

## O 78: Heterogeneous Catalysis and Surface Dynamics II

Time: Thursday 10:30–12:45

Location: TRE Phy

O 78.1 Thu 10:30 TRE Phy

**Data-centric heterogeneous catalysis: identifying rules and materials genes of alkane selective oxidation** — ●LUCAS FOPPA<sup>1</sup>, FREDERIK RÜTHER<sup>2</sup>, MICHAEL GESKE<sup>2</sup>, GREGOR KOCH<sup>3</sup>, FRANK GIRGSDIES<sup>3</sup>, PIERRE KUBE<sup>3</sup>, SPENCER J. CAREY<sup>3</sup>, MICHAEL HÄVECKER<sup>4</sup>, OLAF TIMPE<sup>3</sup>, ANDREY TARASOV<sup>3</sup>, MATTHIAS SCHEFFLER<sup>1</sup>, FRANK ROSOWSKI<sup>2</sup>, ROBERT SCHLÖGL<sup>3,4</sup>, and ANNETTE TRUNSCHKE<sup>3</sup> — <sup>1</sup>The NOMAD Lab. at the FHI of the MPG and IRIS-Adlershof of HU Berlin — <sup>2</sup>BasCat Lab. at TU Berlin — <sup>3</sup>FHI of the MPG — <sup>4</sup>Max Planck Institute for Chemical Energy Conversion

Artificial Intelligence (AI) can accelerate materials design by identifying the key parameters correlated with the performance. However, widely used AI methods require big data, and only the smallest part of catalysis-research data meets the quality requirement for data-efficient AI. We use rigorous experimental procedures[1] to measure 55 physicochemical parameters as well as the reactivity of 12 catalysts towards ethane, propane, and *n*-butane oxidation. By applying the sure-independence-screening-and-sparsifying-operator approach to the so-obtained data set, we identify nonlinear property-function relationships depending on several key parameters and reflecting the intricate interplay of processes governing selective oxidation.[2,3]

[1] A. Trunschke, *et al.*, *Top. Catal.* **63**, 1683-1699 (2020).

[2] L. Foppa, *et al.*, *MRS Bull.* **46**, 1 (2021).

[3] L. Foppa, *et al.*, *ChemRxiv*, 10.26434/chemrxiv-2022-xmg75 (2022).

O 78.2 Thu 10:45 TRE Phy

**Adaptive Experimental Designs for the Unsupervised Exploration of Reaction Kinetic Phase Diagrams** — ●FREDERIK FELSEN, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut der MPG, Berlin, Germany

In heterogeneous catalysis the interplay of various elementary processes taking place at the catalytic interface gives rise to complex kinetic phase diagrams [1]. Characteristic for such phase diagrams are regimes of smooth kinetic behavior separated by phase transitions going along with drastic changes in effective kinetics. Generally it is difficult to reconstruct the kinetic regime topology of a given process without a detailed understanding of the underlying reaction mechanism. Here, we tackle this issue by approximating the reaction kinetics using statistically robust effective rate laws [2]. Locally fingerprinting the apparent behavior of a chemical reaction, we can generate point-wise regime labels as a basis for estimates of the position of the phase transitions. In order to achieve this in a data efficient way, we propose an iterative adaptive design algorithm, bridging between the classical theory of experimental design [3] and modern statistical learning and optimization. Using a microkinetic model, we illustrate the potential of this approach by investigating the kinetic phase diagram of CO oxidation over RuO<sub>2</sub>.

[1] V. Zhdanov *et al.*, *Surf. Sci. Rep.* **20**, 113, (1994).

[2] F. Felsen *et al.*, *Chem. Eng. J.* **433**, 134121, (2022).

[3] V. Fedorov, *Theory of Optimal Experiments* (1972).

