

## O 119: Oxides III: Single-Atom Catalysis, Iron Oxides

Time: Friday 10:30–12:45

Location: REC C 213

**Invited Talk**

O 119.1 Fri 10:30 REC C 213  
**theoretical studies on the state and fate of single atom catalysts: from hydroformylation to CO oxidation** — ●FELIX STUDDT — Karlsruhe Institute of Technology, Institute of Catalysis Research and Technology, Eggenstein-Leopoldshafen, Germany

Single atom catalysts (SAC) are attracting widespread attention as they promise the highest achievable atom efficiency in heterogeneously catalyzed reactions. Herein, we show theoretical calculations of the state, stability and activity of SAC supported on different oxide surfaces for the hydroformylation reaction and evaluate differences between the homogeneous catalysts that are used nowadays. Additionally, we use quantum chemical calculations to reveal the reaction mechanism of SAC for a highly selective tandem olefin isomerization-hydrosilylation process. Finally, we will show how the stability of Pt single atoms supported on ceria depend on reaction conditions and how their state relates to CO oxidation activity.

O 119.2 Fri 11:00 REC C 213  
**Probing structural changes upon carbon monoxide coordination to single metal adatoms** — ●PAUL T. P. RYAN<sup>1,2</sup>, MATTHIAS MEIER<sup>3,4</sup>, ZEDENEK JAKUB<sup>3</sup>, JAN BALAJKA<sup>4</sup>, JAN HULVA<sup>3</sup>, DAVID J. PAYNE<sup>2</sup>, TIEN-LIN LEE<sup>1</sup>, CESARE FRANCHINI<sup>4</sup>, FRANCESCO ALLEGRETTI<sup>5</sup>, GARETH S. PARKINSON<sup>3</sup>, and DAVID A. DUNCAN<sup>1</sup> — <sup>1</sup>Diamond Light Source, Didcot, OX11 0QX UK — <sup>2</sup>Department of Materials, Imperial College London, SW7 2AZ UK — <sup>3</sup>Institute of Applied Physics, TU Wien, Austria — <sup>4</sup>Faculty of Physics and Center for Computational Materials Science, University of Vienna, Austria — <sup>5</sup>Physics Department E20, Technical University of Munich, 85748 Garching, Germany

The application of highly accurate, but yet computationally cheap, density functional theory (DFT) calculations allows for the fine tuning of catalyst development. However, it is necessary to have stringent benchmarks against which these calculations are tested. In this work, the adsorption height of Ag adatoms on the Fe<sub>3</sub>O<sub>4</sub>(001) surface after exposure to CO was determined using normal incidence X-ray standing waves. The Ag adatoms bound to CO (Ag<sup>CO</sup>) are found to be pulled out of the surface to an adsorption height of 1.15 ± 0.08 Å, compared to the previously measured height of 0.96 ± 0.03 Å for bare Ag adatoms[1]. Utilising DFT+vdW+U calculations with the substrate unit cell dimension fixed to the experimental value, the predicted adsorption height for Ag<sup>CO</sup> was 1.16 Å, in remarkably good agreement with the experimental results. [1] M. Meier et. al., *Nanoscale* 10, 2226 (2018)

O 119.3 Fri 11:15 REC C 213  
**Atomic-Scale Studies of Hydroformylation on Rh<sub>1</sub>/Fe<sub>3</sub>O<sub>4</sub>(001)** — ●MANUEL ULREICH<sup>1</sup>, ZDENĚK JAKUB<sup>1</sup>, FLORIAN KRAUSHOFER<sup>1</sup>, MATTHIAS MEIER<sup>1,2</sup>, MICHAEL SCHMID<sup>1</sup>, ULRIKE DIEBOLD<sup>1</sup>, CESARE FRANCHINI<sup>2</sup>, and GARETH S. PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, 1040 Vienna, Austria — <sup>2</sup>Center for Computational Materials Science, University of Vienna, 1090 Vienna, Austria  
 Hydroformylation (alkene + CO + H<sub>2</sub> → 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 Rh<sub>1</sub> adatoms on Fe<sub>3</sub>O<sub>4</sub>(001), a critical first step in the hydroformylation reaction. Our results show that 2-fold coordinated Rh<sub>1</sub> adatoms on Fe<sub>3</sub>O<sub>4</sub>(001) are able to coadsorb C<sub>2</sub>H<sub>4</sub> and CO, but 5-fold coordinated Rh<sub>1</sub> adatoms cannot. We conclude that gaining control of the active site geometry is key to the development of highly-selective single-atom catalysis.

