

## O 31: Heterogeneous Catalysis: Theory

Time: Tuesday 10:30–13:00

Location: S053

O 31.1 Tue 10:30 S053

**Analyzing the case for bifunctional catalysis** — ●MIE ANDERSEN<sup>1</sup>, ANDREW J. MEDFORD<sup>2,3</sup>, JENS K. NØRSKOV<sup>2,3</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Theoretical Chemistry, Technische Universität München, Germany — <sup>2</sup>SUNCAT Center for Interface Science and Catalysis, SLAC National Accelerator Laboratory, CA, USA — <sup>3</sup>Department of Chemical Engineering, Stanford University, CA, USA

Computational screening based on scaling relations has proven highly successful in rationalizing, why efficient catalysts are often found within only a narrow range of binding energies that allow the dissociation of reactants without hindering the formation of products [1]. It has been suggested that these severe limitations in material space could be overcome by bifunctional catalysts, which couple two active sites, each catalyzing a particular reaction step. Using global optimization techniques and microkinetic modeling in the mean-field (MF) approximation, we explore the theoretical limits for such a bifunctional gain for a wide range of model reactions. This analysis suggests that bifunctional catalysts made from two active sites of similar type, i.e. controlled by similar scaling relations, will in general not reach higher activities than single-site catalysts. We correspondingly aim to quantify how "different" the two active sites must be in order for the idea of bifunctionality to work.

[1] J. K. Nørskov et al., *Nature Chem.* **1**, 37 (2009)

O 31.2 Tue 10:45 S053

**NO-induced inhibition of oxide formation on Pd catalysts: A first-principles kinetic Monte Carlo study** — ●JUAN MANUEL LORENZI<sup>1</sup>, SEBASTIAN MATERA<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Technische Universität München, Germany — <sup>2</sup>Freie Universität Berlin, Germany

In the context of NO<sub>x</sub> Storage Reduction (NSR) catalysts, in which oxidation of NO into NO<sub>2</sub> is a critical intermediate step, interest shifts to understanding the oxidation properties of typically employed Pt-group catalysts under the simultaneous exposure to CO, NO and O<sub>2</sub>. We assess this for a model Pd(100) catalyst by means of a comprehensive first-principles kinetic Monte Carlo study, which is based on an extensive set of density-functional theory derived rate constants and which explicitly resolves lateral interactions among all surface species. Multiple studies on Pd(100) in a pure CO + O<sub>2</sub> atmosphere had indicated a strong propensity to surface oxide formation under technologically relevant gas-phase conditions (e.g. [1]). In contrast to this we find that already small amounts of NO in the feed lead to a substantial reduction of the O coverage even in oxygen-rich environments. While NO thus efficiently inhibits oxide formation, the total activity of the resulting metal surface towards NO (and CO) oxidation is still comparable to the one predicted previously for the oxidized surface [2]. [1] S. Blomberg *et al.*, *Phys. Rev. Lett.* **110**, 117601, (2013). [2] J. Jelic, K. Reuter, and R. Meyer, *Chem. Cat. Chem.* **2**, 658 (2010).

O 31.3 Tue 11:00 S053

**First-principles computational screening of dopants to improve the Deacon process over RuO<sub>2</sub>(110)** — ●ZHEN YAO, FARNAZ SOTOODEH, and KARSTEN REUTER — TU München, Germany

Cl<sub>2</sub> is widely used in many chemical industries which produce HCl as byproduct. Recycling HCl back to high purity Cl<sub>2</sub> is therefore mandatory for a sustainable operation. RuO<sub>2</sub> shows unique activity for the corresponding route along the Deacon process, i.e. the catalytic oxidation of HCl to chlorine and water.

One possibility to further improve this performance is a doping of the oxide matrix. With the aim of guiding experimental activities through chemical compound space, we perform a density-functional theory based computational screening study over a wide range of transition metal dopants. Previous work suggested the chlorine desorption from the surface as a rate-controlling step [1,2]. We correspondingly employ the Cl adsorption energy and dopant segregation energy as descriptors to assess activity and stability. Among the metals screened, Cu, Ag, and Zn emerge as most promising dopants.

