

O 52: Poster Wednesday: Adsorption and Catalysis 2

Time: Wednesday 18:00–20:00

Location: P4

O 52.1 Wed 18:00 P4

Investigation of the influence of the spin in adsorption structures of oxygen on a cerium chloride catalyst surface in the Deacon process using computational methods — ●KATHRIN NIESWIEC and FRANZISKA HESS — Technische Universität Berlin, Institut für Chemie, Straße des 17. Juni 124, 10623 Berlin, Germany

CeO₂-based catalysts in the HCl oxidation undergo reversible deactivation by forming CeCl₃. This work examines the interaction of the CeCl₃-(110)-surface with O₂ during the reoxidation of CeCl₃. CeCl₃ is an insulator, where Ce is 9-fold coordinated that exposes different adsorption sites at the surface. Different adsorption structures of atomic and molecular oxygen on the CeCl₃-(110)-surface are examined in terms of energy, electronic state and magnetization. Cerium-based catalyst systems are investigated by DFT calculations in the PAW approach with the PBE functional including Hubbard-U correction. Ab-initio thermodynamics are employed to analyze temperature and pressure-dependency of oxygen adsorption on the surface. Upon adsorption of oxygen on the surface, Ce³⁺ can be locally oxidized to Ce⁴⁺, resulting in different spin and charge density distributions. Consequently, the adsorption energies of oxygen can vary by over 1 eV, depending on the initial spin state. The ab-initio thermodynamics analysis based on the obtained oxygen adsorption energies suggests that the CeCl₃ surface is expected to be covered by oxygen due to the strong Ce-O bond. These results suggest that spin must be explicitly included when examining adsorption on CeCl₃ surfaces in order to obtain correct adsorption energies for catalysis applications.

O 52.2 Wed 18:00 P4

Influence of the Substrate Orientation Dependent Reactivity on the On-surface Ullmann Coupling Reaction of 2,2-Dibromobiphenyl Studied by XPS — ●PAUL SCHWEER and KARINA MORGENSTERN — Chair of Physical Chemistry I, Ruhr-University of Bochum, Germany

The Ullmann coupling reaction is considered the leading approach for accessing low dimensional covalent organic structures in the context of on-surface synthesis. Despite extensive studies on the influence of the halogen substitution pattern of the halogen-aryl precursor on the reaction mechanism and product formation, the impact of ortho-substitution is barely investigated. Hence, this work aims to reveal the temperature-induced reaction steps for 2,2-dibromobiphenyl on low-index Cu surfaces. For this purpose, the precursor is deposited in ultra-high vacuum at 86 K and stepwise annealed to 600 K. By using X-ray photoelectron spectroscopy, chemical changes of the organic species and the bromine atoms are identified and assigned to the typical Ullmann reaction steps: dissociation of the halogen-carbon bond, surface bonding, and C-C coupling. Here, we further discuss different precursor reactivities on Cu(111) and Cu(110) and an additional binding energy shift on Cu(110), indicating a structural change of the surface bound biphenyl before C-C coupling at a higher temperature.

O 52.3 Wed 18:00 P4

Surface Chemistry of the MOST Energy Storage System 2-Carbethoxy-3-Phenyl-Norbornadiene/Quadracyclane — ●FELIX HEMAUER, CORNELIUS WEISS, JOHANN STEINHAUER, VALENTIN SCHWAAB, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Friedrich-Alexander-Universität, Erlangen, Germany

The intermittent character of renewable energy sources gives the necessity for novel energy storage technologies. So-called molecular solar thermal (MOST) energy systems directly combine the light-harvesting process with storing the gained energy as molecular strain. In a photo-conversion reaction, the energy-lean norbornadiene (NBD) is converted to its energy-rich valence isomer quadracyclane (QC). By derivatization of the molecular framework, the light-harvesting properties of the molecules are optimized.

The pair 2-carbethoxy-3-phenyl-NBD/QC was investigated as model system for heterogeneously catalyzed energy release. X-ray photoelectron spectroscopy was employed to study the adsorption and thermal evolution on a Ni(111) and Pt(111) surface, respectively. An unambiguous identification of the QC and NBD derivatives at low temperature was possible on both surfaces. In case of nickel, no cycloreversion of the QC derivative to NBD was found, but individual decomposition routes setting in at about 170 K. For platinum, the back conversion

under energy release was found to start at 150 K and being completed at 230 K. Above 300 K, a fragmentation into carbonaceous species occurred. The work was supported by the DFG (Project No. 392607742) and the HZB for allocation of synchrotron radiation beamtime.

