

O 81: Oxide and Insulator Surfaces I: Adsorption and Reaction of Small Molecules

Time: Thursday 15:00–18:00

Location: CHE 91

O 81.1 Thu 15:00 CHE 91

Adsorption of phosphonic acids on Fe₃O₄ (001) surfaces - a DFT study — WERNFRIED MAYR-SCHMÖLZER, JOHANN FLEISCHHAKER, SOMAK BANERJEE, KAI SELLSCHOPP, and ●GREGOR VONBUN-FELDBAUER — Institute of Advanced Ceramics, TU Hamburg, Germany

The usage of magnetite nanoparticles is interesting for diverse applications from catalysis to hybrid materials. In organic-inorganic hybrids, organic linker molecules are used to allow for the self-assembly of functionalized nanoparticles. The impact of linkers with different functional groups on the, e.g., mechanical properties of assembled materials is not fully clear yet. Here, we present results from investigating the adsorption of small phosphonic acids on the magnetite (001) surface using density functional theory calculations to shed light on this essential interface. For the surface a distorted bulk truncated termination and the sub-surface cation vacancy reconstruction model are used. The adsorption configuration space is sampled and configurations as input for DFT calculations are selected using unsupervised machine learning approaches. Structural, energetic, electronic, and vibrational results are presented and compared to carboxylic acids. Potentials for multi-scale modeling approaches are sketched.

O 81.2 Thu 15:15 CHE 91

Predicting platinum adatom geometries on hematite for single-atom catalysis — ●FLORIAN BUCHNER, RALF WANZENBÖCK, JESÚS CARRETE, and GEORG K. H. MADSEN — Institute of Materials Chemistry, TU Wien, 1060 Vienna, Austria

In single-atom catalysis, where isolated adatoms anchored on a support are used as catalysts, performance is highly sensitive to the charge state and coordination of the adatoms. This offers new avenues to design and tune catalysts. But to do so efficiently, a detailed understanding of the potential energy surface (PES) of the adatom-substrate system is needed.

In this theoretical study, we present an application of an evolutionary algorithm, the covariance matrix adaptation evolution strategy (CMA-ES) [M. Arrigoni *et al.*, npj Comput Mater 7, 1–13 (2021)], to the prediction of Pt adatom configurations on the (1102) surface of hematite (α -Fe₂O₃).

We find a rich PES that is not only governed by the large-scale adatom geometry but also reflects competing electron localization between the Pt and substrate Fe atoms, giving rise to sets of geometrically almost identical structures whose energies nonetheless span an appreciable range. We further discuss the effect of substrate doping on this localization and argue that a combination of different experimental methods and theory is required to understand observed adatom geometries.

O 81.3 Thu 15:30 CHE 91

Growth and adsorption studies of magnetite nanoparticles on Al₂O₃ — ●MOHAMMAD EBRAHIM HAJI NAGHI TEHRANI^{1,2}, MARCUS CREUTZBURG¹, HESHMAT NOEI¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron (DESY), D-22603 Hamburg, Germany — ²Fachbereich Physik Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany

Magnetite (Fe₃O₄) is an important transition metal oxide with diverse applications in catalysis, data storage and biomedical imaging. In this study, we grow model catalyst magnetite nanoparticles on Al₂O₃(0001) surface under UHV conditions and at different temperatures: 150, 300, 500, and 700°C. Grazing incidence X-ray diffraction (GIXRD) and microscopy techniques were assisted in defining the facet and morphology of the developed nanoparticles, respectively. GIXRD outcomes indicated the formation of 111 oriented nanoparticles. Fourier transmission infrared reflection-absorption spectroscopy (FTIRRAS) was performed to study the adsorption of formic acid on magnetite/Al₂O₃ samples. The results demonstrate different types of adsorption and dissociation of formic acid. The results of this study can be applied as a paradigm in order to provide insight into the fundamental surface science of the next generation of the hierarchical organic-linked magnetite.

