

O 62: Surface Reactions and Heterogeneous Catalysis 1

Time: Thursday 10:30–12:45

Location: H4

O 62.1 Thu 10:30 H4

Gaussian Approximation Potentials for Surface Catalysis — ●SINA STOCKER^{1,2}, GÁBOR CSÁNYI³, KARSTEN REUTER¹, and JOHANNES T. MARGRAF¹ — ¹Fritz Haber Institut der Max Planck Gesellschaft, Berlin, Germany — ²Technische Universität München, Germany — ³University of Cambridge, United Kingdom

Predictive-quality first-principles based microkinetic models are increasingly used to analyze (and subsequently optimize) reaction mechanisms in heterogeneous catalysis. In full rigor, such models require the knowledge of all possible elementary reaction steps and their corresponding reaction barriers. Unfortunately, for complex catalytic processes (such as the generation of ethanol from syngas) the number of possible steps is so large that an exhaustive first-principles calculation of all barriers becomes prohibitively expensive.

To overcome this limitation, we develop machine learned (ML) interatomic potentials to model syngas conversion on Rhodium. These ML potentials can be used to determine free energy reaction barriers for a large number of adsorbates at various CO coverages and at a fraction of the computational cost of the underlying first-principles method. Specifically, we use here the Gaussian Approximation Potential (GAP) framework and explore iterative training in combination with umbrella sampling.

O 62.2 Thu 10:45 H4

Hydrogen adsorption on Pd surfaces and its effect on CO₂ activation — ●HERZAIN I. RIVERA-ARRIETA¹, IGOR KOWALEC², LUCAS FOPPA¹, ANDREW LOGSDAIL², DAVID WILLOCK², and MATTHIAS SCHEFFLER¹ — ¹The NOMAD Laboratory at the Fritz Haber Institute of the Max Planck Society and the Humboldt-Universität zu Berlin, Germany — ²Cardiff Catalysis Institute, Cardiff University, UK

Understanding the reactivity of Pd-based catalysts in hydrogenation processes requires an accurate description of its surfaces at realistic temperature (T) and hydrogen pressure (p_{H_2}). Herein, by modeling the surface phase diagram of Pd (111) and (100) as a function of T , p_{H_2} via *ab initio* atomistic thermodynamics [1], we predict 1 monolayer (ML) coverage of H as the most stable configuration under common experimental reaction conditions [2]. Taking a particular interest in the activation of CO₂, we performed simulations concerning the interaction of the molecule with the surfaces as the H-coverage increases from 0 to 1ML. Our results show how 1 ML of H inhibits the formation of chemisorbed CO₂^{*}, the initial intermediate in the CO₂ hydrogenation reaction. The generated data will be combined with information from other metal surfaces, and the subgroup-discovery artificial-intelligence approach [3] will be applied to identify which basic materials parameters correlate with indicators of CO₂ activation, e.g. the adsorption energy or the C-O bond elongation.

[1] C. Stampfl, *et al.*, *Appl. Phys. A*, **69**, 471 (1999).

[2] H. Bahruji, *et al.*, *J. Catal.*, **343**, 133 (2016).

[3] B. R. Goldsmith, *et al.*, *New J. Phys.*, **19**, 013031 (2017).

O 62.3 Thu 11:00 H4

Atomic steps as active sites in the Co-catalyzed Fischer-Tropsch synthesis: Evidence from an operando STM study on a stepped model catalyst — ●KATHARINA GOLDER and JOOST WINTTERLIN — Ludwig-Maximilians-Universität München, Germany

Atomic steps are often assumed to represent the active sites on the surface of a heterogeneous catalyst. This assumption is based on turnover data that display a certain scaling of the activity with the particle sizes of the catalysts. However, this evidence is indirect and often controversial. We have recently shown that the activity of a Co(0001) single crystal surface in the Fischer-Tropsch synthesis of hydrocarbons is proportional to the density of atomic steps. This is a quite direct evidence for the activity of atomic steps, but it was obtained for a flat model system. Here we present results of investigations on a Co(101 $\bar{1}$ 5) surface that has a similar step density as the Co particles of the industrial Fischer-Tropsch catalyst. The experiments were performed with a scanning tunneling microscope (STM) at a syngas (2H₂+CO) pressure of \sim 1 bar and a temperature of 503 K. Hydrocarbon products were detected by a special gas chromatograph (GC). The STM data show that the morphology of the stepped surface is stable under operando conditions. The activity measured by GC is considerably higher than that of the Co(0001) sample. It is close to the activities

reported for supported Co catalysts, a result that bridges the materials gap between model systems and the industrial Fischer-Tropsch catalysts.

