O 33: Poster: Supported Nanoclusters and Catalysis

Time: Tuesday 18:00–20:00 Location: Poster C

O 33.1 Tue 18:00 Poster C

HR-XPS Study on the Adsorption of CO on Graphene-Supported Co Clusters — •Natalie Waleska-Wellnhofer[1], Fabian Düll[1], Udo Bauer[1], Phillip Bachmann[1], Johann Steinhauer[1], and Christian Papp[1,2] — [1]Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — [2]Freie Universität Berlin, Germany

Cobalt plays an important role as catalytic active material for the industrial production of hydrocarbons by Fischer-Tropsch synthesis. To overcome the material gap, we investigated graphene-supported Co clusters as model catalyst by HR-XPS to gather more information about the catalysts' properties. Using CO as a probe molecule, we were able to determine the available adsorption sites on the as-prepared clusters which are edge/top and bridge/hollow sites. The desorption temperatures of CO from these sites were determined by temperature-programmed XPS to be 360 and 240 K, respectively. Additionally, CO dissociation was observed. The dissociation products were used to study the influence of C and O on the reactivity of the clusters. For the precovered clusters, no CO adsorption at edge sites was observed due to site blocking. Furthermore, no CO dissociation was found. Thus, the edge sites are determined to be the most active sites. Moreover, the desorption temperature of CO decreased as a result of a change in the adsorption energy on the precovered clusters.

We thank Helmholtz-Zentrum Berlin for allocation of beamtime and BESSY II staff for support during beamtime. This work was funded by the DFG within SFB 953.

O 33.2 Tue 18:00 Poster C

Photocatalytic Alcohol Reforming on Platinum Cluster Co-Catalyst Loaded Titania(110) — •Anna Lemperle, Philip Petzoldt, Lucia Mengel, Martin Tschurl, and Ueli Heiz — Chair of Physical Chemistry, School of Natural Sciences & Catalysis Research Center, Technische Universität München, Lichtenbergstr. 4, 85748 Garching, Germany

Sunlight is a widely abundant resource, whose potential applications have come into focus in the face of environmental challenges. The field of photocatalysis aims to use light to power chemical reactions, thereby storing its energy inside chemical bonds. However, state of the art catalysts are limited in their performance. To systematically optimise the efficiency of photocatalysts, fundamental understanding of reaction mechanisms is essential. Only well-defined model systems allow to trace back catalytic results to distinct catalyst features and elucidate individual reaction steps. Alcohol reforming on metal loaded semiconductor single crystals under ultra-high vacuum conditions represents an ideal model reaction to enable such mechanistic studies. Encapsulation of clusters with a metal oxide overlayer caused by strong metal-support interactions are of particular interest, as it affects both turnover-frequency and selectivity of the catalyst.

In this poster, mechanistic insights gained from photocatalytic conversion of methanol over platinum cluster loaded $TiO_2(110)$ single crystals will be presented. In particular, we will focus on the effects of reductive heating on the co-catalyst and support demonstrating the importance of a profound understanding of their interplay.

O 33.3 Tue 18:00 Poster C

Investigation of highly efficient black titania nanotube photocatalyst by soft X-ray spectroscopy — •Hesham Hamad[1] and Giuliana Aquilanti[2] — [1]Fabrication Technology Research Department, Advanced Technology and New Materials Research Institute (ATNMRI), City of Scientific Research and Technological Applications (SRTA-City), New Borg El-Arab City, 21934, Alexandria, Egypt — [2]Elettra – Sincrotrone Trieste, s.s. 14 - km 163,5 in AREA Science Park, 34149 Basovizza, Trieste, Italy

The recent discovery of black TiO2 nanoparticles with enhancing solar absorption will trigger an explosion of interest; but black TiO2 nanoparticles remain a mystery. Here we elucidate more properties and try to understand the inner workings of black TiO2 nanotubes with hydrogenated disorders in a surface layer surrounding a crystalline core. In this work, TiO2 nanotubes (TNT) and its black hydrogenated TiO2 nanotubes (BTNT) were synthesized and investigated by characterization techniques. The merit of this project is to investigate the prepared synchrotron-based X-ray absorption fine structures (XAFS). It probed the unoccupied and occupied molecular orbitals of densities of states for O 2p and Ti 3d hybrid orbital characteristics, respectively. The reduction behavior and electronic and crystalline structure of a series of TNT and BTNT as photocatalysts will be investigated by using synchrotron-based XAFS. These techniques provide novel opportunities for tackling the structure and the dynamics of chemical and physical systems in solution.

