

## O 8: Surface Chemical Reactions and Heterogeneous Catalysis I

Time: Monday 10:30–13:15

Location: H33

O 8.1 Mon 10:30 H33

**Influence of the nanometer scale on the reactivity of cerium dioxide** — ●KOSTIANTYN KULYK and MYKOLA BORYSENKO — Chuiko Institute of Surface Chemistry, National Academy of Sciences of Ukraine, General Naumov Str. 17, 03164 Kyiv, Ukraine

Cerium dioxide is considered as the most widely used rare-earth oxide in industry due to its unique redox properties and elevated oxygen storage capacity. However, the preparation of ceria nanoparticles with desired size still remains a challenge and to date little is known about how the nanometer scale of the ceria particles effect its chemical behavior. My talk will illustrate the crucial points of our novel method of synthesis of ceria nanoparticles supported on fumed silica. The proposed method allows us to synthesize nanocomposites with a controllable size of cerium dioxide crystallites from 3 to 24 nm (XRD, Solid State MAS  $^{29}\text{Si}$  NMR, Raman, IR, SEM, UV-vis). Comparison of reactivity of nanosized  $\text{CeO}_2$  and micrometer scale  $\text{CeO}_2$  will be demonstrated by studying the interaction of nanocomposites with cerium acetylacetonate, acetylacetone, acetic acid, thiazolyl- and benzothiazolyl substituted coumarins. Mechanisms and kinetics ( $n$ ,  $E_{act}$ ,  $k_o$ ,  $dS$ ) of surface reactions were studied using a temperature programmed desorption mass spectrometry (TPD-MS) and TG/DTG/DTA. The main part of my speech will be devoted to the phenomena of dramatic enhancement of the reactivity of ceria nanoparticles resulting in its ability to chemisorb acetylacetone at room temperature and form grafted ceriumacetylacetonate groups. The mechanism of the nanoeffect will be presented and described in details.

O 8.2 Mon 10:45 H33

**Adsorption and decomposition of acetic acid on ceria-based model catalysts** — ●A. NEITZEL<sup>1</sup>, Y. LYKHACH<sup>1</sup>, V. JOHÁNEK<sup>2</sup>, N. TSUD<sup>2</sup>, T. SKÁLA<sup>3</sup>, K. C. PRINCE<sup>3</sup>, V. MATOLÍN<sup>2</sup>, and J. LIBUDA<sup>1</sup> — <sup>1</sup>FAU Erlangen-Nürnberg, Germany — <sup>2</sup>Charles University in Prague, Czech Republic — <sup>3</sup>Sincrotron Trieste, Italy

The adsorption and decomposition of acetic acid on stoichiometric  $\text{CeO}_2(111)$ , partially reduced  $\text{CeO}_{2-x}$ , and  $\text{Pt/CeO}_2$  thin films prepared on  $\text{Cu}(111)$  were investigated by synchrotron radiation and resonant photoelectron spectroscopy. Molecular acetic acid and acetate are the major species formed upon adsorption at 150 K. Decomposition of these species on  $\text{CeO}_2(111)$  does not alter the oxidation state of cerium cations. In contrast, decomposition of acetic acid on  $\text{CeO}_{2-x}$  results in re-oxidation between 250 and 400 K, followed by reduction of ceria and C-C bond cleavage above 400 K. Intermediate decomposition products like formate, alkoxy, and alkyl species were identified on the surface. These were converted into thermally stable carbonaceous species above 600 K. On  $\text{Pt/CeO}_2$ , hydrogen spillover and reverse spillover were observed during annealing. Furthermore, CO, alkoxy, alkyl moieties, and elemental carbon were detected. Above 500 K, reverse oxygen spillover from ceria to Pt particles resulted in oxidative removal of carbonaceous species. It was found that C-C bond cleavage is promoted in presence of oxygen ad-atoms on  $\text{Pt}(111)$  and  $\text{Pt/CeO}_2$ . As a result, formation of methoxy species and hydroxyl groups on Pt was observed. On  $\text{Pt/CeO}_2$ , pre-exposed to oxygen, hydrogen reverse spillover was found to be suppressed.