O 78.3 Thu 11:00 TRE Phy

**Machine-learning Gaussian Approximation Potentials to discover RuO<sub>2</sub> surface reconstructions** — ●YONGHYUK LEE, JAKOB TIMMERMANN, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der MPG, Berlin, Germany

Machine-learning Gaussian Approximation Potentials (GAPs) have recently evolved into a powerful class of surrogate models for computationally demanding first-principles calculations. Combined with structure exploration techniques, they enable us to examine the potential energy surface of interest with a hitherto unforeseen combination of physical accuracy and computational efficiency and to achieve global surface structure determination (SSD) for increasingly complex systems. This can be exploited, e.g., to discover novel surface motifs, which are critical in understanding the dynamics of heterogeneous catalysts under operating conditions. In our preceding study on IrO<sub>2</sub>, this methodology was extended by a general and data-efficient active-learning framework that allows for the on-the-fly generation of GAPs via the actual surface exploration process. During the iterative GAP refinement for RuO<sub>2</sub>, we have now identified plenty of unknown low-energy reconstructions of RuO<sub>2</sub> low index facets. Intriguingly, by extending the searching space to larger surface unit cells, we discovered

$c(2 \times 2)$  reconstructions of RuO<sub>2</sub>(100), which provide solutions to long-standing questions in heterogeneous catalysis and experiments.

[1] J. Timmermann *et al.*, *Phys. Rev. Lett.* **125**, 206101 (2020)

[2] J. Timmermann *et al.*, *J. Chem. Phys.*, **155**, 244107 (2021)

O 78.4 Thu 11:15 TRE Phy

**Exploration of IrO<sub>2</sub> electrocatalyst deactivation via machine learning potentials** — ●HAO WAN, HENDRIK HEENEN, SIMON WENGERT, CHRISTOPH SCHEURER, and KARSTEN REUTER — Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

IrO<sub>2</sub> catalysts are one of the best performing oxygen evolution reaction (OER) catalysts in terms of both catalytic activity and stability under harsh acidic conditions. Yet, they still suffer from deactivation under long term OER conditions due to possible changes in surface compositions and morphology. To shed light into these deactivation processes, characterization of the microscopic structure and composition of IrO<sub>2</sub> interfaces is necessary. The involved phase space, however, is vast and its exploration requires extensive sampling and automatic (surface) structure searches which are unfeasible via Density Functional Theory (DFT) calculations. Enabling the intensive computations, machine learning interatomic potentials (MLIP) retain DFT accuracy to within a few meV per atom while reducing the computational cost by up to three orders of magnitude.

In this contribution, we present a reliable MLIP based on Gaussian approximation potentials to investigate IrO<sub>2</sub> deactivation. Stable and metastable IrO<sub>2</sub> surfaces at various surface oxidation states have been extensively sampled using parallel tempering. Relevant surfaces are suggested by evaluating their relative stability compared to rutile-IrO<sub>2</sub>(110), while considering electrochemical conditions. OER activity from these surfaces can be estimated using established reaction descriptors which will help unravel likely deactivation mechanisms.

O 78.5 Thu 11:30 TRE Phy

**Machine Learning Driven Molecular Dynamics Simulation of the M1 Selective Oxidation Catalysts** — ●KYEONGHYEON NAM<sup>1</sup>, YONGHYUK LEE<sup>1</sup>, LIUDMYLA MASLIUK<sup>2</sup>, THOMAS LUNKENBEIN<sup>2</sup>, ANNETTE TRUNSCHKE<sup>2</sup>, CHRISTOPH SCHEURER<sup>1</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Theory, Fritz-Haber-Institut der MPG — <sup>2</sup>Inorganic Chem. Dept., Fritz-Haber-Institut der MPG, Berlin, Germany