O 119.4 Fri 11:30 REC C 213  
**Influence of Surface Dynamics on Oxidation Processes: Case Study of H<sub>2</sub>O<sub>surf</sub> Desorption on Fe<sub>3</sub>O<sub>4</sub>(001)** — ●MATTHIAS MEIER<sup>1,2</sup>, JAN HULVA<sup>1</sup>, ZDENĚK JAKUB<sup>1</sup>, FLORIAN KRAUSHOFER<sup>1</sup>,

MANUEL ULREICH<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, ULRIKE DIEBOLD<sup>1</sup>, CESARE FRANCHINI<sup>2</sup>, and GARETH S. PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien — <sup>2</sup>Center for Computational Materials Science, Faculty of Physics, University of Vienna

Experiments performed under UHV, on so called “model systems”, where surfaces are well defined and controlled, are combined with DFT calculations to propose reaction mechanisms and determine activation barriers of relevant chemical processes.

Fe<sub>3</sub>O<sub>4</sub>(001) is such a model system. It is debatable whether the observed surface in UHV is also maintained under real catalytic conditions, such as high pressure, or electrochemical environments. Our results indicate that the surface undergoes modifications, already in UHV and in some cases even below room temperature. O distortions and Fe displacements can occur for any given transition state along a reaction path, if energetically favored. So if their costs are at least compensated by the gain in adsorption energies of present adsorbates or the reduction of activation barriers.

We show here an example of how these surface dynamics influence H mobility, the formation and extraction of H<sub>2</sub>O<sub>surf</sub> and their consequences on experimental observations.

O 119.5 Fri 11:45 REC C 213  
**Formic acid adsorption and dissociation on magnetite (111)** — ●KAI SELLSCHOPP<sup>1</sup>, MARCUS CREUTZBURG<sup>2,3</sup>, BJÖRN ARNDT<sup>2,3</sup>, HESHMAT NOEI<sup>2</sup>, ANDREAS STIERLE<sup>2,3</sup>, STEFAN MÜLLER<sup>1</sup>, and GREGOR VONBUN-FELDBAUER<sup>1</sup> — <sup>1</sup>Institute of Advanced Ceramics, Hamburg University of Technology — <sup>2</sup>DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — <sup>3</sup>Fachbereich Physik, Universität Hamburg

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) nanoparticles are utilized in different fields like waste water treatment, single-atom catalysis or hybrid materials. Formic acid molecules are usually present in atmospheric conditions. Further, they can be seen as the smallest representative of the carboxylic acid family. Therefore, studying the interaction of formic acid with the major facets of magnetite nanoparticles, namely the {111} and {001} facets, is highly interesting for their various applications. Here, we present results on the adsorption of formic acid on magnetite (111) studied through calculations based on Density Functional Theory (DFT). In agreement with surface science experiments, the formation of a (√3 × √3)R30° superstructure and two different binding modes, a quasi-bidentate and a chelating mode, are found. Independent of the binding mode, the formic acid dissociates on the surface into formate and hydrogen. Calculated surface phase diagrams give further insights in the processes involved under experimental conditions and indicate a separation of the formate and the residual hydrogen originating from the formic acid dissociation.

O 119.6 Fri 12:00 REC C 213  
**Formic acid induced superstructure formation on magnetite (111)** — ●MARCUS CREUTZBURG<sup>1,2</sup>, HESHMAT NOEI<sup>1</sup>, BJÖRN ARNDT<sup>1,2</sup>, VEDRAN VONK<sup>1</sup>, ELIN GRÄNÄS<sup>1</sup>, KAI SELLSCHOPP<sup>3</sup>, GREGOR VONBUN-FELDBAUER<sup>3</sup>, and ANDREAS STIERLE<sup>1,2</sup> — <sup>1</sup>DESY NanoLab, Deutsches Elektronen-Synchrotron, Hamburg — <sup>2</sup>Fachbereich Physik, Universität Hamburg — <sup>3</sup>Institute of Advanced Ceramics, Hamburg University of Technology

Magnetite (Fe<sub>3</sub>O<sub>4</sub>) 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]. In material science magnetite nanoparticles are linked by oleic acid to form supercrystals with exceptional mechanical properties [2]. However, the oxide/carboxylic acid interface is not fully understood. In this contribution the adsorption of formic acid on the magnetite (111) single crystal surface is studied under UHV conditions at room temperature. Formic acid dissociates upon adsorption and forms a (√3 × √3) R30° superstructure, which is investigated using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). Fourier transform infrared reflection-absorption spectroscopy (FT-IRRAS) results indicate two different formic acid adsorption sites. Density functional theory (DFT) calculations of the two adsorption structures prove that both configurations form the superstructure and are the most stable under our experimental working conditions.

