O 50: Supported Nanoclusters: Structure, Reaction, Catalysis

Time: Wednesday 10:30–12:30 Location: TC 006

O 50.1 Wed 10:30 TC 006

Interaction of Formate with Magnetite Nanoparticles Supported by Al_2O_3(0001) — •Mohammad Ebrahim Haji Naghi Tehrani[1,2], Daniel Silvan Dolling[1,2], Jan-Christian Schober[1,2], Esko Erick Beck[1,2], Mona Kohantorabi[1], Arno Jeromin[1], Thomas F. Keller[1], Vedran Vonk[1], Heshmat Noei[1,3], and Andreas Stierle[1,2] — [1]Deutsches Elektronen-Synchrotron (DESY), D-22603 Hamburg, Germany — [2]Fachbereich Physik Universität Hamburg, Jungiusstrasse 9, 20355 Hamburg, Germany — [3]Hamburg Centre for Ultrafast Imaging, Universität Hamburg, Hamburg, Germany

We studied the growth and adsorption properties of magnetite nanoparticles (NPs) grown on Al_2O_3(0001) support by means of physical vapor deposition. Grazing incidence X-ray diffraction (GIXRD) characterization indicated the formation of epitaxial (111)-oriented NPs. Scanning electron microscope (SEM) showed triangular-shaped NPs. Adsorption of formic acid as a probe molecule was studied on the magnetite NPs using Fourier transmission infrared reflection-absorption spectroscopy (FTIRRAS). According to the results, formate adsorbs in the forms of chelating and quasi-bidentate geometries on these NPs, similar to what we recently evidenced on a (111) magnetite single crystal surface. Moreover, X-ray photoelectron spectroscopy (XPS) proved a possible phase transition from magnetite to maghemite after air exposure. Our model system can be applied in order to design the next generation of hierarchical organic-linked magnetite.

O 50.2 Wed 10:45 TC 006

Elucidating the Role of the Degree of Reduction in the Alcohol Photooxidation over Titania(110) Photocatalysts — •Philip Petzoldt, Lucia Mengel, Anna Lemperle, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Titania is one of the most widely investigated metal-oxides in surface science and often considered the archetypical heterogeneous photocatalyst. Fundamental studies have deepened the understanding of its thermal and photochemical reactivity on the atomic scale as well as the interplay with nanoparticulate co-catalysts. However, a critical but commonly neglected parameter of titania is the degree of its reduction and consequential impacts on the (photo)reactivity.

In this contribution, we address this aspect by investigating the alcohol photooxidation reaction over Pt cluster-loaded Titania(110) single crystals, while systematically changing the degree of reduction of the photocatalyst. Our results provide new insights into different factors governing the photoreactivity and underline the importance of kinetics in photocatalysis.

O 50.3 Wed 11:00 TC 006

Influence of the Strong Metal-Support Interaction on the Photoactivity of Pt-loaded TiO_2(110) — •Lucia Mengel, Philip Petzoldt, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Pt-loaded TiO_2(110) is well-known for its capability of alcohol photoreforming. The hole-mediated photooxidation reaction yields hydrogen next to valuable organic compounds such as formaldehyde. The concept of encapsulation of clusters or nanoparticles by a metal oxide overlayer under reductive conditions is well established and has been extensively studied using a variety of techniques. Such encapsulations caused by the strong metal-support interaction (SMSI) are a promising tool in photo-/electrocatalysis to improve catalyst selectivity and high-temperature stability. However, the mechanistic influence of an SMSI overlayer on the photocatalytic hydrogen evolution reaction on Pt-loaded TiO_2(110) is still under investigation.

In our work, we focus on SMSI-induced effects on the hydrogen evolution reaction on Pt_{10}-loaded TiO_2(110) under ultra-high vacuum conditions. In particular, we investigate the SMSI state of the Pt_{10} clusters by thermal-programmed desorption of probe molecules. We employ methanol photoreforming as model reaction to study the evolution of hydrogen on the Pt_{10} clusters in the SMSI state.

O 50.4 Wed 11:15 TC 006

Cu Oxide Nanoparticles for Virus Inactivation — •Daniel Silvan Dolling[1,2], Miguel Blanco Garcia[1,2], Jan-Christian Schober[1,2], Mohammad Ebrahim Haji Naghi Tehrani[1,2], Ming Chao Kao[1,2], Andreas Stierle[1,2], and Heshmat Noei[2] — [1]Deutsches Elektronen Synchrotron (DESY) — [2]Universität Hamburg

Copper and its oxides are well known for their antiviral and antibacterial properties, more recently including the inactivation of SARS-CoV-2 [1, 2, 3]. The combination of Cu oxides with TiO2 has attracted interest due to the photocatalytic activity of the combined system. For the photocatalytic activity, the specific oxidation state of Cu is paramount, as the oxidation states offer different pathways for visible light activity. Up to now, most research regarding virus inactivation has focused on powder systems. Here, we investigate the effects of different Cu nanoparticle sizes and coverages on single crystalline TiO2(110) surface by X-ray photoelectron spectroscopy(XPS). Moreover, as the oxide state is playing a major role in the (photo-)activity, we investigate the in-situ oxidation of Cu nanoparticles via XRD, XPS and SEM. [1] M. Hosseini et al., Scientific Reports 12 (2021), 5919-5928. [2] A. Purniawan et al., Scientific Reports 12 (2022). [3] M. Liu et al., J. Mater. Chem. A 3 (2015), 17312-17319.

