

O 20: Surface Chemical Reactions and Heterogeneous Catalysis II

Time: Monday 16:00–19:00

Location: H33

O 20.1 Mon 16:00 H33

Charge Flow and Catalysis at the Metal-Support Interface: The Molecular Nature of Acid-Base Catalysis on Surfaces —

•ROBERT BAKER and GABOR SOMORJAI — University of California, Berkeley - Berkeley, CA, USA

The role of charge transfer to control the activity and selectivity of supported metal catalysts is studied at a molecular level by a range of techniques. Using a platinum/n-type silicon charge-based device, external control of surface oxygen activity is demonstrated using both an electrical bias and a photo-induced current flow. This allows the rate of carbon monoxide oxidation on platinum to be controlled non-thermally with an external bias or with visible light. Analogously, electronic control of surface chemistry is also achieved by substrate doping. Highly n-type, fluorine-doped titanium oxide behaves as an electronically active support for platinum catalysts improving both the rate and selectivity of carbon monoxide oxidation and methanol oxidation by charge transfer to surface oxygen. Finally, sum frequency generation vibrational spectroscopy is used to directly monitor reaction intermediates on supported platinum catalysts. The results show that charge transfer from a titanium oxide support selectively enhances the rate of aldehyde hydrogenation to alcohols by a charge transfer mechanism. These combined studies reveal at a molecular level how charge flow in supported metal catalysts controls surface reaction kinetics and this represents the molecular foundation of heterogeneous acid-base catalysis.

O 20.2 Mon 16:15 H33

CO₂ Capture by Liquid Amine Solutions: A DFT-based Evaluation — •TUGBA DAVRAN-CANDAN and KARSTEN REUTER — TU München, Germany

Removal of CO₂ from exhaust gases by making use of aqueous amine solutions is a most viable technique to reduce CO₂ emissions that are generally believed to be the major cause of global warming. The amine capture molecules bind CO₂ chemically either in the form of stable carbamates or bicarbonates. However, to date there is no clear understanding of how the specific amine structure favors either of the two binding modes and how it relates to the bond strength. To this end, we perform systematic density-functional theory (DFT) calculations and evaluate the product stabilities (carbamate or bicarbonate) for a wide range of amine molecules. As a reference we compare to the widely investigated monoethanolamine (MEA), where a too high carbamate stability leads to unfavorably high regeneration costs.

O 20.3 Mon 16:30 H33

Bistability during CO oxidation at Pd(100): Atomistic origin from first-principles kinetic Monte Carlo simulations —•MAX HOFFMANN¹, MATTHIAS SCHEFFLER², and KARSTEN REUTER¹ — ¹TU München, Germany — ²Fritz-Haber-Institut, Berlin, Germany

Despite numerous studies on Palladium as a catalyst for CO oxidation the nature of the active surface remains debated. Focusing on the (100) surface the pristine metallic surface, an ultra-thin surface oxide, and thicker oxide layers were each suggested as *the* active surface. However, already the fact that the surface state depends sensibly on the reaction conditions challenges the quest to understand the catalytic function in terms of *one* surface state. Hendriksen *et al.* [1] even observed an overlap in stability conditions between a smooth metal surface and a rough oxidic surface state. The two surfaces states were not only found to coexist in different places of the surface, but the entire surface was stabilized in either of the two states at identical reaction conditions.

Using first-principles kinetic Monte Carlo models for the pristine Pd(100) surface and the PdO(101) surface oxide we can reproduce this bistability behavior and furthermore elucidate its atomistic origin. The predicted bistable regime spans stoichiometric and technological reaction conditions. In fact, within this range we find that both surface states exhibit very similar intrinsic reactivity, which puts further doubts on attempts to assign the catalytic function to one *active* state. [1] B.L.M. Hendriksen, S.C. Bobaru, and J.W.M. Frenken, *Catalysis Today* 105, 234 (2005).

