

O 16: Nanoscale Heterogeneous Catalysis

Time: Monday 15:00–18:15

Location: TRE Ma

O 16.1 Mon 15:00 TRE Ma

Nickel and Platinum Clusters in Methanol Photocatalysis on Rutile Titania — ●MORITZ EDER, CARLA COURTOIS, MARTIN TSCHURL, and UELI HEIZ — Chair of Physical Chemistry, Department of Chemistry & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

We investigate the role of metal clusters in the photocatalytic alcohol conversion on an n-type semiconductor single crystal surface. It is known that small platinum clusters enable the desorption of molecular hydrogen from the surface, preventing catalyst deactivation and making alcohol photoconversion truly catalytic. This work focuses on the role of nickel clusters in methanol chemistry on reduced a titania(110)surface. Strong parallels to the thermal reactivity of platinum are evident, and the photochemistry is still governed by the semiconductor. However, catalyst deactivation is observed. Its likely causes are discussed with respect to certain pre-treatments.

O 16.2 Mon 15:15 TRE Ma

Hydrogenation of small organic molecules on size-selected Pd-clusters supported on MgO — ●KEVIN BERTRANG, MAXIMILIAN KRAUSE, MARIAN DAVID RÖTZER, ANDREW SCOTT CRAMPTON, and UELI HEIZ — Technische Universität München, Lichtenbergstr. 4, D-85748 Garching, Germany

Heterogeneous catalysis on size-selected clusters supported on metal-oxide films opens up a huge pallet of potential catalysts. The unique, non-scalable particle size dependency down to differences of only one atom lead to unique chemical and physical proprieties reflected by drastic changes in chemical activity and selectivity. Cluster-size portrays only one of a manifold of tunable variables. Properties of the support (i.e. metal-oxide thin films grown on metal single crystals) influence the cluster charge: film thickness, acidity and reducibility, (local) crystal work function, interface interactions. Control of these quantities allows to induce drastic changes in a catalyst's performance. Beside activity the selectivity of a catalyzed reaction is a fundamental concept in heterogeneous catalysis. Great emphasis is put on tailoring catalytic systems to stir their selectivity towards chemically desirable products. In this regard we studied the ripening of size-selected supported Pd_n-clusters (n ≤ 30) and the adsorption properties of acrolein, crotonaldehyde and prenal on MgO by means of electronic (UPS, MIES) and vibrational (IRRAS) spectroscopy. Further, the activity and selectivity towards the hydrogenation of small organic molecules is investigated by means of pulsed molecular beam reactive scattering and temperature programmed desorption.

Invited Talk

O 16.3 Mon 15:30 TRE Ma

Nanotuning via local work function control: Ethylene hydrogenation on supported Pt nanoclusters — ●UELI HEIZ¹, MARIAN D. RÖTZER¹, MAXIMILIAN KRAUSE¹, ANDREW S. CRAMPTON¹, BOKWON YOON², and UZI LANDMAN² — ¹Lehrstuhl für Physikalische Chemie, Catalysis Research Center & Chemistry Department, Technische Universität München, Lichtenbergstraße 4, 85748 Garching, Germany — ²School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

Prevention of blocking and deactivation of the hydrogenation of unsaturated hydrocarbons resulting from carbonaceous coke formation is a major challenge. Here we demonstrate experimentally and theoretically that the activity, selectivity, specificity and deactivation of size-selected platinum clusters can be controllably tuned by manipulating the local electronic density of the catalyzing Pt cluster via appropriate choice of the support system. We show that along with interfacial particle-to-support bonding effects, electron transfer and charge balance on the supported sub-nanometer metal clusters, controlling the catalysts activity, can be tuned by the local work function of the catalysts support. Control of this materials property was demonstrated through synthesis of ultra-thin amorphous silica, a-SiO₂, films on single crystals with differing work-functions, Pt(111) or Mo(211), serving as supports for the active sub-nanometer cluster component. The new catalytic control factor introduced here, akin to support-doping, allows steering of the chemical catalytic activity and may be used to inhibit undesirable catalyst poisoning and coke formation.