O 8.3 Mon 11:00 H33

**Dehydrogenation of dodecahydro-N-Ethylcarbazole on Pt(111)** — ●CHRISTOPH GLEICHWEIT, MAX AMENDE, STEFAN SCHERNICH, WEI ZHAO, OLIVER HÖFERT, JÖRG LIBUDA, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen (Germany)

The dehydrogenation of the liquid organic hydrogen carrier dodecahydro-N-ethylcarbazole ( $\text{H}_{12}$ -NEC) on  $\text{Pt}(111)$  was studied by high-resolution X-ray photoelectron spectroscopy (HR-XPS) in order to elucidate its dehydrogenation mechanism.  $\text{H}_{12}$ -NEC was adsorbed under ultra high vacuum (UHV) conditions by physical vapor deposition, and subsequently the reaction was monitored during heating. Although the molecules are quite complex, we identified the reaction steps after detailed analysis of the C1s and N1s core levels. During adsorption at low temperatures the development of monolayer and multilayer peaks was observed. Interestingly the N1s peak assigned to the multilayer is found at lower binding energy than the monolayer peak.

When heating the sample continuously, the multilayer desorbs up to temperatures of about 285 K while the signature of the monolayer increases due to decreased damping. Subsequently, the dehydrogenation of the  $\text{H}_{12}$ -NEC to NEC follows successively in the range of 280 K to 500 K. Above 430 K the dealkylation reaction of the NEC to carbazole is observed. Upon further heating to 1000 K decomposition to adsorbed carbon takes place. We acknowledge the cluster of excellence "Engineering of Advanced Materials".

O 8.4 Mon 11:15 H33

**O K-edge NEXAFS for Silica-Supported Molybdena at Different Loadings: theoretical cluster studies** — ●LILI SUN<sup>1</sup>, KLAUS HERMANN<sup>1</sup>, KAZUHIKO AMAKAWA<sup>1</sup>, MICHAEL HÄVECKER<sup>2</sup>, ANETTE TRUNSCHKE<sup>1</sup>, and ROBERT SCHLÖGL<sup>1</sup> — <sup>1</sup>Inorganic Chemistry Department, Fritz-Haber-Institut der MPG, Faradayweg 4-6, D-14195 Berlin (Germany). — <sup>2</sup>Department of Solar Energy Research, Helmholtz-Zentrum Berlin/BESSY II, Albert-Einstein-Str. 15, 12489 Berlin, Germany.

Oxygen core excitations in different molybdena-silica clusters are evaluated using density-functional theory to explain the X-ray absorption fine structure (NEXAFS) near the O K-edge measured for molybdena supported by SBA-15 silica. Different oxygen species in the molybdena-silica clusters with molybdenum in different coordination can be clearly distinguished in the theoretical spectrum. The experimental NEXAFS spectra at low molybdenum loadings (< 6.6%) exhibit a double-peak structure in the O 1s to Mo 4d / O 2p excitation range of 529-536eV. This is reproduced by the theoretical results for tetrahedral dioxo  $\text{MoO}_4$  units, singly or doubly connected with the silica substrate. The experimental spectrum shows a transition from a double- to a broad asymmetric single-peak structure at high molybdenum loadings (about 13.3%). This can be modeled by decreasing the distance between the two molybdenyl oxygen atoms in the dioxo  $\text{MoO}_4$  unit leading to direct O-O coupling. Thus, the spectral transition may be explained by a simple structural effect resulting from the increased density (squeezing) of  $\text{MoO}_4$  units at the SBA-15 silica surface.