O 20.4 Mon 16:45 H33

Sabatier based Methanation of carbon dioxide and Catalyst stability against contaminations — •FABIAN RACHOW, KLAUS

MÜLLER, and DIETER SCHMEISSER — Brandenburg University of Technology, Applied Physics and Sensors, Konrad-Wachsmann-Allee 17, 03046 Cottbus, Germany

The Sabatier-Reaction [$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$] represents a possible way for the reduction and utilization of CO₂ produced in the oxy-fuel combustion process. While using different ruthenium and nickel based catalysts we studied the catalytic performance with quadrupole mass spectroscopy and IR-spectroscopy in terms of conversion of CO₂, yield of CH₄, selectivity and stability. Conversions of up to 90% and a selectivity of well above 95% could be achieved. Further studies focus on the long term stability, especially with the influence of contaminations like SO_x and NO_x as they may occur in oxy-fuel or flue gas and could greatly reduce the life time of a catalyst. We investigate the limits of Ni based catalysts for those additives. However, technical oxy-fuel gas seems to have no particular effect on the activity of a commonly used NiO-catalyst when compared to quasi pure CO₂, showing only a small drop of performance after five days with a constant conversion rate of over 80% at the end.

O 20.5 Mon 17:00 H33

Reaction kinetics of the Sabatier Reaction in a demonstration plant — •JOHANNES ISRAEL, KLAUS MÜLLER, FABIAN RACHOW, GUIDO BEUCKERT, and DIETER SCHMEISSER — Technische Universität Cottbus, Applied Physics / Sensor Technologie, Germany

We currently build up a demonstration plant for the direct catalytic conversion of CO₂ into methane according to the Sabatier reaction $CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$.

We have already reached conversion rates higher than 90% and a selectivity close to unity in our laboratory experiments with NiO based catalysts. A good long term stability was obtained with a reactant gas flow density of $0.8l/min \cdot cm^2$ at 350°C.

We will study the process now on a larger scale with a factor 10000. The process is controlled via mass flow controllers with a throughput of $20m^3/h H_2$ and $5m^3/h CO_2$ at an inlet gas pressure of up to 15bar, the temperature is regulated by a PID multichannel controller. As water is a by-product we use an efficient cooling trap for its separation from the obtained methane. The reaction products are analyzed by a quadrupole mass spectrometer under reaction conditions.

We start our experiments in using clean CO₂ and H₂. Later experiments will involve industrial quality (oxy-fuel) conditions also. Goal of this project is to determine the performance of the catalytic process under conditions which enable an industrial implementation in energy storage concepts. In this contribution we report of the design of a demonstration plant and on first experiments concerning the kinetics within the system.

O 20.6 Mon 17:15 H33

Mass transfer effects during near-ambient CO oxidation at Pd(100) in non-ideal reactor chambers — •SEBASTIAN MATERA, MAX J. HOFFMANN, and KARSTEN REUTER — TU München

A central goal in in-situ studies of defined model catalysts has been to obtain (at best) as resolved spectro- or microscopic information as has been established in UHV surface science. With this focus possible heat and mass transport limitations in the ambient environments have not received much attention. In parts they are even unavoidable, considering the often significant constraints that in-situ techniques impose on the design of the reactor chamber. We investigate such effects with our newly developed first-principles based multi-scale modeling approach integrating kinetic Monte Carlo simulations into a fluid dynamical treatment [1]. Apart from the conceptual discussion in idealized reactor geometries [2], it is in particular the recent integration of our scheme into the general purpose CatalyticFOAM solver [3] that now enables us to also explicitly address the complex flow profiles in actual in-situ reactor chambers. We demonstrate the crucial role of heat and mass transfer limitations, in particular for the unselective and therefore high turnover CO oxidation in the context of recent in-situ XPS and Planar Laser Induced Fluorescence (PLIF) measurements over Pd(100) [4]. [1] S. Matera and K. Reuter, *Catal. Lett.* 133, 156 (2009). [2] S. Matera and K. Reuter, *Phys. Rev. B* 82, 085446 (2010); *J. Catal.* 295,261 (2012). [3] M. Maestri and A. Cuoci, *CatalyticFOAM*, www.catalyticfoam.polimi.it [4] S. Blomberg, J. Gustafson, E. Lundgren *et al.*, in preparation.