O 52.4 Wed 18:00 P4

Temperature-induced surface reactions of 1-cyclohexylethanol and acetophenone on Pt(111) — ●VALENTIN SCHWAAB, FELIX HEMAUER, EVA MARIE FREIBERGER, NATALIE WALESKA, HANS-PETER STEINRÜCK, and CHRISTIAN PAPP — Friedrich-Alexander-Universität, Erlangen, Germany

1-Cyclohexylethanol (1-CHE) is an interesting candidate when it comes to molecular energy storage systems. Such secondary alcohols can function as electrofuel, whereby their oxidation over a platinum electrode yields the respective ketone together with two electrons and two protons. Additionally, 1-CHE and acetophenone (APH) represent an attractive liquid organic hydrogen carrier (LOHC) pair, as the complete dehydrogenation of the former leads to the release of four equivalents of H₂.

To gain fundamental insights into the surface reaction of both molecules, high-resolution temperature-programmed X-ray photoelectron spectroscopy experiments (HR-TPXPS) were carried out on a Pt(111) model catalyst. Based on the obtained C 1s and O 1s data, the dehydrogenation reaction of the alcohol and the formation of potential catalyst poisoning decomposition products are discussed.

We acknowledge financial support by the Bavarian Ministry of Economic Affairs, Regional Development and Energy, and by the DFG (Project No. 419654270). We thank HZB for the allocation of synchrotron radiation beamtime.

O 52.5 Wed 18:00 P4

Force-induced single-molecular switch of graphene-nanoribbon-fused helicene by atomic force microscopy — ●AKITOSHI SHIOTARI^{1,2}, AYUMU ISHII¹, and YOSHIKI SUGIMOTO¹ — ¹The University of Tokyo, Kashiwa, Japan — ²Fritz-Haber Institute of the Max-Planck Society, Berlin, Germany

On-surface synthesis is an effective bottom-up method to fabricate nanocarbon materials, such as graphene nanoribbons (GNRs), in an atomically precise manner. In this study, using the on-surface method with multiple precursors, we successfully synthesized new helicene-derivative molecule fused by seven-atom-wide armchair GNRs on an Au(111) surface. Atomic resolution imaging with non-contact atomic force microscopy (AFM) identified the molecular structure and the helicity (i.e., chirality of the twisted terminal of the GNR). Although the helicities of individual GNRs on the surface remained stable during observation, the approach of the AFM tip to the helicene-type terminal caused repulsive interactions, leading to the inversion of the twisted structure in a selective and reversible manner. This finding would contribute to the advanced design of switchable molecules and control of chiral-molecule-based devices and machines.

O 52.6 Wed 18:00 P4

On-Surface Synthesis of Kekulene and Isokekulene — ●TIM NAUMANN, QITANG FAN, LUKAS HEUPLICK, LUKAS RUPPENTHAL, SIMON WERNER, TOBIAS VOLLGRAFF, JÖRG SUNDERMEIER, and J. MICHAEL GOTTFRIED — Fachbereich Chemie, Philipps-Universität Marburg, Marburg (Germany)

The concept of aromaticity explains the exceptional stability of monocyclic, planar, conjugated molecules. When extending this concept on cycloarenes, however, the question arises whether the π -electron system is best described by the Clar model or rather by annulenic aromaticity, i.e. delocalization in the inner and outer annulene ring. This question has been discussed especially in the context of kekulene, an alternant benzenoid cycloarene. On-Surface techniques offer the possibility to synthesize kekulene and to investigate its resonance stabilisation. To create complete monolayers of kekulene for further spectroscopic studies, we developed a high-yield on-surface synthesis of kekulene on Cu(111) from vapor-deposited 1,4,7(2,7)-triphenanthrenacyclonaphane-2,5,8-triene, which undergoes cyclodehydrogenation upon annealing, resulting in extended (up to 100 nm) well-ordered domains of kekulene. While the reaction is highly selective towards kekulene on Cu(111), reaction on Cu(110)

leads to an isomer of kekulene with a lower symmetry, named isokekulene. The precursor and the products were analyzed with scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and other methods. Further annealing leads to peripheral C-H bond activation and linking towards chains and islands.