O 81.4 Thu 15:45 CHE 91

Fe₃O₄(111): surface structure and CO adsorption — ●JOHANNA HÜTNER¹, FLORIAN KRAUSHOFER¹, MATTHIAS MEIER^{1,2},

ZDENEK JAKUB³, CESARE FRANCHINI^{2,4}, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, GARETH S. PARKINSON¹, and JAN BALAJKA¹ — ¹Institute of Applied Physics, TU Wien, Austria — ²Computational Materials Physics, University of Vienna, Austria — ³CEITEC, Brno University of Technology, Czech Republic — ⁴Department of Physics and Astronomy, Università di Bologna, Italy

The surface structure of Fe₃O₄(111) has been the subject of an ongoing debate. The most stable termination, over a wide range of oxygen chemical potentials, has a layer of tetrahedrally coordinated iron atoms (Fe_{tet1}). We present AFM data that show an almost perfect grid of Fe_{tet1} atoms. In filled states STM images, iron atoms exhibit varying contrast, suggesting electronic structure variations among the cation sites. We study the adsorption of CO as a probe molecule on the Fe₃O₄(111) surface with noncontact AFM. The data show that CO adsorbs on top of Fe_{tet1} atoms at all coverages. We identify coverage-dependent adsorption structures with varying CO–CO spacings. We propose that the apparent CO–CO repulsion is a substrate-mediated effect that could be explained by charge redistribution in the surface. The CO ordering on a defect-free Fe₃O₄(111) surface is consistent with previously measured temperature programmed desorption data. Our findings contribute to the understanding of the electronic structure of the Fe₃O₄(111) surface and will be a requisite for modeling the adsorption of more complex molecules.

O 81.5 Thu 16:00 CHE 91

Reactivity and Influence of Catalytic Support Materials - a combined in situ and operando Infrared Study of CeO₂ —

●ERIC SAUTER¹, LACHLAN CAULFIELD¹, ALEXEI NEFEDOV¹, FLORIAN MAURER², DARIA GASHNIKOVINA², JAN-DIRK GRUNWALDT², and CHRISTOPH WÖLL¹ — ¹Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany — ²Institute for Chemical Technology and Polymer Chemistry (ITCP), Karlsruhe Institute of Technology (KIT), Engesserstraße 20, 76131 Karlsruhe, Germany

For most catalytic reactions the morphology, oxidation state and support were found to have a strong influence on the catalytic activity. Investigation of the most active sites, the support material and its behavior under model as well as realistic conditions is a prerequisite for a comprehensive understanding of catalytic processes. With Infrared Spectroscopy the surface composition and interaction with water, as well as carbon monoxide, can be investigated. The combination of low temperature, UHV gas adsorption as well as operando DRIFTS was used to characterize CeO₂ as catalytic support material. The adsorption of CO on single crystals was used as reference for the interpretation of more complicated spectra like powders or nanoparticles. The interactions with water have shown the high reactivity of the cerium oxide surface, which at the end leads to hydroxyl termination. With the use of in situ and operando Infrared spectroscopy the behavior of catalysts and their support material can be investigated, under realistic reaction conditions, into more detail.

O 81.6 Thu 16:15 CHE 91

Reduction of ceria with carbon monoxide - A high resolution, operando DRIFTS study — ●LACHLAN CAULFIELD, ERIC SAUTER, and CHRISTOPH WÖLL — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, 76344, Germany

In the last decades, ceria-based systems have seen an increase in popularity, due to its unique redox behavior and catalytic characteristics. Ceria powders are widely used in exhaust catalysts as well as other catalytic cycles, in particular due to the cheap and simple preparation methods. To gain a better understanding of the chemical and structural behavior of ceria nanoparticles and their interaction with gaseous molecules, an operando DRIFTS study was carried out. Following the complete oxidation of the powder samples, they were introduced in a carbon monoxide atmosphere at room temperature. By tuning the pressure of carbon monoxide gas as well as the reaction temperature inside the catalytic cell it was possible to observe the reduction and structural changes of ceria, induced by the presence of carbon monoxide. Using operando DRIFTS with carbon monoxide as a reducing agent as well as a probe molecule, the chemical and structural changes

of ceria can be easily investigated.

