

## O 7: Poster Session I: Heterogeneous catalysis I

Time: Monday 10:30–12:30

Location: P

O 7.1 Mon 10:30 P

**Diffusion of oxygen atoms on a highly CO-covered Ru(0001) surface** — ●HANNAH ILLNER, ANN-KATHRIN HENSS, and JOOST WINTTERLIN — Chemie Department, Ludwig-Maximilians-Universität München, Deutschland

It was recently shown that oxygen atoms on a Ru(0001) surface covered with 0.33 monolayers (ML) of coadsorbed CO could travel through the CO layer by means of a new diffusion mechanism (Henß et al., Science 2019). The term "door-opening mechanism" indicated that the diffusion of the O atoms was facilitated by fluctuations in the CO layer that frequently opened low-energy paths for the oxygen. Here we report about investigations at higher CO coverages (0.50 ML). The experiments were performed between 239 and 280 K by means of a variable-temperature, high-speed STM that achieves imaging rates of up to 60 frames per second. In the investigated temperature range an ordered ( $2\sqrt{3} \times 2\sqrt{3}$ )R30° CO structure, which was observed at 70 K, had undergone an order-disorder transition. The trajectories of the O atoms through the disordered CO layer were analyzed, and hopping frequencies and an activation energy were extracted. It turned out that the surface diffusion of the O atoms was even faster than at the lower CO coverage and also faster than on the bare surface. We explain this finding by the weakened binding strength of the O atoms to the surface caused by CO.

O 7.2 Mon 10:30 P

**Kinetic Monte Carlo simulations of methane and higher oxygenate synthesis over Rh-based catalysts** — MARTIN DEIMEL<sup>1</sup>, HECTOR PRATS GARCIA<sup>2</sup>, ●MICHAEL SEIBT<sup>1</sup>, KARSTEN REUTER<sup>1,3</sup>, and MIE ANDERSEN<sup>1</sup> — <sup>1</sup>Chair for Theoretical Chemistry, Technical University of Munich, Garching, Germany — <sup>2</sup>Department of Materials Science and Physical Chemistry, University of Barcelona, Spain — <sup>3</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany

The kinetic Monte Carlo method (KMC) is a powerful tool for microkinetic modeling of heterogeneous catalysis since it provides a statistically correct description of fluctuations and correlations in the coverage and binding sites of adsorbates and allows to take into account lateral interactions between the adsorbates through e.g. cluster expansion methods [1]. However, simulations can become computationally demanding through complexity in the lateral interactions or when processes with highly disparate timescales are present [2]. Here we present some new implementations in our in-house KMC code *kmoss* aimed at tackling these challenges and apply these to a highly complex reaction network involving methane and higher oxygenate synthesis over Rh-based catalysts. We carefully analyze how lateral interactions affect the effective barriers in the reaction network and show that their inclusion can lead to mechanistic changes regarding the preferred reaction pathways.

[1] M. Andersen *et al.*, Front. Chem. **7**, 202 (2019)[2] M. Andersen *et al.*, J. Chem. Phys. **147**, 152705 (2017)

O 7.3 Mon 10:30 P

**Active Site Representation in First-Principles Microkinetic Models: Data-Enhanced Computational Screening for Improved Methanation Catalysts** — ●MARTIN DEIMEL<sup>1</sup>, KARSTEN REUTER<sup>1,2</sup>, and MIE ANDERSEN<sup>1</sup> — <sup>1</sup>Chair for Theoretical Chemistry, Technical University of Munich, Garching, Germany — <sup>2</sup>Fritz Haber Institute of the Max Planck Society, Berlin, Germany

In heterogeneous catalysis first-principles microkinetic models have largely contributed to our trend understanding of transition metal (TM) and TM alloy catalysts. Within prevalent screening approaches, the computational costs are kept tractable through the use of reductionist models that only resolve a minimal amount of active site motifs at the surface. This reduces the required input to only a few adsorption energies of key reaction intermediates, while the predictive power might be jeopardized. Here, we scrutinize this common practice by systematically comparing the screening predictions for the CO methanation reaction when using microkinetic models that resolve an increasing number of sites at stepped TM and binary TM alloy catalysts. The excessive amount of predictive-quality adsorption energetics required is obtained from a compressed sensing descriptor that once trained provides these data for a new material from a single DFT calculation of the clean surface.<sup>[1]</sup> We show that the explicit consideration of hith-

erto neglected step and terrace sites yields new mechanistic insights and highly active materials.<sup>[2]</sup>

