

O 88: Poster Session VII: Oxides and insulators: Adsorption and reaction of small molecules I

Time: Thursday 10:30–12:30

Location: P

O 88.1 Thu 10:30 P

Electron Stimulated Desorption of Vanadyl-Groups from Vanadium Oxide Thin Films on Ru(0001) probed with STM — ●PIOTR IGOR WEMHOFF, YING WANG, and NIKLAS NILIUS — Carl von Ossietzky University, Institute of Physics, D-26111 Oldenburg,

Low-temperature STM is employed to study electron-stimulated desorption of V=O groups from a vanadium oxide film grown on Ru(0001). The film is built of an ordered network of three, six and twelve membered V-O rings, the former ones capped by upright vanadyls. These V=O groups can be reproducibly desorbed by electron injection from the STM tip. From hundreds of experiments, desorption rates are determined as a function of bias voltage and tunneling current. The rates show a threshold behavior with +3.3 V and -2.6 V bias onsets, and depend quadratically (cubically) on current for positive (negative) polarity. Apparently, V=O desorption is a multi-electron process that proceeds via resonant tunneling into bonding (anti-bonding) resonances of the V=O system followed by vibrational ladder climbing in the binding potential. The involved electronic states are identified in STM conductance spectra of the oxide surface.

O 88.2 Thu 10:30 P

Heterogeneous Adsorption and Local Ordering of Formic Acid on Magnetite (111) — ●MARCUS CREUTZBURG^{1,2}, KAI SELLSCHOPP³, STEFFEN TOBER^{1,2}, VEDRAN VONK¹, HESHMAT NOEI¹, GREGOR B. VONBUN-FELDBAUER³, and ANDREAS STIERLE^{1,2} — ¹DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — ²Fachbereich Physik, Universität Hamburg — ³Institut für Keramische Hochleistungswerkstoffe, Technische Universität Hamburg

Magnetite (Fe₃O₄) is an important and diverse transition metal oxide with applications as a catalyst in various industrial processes such as the water-gas shift reaction [1]. Formic acid (HCOOH), as the elementary carboxylic acid, is proposed to occur as an intermediate during this reaction. In material science magnetite nanoparticles are linked by larger carboxylic acids to form supercrystals with exceptional mechanical properties [2]. Thus, a detailed atomic understanding of the interaction at the magnetite surface/carboxylic acid interface is vital. In this contribution the adsorption of formic acid on the magnetite (111) single crystal surface is studied under UHV conditions at room temperature. Our FT-IRRA spectroscopy results and DFT calculations show dissociative adsorption of formic acid in quasi-bidentate and chelating geometries, the latter being stabilized by the presence of tetrahedral iron vacancies at the surface. The locally observed ($\sqrt{3} \times \sqrt{3}$)R30° superstructure by STM consists of formate in a triangular arrangement, adsorbed predominantly in chelating geometry.

[1] M. Zhu *et al.*, ACS Catal. **6**, 722-732 (2016)[2] A. Dreyer *et al.*, Nat. Mater. **15**, 522-528 (2016)

O 88.3 Thu 10:30 P

Atomic-Scale Studies of Hydroformylation on Rh₁/Fe₃O₄(001) — ●MANUEL ULREICH¹, ZDENEK JAKUB¹, FLORIAN KRAUSHOFER¹, MATTHIAS MEIER^{1,2}, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, CESARE FRANCHINI², and GARETH S. PARKINSON¹ — ¹Institute of Applied Physics, TU Wien, 1040 Vienna, Austria — ²Center for Computational Materials Science, University of Vienna, 1090 Vienna, Austria

Hydroformylation (alkene + CO + H₂ → aldehyde) is an important industrial reaction typically performed in solution using highly-selective mononuclear complexes. Recently, Rh-based “single-atom” catalysts (SACs) have been shown to catalyze this reaction heterogeneously with similar levels of selectivity, suggesting SAC can be a strategy to heterogenize problematic reactions. The main advantage of heterogeneous catalysis is easy separation of the catalyst from the products. SAC is intended to unify this advantage with the high selectivity and activity of homogeneous catalysis. In this talk, TPD and XPS are used to study the coadsorption of ethylene and carbon monoxide on isolated Rh₁ adatoms on Fe₃O₄(001), a critical first step in the hydroformylation reaction. Our results show that 2-fold coordinated Rh₁ adatoms on Fe₃O₄(001) are able to coadsorb C₂H₄ and CO, but 5-fold coordinated Rh₁ adatoms cannot. We conclude that gaining control of the active site geometry is key to the development of highly-selective single-atom catalysis.