[1] S. Zweidinger *et al.*, *J. Phys. Chem. C* **112**, 9966 (2008).

[2] A. P. Seitsonen *et al.*, *J. Phys. Chem. C* **114**, 22624 (2010).

O 31.4 Tue 11:15 S053

**Embedding of Vanadium Atoms into the Anatase TiO<sub>2</sub>(101)**

**Surface** — STIG KOUST<sup>1</sup>, LOGI ARNARSON<sup>1,2</sup>, PAUL GEORG MOSES<sup>2</sup>, IGOR BEINIK<sup>1</sup>, ZHESHEN LI<sup>1</sup>, JEPPE VANG LAURITSEN<sup>1</sup>, and ●STEFAN WENDT<sup>1</sup> — <sup>1</sup>Interdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, DK-8000 Aarhus C, Denmark — <sup>2</sup>Haldor Topsøe Research Labs, DK-2800 Lyngby, Denmark

Selective catalytic reduction (SCR) catalysis is widely used to reduce NO<sub>x</sub> into N<sub>2</sub> and H<sub>2</sub>O in flue and exhaust gasses, often using ammonia (NH<sub>3</sub>) as H source. SCR reactions are best catalyzed by anatase TiO<sub>2</sub>-supported submonolayer VO<sub>x</sub>-catalysts that are promoted with W and/or Mo. Here we present atomically resolved STM images of sub-monolayer V on anatase TiO<sub>2</sub>(101). Following V deposition at 100 K, the surface was covered with small isolated V clusters that were distributed homogeneously on the terraces. Our STM studies revealed an embedding of V into the near-surface region upon warming the sample to room temperature. A significant decrease in the density of V clusters was observed and new features in the STM images appeared, which we assign to monomeric V at regular Ti surface sites. Thus, surface Ti atoms are substituted by V atoms. Additional XPS characterization revealed the oxidation state of V being 2+ directly after deposition at 100 K, indicating a preferred binding between V clusters and surface O atoms. Characteristic changes were observed in the V 2p region after warming the sample to room temperature, corroborating our STM data.

O 31.5 Tue 11:30 S053

**Hydrogen coadsorption effects on C-C bond formation on Ru(0001) at realistic temperatures and pressures: An ab initio study** — ●XUNHUA ZHAO, SERGEY V. LEVCHENKO, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut der MPG, Berlin

Hydrogen coadsorption is a crucial component of heterogeneous catalysis of hydrocarbons. Our recent study [1] demonstrated the critical role of hydrogen coadsorption in the stabilization of CH<sub>2</sub> species on the Ru(0001) surface. In the present work, we report a DFT-PBE study of hydrogen coadsorption effects on C-C bond formation reactions at realistic conditions up to typical temperature and hydrogen pressure of Fischer-Tropsch synthesis (FTS) [2]. *Ab initio* atomistic thermodynamics is employed to assess the relative thermo-stability of CH<sub>x</sub> species, and the string method is used to evaluate the minimum-energy paths for C-C bond formation. CH<sub>x</sub>+CH<sub>y</sub> and CH<sub>x</sub>+C<sub>2</sub>H<sub>z</sub> ( $x, y = 1, 2, 3$  and  $z = 3 - 6$ ) coupling reactions at the monolayer coverage for coadsorbed hydrogen plus reactants are studied to identify possible chain-growth paths in FTS. For comparison, coupling reactions without hydrogen coadsorption are also calculated. It is found that in general hydrogen coadsorption shifts the relative stability to more hydrogen-saturated species (larger  $x$  in CH<sub>x</sub> for instance). Hydrogen coadsorption is found to have a profound influence on the C-C coupling reaction barriers: While it generally reduces all the barriers, some reaction paths become more favoured in the presence of the coadsorbed hydrogen. — [1] H. Kirsch, X. Zhao et. al., *J. Catal.* **320**, 89 (2014); [2] R. A. Van Santen et. al., *Adv. Catal.* **54**, 127 (2011)

