O 57: Surface Chemical Reactions and Heterogeneous Catalysis II

Time: Thursday 15:45–18:30 Location: H38

O 57.1 Thu 15:45 H38

Determination of the CO adsorption energy on Au/TiO$_2$ model catalysts at elevated pressures — •THOMAS DIEMANT, JOACHIM BANSMANN, and ROLF JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm

The adsorption of CO on Au/TiO$_2$/Ru(0001) model catalysts has been studied by in-situ IR measurements at elevated pressures up to 50 mbar. From a quantitative analysis of the integrated IR intensities it is possible to calculate the CO adsorption energy on the Au particles of the model catalyst surface. We have determined the CO adsorption energy with this method for pure CO and for CO/O$_2$ mixtures using model catalysts with different Au coverages. Comparing the results for both gas compositions, we can quantify the influence of (co-adsorbed) oxygen on the CO adsorption. From the results for different Au coverages, the influence of the Au particle size on the CO binding strength is derived. The results of this study will be compared to results of UHV studies on the CO adsorption of Au model catalysts using either TPD measurements or a similar analysis of IR results.

O 57.2 Thu 16:00 H38

CO adsorption on a surface oxide: A combined DFT and XPS study — •JUTTA ROGAL[1], EDVIN LUNDGREN[2], JESPER ANDERSEN[2], and KARSTEN REUTER[1] — [1]Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany — [2]Department of Synchrotron Radiation Research, Institute of Physics, Lund University, Box 118, S-221 00 Lund, Sweden

CO adsorption at some transition metal and bulk oxide surfaces is a well-known showcase for the deficiencies of present-day exchange and correlation (xc) functionals in density-functional theory (DFT). Here we investigate whether similar problems in the determination of the proper adsorption site exist for CO adsorption on a so-called surface oxide, i.e. a nanometer thin oxide film. For this we focus on the $(\sqrt{5} \times \sqrt{5})R27°$ surface oxide at Pd(100) and combine DFT with high-resolution x-ray photoemission experiments. Comparing the calculated Pd $3d_{5/2}$ and C $1s$ surface core-level shifts with the experimental data allows to unambiguously identify the bridge site as the adsorption site populated in the experiment. While this is also the most stable adsorption site when using the local-density and several gradient-corrected xc functionals in the DFT calculations, the absolute values of the binding energy at this bridge site is found to vary significantly for the different xc functionals. Suitably combining the computed binding energies and diffusion barriers in kinetic Monte Carlo simulations provides finally first insight into kinetic limitations to the ordering behavior of the CO adsorbates under the low-temperature conditions of the experiment.

O 57.3 Thu 16:15 H38

CO oxidation on RuO$_2$(110): Temperature programmed reaction spectra from first-principles kMC simulations — •MICHAEL RIEGER, JUTTA ROGAL, and KARSTEN REUTER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin, Germany

The catalytic oxidation of CO over the RuO$_2$(110) surface has become a frequently studied model system, for which detailed data from steady-state activity measurements and *ex-situ* experiments is available. The steady-state activity of this surface was recently investigated by first-principles kinetic Monte Carlo (kMC) simulations [1], yielding very good agreement with experimental results. Using the same setup, and in particular, the same *ab initio* microscopic parameters, i.e. elementary processes (including desorption, diffusion and reaction events) and process rates based on density-functional theory (DFT) energetics, we now also reproduce detailed temperature programmed desorption (TPD) and reaction (TPR) data for this system [2]. We focus in particular on the experimentally found dependence of the CO$_2$ yield on the surface coverage, which could not be explained within a simple mean-field picture. Analyzing our simulation results, we can rationalize the observed non-intuitive dependence as the result of a coverage dependent interplay of different possible reaction processes taking place at the surface.

[1] K. Reuter, D. Frenkel, and M. Scheffler, Phys. Rev. Lett. **93**, 116105 (2004); K. Reuter and M. Scheffler, Phys. Rev. B **73**, 045433 (2006).
[2] S. Wendt, M. Knapp, and H. Over, J. Am. Chem. Soc. **126**, 1537 (2004).

O 57.4 Thu 16:30 H38

Is there a "rate determining step" in the catalytic oxidation of CO over RuO$_2$(110)? — •HAKIM MESKINE, KARSTEN REUTER, and MATTHIAS SCHEFFLER — Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin

Out of the several elementary processes in the catalytic cycle, one step is frequently believed to be particularly important, and limiting the overall product formation. We check on this assumption of a rate determining step, using the CO oxidation at RuO$_2$(110) as a model case. The chemical kinetics is determined with kinetic Monte Carlo simulations, based on rate constants determined by density-functional theory and transition-state theory. The composition and structure of the catalyst surface are computed in reactive environments ranging from ultra-high vacuum (UHV) to technologically relevant conditions (pressures of several atmospheres and elevated temperatures). We employ several forms of sensitivity analyses to identify the rate determining steps under the different environmental conditions. Under UHV conditions we find the catalytic activity indeed predominantly dependent on only one process step, namely the reactant adsorption. However, under catalytically really relevant gas phase conditions, it is not one, but a larger number of elementary processes that contributes equally to the total rate of product formation. The bearings of these findings for the frequently employed approach to extract apparent activation barriers from Arrhenius-type activity plots is critically discussed.