[1] M. Andersen *et al.*, ACS Catal. **9**, 2752 (2019)[2] M. Deimel *et al.*, ACS Catal. **10**, 13729 (2020)

O 7.4 Mon 10:30 P

**The Water Forming Reaction on Palladium Nanoparticles Studied by Kelvin Probe Force Microscopy** — ALI EL BARAJ, BAPTISTE CHATELAIN, and ●CLEMENS BARTH — Aix-Marseille University, CNRS, CINaM, 13288 Marseille, France

The adsorption of atomic or molecular species on metal nanoparticles (NP), the absorption of atomic species like carbon, hydrogen or oxygen inside NPs and chemical reactions at NPs are of key interest in heterogeneous catalysis. Such phenomena strongly depend on the NP's size and shape so that a characterization at the single NP level is desired. A solution is to use Kelvin probe force microscopy (KPFM) and noncontact AFM (nc-AFM) in UHV. Because adsorbed or absorbed species almost always create a surface dipole, their presence can be directly put into evidence by measuring the change of work function (WF) of the NP as recently demonstrated with oxygen and PdNPs [1].

In this contribution, we show that KPFM can be used to monitor the O+H water forming reaction on PdNPs, which is of general importance in astrophysics and for fuel cells. We discuss the reaction itself but also phenomena, which involve possible subsurface oxygen creation and carbon de-activation.

[1] Grönbeck, H.; Barth, C. J. Phys. Chem. C 2019, 123, 24615–24625.

O 7.5 Mon 10:30 P

**What we can learn from pushing atoms around: Design of experiment approach to support effects in heterogeneous catalysis** — ●FREDERIC FELSEN, KARSTEN REUTER, and CHRISTOPH SCHEURER — Fritz-Haber-Institut, Berlin, Germany

Intricate interface structures are characteristic for most commonly employed heterogeneous catalysts in industrial applications. Understanding concomitant surface effects is key for a rational improvement and design of future catalysts. Electronic and steric effects of the support material on presumably active metal particles have been shown to interfere with scaling relations for the estimation of adsorption energies in multi-component catalysts[1]. This implies severe limitations for many established screening approaches and points to the need for suitable descriptors in more complex systems.

We present an approach to efficiently characterize solid-solid interface structures by a well defined set of single-point DFT calculations. Instead of brute forcing a full structural relaxation of the complex interface structure we actively introduce geometric distortions using statistical experimental design and evaluate the resulting changes in electronic properties. Encoding information on elementary distortions in a system-specific fingerprint, we introduce a descriptor capable of capturing the main support effects. As a first test case geometric distortions are applied to thin metal films supported on alkaline earth metal oxides.

[1] P. Metha *et al.*, ACS Catal. **7**, 4707 (2017).

O 7.6 Mon 10:30 P

**A highly sensitive gas chromatograph for operando STM of catalytic reactions** — ●KATHARINA MARIA DURNER<sup>1</sup>, BERNHARD BÖLLER<sup>1</sup>, GÜNTER STIENEN<sup>2</sup>, and JOOST WINTTERLIN<sup>1</sup> — <sup>1</sup>Chemie Department, Ludwig-Maximilians-Universität München, Deutschland — <sup>2</sup>S+H Analytik GmbH, Mönchengladbach, Deutschland

Operando STM experiments of catalytic reactions can provide direct correlations between surface structure elements as possible active sites and catalytic activity. However, a major experimental difficulty is the extremely low product concentrations that result from the small size of the single crystal model catalysts and the usually relatively large volumes of STM cells. We present a special gas chromatograph (GC) that has been developed to solve this problem. The setup combines a common GC with a specially designed injection unit. Gas samples, produced at typical experimental pressures between 100 mbar and 1 bar, are compressed to the working pressure of the GC column. In the column the gas samples are condensed in a liquid nitrogen-cooled trap from which they evaporate during the temperature program. In this

way the gas sample volumes are strongly enhanced without causing peak broadening. The GC has been used in operando STM experiments on the Fischer-Tropsch synthesis. Hydrocarbons from C1 to C4

produced well separated peaks, and a detection limit of 0.45 ppb was reached.