O 31.6 Tue 11:45 S053

**CH<sub>2</sub> stabilization and dissociation at steps on Ru(0001) in UHV** — ●HARALD KIRSCH, XUNHUA ZHAO, SERGEY LEVCHENKO, and R. KRAMER CAMPEN — Fritz-Haber-Institut Berlin, Faradayweg 4-6, 14195 Berlin

In this study we investigated the dissociation of defect(step) bonded CH<sub>2</sub>, produced by methane dissociation on Ru(0001) under UHV conditions. Dissociated sticking of CH<sub>4</sub> was performed by using a supersonic molecular beam source. By using vibrational sum frequency generation(SFG) spectroscopy, we found the characteristic CH-stretch vibration of step adsorbed CH<sub>2</sub> at 2925cm<sup>-1</sup>. The observed species saturated at coverages of about 3-5% of a monolayer of carbon. An Arrhenius analysis of the temperature dependent stability gave an activation energy for the depletion of our signal of 45 kJ/mol. This value is 3 times higher than the calculated dissociation barrier of isolated CH<sub>2</sub> at terrace sites. DFT calculations, performed on this system rationalize this observation by a two step process. First by the diffusion and subsequent dissociation of CH<sub>2</sub> to CH + H, when moving from a step to a nearby terrace site(barrier ≈ 14 kJ/mol). This CH stabilizes remained CH<sub>2</sub> at steps, produced by ongoing dosing of methane,

by increasing the combined diffusion and dissociation barrier to  $\approx 37$  kJ/mol. These results may contribute to a better understanding of the active species in the Fischer-Tropsch Synthesis.

O 31.7 Tue 12:00 S053

**Decomposition of formic acid on Pd-Au surfaces** — ●HOLGER EUCHNER, JAN KUCERA, and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Pd-based catalysts have shown promising activity towards heterogeneous [1] and electrochemical [2] dehydrogenation of formic acid (FA), envisioned to be integrated into future H<sub>2</sub> energy technologies. However, the performance of current catalysts so far has not met the technological demands and, unfortunately, rational strategies towards better catalysts are not easy to establish. This is, despite the apparent simplicity of the overall reaction, mainly due to complexity of FA decomposition.

To provide insight into underlying mechanisms and potential for improvement, we have conducted a computational study of the decomposition of FA on Pd-based surfaces. Using dispersion corrected periodic density functional theory (DFT-D3), the effect of replacing sub-surface Pd by Au is investigated. The impact of changing electronic structure on the decomposition pathway of FA, caused by the vertical ligand effect, is studied and discussed with respect to desired dehydration and undesired dehydrogenation reaction. In a further step, to approach a more realistic modeling, the effect of hydrogen as a co-adsorbent, being at the same time a reaction intermediate, is studied.

[1] Grasmann et al., Energy Environ. Sci. **5**, 8171 (2012).

[2] Jiang et al., Phys. Chem. Chem. Phys. **16**, 20360 (2014).

O 31.8 Tue 12:15 S053

**Formic acid dehydrogenation over Au/CeO<sub>2</sub> catalysts: Theoretical DFT study** — ●JAN KUČERA and AXEL GROSS — Institute of Theoretical Chemistry, Ulm University, D-89069 Ulm/Germany

Heterogeneous catalysts based on nano-sized Au supported on various oxides (e.g., TiO<sub>2</sub>, CeO<sub>2</sub>, or SiO<sub>2</sub>) can selectively decompose formic acid (FA) to provide pure hydrogen already at low temperatures - a process of high technological relevance in the context of hydrogen technology as part of a sustainable energy concept. Despite of the activity ascribed to Au, the decomposition mechanism depends strongly on the nature of the oxide. Unfortunately, the mechanistic understanding of the function of the support remains unclear, which hampers to establish a route towards better catalysts.

