

O 70: Supported nanoclusters: Structure, Reactions, Catalysis

Time: Thursday 15:00–17:45

Location: H6

Topical Talk

O 70.1 Thu 15:00 H6
Stability and dynamics of cluster catalysts and their supports — SEBASTIAN KAISER, JOHANNA PLANSKY, FABIAN KNOLLER, ALEXANDER BOURGUND, KE ZHANG, UELI HEIZ, FRIEDRICH ESCH, and BARBARA A. J. LECHNER — Department of Chemistry & Catalysis Research Center, Technical University of Munich, Germany

The intrinsic metastability of supported clusters can induce a vast range of dynamics that strongly influence their physical and chemical properties, while being experimentally highly challenging to investigate. Here, I will present a range of surface dynamics that occur in supported cluster dynamics, ranging from confined cluster diffusion, cluster encapsulation, support mobility and reactant spillover to lateral diffusion linked to reactivity. Our experimental approach is to combine static, statistically sound, and dynamic, time-resolved scanning tunneling microscopy (STM) to investigate the diffusion, sintering, and restructuring of size-selected clusters on weakly and strongly interacting supports.

O 70.2 Thu 15:30 H6
The role of water in oxidation of the Pt/Co₃O₄ interface — YAROSLAVA LYKHACH¹, LUKÁŠ FUSEK^{1,2}, MAXIMILIAN KASTENMEIER¹, TOMÁŠ SKÁLA², NATALIYA TSUD², VIKTOR JOHÁNEK², SASCHA MEHL³, JOSEF MYSLIVEČEK², OLAF BRUMMEL¹, and JÖRG LIBUDA¹ — ¹Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — ²Charles University, Prague, Czech Republic — ³Elettra-Sincrotrone Trieste SCpA, Basovizza-Trieste, Italy

Electronic metal-oxide interactions (EMSI) play a major role in the design of advanced functional materials for applications in catalysis. We investigated the influence of the EMSI on the oxidation state of ultra-small Pt particles supported on a well-ordered Co₃O₄(111) substrate in the presence of co-adsorbates, i.e. hydroxyl groups and molecularly adsorbed water, by means of synchrotron radiation photoelectron spectroscopy and scanning tunneling microscopy. The EMSI gives rise to charge transfer across the metal-oxide interface and results in partial oxidation of Pt deposits coupled with partial reduction of Co₃O₄(111). We detected ultra-small Pt^{δ+} aggregates in combination with atomically dispersed Pt^{2+/4+} species. While the oxidation degree of Pt deposits is not influenced by the presence of co-adsorbates, the magnitude of the charge transfer is enhanced in the presence of molecularly adsorbed water. Subsequent annealing in UHV leads to re-oxidation of Co₃O₄(111) accompanied by an increase in the amount of Pt⁴⁺ species. This observation suggests the re-dispersion of Pt^{δ+} aggregates to Pt⁴⁺ species triggered by the dissociation of water.

O 70.3 Thu 15:45 H6
Ripening mechanism changes with cluster size: *In situ* observation of Pt cluster diffusion on Fe₃O₄(001) — SEBASTIAN KAISER, JOHANNA PLANSKY, UELI HEIZ, BARBARA A. J. LECHNER, and FRIEDRICH ESCH — Technical University of Munich, Garching, Germany

Ripening of small oxide-supported metal clusters is a common deactivation mechanism in heterogeneous catalysis. We use scanning tunneling microscopy (STM) to follow the diffusion and ripening of size-selected Pt clusters on an Fe₃O₄(001) support. Thanks to a strong cluster-support bonding, ripening and coalescence only set in at elevated temperatures. Particle size analysis of our STM images reveals that Pt₁₉ exhibits Ostwald ripening at temperatures above 800 K, i.e. with cluster growth by atom diffusion. In contrast, the smaller Pt₅ and Pt₁₀ clusters show Smoluchowski ripening, i.e. the diffusion of entire clusters, already in the temperature range of 600 to 800 K and Ostwald ripening >800 K. We not only observe the ripened clusters in STM, but could successfully follow the diffusion process *in situ* by STM movies. Surprisingly, temperature programmed desorption (TPD) measurements of CO molecules show that in this temperature range the clusters get concomitantly encapsulated by iron oxide via strong metal support interaction (SMSI). Cluster diffusion thus occurs despite a strong interaction with the magnetite support and the diffusing species is most likely a cluster with Fe and O atoms on top.

