

O 29: Supported Nanoclusters: Structure, Reactions and Catalysis

Time: Tuesday 10:30–13:00

Location: CHE 91

O 29.1 Tue 10:30 CHE 91

There is life after coking for Ir nanocatalyst superlattices — ●ANTONIO J MARTÍNEZ-GALERA^{1,2}, HAOJIE GUO³, MARIANO D JIMÉNEZ-SÁNCHEZ³, STEFANO FRANCHI⁴, KEVIN C PRINCE⁴, and JOSÉ M GÓMEZ-RODRÍGUEZ^{2,3,5} — ¹Departamento de Física de Materiales, Universidad Autónoma de Madrid, E-28049 Madrid, Spain — ²Instituto Nicolás Cabrera, Universidad Autónoma de Madrid, E-28049 Madrid, Spain — ³Departamento de Física de la Materia Condensada, Universidad Autónoma de Madrid, E-28049 Madrid, Spain — ⁴Eletra-Sincrotrone Trieste S.C.p.A., in Area Science Park, 34149 Basovizza (Trieste), Italy — ⁵Condensed Matter Physics Center (IFI-MAC), Universidad Autónoma de Madrid, E-28049 Madrid, Spain

Achieving superior performance of nanoparticle systems is a major challenge in catalysis. Two main phenomena, occurring during the reactions, hinder the development of the full potential of nanoparticle catalysts: sintering and contamination with carbon containing species, sometimes called coking. Here, we show that Ir nanocrystals, periodically arranged on h-BN supports, can be restored without sintering after contamination by persistent carbon. This restoration yields the complete removal of carbon from the nanocrystals, which keep their crystalline structure, allowing operation without degradation. These findings, together with the possibility of fine tuning the nanocrystals size, confer this nanoparticle system a great potential as a testbed to extract key information about catalysis-mediated oxidation reactions. For the case of the CO oxidation by O₂, the existence of chemical processes not observed before in other nanoparticle systems is proven.

O 29.2 Tue 10:45 CHE 91

Formation of the Pd/Co3O4 interface — ●YAROSLAVA LYKHACH¹, MAXIMILIAN KASTENMEIER¹, LUKÁŠ FUSEK^{1,2}, MATTEO FARNESI CAMELLONE³, TOMÁŠ SKÁLA², NATALIYA TSUD², VIKTOR JOHÁNEK², SASCHA MEHL⁴, JOSEF MYSLIVEČEK², SIMONE PICCININ³, OLAF BRUMMEL¹, STEFANO FABRIS³, and JÖRG LIBUDA¹ — ¹Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — ²Charles University, Prague, Czech Republic — ³Istituto Officina dei Materiali, CNR-IOM, Trieste, Italy — ⁴Eletra-Sincrotrone Trieste SCpA, Basovizza-Trieste, Italy

Metal-oxide interfaces play a major role in the design of advanced functional materials for applications in catalysis, energy storage, and nanoelectronics. We investigated the formation of the metal/oxide interface during deposition of Pd nanoparticles onto a well-ordered Co₃O₄(111) substrate by means of synchrotron radiation photoelectron spectroscopy (SRPES), density functional theory (DFT), and scanning tunnelling microscopy (STM). DFT predicted strong interaction between Pd and Co₃O₄(111) which resulted in the growth of two-dimensional Pd islands densely covering the substrate. We observed a charge transfer across the metal/oxide interface resulting in partial oxidation of Pd deposits and partial reduction of Co₃O₄(111). Based on the analysis of the degree of the reduction of Co₃O₄(111), we found that the charge transfer at the Pd/Co₃O₄(111) is confined to the near-surface region of Co₃O₄(111).

O 29.3 Tue 11:00 CHE 91

Structure of PdPt/CeO₂/YSZ model systems in operando methane oxidation — ●JAN-CHRISTIAN SCHOBER^{1,2}, SILVAN DOLLING^{1,2}, THOMAS F. KELLER¹, and ANDREAS STIERLE^{1,2} — ¹DESY, Centre for X-ray and Nanoscience CXNS, Hamburg, Germany — ²Universität Hamburg, Germany

Due to the high ecological impact of gasoline and diesel fuels, natural gas and biofuel alternatives become more important than ever. Methane is a major component of natural gas and many bio fuels and has a much higher environmental impact than carbon dioxide. Thus, it is vital to ensure the elimination of methane in exhaust gas treatment systems. Pd and PdPt alloy NPs supported by ceria, are among the most active catalysts for the oxidation of methane. Yet, many questions about the interplay of the noble metals with the support, the involvement of palladium oxide species, the role of Pt, and the exact reaction mechanism in the low-temperature regime remain [1,3].

In order to track the active sites and elucidate structure function relationships on an atomistic level we prepare fully epitaxial model systems of PdPt alloy NPs supported by ceria thin films on YSZ single crystals. Using grazing incidence X-ray diffraction techniques in

conjunction with our operando catalysis environments we were able to track activity by in-line mass spectrometry and structure of the model catalysts by following the ceria CTRs, as well as Pd, Pt, and their respective oxide Bragg peaks under operando conditions.

