O 111: Heterogeneous Catalysis II

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

O 111.1 Fri 10:30 TC 006

Fast Screening of Metal Alloys for CO_2 Activation by Ab initio Calculations and Local AI Rules — •Herzain I. Rivera-Arrieta, Matthias Scheffler, and Lucas Foppa — The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin

Metal alloy catalysts can weaken the bonds in CO_2, enabling reactions to convert the molecule into valuable products such as methanol. However, the immense compositional and configurational space of alloys hinders the direct high-throughput screening of novel materials. Herein, through DFT-mBEEF calculations, we modeled the CO_2 interaction with surfaces of Single-Atom Alloys, i.e., systems with one atomic dopant embedded in a host metal [1]. Then, out of 24 offered candidate properties, we used the Subgroup Discovery (SGD) approach [2] to unveil rules connecting key electronic and geometric properties of the adsorption sites in SAA with the CO_2 activation process. These rules, which constrain the values of the key properties, allow us to focus on the regions in materials space where the promising catalysts may be located. Besides applying the rules for screening new SAA, we also tested them to search promising Dual-Atom Alloys (DAA), i.e., structures with two dopant atoms [3]. Further calculations confirmed that the selected SAA and DAA can indeed activate CO_2.

[1] R. T. Hannagan, *et al.*, *Chem. Rev.*, **120**, 12044 (2020).

[2] S. Wrobel, *1st Europ. Symp. on Princ. of Data Min. and Knowl. Discov.*, **19**, 78 (1997).

[3] D. Behrendt, *et al.*, *J. Am. Chem. Soc.*, **145**, 4730 (2023).

O 111.2 Fri 10:45 TC 006

Ni-In Synergy in CO_2 Hydrogenation to Methanol Explained by Microkinetic Models — •Francesco Cannizzaro, Bart Klumpers, Ivo A. W. Filot, and Emiel J. M. Hensen — Laboratory of Inorganic Materials and Catalysis, Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, 5600 MB Eindhoven, The Netherlands

Highly dispersed Ni-In clusters can promote In_2O_3 catalysts for the hydrogenation of CO_2 to CH_3OH, a key reaction in the fight against global warming. However, fundamental understanding of the role of such clusters is lacking, hampering large-scale application of Ni-In_2O_3 catalysts. Herein, we employed density functional theory (DFT) and microkinetic modeling to study the influence of the composition of In_2O_3-supported Ni-In clusters on CO_2 hydrogenation. Lowest-energy Ni_nIn_{8-n} clusters ($n = 0 - 7$) were identified by combining genetic algorithms with an artificial neural network potential trained by DFT. At higher Ni content, the clusters expose more Ni atoms. The mechanistic pathways for CO_2 hydrogenation were computed for In_2O_3-supported Ni_2In_6 and Ni_6In_2 clusters, representing In-rich or Ni-rich clusters. Microkinetic simulations show that only the Ni_6In_2 cluster catalyzes methanol via hydrogenation of adsorbed CO_2 to formate, the precursor to methanol, by Ni-H species. Methanol formation competes with direct CO_2 dissociation, which becomes the dominant reaction pathway at high temperatures due to low H coverage. The supported Ni_2In_6 cluster exposes In atoms, which do not stabilize surface hydrides, explaining the low methanol activity and predominant CO formation.

O 111.3 Fri 11:00 TC 006

Systematic evaluation of trends in CO_2 reduction on metal–nitrogen–carbon systems from first principles — •Sze-Chun Tsang, Sihang Liu, and Georg Kastlunger — Catalysis Theory Center, Technical Univ. of Denmark, 2800 Kgs. Lyngby, Denmark

The electrochemical CO_2 reduction reaction (e-CO_2RR) can be a crucial aspect of sustainability. Metal–nitrogen–carbon (MNC) single-atom catalysts (SACs) hold promises towards electroreduction, besting transition-metal (TM) surface catalysts in suppressing side reactions and unlocking new energetic degrees-of-freedom. However, adsorbates on MNCs are often poorly modeled; and the oft-assumed and -used analogy between graphene-based (G-) and molecular MNCs has yet to be examined.