O 8.5 Mon 11:30 H33

**DFT study of Redox-Active Metal-Organic Frameworks** — ●JELENA JELIC<sup>1</sup>, DMYTRO DENYSENKO<sup>2</sup>, DIRK VOLKMER<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>TU Munich, Germany — <sup>2</sup>University of Augsburg, Germany

Next to applications in gas storage or drug delivery, metal-organic frameworks (MOFs) also receive increasing attention as redox active catalysts. We have recently reported on a Co-based MOF within the robust and modular MFU-4 structural family that shows promising reversible gas-phase oxidation properties [1]. We here present a density-functional theory (DFT) based computational screening approach to identify other coordinatively unsaturated metal centers or ligands that yield even more redox-active frameworks. A central concern is the accuracy of present-day DFT functionals, and we elucidate systematic shortcomings of semi-local DFT in order to establish it as a reliable and computationally efficient tool for extended in-silico searches. Among the tested ligands hydrides seem particularly promising and we further scrutinize this by detailed mechanistic analysis of potential oxidation reactions.

[1] D. Denysenko, T. Werner, M. Grzywa, A. Puls, V. Hagen, G. Eickerling, J. Jelic, K. Reuter, and D. Volkmer, Chem. Commun., 1236 (2012)

O 8.6 Mon 11:45 H33

**Identifying Cu(I) Cationic Positions in SSZ-13 by Modeling Infrared and Diffuse Reflectance Spectra** — ●FLORIAN GÖLTL<sup>1</sup>, PHILIPPE SAUTET<sup>1</sup>, KERSTIN HUMMER<sup>2</sup>, GEORG KRESSE<sup>2</sup>, and JÜRGEN HAFNER<sup>2</sup> — <sup>1</sup>University of Lyon I, ENS Lyon, Allée d'Italie 46, 69342 Lyon, France — <sup>2</sup>University of Vienna, Faculty of Physics, Computational Materials Physics, Sensengasse 8/12, 1090 Vienna, Austria

Copper containing zeolites are prime candidates in removing nitrous oxides from exhaust gases. Recently an especially high activity of Cu containing SSZ-13 for the given reaction has been shown in experiment. However, the exact cationic positions within this material have been debated. Based upon the catalyst preparation process we suggest a new type of Cu(I) site within SSZ-13. We use density functional to

model different active sites and the IR spectrum of adsorbed CO. We find two different peaks, one redshifted by 2-5  $\text{cm}^{-1}$ , the other one red-shifted by 15  $\text{cm}^{-1}$ . Furthermore we calculate the optical absorption spectra of those sites using Bethe-Salpeter Equation on top of self consistent  $\text{GW}_0$  calculations. Compared to hybrid functional calculations the  $\text{GW}_0$  approximation increases the energy gap between Cu 3d- and 4s states by about 2 eV. On the other hand, excitonic effects calculated within Bethe-Salpeter Equation reduce this gap upon optical absorption by about 3 eV, which leads to absorption maxima for the Cu d-s transition of 4 eV and between 4.5 and 4.7 eV for different cationic sites. Our calculations agree perfectly with experiment.

O 8.7 Mon 12:00 H33

**Interfacial complexation reaction in vacuo by metal-organic chemical vapour deposition** — ●ANTHOULA C. PAPAGEORGIOU<sup>1</sup>, SYBILLE FISCHER<sup>1</sup>, SEUNG CHEOL OH<sup>1</sup>, FRANCESCO ALLEGRETTI<sup>1</sup>, ALISSA WIENGARTEN<sup>1</sup>, KNUD SEUFERT<sup>1</sup>, SARANYAN VIJAYARAGHAVAN<sup>1</sup>, KATHARINA DILLER<sup>1</sup>, ROBERT G. ACRES<sup>2</sup>, KEVIN C. PRINCE<sup>2</sup>, FLORIAN KLAPPENBERGER<sup>1</sup>, WILLI AUWÄRTER<sup>1</sup>, JOACHIM REICHERT<sup>1</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>Physik Department E20, Technische Universität München, 85748 Garching, Germany — <sup>2</sup>Sincrotrone Trieste, 34149 Basovizza, Italy