O 81.7 Thu 16:30 CHE 91

Tailoring photolytic reaction products by application of a low interacting rare gas decoupling layer — ●INGA LANGGUTH¹, JULIEN ROWEN², WOLFRAM SANDER², and KARINA MORGENSTERN¹ — ¹Chair of Physical Chemistry I, Ruhr-Universität Bochum, Germany — ²Chair of Organic Chemistry II, Ruhr-Universität Bochum, Germany

While carbene molecules are known to be highly reactive and short living reactants in gas phase, they are passivated on metal surfaces upon chemisorption. Thin solid rare gas films on coinage metal surfaces are a novel type of decoupling layer applicable for STM investigations. Thus, it is taken advantage of the low interacting chemical environment of xenon (Xe) monolayer on Ag(110) in order to investigate the photolytic reactions of classical carbenes. The reaction products of the carbene coupling formed on the Xe layer adsorbed on the metal are straightforwardly accessed by subsequent Xe desorption. Vast structural differences reveal that the reaction products formed on the Xe substantially differ from the species formed under the same conditions on the metal surface. Both reaction products are compared, revealing the tool function of the non-ionic, low interacting rare gas decoupling layer for tailoring reaction pathways.

O 81.8 Thu 16:45 CHE 91

Methanol and water compete for the same adsorption sites on In₂O₃(111) — CHIARA WAGNER¹, ANDREAS ZIEGLER², MICHAEL SCHMID¹, BERND MEYER², ULRIKE DIEBOLD¹, and ●MARGARETA WAGNER¹ — ¹Institute of Applied Physics, TU Wien, Austria — ²Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Germany

Indium oxide, a transparent conductive oxide, has been discovered to be a highly selective catalyst for methanol synthesis by CO₂ hydrogenation. The large surface unit cell of In₂O₃(111) exhibits a variety of Lewis acid and base sites for methanol and water adsorption. We compare the adsorption of both molecules under UHV conditions by employing AFM, STM, XPS, and TPD, together with DFT calculations. For medium coverages up to 9 molecules per surface unit cell we find a similar behavior: Initially, at room temperature, both molecules dissociate and protonate the most reactive O sites of the unit cell. When both molecules are dosed consecutively, methanol readily replaces water, while water is less efficient to substitute methanol. Below 300 K, both methanol and water adsorb molecularly in less-favored regions of the unit cell, still occupying the same sites and thus forming the same structural motifs. However, at coverages beyond 9 molecules per unit cell significant difference are found due to the ability of water to form and receive two hydrogen bonds instead of only one in the case of methanol.

O 81.9 Thu 17:00 CHE 91

How the (2x1) Reconstruction of Calcite (10.4) dominates the Desorption Kinetics of Water and Ethanol — ●TOBIAS DICKBREDER¹, DIRK LAUTNER², ANTONIA KÖHLER¹, LEA KLAUSFERING¹, RALF BECHSTEIN¹, and ANGELIKA KÜHNLE¹ — ¹Physical Chemistry I, Bielefeld University, 33615 Bielefeld, Germany. — ²Institute of Physical Chemistry, Johannes Gutenberg University Mainz, Duesbergweg 10-14, 55099 Mainz, Germany.

Calcite, the most abundant carbonate mineral in the Earth's crust, plays a dominant role in a variety of environmental processes. Upon cleavage, calcite exposes the (10.4) cleavage plane with a rectangular unit cell. Interestingly, several experiments have been presented that suggest a (2x1) surface reconstruction. However, clear experimental evidence and a theoretical confirmation were long missing. Recently, an atomic force microscopy study provided convincing experimental indication for a (2x1) reconstruction at 5 K. Nevertheless, it remained unclear how the (2x1) reconstruction affects the surface properties of calcite. Here, we present temperature-programmed desorption (TPD) curves of water and ethanol desorbing from calcite (10.4) around room temperature. Our experiments can be excellently described by a kinetic model considering two different adsorption positions, as would be present in case of a (2x1) reconstruction. This finding applies to the desorption of water and ethanol, suggesting that the effect is not molecule specific, but characteristic for the calcite cleavage plane. Our results, thus, demonstrate that the (2x1) reconstruction has significant impact on the interfacial properties of calcite.

