

## O 3: Focus Session: Single Atom Catalysis 1

The field of single atom catalysis has emerged rapidly in recent years out of the desire to utilize less and less precious metals, and remarkable successes have been reported in thermo-, electro-, and photocatalysis. While much of the early focus was on establishing synthesis routes to achieve atomic dispersion, it has become clear that "single atom" systems cannot be considered as the smallest possible nanoparticle. Because isolated adatoms are stabilized by chemical bonds to the support, they have much more in common with mononuclear complexes used in homogeneous catalysis. Thus, the focus has now changed towards understanding the role of coordination of the active site, and developing ways to tailor it toward specific processes. This has led to much interest in fundamental work, which opens up a tremendous opportunity for surface science to contribute to a hot topic in catalysis.

Organizer: Gareth Parkinson (Technical University Vienna), Matthias Meier (University of Vienna)

Time: Monday 10:30–12:45

Location: H4

### Topical Talk

O 3.1 Mon 10:30 H4

**Rational design of single atom electrocatalysts: handle with care** — ●GIANFRANCO PACCHIONI — Dipartimento di Scienza dei Materiali, Università Milano-Bicocca, Milano, Italy

One of the objectives of electronic structure theory is to predict chemical and catalytic activities. This is a challenging target due to the large number of variables that determine the performance of a heterogeneous catalyst. The complexity of the problem has reduced considerably with the advent of single atom catalysts (SAC) and, in particular, of graphene-based SACs for electrocatalytic reactions such as the oxygen reduction (ORR), the oxygen evolution (OER) and the hydrogen evolution (HER) reactions. In this context we assist to a rapidly growing number of theoretical studies based on density functional theory (DFT) and of proposals of universal descriptors that should provide a guide to the experimentalist for the synthesis of new catalysts. In this talk we critically analyze some of the current problems connected with the prediction of the activity of SACs based on DFT: accuracy of the calculations, neglect of important contributions in the models used, physical meaning of the proposed descriptors, inaccurate data sets used to train machine learning algorithms, not to mention some severe problems of reproducibility. It follows that the 'rational design' of a catalyst based on some of the proposed universal descriptors or of the DFT screening of large number of structures should be considered with great caution.

O 3.2 Mon 11:00 H4

**Single atom co-catalyst dispersion on KTaO<sub>3</sub> (001) by surface polarity compensation.** — ●AJI ALEXANDER<sup>1</sup>, JESÚS REDONDO<sup>1</sup>, DOMINIK WRANA<sup>1</sup>, LUKÁŠ FUSEK<sup>1</sup>, VIKTOR JOHÁNEK<sup>1</sup>, JOSEF MYSLIVEČEK<sup>1</sup>, and MARTIN SETVIN<sup>1,2</sup> — <sup>1</sup>Department of Surface and Plasma Science, Faculty of Mathematics and Physics, Charles University, Prague, Czech Republic — <sup>2</sup>Institute of Applied Physics, TU Wien, Vienna, Austria

Redox chemistry on perovskite surfaces attracts attention due to these materials\* promising catalytic properties, good ability to separate electron-hole pairs in light-harvesting, and the presence of ferroelectricity in many perovskites. This work focuses on enhancing catalytic activity achieved by activating the perovskite surface with extrinsic metals. Combined STM/AFM measurement together with XPS data shows the tendency of the cobalt atoms to disperse in the form of single adatoms on the polarity uncompensated KTaO<sub>3</sub> (001) surface [1]. The interaction of cobalt with KTO surfaces was studied under various reducing and oxidizing conditions, as well as a function of temperature. This, in turn, will allow characterization of the metallic, oxide, and hydroxide phases of cobalt in dependence on the environment. The work was supported by projects GACR 20-21727X and GAUK Primus/20/SCI/009. [1] M. Setvin, M. Reticcioli, F. Poelzleitner et al., *Science* 359, 572 (2018)

O 3.3 Mon 11:15 H4

**Comparison study of different transition metals on two TiO<sub>2</sub> model supports: anatase TiO<sub>2</sub>(101) and rutile TiO<sub>2</sub>(110)** — ●LENA PUNTSCHER<sup>1</sup>, KEVIN DANINGER<sup>1</sup>, PANUKORN SOMBUT<sup>1,2</sup>, MATTHIAS MEIER<sup>2</sup>, MICHAEL SCHMID<sup>1</sup>, CESARE FRANCHINI<sup>2</sup>, ULRIKE DIEBOLD<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, University of Vienna, Vienna, Austria