O 62.4 Thu 11:15 H4

Predicting Binding Motifs of Complex Adsorbates Using Machine Learning with a Physics-inspired Graph Representation — ●WENBIN XU¹, KARSTEN REUTER¹, and MIE ANDERSEN² — ¹Fritz-Haber-Institut der MPG, Berlin, Germany — ²Aarhus Institute of Advanced Studies and Department of Physics and Astronomy, Aarhus University, Denmark

Complex adsorbates are involved in many surface catalytic reactions such as Fischer-Tropsch, methanol, or higher oxygenate synthesis. The modeling of these species at transition metal catalysts must account for their ability to exhibit a wide range of adsorption motifs, including mono- and multi-dentate adsorption modes. Given the combinatorial explosion of possible adsorption motifs and the computational cost of density functional theory, it is desirable to develop machine learning (ML) models for predicting the binding motifs and their associated adsorption enthalpies. Most ML models to date are only applicable to simple adsorbates. In this work, we overcome this limitation and propose a kernelized ML model with a physics-inspired graph representation for the prediction of complex species. The model is data-efficient and its good extrapolation ability makes it promising for comprehensively exploring complex reaction networks on novel catalysts. Furthermore, we show that the outliers with large prediction errors can be reliably captured from an ensemble uncertainty prediction approach.

O 62.5 Thu 11:30 H4

Machine-Learning Driven Global Optimization of Surface Adsorbate Geometries — ●HYUNWOOK JUNG, SINA STOCKER, KARSTEN REUTER, and JOHANNES T. MARGRAF — Fritz-Haber-Institut der MPG, Berlin, Germany

The adsorption energy is an essential descriptor for predicting catalytic activity in theoretical models of heterogeneous catalysis. Although established scaling relations facilitate the prediction of adsorption energies for small adsorbates like OH, they are not applicable to larger adsorbates that are frequently encountered in syngas chemistry. Such systems often feature complex potential energy surfaces due to their flexibility and the possibility of multidentate binding to the surface. Consequently, computing adsorption energies for such adsorbates implies a complex global optimization to find the ground state geometry. This is prohibitively expensive at the density functional theory (DFT) level for routine applications. To tackle this issue, we present a global optimization protocol for adsorbate geometries which trains a surrogate Gaussian Approximation Potential on-the-fly. The approach is applicable to generic surface models (i.e. without defining surface sites) and minimizes both user intervention and the number of DFT calculations by iteratively updating the training set with configurations explored by the algorithm. We demonstrate this approach for diverse adsorbates on the Rh (111) and (211) surfaces.

O 62.6 Thu 11:45 H4

New catalysts for oxidative-coupling of methane: theoretical search and experimental validation — ●ALIAKSEI MAZHEIKA¹, MICHAEL GESKE¹, MATTHIAS MUELLER², STEPHAN SCHUNK², FRANK ROSOWSKI^{1,3}, and RALPH KRAEHNERT¹ — ¹Technische Universität, Berlin, DE — ²hte GmbH, Heidelberg, DE — ³BASF SE, Ludwigshafen, DE

Oxidative-coupling of methane (OCM) is a direct way for conversion of methane to higher hydrocarbons - ethane, ethylene. Despite many years spent for the search of an efficient catalyst, still a material which would satisfy industrial rentability has not been found. In our study we proceed from an experimentally observed volcano-like dependence of C₂-yields on formation energies of carbonates on oxide catalysts [1]. We developed a new method which allows to calculate carbonates formation energies from CO₂ adsorption energies on the surfaces of corresponding oxides. In combination with artificial intelligence methods (data mining and symbolic regression) this was used in the high-throughput screening. The latter is done in a way of active-learning, and we demonstrate its advantages compared to traditional scheme. Several catalysts obtained from the screening have been synthesized

and experimentally tested together with less promising materials. Obtained C₂-yields follow the same volcano-type dependence that formed initial basis for the employed strategy. The best catalyst candidates reach maximum C₂-yields comparable to the well-known OCM catalysts and outperform them at lower temperatures.