O 81.10 Thu 17:15 CHE 91

Identification of Intermediates in the Reaction Pathway of SO₂ on the CaO surface: From Physisorption to Sulfite to Sulfate — ●NILS SCHEWE¹, FARAHNAZ MALEKI², GIOVANNI DI LIBERTO², HICHAM IDRIS¹, GIANFRANCO PACCHIONI², and CHRISTOPH WÖLL¹ — ¹Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, Eggenstein-Leopoldshafen, 76344, Germany — ²Department of Materials Science, University of Milano-Bicocca, 20125 Milano, Italy

We report on the results of a combined experimental and theoretical study of the interaction of sulfur dioxide with a calcium oxide single crystal surface. Our investigation of this model system for flue gas desulfurization was carried out on the CaO (001) surface under ultra-high-vacuum conditions. Combining UHV infrared reflection absorption spectroscopy (IRRAS) with x-ray photo electron spectroscopy (XPS) and ab initio density functional theory (DFT) calculations, we were able to identify a three-step reaction path way. After the physisorption of SO₂ at temperatures below 70 K on the ubiquitously hydroxylated surface, increasing the temperature leads to insertion of the SO₂ into surface hydroxyl groups. Around 110 K the first insertion leads to a surface hydrogen-sulfite, which evolves into a surface hydrogen-sulfate with the second insertion into another OH-group above 160 K. The surface state was confirmed by DFT, where the predicted IR vibrational frequencies align with the experimentally observed ones.

O 81.11 Thu 17:30 CHE 91

Interaction and structural behavior of thymidine on polycrystalline cerium oxide films — ●SASCHA MEHL¹, ANASTASIA DEINEKO², VIACHESLAV KALINOVYCH², TOMÁŠ SKÁLA², IVA MATOLINOVÁ², VLADIMÍR MATOLÍN², KEVIN C. PRINCE¹, and NATALIYA TSUD² — ¹Elettra-Sincrotrone Trieste S.C.p.A., in Area Science Park, Strada Statale 14, km 163.5, Basovizza (Trieste), 34149, Italy — ²Charles University, Faculty of Mathematics and Physics, Department of Surface and Plasma Science, V Holešovičkách 2, Prague, 18000, Czech Republic

Thymidine (dT) is a nucleoside and therefore important for the contribution to in-depth studies of cerium oxide as a potential sensing material applicable for analytes such as DNA. This topic contributes to a survey which embraces from simple nucleobases to more complex DNA components as probe molecules on a wide array of different CeO₂ films. Consequently, bridging the material gap and deposition of dT from aqueous solution on compact CeO₂ allows us to get closer towards more realistic conditions. The goals of the present study were the elucidation of the electronic structure of the biomolecule-cerium oxide interface, as well as the adsorption geometry and thermal stability of the nucleoside. Adsorption studies were carried out by using SRPES, RPES and NEXAFS techniques. A noteworthy result was the successful deposition of dT from solution and in gas phase without decomposition, which was never previously reported in the literature. The analysis of the experimental data revealed that dT molecules anchor on CeO₂ film via two carbonyl oxygen atoms and an amino group.

O 81.12 Thu 17:45 CHE 91

Modeling Bio-MOFs for Anesthetic Xenon Recovery: The Role of Noncovalent Host-Guest Interactions — ●YELIZ GURDAL — Lehrstuhl für Theoretische Chemie II, Ruhr-Universität Bochum, 44780 Bochum, Germany — Research Center Chemical Sciences and Sustainability, Research Alliance Ruhr, 44780 Bochum, Germany — Department of Bioengineering, Adana Alparslan Türkeş Science and Technology University, 01250 Adana, Türkiye

Taking advantage of metal organic frameworks (MOFs) for anesthetic Xe recovery has been a recent topic studied rarely in the literature. In this work, Xe recovery performances of 43 biological MOFs (Bio-MOFs) consisting of biocompatible cations and linkers have been studied by means of Grand Canonical Monte Carlo, Density Functional Theory, and Molecular Dynamics simulations. Results reveal that Xe-host interactions are maximized mainly due to noncovalent interactions of Xe, such as charge-induced dipole and aerogen- π interactions. Polarized Xe atoms in the vicinity of cations/anions as well as π systems suggest enhanced guest-host interactions. The results of this work depict examples of superficially studied aerogen interactions playing an important role in selective adsorption of Xe in porous materials. This study has received funding from the TUBITAK under the 1002 Short Term R&D Funding Program (grant agreement No: 120Z160).