O 47: Metal Substrates I

Time: Wednesday 10:30–12:15 Location: MA 043

O 47.1 Wed 10:30 MA 043

Studying facet-selective adsorption of CO on Cu using the random phase approximation — •Seungchang Han and Stefan Ringe — Department of Chemistry, Korea University

Electrochemical CO2 reduction is a promising sustainable strategy for producing valuable chemicals and fuels. Cu is the only catalyst that produces significant amounts of higher reduced products like ethylene, ethanol, or methane. The product selectivity depends critically on the Cu active site environment, defined by the coverage and distribution of the central *CO intermediate. Unfortunately, one of the most successful approaches to studying adsorption events, the Perdew-Burke-Ernzerhof (PBE) functional based on generalized gradient approximation (GGA), has been shown to benefit from error compensation, which can affect their transferability to unknown systems. It also leads to a wrong prediction of adsorption trends across different surface facets and adsorption sites. Adding many-body corrections based on the random phase approximation (RPA) has been shown to critically improve the prediction of adsorption energies and long-range interactions. In this work, we first present a simple extrapolation scheme to overcome the difficulty of getting converged RPA-based adsorption energies. We then demonstrate the first trends of adsorption energies as well as the coverage dependence and compare them to conventional functionals.

O 47.2 Wed 10:45 MA 043

Electronic Structure Benchmark Calculations for CO2 Reduction Products on Cu(111)-Clusters from Projection-Based Embedding Theory — •Elena Kolodzeiski and Christopher Stein — TU Munich, TUM School of Natural Sciences, Department of Chemistry, Lichtenbergstr. 4, 85748 Garching, Germany

Copper surfaces are promising catalysts for the conversion of carbon dioxide. Despite the immense interest in such systems, current theoretical approaches have limitations either in numerical cost or accuracy. We propose the use of a cluster model described by the projection-based embedding theory (PBET) as a balanced compromise. This approach involves partitioning the system into an active system and an environmental, focusing the computational efforts on the active subsystem. The system partitioning is based on our recently developed ACE-of-SPADE algorithm, which has been proven to enable consistent active orbital space selection even for such challenging systems as transition metal clusters. Here, we present a benchmark study validating the accuracy of the cluster embedding approach for calculating the binding energy of a series of CO2 reduction products on Cu(111)-clusters. The cluster approach is first verified by comparison to PBE plane-wave calculations and then extensively validated regarding the impact of different cluster models. We showed that the proposed QM/QM embedding strategy considerably improves the accuracy compared to PBE plane-wave calculations. PBET, in combination with the ACE-of-SPADE algorithm, provides a highly accurate method for studying chemical reactions on cluster models of metal surfaces.

Topical Talk O 47.3 Wed 11:00 MA 043

Adsorbate motors for unidirectional translation and transport — •Grant J. Simpson[1], Mats Persson[2], and Leonhard Grill[1] — [1]University of Graz, Graz, Austria — [2]University of Liverpool, Liverpool, UK

Inspired by their biological counterparts, artificial molecular motors aim to convert external energy into unidirectional motion. However, despite having some form of inherent directionality imprinted into their chemical structure, synthetic motors often lose functionality when taken from their native aqueous phase and deposited onto a metallic surface. Here, we demonstrate a new concept in molecular motors which uses a small and simple chemical structure to achieve perfect unidirectionality when deposited onto a Cu(110) surface [1]. The motion is observed and quantified using scanning tunnelling microscopy and is shown to be triggered by an intramolecular proton transfer. We further demonstrate that this unidirectional motion can be harnessed to perform meaningful work by transporting small cargo molecules across the surface.