O 57.5 Thu 16:45 H38

Comparison of phenomenological kinetics and kMC modelling of CO oxidation at RuO$_2$(110) — •SEBASTIAN MATERA[1], HAKIM MESKINE[1], KARSTEN REUTER[1], MATTHIAS SCHEFFLER[1,2], and HORIA METIU[2] — [1]Fritz-Haber-Institut, Faradayweg 4-6, D-14195 Berlin — [2]University of California at Santa Barbara, Santa Barbara CA 93106

Neglecting the explicit spatial distribution of the chemicals at the catalyst surface is a frequently employed concept in phenomenological kinetics (PK). We scrutinize this concept by comparing with results from kinetic Monte Carlo (kMC) simulations, which do not need to rely on this mean-field approximation. For the model system CO oxidation at RuO$_2$(110) we compute the surface composition and activity of the catalyst surface in reactive environments ranging from ultra-high vacuum to technologically relevant conditions (pressures of several atmospheres and elevated temperatures). Using the same first-principles rate constants in both approaches, we find the PK modeling to be in serious error, and even failing to identify the correct dominant reaction mechanism. Approaches to improve on this situation, by explicitly including diffusion events and site correlations in the PK modeling, will be discussed.

O 57.6 Thu 17:00 H38

Ultrafast reaction dynamics of the associative desorption of C+O from Ru(001) — •CHRISTIAN FRISCHKORN, STEFFEN WAGNER, HENRIK ÖSTRÖM, and MARTIN WOLF — Freie Universität Berlin, Fachbereich Physik, Arnimallee 14, 14195 Berlin

Femtosecond laser excitation of Ru(001) covered with atomic carbon and oxygen results in the recombinative desorption of CO molecules from the surface. A nonlinear fluence dependence of the reaction yield is found for excitation wavelengths of 400 and 800 nm. The higher reaction yield obtained for the 400-nm as compared to the 800-nm excitation can be attributed to the different optical penetration depths in Ru(001). As a consequence, higher surface temperatures rather than significant contributions of non-thermalized hot electrons cause the stronger laser-induced desorption with 400-nm pulses. Furthermore, the reaction mechanism of the CO recombination is investigated with two-pulse correlation measurements which exhibit a FWHM of $\approx$ 20 ps. However, despite this relatively wide two-pulse correlation (which usually is taken as an indication for a purely phonon-mediated energy flow), all experimental data are only consistently reproduced in the framework of frictional coupling between the substrate and the adsorbate, if both phonon *and* electronic contributions are included.

O 57.7 Thu 17:15 H38

Site specific analysis of CO dissociation on Ni(111) with

STM — •Sebastian Horch, Martin Andersson, Frank Abild-Pedersen, and Jens Nørskov — Center for Atomic-scale Materials Design (CAMD), NanoDTU, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

One of the most important problems in heterogeneous catalysis is the analysis of the "active site" (cf. our contribution on the experimental identification of the active site on MoS_2). Only when this site and its relative abundance are known, it is –at least in principal– possible to determine e.g. turnover-rates per active site.

There are not many methods that can perform such site-specific measurements. While STM is the method of choice for atomic-scale visualization of the active site, it is much too slow for a real-time investigation of catalytic reactions at this site. If, however, the reaction leaves a clear footprint at the active site, one might use this to learn more about the reaction itself.

We have used this approach to investigate the dissociation of CO on Ni(111) using STM. The footprint is here the formation of carbide islands at the upper step edges. The steps provide the active site in this process, as can be shown e.g. by step blocking. By measuring the carbon uptake *per step length* for different temperatures and CO pressures, we can learn more about the processes involved and shed some more light onto the long-term debate about the barrier for CO dissociation on Ni surfaces.

O 57.8   Thu 17:30   H38

Dehydrogenation kinetics of methyl on various Pt surfaces as studied by temperature-programmed XPS. — •Christian Papp, Barbara Tränkenschuh, Regine Streber, Reinhard Denecke, and Hans-Peter Steinrück — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

We studied the reaction of methyl (CH_3) on different platinum surfaces by temperature-programmed XPS at the synchrotron radiation facility BESSY II in Berlin [1]. The quantitative analysis yielded the transition temperatures for the subsequent dehydrogenation steps from CH_3 to CH to atomic C, which depend on the crystallographic orientation of the substrate. Corresponding experiments with deuterated methyl (CD_3) show the same dehydrogenation sequence; however, the transition temperatures are approx. 20 K higher, due to the kinetic isotope effect. By assuming first order reaction kinetics and by applying a simple Redhead analysis [2] to our data, we were able to estimate the activation energies. The difference in the activation barriers for dehydrogenation of deuterated and non-deuterated methyl to methylidyne agrees well with the difference in zero-point energies of the C-H and C-D vibrations. This result is in agreement with expectations from DFT calculations [3], which show that the rate limiting step in methyl dissociation should be the breaking of the first C-H bond.

