compounds and of real catalytic materials in order to determine structural properties of silica-supported vanadia nanoparticles. This procedure provides an unambiguous discrimination of all different oxygen species inside the particles and overcomes limitations of previous studies using vibrational spectroscopy where the particle-support interaction was found to hide essential structural information.

As a result, we are able to identify unique spectroscopic features characterizing bridging V-O-V oxygen that can be used as a fingerprint of polymeric vanadia species. The O 1s excitations of the silica support are found to contribute to the NEXAFS spectrum at higher energies compared with those of the vanadia particle such that the two contributions can easily be separated in the experiment.

O 13.2 Mon 14:15 HE 101

**Adsorption and dehydrogenation of ammonia at the V<sub>2</sub>O<sub>5</sub>(010) surface: DFT cluster studies** — ●MATHIS GRUBER and KLAUS HERMANN — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin, Germany

Transition metal oxide catalysts are widely used for selective oxidation reactions. However, in many cases details of the catalytic reaction mechanisms are still under discussion. One prominent example is the ammoxidation of propylene to acrylonitrile at transition metal oxide surfaces (SOHIO process). This catalytic reaction includes, amongst other steps, the adsorption and dehydrogenation of NH<sub>x</sub>,  $x < 4$ , at the catalyst surface. We have performed theoretical studies on these reaction steps where the catalyst is simulated by a finite section of the V<sub>2</sub>O<sub>5</sub>(010) surface. The calculations use density-functional theory combined with clusters modeling the surface and adsorbate system. Calculations for the clean V<sub>2</sub>O<sub>5</sub>(010) surface show that binding energies of the H atom are always significantly larger than of the NH<sub>x</sub> species. Further, the substrate is found to lower corresponding dehydrogenation energies compared with values for the gas phase reaction. However, the lowering is too small to make dehydrogenation likely to happen under ammoxidation reaction conditions. This suggests that surface defects such as oxygen vacancies become important for the reaction. Therefore, the role of oxygen vacancies for the dehydrogenation of NH<sub>x</sub> will be discussed in detail.

O 13.3 Mon 14:30 HE 101

**Kinetische Monte Carlo Simulation von Oberflächenreaktionen auf Nanopartikeln** — ●LOTHAR KUNZ und OLAF DEUTSCHMANN — Institut für Technische Chemie und Polymerchemie, Universität Karlsruhe (TH), Engesserstr. 20, 76131 Karlsruhe

Eine Erweiterung der kinetischen Monte Carlo Methode erlaubt die detaillierte Betrachtung von Oberflächenreaktionen auf geträgerten Nanopartikeln und deren Support. Dabei kann zwischen Adsorptionsplätzen auf Flächen, Kanten und Ecken der Partikel differenziert werden. Die Methode läßt sich als Brücke zwischen Dichtefunktionalrechnungen der Elementarprozesse und Mean-Field-Simulationen in der heterogenen Katalyse einsetzen.

Es wird die Erweiterung der Methode sowie deren Anwendungsmöglichkeiten vorgestellt. Eine generische Implementierung sowie ein Editor für die Eingabe des Gitters der Oberfläche und die Formulierung der Elementarprozesse wie Adsorption, Desorption, Diffusion und Reaktion erlauben eine effiziente Übertragung auf unterschiedliche Partikelformen und Reaktionen.

O 13.4 Mon 14:45 HE 101

**Influence of the substrate on the catalytic activity of Au/TiO<sub>2</sub>(110) model catalysts** — ●STEFAN KIELBASSA, MENHILD

EYRICH, JOACHIM BANSMANN, and ROLF-JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany

In recent years, oxide supported Au catalysts and, in particular, the low temperature CO oxidation have intensively been examined. However, various topics, like the influence of the support on the catalytic activity, are still controversially discussed. Here, we present results on the influence of the chemical nature of the TiO<sub>2</sub>(110) support on the activity of Au/TiO<sub>2</sub>(110) model catalysts. Substrates with different surface structures and (bulk) oxidation states were prepared by using different preparation cycles (such as annealing and sputtering steps). After deposition of Au nanoparticles by thermal evaporation ( $\Theta = 0.5$  ML), the activity of the model catalysts was examined in a micro-flow reactor. Samples with fully oxidized substrates are nearly catalytically inactive, while for catalysts based on bulk-reduced substrates or thin TiO<sub>2</sub> films, the activity is up to 50 times higher. Atomic force microscopy (AFM) images of the surfaces show that, on the bulk-reduced supports, Au particle densities and sizes do not differ significantly and thus cannot be made responsible for the observed variations in the activity. A high activity of oxygen surface vacancies is discussed as origin of the enhanced activity of these catalysts.

