O 39: Oxides and Insulator Surfaces: Adsorption and Reaction of Small Molecules I

Time: Tuesday 14:00–15:30 Location: H4

O 39.1 Tue 14:00 H4

Instrumental Innovations for Model Single-Atom Catalysis — •Jiří Pavelec, David Rath, Chunlei Wang, Nail Barama, Panukorn Sombut, Matthias Meier, Michael Schmid, Ulrike Diebold, and Gareth S. Parkinson — TU Wien, Vienna, Austria

Single-atom catalysts (SACs) reduce reliance on precious materials by using individual atoms as active sites. Infrared spectroscopy of adsorbed CO is widely used to probe these sites, but spectral interpretation and charge-state assignment remain debated. Surface science studies of model SACs could provide valuable benchmarks, but progress has been hindered by a lack of model systems and challenges in detecting low coverages of intermediates.

Here, I introduce a novel approach to infrared reflection absorption spectroscopy (IRAS) that adjusts the incidence angle, which resolves signal-to-noise issues on dielectrics [1]. As a case study, we investigated CO titration of rhodium-based SACs on a $Fe_3O_4(001)$ support. The spectra reveal Rh_1CO monocarbonyls as the dominant species. Meanwhile, the $Rh_1(CO)_2$ gem-dicarbonyl arises solely from the breakup of minority Rh_2 dimers, as confirmed by STM movies and theoretical modeling [2]. Though less prevalent in our UHV study, $Rh_1(CO)_2$ may play a critical role under realistic conditions.

Combining advancements in IRAS with a detailed understanding of model SACs provides valuable benchmarks for theoretical studies and spectral references for researchers working with less-defined, high-surface-area powder catalysts. [1] D. Rath et al., Rev. Sci. Instrum. 95, (2024). [2] C. Wang et al., Angew. Chem. Int. Ed. 63, (2024).

O 39.2 Tue 14:15 H4

Structure and oelic acid adsorption properties of magnetite nanoparticles on $SrTiO_3$ — •mohammad ebrahim haji naghi tehrani[1,2], lucio martinelli[3], daniel silvan dolling[1,2], marcus creutzburg[1], ming chao kao[1,2], alexander meinhardt[1,2], mona kohantorabi[1], heshmat noei[1], and andreas stierle[1,2] — [1]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — [2]Fachbereich Physik Universität Hamburg, Hamburg, Germany — [3]Institut Néel, CNRS, Grenoble INP, Université Grenoble Alpes, Grenoble, France

The underlying explanation for the exceptional mechanical properties of hierarchically arranged magnetite nanoparticle super-crystals is closely linked to understanding the oxide-organic interface between the magnetite nanoparticles (NPs) and the oleic acid (OA) molecules. We studied the shape and surface structure changes of the magnetite NPs induced by crosslinking the OA molecules. In this regard, magnetite NPs were grown by reactive physical vapor deposition on a strontium titanate single crystalline surface (STO(001)). The structural and morphological changes in the NPs were monitored under ultra-high vacuum (UHV) conditions employing synchrotron-based grazing incidence X-ray diffraction (GIXRD). We evidenced the growth of (001) oriented magnetite NPs with predominant (111) side facets. Additionally, our results indicate an increase in the NP lattice constant after OA adsorption, which may be attributed to the incorporation of oxygen vacancies.

O 39.3 Tue 14:30 H4

Towards Understanding the Photoreactivity of $SrTiO_3$ through Studies in Ultra-High Vacuum — •Anna Lemperle, Philip Petzoldt, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Heterogeneous photocatalysis offers the prospect of utilising solar energy for the zero-carbon production of hydrogen from water. The most prominent photocatalytic materials currently employ $SrTiO_3$ as the light harvesting semiconductor. While these catalysts have been shown to promote a stoichiometric reaction, their photocatalytic performance is still insufficient for economically viable application. As their structural complexity impedes mechanistic studies, model systems are necessary to elucidate individual reaction steps and connect catalytic results to distinct catalyst properties. This approach aims to attain a molecular understanding of the reaction mechanisms involved in water splitting in order to enable a more targeted design of photocatalysts. In this contribution, we discuss first results on the reactivity of water and oxygen on the bare $SrTiO_3(110)$ surface. Results obtained by combining temperature programmed desorption and studies under illumination highlight the importance of bulk and surface oxygen for the reactivity of $SrTiO_3$.