O 16.4 Mon 16:00 TRE Ma

Palladium nanoparticles supported on sapphire (0001): Decomposition of metastable palladium carbide under LOHC and under inert gas atmosphere — ●RALF SCHUSTER¹, MANON BERTRAM¹, HENNING RUNGE², SIMON CHUNG², VEDRAN VONK², HESHMAT NOEI², YAROSLAVA LYKHACH¹, ANDREAS STIERLE², and JÖRG LIBUDA¹ — ¹Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen — ²Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, D-22607 Hamburg

Surface carbon species can be formed by unselective decomposition during heterogeneously catalyzed dehydrogenation of liquid organic hydrogen carriers (LOHCs). These species may diffuse into the bulk of the catalyst, forming a metal carbide phase. For palladium, however, the carbide phase is metastable with respect to palladium and graphite. Therefore, we studied the stability of palladium carbide on sapphire-supported Pd nanoparticle model catalysts. Two different particle sizes were investigated under reaction conditions (500 K, 1 bar) by high-energy grazing incidence X-ray diffraction. For small particles and low gas flow rate, the carbide formed is stable in LOHC atmosphere but decomposes under pure argon. Increasing the gas flow rate results in immediate decomposition of the carbide even in the presence of LOHC. Studies on bigger particles at low gas flow rate show a different behavior. Here, the carbide is stable in the presence of LOHC only for a limited amount of time before it decomposes in further contact with the LOHC.

O 16.5 Mon 16:15 TRE Ma

Coupled Cluster Embedding of Metal Nanoparticles — ●WILKE DONONELLI — Department of Physics and Astronomy, Aarhus University, Denmark

In a recent study, we calculated CCSD(T) adsorption energies on metal nanoparticles (NPs) of varying sizes [1]. We were able to show that it is possible to calculate adsorption energies and activation barriers for different sizes of NPs at the CCSD(T) level of theory by using ONIOM as a QM/QM* embedding scheme and discussed the results with respect to full CCSD(T) and DLPNO-CCSD(T) energies for small 13 atom coinage metal NPs [2]. Another way of calculating energies at higher levels of theory is using either the method of increments (see e.g. ref [3]) or a simpler similar approach (without usage of localized molecular orbitals from an all electron calculation) the many body expansion (MBE). The advantage of using a MBE is that the estimated total energy can be calculated from a pre-calculated database or can be estimated e.g. with neural networks [4]. In our new approach we are trying to use a MBE in the framework of the before mentioned QM/QM* embedding scheme [1] in order to overcome some problems related to neglecting the overall electronic structure of a system when using the MBE.

References [1] W. Dononelli and T. Klüner; Faraday Discuss. 208, 105 (2018) [2] R. Arrigo et. al, Faraday Discuss. 208, 147 (2018) [3] E. Voloshina, Phys. Rev. B 85, 045444 (2012) [4] K. Yao, J. E. Herr and J. Parkhill, J.Chem.Phys. 146, 014106 (2017)

O 16.6 Mon 16:30 TRE Ma

Cluster superlattice membranes — TOBIAS HARTL¹, ●MORITZ WILL¹, SOPHIA DELLMANN¹, DAVOR ČAPETA², VIRGÍNIA BOIX DE LA CRUZ³, RAJENDRA SINGH⁴, DANIEL SCHEINECKER⁴, PAOLO LACOVIG⁵, SILVANO LIZZIT⁵, JANI KOTAKOSKI⁴, MARKO KRALJ², JAN KNUDSEN³, THOMAS MICHELY¹, and PANTELIS BAMPOULIS¹ — ¹II. Physikalisches Institut, University of Cologne — ²Institut za fiziku, Zagreb — ³MAX-IV Lab, Lund — ⁴Faculty of Physics, University of Vienna — ⁵ELETTRA Sincrotrone, Trieste

We demonstrate the fabrication of a free-standing material consisting of a dense array of perfectly ordered and similar-sized metal nanoclusters sandwiched between sp²/sp³-hybridized carbon and graphene, highly stable under reaction conditions. The nanometer-thick membrane is prepared by conformal embedding of pre-formed Ir cluster arrays on graphene/Ir(111) with elemental carbon in ultra-high vacuum and subsequent ex situ transfer from the Ir(111) crystal by the hydrogen bubbling method. High resolution transmission electron microscopy of the free-standing membrane confirms the perfect order and crystallinity of the encapsulated metal clusters, with super-lattice constant of 2.51nm and Ir nearest-neighbor distance of 2.5Å. The approach

presented in this study can be extended to different cluster materials and sizes. It paves the way for synthesizing cluster membranes with tunable functionalities which have potential applications in optoelectronics, nanomagnetism and catalysis.