O 88.4 Thu 10:30 P

Comparison of single Rh adatoms on α -Fe₂O₃(1 $\bar{1}$ 02) and TiO₂(110) stabilized by adsorbed water — ●LENA HAAGER¹, FLORIAN KRAUSHOFER¹, MORITZ EDER², ALI RAFSANJANI-ABBASI¹, GIADA FRANCESCHI¹, MICHELE RIVA¹, PANUKORN SOMBUT¹, MARLENE ATZMUELLER¹, MICHAEL SCHMID¹, CESARE FRANCHINI^{3,4}, ULRIKE DIEBOLD¹, and GARETH S. PARKINSON¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²Chair of Physical Chemistry, TU München, Germany — ³University of Vienna, Vienna, Austria — ⁴Università di Bologna, Bologna, Italy

Despite its high cost, rhodium is a widely applied catalyst primarily used in nanoparticle form for converting toxic gases in automobiles. It is also utilized in organometallic complexes, such as the Wilkinson catalyst, for the hydrogenation of olefins and for converting alkenes to aldehydes through a process known as hydroformylation. So-called “single-atom” catalysis offers an opportunity to reduce the amount of Rh required for traditional heterogeneous catalysis, and a path to heterogenize homogeneous reactions, with the advantage of easy separation of catalyst and product.

Using STM, nc-AFM and XPS we compare the stability of Rh adatoms on two different model supports: α -Fe₂O₃(1 $\bar{1}$ 02) and TiO₂(110), both in UHV and 2 * 10⁻⁸ mbar of water. We show that the Rh adatoms on α -Fe₂O₃(1 $\bar{1}$ 02) sinter in UHV, but are stabilized by water up to 150 °C through coordination to 2-3 OH ligands. In contrast, Rh adatoms on TiO₂(110) could not be stabilized above room temperature in either environment.

O 88.5 Thu 10:30 P

Unravelling CO Adsorption on Model Single-Atom Catalysts (SAC) — JAN HULVA¹, ●MATTHIAS MEIER^{1,2}, ROLAND BLIEM¹, ZDENEK JAKUB¹, FLORIAN KRAUSHOFER¹, MICHAEL SCHMID¹, ULRIKE DIEBOLD¹, CESARE FRANCHINI^{2,3}, and GARETH S. PARKINSON¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²Computational Materials Physics, University of Vienna, Vienna, Austria — ³Alma Mater Studiorum, Università di Bologna, Bologna, Italy

The electronic structure of a surface atom is crucial when it comes to predicting and understanding its binding to adsorbates. This has been demonstrated in depth on metal surfaces, where the d-band center of mass and d-band filling are two of the main descriptors when it comes to defining the adsorption of small molecules. We propose an extension of this model towards oxide surfaces and SACs, based on a combination of density functional theory (DFT) and surface sensitive techniques (Hulva *et al.*, Science (in press)). The same rules regarding the electronic structure of the binding atom apply and govern the adsorption energies. But additionally, the exact local environment, affecting the electronic states, also leads to two particular deviations. Firstly, if the surface atom is saturated in ligands, no matter the electronic structure, the atom will bind CO poorly, and therefore the metal will be almost inert. On the other hand, if the coordination of the metal atom at the surface is low and the CO adsorption geometry is not ideal, CO-induced relaxations occur. This can lead to strong offsets with respect to the adsorption energy estimated by the electronic structure alone.

