

O 20: Poster Session II: Heterogeneous catalysis II

Time: Monday 13:30–15:30

Location: P

O 20.1 Mon 13:30 P

Data-Driven Descriptor Engineering and Refined Scaling Relations for Predicting Transition Metal Oxide Reactivity — ●WENBIN XU¹, MIE ANDERSEN¹, and KARSTEN REUTER^{1,2} — ¹Chair for Theoretical Chemistry, Technical University of Munich, Garching, Germany — ²Fritz Haber Institute of the Max Planck Society, Berlin, Germany

Screening of transition metal (TM) and TM alloy catalysts is often carried out using the comparatively simple d-band model and related scaling relations to predict adsorption enthalpies. Unfortunately, these methodologies do not extend to TM oxides due to their more localized and intricate electronic structure. Multiple geometric and electronic properties could in principle govern the adsorption enthalpies at these more complex compound materials. Given the immense number of candidates, we here apply a data-driven compressed sensing method^[1] to tackle the search for best-performing multidimensional descriptors expressed as nonlinear functions of intrinsic properties of the clean surface. Our descriptors largely outperform previously highlighted descriptors in terms of accuracy and computational cost. Furthermore, we identify properties related to the local charge transfer to be the missing ingredient in standard scaling relations and show that their inclusion is crucial for the correct identification of promising catalyst materials for the oxygen evolution reaction.^[2]

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

[2]W. Xu *et al.*, ACS Catal. **11**, 734 (2021)

O 20.2 Mon 13:30 P

Microscopy of Gold Oxide Formation on TiO₂/Au(111) Model Catalysts for CO Oxidation — ●SABINE WENZEL and IRENE M. N. GROOT — Leiden Institute of Chemistry, The Netherlands

Hydrogen produced from methanol has to be cleaned from traces of CO for its use in fuel cells [1]. Gold-based catalysts have been shown to selectively oxidize CO in H₂ environment at low temperatures [2]. There is ample evidence for strong interactions between gold and typically used supports such as TiO₂ [3]. However, the exact oxidation state of the active phase of gold as well as the role of oxide supports and water remain under debate [4,5,6]. Our set-up [7] allows for the controlled preparation and characterization of model catalyst surfaces in ultra-high vacuum combined with scanning tunneling microscopy at atmospheric pressures. A TiO₂/Au(111) model catalyst was prepared via physical vapor deposition and exposed to CO oxidation reaction conditions. We present evidence for the formation of a surface gold oxide in this environment. Our findings suggest that transfer of atomic oxygen from the titania nanoparticles to the gold substrate does not occur but that contaminants can promote the oxidation of gold.

References: [1] Dhar *et al.*, J. Electrochem. Soc. 1987, 134, 12, 3021 [2] Haruta, The Chemical Record 2003, 3, 75 [3] Palomina *et al.*, ACS Sustainable Chem. Eng. 2017, 5, 10783 [4] Min *et al.*, Chem. Rev. 2007, 107, 2709 [5] Klyushin *et al.*, ACS Catal. 2016 **6**, 3372 [6] Kettemann *et al.*, ACS Catal. 2017, 7, 8247 [7] Herbschleb *et al.*, Rev. Sci. Instrum. 2014, 85, 083703

O 20.3 Mon 13:30 P

surface structure and stoichiometry of PdZn alloys under realistic (*T*, *p*) conditions — ●YUANYUAN ZHOU¹, LARA KABALAN², IGOR KOWALEC², LUCA M. GHIRINGHELLI¹, SERGEY LEVCHENKO¹, ANDREW LOGSDAIL², RICHARD CATLOW², and MATTHIAS SCHEFFLER¹ — ¹NOMAD Laboratory, Fritz Haber Institute of the Max Planck Society, Berlin, Germany — ²School of Chemistry, Cardiff University, Cardiff, United Kingdom