Single-atom catalysis (SAC) offers an opportunity to minimize the amount of precious catalyst material required for traditional heteroge-

neous catalysis and to heterogenize reactions presently requiring homogeneous catalysis. Unravelling how metal atoms bind to oxide supports is crucial for a better understanding of the SACs catalytic properties. Using STM and XPS, we compare the adsorption geometry and stability of several transition metals (Pt, Rh, Ir and Ni) on TiO<sub>2</sub> model supports: anatase TiO<sub>2</sub>(101) and rutile TiO<sub>2</sub>(110), and the influence of water on the dispersion of these systems. While most of the metals rapidly sinter on both surfaces, there are a few exceptions: Ir forms stable adatoms on the anatase support. Ni is much more dispersed when water vapor is added to the deposition and a very low coverage of Pt single atoms can be stabilized in oxygen vacancies formed on rutile (110), which are only stable in UHV conditions. This study points out the importance of metal-support interaction and the surprisingly different behaviour of the transition metals on TiO<sub>2</sub> model supports.

O 3.4 Mon 11:30 H4

**Methane Activation by Free Tantalum Cluster Cations: When the Atomic System is Different** — ●MARTIN TSCHURL, JAN ECKHARD, and UELI HEIZ — Physical Chemistry, Department of Chemistry and Catalysis Research Center, Technical University of Munich

The efficient conversion of methane into valuable chemicals represents a challenge in chemistry in general. It also carries the potential of becoming a key technological process, given the availability of the substance from fossil, as well as agricultural, sources. Despite decades of research, only steam reforming is used today on commercially relevant scales. Nevertheless, the interest in the topic remains steadily strong, in particular in heterogeneous catalysis. Studies of ion-molecule reactions have already provided substantial contributions to the field and enabled the identification of fundamental reaction pathways and key properties governing them. We use of this approach in order to reveal pathways and reaction kinetics in the C-H bond activation in methane. This way, we comprehensively elucidate the size-dependent reactivity of different cluster cations of tantalum - a metal, which has already been noted as a prospective candidate in the activation of C-H bonds. One of our main findings, in the combined experimental and theoretical study, reveals a significant difference in the reaction of single atoms compared to that of larger clusters. The single atom is the only size that facilitates an often-desired C-C coupling, which further suggests a possible intrinsic benefit of single atoms over clusters in the catalytic conversion of methane.

O 3.5 Mon 11:45 H4

**Assessing the environmental benefit of palladium-based single-atom heterogeneous catalysts for Sonogashira coupling** — ●DARIO FAUST AKL<sup>1</sup>, DARIO POIER<sup>1,2</sup>, SHARON MITCHELL<sup>1</sup>, ROGER MARTI<sup>2</sup>, GONZALO GULLÉN-GOSÁLBEZ<sup>1</sup>, and JAVIER PÉREZ-RAMÍREZ<sup>1</sup> — <sup>1</sup>Institute of Chemical and Bioengineering, ETH Zurich, Switzerland — <sup>2</sup>ChemTech, HEIA Fribourg, Switzerland

The Pd-Cu catalyzed Sonogashira coupling of terminal alkynes and aryl halides is a cornerstone organic transformation. A cradle-to-gate life cycle analysis (LCA) reveals a two orders of magnitude potential improvement in process footprint when replacing an organometallic Pd catalyst with a heterogeneous analogue. The latter could be easily separated permitting full Pd recovery and catalyst reuse. Heterogeneous catalysts based on isolated metal atoms (single-atom catalysts, SACs) demonstrate promising potential to synergize the benefits of solid and molecular catalysts for efficient Pd utilization. By anchoring Pd atoms on nitrogen-doped carbon we achieve full recovery of the metal, al-

lowing catalyst reuse over multiple cycles. A hybrid process using the Pd-SAC with a homogeneous CuI cocatalyst is more productive than a fully heterogeneous bimetallic Pd-Cu SAC, which deactivates severely due to copper leaching. In some scenarios, the LCA-based metrics demonstrate the process footprint of the hybrid SAC system is leaner than the purely homogeneous counterpart already upon single reuse. Combining LCA with experimental evaluation could guide the design of reusable catalysts for more sustainable organic transformations.

O 3.6 Mon 12:00 H4

**Nature of the active species in low-temperature CO oxidation over Pt-CeO<sub>2</sub> model catalysts** — ●ALEXANDER SIMANENKO<sup>1</sup>, MAXIMILIAN KASTENMEIER<sup>1</sup>, LESIA PILIAI<sup>2</sup>, TOMÁŠ SKÁLA<sup>2</sup>, YULIYA KOSTO<sup>2</sup>, NATALIYA TSUD<sup>2</sup>, SASCHA MEHL<sup>3</sup>, MYKHAILO VOROKHTA<sup>2</sup>, IVA MATOLÍNOVÁ<sup>2</sup>, YAROSLAVA LYKHACH<sup>1</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — <sup>2</sup>Charles University, Prague, Czech Republic — <sup>3</sup>Elettra-Sincrotrone Trieste SCpA, Basovizza-Trieste, Italy