The fabrication and control of metal coordination compounds or architectures at well-defined interfaces is a thriving research domain with promise for various areas, including single-site catalysis, molecular magnetism, light-harvesting and molecular rotors and machines. To date such systems have been realized either by grafting prefabricated metal-organic complexes or by protocols combining molecular linkers and single metal atoms at the interface. Here we report a different pathway employing metal-organic chemical vapour deposition, as exemplified by the reaction of meso-tetraphenylporphyrin derivatives on atomistically clean Ag(111) with a metal precursor under vacuum conditions. STM, XPS and NEXAFS reveal the formation of a meso-tetraphenylporphyrin cyclodehydrogenation product that readily undergoes metalation after exposure to the metal precursor vapour and thermal treatment. A self-terminating porphyrin metalation protocol, which proceeds without additional surface-bound by-products, yielding a single, thermally robust layer of metalloporphyrins, is discovered.

O 8.8 Mon 12:15 H33

**Surface activated dedeuteration of deuterofullerenes** — SEYITHAN ULAS, PATRICK WEIS, ●ARTUR BÖTTCHER, and MANFRED KAPPES — Institute of Physical Chemistry, Karlsruhe Institute of Technology (KIT), Fritz-Haber-Weg 2, 76131 Karlsruhe, Germany

Deuterofullerenes have been created by exposing  $\text{C}_{60}$  films grown on Au(111) to atomic deuterium. The composition of the films created is dominated by  $\text{C}_{60}\text{D}_{18}$  and  $\text{C}_{60}\text{D}_{36}$ . The thermally induced decomposition of the deuterofullerenes proceeds via emission of  $\text{D}_2$ ,  $\text{C}_{60}$  and  $\text{C}_{60}\text{D}_{x<46}$ . The  $\text{C}_{60}\text{D}_x/\text{Au}(111)$  interface has been found to be responsible for the  $\text{D}_2$  emission observed. The catalytic role of the Au(111) surface resembles the activated dedeuteration of deuterofullerenes as induced by alkali metal doping  $/1/$ . A lower limit to the  $\text{D}_2/\text{D}$  conversion yield (integrated  $\text{D}_2$  emission/ $\text{D}$  exposure) as induced by  $\text{C}_{60}$  on Au(111) has been estimated to be higher than  $10^{-4}$ .  $\text{D}_2$  emission competes with cage fragmentation which leads to gradual graphitization of the Au(111) surface. The latter process corresponds to poisoning of the catalyst.

$/1/$  D. Löffler et al. J. Phys. Chem. C, 112 (2008) 13796

O 8.9 Mon 12:30 H33

**Density Analysis of 1-Octadecanethiol (CH<sub>3</sub> (CH<sub>2</sub>)<sub>17</sub>-SH) and 1-Hexadecanethiol (CH<sub>3</sub> (CH<sub>2</sub>)<sub>15</sub>-SH) Self-Assembled Monolayers (SAMs) on Gold and Silver by Impedance Spectroscopy** — ●UDDIN MD. JALAL, NIVEDITA YUMNAM, and VEIT WAGNER — School of Engineering and Science, Jacobs University, Campusring 1, D-28759 Bremen, Germany

Self-assembled monolayers (SAMs) have significantly contributed to the field of interfacial electron transfer, to developing electrodes, to fabricating lipid bilayers on electrodes among others. For applications high quality self-assembled monolayers (SAMs) with low leakage currents and without pinholes are important.

