

## O 10: Focus Session: Single Atom Catalysis 2

Time: Monday 15:00–17:30

Location: H4

## Topical Talk

O 10.1 Mon 15:00 H4

**Atomically-precise design of low-nuclearity catalysts** — ●SHARON MITCHELL and JAVIER PÉREZ-RAMÍREZ — ETH Zurich, Zurich, Switzerland

Nanostructured catalysts incorporating supported metal atoms or small clusters of defined size and chemical composition attract considerable attention because of their potential to maximize resource efficiency. When optimally assembled, all the metal nuclei can participate in the catalytic cycle with properties tailored to deliver high specific activity and stable performance. Over the past decade, the number and diversity of reported systems have exploded as researchers attempted to control the nanostructure with increasing atomic precision. Nonetheless, spatially resolving the architecture and properties of supported low-nuclearity catalysts using existing analytical methods remains challenging. This talk will discuss approaches to prepare and characterize catalytic materials integrating low-nuclearity metal species. Topical case studies will introduce recent achievements and challenges, including the synthesis of single-atom catalyst libraries with controlled density, the precision synthesis of low-nuclearity species, tools for metal speciation analysis in electron-beam-sensitive materials, and an automated image analysis approach for atom detection and classification.

O 10.2 Mon 15:30 H4

**Synthesis of single-atom model catalysts via atomic layer deposition for CO oxidation** — ●CHUNLEI WANG<sup>1</sup>, HÉLOÏS TISSOT<sup>1</sup>, JOAKIM HALLDIN STENLID<sup>2</sup>, MARKUS SOLDEMO<sup>1</sup>, SARP KAYA<sup>3</sup>, and JONAS WEISSENRIEDER<sup>1</sup> — <sup>1</sup>Materials and Nano Physics, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden — <sup>2</sup>Department of Physics, Stockholm University, SE-106 91 Stockholm, Sweden — <sup>3</sup>Department of Chemistry, Koc University, 34450 Istanbul, Turkey

Single-atom model catalysts, with individual metal atoms anchored on well-defined single crystals under ultra-high vacuum conditions, can provide an atomic-scale insight into active sites and reaction mechanisms for applied catalysis, thus promoting the design of better industrial catalysts. The metal growth of model catalyst is usually synthesized by physical vapor deposition method. Here, we applied a novel atomic layer deposition strategy to model systems for the synthesis of single-atom FeO<sub>x</sub> catalysts on Cu<sub>2</sub>O(100) and Pt(111). The coordination configuration was determined through a combination of scanning tunneling microscopy, synchrotron radiation X-ray photoelectron spectroscopy (XPS), and density functional theory calculations. The redox properties of single atoms were investigated using ambient-pressure XPS under mbar level of reactant gas.

O 10.3 Mon 15:45 H4

**A Customized IRAS System for Investigations of Adsorbates on Metal-Oxide Single Crystals** — ●DAVID RATH, JIRI PAVELEC, ULRIKE DIEBOLD, MICHAEL SCHMID, and GARETH S. PARKINSON — Institute of Applied Physics, TU Wien, Austria

The IRAS system GRISU (GRazing incident Infrared absorption Spectroscopy Unit) was developed to investigate adsorbates on metal oxide single crystals in the research field of single-atom catalysis [1]. It combines the commercially available FTIR spectrometer Bruker Vertex 80v with an UHV chamber [2]. The compact design requires only one CF150 port for the main optical components, features five mirrors for beam guidance placed in HV and UHV environment and optimises the system's performance, flexibility, and usability. The result is a small controllable focal-spot diameter (max. 3 mm) on the sample, motorised optical components, and an aperture limiting the incidence angle range (variable, 49° to 85°) on the sample. The simulated system (done with a ray-tracing program and a simplified spectrometer model) shows an efficiency of 13 %, i.e., 13 % of the radiation passing through the first aperture (Ø 6 mm) after the IR source in the FTIR spectrometer reaches the detector after being reflected from the molecular beam spot (Ø 3.5 mm) on the sample. Compared to a commercially available system with two parabolic mirrors with a focal length of 250 mm, the efficiency is about 20× higher. First measurements demonstrate the performance of the system.