O 50.5 Wed 11:30 TC 006

Structure of Pd/CeO2/YSZ and Pd/Al2O3 model systems during methane oxidation light-off — •Jan Schober[1,2], Mona Kohantorabi[1], Birger Holtermann[3], Nadejda Firman[3], Thomas Keller[1], Vedran Vonk[1], Yolita Eggeler[3], and Andreas Stierle[1,2] — [1]DESY, Hamburg, Germany — [2]UHH, Hamburg, Germany — [3]KIT (LEM), Karlsruhe, Germany

High ecological impact of gasoline and diesel fuels causes a shift to natural gas and biofuel alternatives. Methane is one of the major components of these fuels and has a much higher greenhouse gas effect. To eliminate methane from exhaust gases, heterogeneous catalysts using noble metal NPs of the Pt group with oxides such as Al2O3 and CeO2 as support. [1,2]. To track the active sites and elucidate structure function relationships on an atomistic level we prepare fully oxidized and epitaxial CeO2 thin films for NP support, suitable for catalytic studies using grazing incidence X-ray diffraction. This allows us to investigate open questions about the interplay of the NPs with the support, role of the support in the reaction, sintering behavior and reaction mechanism in the low-temperature regime [1]. Using our operando catalysis environments, we investigated Pd/Al2O3 and Pd/CeO2/YSZ catalysts during methane oxidation light-off experiments at ID31, ESRF with HEGIXRD. With in-line mass spectrometry we were able to track activity while capturing detailed structural information on NPs and support by continuously tracking high-symmetry planes of reciprocal space. [1] DOI: 10.1021/acscatal.0c03338. [2] DOI: 10.1016/j.susc.2013.06.014.

O 50.6 Wed 11:45 TC 006

Bimetallic Pd-Rh core-shell nanoparticles supported on Co3O4(111): atomic ordering and stability — •Yaroslava Lykhach[1], Alexander Simanenko[1], Lukáš Fusek[1,2], Tomáš Skála[2], Nataliya Tsud[2], Sascha Mehl[3], Olaf Brummel[1], and Jörg Libuda[1] — [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany — [2]Charles University, Prague, Czech Republic — [3]Elettra-Sincrotrone Trieste SCpA, Basovizza-Trieste, Italy

The activity of bimetallic Pd-Rh catalysts can be efficiently tuned by geometric and electronic effects resulting from the atomic arrangement and bimetallic interactions between the Pd and Rh atoms. Additional functionalities arising from the electronic metal-support interaction (EMSI) can be introduced by the use of reducible oxide supports. We investigated the impact of the EMSI on the atomic ordering and stability of bimetallic Pd@Rh and Rh@Pd core@shell nanostructures supported on well-ordered Co3O4(111) films by means of synchrotron radiation photoelectron spectroscopy (SRPES). Depth profile analysis of the charge transfer and the oxidation states of Rh and Pd was performed using tunable synchrotron light during the preparation and annealing of the model systems in UHV. We found that the EMSI yields a fraction of Rh3+ species at the interface between metallic Rh nanoparticles and Co3O4(111). Annealing the model systems triggers atomic rearrangement in the core@shell nanostructures, leading to the formation of thermodynamically favorable Pd-rich shells and Rh-rich cores in both core@shell systems.

O 50.7 Wed 12:00 TC 006

Identifying Partial Reaction Steps in the Photocatalytic Conversion of Alcohols on Rutile Titania by Isotopic Labeling

— •Martin Tschurl, Philip Petzoldt, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

The substitution of particular isotopes is a powerful method to uncover partial reactions in complex networks and to identify rate-determining steps by ascertaining kinetic isotope effects. Utilizing this methodology, we study the reaction of methanol on a rutile $TiO_2(110)$ single crystal decorated with Pt_{10} clusters under UV illumination in an ultra-high vacuum environment. By applying alcohols with different degrees of deuteration, we exemplarily reveal the reaction sequence in the photocatalysis of co-catalyst-loaded rutile titania for this class of molecules.

O 50.8 Wed 12:15 TC 006

Photocatalytic Reforming of Tertiary Alcohols at Ambient Conditions

— •Paula Neumann, Clara Aletsee, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

The selective oxidation of tertiary alcohols by heterogeneous photocatalysis is a mild alternative compared to harsh methods commonly employed in organic chemistry. What was first shown in a UHV study using a titania single crystal as a photocatalyst, we transferred to ambient conditions by means of our gas phase micro-reactor enabling sensitive and time-resolved product detection in a well-defined environment under the exclusion of oxygen. The results observed for a titania powder catalyst are in good agreement with UHV findings suggesting the absence of a significant pressure gap wich allows for a comprehensive interpretation of the surface photochemistry. Lastly, we discuss the impact of co-catalyst loading on the reaction and present the underlying mechanistic processes.