The activity and selectivity of realistic heterogeneous catalysts can be altered noticeably by small changes in a multitude of factors such as bulk composition, dopants, defects, reaction conditions, etc. Their effects are furthermore interrelated in non-trivial ways. As an important first step to rationally disentangle them, we here aim to understand their influences on the evolution of local atomic-scale structural motifs presented by the catalyst. Specifically, we do this for the M1 structural modification of (Mo,V)O<sub>x</sub> and (Mo,V,Te,Nb)O<sub>x</sub> as an active catalyst for oxidative dehydrogenation of ethane to ethylene. The large primitive cell of the M1 catalyst challenges a detailed study of all surface terminations by means of predictive-quality first-principles calculations. To this end, we deconstruct the primitive cell into ‘rod-like structures’ of surface motifs with various oxygen content. A machine-learned Gaussian Approximation Potential (GAP), trained against this structural library, faithfully reproduces experimental data from electron microscopy [1]. MD simulations of M1 catalyst hk0 prismatic faces with the iteratively improved GAP help to rationalize the influence of vanadium and niobium doping on the active surface structure.

[1] L. Masliuk *et al.*, *J. Phys. Chem. C* **121**, 24093 (2017).

O 78.6 Thu 11:45 TRE Phy

**Studying of rate-limiting steps on CO<sub>2</sub> reduction on ZnO/Cu(111)** — ●SINA DORTAJ<sup>1,2</sup> and SEBASTIAN MATERA<sup>1,2</sup> — <sup>1</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany — <sup>2</sup>Institute for Mathematics, Freie Universität, Berlin, Germany

To simulate the chemical kinetics of heterogeneous catalysts, the kinetic Monte Carlo (kMC) method is a common choice as it allows estimating turnover frequencies and coverages with a tunable accuracy. This advantage comes at much higher computational costs compared to classical kinetic approaches, in addition to stochastic noise on the simulation results. Thus, local sensitivity analysis to determine the rate-limiting step becomes cumbersome. Additionally, rate constants often carry some sizeable uncertainty due to the intrinsic approxima-

tions in quantum chemical methods or the noise in experimental data used to determine reaction barriers that make the use of just local methods obscure. We address both problems, high costs, and parameter uncertainties, by a novel global sensitivity analysis based on the Cramér von Mises distance and a Quasi-Monte Carlo sampling of the space of rate constants. While applicable to any model, our approach is particularly suited for the use of kMC and other Monte Carlo models. We demonstrate the approach on the CO<sub>2</sub> reduction on ZnO/Cu(111) catalysts identifying the key atomic scale factors controlling activity and selectivity.

O 78.7 Thu 12:00 TRE Phy

**Identifying materials genes describing selectivity of catalytic CO<sub>2</sub> hydrogenation: an AI approach with theoretical and experimental data** — ●RAY MIYAZAKI<sup>1</sup>, KENDRA BELTHLE<sup>2</sup>, HARUN TÜYSÜZ<sup>2</sup>, LUCAS FOPPA<sup>1</sup>, and MATTHIAS SCHEFFLER<sup>1</sup> — <sup>1</sup>The NOMAD Laboratory at the FHI of the Max-Planck-Gesellschaft and IRIS-Adlershof of the Humboldt-Universität zu Berlin, Germany — <sup>2</sup>Max-Planck-Institut für Kohlenforschung, Germany

Investigating CO<sub>2</sub> hydrogenation by heterogeneous catalysis that mimics hydrothermal vents leads to a deeper understanding of the origin of organic molecules at the early earth [1]. We focus on cobalt nanoparticles supported on M-SiO<sub>2</sub> where hetero atoms (e.g., Ti or Al) are incorporated into SiO<sub>2</sub>. However, heterogeneous catalysis is governed by an intricate interplay among multi-scale processes. Thus, it is rather difficult, if not impossible, to identify the key physical parameters correlated with the catalytic performance (*materials genes*) directly by theoretical or experimental approaches. In this study, materials properties obtained from density functional theory calculations and experiments, such as adsorption energy of CO<sub>2</sub> and measured pore volume, are used to model the experimental selectivity of each organic molecule (e.g., CH<sub>3</sub>OH, CH<sub>4</sub>) by the sure-independence screening and sparsifying operator (SISSO) AI approach [2]. In order to accelerate catalyst design, we also investigate the accuracy of the models using input parameter sets with the different acquisition cost.