O 33.4 Tue 18:00 Poster C

Fluorescence Carbon dots (CQDs) produced via hydrothermal carbonization incorporated in Graphene Oxide layers — •Daniel Saavedra[1], Marcelo A. Cisternas[2], Donovan E. Diaz-Droguett[1], and Ulrich G. Volkmann[1] — [1]Instituto de Física, Pontificia Universidad Católica de Chile, Santiago, Chile — [2]Escuela de Ingeniería Industrial, Universidad de Valparaíso, Santiago, Chile

Carbon quantum dots (CQDs) have received increasing attention due to their excellent photostability, low toxicity, tunable fluorescence performance [1], high extinction coefficient and brightness. In this study, carbon dots were prepared by carbonization of chitosan via hydrothermal carbonization method [2]. To improve the stability, graphene oxide synthesized by the Hummer method was incorporated. The obtained CQDs were characterized by various techniques including FTIR, AFM, TEM, UV-Vis and fluorescence spectroscopy. The results obtained are aimed at incorporating carbon dots into nanostructured surfaces to enhance hydrogen production by photocatalytic water splitting. Acknowledgements: ANID Ph.D. Fellowship (DS). References: [1] Wu, Q, et al. (2023), Nano Research, 16(2), 1835-1845. [2] Zattar, A. P. P., et al. (2021), Nanotubes and Carbon Nanostructures, 29(6), 414-422.

O 33.5 Tue 18:00 Poster C

In situ observation of Pt encapsulation in powder and single crystalline model catalysts — •Mohammad Salehi[1], Florian Kraushofer[1], Sebastian Kaiser[1], Matthias Krinninger[1], Johanna Reich[1], Virginia Pérez-Dieste[2], Friedrich Esch[1], and Barbara A. J. Lechner[1] — [1]Technical University of Munich, Garching, Germany — [2]ALBA Synchrotron Light Source, Barcelona, Spain

The activity of catalysts supported on reducible oxides is frequently altered significantly at high temperatures due to the strong metal support interaction (SMSI), which leads to an encapsulation layer surrounding the noble metal particles, changing the available active sites. Nevertheless, the effects of oxidizing and reducing treatments on the encapsulation layer under high pressures remain controversial, as ultrahigh vacuum (UHV) analyses often fail to fully understand the intricate nature of these systems. To comprehensively apprehend the atomic-scale structural dynamics and the process of active site formation, it is imperative to employ in situ or operando measurements. In this study, we utilize near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and near-edge X-ray absorption fine structure (NEXAFS) techniques to conduct a comparative analysis between rutile TiO_2 powder catalysts and rutile $TiO_2(110)$ single crystal samples concerning Pt encapsulation in oxygen. We find that on single crystals, Pt encapsulation dynamics depend both on the reduction state of the sample and on the Pt loading. Powder samples behave more similarly to near-stoichiometric crystals than strongly reduced ones but also show qualitative distinctions

O 33.6 Tue 18:00 Poster C

Operando ambient pressure HAXPES studies of Cu/ZnO(10-14) and Cu/ZnO(000-1) model catalysts for methanol synthesis — •Heshmat Noei[1], Robert Gleissner[1], Pauline Schütt[2], Michael Wagstaffe[1], Christopher Goodwin[3], Markus Soldemo[3], Mikhail Shipilin[3], Patrick Lömker[3], Christoph Schlueter[1], Peter Amann[3], Gregor Feldbauer[4], Anders Nilsson[3], and Andreas Stierle[1] — [1]Deutsches Elektronen-Synchrotron (DESY), Hamburg, Germany — [2]Universität Hamburg Department of Physics, Hamburg, Germany — [3]Stockholm Universitet, Department of Physics, Sweden — [4]Institute of Advanced Ceramics, TU Hamburg, Germany

The vicinal ZnO(10-14) facet recently gained scientific interest for its high density of surface steps and outstanding stability [1]. It has the lowest formation energy in comparison with other mixed-terminated facets such as (10-10) or (11-20) and therefor can be expected to play a distinct role in Cu/ZnO/Al2O3 powder catalysts [2]. We investigate the growth and morphology of the Cu nano particles on the vicinal ZnO surface under UHV conditions. Ambient Pressure XPS studies reveal the higher abundance of reaction intermediates for Cu/ZnO(10-14) in comparison to the Cu/ZnO(000-1) system on the surface of these model catalysts. Switching from CO/H2 over CO/CO2/H2 to CO2/H2 conditions and vice versa revealed complete reversibility. References [1] H. Zheng, Phys. Rev. Lett. 2013, 111, 086101. [2] K.S. Chan, Appl. Phys. Lett. 2015, 106, 212102.