O 20.7 Mon 17:30 H33

Addressing structural and catalytic properties of bimetallic surface alloys using kinetic Monte Carlo — ●LUIS MANCERA and AXEL GROSS — Institute of Theoretical Chemistry, University of Ulm, D-89069 Ulm, Germany

Using CO as a probe of the local reactivity, it has been experimentally shown that catalytic activity in PdAg/Pd(111) bimetallic surface alloys is mainly driven by the configuration of Pd adsorption sites.[1] Based on density functional theory (DFT) calculations, these ensemble effects have been theoretically confirmed for the same surface alloy, whereas a mutual cancellation of ligand and strain effects has been obtained from the analysis of local density of d -states.[2] Since an unexpected dependence of the local reactivity and the formation enthalpy on the subsurface layers has been also found from the DFT calculations, in particular for the case of low silver concentrations at the surface combined with complete silver layers at the subsurface, we address here the effect of diffusion of silver atoms to the sublayers. In order to obtain a more detailed understanding of the catalytic properties by including a wider set of structural configurations, we present in this contribution first steps towards DFT-based kinetic Monte Carlo calculations of bimetallic surface alloys, using PdAg/Pd(111) as a model system.

[1] Y. Ma *et al.* *Phys. Chem. Chem. Phys.* **13**, 10741 (2011)

[2] L. A. Mancera *et al.* *Phys. Chem. Chem. Phys.*, accepted for publ., DOI:10.1039/C2CP42914D, (2012)

O 20.8 Mon 17:45 H33

Structure and methanol oxidation reaction on $\text{VO}_x/\text{TiO}_2(110)$ model systems — ●LUCA ARTIGLIA¹, STEFANO AGNOLI¹, ANDREA VITTADINI², ALBERTO VERDINI³, ALBANO COSSARO³, LUCA FLOREANO³, and GAETANO GRANOZZI¹ — ¹Department of Chemical Sciences, University of Padova, Via Marzolo 1, I-35131, Padova, Italy — ²ISTM-CNR, Padova, Italy/PD I-35131, Italy — ³TASC National Laboratory, CNR-IOM, Trieste, Italy/TS I-34149, Italy

During the past years the structure of vanadia (VO_x) thin films supported on TiO_2 rutile (110) and their reactivity towards alcohols oxidation have been extensively studied. The main reaction products are aldehydes, thus the reaction proceeds through oxidative dehydrogenation (ODH) path. In this work we introduce a completely new set of data collected on different amount of VO_x (from 0.2 to 2.0 ML) grown on TiO_2 (110) by V reactive deposition in O_2 , where the V oxidation state is close to +4. A complete surface science characterization (XPS, XPD and STM) and DFT calculations have allowed us to describe the structure and electronic properties of VO_x nanoclusters (NCs), obtained after 0.2 ML V deposition. These NCs resulted to be V_4O_8 tetramers growing aligned along the TiO_2 [001] crystallographic direction. Hence we have focused on the interaction between VO_x/TiO_2 model system and methanol performing TPD experiments. Our results clearly show that on VO_x tetramers ODH reaction takes place at low temperature (ca. 290 K) and that the system selectivity is high. A TPD analysis of higher VO_x coverage (up to 2.0 ML) unravel a desorption peak shift to lower temperatures together with a selectivity decrease.

O 20.9 Mon 18:00 H33

Methanol synthesis on ZnO from molecular dynamics — ●JOHANNES FRENZEL and DOMINIK MARX — LS Theoretische Chemie, Ruhr-Universität Bochum, 44780 Bochum, Germany

Advanced molecular dynamics [1] is demonstrated to be a powerful, comprehensive and general approach to study surface chemical reactions using such as those underlying the heterogeneous catalytic synthesis of methanol from CO on ZnO as a case study[2,3]. This technique opens up a novel dimension in moving closer to the experiment by allowing to explore enormous space of chemical possibilities generating an unexpectedly complex reaction network of apparently simple surface chemical reactions in the first place. In particular, "near-surface states" are identified to be key to some of the steps in the catalytic cycle tanking place at ZnO(0001) surface with oxygen vacancies[4].

Automated exploration techniques in the framework of accelerated molecular dynamics, as opposed to genuinely static approaches, might be the method of choice to address such problems involving competing processes to the molecule-surface interaction.

