

## O 97: Heterogeneous catalysis II

Time: Friday 11:15–13:00

Location: PHY C213

O 97.1 Fri 11:15 PHY C213

**Methanol synthesis on ZnO(000 $\bar{1}$ ): Free energy landscapes, reaction pathways, and mechanistic insights.** — ●JOHANNES FRENZEL<sup>1</sup>, JANOS KISS<sup>1</sup>, NISANTH NAIR<sup>2</sup>, BERND MEYER<sup>3</sup>, and DOMINIK MARX<sup>1</sup> — <sup>1</sup>LS Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany — <sup>2</sup>Dep. of Chemistry, IIT, Kanapur, India — <sup>3</sup>ICMM and CCC, Universität Erlangen-Nürnberg, Germany

The interplay of physical and chemical processes in the heterogeneous catalytic synthesis of methanol on the ZnO(000 $\bar{1}$ ) surface with oxygen vacancies is expected to give rise to a complex free energy landscape. A manifold of intermediate species and reaction pathways has been proposed over the years for the reduction of CO on this catalyst at high temperature and pressure conditions as required in the industrial process. In the present study, the underlying complex reaction network from CO to methanol is generated in the first place by using *ab initio* metadynamics for computational heterogeneous catalysis. After having synthesized the previously discussed intermediates in addition to finding novel species, mechanistic insights into this network of surface chemical reactions are obtained based on exploring the global free energy landscape, which is refined by investigating individual reaction pathways. Furthermore, the impact of homolytic adsorption and desorption of hydrogen at the required reducing gas phase conditions are probed by studying such processes using different charge states of the F-center.

O 97.2 Fri 11:30 PHY C213

**charge localization dynamics induced by oxygen vacancies on the TiO<sub>2</sub>(110) Surface** — ●MATTEO FARNESI CAMELLONE<sup>1</sup>, PIOTR M. KOWALSKI<sup>2</sup>, and DOMINIK MARX<sup>1</sup> — <sup>1</sup>Lehrstuhl für theoretische chemie, ruhr universität bochum, 44780 bochum, germany — <sup>2</sup>helmholtz centre potsdam, telegrafenberg, 14473 potsdam, germany

The dynamics of an F center created by an oxygen vacancy on the TiO<sub>2</sub>(110) rutile surface has been investigated using *ab initio* molecular dynamics (1). These simulations uncover a truly complex, time-dependent behavior of fluctuating electron localization topologies in the vicinity of the oxygen vacancy. Although the two excess electrons are found to populate preferentially the second subsurface layer, they occasionally visit surface sites and also the third subsurface layer. This dynamical behavior of the excess charge explains hitherto conflicting interpretations of both theoretical findings and experimental data.

(1) Phys. Rev. Lett. 105, 146405 (2010)

O 97.3 Fri 11:45 PHY C213

**Oxygen vacancies in different charge states at the MgO(100) surface** — ●NORINA A. RICHTER, SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Berlin (Germany)

Point defects can dramatically change the chemical properties of oxide surfaces. However, the concentration of the defects at realistic conditions is difficult to determine experimentally. In this work, we calculate electronic structure and formation energies of neutral and charged oxygen vacancies in the bulk and at the MgO(100) surface [1], and estimate their concentration and distribution at realistic temperatures and pressures using the *ab initio* atomistic thermodynamics approach [2]. We determine the stability of different charge states of the oxygen vacancy as a function of the Fermi level position within the band gap (simulating the global effect of doping). We also analyze how the proximity of a dopant providing localized acceptor states changes the vacancy formation energies (local effect of doping). We use the Li substitutional defect as a prototype of such a dopant. The effects of electron exchange and correlation on our results, in particular the self-interaction error and the band-gap problem, are discussed, based on comparison of LDA with the HSE06 functional with different values of the exchange screening parameter.

O 97.4 Fri 12:00 PHY C213

**Exploring Morphology-Activity Relationships: Ab Initio Thermodynamics Wulff Construction of RuO<sub>2</sub>** — ●JELENA JELIC<sup>1,2</sup> and KARSTEN REUTER<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin — <sup>2</sup>Technische Universität München

Systematic studies on polycrystalline powders are an appealing link between detailed Surface Science work on single crystals and the supported nanoparticles in real catalysis. On the other hand, the cat-

alytic activity of the powder is sensitively influenced by the preparation procedure, with structure-morphology-activity relationships still only scarcely understood and controlled. A prominent example in this respect are the recently reported, largely different induction times for the CO oxidation over RuO<sub>2</sub> powder [1,2]. Suspecting differing calcination temperatures behind these findings we use *ab initio* thermodynamics for a Wulff construction of RuO<sub>2</sub> crystallites in contact with an oxygen gas-phase. Depending on the calcination temperature we indeed obtain distinctly different equilibrium shapes. Correlating the exposed facets with the reported activity data points to a prominent role of the hitherto not much studied (101) and (111) facets. [1] V. Narkhede, J. Assmann, and M. Muhler, Z. Phys. Chem. 219, 979 (2005); [2] D. Rosenthal *et al.*, Z. Phys. Chem. 223, 183 (2009).