[1] G. S. Parkinson, *Catal. Lett.* 149, 1137 (2019)[2] J. Pavelec, et al., *J. Chem. Phys.* 146, 014701 (2017).

## Topical Talk

O 10.4 Mon 16:00 H4

**Design of Model Single-Atom Catalysts: Metal Adatoms, Monomeric Oxide Units, and Mixed Surface Layers on Oxide Surfaces** — ●ZDENEK DOHNALEK — Physical and Computational Sciences Directorate and Institute for Interfacial Catalysis, Pacific Northwest National Laboratory, Richland, WA 99354, USA

Single-atom catalysts have attracted significant attention due to their ultimate metal efficiency and the promise of novel properties. The sublimation of oxides and metals is employed to design monodispersed model systems with supported metal adatoms, monomeric oxide units, and ordered mixed oxide surfaces. Scanning tunneling microscopy, ensemble-averaged electron spectroscopies, and density functional theory are employed to achieve an atomic-level understanding. Specifically, the deposition of (MgO)<sub>1</sub> monomers and (MoO<sub>3</sub>)<sub>n</sub> oligomers is studied on anatase TiO<sub>2</sub>(101) via direct evaporation of MgO and MoO<sub>3</sub> powders. While gas phase (MgO)<sub>1</sub> is readily immobilized at room temperature, (MoO<sub>3</sub>)<sub>n</sub> transiently diffuse, agglomerate, and spontaneously decompose into the (MoO<sub>3</sub>)<sub>1</sub> monomers. The transient mobility of the oligomers is the key to the self-assembly of the ordered overlayers of (MoO<sub>3</sub>)<sub>1</sub>. Metal adatoms and mixed oxide surfaces are synthesized by the sublimation of Rh onto Fe<sub>3</sub>O<sub>4</sub>(001). Higher substrate temperatures facilitate Rh incorporation into the surface, leading to ordered mixed Rh-Fe<sub>3</sub>O<sub>4</sub>(001). Cryogenic deposition temperatures stabilize Rh on the surface and allow for the preparation of the pure Rh adatom phase. The effect of temperature and adsorbates on the stability of such model catalysts is explored.

O 10.5 Mon 16:30 H4

**Rh and Ir single atoms on Fe<sub>3</sub>O<sub>4</sub>(001): local structure affecting catalytic properties** — ●MATTHIAS MEIER<sup>1,2</sup>, ZDENEK JAKUB<sup>1</sup>, JIRI PAVELEC<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, ULRIKE DIEBOLD<sup>1</sup>, CESARE FRANCHINI<sup>2,3</sup>, and GARETH S. PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, Technische Universität Wien, Vienna, Austria — <sup>2</sup>Faculty of Physics and Center for Computational Materials Science, University of Vienna, Vienna, Austria — <sup>3</sup>Department of Physics and Astronomy, Alma Mater Studiorum, Università di Bologna, Bologna, Italy

Single-atom catalysts are often supported by cheap oxides, such as iron oxides. As a model system [1], magnetite (Fe<sub>3</sub>O<sub>4</sub>), specifically its (001) facet has been used because it offers stable sites for single-atom adsorption up to high temperatures. Here, I will demonstrate how important the support is for the stability of single-atoms, as well as their catalytic properties. Rh and Ir [2] single atoms utilize Fe vacancies in the subsurface of the reconstructed Fe<sub>3</sub>O<sub>4</sub>(001) unit cell to incorporate into the surface layer. Changing the positions of Fe atoms in the support as part of the incorporation process enables the single atoms to be accommodated in a more favorable configuration than if they were adsorbing on top of the surface. Their catalytic properties are drastically affected by changes in the atomic environment. Incorporation temperatures vary depending on both coverage and the presence or absence of adsorbates, such as CO.

