

O 61: Heterogeneous Catalysis

Time: Tuesday 18:30–20:30

Location: P2-OG2

O 61.1 Tue 18:30 P2-OG2

Simulation of gas-phase mediated sintering — •ELISABETH DIETZE^{1,2} and PHILIPP PLESSOW^{1,2} — ¹Karlsruhe Institute of Technology (KIT), Karlsruhe, Germany — ²Institute of Catalysis Research and Technology (IKFT), Karlsruhe, Germany Institute of Catalysis Research and Technology (IKFT), Karlsruhe, Germany

It is a longstanding question whether sintering of Pt under oxidizing conditions is mediated by surface migration of Pt species or through the gas phase, by PtO₂. Simulations have shown that ripening through the gas phase is relevant [1]. In addition, experiments have shown how sintering depends on the gas flow and the geometrical setup of the reactor for the sintering of Pt particles in an oxidizing atmosphere [2]. Accurate prediction of gas-phase mediated sintering requires to go beyond continuum approximations and to model mass transport in the gas phase. The transport is modeled through an explicit simulation of single-particle scattering events in the gas phase, using a kinetic Monte Carlo (kMC) model that describes the collision of an explicit molecule within a uniform background of ideal gas that is characterized by its temperature as well as its mass distribution, collision cross section and collective gas-flow. Since Argon is often used as a gas in experiments it is an appropriate model system. First results are promising. The diffusion constant of an Ar⁴⁰ molecule in Ar⁴⁰ could be reproduced.

[1] P. Plessow, F. Abild-Pedersen, ACS Catal. 2016, 6 (10), 7098-7108. [2] T.W. Hansen, A.T. Delariva, S.R. Challa, A.K. Datye, Acc. Chem. Res. 2013, 46 (8), 1720-30.

O 61.2 Tue 18:30 P2-OG2

Ab-initio Study of Photocatalytic Water Splitting on LiNbO₃ — •CHRISTOF DUES, WOLF GERO SCHMIDT, and SIMONE SANNA — Theoretische Physik, Universität Paderborn, D-33095 Paderborn

Photocatalytic water-splitting for hydrogen production promises to offer a way for clean, low-cost and environmentally friendly production of hydrogen by solar energy. Besides titanium dioxide also ferroelectric lithium niobate has been studied as a possible photocatalyst in this context [1]. The internal polarisation in this material is expected to lead to a long lifetime of photo-induced carriers as well as reaction pathways that involve both the positively and negatively charged surface.

In the present work the water splitting at LiNbO₃ Z-Cut surfaces is studied within density functional theory (DFT). Thereby the approach of Nørskov et al. [2] for estimating the free energy profile of the reactions is followed. Saddle points in the potential energy hypersurface are determined using the nudged elastic band method [3] and constrained DFT is used to model the excited configurations.

[1] B. Zielinska et al., J. Phys. Chem. Solids **69**, 236 (2008).
[2] J. K. Nørskov et al., J. Phys. Chem. B **108**, 17886 (2004).
[3] G. Henkelman et al., J. Chem. Phys. **113**, 9901 (2000).

O 61.3 Tue 18:30 P2-OG2

Theoretical Investigation of the Role of CO Adsorption on the Properties of 55-Atom PtCo Nanoalloys — •DIEGO GUEDES-SOBRINHO¹, ANDERSON S. CHAVES², RAFAEL L. H. FREIRE¹, and JUAREZ L. F. DA SILVA¹ — ¹University of São Paulo, São Carlos, Brazil — ²University of Campinas, Campinas, SP, Brazil

The understanding of composition dependent properties of PtCo nanoalloys is crucial for several potential applications, such as catalytic and anti-corrosive capacities. However, our current comprehension of these systems in an atomistic level is far from satisfactory. In this work, we report a density functional theory investigation of the structural, energetic, and electronic properties of PtCo 55-atoms nanoalloys by using Pt_nCo_(55-n) ($n = 0, 6, 13, 20, 28, 35, 42, 49$, and 55) models, in which the CO ligands saturation properties were investigated including van der Waals (vdW) corrections.[A. Tkatchenko *et al.*, JCP **138**, 074106 (2013)] We found that in gas-phase the maximum stability was obtained for icosahedron (ICO-like) structures at all the compositions with both transition metals.[D. Guedes-Sobrinho *et al.* **119** (27), 15669 (2015)] The adsorption of CO ligands on the nanoalloys surface affect drastically the alloy stability, which decrease for high amounts of Pt, in which the effective charge distribution in the CO molecules correlates directly with the nanoalloys composition. The most of compositions remain ICO-like, except for perfect core-shell when the vdW correction are not added, in which the CO ligands pull out all the inner

Co atoms, by yielding a disordered structure.

