O 88: Catalysis and surface reactions III

Time: Thursday 15:00–17:45 Location: TRE/MATH

O 88.1 Thu 15:00 TRE/MATH

Trapping ionomer for efficient proton exchange membrane fuel cells — •Fanpeng Kong — Harbin Institute of Technology, Harbin, China

Both uniformity of ionomer distribution and adsorption dynamics of side-chain sulfonates are paramount in determining the performance of low Pt-loaded membrane electrode assembly (MEA), particularly at high current densities. However, the heterogeneity of Pt/C leads to strong sulfonate anion adsorption on Pt sites and deleterious ionomer aggregation on the carbon support. Here, we synthesize atomic dipole modulated Pt/C (SCDC-Pt) electrocatalysts for low Pt-loaded MEA. Remarkably,this catalyst delivers a superior peak power density (1.4 W cm-2) and only a 15% of activity loss after 30 000 square-wave cycles. Operando characterization and computational analysis demonstrate that surface charged dipole facilitates homogenous ionomer distribution, while mitigating sulfonate poisoning of Pt. Electrochemical diagnostic technique establishes the low sulfonate coverage (˜8%) and local O2 transport resistance (38.6 S m-1).This finding demonstrates the viability of rationally designed high-performance surface composition-homogenization low Pt-loaded MEA.

O 88.2 Thu 15:15 TRE/MATH

Molecular Beam Surface Scattering and PECD to Probe Chirality in Surface Reaction Products — Arved Dorst[1,2], Johannes Diedrich[1,2], Rasika Dissayanake[1,2], and •Tim Schäfer[1,2] — [1]Georg-August-University of Göttingen, Germany — [2]Max-Planck Institute for Multidisciplinary Sciences, Göttingen, Germany

The epoxidation of olefins on Ag/O systems is an important industrial heterogeneous catalytic process. However, the mechanistic details of the surface reaction remain controversial, and it has been highly challenging to reconcile findings obtained under realistic reaction conditions with the highly detailed but static studies performed under ultra-high vacuum (UHV).

An additional level of complexity and opportunity arises when using prochiral olefin molecules. Their epoxidation can yield chiral epoxide products, provided the reaction pathway can be directed toward one enantiomer. In our studies, we combine molecular-beam surface scattering with laser spectroscopy to probe this process. By detecting the photoelectron circular dichroism (PECD) of the reaction products, we are able to determine their absolute chirality.

Our overarching goal is to achieve an atomistic understanding of reaction dynamics on chiral surfaces, ultimately bridging the gap between UHV studies and catalytic behavior under operational conditions.

O 88.3 Thu 15:30 TRE/MATH

From Processes to Mechanisms: Machine-Learning Based Automated Lattice Mapping as Prerequisite to Microkinetic Modeling — •Aditya Kumar[1], Patricia Poths[1], King Chun Lai[2], Christoph Scheurer[1], Sebastian Matera[1], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Max Planck Computing and Data Facility, Garching

Finding the reaction mechanism of a surface reactive system from first principles is a tedious task requiring a lot of human effort and being affected by human bias. To address these points, we have developed the Automatic Process Explorer (APE), which generates a comprehensive library of elementary reaction steps [1]. With easily thousands of steps identified, their manual assembly into a reaction network as a prerequisite to subsequent microkinetic modeling becomes intractable. To this end, we develop an automated framework that infers an effective lattice onto which all APE-discovered elementary steps may be coarse-grained. In this, atomic configurations from APE are analyzed using density-based hierarchical clustering, creating a fine-to-coarse hierarchy of potential lattice sites. All processes are then mapped onto the lattice as discrete occupation changes and, exploiting symmetry, a network of unique elementary reactions on this lattice is generated. We demonstrate the approach for a large set of elementary processes within the initial oxidation of Pd(100) terrace edges, and discuss the feasibility of subsequent efficient lattice-based microkinetic simulations.

[1] K.C. Lai *et al.*, Phys. Rev. Lett. **134**, 096201 (2025).