PdZn is known to efficiently catalyze CO₂ to methanol.[1] However, the microscopic understanding of the underlying chemical reactions at the surface is lacking, for example, the stoichiometry and structure of the surface under catalytic *T*, *p* conditions. The talk will, address the first and crucial step for achieving an improved understanding needed

for predicting better catalysts in the family of bi- and tri-metallic materials. Specifically, we will analyze the composition and structure of PdZn(101) in a constrained thermal equilibrium with CO₂ and H₂ gases using density-functional theory and *ab initio* atomistic thermodynamics [2], considering a bulk composition of 1:1. Exposure to H₂ induces a restructuring of the surface and an enhancement of the Pd concentration. This is understood in terms of the stronger Pd-H bonds compared to Zn-H. Importantly, the adsorption of CO₂ is stronger in the presence of surface hydrogen. We discuss the various restructurings, order/disorder adsorbate phases, and the possibility of the formation of a surface hydride.

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

[2]K. Reuter and M. Scheffler, Phys. Rev. B. 65, 035406 (2001).

O 20.4 Mon 13:30 P

Performance and predictions of kinetic models for MgO-catalyzed ethanol conversion to butadiene — ●ASTRID BOJE¹, WILLIAM E. TAIFAN², HENRIK STRÖM¹, TOMÁŠ BUČKO^{3,4}, JONAS BALTRUSAITIS², and ANDERS HELLMAN¹ — ¹Chalmers University of Technology, Göteborg, Sweden. — ²Lehigh University, Bethlehem, USA. — ³Comenius University in Bratislava, Bratislava, Slovak Republic. — ⁴Slovak Academy of Sciences, Bratislava, Slovak Republic.

Formation of 1,3-butadiene from ethanol is a sustainable alternative to conventional synthesis; however, selectivity is challenging and there is significant sensitivity to catalyst composition and conditions. We employ a combination of first-principles-informed energetic span and microkinetic models to interrogate the kinetic behavior of this system on a model MgO catalyst, demonstrating the utility and limitations of both perspectives. The microkinetic model was developed based on the extensive DFT mechanism of Taifan *et al.* [1], comprising several possible pathways. Both models allow quantification of rate-determining states and turnover, with the microkinetic model characterizing kinetic limitations due to coverage and adsorption/desorption effects. The dominance of the pathways varied with temperature. We considered the impact of uncertainty in the free energy landscape on kinetic predictions by sampling from a correlated error model, finding that the microkinetic model was less robust but both models predicted similar median outcomes. The two models thus provide valuable and complementary insights into the operation of a complex, selectivity-limited process. [1] Taifan, W. E., *et al.*, J. Catal. **346**, 78 (2017).

O 20.5 Mon 13:30 P

Interfacial catalysis over well-defined Cu₂O nanostructures — ●FAN YANG — School of Physical Science and Technology, ShanghaiTech University, Shanghai 201210, China

The catalytic properties of nano-oxides are increasingly recognized and currently explored for a wide range of applications. However, the nature of the active sites of these nano-oxides, as well as their catalytic chemistry, remain poorly understood, because of the difficulties to access these surface/interfacial sites at the atomic level. Using molecular beam epitaxy, we construct well-defined oxide nanostructures (NSs) on planar metal or oxide surfaces, which serve as the model systems for understanding the catalytic chemistry of the metal-oxide interface and nano-oxides. In this talk, we report our recent progress in the studies of low temperature CO oxidation using supported Cu₂O NSs as the model catalyst. The Cu₂O-M interface has been suggested as catalytic active sites for low temperature CO oxidation and a series of selective oxidation reactions. Combining microscopic and spectroscopic methods, CO oxidation was investigated at the Cu₂O-M interface, to understand the mechanism of low temperature CO oxidation and the catalytic properties of the metal-oxide interface. A highly dynamic behavior of the catalytically active interfacial sites were observed, which accounts for the enhanced activities and stability of supported oxide NSs for oxidation reactions. Overall, we wish to demonstrate that the control over supported oxide NSs could enable a wide range of catalytic properties for the rational design of highly efficient catalysts.