O 16.7 Mon 16:45 TRE Ma
Shape-controlling effects of hydrohalic and carboxylic acids in TiO₂ nanoparticle synthesis — KAI SELLSCHOPP¹, WOLFGANG HECKEL¹, JOHANNES GÄDING¹, CLEMENS SCHRÖTER², ANDREAS HENSEL², TOBIAS VOSSMEYER², HORST WELLER², STEFAN MÜLLER¹, and ●GREGOR VONBUN-FELDBAUER¹ — ¹Institute of Advanced Ceramics, Hamburg University of Technology — ²Institute of Physical Chemistry, University of Hamburg

Shape-controlled synthesis of nanoparticles (NP), here titania (TiO₂), is paramount for various fields from catalysis to materials design. In thermodynamic equilibrium, the NP shape is governed by the stability of competing surface facets which also determine characteristics of NPs such as the reactivity or the mechanical properties of assembled NPs. Combining density functional theory (DFT) calculations with experimental techniques such as TEM, we studied the influence of various adsorbates on the NP shape during synthesis. This effort allowed the identification of mechanisms stabilizing different facets and the detailed characterization of the NPs which shows the agreement between computational and experimental work. Investigating the effects of variations in the physical conditions and chemical environments, e.g. via changes in the chemical potentials, highlights potentials for new synthesis routes and NP shapes.

O 16.8 Mon 17:00 TRE Ma
Ru/TiO₂ catalysts in the CO₂ methanation: chemical nature of Ru nanoparticles investigated by operando X-ray absorption spectroscopy — ●JOACHIM BANSMANN, ALI ABDEL-MAGEED, SHILONG CHEN, KLARA WIESE, and R. JÜRGEN BEHM — Institute of Surface Chemistry and Catalysis, Ulm University, Albert-Einstein-Allee 47, D-89081 Ulm, Germany

The CO₂ methanation (known as Sabatier reaction) is an important catalytic process for the conversion of CO₂ to methane in H₂ rich gas mixtures over Ni and Ru catalysts and has recently gained increasing interest due to its application in the power-to-gas technology. In this contribution, we concentrate on the physical and chemical properties of Ru nanoparticles on Ru/TiO₂ catalysts in the CO₂ methanation using TiO₂ (P90) supports. 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 a CO₂ reformat gas mixture at atmospheric pressure (15.5% CO₂, balance H₂) at 190C. Additionally, we applied a stepwise increase in the temperature up to 350C in the reaction gas mixture in order to activate the catalysts followed by measurements at 190C. XANES data showed a very high content of metallic Ru species during the activation period. The effect of the activation step on the activity and deactivation of the catalyst will be discussed based on simultaneously recorded IR/GC data. Furthermore, the results will be compared to recently obtained operando XAS in the CO methanation over Ru/TiO₂ catalysts used in our group.

O 16.9 Mon 17:15 TRE Ma
Nanoscale surface chemistry of Au-based catalysis studied by field emission techniques — LUC JACOBS¹, THIERRY VISART DE BOCARME¹, AUSTIN AKEY², DAVID BELL², and ●CÉDRIC BARROO^{1,2} — ¹Université Libre de Bruxelles — ²Harvard University

To improve the efficiency of binary catalysts, it is crucial to understand the surface composition/reactivity relationships. Here, we studied the AuAg system exhibiting high activity and selectivity for deNO_x and selective oxidation reactions. The catalytic performance of AuAg is attributed to the presence of traces of silver allowing to provide adsorbed atomic oxygen, the key factor for activity/selectivity on gold surfaces. To do so, we used field ion microscopy (FIM), field emission microscopy (FEM) and atom probe tomography (APT). APT is used to characterize the structure of nanoporous gold catalysts and to study the non-homogeneous distribution of Ag within the 3D-structure. The size of a single ligament corresponds to ~50nm and can be modelled by sharp tips. Such samples are analyzed with atomic-scale resolution by FIM to study the structure before and after reaction; but also by FEM to observe the structure-reactivity relationships during the ongoing process. N₂O+H₂ was selected for its ability to provide atomic oxygen at the surface, and the experiments provide insights into the local reactivity of the sample: within a very strict temperature range, we can study the relative reactivity of different crystallographic ori-

entations. Further experiments were performed during O₂+H₂ and CH₃OH+O₂ reactions. These results prove the relevance of field emission techniques to study the catalytic activity of alloys.