[1] M. Zhu et al., *ACS Catalysis*. 6, 722-732 (2016).

[2] A. Dreyer *et al.*, Nature Materials **15**, 522-528 (2016)

O 119.7 Fri 12:15 REC C 213

**Atomistic modelling of the structural and dynamical behaviour of interfaces between biomolecules and magnetite** — MINE KONUK<sup>1</sup>, KAI SELLSCHOPP<sup>2</sup>, GREGOR VONBUN-FELDBAUER<sup>2</sup>, and ●ROBERT HORST MEISSNER<sup>1,3</sup> — <sup>1</sup>Institute of Polymer and Composites, Hamburg University of Technology — <sup>2</sup>Institute of Advanced Ceramics, Hamburg University of Technology — <sup>3</sup>MagIC Magnesium Innovation Centre, Institute of Materials Research, Helmholtz Zentrum Geesthacht

Based on a newly developed force field for magnetite surfaces that mimics the charge migration of a Bader charge analysis, results of atomic-level calculations on the stability of (001) and (111) magnetite surfaces are presented. The recently proposed subsurface cation vacancy (SCV) termination on Fe<sub>3</sub>O<sub>4</sub>(001) or the distorted bulk truncation (DBT) are now stable configurations in MD simulations using typical experimental conditions. Within this formalism, the electrostatic interactions between magnetite surfaces and organic molecules with a bidental or quasi-bidental binding motif are also optimized. The results for formic acid adsorption on the (111) or (001) magnetite surface are well in line with the latest experimental findings and *ab initio* calculations. The stability of molecular and dissociated water clusters on SCV and DBT surfaces is additionally investigated and it is further shown that on a DBT surface model a layer of ordered water rows, forming a network of hydrogen bonds, is thermodynamically more stable at room temperature than the same amount of water adsorbed on a SCV termination.

O 119.8 Fri 12:30 REC C 213

**Near-surface diffusion of Fe<sub>3</sub>O<sub>4</sub> (001) observed by nuclear forward scattering** — ●STEFFEN TOBER<sup>1,2</sup>, JAN-CHRISTIAN SCHOBER<sup>1,2</sup>, ESKO ERIK BECK<sup>1,2</sup>, GUILHERME DALLA LANA SEMIONE<sup>1,2</sup>, SIMON CHUNG<sup>1,2</sup>, KAI SCHLAGE<sup>1</sup>, OLAF LEUPOLD<sup>1</sup>, ILYA SERGEEV<sup>1</sup>, RENÉ STEINBRÜGGE<sup>1</sup>, HANS-CHRISTIAN WILLE<sup>1</sup>, HESHMAT NOEI<sup>1</sup>, VEDRAN VONK<sup>1</sup>, and ANDREAS STIERLE<sup>1,2</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron, Hamburg — <sup>2</sup>Universität Hamburg, Fachbereich Physik

The near surface defect structure is of key importance to tune the performance of magnetite (Fe<sub>3</sub>O<sub>4</sub>) in catalysts and spintronic devices. Recent observations of the formation and lifting of the subsurface cation vacancy reconstruction on the (001) surface indicate the presence of a near surface transport process influencing surface phenomena [1,2]. The near surface cation transport between a homoepitaxially grown <sup>57</sup>Fe<sub>3</sub>O<sub>4</sub> layer and a (001) oriented Fe<sub>3</sub>O<sub>4</sub> single crystalline substrate was studied by nuclear forward scattering at the P01 Beamline of PETRAIII. A smearing of the isotope distribution at the film/substrate interface was observed by nuclear resonant reflectivity [3] as a function of temperature in vacuum or oxygen, indicating interfacial cation transport. The sample's chemical state was monitored by time spectra. These results allow to quantify the mobility of near surface cations in magnetite.

[1] Arndt, B. *et al.* Chem. Comm. 1, 92 (2019)

[2] Arndt, B. *et al.* Surf. Sci. 653, 76 (2016)

[3] Andreeva *et al.*, Mosc. Univ. Phys. Bull. 63, 132 (2008)