O 97.5 Fri 12:15 PHY C213

**Analysis of Silica-Supported Molybdena by X-ray Absorption Spectroscopy: theoretical cluster studies** — ●CHUNSHENG GUO and KLAUS HERMANN — Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin and Sfb 546, (Germany)

We have performed density-functional theory (DFT) calculations on oxygen core excitations in different molybdena-silica model clusters in order to analyze structural details of the molybdena species. Differently binding oxygen, characteristic for specific molybdena species and coordination of the corresponding molybdenum centers, tetrahedral, pentahedral, and octahedral, can be clearly distinguished in the theoretical spectra. Further, the oxygen of the silica support is found to contribute to the NEXAFS spectrum in an energy range well above that of the molybdena units. The theoretical results can be compared with X-ray absorption fine structure (NEXAFS) measurements near the O K-edge of molybdena model catalysts supported by SBA-15 silica. The experimental NEXAFS spectra exhibit a symmetric double-peak structure in the O 1s to Mo4d/O2p excitation range at 529 - 536 eV. The comparison with the present theoretical data gives clear indications that molybdena species with tetrahedral dioxo MoO<sub>4</sub> units, singly or doubly connected with the silica substrate, dominate the experimental spectrum. This is different from results for MoO<sub>3</sub> bulk material where octahedral MoO<sub>6</sub> units exist and lead to a strongly asymmetric peak structure in the O K-edge NEXAFS spectrum, in agreement with the theoretical result.

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**Selective Catalytic Reduction of NO with NH<sub>3</sub> at V<sub>2</sub>O<sub>5</sub>(010) and Silica supported Vanadium Oxide: DFT Studies.** — ●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<sub>x</sub> with NH<sub>3</sub> over vanadium based metal-oxide (VO<sub>x</sub>) catalysts has been proven to be one of the most effective NO<sub>x</sub> reduction processes. Details of the reaction mechanism are still under debate. Adsorption, (de)hydrogenation, reactions with NO, and surface water formation at the VO<sub>x</sub> catalyst contribute elementary steps. These processes are examined in theoretical studies employing density-functional theory together with gradient corrected functionals. The VO<sub>x</sub> substrate is modeled by clusters cut out from the clean V<sub>2</sub>O<sub>5</sub>(010) surface where peripheral oxygen bonds are saturated by hydrogen. Reduced surfaces are represented by introducing oxygen vacancies. In addition, silica supported vanadium oxide clusters are considered. NH<sub>3</sub> is found to interact with the clean V<sub>2</sub>O<sub>5</sub>(010) surface only in the presence of OH groups (Brønsted acid sites) where it can form a rather stable surface NH<sub>4</sub><sup>+</sup> species. Further, NH<sub>3</sub> can adsorb at vanadium centers of lower coordination at the reduced surface (Lewis acid sites). This leads to two different SCR reaction scenarios transferring NH<sub>3</sub> and NO to N<sub>2</sub> and H<sub>2</sub>O which are discussed by corresponding reaction paths and intermediates.

O 97.7 Fri 12:45 PHY C213

**Theoretical Investigations on the Structure of Copper Catalysts at Zinc Oxide Surfaces** — ●BJÖRN HILLER and JÖRG BEHLER — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, D-44801 Bochum, Deutschland

The Cu@ZnO system is an important catalyst, e.g. in methanol synthesis. From experiments it is known that the structure of the copper particles strongly depends on the gas phase composition. In addition

there is some evidence for strong interactions between the copper particles and the oxide support. To understand this system it is crucial to investigate the structure of the involved copper surfaces in different gaseous environments and the structure of the interface between the copper particles and the zinc oxide support.

Using density-functional theory we determine the relative stabilities of a variety of possible oxygen and hydrogen adsorbate phases on copper surfaces to predict the shape of copper clusters under catalytic conditions. Moreover some results concerning the structure of the interface between copper and zinc oxide are presented.