[1] K. S. Belthle *et al.*, *J. Am. Chem. Soc.*, in press (2022).

[2] R. Ouyang *et al.*, *Phys. Rev. Mater.*, **2**, 083802 (2018).

O 78.8 Thu 12:15 TRE Phy

**Structural and Electronic Properties of Iron Nanoparticles onto Well-Defined Ceria Thin Films** — ●LESIA PILIAI<sup>1</sup>, MYKHAILO VOROKHTA<sup>1</sup>, PETER MATVIJA<sup>1</sup>, TOMÁŠ SKÁLA<sup>1,2</sup>, IVAN KHALAKHAN<sup>1</sup>, and IVA MATOLÍNOVÁ<sup>1</sup> — <sup>1</sup>Charles University, Prague, Czech Republic — <sup>2</sup>Elettra-Sincrotrone, Elettra-Sincrotrone, Italy

The interaction of iron with ceria using model Fe/ceria systems consist-

ing of Fe nanoparticles vapor deposited on well-ordered CeO<sub>x</sub>(x=1,5;2) thin films grown on Cu(111) has been investigated by X-ray photoelectron spectroscopy (XPS), synchrotron radiation photoemission spectroscopy (SRPES), and scanning tunneling microscopy (STM). The Fe atoms are oxidized to Fe<sup>3+</sup> and Fe<sup>2+</sup> species upon deposition on CeO<sub>2</sub> at 300 K at the cost of the reduction of Ce<sup>4+</sup> to Ce<sup>3+</sup>. With increasing the Fe coverage, the concentration of Ce<sup>3+</sup> increases monotonically. The notable growth of Fe<sup>2+</sup> species was observed upon deposition on CeO<sub>2</sub> at 300 K, but Fe<sup>3+</sup> species remain predominant in Fe/CeO<sub>x</sub> systems. Our studies demonstrate that in comparison with other transition metals, Fe remains oxidized on ceria even at higher coverage and exhibits a small particle size, likely arising from strong metal\*support interactions. Combining the SRPES and STM data suggests that annealing to higher temperatures leads to the formation of an iron-ceria solid solution. These results illustrate that Fe modifies both the electronic and structural properties of ceria depending on external conditions.

O 78.9 Thu 12:30 TRE Phy

**In situ characterization of cerium oxide on Au(111) under reducing and oxidizing conditions by low-energy electron microscopy** — ●RUDI TSCHAMMER<sup>1</sup>, LARS BUSS<sup>1,2</sup>, CARLOS MORALES<sup>1</sup>, SANJAYA SENANAYAKE<sup>3</sup>, JENS FALTA<sup>2,4</sup>, and JAN INGO FLEGE<sup>1</sup> — <sup>1</sup>Applied Physics and Semiconductor Spectroscopy, BTU Cottbus-Senftenberg, Cottbus, Germany — <sup>2</sup>Institute of Solid State Physics, University of Bremen, Bremen, Germany — <sup>3</sup>Chemistry Division, Brookhaven National Laboratory, Upton, NY 11973, USA — <sup>4</sup>MAPEX Center for Materials and Processes, University of Bremen, Bremen, Germany

The development of novel catalysts for a variety of applications is a key challenge for modern catalysis. Inverse metal oxide catalysts consisting of oxide nanoparticles dispersed on a metal support have recently attracted much attention, showing higher activity and selectivity compared to traditional catalytic systems, harnessing synergistic effects attributed to the so-called metal-support interaction. To gain further insights, we deposited cerium oxide nanoparticles on Au(111) and studied this system by low-energy electron microscopy (LEEM) and low-energy electron diffraction (LEED). The prepared samples demonstrate a distinct correlation between the deposition temperature and the structural order of the nanoparticles. This has been expanded upon by exploring the changes induced by reduction with H<sub>2</sub> and reoxidation with O<sub>2</sub> or CO<sub>2</sub>, again exhibiting a connection between structural order and activity, while also showing the influence of the oxide-metal interaction on the stability of cerium oxide under reducing conditions.