The low-temperature CO oxidation has wide applications in energy production and exhaust gas cleaning. Pt-CeO<sub>2</sub> catalysts with high Pt content allow achieving 100% CO conversion below room temperature. We investigated the nature of active sites on Pt-CeO<sub>2</sub> catalysts under the conditions of low-temperature CO oxidation by means of synchrotron radiation photoelectron spectroscopy, resonant photoemission spectroscopy, and near ambient pressure XPS. Model Pt-CeO<sub>2</sub> systems were prepared by reactive physical vapor co-deposition and annealed in UHV or O<sub>2</sub> in order to obtain different types of platinum species on the surface. These included mainly Pt<sup>2+</sup> species accompanied by a small number of Pt<sup>4+</sup> species that were reduced to Pt<sup>2+</sup> or metallic Pt during annealing. Exclusively, stable Pt<sup>4+</sup> species were formed on a thick Pt-CeO<sub>2</sub> catalyst with high Pt content after annealing in oxygen at NAP conditions. The results of our study showed that there is no reduction or oxidation of the Pt-CeO<sub>2</sub> catalysts by CO below 450 K. These observations suggest that low-temperature CO oxidation on Pt-CeO<sub>2</sub> catalyst does not follow a Mars-Van Krevelen mechanism.

O 3.7 Mon 12:15 H4

**Adsorption sites and thermal stability of Pt adatoms on Fe<sub>2</sub>O<sub>3</sub>(1102)** — ●ALI RAFSANJANI ABBASI, FLORIAN KRAUSHOFER, LENA HAAGER, MORITZ EDER, JIRI PAVELEC, GIADA FRANCESCHI, MICHELE RIVA, MICHAEL SCHMID, ULRIKE DIEBOLD, and GARETH S.

PARKINSON — Institute of Applied Physics, TU Wien, Austria

Oxide-supported Pt catalysts offer superior performance because of their high activity and/or selectivity for many important chemical reactions. However, the high cost of Pt and its susceptibility to CO poisoning are two drawbacks to its role as a catalyst. Downsizing catalyst clusters to single atoms is an effective way to reach maximum efficiency, and so-called “single-atom catalysis” is now an important field of research [1]. Nevertheless, stabilizing single Pt atoms on oxide supports without compromising catalytic activity is still a key challenge. Here, we present a surface science study to investigate the local binding environment of Pt adatoms deposited on Fe<sub>2</sub>O<sub>3</sub>(1102) – (1 × 1) under UHV conditions. Extensive STM and XPS studies at different Pt surface coverages on Fe<sub>2</sub>O<sub>3</sub>(1102) revealed that Pt single atoms are highly stable at room temperature. STM images showed that Pt single atoms are adsorbing at two distinct sites with different apparent heights. Through an atom-by-atom analysis, the relative contributions of two types of Pt adsorption sites were determined for different surface coverages. Moreover, thermally induced sintering of the Pt single atoms is traced by means of XPS and STM.

[1] G. S. Parkinson, *Catal. Lett.* 149, 1137 (2019).

O 3.8 Mon 12:30 H4

**Comparison of Single Metal Atoms on a Fe<sub>2</sub>O<sub>3</sub> Model Support** — ●GARETH PARKINSON<sup>1</sup>, ALI RAFSANJANI-ABBASI<sup>1</sup>, LENA PUNTSCHER<sup>1</sup>, FLORIAN KRAUSHOFER<sup>1</sup>, PANUKORN SOMBUT<sup>1</sup>, CHUNLEI WANG<sup>1</sup>, MATTHIAS MEIER<sup>1,2</sup>, MORITZ EDER<sup>1</sup>, JIRI PAVELEC<sup>1</sup>, GIADA FRANCESCHI<sup>1</sup>, MICHELE RIVA<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, CESARE FRANCHINI<sup>2,3</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>TU Wien, Vienna, Austria — <sup>2</sup>University of Vienna, Vienna, Austria — <sup>3</sup>Università di Bologna, Bologna, Italy

Understanding how the local environment of a “single-atom” catalyst affects stability and reactivity remains a significant challenge. Fe<sub>2</sub>O<sub>3</sub> is the most common iron-oxide support material utilized for SAC, but little is known about how metal adatoms bind at its surfaces. In this talk, I will compare and contrast the behavior of Pt, Rh, and Ir atoms on the flat, well-ordered (1x1) termination of Fe<sub>2</sub>O<sub>3</sub>(1-102). Using a combination of scanning probe microscopy and spectroscopic data, as well as theoretical calculations, I will demonstrate significant differences between the adsorption site and thermal stability of the metals, as well as differences in their interaction with water and CO.