[1] G. J. Simpson, M. Persson, L. Grill, Nature, 621, 82-86 (2023)

O 47.4 Wed 11:30 MA 043

Functionalization of Cu and CuxO surfaces with heterocyclic molecules: a joint experimental and computational study — •Sergio Tosoni[1], Felix Landwehr[2], Mowpriya Das[3], Maximilian Koy[3], Jared P. Bruce[2], Ankita Das[3], Juan J. Navarro[2], Markus Heyde[2], Gianfranco Pacchioni[1], Frank Glorius[3], and Beatriz Roldan Cuenya[2] — [1]Dipartimento di Scienza dei Materiali, Università di Milano-Bicocca, Via Cozzi 55, 20125 Milano, Italy — [2]Fritz-Haber Institute of the Max Planck Society, Department of Interface Science, Faradayweg 4 6, 14195 Berlin, Germany — [3]Westfälische Wilhelms-Universität, Organisch-Chemisches Institut Corrensstraße 40, 48149 Münster, Germany)

N-Heterocyclic Carbenes (NHCs) and Olefins (NHOs) form strong chemical bonds to surfaces, which enables their use in surface functionalization for gas sensing, optoelectronics and (photo)catalysis. We deposit and characterize NHCs on clean and oxidized copper. State-of-the-art DFT calculations are used to interpret the results of STM and XPS measurements. We compare the adsorption and diffusion of NHCs and NHOs on Cu, also considering the important effect of the steric hindrance exerted by the side substituents. NHCs are bound stronger than NHOs on clean copper. Interestingly, bonds to oxygen are preferentially formed by NHCs on an oxidized Cu surface. The intriguing different behaviour shown by NHCs on Cu(111) and Cu(100) is analysed in details.

O 47.5 Wed 11:45 MA 043

Cluster formation and ordering at high CO coverages on Ru(0001): A combined DFT and STM study — •Hannah Illner[1], Sung Sakong[2], Axel Gross[2], and Joost Wintterlin[1] — [1]Ludwig-Maximilians-Universität München, Germany — [2]Universität Ulm, Germany

Dense coverages of adsorbates on metal surfaces provide insight into the relation between metal-adsorbate and adsorbate-adsorbate interactions. Depending on the variation of the adsorption energy with binding site, different types of structures can be formed in dense layers, namely moiré structures, structures formed by domain boundaries, and cluster structures. On Ru(0001), CO at 0.58 monolayers (ML) forms a closed ring cluster structure consisting of seven molecules in $(2\sqrt{3} \times 2\sqrt{3})$R 30° symmetry. Here we present a study in which CO at higher coverages than 0.58 ML is investigated by low-temperature STM and DFT simulations. We identify six compact cluster structures, which are separated by CO-free Ru rows and a triangular arrangement of CO molecules at the junctions. We discuss how the local configurations stabilize the cluster configuration. By analyzing the Fourier transform of the STM image we provide a new explanation of the LEED pattern of the CO adlayer, that previously has been interpreted as resulting from a moiré structure. The newly identified structures clarify the long-standing conflict between the assumed structure and the vibrational spectroscopy data.

O 47.6 Wed 12:00 MA 043

Single-molecule study of Heck cross-coupling with Pd nano-islands on Au(111) surface — •Donato Civita[1], Friedrich Esch[2], and Leonhard Grill[1] — [1]Department of Physical Chemistry, University of Graz, Austria — [2]Fakultät für Chemie, TU München, Germany

The interaction of organic molecules with metallic structures is particularly important in heterogeneous catalysis. It has been shown that model heterogeneous catalysts based on metal single crystals can be investigated by scanning tunnelling microscopy (STM) to determine the role of steps as active sites for dissociation or to study a thermally induced Heck cross-coupling [1]. Moreover, nanostructured catalysts are advantageous to obtain specific electronic properties, a large number of undercoordinated sites, and to reduce the amount of precious catalyst material. However, instability effects like leaching of catalyst atoms from the nanostructure or sintering of small particle into large ones requires a systematic investigation at the atomic scale.

Here, these questions are addressed by studying a Heck cross-coupling reaction catalysed by Palladium nano-islands on Au(111) surface by low temperature STM. A statistical analysis of the products and the Pd islands size, together with STM tip manipulation experiments of single intermediates, give insight into the activity and stability of this catalyst, and the dependence on its morphology.

[1] Shi, K.-J., et al., On-Surface Heck Reaction of Aryl Bromides with Alkene on Au(111) with Palladium as Catalyst. Organic Letters, 2017. 19(11): p. 2801.