[1] H. Wang *et al.*, <https://doi.org/10.26434/chemrxiv-2022-gxt5n>

O 62.7 Thu 12:00 H4

Finding catalyst genes with subgroup discovery — ●ALIAKSEI MAZHEIKA¹, YANGGANG WANG², ROSENDO VALERO³, FRANCESC VINES³, FRANCESC ILLAS³, LUCA M. GHIRINGHELLI⁴, SERGEY V. LEVCHENKO⁵, and MATTHIAS SCHEFFLER⁴ — ¹Technische Universität, Berlin, DE — ²University of Science and Technology, Shenzhen, CN — ³Universitat de Barcelona, Barcelona, ES — ⁴The NOMAD Laboratory at the Fritz Haber Institute and Humboldt University, Berlin, DE — ⁵Moscow

Catalytic-materials design requires predictive modeling of the interaction between catalyst and reactants. This is challenging due to the complexity and diversity of structure-property relationships across the chemical space. Here, we report a strategy for a rational design of catalytic materials using the artificial intelligence approach (AI) subgroup discovery. We identify catalyst genes (features) that correlate with mechanisms that trigger, facilitate, or hinder the activation of carbon dioxide (CO₂) towards a chemical conversion. The AI model is trained on first-principles data for a broad family of oxides. We demonstrate that surfaces of experimentally identified good catalysts consistently exhibit combinations of genes resulting in a strong elongation of a C-O bond. The same combinations of genes also minimize the OCO-angle, the previously proposed indicator of activation, albeit under the constraint that the Sabatier principle is satisfied. Based on these findings, we propose a set of new promising catalyst materials for CO₂ conversion.—A. Mazheika *et. al.* Nature Comm. 2022, 13, 419.

O 62.8 Thu 12:15 H4

Selectivity in single-molecule reactions by tip-induced redox chemistry — ●FLORIAN ALBRECHT¹, SHADI FATAYER^{1,2}, IAGO POZO³, IVANO TAVERNELLI¹, JASCHA REPP⁴, DIEGO PENA³, and LEO GROSS¹ — ¹IBM Research - Zurich, 8803 Rüschlikon (Switzerland) — ²Physical Science and Engineering Division, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal (Saudi Arabia) — ³Centro Singular de Investigación en Química Biolóxica e Ma-

teriaisMoleculares (CiQUS) and Departamento de Química Orgánica, Universidade de Santiago de Compostela, 15782 Santiago de Compostela (Spain) — ⁴Institute of Experimental and Applied Physics, University of Regensburg, 93053 Regensburg (Germany)

Since the first experiments by S.-W. Hla in 2000 [1], tip-induced on-surface synthesis is an active field. Not only in on-surface chemistry, selective control over the outcome of a reaction is a major quest. Here, we activate a molecule adsorbed on ultrathin insulating films by dehalogenation and perform selective constitutional isomerization reactions in a low temperature UHV combined STM and AFM. The selectivity is controlled by the polarity and amplitude of applied voltage pulses. The insulating films stabilize the isomers in different charge states and allow for their characterization. The importance of molecular charge state on the reaction is supported by DFT-derived isomerization energy landscape. [1] S.-W. Hla *et al.*, Phys. Rev. Lett. 85, 2777 (2000).

O 62.9 Thu 12:30 H4

Abiotic Formation of an Amide Bond via Surface-Supported Direct Carboxyl-Amine Coupling — ●BIAO YANG^{1,2}, KAIFENG NIU^{1,3}, FELIX HAAG², NAN CAO^{1,2}, JUNJIE ZHANG¹, HAIMING ZHANG¹, QING LI¹, FRANCESCO ALLEGRETTI², JONAS BJÖRK³, JOHANNES BARTH², and LIFENG CHI¹ — ¹Institute of Functional Nano and Soft Materials (FUNSOM), Soochow University, Suzhou 215123 (P. R. China) — ²Physics Department E20, Technical University of Munich, D-85748 Garching, (Germany) — ³Department of Physics, Chemistry and Biology, IFM, Linköping University, 58183 Linköping (Sweden)

Amide bond formation is one of the most important reactions in biochemistry, notably being of crucial importance for the origin of life. Herein, we combine scanning tunneling microscopy and X-ray photoelectron spectroscopy studies to provide evidence for thermally activated abiotic formation of amide bonds between adsorbed precursors through direct carboxyl-amine coupling under ultrahigh-vacuum conditions by means of on-surface synthesis. Complementary insights from temperature-programmed desorption measurements and density functional theory calculations reveal the competition between cross-coupling amide formation and decarboxylation reactions on the Au(111) surface. Furthermore, we demonstrate the critical influence of the employed metal support: whereas on Au(111) the coupling readily occurs, different reaction scenarios prevail on Ag(111) and Cu(111).[1] [1] Biao Yang⁺, Kaifeng Niu⁺, *et al.* Angew. Chem. Int. Ed. anie.202113590 (2021)