O 39.4 Tue 14:45 H4

Effect of Mn and V Doping on the OER activity of $Co_3O_4(001)$: insights from DFT+U calculations — •Palani Muthu Kumar and Rossitza Pentcheva — Department of Physics, University of Duisburg-Essen

Using density functional theory calculations with a Hubbard U term (DFT+U), we study the effect of Mn and V doping on the oxygen evolution reaction (OER) at the $Co_3O_4(001)$ surface. In bulk, both dopants favor the octahedral over the tetrahedral site, providing a foundation for understanding the incorporation at the surface. Both at the A and the B-terminations of $Co_3O_4(001)$, Mn doping at a surface octahedral site enhances the overpotential, reducing overall the OER efficiency. In contrast, at the B-layer, V doping at a surface octahedral site reduces the overpotential from 0.48V (pristine) to 0.43 V, retaining the Co_{oct} reaction site. At the pristine A-surface, η is higher for a tetrahedral (0.74 V) vs. octahedral surface Co site (0.55 V). This trend is reversed for V-doping in the subsurface octahedral site which leads to the lowest overpotential of 0.18 V at the Co_{tet} reaction site. In all studied cases, the potential determining step is the deprotonation of *OH to *O. The improved catalytic activity due to V doping is attributed to a modified charge redistribution on the surface, leading to favorable binding energies of the intermediates. Funding by DFG within CRC247 and computational time at the Leibniz Rechenzentrum are gratefully acknowledged.

O 39.5 Tue 15:00 H4

Complex structural arrangements at the $CO_2/In_2O_3(111)$ interface — Sarah Tobisch[1], Andreas Ziegler[2], Marco Knapp[1], Michael Schmid[1], Ulrike Diebold[1], Bernd Meyer[2], and •Margareta Wagner[1] — [1]Institut für Angewandte Physik, TU Wien — [2]ICMM & CCC, FAU-Erlangen-Nürnberg

Promising catalysts for the hydrogenation of CO_2 to methanol are highly desired to address the pressing issue of rising carbon emissions. Since reactions take place at the interface, understanding the fundamental properties and behavior of molecular species on well-defined surfaces is crucial for designing model catalysts.

In_2O_3 has gained attention as catalytic material due to its high selectivity for methanol synthesis via CO_2 reduction. In this work, the adsorption and interaction of CO_2 molecules on $In_2O_3(111)$ were investigated in detail at the atomic scale and under UHV conditions. We employ non-contact atomic force microscopy (AFM) and compared our findings with results from temperature programmed desorption (TPD) and x-ray photoelectron spectroscopy (XPS) measurements, as well as density functional theory (DFT) calculations. AFM images of the $In_2O_3(111)$ surface show 10 molecular features per surface unit cell arranged in a systematic and uniform order, albeit breaking the threefold symmetry of the substrate surface. The adsorption sites of all individual molecules were identified; some of them are carbonate species, in agreement to XPS showing a mixture of CO_2 molecules and CO_3^{2-}. Moreover, the desorption and structural evolution with increasing temperature was studied.

O 39.6 Tue 15:15 H4

Adsorption and activation of CO_2 on CeO_2 surfaces — •Zairan Yu, Shuang Chen, Wangtao Li, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

CO_2 activation and its subsequent transformation into valuable chemicals pose significant challenges in heterogeneous catalysis. Most studies have focused on powdered catalysts with various facets and unknown defect densities, whereas much less is known about the surface chemistry of CO_2 on well-defined oxide surfaces. Here, we investigate CO_2 adsorption and activation on fully oxidized $CeO_2(111)$ single-crystal surfaces using polarization-resolved IR reflection absorption spectroscopy (IRRAS). The comprehensive IRRAS data reveal that CO_2 is weakly bound to $CeO_2(111)$ at 117 K in a linear, physisorbed state. At elevated temperatures (300 K) and pressures, CO_2

undergoes activation forming an unusual horizontal carbonate. Additionally, in the presence of surface hydroxyl groups, formate and HCO_3 species are identified. These experimental findings are supported by complementary theoretical analysis. Furthermore, the IRRAS results are in excellent agreement with the in situ transmission IR data obtained for CO adsorption on octahedral ceria nanoparticles, which predominantly expose (111) facets. This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) -Project-ID 426888090- SFB 1441.