O 35: Heterogeneous catalysis II

Time: Tuesday 15:00–16:30 Location: H33

O 35.1 Tue 15:00 H33

ReactorAFM; imaging supported catalysts at work — •M.E. Cañas-Ventura[1], A. Ofitserov[2], W. Onderwaater[1], P.C. van der Tuijn[1], G.J.C. van Baarle[2], R.C.T. Koehler[1], and J.W.M. Frenken[1] — [1]Kamerlingh Onnes Laboratory, Leiden Uni, Netherlands — [2]Leiden Probe Microscopy BV, Netherlands

The atomic-scale investigation of supported catalysts is on the move towards experiments with state-of-the-art techniques close to industrial conditions: high pressures (P) and high temperatures (T). After successful experiments with a ReactorSTM[1], a miniature flow reactor integrated with a STM, we feel urged to widen range of model catalysts that can be studied under reaction conditions with atomic/near-atomic resolution, to the oxide-supported metal nanoparticle geometry. In this way we bridge not only the so-called "P gap" but also the "materials gap". For this purpose we have now developed the ReactorAFM. With special attention paid to vibration isolation, low-expansion materials and fast electronics, the instrument operates at T up to 570 K, P up to 5 bar and relatively high speeds. A new gas-flow system provides full control over the gas mixture and excellent time resolution and precise distribution of reaction products. The AFM is housed in a UHV system with several additional preparation and surface analysis techniques. The ReactorAFM also measures a tunneling current, which allows operation in a variety of modes with a wide range of simultaneously acquired signals. First scans and Δf vs. Z curves demonstrate the good behavior of the new setup.[1]B.L.M.Hendriksen et al.PRL 89,046101(2002)

O 35.2 Tue 15:15 H33

Steps to detect catalytic ethylene oxide formation on single crystals — •Sebastian Böcklein, Sebastian Günther, Robert Reichelt, Markus Seibald, Andreas Preimesser, Martin Ehrensberger, Gergely Rozsa, and Joost Wintterlin — Ludwig-Maximilians-Universität, 81377 München, Germany

As part of a project to bridge the "pressure gap" for the catalytic synthesis of ethylene oxide (EtO) on Ag surfaces we have undertaken extensive studies in a model reactor. The investigations aimed at finding conditions under which the production of EtO can be unambiguously and quantitatively detected on single crystal Ag surfaces, a challenging task because of the extremely low ethylene-to-EtO reaction probability. The experiments were performed in a specially designed reactor, and they involved the variation of partial pressures, temperature, and type of Ag samples (powders and polycrystalline sheets), and great effort was expended for proper background subtraction. We find that for the sheets an essential ingredient is an activation treatment by annealing in oxygen, which raises the activity by more than one order of magnitude. There are indications that subsurface O atoms are created by this pretreatment. The maximum values obtained for activity, selectivity, yield, and reaction probability allow us to predict that EtO produced on a single Ag crystal can indeed be detected under flow conditions in a UHV chamber. Experiments on the deactivation show that sintering plays an important role for the dispersed samples, but that there is an additional deactivation process for the sheets that is not caused by sintering or poisoning.

O 35.3 Tue 15:30 H33

The role of surface oxides in NOx storage reduction (NSR) catalysts — •Jelena Jelic[1,2], Randall Meyer[1], and Karsten Reuter[2,3] — [1]Univ. of Illinois at Chicago (USA) — [2]Fritz-Haber-Institut Berlin (Germany) — [3]TU München (Germany)

In the NSR approach to lean burn automotive emissions a longer O-rich mode in the cyclic operation first oxidizes and stores the excess NO before a short O-poor mode reduces the stored NOx. Bulk oxide formation in the oxidizing environment is commonly perceived as detrimental to the catalytic activity of the employed platinum metals. To qualify this notion we perform first-principles atomistic thermodynamics and kinetic Monte Carlo simulations determining the surface structure and composition, as well as catalytic performance of Pd(100) under gas-phase conditions typical for the NO oxidation. With bulk oxide formation prevented on the time scale of the O-rich mode, we identify an ultrathin PdO(101)/Pd(100) surface oxide film as the stable surface termination. Moreover, its turnover frequencies are similar to those measured for platinum metal, demonstrating that a surface oxide may be a viable catalyst for NO oxidation.