O 52.7 Wed 18:00 P4

2D arrays of reaction centers for CO oxidation over Pt/SiO₂/Si interface — ●ARTUR BÖTTCHER¹, DAVID RETTINGER¹, JAKOB HAUNS¹, MANFRED KAPPES¹, DANIELA EXNER², RAHUL PARMER³, MATTEO AMATI³, and LUCA GREGORATTI³ — ¹Institute of Physical Chemistry, KIT, 76131 Karlsruhe, Germany — ²Institute for Applied Materials, KIT, 76344 Karlsruhe, Germany — ³Elettra - Sincrotrone Trieste ScPA, Area Science Park, 34149 Basovizza-Trieste, Italy

We created arrays of tailored reaction centers on the SiO₂/Si-wafer by annealing thin Pt layers deposited on He⁺-beam patterned Graphene/SiO₂/Si substrates.[1] The resulting spots have been identified as amorphous areas consisting of silicon carbides and silicon oxycarbides. These defected surface regions are expected to act as pinning sites for migrating Pt atoms. By thermally activating the surface diffusion of Pt adatoms (1h, 600°C, UHV), the migrating atoms become immobilized thus forming chemical bonds with compounds created in the defected surface regions, resulting in 2D arrays of tailored Pt-based islands. The chemical state of individual islands has been studied by monitoring core level states (ESCA microscopy). The islands consist of Pt, PtSix and PtOx compounds and appear to be chemically resistant under exposure to molecular oxygen and carbon monoxide at T=550°C, p= 0.4 mbar, 0.5 h. The CO₂-light-off curves enable to estimate the contribution of the artificial reaction centers to the total CO->CO₂ conversion yield.

[1] A. Böttcher et al. 2020 Nanotechnology 31 505302

O 52.8 Wed 18:00 P4

CO→CO₂ conversion over Pt/SiO₂/Si model catalyst — ●ARTUR BÖTTCHER¹, PASCAL WEISENBURGER¹, DAVID RETTINGER¹, JAKOB HAUNS¹, RAHUL PARMER², MATTEO AMATI², LUCA GREGORATTI², and MANFRED KAPPES¹ — ¹Institute of Physical Chemistry, KIT, 76131 Karlsruhe, Germany — ²Elettra - Sincrotrone Trieste ScPA, Area Science Park, 34149 Basovizza-Trieste, Italy

We studied the thermal stability of the Pt/SiO₂/Si interface as the model catalyst for CO oxidation reaction. The 2D catalysts were prepared under UHV conditions by growing very thin Pt films on the SiO₂/Si wafer and subsequently performing a long-term annealing of the interface at elevated temperatures, T*(700-900K). Such a treatment results in the formation of the submicron-sized islands. The size/shape distribution of the islands scales primarily with the thickness of the Pt film. The chemical state of the islands as probed by ESCA microscopy (Elettra) evidences the formation of PtSinOm alloys as the dominating component of the islands. The CO₂ light-off curves taken for Pt/SiO₂/Si interfaces fabricated at room temperature reveal the highest CO/CO₂ conversion yield, Y, and the lowest activation temperature, T_A ~400 K. Increasing alloying degree considerably quenches the conversion yield and shifts up the CO/CO₂ conversion onset.

O 52.9 Wed 18:00 P4

Adsorption and photocatalytic inactivation of Corona-virus like particles by anatase TiO₂(101) — ●MONA KOHANTORABI, MICHAEL WAGSTAFFE, HESHMAT NOEI, and ANDREAS STIERLE — Centre for X-ray and Nano Science (CXNS), Deutsches Elektronen-Synchrotron (DESY), 22607 Hamburg, Germany

The adsorption of corona-virus like particles (VLPs), on the surface of the model catalyst TiO₂(101) was investigated using different spectroscopic and microscopic techniques.

Two different methods were employed to inactivate the virus after it was loaded on the surface of TiO₂: 1) UV light and 2) thermal treatment. The adsorbed virus morphology and virus particle arrangement on the surface of TiO₂ were investigated using grazing-incidence small-angle scattering. Microscopic studies demonstrate that the denatured spike proteins and other virus proteins dissociate from VLPs and adsorb on the surface of TiO₂.

Clarification of the interaction of the virus with the surface of semiconductor oxides will aid in obtaining a deeper understanding of the chemical processes involved in photo-inactivation of microorganisms which is important for the design of effective photocatalysts for air purification and self-cleaning materials.

