O 21: Poster Heterogeneous Catalysis

Time: Monday 18:00–20:00 Location: P2

O 21.1 Mon 18:00 P2

Disentangling Transport and Kinetics in Complex Reaction Chambers by Novel Reduced-Order Modeling Approaches — •Tobias Hülser[1], Maryke Kouyate[1], Uzair Qureshi[2], Daniel Runge[3], Georg Brösigke[2], Christian Merdon[3], Jürgen Fuhrmann[3], Karsten Reuter[1], Christoph Scheurer[1], and Sebastian Matera[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Technische Unviversität Berlin — [3]Weierstraß-Institut für Angewandte Analysis und Stochastik, Berlin

Operando catalytic characterization chambers are governed by mass transport interplaying with highly-nonlinear chemical kinetics, which needs to be accounted for by corresponding coupled simulations. Often, these chambers can not be modelled with established reactor models, instead requiring high-cost Computational Fluid Dynamics simulations. We have developed reduced-order methods which disentangle the computational treatment for transport and kinetics into an offline (OffPh) and online phase (OnPh). In the OffPh, we determine a suitable solution space of the transport operator, which is independent of the employed kinetic model and therefore reusable. In the OnPh, the solution from this space is determined from the balance of transport and kinetics at the catalytic surfaces. This drastically reduces the costs as the OffPh is a linear problem and, particularly, the nonlinear online phase typically involves only very few degrees of freedom. We demonstrate this idea on mesoscale core-shell particles, an asymptotic expansion for small catalyst samples and a quasi-exact reduced basis strategy for general problem settings.

O 21.2 Mon 18:00 P2

Bayesian Inference of Kinetic Models of Heterogeneous Catalysis by Normalizing Flows — •Andreas Panagiotopoulos[1], Javed Mudassar[2], Jens-Uwe Repke[2], Georg Brösigke[2], and Sebastian Matera[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Technical University Berlin

Estimating kinetic parameters is typically done by classical fitting a model to experimental reactor data, which, however, suffers from a number of fundamental problems like ill-posedness, multiple possible solutions and the lack of reliable uncertainty estimates. By reformulating the problem in a probabilistic language, Bayesian inference cures these problems, but also requires to sample from a high-dimension probability distribution. Because of their high non-linearity and sensitivity, this becomes challenging for kinetic models and established sampling approaches become inefficient. We investigate Normalizing Flows in conjunction with Quasi Monte Carlo sampling to address this problem. In this approach, a bijective nonlinear parameter transformation is sequentially learned such that a uniform sampling from the transformed parameters leads to a good importance sampler of the Bayesian posterior. We investigate the performance of the proposed approach on an empirical model for methanol synthesis on Cu based catalysts using synthetic and experimental data.

O 21.3 Mon 18:00 P2

Model Catalytic Studies on the Thermal Dehydrogenation of the Benzaldehyde/Cyclohexylmethanol LOHC System on Pt(111) — •Marius Steinmetz[1], Valentin Schwaab[1,2], Felix Hemauer[1,2], Eva Marie Freiberger[2], Natalie J. Waleska-Wellnhofer[2], Hans-Peter Steinrück[2], and Christian Papp[1] — [1]Angewandte Physikalische Chemie, Freie Universität Berlin (FU Berlin), Arnimallee 22, 14195 Berlin, Germany — [2]Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Egerlandstr. 3, 91058 Erlangen, Germany

We investigated the dehydrogenation reaction and the thermal decomposition of the liquid organic hydrogen carrier (LOHC) pair benzaldehyde/cyclohexylmethanol on a Pt(111) model catalyst via temperature-programmed desorption experiments and synchrotron radiation photoelectron spectroscopy. The LOHC pair has a hydrogen storage capacity of 7.0 mass%, stored in a cyclohexyl ring and a primary alcohol group. We observed a stepwise dehydrogenation mechanism, starting with the dehydrogenation of the alcohol group, followed by the dehydrogenation of the cyclohexyl ring. We also observed different dehydrogenation behaviors for low and high coverages, probably caused by steric hindrance for high coverages. Even though the LOHC pair achieves high hydrogen storage capacity, early decomposition at low temperatures between 250 and 350K limits the use of the molecule pair as a reversible hydrogen carrier.

O 21.4 Mon 18:00 P2

Size-selected metal nanoparticles on tungsten: influence of the deposition angle — •Sumanasa Begur Prakash and Mathias Getzlaff — Institute of Applied Physics, University of Düsseldorf

Metal nanoclusters and nanoparticles, especially those composed of iron (Fe), nickel (Ni), and their alloys, are fascinating due to their unique electronic and magnetic properties which vary significantly with particle size. This feature makes them not only interesting for fundamental research but also highly promising for advanced technologies including catalysis, magnetic storage, and sensing. However, interaction with the substrate during and after deposition significantly influences the particle's properties.

Our contribution is focused on size-selected Fe, Ni, and Fe-Ni alloy nanoparticles which are deposited on a W (110) substrate. Using a magnetron sputter source (Haberland-type) we vary the deposition angle to understand how this parameter influences the particle size, structure, and overall distribution of nanoparticles on the substrate surface. This approach allows us to probe the relationship between deposition conditions and particle characteristics. The size and structural properties are investigated by scanning tunneling microscopy (STM) and low energy electron diffraction (LEED) under ultra-high vacuum (UHV) conditions.

