

O 75: Fundamentals of Catalysis I

Time: Thursday 10:30–13:00

Location: H5

O 75.1 Thu 10:30 H5
Coordination Effects in Model Rh1/Fe3O4 and Ir1/Fe3O4 Single-Atom Catalysts — ●GARETH PARKINSON¹, JAN HULVA¹, ZDENEK JAKUB¹, MATTHIAS MEIER^{1,2}, ROLAND BLIEM¹, CESARE FRANCHINI^{1,2}, MICHAEL SCHMID¹, and ULRIKE DIEBOLD¹ — ¹Institute of Applied Physics, TU Wien, Vienna, Austria — ²University of Vienna, Vienna, Austria

The coordination of the active site is thought to play a significant role in single atom catalysis, but precisely determining the local structure on high-area catalysts is extremely difficult. In this talk, I will report scanning probe microscopy, x-ray photoelectron spectroscopy (XPS) and temperature programmed desorption (TPD) results on the structure of Ir1/Fe3O4(001) and Rh1/Fe3O4(001) model single atom catalysts, and show that the coordination has dramatic consequences on CO adsorption. As prepared at room temperature, adatoms are twofold coordinated to surface oxygen, and hold on to CO until 650 K. Annealing the catalyst to successively higher temperatures results in five- and six-fold coordinated species, which adsorb CO even progressively more weakly. These results show that control of the local coordination environment is critical to design so-called single-atom catalysts, and that incorporation into the support can be as critical a deactivation mechanism for single atom catalysts as thermal sintering.

O 75.2 Thu 10:45 H5
CO-assisted stabilisation of single-atom Pt on ceria — ●NATHAN DAELMAN, MARÇAL CAPDEVILA-CORTADA, and NÚRIA LÓPEZ — Institute of Chemical Research of Catalonia, Tarragona, Spain

Single-atom Pt on ceria has been proposed as a potential car exhaust catalyst that can achieve the DOE <150° challenge set forth by the EU.[1] Our work focuses on the system's applications in CO oxidation. The relevance of this reaction is far-reaching, since it is widely employed for single-atom detection. Nonetheless, its reactivity compared to nanoparticles is still under debate.[2,3]

We have identified a novel anchoring site for dispersed Pt atoms which yields a meta-stable catalyst on the oxygen-terminated (100) surfaces. Carbon monoxide stabilizes the single-atom site upon adsorption. Under oxygen-rich conditions O₂ then integrates into the lattice. From there on, the system converts through a percarbonate transition state to CO₂ gas. One oxygen anion remains in the lattice, effectively reducing the surface.

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[1] Betz, B., Müller, E., et al., 3rd Fundamentals and applications of Cerium Dioxide in catalysis, 2018, OP-2.1.

[2] Jones, J., Xiong, H., et al., Science, 2016, 353, 150-154.

[3] Ding, K., Gulec, A., et al., Science, 2015, 350, 189-192.

Invited Talk O 75.3 Thu 11:00 H5
Structure evolution of oxide-supported metal nanoparticles under different conditions — ●YUEMIN WANG — Institute of Functional Interfaces, Karlsruhe Institute of Technology, Germany

A fundamental understanding of nanostructured metal oxides and oxide-supported metal nanoparticles (NPs) is among the most important and challenging topics in catalysis and nanoscience. Here, we present our recent work on various metal/oxide NPs (Cu/CeO₂, Pt/CeO₂ and Pt/Al₂O₃). The study combining in-situ IR spectroscopy (polarization-resolved IRRAS on model systems and IR transmission on powders), high-resolution TEM and DFT calculations allowed us to gain deep insight into structural, electronic and reactive properties of the metal/oxide systems under different conditions. The results revealed that the atomic structure of pristine and metal-decorated oxide surfaces can vary substantially depending on activation or reaction conditions. For Cu/CeO₂, we will discuss the atomic structure of ultrafine copper clusters (bilayer, 1.0-1.5 nm) and the dynamic behavior under reactive gases at elevated temperatures. For Pt/CeO₂ and Pt/Al₂O₃ systems, we will focus on the structure evolution of various Pt clusters during the course of activation or reaction.