O 70.4 Thu 16:00 H6
Tuning SMSI Kinetics on Pt-loaded TiO₂(110) by Choos-

ing the Pressure — PHILIP PETZOLDT¹, MORITZ EDER¹, SONIA MACKEWICZ¹, MONIKA BLUM^{2,3}, TIM KRATKY⁴, SEBASTIAN GÜNTHER⁴, MARTIN TSCHURL¹, UELI HEIZ¹, and BARBARA LECHNER⁵ — ¹Physical Chemistry, Department of Chemistry and Catalysis Research Center, Technical University of Munich — ²Advanced Light Source, Lawrence Berkeley National Laboratory — ³Chemical Sciences Division, Lawrence Berkeley National Laboratory — ⁴Physical Chemistry with Focus on Catalysis, Department of Chemistry and Catalysis Research Center, Technical University of Munich — ⁵Functional Nanomaterials, Department of Chemistry and Catalysis Research Center, Technical University of Munich

The encapsulation of noble metal particles on reducible supports due to a strong metal-support interaction (SMSI) has already been extensively studied. However, there is still an ongoing debate on important aspects such as the influence of oxygen or hydrogen treatments on the encapsulating overlayer. We have utilized synchrotron-based NAP-XPS in order to investigate the SMSI for Pt-loaded TiO₂(110) single crystals under the influence of H₂ and O₂ at different pressures. In an O₂ atmosphere two different, pressure-dependent phenomena, namely, an oxidation of Pt particles and a loss of Pt signal intensity, are observed at 800 K. While the oxidation is partially reversed in vacuum, the intensity of the platinum signal cannot be recovered. H₂ annealing has no significant additional effect compared to vacuum annealing. In the presentation, we discuss possible origins of these observations.

O 70.5 Thu 16:15 H6
Deposition and annealing of FeNi nanoparticles on surfaces — MAHBOOBEH RAVANKHAH¹, MATHIAS GETZLAFF¹, GERHARD DEHM², and PHILIPP WATERMEYER² — ¹Institut für Angewandte Physik, Universität Düsseldorf — ²Max-Planck-Institut für Eisenforschung GmbH, Düsseldorf

3d bimetallic nanoparticles have received lots of attention due to their technological applications in ultrahigh density information storage, catalysis and biomedicine. The thermal stability and the magnetic properties of the in-vacuo prepared bimetallic nanoparticles are shown to depend on the composition and their structure. Here we report on new findings of structure and composition of Fe-Ni nanoparticles, synthesized via a magnetron sputtering source and deposited on a Tungsten crystal surface. The elemental distribution of nanoparticles is determined by high resolution transmission electron microscopy (HRTEM) and electron energy loss spectroscopy (EELS). It is found that the nanoparticles have a shell formed by Fe atoms and a core composed of Fe and Ni with the gradient of composition from core to the surface. The melting behavior of nanoparticles was studied under UHV conditions by scanning tunneling microscopy (STM) as a function of heating temperature. The unrolling carpet, surface diffusion and anisotropy spreading are driving processes to form monolayer high islands above the melting point. The relevant result could be helpful for the design and preparation of stable and controllable bimetallic nanoparticles for technological applications.

O 70.6 Thu 16:30 H6
Reaction Pathways in Alcohol Photoreforming on Cluster Co-Catalyst Loaded TiO₂(110) — SONIA MACKEWICZ, MORITZ EDER, PHILIP PETZOLDT, MARTIN TSCHURL, and UELI HEIZ — Physical Chemistry, Department of Chemistry and Catalysis Research Center, Technical University of Munich

Heterogeneous photocatalysis offers the prospect of utilizing solar energy for the environmentally benign production of chemical fuels such as hydrogen. State-of-the-art materials often comprise co-catalyst loaded semiconductors, but these systems are still limited in efficiency. In order to systematically optimize photocatalysts, a profound knowledge of reaction mechanisms is crucial, whose details are so far little understood. Alcohols are an ideal model system to investigate reaction mechanisms in photocatalysis. Furthermore, they may serve as renewable sources for hydrogen in the future. In this talk, we give insights into the mechanistic of the alcohol photoreforming reaction on co-catalyst loaded TiO₂(110). It is shown that semiconductor photocatalysis selectively enables new reaction pathways, which are not accessible by thermal or conventional chemical methods.

O 70.7 Thu 16:45 H6

Electron transfer reaction by time resolved (TRS) and core level spectroscopy (XPS) and STM on Au/TiO₂(110) single crystal systems. — •HICHAM IDRIS — Institute of functional Interfaces, KIT, Karlsruhe

Charge transfer from or to a metal deposited on an oxide semiconductor are central to photocatalysis. In order to probe into this phenomenon, the effect of gold coverage on the chemical state of Ti cations, upon photoexcitation of rutile TiO₂(110) single crystal, was investigated by X-ray photoelectron spectroscopy (XPS). Photocatalytic reaction of gas phase ethanol (a hole scavenger) on TiO₂(110) and Au/TiO₂(110) resulted in the formation of Ti³⁺ cations. Increasing the Au coverage resulted in the gradual decrease of these Ti³⁺ cations. The "quasi" total consumption of these reduced states was found at a ratio Au atoms to reacted Ti³⁺ close to one; this corresponded to about 0.50 at. % of Au. The relationship suggests that electron transfer occurs from the excited semiconductor to Au atoms during the catalytic reaction. In order to complement the work H2 production rates of an electron donor, such as ethanol, over Au clusters with different sizes and coverage deposited on single crystal rutile TiO₂(110) were studied by scanning tunneling microscopy, online mass spectrometry and complemented by femto second pump probe spectroscopy. It was also found that there is a non-linear increase of the H₂ production rate with increasing gold coverage. The key determining factor appears to be the Au inter-particle distance. Increasing this distance resulted in an increase in the normalized reaction rate.