Using density-functional theory, we compare the adsorption energetics relevant to the CO_2RR on G-MNCs and molecular MNCs. We will show energetic trends to be largely metal-dependent and consistent across SAC geometries. We also demonstrate that higher-level theories like the exact-exchange functional are crucial towards capturing said energetics. Further, we examine the pairwise correlation, or the lack thereof, between reaction-intermediate formation energies on $3d$-TM-based MNCs. Finally, we discuss several caveats: (1) the sampling of spin states and its energetic ramifications; and (2) the tendencies for protons to potentially destabilize the active site. These results emphasize the importance of and highlight the difficulties in correctly describing MNC systems, illuminating key theoretical insights into this distinguished class of catalysts.

O 111.4 Fri 11:15 TC 006

High-throughput catalyst screening for CO_2 to methanol conversion with machine-learned force-fields — •Ondřej Krejčí, Prajwal Pisal, and Patrick Rinke — Department of Applied Physics, School of Science, Aalto University, Espoo, Finland

The search for new and better catalysts is one of the key research directions in material science, as heterogeneous catalysis is essential in converting CO_2 to fuel in a closed loop carbon cycle. Approximative predictions of activity, like the Sabatier principle, have been very popular for catalytic screening. However, to take the nanostructure of real thermocatalysts into account, we need to scan the adsorption energies (AEs) for a variety of different facets and binding sites.

In this work, we will present our current workflow for obtaining the relevant AEs in CO_2 thermoreduction to methanol. We employ trained machine learning force-field from the Open Catalyst Project [1], to accelerate the search for ideal catalysts. We have calculated the surface stabilities for various facets with all Miller indices $\in \{-2, -1, 0, 1, 2\}$ and picked the most stable cuts for each facet. Subsequently, we have created all possible high symmetry binding sites on those facets and predicted AEs for the reaction key semi-products: *H, *OH, *OCHO and *OCH_3. The AE distributions are further analysed for material*s activity.

[1] L. Chanussot et al., ACS Catal. **11**, 6059-6072 (2021); R. Tran et al., ACS Catal. **13**, 3066-3084 (2023); https://opencatalystproject.org/

O 111.5 Fri 11:30 TC 006

Exploring Unsupervised Learning for Analysis of Adsorption Energy Distributions in CO2 to Methanol Synthesis — •Prajwal Pisal, Ondrej Krejci, and Patrick Rinke — Department of Applied Physics, Aalto University, P.O.Box 11100, FI-00076 AALTO, Finland

Synthesis of methanol from carbon dioxide using heterogeneous catalysts is a reaction of great relevance from an industrial and environmental perspective, underscoring the need for extensive catalytic exploration. Understanding the adsorption energy distributions (AE) of reactants on catalytic surfaces is crucial for evaluating material reactivity, as catalyst reactivity is often linked to AE.

In this work, we leverage our extensive database of AE for more than 100 catalytic materials using the Open Catalyst Project infrastructure [1]. We perform statistical analysis and unsupervised machine learning, like dimensionality reduction and clustering, on the dataset for recognition of features and patterns in the AE distributions. Utilizing these tools, we classify the materials under study and compare with experimental and literature data (e.g. [2]). This analysis provides a deeper understanding of the key properties of the materials that enhance the catalytic activity. The data obtained will further aid us in building predictive models to maximize methanol yield as a function of AE distributions and experimental conditions.

[1] L. Chanussot et al., ACS Catal. 11, 6059-6072 (2021); R. Tran et al., ACS Catal. 13, 3066-3084 (2023)

[2] A. J. Medford et al, J. Catal. 328, 36-42 (2015).