O 52.10 Wed 18:00 P4

Calculation of XPS Core-Level Fingerprints of Intermediates in Methanol Synthesis on Cu Surfaces — ●MATTIS GOSSLER, AZAD KIRSAN, and BERND MEYER — Interdisciplinary Center for Molecular Materials and Computer Chemistry Center, FAU Erlangen-Nürnberg, Germany

Cu/ZnO/Al₂O₃ is used as a highly efficient catalyst in industry for the synthesis of methanol from syn gas, i.e. H₂, CO and CO₂. Despite intensive research efforts over the past decades, the precise reaction pathway and the relevant intermediates in the synthesis process are still under debate. New insights can be provided by recently performed ambient pressure x-ray photoelectron spectroscopy (AP-XPS) measurements on ZnO-supported Cu clusters with well-defined crystal terminations [1]. In order to assist the interpretation of the measured AP-XP spectra, we determined the C-1s and O-1s core level shifts for a series of intermediates in the methanol synthesis process on a variety of Cu surfaces using DFT calculations. First, a careful search for the most stable structure of all intermediates on each surface was performed. Core-level shifts were then calculated by an ΔSCF approach after removing a core electron. This fingerprint data allows us to identify the most relevant intermediates present in the AP-XPS experiments and to assess the importance of different Cu surfaces for the overall reactivity.

[1] R. Gleissner, H. Noei, S. Chung, G.D.L. Semione, E.E. Beck, A.-C. Dippel, O. Gutowski, G. Gizer, V. Vonk, A. Stierle, J. Phys. Chem. C **125** (2021) 23561–23569

O 52.11 Wed 18:00 P4

The relation between structure sensitivity and doping of ceria(111) vs. ceria(100) — EMILIA POZAROWSKA¹, LINUS PLEINES², MAURICIO J. PRIETO³, LIVIU C. TĂNASE³, LUCAS DE SOUZA CALDAS³, AARTI TIWARI³, THOMAS SCHMIDT³, JENS FALTA², CARLOS MORALES¹, and ●JAN INGO FLEGE¹ — ¹Applied Physics and Semiconductor Spectroscopy, BTU Cottbus-Senftenberg, Cottbus, Germany — ²Institute of Solid State Physics, University of Bremen, Bremen, Germany — ³Department of Interface Science, Fritz-Haber Institute, Berlin, Germany

CeO_x-Cu inverse catalysts have been shown to convert CO₂ into valuable chemicals through catalytic hydrogenation. The catalytic activity may further be enhanced by alloying ceria with trivalent, catalytically active metals, such as Sm, promoting the formation of Ce³⁺ active sites. In this work, the structural and chemical properties of (111)- and (100)- oriented CeO_x islands alloyed with samarium were explored by low-energy electron microscopy and X-ray photoemission electron microscopy. After Sm deposition on the as-grown CeO_x islands, the near-surface region of (100)-oriented CeO_x is reduced after exposure to H₂ at 470 °C, whereas the deeper layers as well as the whole (111)-oriented islands retain the Ce⁴⁺ state. Subsequent reoxidation with O₂ leads to the complete Ce⁴⁺ state recovery, suggesting the healing of oxygen vacancies. Additional annealing at 470 °C induces samarium diffusion into the ceria matrix. Yet, subsequent exposure to H₂ reduces neither the (111)- nor the (100)-oriented CeSmO_x islands, suggesting a quite unexpected stability of this system.

O 52.12 Wed 18:00 P4

Operando studies of CuZn catalysts for methanol synthesis — ●DAVID KORDUS^{1,2}, NURIA JIMENEZ DIVINS², JANIS TIMOSHENKO¹, and BEATRIZ ROLDAN CUENYA¹ — ¹Departement of Interface Science, Fritz Haber Institute of the Max Planck Society — ²Departement of Physics, Ruhr University Bochum

Methanol is an essential feedstock for the chemical industry and may be a key component when switching to renewable resources. Industrially methanol production uses a ternary Cu/ZnO/Al₂O₃ catalyst. Especially the interaction between Cu and ZnO is critical for a high activity of the catalyst. Multiple model catalysts were synthesized to target different aspects of this system, but particularly the Cu-ZnO interactions. In-situ and operando spectroscopy methods (XAS, XPS, Raman) together with microscopy and measurements of the catalytic performance allow us to follow the chemical and structural changes of the catalysts under reaction conditions. We investigated size-selected Cu and CuZn nanoparticles on multiple support materials (SiO₂, Al₂O₃ and ZnO/Al₂O₃) to obtain a better insight into particle-support interactions. These studies show that the formation of metallic Zn for CuZn particles on SiO₂ is detrimental for the catalysts activity, as it coincides with a deactivation. On Al₂O₃ in contrast, ZnO is incorporated into the support and forms a spinel structure similar to ZnAl₂O₄.

In another catalyst shaped Cu particles are used to create preferential facets on the surface of our catalysts. These unlike surface structures

will then lead to different catalytic behavior. Here, a higher activity was observed for cubic particles.