

## O 64: Oxides and Interfaces: Adsorption II

Time: Wednesday 15:00–17:30

Location: H6

O 64.1 Wed 15:00 H6

**Ab initio wave-function-based methods for highly accurate description of adsorption** — ●DENIS USVYAT — Institut für Physikalische und Theoretische Chemie, Universität Regensburg, 93040 Regensburg, Deutschland

The wave-function-based hierarchy of electronic structure models represents a convergent theory in a sense that it systematically approaches the exact solution within the Born-Oppenheimer approximation. Conventionally these models are computationally quite intensive and for decades were hardly applicable to extended systems. We show that by employing local approximations for the electronic correlations it becomes possible to overcome the issues of the computational complexity and treat periodic systems at a very high ab initio level. Furthermore, a combined periodic/finite-cluster approach allows one even to reach accuracy that surpasses the experimental one.

Physisorption on surfaces is one of the fields, where this technique is especially powerful. Indeed, the small energy scale and shallowness of the potential energy surfaces set high demands on the accuracy. On several examples we demonstrate that progressive elimination of various sources of errors, which is possible within the hierarchical wave-function-based treatment, leads to a sub-kJ/mol (or meV) accuracy in the interaction energies for small molecules adsorbed on non-conducting surfaces. Due to the unbiased character of this approach, it can be used to resolve experimental controversies, which are common in studies of physisorption.

O 64.2 Wed 15:15 H6

**Effects of Flexibility and Entropy on the Adsorption and Growth of Functional Molecules** — ●DAVID GAO<sup>1</sup>, JULIAN GABERLE<sup>1</sup>, MATTHEW WATKINS<sup>2</sup>, FILIPPO FEDERICI CANOVA<sup>3</sup>, CHRISTIAN LOPPACHER<sup>4</sup>, LAURENT NONY<sup>4</sup>, ANIA AMROUS<sup>4</sup>, FRANCK BOCQUET<sup>4</sup>, FRANCK PARA<sup>4</sup>, and ALEXANDER SHLUGER<sup>1,5</sup> — <sup>1</sup>University College London, London, UK — <sup>2</sup>University of Lincoln, Lincoln, UK — <sup>3</sup>Aalto University, Espoo, Finland — <sup>4</sup>Aix-Marseille University CNRS, Marseille, France — <sup>5</sup>WPI-AIMR Tohoku University, Sendai, Japan

In this work we combined noncontact atomic force microscopy (NCAFM) experiments and theoretical calculations to study the effects of molecular flexibility on the adsorption and self-assembly of organic molecules on KCl(001).

Rigid 1,3,5-tri-(4-cyano-4,4 biphenyl)-benzene (TCB) and flexible 1,4-bis(cyanophenyl)-2,5-bis(decyloxy)benzene (CDB) molecules were synthesized, deposited onto a KCl (110) surface, and imaged using NCAFM. Both molecules were observed to form ordered monolayer structures at room temperature. However, the dewetting properties and growth modes of these two molecules were qualitatively different. We performed density functional theory (DFT) and classical molecular dynamics (MD) calculations to consider both enthalpic and entropic contributions to adsorption energy. Our results show that entropic effects are significant for flexible molecules (such as CDB) and can have a pronounced effect on the mechanisms of self-assembly and structural stability.

O 64.3 Wed 15:30 H6

**Copper deposition on stoichiometric and reduced ceria films** — ●BORIS GROSS and NIKLAS NILIUS — Carl-von-Ossietzky Universität Oldenburg, Institut für Physik, D-26111 Oldenburg, Germany

Nearly stoichiometric and oxygen-deficient CeO<sub>2-x</sub>(111) films, grown on Ru(0001), have been titrated with Cu nanoparticles in order to explore the interaction of noble metals with reducible oxides. In contrast to Ag and Au that preferentially bind along oxide step edges, Cu randomly nucleates even on mildly reduced ceria, as revealed from low-temperature STM measurements. The observed nucleation behavior indicates a considerable Cu interaction with O vacancies in the surface. Moreover, a distinct bimodal size distribution is revealed for the Cu particles, with the mean size substantially varying on adjacent and even on single oxide terraces. As recorded particle sizes display a strong dependence on the STM bias voltage used for imaging, an electronic origin for the bimodal size distribution is anticipated. We discuss self-limiting Cu growth as a result of charge-transfer from underlying Ce<sup>3+</sup> ions as well as a variable O vacancy concentration in differently thick ceria patches as possible reasons for the observed effect.