O 70.8 Thu 17:00 H6

Surface Ligand Infrared Spectroscopy: In-Situ Characterization of Noble Metal Clusters and Metal Oxides at Work — •ERIC SAUTER¹, DARIA GASHNIKOVA², FLORIAN MAURER², ALEXEI NEFEDOV¹, STEFAN HEISSLER¹, YUEMIN WANG¹, JAN-DIRK GRUNWALD², and CHRISTOF WÖLL¹ — ¹Institute of Functional Interfaces, KIT, Eggenstein-Leopoldshafen, Germany — ²Institute of Chemical Technology and Polymer Chemistry, KIT, Karlsruhe, Germany

To achieve a full understanding of chemical processes at exposed surfaces in-situ and operando investigations are required. For studies of catalytic processes under real conditions, IR spectroscopy offers a number of advantages. In the present study, surface ligand infrared spectroscopy was used to perform an in-situ investigation of the surface characteristics of cerium oxide single crystals as well as catalytic active NM-clusters on cerium oxide nanoparticles. Low temperature adsorption of carbon monoxide was used to identify the surface structure and morphology, visible through distinctive adsorption bands blue shifted in respect to the gas phase, which can be used as reference for the interpretation of more complicated spectra like powders or nanoparticles. Additionally, noble-metal clusters were investigated in pristine condition as well as in the reduced state. Upon heating, desorption of the probe molecule occurred and at higher temperatures deformation and sintering of the clusters was observed. The investigation shows

the power of infrared spectroscopy as a tool for in-situ investigations and characterization of NM-clusters and metal oxides at work.

O 70.9 Thu 17:15 H6

AI with Experimental and Theoretical Data toward the Understanding CO₂ Hydrogenation Catalysis: The Role of the Support Materials — •RAY MIYAZAKI¹, KENDRA BELTHLE², HARUN TÜYSÜZ², LUCAS FOPPA¹, and MATTHIAS SCHEFFLER¹ — ¹The NOMAD Laboratory at the Fritz Haber Institute of the Max Planck Society, Germany — ²Max-Planck-Institut für Kohlenforschung, Germany

The genesis of organic molecules from CO₂ at a hydrothermal vent, which is a fissure on the seafloor, is one of the theories for the origin of life [1]. We focus on CO₂ hydrogenation catalyzed by cobalt nanoparticles supported on SiO₂, which mimic the environment of a hydrothermal vent. In particular, we investigate the role of support materials by using several amorphous SiO₂ supports incorporating different elements (e.g., Ti, Zr). In this study, the experimental selectivity toward organic molecules (e.g., methanol, formic acid) is modeled by the sure-independence screening and sparsifying operator (SISSO) AI approach [2]. Both experimental and theoretical data are adopted as the input features for SISSO, such as atomic-scale features calculated by density functional theory and experimental characterization data. Our approach identifies the key descriptive parameters correlated to the selectivity, which lead to a better understanding of the origin of life and to design of novel CO₂ hydrogenation catalysts.

[1] M. Preiner *et al.*, *Nat. Ecol. Evol.*, **4**, 534-542 (2020).

[2] R. Ouyang *et al.*, *Phys. Rev. Mater.*, **2**, 083802 (2018).

O 70.10 Thu 17:30 H6

Near-ambient pressure studies of size selected clusters on ultrathin silica films — •MATTHIAS KRINNINGER, FLORIAN KRAUSHOFER, FRIEDRICH ESCH, and BARBARA A.J. LECHNER — Department of Chemistry, Technical University of Munich, 85748 Garching, Germany

Silicon oxide is a widely used catalyst support material for clusters and nanoparticles. Understanding the relationship between these clusters and the support is challenging, however, because SiO₂ is insulating, and in most applications not crystalline, which limits the use of diffraction-based experimental techniques. Some progress has been made by growing ultrathin, quasi-2D silica bilayer films on a variety of metal supports [1], which can then be measured by scanning tunneling microscopy (STM). Here, we show first results for ultrathin silica films grown on Pt(111) and their interaction with deposited metal clusters, examined by near-ambient pressure (NAP) XPS and NAP-STM. We investigate the stability of the films, their ability to stabilize small clusters without sintering, and the dependence of this stability on the crystallinity of the film.

[1] C. Büchner, M. Heyde, Two-dimensional silica opens new perspectives, *Prog. Surf. Sci.*, **92** (2017) 341-374.