[1] A. Laio and M. Parrinello, *PNAS* **99** (2002) 12562; M. Iannuzzi, A. Laio and M. Parrinello, *Phys. Rev. Lett.* **90** (2003) 238302

[2] J. Kiss, J. Frenzel, N. N. Nair, B. Meyer and D. Marx, *JCP* **90**

(2011) 064710

[3] J. Frenzel, J. Kiss, N. N. Nair, B. Meyer and D. Marx, submitted

[4] J. Kiss, A. Witt, B. Meyer and D. Marx, *JPC* **130** (2009) 184706

O 20.10 Mon 18:15 H33

Flow-Reactor Investigations of Clean and Cs-promoted Ag foils as Catalysts in the Ethylene Epoxidation Reaction — GERGELY ROZSA, ●REGINA WYRWICH, SEBASTIAN BÖCKLEIN, MAXIMILIAN GANIEK, and JOOST WINTTERLIN — Department Chemie, Ludwig-Maximilians-Universität München, Germany

The selective epoxidation of ethylene over Ag is a large scale industrial process. Nevertheless the reaction mechanism is still heavily debated. In the commercial process a supported catalyst is used and Cs is added as a promoter to improve the selectivity. Despite intense investigations on model systems the role of Cs remains unclear. Both a site blocking effect as well as an electronic effect are discussed. In the context of an extensive catalytic study we investigated the behaviour of Cs-promoted polycrystalline Ag-foils under reaction conditions. We report about a procedure to reproducibly deposit Cs on sputter-cleaned Ag foils by dip-coating in aqueous CsOH solutions. Based on x-ray photoelectron spectroscopy (XPS) measurements a Langmuir-type behaviour of the deposition process is observed. Evaluation and comparison of the catalytic performance (activity and selectivity) of the Cs-promoted and clean Ag foils is done in a flow-reactor setup with quadrupole mass spectrometry (QMS) for product analysis. A crucial dependency upon the activation procedure (thermal treatment at 500 °C in Ar or O_2) is found in this case. A potential influence of Cs seems to arise at higher pressures of the reactant gases indicating a site blocking effect of Cs.

O 20.11 Mon 18:30 H33

Ethylene Oxide Formation over Ag(111): Reactivity and Spectroscopy Investigation of the Active Oxygen Species — ●SEBASTIAN BÖCKLEIN¹, SEBASTIAN GÜNTHER², and JOOST WINTTERLIN¹ — ¹Ludwig-Maximilians-Universität München, Germany — ²Technische Universität München, Germany

Despite intensive investigation the ethylene oxide (EtO) formation over Ag catalysts remains an unsolved problem. By applying a special preparation procedure we were able to obtain and characterize the catalytically active oxygen phase on Ag(111). Reactivity experiments of this species with ethylene using temperature-programmed reaction (TPR) show formation of EtO. X-ray photoelectron spectroscopy (XPS) gives an O 1s signal in the range of 530-531 eV. A closer investigation of the XPS data shows that it consists of two distinct oxygen species (O 1s BE 530.2 and 530.7 eV). The ratio depends on the simultaneous presence of the $\text{p}(4 \times 4)\text{O}$ reconstruction and on the sample temperature. Temperature dependent XPS (TDXPS) measurements show that the 530.2 eV-species increases with temperature, and a quantitative analysis indicates a reversible transformation between the two species. By angle resolved XPS (ARXPS) depth profiles for these species could be evaluated resulting in a model for this system. Using in situ scanning tunneling microscopy (STM) we could follow the reaction of this reactive oxygen phase with ethylene. The reaction is connected with massive changes of the catalyst surface and with the appearance of new ordered structures like a (2×2) or a chain-like phase.

O 20.12 Mon 18:45 H33

Bonding of ammonia and its dehydrogenated fragments on Ru(0001) — ●SABINE MAIER¹, INGEBORG STASS², JORGE CERDA³, and MIQUEL SALMERON⁴ — ¹University of Erlangen-Nürnberg, Department of Physics, Erlangen, Germany — ²Freie Universität Berlin, Institut für Experimental Physik, Berlin, Germany — ³CSIC, Instituto de Ciencia de Materiales, Madrid, Spain — ⁴Lawrence Berkeley National Laboratory, Materials Science, Berkeley, CA, United States

The catalytic ammonia decomposition has recently attracted attention due to the high hydrogen storage capacity of ammonia and the possibility to produce hydrogen without toxic or greenhouse gases as byproducts, making ammonia a potential candidate as an energy carrier for fuel cells. Here we present low temperature scanning tunneling microscopy experiments and density functional theory calculations that unambiguously establish the adsorption sites of the NH_x ($x=0-3$) species and give insights into the dissociation pathways of ammonia on Ru(0001). All the N-H bond cleavage reactions were induced by controlled tip manipulation to produce each of the NH_x ($x=0-2$) intermediates. Further, the interaction of ammonia with surface hydrogen and the ammonia dimer formation will be discussed.