O 64.4 Wed 15:45 H6

**Exploring Pd adsorption, diffusion, permeation, and nucleation on bilayer SiO<sub>2</sub>/Ru as a function of hydroxylation and precursor environment; from UHV to catalyst preparation** — SASCHA POMP<sup>1,2</sup>, WILLIAM KADEN<sup>2</sup>, ●MARTIN STERRER<sup>1,2</sup>, and HANS-JOACHIM FREUND<sup>2</sup> — <sup>1</sup>Institute of Physics, University of Graz, Graz, Austria — <sup>2</sup>Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

The hydroxylation-dependent permeability of bilayer SiO<sub>2</sub> supported on Ru(0001) was investigated by XPS and TDS studies. For this, the thermal behavior of Pd evaporated at 100 K, which results in surface and sub-surface binding arrangements, was examined relative to the extent of pre-hydroxylation. Samples containing only defect-mediated hydroxyls showed no effect on Pd diffusion through the film. If, instead, the concentration of strongly bound hydroxyl groups and associated weakly bound water molecules was enriched by an electron-assisted hydroxylation procedure, the probability for Pd diffusion through the film is decreased via pore-blocking. Above room temperature, all samples showed similar behavior, reflective of particle nucleation above the film. When depositing Pd onto the same SiO<sub>2</sub>/Ru model-support via adsorption of [Pd(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> from alkaline (pH 12) precursor solution, we observe notably different adsorption and nucleation mechanisms. The Pd adsorption complexes follow established decomposition pathways to produce model-catalyst systems compatible with those created exclusively within UHV despite lacking the ability to penetrate the film due to the increased size of the initial Pd precursor groups.

O 64.5 Wed 16:00 H6

**Single Rh adatoms at the Fe<sub>3</sub>O<sub>4</sub>(001) surface and their interaction with gas molecules** — ●ROLAND BLIEM, ADAM ZAVODNY, MICHAEL SCHMID, PETER BLAHA, ULRIKE DIEBOLD, and GARETH STEVEN PARKINSON — TU Wien, Vienna, Austria

Single-atom catalysis is a hot topic in catalysis research, aiming for high activity at optimum efficiency in the usage of precious metals. Understanding the reaction mechanisms in this emerging field requires atomic-scale information about the interaction of single metal adatoms with gas molecules. The Fe<sub>3</sub>O<sub>4</sub>(001) surface is an ideal model system to study adatom-gas interactions as well as a promising support material for single-atom catalysis, because its ( $\sqrt{2} \times \sqrt{2}$ )R45° reconstruction [1] provides strong adsorption sites stabilizing single metal adatoms up to temperatures as high as 700K [2,3].

Here, we present a room-temperature study of Rh adatoms and their interaction with O<sub>2</sub>, NO, CO, and H<sub>2</sub>O using scanning tunnelling microscopy (STM) and density functional theory (DFT+U). Rh adatoms interact with each gas in a different way: O<sub>2</sub> adsorbs strongly, causing adatom mobility and sintering. NO adsorption also leads to mobility but hardly any clustering is observed. In contrast, CO adsorption does not induce mobility but poisons the activity for O<sub>2</sub> adsorption. Furthermore, Rh adatoms facilitate water splitting. DFT calculations yield bond strengths of O<sub>2</sub> and CO and metal-adsorbate bond lengths.

[1] Bliem et al. Science 346, 1215-1218 (2014).

[2] Novotny et al. Phys. Rev. Lett. 108, 216103 (2012).

[3] Bliem et al. ACS Nano 8, 7531-7537 (2014).