O 13.5 Mon 15:00 HE 101

**Olefin conversions on supported Pd model catalysts: Molecular origins of selectivity towards isomerization and hydrogenation** — ●WIEBKE LUDWIG<sup>1</sup>, BJÖRN BRANDT<sup>1</sup>, JAN-HENRIK FISCHER<sup>1</sup>, SWETLANA SCHAUERMANN<sup>1</sup>, FRANCISCO ZAERA<sup>2</sup>, and HANS-JOACHIM FREUND<sup>1</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — <sup>2</sup>University of California, Riverside, USA

Understanding the mechanisms governing alkene conversions, isomerization and hydrogenation in particular, is an important goal in catalytic research and significant for industrial processes.

Whereas no hydrogenation is observed on Pd single crystals, it was recently shown that hydrogenation readily occurs on small Pd particles, presumably due to the formation of weakly-bound subsurface hydrogen species [1].

Under realistic conditions, these reactions take place over catalysts covered with carbonaceous species originating from the decomposition of alkenes. The exact role of these strongly bound species is however still not clear.

In this study, we present results on the conversion of *cis*- and *trans*-2-butene with deuterium over a Pd model catalyst supported on a Fe<sub>3</sub>O<sub>4</sub> oxide film. To investigate the influence of carbonaceous species on the reaction kinetics, we performed isothermal molecular beam experiments combined with TPD measurements on both clean and carbon-precovered catalysts.

[1] A.M. Doyle et al., *Angew. Chem. Int. Ed.* 2003, 42, 5240-5243.

O 13.6 Mon 15:15 HE 101

**CO oxidation on Palladium(111): Rate hysteresis and periodic breakdowns** — ●STEFAN KARPITSCHKA<sup>1</sup>, STEFAN WEHNER<sup>1</sup>, HELMUT BRAND<sup>2</sup>, and JÜRGEN KÜPPERS<sup>1,3</sup> — <sup>1</sup>Experimentalphysik III, Universität Bayreuth, 95440 Bayreuth, Germany — <sup>2</sup>Theoretische Physik III, Universität Bayreuth, 95440 Bayreuth, Germany — <sup>3</sup>Max-Planck-Institut für Plasmaphysik (EURATOM Association), 85748 Garching, Germany

A rate-measurement-study of the catalytic oxidation of carbon monoxide on Pd(111) surfaces in the high vacuum pressure range is presented. The total flux of the feed gas to the surface was held constant while its CO-fraction was varied. The existence of a regime in the feed gas composition in which the system exhibits bistable behavior was shown by long-time measurements. Pulse-like modulations of the feed gas revealed that the experimentally observed high CO-fraction border of the bistable region is determined by the equistability condition of both phases. This behavior could be caused by the presence of predominantly CO-covered defects exceeding the critical size for nucleation. The experimental results and their temperature dependence are well described by a simple mean field model containing no fit parameters.

Applying high CO-fractions in the feed gas just within the bistable range, we furthermore observed periodic breakdowns in the catalytic activity at a very low frequency, which were not yet reported for this surface. Growth and decay of surface oxides as well as noise have been

tested as an origin of these periodic breakdowns.

O 13.7 Mon 15:30 HE 101

**Methane Oxidation on Gold** — ●GUIDO WALTHER<sup>1</sup>, GLENN JONES<sup>1</sup>, SØREN JENSEN<sup>2</sup>, and SEBASTIAN HORCH<sup>1</sup> — <sup>1</sup>CAMD, Department of Physics, DTU, 2800 Lyngby, Denmark — <sup>2</sup>MIC, Department of Micro and Nanotechnology, DTU, 2800 Lyngby, Denmark

Since transportation of methane from the sources to the consumers requires low temperature and high pressure, there is a keen interest in transforming methane into methanol. This study aims at investigating the fundamental process of methane oxidation on gold.

In a millireactor setup, methane oxidation was studied on various gold catalysts. The reaction products were analyzed using a gas chromatograph and a mass spectrometer. To study the trend in activity of gold, a couple of catalysts of different particle sizes were used. Additional experiments were performed on a few gold catalysts of the same particle size, but different support materials, to emphasize the support effect in terms of trends in stability. TEM analysis before and after catalytic reactions document changes in particle size and shape.

Partial methane oxidation could not be observed on these catalysts. This is consistent with the thermodynamics, which show that there is a strong tendency of CO<sub>2</sub> formation.