- [1] J. Dong et al., ACS Catal. 10 (23), pp. 14304-14314.
[2] T. Adriana et al. Surface Science 616, pp. 206-213.

O 29.4 Tue 11:15 CHE 91

Methane activation towards H₂ evolution with sub-nanometer Ta clusters supported on Pt(111) — ●TOBIAS HINKE, KEVIN BERTRANG, MATTHIAS KNECHTGES, SEBASTIAN KAISER, and UELI HEIZ — TU Munich, School of Natural Sciences & CRC, Physical Chemistry

The tremendous global energy demand leads to resource shortages as well as environmental consequences. Employing H₂ as an alternative energy carrier from abundant feedstocks such as natural gas is one strategy to tackle these issues. However, efficient hydrogen evolution demands for a fundamental understanding to increase H₂ availability. For this, model systems can be used to elucidate basic principles in chemical reactions, facilitating the design of tailored catalytic systems. Studies of small cationic Ta-clusters and their oxides in the gas phase exhibit high activity towards the activation of highly inert CH₄, yielding Hydrogen, whereas the cluster charge was identified as a key parameter.

These studies are now extended to their supported analogues to approach common catalytic structures. Therefore, Ta_n-clusters (n < 30) supported on metal single crystal substrates are investigated under mild conditions in UHV, with regards to their activity towards H₂ evolution from CH₄ via TPD. Characterization was performed via XPS and STM. Supported Ta₈ clusters exhibit size dispersive stability at room temperature and are active towards H₂ evolution from CH₄.

- [1] N. Levin et al. *J. Am. Chem. Soc.* **2020**, 142, 12, 5862-5869

O 29.5 Tue 11:30 CHE 91

Ta atoms & clusters on Pt(111) - an XPS study — ●KEVIN BERTRANG, TOBIAS HINKE, MATTHIAS KNECHTGES, FEDERICO LOI, ALESSANDRO BARALDI, SEBASTIAN KAISER, and UELI HEIZ — Physical Chemistry, School of Natural Sciences, & Catalysis Research Center, Technical University of Munich

Thin films comprising Ta/Ta_xO_y have been extensively studied on Pt surfaces. There is still a lack of profound understanding concerning the chemical interaction in the Ta/Pt interface and how it is affected during film growth and oxidation. In particular, an unambiguous attribution of the oxidation state of Ta is lacking which is largely complicated due to the numerous oxides and sub-oxides it can form.

In a bottom up approach we deposited low coverage of Ta atoms & clusters on a Pt(111) surface and probed the system by means of XPS using synchrotron radiation. Oxidation was studied using both atomic and molecular O₂. Stability and surface mobility was studied. At liquid He a high variety of features are observed. In contrast at liquid N₂ most Ta species are mobile and agglomerate to form structures stable up to high temperatures.

O 29.6 Tue 11:45 CHE 91

Cu Nanoparticles on Vicinal and Basal ZnO as Model Catalysts for Methanol Synthesis — ●ROBERT GLEISSNER^{1,2}, SIMON CHUNG¹, ESKO ERIK BECK^{1,2}, GUILHERME D. L. SEMIONE^{1,2}, MICHAEL WAGSTAFFE¹, LEON JACOBSE¹, STEFFEN TOBER^{1,2}, GÖKHAN GIZER⁴, CHRISTOPHER GOODWIN³, MARCUS SOLDEMO^{3,6}, MIKHAIL SHIPILIN^{1,3}, PATRICK LÖMKER^{1,3}, CHRISTOPH SCHLUETER¹, PETER AMANN³, OLOF GUTOWSKI¹, ANN-CHRISTIN DIPPEL¹, MATTHIAS MUNTWILER⁵, VEDRAN VONK¹, HESHMAT NOEI¹, and ANDREAS STIERLE^{1,2} — ¹Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — ²Universität Hamburg, Germany — ³University of Stockholm, Sweden — ⁴Helmholtz-Zentrum hereon, Gesthaacht, Germany — ⁵Paul-Scherrer Institut, Villigen, Switzerland — ⁶Stanford University, Stanford, USA

Over recent years, the vicinal ZnO(10-14) surface garnered increased scientific interest, as it combines a high density of surface steps with high stability. However, the role of vicinal ZnO in Cu/ZnO catalysts

remained to be investigated. In this study, Cu nanoparticles were grown on vicinal and basal ZnO and studied by STM, LEED, SEM, and ambient pressure XPS, GIXRD, and XRR. On vicinal ZnO, the Cu nanoparticles show a high prevalence of stepped Cu facets, which are interesting for catalytic reactions. Our study elucidates the morphology of the Cu nanoparticles, their interplay with the ZnO support, their stability under oxidation/reduction conditions, and the prospects for improving the activity of Cu/ZnO-based catalysts for methanol synthesis.