O 88.4 Thu 15:45 TRE/MATH

Investigating the Promotion Mechanism of Lanthanum on Cobalt Model Catalysts for Ammonia Production — •Clara C. Aletsee, Lau H. Wandall, Emanuel Biletter, and Ib Chorkendorff — DTU, Copenhagen, Denmark

Developing catalysts for ammonia synthesis under milder conditions than the Haber-Bosch process has gained significant interest. Recent studies demonstrate that usually unreactive magnetic materials, such as cobalt, can be activated for NH_3 synthesis by adding lanthanum.(1,2) According to theoretical calculations, this is attributed to not only an electrostatic, but also a beneficial spin promotion effect.(3) Herein, we examine the role of the promoter form on the catalytic performance. For this, either metallic La or La_2O_3 was deposited on a stepped Co(10-115) single crystal surface via e-beam evaporation. Additionally, mass-selected Co nanoparticles were deposited on two different magnetron-sputtered film supports: LaN and La_2O_3. All catalysts were characterized by X-ray photoelectron spectroscopy and low-energy ion scattering before and after reaction, and their activity was measured between 350-500°C at 1 bar in a UHV-compatible cell.(4) We show that Co/La_2O_3 exhibits the same activity as the LaN supported catalyst system at 350°C, but the stability decreases at higher temperatures.

References: (1) K. Zhang et al., Science 383, 1357 (2024). (2) T. N. et al., Nature 583, 391 (2020). (3) A. Cao et al., Nat Commun. 13 (2022). (4) K. Zhang et al., Rev. Sci. Instrum. 94, 114102 (2023).

O 88.5 Thu 16:00 TRE/MATH

Bridging the Pressure and Materials Gaps in NO Adsorption on Ceria — •Lukas Bolz[1], Ali Essa[1], Zairan Yu[1], Alexei Nefedov[1], Julia Vecchietti[2], Adrian Bonivardi[3], Yuemin Wang[1], and Christof Wöll[1] — [1]Insitute of Functional Interfaces, KIT, Eggenstein-Leopoldshafen, Germany — [2]Instituto de Desarrollo Tecnológico para la Industria Química, UNL, Santa Fe, Argentina — [3]Facultad de Ingenieria, UBA, Buenos Aires, Argentina

Nitric oxide (NO) is well known to have adverse effects on human health and the environment. One effective approach to decrease its emission is the selective catalytic reduction of NO over metal oxide surfaces. Understanding the reaction mechanisms, by tracking the structural changes of the active sites and intermediates as a function of reaction atmosphere and temperature, is crucial. Here, we present results on UHV-IRRAS and FTIRS as well as in situ/operando DRIFTS studies at atmospheric pressures and elevated temperatures to investigate the interaction between NO and ceria (CeO_2). A reliable assignment of the IR bands observed in the complex DRIFTS spectra was achieved based on accurate references obtained for NO molecules adsorbed on single crystal surfaces and nanocrystalline powders, thereby bridging the material and pressure gap for oxidic catalysts. The combined results enabled the tracking of facet-dependent surface transformations, the adsorption and reaction of NO, and the formation of intermediates such as nitrous oxide (N_2O). This work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) - Project-ID 426888090 - SFB 1441, project B03 and A04.

O 88.6 Thu 16:15 TRE/MATH

Competing reaction pathways in decomposition of 2-propanol over V-doped Co3O4(111) model catalyst: a mechanistic study. — •Patrick Hubert[1], Jan Smyczek[1], Maximilian Galinski[1], Lina Marquardt[1], Justin Girschik[1], Philipp Fredersdorff[1], Paul Fröhlich[1], Bernd Hartke[1], Guntram Rauhut[2], and Swetlana Schauermann[1] — [1]Institute of Physical Chemistry, Christian-Albrechts-University Kiel, Max-Eyth-Str. 1, 24118 Kiel, Germany. — [2]Insitute of Theoretical Chemistry, University of Stuttgart, Pfaffenwaldring 55, 70569 Stuttgart, Germany.