O 16.10 Mon 17:30 TRE Ma
In situ SEM as surface-sensitive tool to study catalytic reactions — ●CÉDRIC BARROO¹, ZHU-JUN WANG², and MARC WILLINGER² — ¹Université Libre de Bruxelles — ²ETH Zurich

Non-equilibrium reactions are observed in a variety of reactive systems, including at the surface of catalytic materials. Probing such reactions and their dynamics during the ongoing processes remains challenging due to the scarcity of techniques allowing for in situ experiments. Here we report the observation and analysis of nonlinear behaviours during NO₂+H₂ on Pt catalysts using in situ environmental scanning electron microscopy (ESEM), a technique sensitive to the variations of work function due to the presence of adsorbates. The ESEM instrument allows to study samples with various morphologies, allowing to bridge the materials-gap, and can be used with gas pressures up to tens of Pa. Experiments during the NO₂ hydrogenation were performed on Pt single crystals and on Pt foils, and several types of nonlinear behaviours were observed, mainly in the form of spiral patterns. Different brightness levels can be distinguished on a single propagating wave, sign of different surface adsorbate composition. These patterns were observed on regions as large as 100 *m and over a wide range of pressures: from 10-3 to 20 Pa. ESEM can be used to observe similar phenomena over different pressure conditions, allowing to, somewhat, bridge the pressure-gap; but also analysing the same reaction on single crystal and foils: it is then possible to study the various reaction behaviors, the structure sensitivity of the reaction, the spillover between different facets, and how the presence of boundaries affects the reactivity.

O 16.11 Mon 17:45 TRE Ma
Molecular Dynamics Simulations of Silver Tarnishing — ●GABRIELE SALEH^{1,3}, CHEN XU², and STEFANO SANVITO³ — ¹Istituto Italiano di Tecnologia, Via Morego 30, Genova 16163 Italy — ²Nokia Bell Labs, 600 Mountain Avenue, Murray Hill, NJ, USA — ³a School of Physics, AMBER and CRANN institute, Trinity College Dublin, College Green, Dublin 2, Ireland

Silver is broadly adopted in electronics, although its tendency to degrade by reacting with the environment (Ag tarnishing) represents a severe limitation. Ag is easily tarnished by sulphur compounds, even at ppb concentrations, but hardly reacts with O₂, despite thermodynamics predicts both sulphide and oxide to form favorably at ambient conditions[1]. The reactivity disparity is thus to be sought in the reaction dynamics, that is the focus of this contribution. We performed extensive Molecular Dynamics (MD) simulations of Ag/S and Ag/O reactions by employing reactive force fields (ReaxFF [2]). We unearth the different mechanisms of silver oxidation and sulphidation[3], thereby explaining why the latter but not the former takes place. The influence of various defects on Ag reactivity is also considered. Ab initio calculations are performed to confirm and further rationalize the MD findings. Additionally, our results recover (and explain) a number of experimental results from literature. Importantly, for this study we developed new ReaxFF force fields that was extensively tested against ab initio results. [1] P. Patnaik *Handbook of Inorganic Chemicals* [2] A.C.T. van Duin et al., J. Phys. Chem. A 105, 9396 (2001) [3] G. Saleh et al., Angew. Chem. 58, 6017 (2019)

O 16.12 Mon 18:00 TRE Ma
Water-Gas Shift Activity on Au-Clusters Supported over TiO₂(110) Surface: The Role of Planar Versus Non-Planar Au-Clusters — ●BHUMI BARAIYA¹, VENU MANKAD², and PRAFULLA JHA¹ — ¹Department of Physics, Faculty of Science, The M. S. University of Baroda, Vadodara-390002, Gujarat, India — ²Department of Physics, School of Technology, GITAM, Hyderabad Campus, Hyderabad -502329, Telangana, India

Water-gas shift (WGS) reaction over transition metal nanoclusters supported on reducible oxides achieved noticeable attention by the surface scientists due to its great potential to improve catalytic activity compared to conventional catalysts. The two key factors for this reaction is a matter of intense debate, (1) the adsorption strength of carbon monoxide (CO) and (2) the dissociation of water (H₂O). Herein, we have adopted dispersion-corrected density functional theory (DFT-D2) calculations to investigate WGS activity for the production of hydrogen (H₂) over planar and non-planar Au clusters supported over TiO₂(110) rutile surface. In quest of the most preferable site for co-adsorption, we studied adsorption energetics of H₂O, CO and carboxyl (COOH)

intermediate over various sites of Au over TiO₂(110) rutile surface. Strong metal*support interactions stabilize Au-clusters which favor the formation of COOH through the dissociation of O*H bonds. The

neighboring edges of non-planar Au-cluster are more suitable for CO and H₂O adsorption for the formation of COOH by lowering the energy barrier below 0.5 eV compared to planar Au-clusters.