

## O 4: Heterogeneous catalysis I

Time: Monday 11:15–13:00

Location: H33

O 4.1 Mon 11:15 H33

**First-Principles statistical mechanics simulations of catalytic oxidation of ammonia at RuO<sub>2</sub>(110)** — ●CLAUDIA MANGOLD<sup>1</sup> and KARSTEN REUTER<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut, Berlin (Germany) — <sup>2</sup>Technische Universität München (Germany)

RuO<sub>2</sub>(110) has evolved into a frequently studied model oxide surface, with appealing catalytic properties for a range of reactions. Recent experiments by Wang *et al.* [1] determined an almost 100% selectivity for the oxidation of ammonia, adding this first step of the Ostwald process to the list. In order to understand the mechanistic details behind this high selectivity we perform first-principles statistical mechanics simulations, based on density-functional theory for a quantitative account of the surface energetics. The atomistic thermodynamics phase diagram, constructed for a constrained equilibrium with the NH<sub>3</sub> and O<sub>2</sub> gas phase, points at a prominent role of the coordinatively unsaturated sites offered by the surface. First kinetic Monte Carlo simulations concentrate on the kinetics at these sites and reveal severe diffusion limitations at the nanostructured RuO<sub>2</sub>(110) surface.

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

O 4.2 Mon 11:30 H33

**Size effects in C<sub>2</sub>H<sub>4</sub> dehydrogenation studied by HR-PES: Pt(111) versus Pt/CeO<sub>2</sub>/Cu(111) model catalysts.** — ●YAROSLAVA LYKHACH<sup>1</sup>, THORSTEN STAUDT<sup>1</sup>, NATALIA TSUD<sup>2</sup>, TOMAS SKALA<sup>3</sup>, VLADIMIR MATOLIN<sup>2</sup>, KEVIN C. PRINCE<sup>3</sup>, and JOERG LIBUDA<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, D-91058 Erlangen, Germany — <sup>2</sup>Charles University, Department of Plasma and Surface Science, 18000 Prague 8, Czech Republic — <sup>3</sup>Sincrotrone Trieste, 34012 Basovizza-Trieste, Italy

Complex catalysts consisting of noble metal particles on reducible CeO<sub>2</sub> supports show unique reactivity and reduced carbon precipitation during hydrocarbon reforming. In order to explore these effects at the microscopic level, we have studied the adsorption and dehydrogenation of C<sub>2</sub>H<sub>4</sub> on a Pt/CeO<sub>2</sub>(111)/Cu(111) and Pt(111) model catalysts. Reaction and decomposition of C<sub>2</sub>H<sub>4</sub> are investigated by means of HR-PES as a function of the CeO<sub>2-x</sub> stoichiometry and Pt particle size. In contrast to the behavior on Pt(111), where molecular adsorption of C<sub>2</sub>H<sub>4</sub> is observed, dissociation intermediates, namely CCH<sub>3</sub> and CHCH<sub>3</sub>, were found on the Pt nanoparticles even at 100 K. The dehydrogenation of these products to carbonaceous deposits is accompanied by the hydrogen spillover and formation of hydroxyl groups on ceria. The decomposition of the hydroxyl groups and desorption of H<sub>2</sub> occurs at 450 K. At higher temperatures, carbonaceous species react with oxygen, which is supplied via reverse spillover from the ceria and, subsequently, desorb in the form of CO and/or CO<sub>2</sub>.

O 4.3 Mon 11:45 H33

**Nanostructured Cerium Oxide Based Model Catalysts: Structure, Morphology and Reactivity** — ●THORSTEN STAUDT<sup>1</sup>, YAROSLAVA LYKHACH<sup>1</sup>, MICHAEL PETER ANDREAS LORENZ<sup>1</sup>, REGINE STREBER<sup>1</sup>, LUTZ HAMMER<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, ALEXANDER SCHNEIDER<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen — <sup>2</sup>Lehrstuhl für Festkörperphysik, Friedrich-Alexander-Universität Erlangen

Nanostructured cerium oxide based catalysts offer unique properties in the field of heterogeneous catalysis, e.g. involving the activation of CO<sub>2</sub>. In our study we prepare model systems starting from CeO<sub>2</sub>(111) films on a Cu(111) substrate. Ultra-thin films are grown by PVD in O<sub>2</sub> at different sample temperatures. The morphology is analyzed by STM and LEED [1], showing a (1.5x1.5) superstructure. STM reveals a 3d growth mode for films grown at elevated temperatures (520K). Using kinetically limited growth at 100K and subsequent annealing, closed layers of ceria with atomically flat terraces can be prepared, even in the ultra-thin regime (1.5 ML). Via homoepitaxial growth of ceria on this initial film, closed films with larger thickness (3 ML) are available.

In a second step, the ceria substrate is modified by deposition of MgO, which offers basic sites and may further enhance the reactivity. We have investigated the influence of surface structure, oxidation state and composition of these samples on their interaction with CO<sub>2</sub>. [2] Systematic XPS studies show that two CO<sub>2</sub> related species are formed,

which are assigned to carbonates and carboxylates. [1] T. Staudt *et al.*, *Surface Science* **603** (2009) 3382 [2] Y. Lykhach *et al.*, submitted

O 4.4 Mon 12:00 H33

**CO oxidation on Au/TiO<sub>2</sub>(110) model catalysts - support oxidation state and Au particle size effects** — ●MENHILD EYRICH, CIHAN TOPKAYA, JOACHIM BANSMANN, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

Since Haruta [1] discovered the unusual catalytic activity of small Au particles on transition metal oxide supports in the late 1980s, numerous studies were carried out on the catalysts to understand the physical origin of the high activity. Especially for the CO oxidation on TiO<sub>2</sub> supported Au catalysts, the reaction mechanism is still not completely resolved. Analogously to the respective powder catalysts, also the activity of the planar model catalysts strongly depends on the pretreatment of the catalyst and on the size of the Au nanoparticles. Here, we report the results of a study on fully oxidized and reduced planar Au/TiO<sub>2</sub> model catalysts. For each model system, the reaction rates for different Au nanoparticle sizes were determined. The results will be compared to other Au/TiO<sub>2</sub> catalysts and possible reasons for the strong influence of the Au nanoparticle size and the oxidation state of the support on the catalytic activity will be discussed.