[1] Papp et al., J. Phys. Chem. C accepted.
[2] Redhead, Vacuum 62 (1962) 203.
[3] Petersen et al., J. Phys. Chem. B 108 (2004) 5909.

O 57.9   Thu 17:45   H38

H laserdesorption experiments from HOPG with VUV photonenergies at the FLASH facility in Hamburg — •Carsten Thewes, Björn Siemer, Tim Hoger, and Marco Rutkowski — Physikalisches Institut, Westfälische Wilhelms-Universität, 48149 Münster

During the past years, the understanding of the interaction of atomic and molecular hydrogen with carbon surfaces has gained new attention for the fields of hydrogen storage [19 and molecular hydrogen formation in the interstellar medium [2, 3]. Our recent experiments concerning the desorption of H and D atoms adsorbed on highly oriented pyrolytic graphite (HOPG) will be surveyed. The experiments are performed at the Free Electron Laser facility FLASH at DESY using 32.5 nm XUV photons. The recording of arrival time distributions via a delayable laser detection scheme (hydrogen 2s ← 1s excitation REMPI process), information about possible reaction mechanisms is accessible. Based on this background an insight to the so far evaluated data and results will be given. The analysis of the kinetic energy distribution of the desorbing neutral hydrogen atoms reveals different contributions peaking at around 2, 8 and 25 meV. The new experimental data is discussed in the model of Hammer et al. [3]. [1] L. Schlapbach, A. Züttel, Nature 414, 353 (2001) [2] N.Rougeau, D. Teillet-Billy and V. Sidis, Chem. Phys. Let., 431, 135138 (2006) [3] L. Hornekær, E. Rauls, W. Xu, Z. Sljivančanin, R. Otero, I. Stensgaard, E. Lægsgaard, B. Hammer, F. Besenbacher, Phys. Rev. Let. 97 (18), 186102 (2006)

O 57.10   Thu 18:00   H38

Surface studies of simple and complex ionic liquid systems using XPS — •Manuela Killian[1], Christian Potzner[1], Till Cremer[1], Jörg Michael Gottfried[1], Natalie Müller[2], Dirk Gerhard[2], Peter Wasserscheid[2], Florian Maier[1], and Hans-Peter Steinrück[1] — [1]Lehrstuhl für Physikalische Chemie II, Universität Erlangen, Egerlandstr. 3, 91058 Erlangen — [2]Lehrstuhl für Chemische Reaktionstechnik, Universität Erlangen

Ionic liquids (ILs) - organic salts with melting points below $100°C$ - represent a new class of materials in liquid phase physics and chemistry. In surface science, ILs open up unprecedented possibilities for surface studies of phenomena related to liquids in general because of their negligible vapour pressures even at elevated temperatures. Our studies focus on two ILs consisting of the same cation but different anions, namely 1-ethyl-3-methylimidazolium ethylsulfate (EMIM EtSO4) and 1-ethyl-3-methylimidazolium bis(tri-fluoromethane-sulfon)amide (EMIM BTA). To determine surface composition and molecular orientation, angle dependent XP spectra were recorded for the pure ILs, their mixtures, and solutions comprising a dissolved platinum salt as model catalyst. In the latter case, we demonstrate a selective enrichment of the platinum cation at the surface.[1] The basic understanding of surface/interface enrichment effects is important for all kinds of multiphasic catalysis operations employing ionic liquids. This work was supported by the DFG through SPP1191.

[1] F. Maier et al., Angew. Chem. Int. Ed. 45 (2006) 7778.

O 57.11   Thu 18:15   H38

Plasma modified bimetallic nanocolloid arrays - a model system for structural and order effects in particle catalysis — •Bernhard Gehl[1], Jan Ingo Flege[2], Vesna Aleksandrovic[3], Thomas Schmidt[2], Sigrid Bernstorff[4], Jens Falta[2], Horst Weller[3], and Marcus Bäumer[1] — [1]Institut für Angewandte und Physikalische Chemie, Universität Bremen, Leobener Strasse NW2, 28359 Bremen, Germany — [2]Institut für Festkörperphysik, Universität Bremen, Otto-Hahn-Allee, 28359 Bremen, Germany — [3]Institut für Physikalische Chemie, Universität Hamburg, Grindelallee 117, 20146 Hamburg, Germany — [4]Sincrotrone Trieste, Strada Statale 14, km 163.5, in Area Science Park, 34012 Basovizza / Trieste, Italy

The high surface to volume ratio and special chemical properties of nanoparticles have made them a very common class of materials for catalytic coatings. Well-defined monolayers of nanoparticles were obtained by spin-coating of bimetallic colloidal particles on oxidic substrates. Plasma treatment and thermolysis were applied to strip the particles of the organic ligands serving as stabilizers in the liquid phase and as spacers during deposition. With SEM, GISAXS, and XPS the structural and chemical changes induced by both cleaning methods were examined.