O 21.5 Mon 18:00 P2

Optimized BiVO4/g-C3N4 Heterojunctions for Efficient Photocatalytic Green Ammonia Production — •Susana D. Rojas[1], Nicolás A. Soto[1], Pablo E. Salinas[1], Daniel Saavedra[2], Marcelo A. Cisternas[1], and Ulrich G. Volkmann[2] — [1]Escuela de Ingeniería Industrial, Universidad de Valparaíso, Santiago, Chile — [2]Instituto de Física, Pontificia Universidad Católica de Chile, Santiago, Chile

BiVO4 nanostructures were synthesized via a hydrothermal method, and g-C3N4 nanosheets by urea pyrolysis. The materials were characterized using Fourier transform IR spectroscopy (FTIR), UV-Vis and X-ray photoelectron spectroscopy, X-ray diffraction, and scanning electron microscopy to confirm their chemical and morphological structures. Photocatalytic ammonia production was evaluated in a cylindrical reactor with a Xenon discharge lamp, using an aqueous catalyst dispersion under magnetic stirring and a nitrogen flow at atmospheric pressure. Ammonia production was analyzed via the Nessler method with ammonium chloride (NH4Cl) calibration curves for the aqueous phase and in situ FTIR spectroscopy with a 16 m optical path gas cell for the gas phase [1, 2]. This work advances the understanding of photocatalytic processes for sustainable ammonia production and the development of efficient, eco-friendly methods for synthesizing this essential compound. Acknowledgements: ANID project SIA77210032 (SR, MC), UVA22991 (SR, MC), ANID Fellowship (DS), and Puente UC 2024-25 (UV). Ref.: [1] P. Huang, et al., Nature Comm. 13, 7908 (2022). [2] S.Z. Andersen, et al., Nature 570, 7762, 504-508 (2022).

O 21.6 Mon 18:00 P2

Tuning the ceria island orientation: from (111) to (100)-oriented islands — •Maja Atlas, Raquel Sanchez-Barquilla, and Jan Ingo Flege — Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology Cottbus-Senftenberg, Germany

Inverse catalysis systems, where the reducible oxide is anchored on the metallic support, have shown a better performance compared with its traditional counterparts due to the strong metal support interaction. Among catalytic materials, ceria (CeO_2) is used in a wide range of applications, due to its oxygen storage and redox properties. In particular, the catalytic activity of Cu(111) can be substantially enhanced when depositing CeO_x on top, achieving direct methanol production from CO_2. In situ near ambient pressure X-ray photoemission spectroscopy (NAP-XPS) measurements have shown that the activated CO_2 molecule is stabilized by Ce^{3+} sites during the reaction. Moreover, epitaxially grown CeO_2 islands can have two different orientations on Cu(111): the (111)-oriented islands appear first and with lower oxygen pressure, while the (100)-oriented phase can be enhanced by increasing the oxygen exposure. Here, we present a structural and chemical study of the ceria islands growth as a function of temperature, oxygen pressure and deposition rate. By varying these parameters, we can study the relation between the phase and the Ce^{3+}/Ce^{4+} ratio, using XPS, low energy electron diffraction (LEED) and scanning tunneling microscopy (STM).

O 21.7 Mon 18:00 P2

Structure and chemical properties of Pt clusters and particles deposited on $CeO_2(111)$

— •Shuang Chen, Zairan Yu, Alexei Nefedov, Christof Wöll, and Yuemin Wang — Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), 76344 Eggenstein-Leopoldshafen, Germany

CeO_2-supported Pt nanoparticles are of significant technological interest due to their unique catalytic properties and wide range of applications in numerous chemical reactions. However, the catalytic performance of various Pt species remains a highly debated topic. This arises primarily from the complexity of Pt/CeO_2 powder catalysts and the scarcity of accurate reference data obtained from well-defined model systems. Here, we report systematic IR reflection absorption spectroscopic (IRRAS) investigations of Pt deposited on oxidized $CeO_2(111)$ single-crystal surfaces. By employing polarization-resolved IRRAS with CO as a probe molecule and grazing-emission XPS, we were able to track the structural and electronic evolution of Pt on $CeO_2(111)$ as a function of the deposition amount. Various Pt species, ranging from single atoms to small clusters and large particles, were identified. Our results provide solid evidence of strong electronic interactions between Pt and the ceria substrate, offering profound insights into the dynamic behavior of Pt clusters under different conditions.

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O 21.8 Mon 18:00 P2

Photoelectrochemical nitrate reduction by copper oxide-based semiconductors

— •Jasmin A. Zitzmann[1,2], Maximilian Christis[1,2], Saswati Santra[1,2], and Ian D. Sharp[1,2] — [1]Walter Schottky Institute, Technical University of Munich, Germany — [2]Physics Department, TUM School of Natural Sciences, Technical University of Munich, Germany

The photoelectrochemical nitrate reduction reaction (PEC-NO_3RR) offers a route to ambient ammonia (NH_3) synthesis and recycling of NO_3^- pollutants. Copper oxide-based semiconductors, such as Cu_2O, CuO and $CuBi_2O_4$ exhibit suitable band energetics to drive this reaction. While Cu_2O is reported for PEC-NO_3RR, further studies are required to optimize reaction conditions and minimize photocorrosion. With this aim, the PEC-NO_3RR performance characteristics of Cu_2O, CuO and $CuBi_2O_4$ are investigated in alkaline and neutral aqueous electrolytes. The dominant reaction product observed is nitrite (NO_2^-) with Cu_2O producing the highest yields. In addition, NH_3 is generated by Cu_2O, with an increase in selectivity at lower potentials. Photocorrosion is most pronounced for CuO, whereas $CuBi_2O_4$ shows the most consistent PEC stability. Our findings indicate the potential-dependent PEC-NO_3RR product selectivity, with further research necessary to optimize the electrochemical conditions to improve PEC-NO_3RR stability and NH_3 yield using these promising copper oxide-based semiconductors.