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**N<sub>2</sub>O to N<sub>2</sub> conversion on reduced ceria surface: NEXAFS and IRRAS studies** — ●ALEXEI NEFEDOV, CHENGWU YANG, and CHRISTOF WÖLL — Karlsruhe Institute of Technology, Karlsruhe, Germany

Ceria, one of the most reducible metal oxides, has proven to be a highly active catalyst for NO<sub>x</sub> reduction to N<sub>2</sub>. To monitor this conversion the NEXAFS and IRRAS spectroscopies have been applied in a time-resolved fashion. The stoichiometric CeO<sub>2</sub> single crystals and powders were annealed at elevated temperatures in vacuum to create surface oxygen vacancies. N<sub>2</sub>O exposure was achieved by backfilling up to 10<sup>-9</sup> mbar at sample temperatures typically below 120 K. The NEXAFS measurements were carried out at the synchrotron facility BESSY II and for IRRAS experiments we used a novel UHV-IR spectrometer. In the NEXAFS spectra, two intense resonances (401.2 eV and 404.8 eV) with equal intensities are observed. These resonances decrease in parallel over time and this decrease is explained by conversion of N<sub>2</sub>O to N<sub>2</sub> over reduced CeO<sub>2</sub>. IRRAS data confirm NEXAFS results. Af-

ter N<sub>2</sub>O adsorption only one band at 2250 cm<sup>-1</sup> is observed, which can be described as a nitrogen-nitrogen asymmetric stretching vibration. After the temperature increase as well as after the UV irradiation the band intensity goes down. Comparison of grazing emission XP spectra before and after N<sub>2</sub>O treatment indicates N<sub>2</sub>O donated oxygen atom to the oxygen vacancy and re-oxidized the reduced CeO<sub>2</sub>.

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**CO<sub>2</sub> and Water Adsorption on the Fe<sub>3</sub>O<sub>4</sub>(001) Surface** — ●JIRI PAVELEC, JAN HULVA, ROLAND BLIEM, OSCAR GAMBA, DANIEL HALWIDL, MARTIN SETVIN, MICHAEL SCHMID, ULRIKE DIEBOLD, and GARETH PARKINSON — TU Wien, Vienna, Austria

The recently solved Fe<sub>3</sub>O<sub>4</sub>(001) surface [1] is an exciting model system to investigate catalysis by supported single atoms [2] and sub-nano clusters [3]. However, understanding the interaction of the clean surface with the relevant molecules is an essential prerequisite to studying such composite systems.

Here we report a study of water and CO<sub>2</sub> adsorption using a new multi-technique vacuum system constructed at the TU Wien that combines molecular beam methods, UPS, XPS and TPD. Together with STM results these data are used to characterize the state of the molecules over a broad temperature range (50K - 600K).

CO<sub>2</sub> is physisorbed up to 115K, and desorbs with first-order kinetics from regular lattice sites. A small peak at 125K provides a quantitative measure of the surface defect concentration.

Water adsorbs molecularly at 100K, and most of the molecules in the first monolayer desorb in four peaks up to 250 K. Isotopic labelling suggest that the two smaller peaks at 320K and 520K are related to defects, the latter involving exchange of O with the surface.

[1] R. Bliem et al., *Science* 2014, doi:10.1126/science.1260556

[2] Parkinson et al., *Nature Materials* 2013, doi:10.1038/nmat3667

[3] R. Bliem et al., *Angewandte Chemie* 2015, doi:10.1002/anie.201507368

O 64.8 Wed 16:45 H6

**On-surface generation and imaging of reactive intermediates by atomic force microscopy** — ●NIKO PAVLIČEK<sup>1</sup>, BRUNO SCHULER<sup>1</sup>, SARA COLLAZOS<sup>2</sup>, NIKOLAJ MOLL<sup>1</sup>, DOLORES PÉREZ<sup>2</sup>, ENRIQUE GUITIÁN<sup>2</sup>, GERHARD MEYER<sup>1</sup>, DIEGO PEÑA<sup>2</sup>, and LEO GROSS<sup>1</sup> — <sup>1</sup>IBM Research-Zurich, 8803 Rüschlikon, Switzerland — <sup>2</sup>CIQUS and Departamento de Química Orgánica, Universidade de Santiago de Compostela, Santiago de Compostela 15782, Spain

Atomic force microscopy with functionalized tips allows imaging of the chemical structure of surface-adsorbed molecules [1].