This study investigated catalytic decomposition of 2-propanol over $Co_3O_4(111)/Au(111)$ and $VO_x/Co_3O_4(111)/Au(111)$ model catalysts to unravel competing reaction pathways toward acetone or propene. Ultra-high vacuum (UHV) surface science techniques were employed, including scanning-tunneling microscopy (STM), molecular-beam methods, infrared reflection absorption spectroscopy (IRAS), and temperature-programmed desorption (TPD). The $VO_x/Co_3O_4(111)/Au(111)$ surface exhibits structures with V^{3+}, V^{4+} adsorption sites and vanadyl groups (V=O). TPD measurements showed propene desorption at 480 K from 2-propanol adsorbed at

100 K on surfaces exceeding 0.6 ML VO_x coverage. At 180 K, 2-propanol dissociatively adsorbs on VO_x, consuming vanadyl groups during OH deprotonation, forming tilted 2-propoxy with surface-proximal methyl groups. At 400 K, a second intermediate forms via C-O bond scission and methyl deprotonation. IR spectra suggest this intermediate is a surface-bound propene-derived species.

O 88.7 Thu 16:30 TRE/MATH

Beyond U-Ce charge transfer: stabilization of Ce^{3+} states in epitaxial $Ce_{1-x}U_xO_2$ films grown on Ru(0001) — •Carlos Morales[1], Rudi Tschammer[1], Thomas Gouder[2], Hicham Idriss[3], and Jan Ingo Flege[1] — [1]Applied Physics and Semiconductor Spectroscopy, Brandenburg University of Technology, Cottbus, Germany — [2]European Commission, Joint Research Centre (JRC), Karlsruhe, Germany — [3]Institute of Functional Interfaces (IFG), Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany

Cerium oxide (CeO_2) stands out among reducible metal oxides for its stability and activity. Yet, promoting Ce^{3+} active states requires high energy. The conversion of Ce^{4+} to Ce^{3+} at lower temperatures for the thermochemical splitting of H_2O or CO_2 can be enhanced by doping ceria with other elements. Particularly, ceria mixing with uranium has been proven successful: substituting a fraction of Ce^{4+} by U^{4+} results in a charge transfer that promotes the formation of Ce^{3+} and U^{5+} states. We have explored the redox properties of 8 nm thick epitaxial (111)-oriented $Ce_{1-x}U_xO_2$ on Ru(0001). In line with previous studies focused on polycrystalline powders, the as-grown films exhibit a high Ce^{4+} to Ce^{3+} conversion, with a maximum reduction corresponding to approximately 20 % of U content. However, the concentration of Ce^{3+} states and oxygen is higher than predicted by density function theory (DFT) calculations for various U contents and spatial ordering. The observed behaviour could be likely related to the lattice distortion caused by the significant difference in the ionic radii of Ce^{3+} and U^{5+}. This effect has not been considered before in $Ce_{1-x}U_xO_2$ mixed oxides.

O 88.8 Thu 16:45 TRE/MATH

Product Selectivity in Fischer-Tropsch Synthesis — •Benjamin Rasmus Grimm, Luis Antonio Cipriano Marcos, Oliver Christensen, and Jens Kehlet Nørskov — DTU Physics, Kongens Lyngby, Denmark

The product selectivity and activity of Fischer-Tropsch synthesis (FTS) is important for producing synthetic fuels and chemicals from natural gas, coal, or biomass. Some catalysts generate mainly undesired methane, whereas others show higher selectivity toward longer hydrocarbons. In this study, density functional theory (DFT) is employed to calculate the activity- and selectivity-determining reaction steps and energy barriers of FTS on cobalt-based catalysts. Reaction rates and product selectivities are then evaluated using a microkinetic model that incorporates the rate- and selectivity-determining steps of the FTS mechanism. To describe the catalyst as realistically as possible, adsorbate coverage and migration effects under experimental conditions are taken into account. Finally, strategies to improve reaction rates and selectivity are discussed.