O 13.8 Mon 15:45 HE 101

**Reactivity of Nickel on oxide surfaces: evidence of surface oxygen** — ●YAN-CHUN LIU, HEIKO STRAUSS, ANDREA BERLICH, and HARALD MORGNER — Wilhelm-Ostwald-Institute for Physical and Theoretical Chemistry, University of Leipzig, Linnéstraße 2, D-04103 Leipzig

The role of surface and subsurface oxygen during catalytic processes on oxide supported metal catalysts remains a question of debate in some cases [1,2,3]. Some controversy arises from the difficulties to identify the position of the oxygen. Using Metastable Induced Electron Spectroscopy (MIES) we have been able to identify adsorbed oxygen on top of the metallic Nickel deposits on NiO layers. Furthermore, detailed analysis of the MIE spectra provides evidence of an atomically adsorbed Nickel species. The reactivity of the different Ni adsorbates was evaluated by its reaction with oxygen. Results of the growth of Ni on TiO<sub>2</sub> by MIES are also presented.

[1]D. W. Goodman, C. H. F. Peden and M. S. Chen, CO oxidation on ruthenium: The nature of the active catalytic surface. *Surface Science* 601, L124-L126 (2007).

[2]H. Over, M. Muhler and A. P. Seitsonen, Comment on [1] *Surface Science* in Press.

[3]D. W. Goodman, C. H. F. Peden and M. S. Chen, Comment on [2] *Surface Science* in Press

O 13.9 Mon 16:00 HE 101

**Interaction of CO, CO<sub>2</sub>, O<sub>2</sub> and H<sub>2</sub>O with Au/Rutile TiO<sub>2</sub>(011)-(2x1)/Re(10 $\bar{1}$ 0) model catalysts** — ●WILHELMINE

KUDERNATSCH<sup>1</sup>, KARIFALA DUMBUYA<sup>2</sup>, J. MICHAEL GOTTFRIED<sup>2</sup>, HANS-PETER STEINRÜCK<sup>2</sup>, and KLAUS CHRISTMANN<sup>1</sup> — <sup>1</sup>Physikalische und Theoretische Chemie, Freie Universität Berlin, Germany — <sup>2</sup>Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

During the last decade, the peculiar activity of Au/titania catalysts for low-temperature CO oxidation has stimulated a wealth of studies using TiO<sub>2</sub> model catalyst systems. In a first step, we have studied the epitaxy and chemical properties of titanium dioxide films grown on rhenium surfaces under ultra-high vacuum (UHV) conditions. Titania films were prepared by co-deposition of Ti vapor in an O<sub>2</sub> atmosphere of 1x10<sup>-6</sup> mbar at 900 K. On Re(10 $\bar{1}$ 0), this procedure results in the growth of rutile films terminated by a (2x1)-reconstructed (011) surface. Au-containing model catalyst systems were then prepared by controlled vapor deposition of Au onto these films.

In order to characterize the structural and chemical properties of our model catalyst surfaces, we have studied the adsorption of CO, CO<sub>2</sub>, and H<sub>2</sub>O on the clean and Au-covered TiO<sub>2</sub>(011)-(2x1) films by means of temperature-programmed desorption (TPD) and low-energy electron diffraction (LEED). To obtain information about the chemical composition of the model catalysts in the presence of the reactants, CO and O<sub>2</sub>, we performed in-situ measurements with high-pressure X-ray photoelectron spectroscopy (XPS) at pressures up to 1 mbar.

O 13.10 Mon 16:15 HE 101

**LEEM, XPS, and STM Characterization of Oxygen Species Relevant for the Ethylene Epoxidation on Silver** — ●R. REICHEL, S. GÜNTHER, and J. WINTERLIN — Ludwig-Maximilians-Universität, 80337 München, Germany

The epoxidation of ethylene on silver catalysts is an extremely complex reaction because of the complicated nature of the Ag/O interaction. Several oxygen species on Ag surfaces have been identified but until now there is no general agreement about their role for the catalytic reaction. Using LEEM, XPS and STM we have investigated oxygen species on Ag(111) that were prepared by thermal decomposition of NO<sub>2</sub>. We find that the species obtained sensitively depend on the preparation conditions which may explain part of the conflicting data from literature. Apart from the (4x4)O phase, another oxygen species, the so called O  $\gamma$  could be obtained by applying several preparation cycles of (4x4)O phase followed by flash annealing it slightly above 570 K. Angle-resolved XPS of O  $\gamma$  shows a surface-like behaviour. However XPS data surprisingly show that it is stable up to 800 K, suggesting a strongly bound species. Another species could be prepared by dosing CO<sub>2</sub> on the (4x4)O structure which meanwhile vanishes in XPS. In STM the local decomposition of (4x4)-patches and related stripe phases evidenced a reaction of the (4x4)O adsorption layer with CO<sub>2</sub>. We can propose the formation of two surface carbonate species evidenced by two well separated CO<sub>2</sub> desorption peaks in TDS. It is also demonstrated that after using NO<sub>2</sub> readsorption of residual gas species can occur, an apparent cause for misinterpretations of spectra.