O 35.4 Tue 15:45 H33

The Selective Catalytic Reduction (SCR) of NO with NH$_3$ at Vanadium Oxide Catalysts: Adsorption, Diffusion, Reaction. — •Mathis Gruber and Klaus Hermann — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin and Sfb 546, (Germany)

The Selective Catalytic Reduction (SCR) of NO$_x$ with NH$_3$ over vanadium based metal-oxide (VO$_x$) catalysts has been proven to be one of the most effective NO$_x$ reduction processes. Even though it is widely used in commercial applications details of the reaction mechanism are still under debate. Experiments show that adsorption, diffusion, and reactions with NO and (de)hydrogenation processes at the VOx surface contribute elementary steps. These processes are examined in theoretical studies employing density-functional theory together with gradient corrected functionals. The VO$_x$ substrate is modeled by clusters cut out from the ideal V$_2$O$_5$(010) surface where peripheral oxygen bonds are saturated by hydrogen. Apart from the perfect oxide surface also differently reduced surfaces are considered by introducing oxygen vacancies. NH$_3$ is found to interact only weakly with the perfect V$_2$O$_5$(010) surface. In the presence of OH groups (Brønsted acid sites) NH$_3$ can form a surface NH$_4^+$ species. NH$_3$ can also interact with the surface near oxygen vacancies, adsorbing at vanadium centers of lower coordination (Lewis acid sites). In contrast, NO interacts much more weakly with the surface. Further, simultaneous NO, NH$_3$ adsorption and SCR reaction scenarios at Brønsted and Lewis acid sites are examined. They result in different reaction paths and intermediates as will be discussed in detail.

O 35.5 Tue 16:00 H33

Electrochemical promotion of catalytic ethylene oxidation on Pt/YSZ catalyst under low pressure conditions — •Arafat Toghan, Liz Michaela Rösken, and Ronald Imbihl — Institut für Physikalische Chemie und Elektrochemie, Universität Hannover, Callinstrasse 3-3a, D-30167 Hannover, Germany

The catalytic oxidation of C2H4 on Pt catalyst film interfaced with the oxygen-ion conducting yttria-stabilized zirconia solid electrolyte (YSZ) has been studied in the 10-5 and 10-4 mbar range. Photoemission electron microscopy (PEEM) was used as spatially resolving method. Under open circuit conditions (VWR= 0 V) the CO2 production increases by rising p(C2H4) and then at a critical point decreases sharply, showing a pronounced hysteresis. The hysteresis and the abrupt rate decrease are attributed to the build-up of a carbonaceous CHx layer inhibiting O2 adsorption and hence poisoning the catalyst. Applying an anodic potential of +1V leads to trigger a transition from the unreactive branch of the reaction to an active branch. The huge non-Faradayicity reported in the literature for this reaction system is explained as an ignition effect caused by the partial removal of the inhibiting carbonaceaous layer. The electrode has been characterized by SEM, XRD and a profilometer.

[1] S. Bebelis and C. G. Vayenas, J. Catal. 1989, 118, 125-146.

O 35.6 Tue 16:15 H33

Formation of islands of substitutional Li defects on the MgO (001) surface — •Sergey V. Levchenko and Matthias Scheffler — Fritz-Haber-Institut der MPG, Berlin, Germany

We use density functional theory (DFT) calculations to evaluate electronic structure and formation energies of the substitutional Li defects in the (001) surface, subsurface, and bulk MgO. We analyze the sensitivity of the results to the approximations in the exchange-correlation functional by comparing semi-local (GGA PBE) and non-local (PBE0 and B3LYP) approximations. Calculated defect formation energy as a function of coverage and layer depth indicates that the Li defects prefer to form islands with molar concentration 50% at the top layer, but not in the deeper layers. The formation energy of an isolated substitutional Li defect increases with the depth of the layer in which the defect is formed [1]. We perform an *ab initio* atomistic thermodynamics [2] analysis to determine the average island size under realistic conditions. This shows that, despite the loss in the configurational entropy due to the island formation, the islands containing 10-20 Li defects are present on the surface at relevant temperatures (900-1000 K). Within the islands, the oxygen vacancy formation energy is greatly decreased due to an electron transfer from the O vacancy state to the lower energy states near the top of the valence band, associated with the Li defects.—[1] Z. Yang, G. Liu, and R. Wu, Phys. Rev. B **65**, 235432 (2002)—[2] K. Reuter and M. Scheffler, Phys. Rev. B **65**, 035406 (2001); C. M. Weinert and M. Scheffler, Mat. Sci. Forum **10-12**, 25 (1986); M. Scheffler and J. Dabrowski, Phil. Mag. A **58**, 107 (1988)