[1] M. Haruta, N. Yamada, T. Kobayashi, S. Iijima, *J. Catal.* **115** (1989), 301-309.

O 4.5 Mon 12:15 H33

**Mechanisms of CO oxidation at nanoporous gold: combined TPD and XPS study** — ●SARAH RÖHE, TOBIAS BECKER, ANDREAS SCHAEFER, ARNE WITTSTOCK, VOLKMAR ZIELASEK, and MARCUS BÄUMER — Universität Bremen, Institut für Angewandte und Physikalische Chemie, Leobener Str. NW2, 28359 Bremen

Unsupported nanoporous gold (NPG) shows high catalytic activity for CO oxidation with molecular oxygen even below room temperature [1]. So far, the mechanisms of how the surface of NPG catalyzes this reaction have been somehow puzzling. In particular, several experiments on various low-index single crystal gold surfaces had demonstrated that the rate of O<sub>2</sub> dissociation at pure gold is negligible - even at higher temperatures and even if the surface had been roughened on the atomic scale by Ar sputtering.

Based on a combined TPD and XPS study in ultrahigh vacuum at NPG we will provide evidence for residual silver in the NPG surface playing a major role for the activation of molecular oxygen for CO oxidation. Since NPG is produced by leaching of silver from Au-Ag alloy, rest silver with total concentrations of 1-5% and up to 20% at the surface remains in the material and was speculated on as an active ingredient in the CO oxidation, before. Our data indicate that at temperatures above 200 K O<sub>2</sub> is dissociated at silver sites and atomic oxygen probably binds at silver but also spills over to gold surrounding silver islands.

[1] V. Zielasek, B. Jürgens, C. Schulz, J. Biener, M.M. Biener, A.V. Hamza, M. Bäumer, *Angew. Chem. Int. Ed.* **45** (2006) 8241.

O 4.6 Mon 12:30 H33

**Oxidation of carbon monoxide on Au/ZnO nanoparticles: an infrared spectroscopy study** — ●HESHMAT NOEI<sup>1</sup>, MARTIN MUHLER<sup>1</sup>, and YUEMIN WANG<sup>1,2</sup> — <sup>1</sup>Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum, Germany — <sup>2</sup>Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, 44801 Bochum, Germany

Recently, supported gold nanoparticles have attracted enormous attention due to their unique catalytic properties for a number of chemical reactions including CO oxidation at low temperatures. In this contribution the catalytic reactivity of different ZnO-supported Au nanoparticles was studied systematically by ultra-high vacuum FTIR spectroscopy (UHV-FTIRS). Exposing negatively charged Au nanoparticles to CO at 110 K leads to the appearance of two C-O stretching bands at 2180 and 2066 cm<sup>-1</sup>, which are assigned to CO species adsorbed on ZnO and Au surfaces, respectively. On oxidized Au/ZnO (with Au<sup>0</sup>) the IR band for CO adsorption on ZnO is observed at 2183 cm<sup>-1</sup>, while two new C-O bands show up at 2105 and 2112 cm<sup>-1</sup>, which are attributed to the CO species adsorbed on Au/ZnO interface

and Au particles, respectively. After further exposing the reduced and oxidized Au/ZnO nanoparticles to oxygen at 110 K, CO oxidation occurs yielding physisorbed CO<sub>2</sub> and carbonate species. It was found that the reduced surfaces favour CO<sub>2</sub> production, whereas on the oxidized surfaces carbonate species are preferentially formed. The catalytic mechanisms of low temperature CO oxidation will be discussed in details.

O 4.7 Mon 12:45 H33

**First-Principles Approach to Heat and Mass Transfer Effects in Model Catalyst Studies** — ●SEBASTIAN MATERA<sup>1</sup> and KARSTEN REUTER<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut Berlin (Germany) — <sup>2</sup>Technische Universität München (Germany)

We assess heat and mass transfer limitations in *in situ* studies of model catalysts with a first-principles based multiscale modeling approach that integrates a detailed description of the surface reaction chemistry

and the macro-scale flow structures. Using RuO<sub>2</sub>(110) as a representative substrate for the frequently studied CO oxidation reaction we find corresponding limitations to significantly mask the intrinsic catalytic function at the high conversion rates reached at near-ambient gas-phase conditions [1]. Two crucial and hitherto largely unappreciated factors specific to the model catalyst reactor geometry are in this respect the degree of heat dissipation at the back of the thin sample and the propensity to build-up a product boundary layer above the flat-faced surface. A qualified discussion of a possibly different surface chemistry across the “pressure gap” requires accounting for resulting temperature and pressure gradients, both in experimental *in-situ* setups and through predictive-quality integrated models as the one presented here. Otherwise wrong mechanistic conclusions may be derived which hamper our progress towards an atomic-scale understanding of the function of heterogeneous catalysts at technologically relevant gas-phase conditions. [1] S. Matera and K. Reuter, *Catal. Lett.* **133**, 156 (2009).