[1] R. Blum et al., *Science* 346, 1215 (2014). [2] Z. Jakub et al., *Angew. Chemie Int. Ed.* 58, 13961 (2019).

O 10.6 Mon 16:45 H4

**Atomic-Level Studies of C<sub>2</sub>H<sub>4</sub> on Clean and Rh<sub>1</sub> Single-Atom Decorated Fe<sub>3</sub>O<sub>4</sub>(001)** — ●PANUKORN SOMBUT<sup>1</sup>, LENA PUNTSCHER<sup>1</sup>, CHUNLEI WANG<sup>1</sup>, MANUEL ULREICH<sup>1</sup>, JIRI PAVELEC<sup>1</sup>, ALI RAFSANJANI-ABASSI<sup>1</sup>, MATTHIAS MEIER<sup>2</sup>, ULRIKE DIEBOLD<sup>1</sup>, CESARE FRANCHINI<sup>2,3</sup>, MICHAEL SCHMID<sup>1</sup>, and GARETH S. PARKINSON<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Austria — <sup>2</sup>Faculty of Physics, Center for Computational Materials Science, University of Vienna, Austria — <sup>3</sup>Alma Mater Studiorum, Università di Bologna, Bologna, Italy

The local binding environment of metal-oxide supported single-atom catalysts (SACs) determines how reactants adsorb and therefore plays a decisive role in catalysis. Here, we study how Fe<sub>3</sub>O<sub>4</sub>(001)-supported Rh<sub>1</sub> adatoms interact with ethylene (C<sub>2</sub>H<sub>4</sub>) using DFT, combined with experimental surface science techniques (TPD, XPS, and STM). We show that C<sub>2</sub>H<sub>4</sub> physisorbs on the clean Fe<sub>3</sub>O<sub>4</sub>(001). We also identify and model different molecule orderings at different coverages that agree nicely with STM images and TPD data. Then, we study C<sub>2</sub>H<sub>4</sub>

adsorption at 2- and 5-fold coordinated Rh sites at the  $\text{Fe}_3\text{O}_4(001)$  surface, and show that the local environment has a strong effect on the adsorption properties: 2-fold Rh can adsorb two  $\text{C}_2\text{H}_4$  molecules, while 5-fold Rh can only host a single  $\text{C}_2\text{H}_4$  molecule. Finally, we investigate coadsorption of  $\text{C}_2\text{H}_4$  with  $\text{CO}$ , a vital step towards enabling the hydroformylation reaction, and show that this is feasible only at 2-fold coordinated Rh sites.

**Topical Talk**

O 10.7 Mon 17:00 H4

**Model catalysis of single atoms on ultrathin solid films —**

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Metal atoms at surfaces play a key role in catalysis and related disciplines. A new strategy is introduced to prepare ultrathin films like oxides on surfaces which are further utilized to prepare stabilized metal atoms. Since the surface free energy of a bulk oxide is much lower than

the chemical potential or free energy of the metal atoms, one can play the game by reducing the thickness of the oxide film, even down to one atomic monolayer, which is grown on a bulk metal substrate. In such a way, the chemical potential of the oxide thin film can be tweaked by the underlying bulk metal substrate. Once the chemical potential or free energy of the ultrathin oxide support is tuned to such an extent that it becomes comparable with those of the metal atoms, one can then stabilize these metal atoms without additional measures. Such an approach may be termed as surface free energy strategy to prepare uncoordinated metal atoms at surfaces. Since the metal atoms are truly unprotected and therefore their physicochemical properties could be intrinsic, in sharp contrast to those of coordinated metal atoms prepared by surface coordination and crystal engineering strategies. In this presentation, several systems of the unprotected metal atoms including alkali and transition metal atoms on ultrathin films such as metallic oxides and carbides grown on bulk metal substrates are employed to explore surface catalysis.