O 75.4 Thu 11:30 H5

Observing diffusion and morphology changes of small metal clusters via scanning tunneling microscopy — ●BARBARA A J LECHNER, KE ZHANG, ALEXANDER BOURGUND, FABIAN KNOLLER, UELI HEIZ, and FRIEDRICH ESCH — Department of Chemistry & Catalysis Research Center, Technical University of Munich, Lichtenbergstr. 4, D-85748 Garching

Metal clusters are partway between molecular and bulk systems and thus exhibit special physical and chemical properties: Atoms can rearrange within a cluster to form different structural isomers, clusters of different size can exhibit a different diffusivity across the same support. Here, we show how scanning tunneling microscopy (STM) can be used to investigate such dynamical behavior of individual clusters. By operating our STM with a specially developed FastSTM add-on module, we followed steady state diffusion of Pd_n (1 ≤ n ≤ 19) clusters and atoms inside the pore of a hexagonal boron nitride nanomesh on Rh(111). While atoms diffuse along the rim of a pore, a small cluster experiences a corrugation in the potential energy landscape and jumps between six sites around the center of the pore. Furthermore, we observed reversible cluster isomerization in situ. In another example, we observed an irreversible decrease in apparent height of Pt_n clusters supported on an Fe₃O₄(001) single crystal surface with increasing temperature. Such a morphological change without concomitant changes in cluster coverage suggests that the cluster-support interface changes with temperature, possibly favoring flattened clusters over spherical ones.

O 75.5 Thu 11:45 H5
Modelling Ostwald ripening beyond mean-field models — ●ELISABETH M. DIETZE and PHILIPP N. PLESSOW — Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology, Karlsruhe, Germany

Transport of atoms and molecules via the gas-phase plays an important role in many processes in heterogeneous catalysis. One of the challenges for heterogeneous catalysts in industry is deactivation due to sintering. For example, platinum particles are widely used in exhaust gas after treatment, but suffer from sintering through ripening by volatile PtO₂ under oxidizing conditions.

We have recently proposed a kinetic Monte Carlo (kMC) model for the explicit simulation of gas-phase mass transport.[1] On small length scales that correspond to typical distances between nanoparticles, transport in model systems was found to deviate significantly from Fick's laws. We are currently exploring, how that affects sintering, when compared with mean-field models suggested in the literature.[2-3]

References: [1] Dietze, E. M.; Plessow, P. N., J. Phys. Chem. C 2018, 122 (21), 11524-11531. [2] Campbell, C. T.; Mao, Z., ACS Catal. 2017, 7 (12), 8460-8466. [3] Plessow, P. N.; Abild-Pedersen, F., ACS Catal. 2016, 6 (10), 7098-7108.

O 75.6 Thu 12:00 H5
Ru/TiO₂ catalysts in the CO methanation: influence of the TiO₂ morphology on the activation and the chemical nature of Ru investigated by operando X-ray absorption spectroscopy — SHILONG CHEN¹, ●JOACHIM BANSMANN¹, ALI ABDELMAGEED¹, DAN LI², WEIXIN HUANG², and R. JÜRGEN BEHM¹ — ¹Institute of Surface Chemistry and Catalysis, Ulm University, D-89069 Ulm, Germany — ²Dept. of Chemical Physics, University of Science and Technology of China, Hefei, China

The selective CO methanation recently proved to be a competitive substitute for the preferential CO oxidation in the purification of CO₂-rich H₂ feed gases. In this contribution, we concentrate on the physical and chemical properties of Ru nanoparticles on Ru/TiO₂ catalysts in the CO methanation using TiO₂ supports with different morphologies. The catalysts were investigated at the ID 24 beamline at the ESRF (Grenoble) using operando X-ray absorption spectroscopy (XAS) at the Ru K edge in an idealized reformat at atmospheric pressure (0.6% CO, 3% N₂, balance H₂) at 190°C. Ru/TiO₂-{001} catalysts experience a much faster activation, however, also a more pronounced deactivation compared to Ru/TiO₂-{100} catalysts. Measurements in the XANES region showed a higher content of oxidic species on Ru/TiO₂-{100} catalysts during the activation period which seems to be related to the lower activity. These findings will be discussed with respect to

simultaneously recorded IR data and results obtained from different Ru/TiO₂ catalysts used in our group.