O 111.6 Fri 11:45 TC 006

Theoretical investigation of bifunctional monolayer catalysts for fuel cell applications — •Thies Reetz and Halil Ibrahim Sözen — Carl von Ossietzky Universität Oldenburg

Road transport is estimated to contribute 10 % of all anthropogenic CO2 emissions. The use of polymer electrolyte membrane fuel cells (PEMFC) is a promising way to reduce these emissions. A problem facing the commercialization of PEMFCs are cell reversal events which occur under hydrogen depletion at the anode leading to the carbon oxidation reaction (COR) at carbon based support materials. In this work novel bifunctional anode catalysts are theoretically designed and investigated which can perform both the hydrogen oxidation reaction (HOR) and the oxygen evolution reaction (OER) simultaneously. The latter reaction is competing with the COR. Therefore by promoting the OER the COR is suppressed and the support material corrosion is slowed down.

The focus in this study was on Platinum and Iridium and bifunctional Pt/Ir alloys. Monolayers of these materials on a rutile support material were investigated in terms of structure and bifunctional catalytic performance and were compared to the performance of pure metal surfaces. The investigation showed that the adsorption energy of important species in the OER and HOR process changes drastically for the monolayer materials compared to the pure metal surfaces. Therefore, bifunctional monolayers on a support material are a possible way to tune PEMFC performance.

O 111.7 Fri 12:00 TC 006

Adaptive Designs for the Efficient Exploration of Catalyst Materials or Reaction Condition Spaces — •Frederic Felsen, Christian Kunkel, Karsten Reuter, and Christoph Scheurer — Fritz-Haber-Institut der MPG, Berlin

Changes of the reaction mechanism often lead to qualitative changes in the performance over a small range of reaction conditions or catalyst compositions. The topology of diagrams that summarize this performance over an investigated domain is therefore typically characterized by extended regimes of smooth behavior separated by narrow such transitions in between (e.g. kinetic phase transitions or peaks of Volcano plots). Such discontinuous topology prevents the efficient exploration with traditional design-of-experiment (DoE) approaches that assume a smoothly varying measurement function over the entire investigated domain.

To this end, we here propose an adaptive DoE algorithm that tackles this issue in a data-efficient way. A support vector machine classification learns and iteratively refines the *a priori* unknown positions of the transitions by optimally designing new data points, i.e. the reaction conditions or catalyst compositions at which the next measurements are to be taken. We illustrate the approach for a vast space of possible promoter compositions for the propane dehydrogenation reaction (PDH). Based on characterization data (Raman spectroscopy and thermogravimetric analysis) for each individual catalyst sample, we identify two distinct regimes, differing not only in automatically identified characterization features but also in catalytic performance.

O 111.8 Fri 12:15 TC 006

Accelerating Catalyst Discovery through Efficient Exploration of a Complex Design Space — •Charles W.P. Pare[1], Christian Kunkel[1], Frederic Felsen[1], Frederik Rüther[2], Sina Stocker[1], Robert Baumgarten[2], Esteban Gioria[1], Raoul Naumann d'Alnoncourt[2], Christoph Scheurer[1], Frank Rosowski[2,3], and Karsten Reuter[1] — [1]Fritz-Haber-Institut der MPG, Berlin — [2]BasCat - UniCat BASF JointLab, Berlin — [3]BASF SE, Catalysis Research, Ludwigshafen

Catalyst promoters often form key components of stable and well-performing industrial heterogeneous catalysts. Yet, today's industrial catalysts often only benefit from one or two promoters. This can often be traced back to the laborious empirical research required to identify promising formulations that jointly act to improve catalyst performance. To overcome such hurdles, we implemented an accelerated catalyst discovery approach by globally exploring a large multi-promoter design space using only a limited number of experiments. Its pillars are an efficient Design-of-Experiment (DoE) planning, a fast parallelized testing protocol and an iterative incorporation of experimental feedback. New and competitive promoter chemistries for the non-oxidative propane dehydrogenation to propylene over Pt on alumina were discovered in less than 100 experiments performed within weeks. The results show the potential of iterative DoE strategies for the data-efficient knowledge-generation and optimization in complex, academically and industrially relevant catalytic systems.