Recently, we applied this method to investigate arynes, a class of reactive intermediates, which are involved in many chemical transformations [2]. Usually, their characterization is a great challenge because of short lifetimes and high reactivities. Here, we demonstrate the generation and characterization of individual polycyclic aryne molecules on an ultrathin insulating film by means of combined low-temperature scanning tunneling and atomic force microscopy. We also show that the aryne reactivity is preserved at cryogenic temperatures.

[1] L. Gross, F. Mohn, N. Moll, P. Liljeroth, and G. Meyer, *Science* 325, 1110 (2009).

[2] N. Pavliček, B. Schuler, S. Collazos, N. Moll, D. Pérez, E. Guitián, G. Meyer, D. Peña, and L. Gross, *Nature Chem.* 7, 623 (2015).

O 64.9 Wed 17:00 H6

**CO adsorption on small Au<sub>n</sub> (n = 1–4) structures supported on magnetite (111) surface** — ●TOMASZ PABISIAK<sup>1</sup>, MACIEJ J. WINIARSKI<sup>1,2</sup>, and ADAM KIEJNA<sup>1</sup> — <sup>1</sup>Institute of Experimental Physics, University of Wrocław, Wrocław, Poland — <sup>2</sup>Institute of Low Temperature and Structure Research, Polish Academy of Sciences, Wrocław, Poland

The adsorption of CO on Au<sub>n</sub> nanostructures (n = 1–4) formed on the Fe-terminated (111) surface of magnetite (Fe<sub>3</sub>O<sub>4</sub>) was studied using density functional theory in the generalized gradient approximation of Perdew-Burke-Ernzerhof form with Hubbard correction U, accounting for strong electron correlations. The structural, energetic, and electronic properties were examined for two classes of configurations of the adsorbed Au<sub>n</sub> structures. The flattened ones of bilayer-like structure, were found energetically more favored than vertical ones. For both classes of structures the adsorption binding energy increases with the number of Au atoms in a gold structure. A detailed analysis of the bonding charge and of the electron charge rearrangements at the Au<sub>n</sub>/oxide contacts is presented. It is found that the CO adsorption binding to the Fe<sub>3</sub>O<sub>4</sub>(111) supported Au<sub>n</sub> is up to twice as strong as to the bare magnetite surface. Analysis of charges on the atoms showed that in each case CO binds to the most positively charged (cationic) atom of the Au<sub>n</sub> structure. Changes in the electronic structure of the Au<sub>n</sub> species and of the oxide support are discussed.

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**The interaction of Li with thin layers of the ionic liquid [BMP][TFSA] adsorbed on rutile TiO<sub>2</sub>(110) and their thermal stability** — ●BENEDIKT UHL<sup>1,2</sup>, MARAL HEKMATFAR<sup>1,2</sup>, FLORIAN BUCHNER<sup>1,2</sup>, and R. JÜRGEN BEHM<sup>1,2</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, D-89069 Ulm, Germany — <sup>2</sup>Helmholtz-Institute Ulm (HIU) Electrochemical Energy Storage, D-89081 Ulm, Germany

Due to their low flammability the use of ionic liquids (IL) as component in Li ion battery electrolytes is one possibility for the development of safer battery systems. To gain a better understanding of the fundamental molecular processes at the electrode|electrolyte interface, the interaction of Li with thin layers of n-butyl-n-methylpyrrolidinium-bis(trifluoromethylsulfonyl)imide [BMP][TFSA] on rutile TiO<sub>2</sub>(110) was investigated by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM) under UHV conditions. Even at 80 K, deposition of Li, either before or after [BMP][TFSA] deposition, leads to a reaction of Li with the TiO<sub>2</sub> substrate, forming Ti<sup>3+</sup> species in the near surface region. Also the [BMP][TFSA] adlayers are partly decomposed in both cases, in the first case by reaction with the formed Ti<sup>3+</sup> species, in the second case by direct reaction with adsorbed Li atoms. The decomposition products of [BMP][TFSA] agree with decomposition mechanisms calculated previously in literature.<sup>1</sup> The thermal stability of the resulting layers is monitored up to 630 K until complete decomposition of the adlayers. <sup>1</sup>M. C. Kroon, *Green Chem.* 2006, 8, 3, 241; *Thermochim. Acta* 2007, 465, 1, 40.