O 88.9 Thu 17:00 TRE/MATH

Low-Temperature CO2 Methanation over Ni/Ce-Sm Oxide Catalysts — •Rachow Fabian, Sichen Liu, Evgenia Charlafti, Raquel Sánchez-Barquilla, and Jan Ingo Flege — Brandenburg University of Technology, Cottbus-Senftenberg, Germany

Nickel catalysts on doped ceria are attractive for CO_2 methanation due to their redox flexibility and potential for improved efficiency and stability. In this work, we investigate Ni supported on mixed Ce–Sm oxides with Ce:Sm ratios of 3:1, 2:1, and 1:1. The catalysts are tested as powders in a fixed-bed flow reactor between 250 and 400°C and benchmarked against a conventional Ni/Al_2O_3 catalyst. Among the compositions, the Ce:Sm ratio of 2:1 shows the highest CO_2 conversion, with a pronounced enhancement in low-temperature activity compared to Ni/Al_2O_3. To relate performance to material properties, we combine X-ray diffraction (XRD), temperature-programmed reactivity (H_2-TPR), Raman spectroscopy, high-resolution transmission electron microscopy (HRTEM/EDX), as well as in-situ X-ray absorption near-edge spectroscopy (XANES) under reaction conditions, elucidating how Sm incorporation and Ce:Sm ratio influence the structural and redox characteristics of the oxide support, oxygen vacancy formation, and Ni dispersion, which together govern catalytic activity and stability. To assess practical applicability and scale-up, the optimized Ni/Ce–Sm (2:1) oxide formulation is deposited on Al_2O_3 spheres and evaluated under conditions representative of packed-bed operation with a limited amount of active material, revealing high conversion and stable, efficient operation in low-temperature CO_2 methanation.

O 88.10 Thu 17:15 TRE/MATH

Heteroepitaxial growth of Sm_2O_3 nanoislands on Cu(111) — •Björn Riedel[1], Raquel Sánchez-Barquilla[1], Lars Buss[1], Iulia Cojocariu[2], Tevfik Onur Mentes[2], Andrea Locatelli[2], and Jan Ingo Flege[1] — [1]Brandenburg University of Technology, Cottbus, Germany — [2]Elettra-Sincrotrone Trieste, Basovizza, Italy

Doping of CeO_2 with samarium can significantly influence its redox behavior by promoting the formation and stabilization of reduced Ce^{3+} species. Yet, studies of well-defined samaria model systems grown on single-crystal surfaces are scarce, leading to a lack of combined structural and spectroscopic studies and, hence, a gap in understanding the relationship between samaria's structure and its chemical behavior. We have investigated hexagonal and monoclinic Sm_2O_3 nanoislands grown on Cu(111) using a multi-method approach with high structural and chemical sensitivity, employing low-energy electron microscopy (LEEM), micro-spot diffraction (μLEED) and intensity-voltage LEEM in combination with X-ray absorption spectroscopy photoemission electron microscopy (XAS-PEEM). To study the influence of different structures and phases on the chemical behavior of Sm_2O_3 islands, we have examined their redox properties under reducing (H_2) and oxidizing (O_2) conditions. The results indicate a highly dynamic system that can be readily adjusted by varying the conditions during deposition, such as growth temperature and oxygen partial pressure.

O 88.11 Thu 17:30 TRE/MATH

Surface Modifications in Complex Mixed Oxide Activation for the Selective Oxidation of Hydrocarbons — •Kyeonghyeon Nam[1], L. Masliuk[1], T. Jones[1], Y. Song[1], A. Trunschke[1], R. Schlögl[1], T. Lunkenbein[1,2], K. Reuter[1], and C. Scheuer[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]Universität Bayreuth

Calcination (thermal activation) is crucial for metal-oxide catalysts, enhancing activity and durability by preparing surface morphology and active sites. However, thermal treatment also induces dynamic surface changes, such as defect formation, reconstruction, and grain reorientation, complicating the continuous monitoring of a catalyst's surface. Here, identical-location STEM imaging of a ternary M1 $(Mo,V)O_x$ catalyst reveals that the (hk0) surface undergoes pronounced modification under calcination and oxidative dehydrogenation (ODH) conditions. The surface evolution is modeled using machine learning force fields. Molecular dynamics (MD) simulations reproduce the reconstruction of extended M1 regions from MoO_2-like motifs, as well as mass transport within the pentagonal motif that further activates the catalyst. Experimentally observed catalytic activity changes can be assigned to the presence of highly charged surface metal centers via DFTB Mulliken charge analysis. These surface transformations strongly influence the catalytic properties of ternary M1 catalysts, suggesting potential applications in improving catalytic performance through controlled surface modifications.