Our computational study focuses on the elucidation of elementary processes behind the FA decomposition over Au/CeO<sub>2</sub>. In particular, the reducible surface of CeO<sub>2</sub> facilitates the dynamical formation of catalytically active subnanometer/atomic Au species detached from Au-nanoparticles [1]. We have employed periodic DFT+U models together with a periodic embedded cluster method (PEECM) to investigate the dehydrogenation process of FA over single-Au species on CeO<sub>2</sub>. We will discuss the influence of the charge transfer between Au and the CeO<sub>2</sub> support on the catalytic mechanism in the presence of various surface defects.

[1] N. Yi *et al.*, ChemSusChem **6**, 816 (2013) 816; Y-G. Wang *et al.*,

Nat. Commun. **6**, 6511 (2015).

O 31.9 Tue 12:30 S053

**(Meta)stability and Dynamics of Nanoclusters at Finite-Temperature** — ●DIEGO GUEDES-SOBRINHO<sup>1</sup>, JUAREZ L. F. DA SILVA<sup>1</sup>, IAN HAMILTON<sup>2</sup>, and LUCA GHIRINGHELLI<sup>3</sup> — <sup>1</sup>University of Sao Paulo, Sao Carlos, Brazil — <sup>2</sup>Wilfrid Laurier University, Waterloo, Ontario, Canada — <sup>3</sup>Fritz Haber Institut der MPG, Berlin, Germany

Due to their catalytic properties, transition-metal nanoclusters have been the focus of a large number of experimental and theoretical studies. However, an atomistic understanding of the temperature effects on their structure are far from satisfactory. In this work, we investigate the (meta)stability and dynamics of Au nanoclusters in a range of sizes where a core-shell structure starts to be formed, namely in the range from 25 to 40 atoms. We use *ab initio* molecular dynamics combined with replica-exchange techniques, in order to obtain an unbiased statistical sampling of the phase space. The energy and forces are described via the PBE exchange-correlation functional, including many-body dispersion interactions [1], as implemented in the all-electron, full potential, numeric atom-centered orbital based FHI-aims package. We find that at room and higher temperature, the gold clusters at the chosen sizes exhibit a dynamical core-shell structure, with a (typically) tetrahedral core loosely bound to the outer liquid-like shell. A suitable structural descriptor, based on the radial distribution function referred to the cluster's center-of-mass, is introduced, in order to capture the invariants along the dynamics of these structures. [1] A. Tkatchenko *et al.*, J. Chem. Phys., **138**, 074106 (2013).

O 31.10 Tue 12:45 S053

**Methanol synthesis over Cu/ZnO from molecular dynamics** — LUIS MARTÍNEZ-SUÁREZ, NIKLAS SIEMER, ●JOHANNES FRENZEL, and DOMINIK MARX — Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Bochum, Germany

In the industrial process of methanol synthesis from CO<sub>2</sub> the presence of dynamical morphological changes is believed to explain the superior performance of the Cu/ZnO catalyst material under reaction conditions. Yet, a highly corrosive syngas atmosphere at elevated temperatures and pressures substantially hampers *in situ* experimental access to identify the underlying reaction mechanisms and active site(s). Using our combined approach [1,2] of advanced *ab initio* molecular dynamics and thermodynamically optimized catalysts models [3,4] a huge space of possibilities emerging from the structural and chemical configurations of both, adsorbates and continuously altering Cu/ZnO catalyst material, is successfully explored by pure computational means.[5] Extensive sampling of the underlying free energy landscape discloses an overwhelmingly rich network of parallel, competing and reverse reaction channels that interconnect a host of C<sub>1</sub> species. Cu/ZnO interface sites and the near surface region over the catalyst surface were identified as key to some pivotal reaction steps in the global reaction network which, ultimately, embodies also important side reactions and catalyst deactivation. Refs.: [1] Frenzel, J. *et al.*, PSS B 250, 1174, [2] Frenzel, J., Marx, D, JCP 141, 124710 [3] Martínez-Suárez, L. *et al.*, PRL 110, 086108 [4] Martínez-Suárez, L. *et al.*, PCCP 16, 26119 [5] Martínez-Suárez, L. *et al.*, ACS Catal. 5, 4201