O 33.7 Tue 18:00 Poster C

Advancing Single-Atom Catalysis: Developing a New Apparatus for Near-Ambient Pressure Applications — •Johannes Filzmoser, Adam Lagin, Jiri Pavelec, Ulrike Diebold, Michael Schmid, and Gareth S. Parkinson — TU Wien - Institute of Applied Physics - Wiedner Hauptstraße 8-10, 1040 Vienna, Austria

Single-atom catalysts (SAC) are much-studied in surface science due to their great potential in heterogeneous catalysis. Model systems consisting of metal adatoms on single-crystal metal-oxide surfaces are being investigated in ultra-high vacuum (UHV) to understand the fundamentals of SAC. A step towards industrial SAC systems is an examination of idealized model systems under more realistic conditions, i.e., at elevated pressures and temperatures. This work aims to develop a UHV-compatible reaction cell, enabling sample exposure to gases at about 1 mbar pressure and temperatures up to 300°C. The composition of the exhaust gas from the reactor is quantitatively analyzed by mass spectrometry. Due to the low number of active sites on model SAC, measuring turnover frequencies presents a significant challenge. Therefore, we are investigating methods to optimize detection techniques.

O 33.8 Tue 18:00 Poster C

Computational Modeling of Metal-Organic Frameworks as Heterogeneous Catalysts for Biomass Conversion — •Manuel A Ortuño[1], Thanh-Hiep T. Le[1], David Ferro-Costas[1,2], and Antonio Fernandez-Ramos[1,2] — [1]Centro Singular de Investigación en Química Biolóxica e Materiais Moleculares (CIQUS), Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain — [2]Departamento de Química Física, Facultade de Química, Universidade de Santiago de Compostela, 15782 Santiago de Compostela, Spain

Metal-organic frameworks (MOFs) have emerged as promising heterogeneous catalysts due to well-defined structure, surface area, and tunable pore size. In particular, MOFs with Zr-based nodes are stable and therefore used as heterogeneous catalysts for a myriad of reactions.

Here we focus on UiO-66, formed by Zr-oxide nodes and 1,4-benzenedicarboxylate linkers, for the catalytic conversion of methyl levulinate into γ-valerolactone. We computed cluster and periodic models at DFT level to unravel the reaction mechanism. The simulations supported a defective node as active site, where the reaction takes place via three main steps: hydrogen transfer, nucleophilic attack, and elimination. Further studies suggested that the presence of Ce in the node might improve catalytic performance. Later, we found that both cluster and periodic models behave similarly, and the choice of density functional does not affect the rate-determining step but it does significantly change the Gibbs energy barriers.

O 33.9 Tue 18:00 Poster C

In situ XPS and SXAS study on CO adsorption on a FeNC catalyst — •Benedikt P. Klein[1,3], Beomgyun Jeong[1], Hafiz Ghulam Abbas[2], Geunsu Bae[2], Adith R. Velmurugan[2], Chang Hyuck Choi[4], Geonhwa Kim[5], Dong Woo Kim[5], Ki-jeong Kim[5], Byeong Jun Cha[6], Young Dok Kim[6], Frederic Jaouen[7], Reinhard J. Maurer[3], and Stefan Ringe[2] — [1]Korea Basic Science Institute, Daejeon, ROK — [2]Korea University, Seoul, ROK — [3]University of Warwick, Coventry, UK — [4]POSTECH, Pohang, ROK — [5]PAL, Pohang, ROK — [6]Sungkyunkwan University, Suwon, ROK — [7]University of Montpellier, France

A reliable way to quantify the number of active sites in a catalyst is crucial to evaluate its performance. One option to achieve this is to utilize strongly adsorbing gas molecules as a probe to identify the catalytically active sites. Once the molecules are adsorbed on the active sites, their surface density can be determined by using spectroscopic techniques. For this approach it is necessary to identify the probe molecules according to their spectroscopic features, a task much helped by the computational simulation of spectra. Here, we present the *in situ* XPS and SXAS study for the adsorption of CO on an iron-nitrogen-carbon (FeNC) catalyst under near-ambient gas pressure. Using the experimental spectroscopic data combined with state-of-the-art DFT based spectroscopy simulations, we determine the active site density for the electrochemical oxygen reduction reaction of this catalyst.

O 33.10 Tue 18:00 Poster C

Oxide formation and oxide/metal interaction in CeO_x/Ni(111) — •Dominic Guttmann, Björn Riedel, Raquel Sánchez-Barquilla, Carlos Morales, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Cottbus 03046, Germany

Ni/ceria catalysts exhibit a high activity for methane to methanol conversion, making them very promising for applications within a sustainable economy. Possibly, their activity may be strongly enhanced due to the facile exchange between Ce^{4+} and Ce^{3+} states, with the latter likely responsible for activating O-H and C-H bonds. Here, we aim to unravel the complex metal-oxide interactions in the inverse CeO_x/Ni(111) system under oxidizing and reducing environments. Using low-energy electron diffraction (LEED) we find that the CeO_x(111) grown by reactive molecular beam epitaxy preferentially aligns with the main directions of the Ni(111) substrate or is azimuthally rotated by ±10°. By using X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS), we find that less NiO is formed during deposition of CeO_x than when it is held without ceria at the same conditions (O_2 partial pressure and temperature). Finally, we observe a complex behavior of the cerium and nickel oxidation states when exposing the system to O_2 or H_2 atmospheres.