O 75.7 Thu 12:15 H5

Density functional study of hydrogen adsorption on 55-atom Pt-Ni nanoclusters — ●OLLI AHLSTEDT¹ and JAAKKO AKOLA^{1,2} — ¹Laboratory of Physics, Tampere University of Technology, Finland — ²Department of Physics, Norwegian University of Science and Technology, Trondheim, Norway

Density functional theory calculations were performed on small 55-atom Pt-Ni nanoclusters to study their activity towards the hydrogen evolution reaction (HER). Two Pt_nNi_{55-n} compositions, Pt₁₂Ni₄₃ and Pt₂₀Ni₃₅, were studied in the gas phase and on an Al₂O₃ support. The critical hydrogen coverages were determined using the method based on the differential free energy of hydrogen adsorption. The free energy of hydrogen adsorption, ΔG_{H}^* , was used as a descriptor of the HER activity.

Ni₃ hollow sites were discovered to be the strongly binding sites for hydrogen. The clusters adsorb approximately four H atoms per facet before the hydrogen adsorption becomes endergonic, therefore the critical hydrogen coverages on the clusters are high. The obtained ΔG_{H}^* descriptor values are smaller than 0.1 eV in the gas phase and on the support, suggesting that the clusters are catalytically active towards HER.

O 75.8 Thu 12:30 H5

Bimetallic PdPt Alloy Nanocluster Arrays on Graphene/Rh(111): Formation, Stability, and Dynamics — ●FABIAN DÜLL, UDO BAUER, FLORIAN SPÄTH, PHILIPP BACHMANN, JOHANN STEINHÄUER, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany

Alloy catalysts often have superior properties compared to their single metal counterparts. We studied bimetallic PdPt alloy nanocluster arrays supported on a chemically inert graphene/Rh(111) Moiré. The clusters are well-ordered, separated, and have a small size distribution; thus, they are an intriguing model system for catalysis bridging the materials gap by introducing various facet and edge sites. Using in situ high-resolution XPS, we followed the site occupation and dynamic

changes of the metal distribution during CO adsorption and thermal treatment [PCCP, 2018, 20, 21294]. Annealing of the as-prepared nanoclusters after exposure to CO to 550 K leads to a restructuring towards a more 3D shape and to a replacement of Pt atoms at the cluster edges by Pd. The facets are dominated by Pt. Additionally, the nanoclusters are stabilized, as repeated CO adsorption and desorption cycles cause no further changes. Interestingly, we observe dynamical changes during heating or when applying a CO- or O₂-stream at constant temperatures: CO molecules rearrange from terrace to edge sites, and Pt atoms move back to the particle edges. These effects are only found at elevated temperatures in the presence of CO and disappear when the system cools down in a vacuum.

O 75.9 Thu 12:45 H5

Coverage and temperature dependent size and distribution variations of entrapped Pt-nanoclusters on h-BN/Rh(111) — ●MANUEL MEUSEL, FABIAN DÜLL, SIMON SCHÖTZ, FLORIAN SPÄTH, UDO BAUER, PHILIPP BACHMANN, JOHAN STEINHÄUER, HANS-PETER STEINRÜCK, ANDREAS BAYER, and CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen, Germany

UHV methods provide a powerful tool to investigate surfaces down to the atomic level. However, a large material gap exists between highly defined single crystalline surfaces under UHV conditions and real life materials. One route to bridge this material gap are, at first, more complex surfaces with steps, followed by nanoclusters with mainly edges and corners. By using the Moiré pattern of hexagonal boron-nitride (h-BN) on Rh(111), it is possible to prepare highly defined arrays of separated metal nanoclusters. These systems are promising candidates as model systems for the complex surfaces of heterogeneous catalysts, while still being accessible to investigations via surface science methods. Therefore, the controlled fabrication and understanding of such systems is crucial. We conducted STM and XPS investigations on the coverage- and temperature-dependence of distribution and size of the Pt nanoclusters in the h BN/Rh(111) nanomesh at sub-monolayer coverages. Above 0.1 ML of Pt, we observe well-ordered nanoclusters with a uniform shape. Below this coverage, an inhomogeneous appearance suggests the presence of smaller, more mobile clusters. Further, we discuss the temperature-dependent sintering behaviour.