O 29.7 Tue 12:00 CHE 91

A hybrid QM/MM framework to study single metal atom adsorption on doped diamond surfaces — ●SHAYANTAN CHAUDHURI¹, ANDREW J. LOGSDAIL², and REINHARD J. MAURER¹ — ¹University of Warwick, Coventry, UK — ²Cardiff University, Cardiff, UK

Polycrystalline boron-doped diamond is widely used as a working electrode material in electrochemistry, and its properties such as a high stability make it an appealing support material for nanostructures for (electro)catalytic applications. Experiments have shown that electrodeposition can lead to the creation of stable small nanoclusters and even single metal adatoms on diamond. We investigate the structural stability and reactivity of single atoms on diamond as predicted by density functional theory. As hybrid functionals are computationally intractable for large-scale periodic surface structures, we use the quantum mechanics/molecular mechanics (QM/MM) methodology to compare different density-functional approximations on equal footing. We investigate the adsorption energy and kinetic stability of metal single atoms on an oxygen-terminated diamond (110) surface and explore the role of structural defects such as vacancies and dopants on metal atom adsorption. Our work forms the foundations for the study of metal nanocluster formation on diamond.

O 29.8 Tue 12:15 CHE 91

Reaction Pathways in Heterogeneous Photoreforming of Tertiary Alcohols — ●MARTIN TSCHURL, CLARA ALETSEE, PAULA NEUMANN, PHILIP PETZOLDT, CARLA COURTOIS, MORITZ EDER, and UELI HEIZ — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

While the oxidation of tertiary alcohols remains a challenge in organic chemistry, heterogeneous photocatalysis opens up new pathways for their conversion. In this contribution, we discuss the selective oxidation of those alcohols under illumination on titania model photocatalysts. We reveal the processes occurring on the surface of a rutile single crystal in studies under ultra-high vacuum conditions and address the role of the pressure gap by comparing those results with reactions of titania powders at ambient pressure. Furthermore, we demonstrate the impact of co-catalyst loading on the selectivity of the reaction and explain the underlying reaction mechanisms.

O 29.9 Tue 12:30 CHE 91

Bottom-up synthesis and transfer of free-standing nanocluster arrays supported by carbon — ●TOBIAS HARTL¹, STEFAN SCHULTE¹, MORITZ WILL¹, PANTELIS BAMPOULIS^{1,2}, RAJENDRA SINGH³, JANI KOTAKOSKI³, JAN KNUDSEN⁴, and THOMAS MICHELY¹ — ¹Universität zu Köln — ²MESA+ Institute for Nanotechnology — ³Universität Wien — ⁴MAX IV Laboratory

Cluster superlattices exhibit unique properties stemming from their small size and dimensionality. However, their use in applications is hampered by their low stability when exposed to application relevant conditions, e.g. ambient pressure or high temperature. We succeeded in synthesizing free-standing cluster superlattice membranes (CSLM) which are stable at these conditions. CSLMs consist of a 2D lattice of similar-sized nanoclusters sandwiched between graphene (Gr) and an amorphous carbon (a-C) matrix. In order to make the membrane useful for experiments in nanocatalysis, it needs to be lifted off from the Ir(111) substrate and flipped over, to expose its Gr bottom side. This enables the removal of the covering Gr sheet and provides access to the clusters in the a-C matrix. Turning the membrane around requires a double transfer process, which is preceded by water and gas intercalation below the membrane. The transfer process consists of a first pick-up with a PDMS stamp, then a second pick-up from the PDMS stamp onto a polycarbonate stamp and finally the transfer to a new substrate. We present the fabrication and transfer processes of the membranes and explore the thermal stability and the physicochemical properties of this novel nanomaterial via XPS, TEM and STM.

O 29.10 Tue 12:45 CHE 91

Changing surface morphology and chemistry by scalable atmospheric pressure plasma treatment — ●TIMO WAGNER¹, NICOLAS WÖHRL¹, VINEETHA VINAYAKUMAR², DORIS SEGETS², and AXEL LORKE¹ — ¹Faculty of Physics and CENIDE, University Duisburg-Essen, Germany — ²Particle Science and Technology (IVG-PST) and CENIDE, University of Duisburg-Essen

Nickel foams provide a large specific surface area. Yet, compared to bulk nickel plates, they are less desirable for industrial applications due to their higher cost and more difficult handling. As part of H2Giga, the hydrogen flagship project by the German Federal Ministry of Education and Research (BMBF), we developed a plasma treatment for industry relevant nickel plates and catalyst particles. In a common manufacturing process for electrolyzers, nickel plates or meshes are first coated with a suspension of catalyst particles. Afterwards the solvents get thermally evaporated, yielding the finished electrode. With our process, the blank nickel surface can be roughened up by exposing it to a nitrogen plasma as a form of pre treatment. Also after coating, an exposure to a nitrogen plasma shows significant morphological changes. The individual particles coalesce to bulbs, that are again interspersed by a sponge-like porous structure. These structures have shown to notably improve the electrochemical performance of the electrodes, decreasing the overpotential by ca. 100mV.