O 88.6 Thu 10:30 P

Rapid surface oxygen exchange at the hematite-water interface — ZDENEK JAKUB¹, MATTHIAS MEIER¹, FLORIAN KRAUSHOFER^{1,2}, JAN BALAJKA¹, JIRI PAVELEC¹, MICHAEL SCHMID¹, CESARE FRANCHINI^{2,3}, ULRIKE DIEBOLD¹, and ●GARETH S. PARKINSON¹ — ¹TU Wien, Vienna, Austria — ²University of Vienna, Vienna, Austria — ³Università di Bologna, Bologna, Italy

It seems natural to assume that low-index surfaces of insoluble minerals do not exchange atoms with their surroundings. Here, we will show using surface science techniques that all oxygen atoms on the *r-cut* (1-102) surface are exchanged with oxygen from surrounding water vapour within minutes at temperatures below 70°C, even though the structure remains intact. Density functional theory computations suggest the oxygen exchange occurs during on-surface diffusion, and that cooperative stabilization of an HO-HOH-OH complex compensates the cost of the lattice oxygen extraction. Such a rapid oxygen exchange mechanism affects the isotope composition in the near-surface region, and the knowledge of the mineral-liquid interface dynamics is relevant for many fields ranging from hydrogen production to paleoclimatology.

O 88.7 Thu 10:30 P

Real-time Dynamics During TiO₂ Photocatalysis — ●MICHAEL WAGSTAFFE¹, LUKAS WENTHAUS^{1,2}, ADRIAN DOMINGUEZ-CASTRO³, THOMAS FRAUENHEIM^{3,4,5}, ADRIEL DOMINGUEZ³, ANGEL RUBIO^{2,6}, WILFRIED WURTH^{1,2,7}, ANDREAS STIERLE^{1,7}, and HESHMAT NOEI¹ — ¹DESY, 22607, Hamburg, Germany — ²CFEL, 22761, Hamburg, Germany — ³BCCMS, 28359, Bremen, Germany — ⁴CSAR, 518110, Shenzhen, China — ⁵CSRC, 100193, Beijing, China — ⁶MPI for the Structure and Dynamics of Matter, 22761, Hamburg, Germany — ⁷Fachbereich Physik Universität Hamburg, 20355, Hamburg, Germany

Studies of photocatalytic reactions on TiO₂ are instrumental to the development of technology used for self-cleaning surfaces and for air and water purification. We utilize femtosecond X-ray laser pulses synchronized with an optical laser to directly follow the reaction dynamics of the photooxidation of CO on the anatase TiO₂(101) surface. Our time-resolved soft X-ray photoemission spectroscopy results, combined with theoretical calculations, allow us to elucidate the mechanism of oxygen activation and provides evidence of ultrafast timescales. The reaction takes place between 1.2 - 2.8 (\pm 0.2) ps after irradiation with an ultrashort laser pulse, resulting in CO₂. No intermediate species were observed on a picosecond time scale. Theoretical calculations predict that the reaction can be initiated following the formation an O₂-TiO₂ charge-transfer complex. This allows the reaction to take place following laser illumination at a photon energy of 1.6 eV (770 nm), following the direct transfer of electrons from TiO₂ to physisorbed O₂.

O 88.8 Thu 10:30 P

Interaction of formic acid with magnetite surfaces – the DFT perspective — ●KAI SELLSCHOPP¹, MARCUS CREUTZBURG^{2,3}, BJÖRN ARNDT^{2,3}, HESHMAT NOEI², ANDREAS STIERLE^{2,3}, STEFAN MÜLLER¹, and GREGOR VONBUN-FELDBAUER¹ — ¹Institute of Advanced Ceramics, Hamburg University of Technology — ²DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — ³Fachbereich Physik, Universität Hamburg

Formic acid (HCOOH) molecules are present in atmospheric conditions and furthermore, can be seen as the smallest representative of the carboxylic acid family. Magnetite (Fe₃O₄) nanoparticles are utilized in various applications, such as waste water treatment, single-atom catalysis or hybrid materials. Therefore, studying the interaction of formic acid with the major facets of magnetite nanoparticles, namely the {111} and {001} facets, is highly interesting for improving their performance. Here, we present results on the adsorption of formic acid on both magnetite (111) and (001) studied through Density Functional Theory (DFT) calculations. In agreement with surface science experiments, the formation of a ($\sqrt{3} \times \sqrt{3}$)R30° superstructure and two different binding modes, a quasi-bidentate and a chelating mode, are found on the (111) surface, and the observed restructuring of the (001) surface is explained. In all studied cases, the dissociation of formic acid into formate and hydrogen is energetically favourable. Calculated surface phase diagrams give further insights in the processes involved under experimental conditions and indicate a stabilisation of iron vacancies on the (111) surface upon formic acid dissociation.