In this study we measured the impedance of 1-Octadecanethiol ( $\text{CH}_3(\text{CH}_2)_{17}\text{-SH}$ ) and 1-Hexadecanethiol ( $\text{CH}_3(\text{CH}_2)_{15}\text{-SH}$ ) based SAMs on gold (Au) and silver (Ag) surfaces prepared on polyethylene terephthalate (PET) flexible substrates to assess the quality of the SAM layers. For optimization of the quality of SAM layers on Au and Ag surfaces, the adsorption time of Octadecanethiol ( $\text{CH}_3(\text{CH}_2)_{17}\text{-SH}$ ) and Hexadecanethiol ( $\text{CH}_3(\text{CH}_2)_{15}\text{-SH}$ ) on gold and silver was systematically varied from 30 seconds to 24 hours. Adsorption times beyond 1 hour were found to have negligible difference in layer quality. To be able to sense leakage current for those high quality layers, low noise and low frequency measurement at 1Hz were necessary. The impedance data analyzed using an R-C model reveals that the SAMs of ( $\text{CH}_3(\text{CH}_2)_{15}\text{-SH}$ ) have lower leakage current in comparison to the SAMs of ( $\text{CH}_3(\text{CH}_2)_{17}\text{-SH}$ ).

O 8.10 Mon 12:45 H33

**Dissociative adsorption of water on stepped metal surfaces** — ●DAVIDE DONADIO<sup>1</sup>, RENGIN PEKOEZ<sup>1</sup>, SVENJA WOERNER<sup>1</sup>, LUCA GHIRINGHELLI<sup>2</sup>, and LUIGI DELLE SITE<sup>3</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Mainz, Germany — <sup>2</sup>Fritz Haber Institute, Berlin, Germany — <sup>3</sup>Freie Universität Berlin, Germany

Water-metal interfaces play a key role in many chemical processes, from catalysis to corrosion and photoelectrochemistry. Whereas water adlayers on atomically flat transition metal surfaces have been investigated in depth, little is known about water on stepped surfaces [1].

Using first-principles simulations we study the adsorption of water on stepped Pt, Pd, Rh, Ni and Ir surfaces. We find that the chemistry of water at steps is in general different and cannot be predicted based on the acquired knowledge on flat surfaces. For example at Pt steps, in contrast with flat surfaces, water molecules dissociate forming mixed hydroxyl/water structures, through an autocatalytic mechanism promoted by hydrogen bonding [2]. Similar effects are analyzed systematically for several metals, and general trends are devised. Together with the attitude of water chains on metal steps to transfer protons via thermally activated hopping, these findings candidate these systems as viable proton wires.

[1] A. Hodgson and S. Haq, Surf. Sci. Rep. 64, 381 (2009).

[2] D. Donadio, L. M. Ghiringhelli and L. Delle Site, J. Am. Chem. Soc. 134, 19217 (2012)

O 8.11 Mon 13:00 H33

**Auto-catalytic creation of active sites?! Step formation during NO reduction at Pt(110)** — ●TONGYU WANG<sup>1</sup>, QIAN LIU<sup>2</sup>, JOOST W.M. FRENKEN<sup>2</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>TU München, Germany — <sup>2</sup>Leiden University, The Netherlands

We report a surprisingly distinct faceting of Pt(110) into vicinal orientations with highly regular step lattices during the near-ambient NO reduction by  $\text{H}_2$ . Reactor Scanning Tunneling Microscopy (STM) measurements demonstrate that the step density can be reversibly tuned by the  $\text{NO}/\text{H}_2$  partial pressure ratio. In view of the potential role of steps in the reaction, this could reflect a unique self-promoting feature. We analyze these observations through first-principles atomistic thermodynamics calculations. They predict the formation of a high-coverage NO phase precisely over the experimentally employed (T,p)-range. Surface stress calculations show that the highly repulsive interaction in this adlayer builds up a huge compressive stress. This stress is accommodated by the expansive, lateral relaxation that the Pt surface can perform, when either space (grooves) or 'overhang'-type geometries (steps) are created. We thus suggest surface stress relaxation as atomic-scale origin behind the observed faceting.