O 61.4 Tue 18:30 P2-OG2

Hydrogenation reactions on Pd nanoparticles studied under UHV conditions — •MARIAN RÖTZER, MAXIMILIAN KRAUSE, FLORIAN SCHWEINBERGER, and UELI HEIZ — Technische Universität München, Lehrstuhl für Physikalische Chemie, München

Hydrogenation reactions of unsaturated hydrocarbons are of major importance for chemical industry. Therefore we investigated the hydrogenation of ethylene and acetylene on supported palladium nanoparticles consisting of 20-40 atoms under ultra-high vacuum conditions (UHV). In order to evaluate the influence of support material on the nanoparticles, two different amorphous silica films are synthesized either on a Mo(211) or a Pt(111) single crystal. The presence of different types of hydrogen species on the particles and how they can be effectively tuned by the support material are tested by temperature-programmed desorption (TPD). A pulsed molecular beam technique is used to study the hydrogenation of ethylene and acetylene under isothermal conditions. A special focus is put on the available reaction pathways for these two reactions on both support systems. Important differences are discussed and how they can be tuned by proper choice of support material based on a mechanistic level.

O 61.5 Tue 18:30 P2-OG2

Ethylene hydrogenation on supported Ni, Pd and Pt nanoparticles: Catalyst activity, deactivation and the d-band model — ANDREW S. CRAMPTON¹, MARIAN D. RÖTZER¹, •MAXIMILIAN KRAUSE¹, FLORIAN F. SCHWEINBERGER¹, BOKWON YOON², UZI LANDMAN², and UELI HEIZ¹ — ¹Technische Universität München, Lehrstuhl für Physikalische Chemie, Zentralinstitut für Katalyseforschung und Fakultät für Chemie, Lichtenbergstr. 4, 85748 Garching, Germany — ²School of Physics, Georgia Institute of Technology, Atlanta, GA 30332-0430, USA

Ethylene was hydrogenated over cluster-ensembles with narrow size distributions. Ni, Pd and Pt particles (1-1.5 nm) were softlanded on an MgO(100)-thin film on Mo(100) (X_n/MgO(100)/Mo(100); X=Ni, Pd, Pt). The pulsed molecular beam reactive scattering (p-MBRS) technique was employed at 300 and 400 K to test the catalytic activity and deactivation of the particles.

While Pt particles showed the highest hydrogenation activity, they were also the most stable particles upon heating to 400 K. A trend within the group of the periodic table was found: Pd particles were less stable and active than Pt, Ni particles the least.

ϵ_c , the position of the d-band centroid taken from density functional theory calculations, correlates with the trend in activity and stability: for Pt ϵ_c lies the farthest away from the Fermi edge, for Ni the nearest.

For further characterization the particles were adsorbed with CO before and after reaction and examined with infrared reflection absorption spectroscopy.

O 61.6 Tue 18:30 P2-OG2

Size dependence of supported Rh nanoclusters in the decomposition of methanol — •TING-CHIEH HUNG¹, TING-WEI LIAO¹, ZHEN-HE LIAO¹, PO-WEI HSU¹, PEI-YANG CAI¹, HSUAN LEE¹, YU-LING LAI², YAO-JANE HSU², HUI-YU CHEN³, JENG-HAN WANG³, and MENG-FAN LUO¹ — ¹Department of Physics, National Central University, Taiwan — ²National Synchrotron Radiation Research Center, Taiwan — ³Department of Chemistry, National Taiwan Normal University, Taiwan

Catalyzed methanol decomposition has been extensively studied as a principal reaction in direct methanol fuel cells. The process provides not only an efficient transformation from chemical energy to electricity but also a convenient source of hydrogen. To shed light on the reaction, we perform experiments on a realistic model system, oxide-supported Rh nanoclusters. We present the study of adsorption and decomposition of methanol on Rh clusters grown on an ordered thin film of θ -Al₂O₃/NiAl(100) by combining infrared absorption spectroscopy (IRAS), temperature programmed desorption (TPD) and synchrotron-based photoemission spectroscopy (PES). The investigation shows that methanol adsorbs at 100 K and the formation of CO begins at about 200 K. The quantities of CO and H₂ (D₂) produced per Rh surface site remain unaltered on clusters of diameter >1.5 nm and height >0.6

nm. In contrast, on clusters with diameter <1.5 nm and height <0.6 nm, the production per Rh surface site increases with decreasing size. In this presentation, we will discuss the size dependence of oxide supported Rh clusters in the decomposition of methanol.

O 61.7 Tue 18:30 P2-OG2

CO-Adsorption on Pt/h-BN nanocluster arrays — FABIAN DÜLL, FLORIAN SPÄTH, JOHANN STEINHAUER, PHILIPP BACHMANN, UDO BAUER, HANS-PETER STEINRÜCK, and ●CHRISTIAN PAPP — Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Egerlandstraße 3, 91058 Erlangen

Nanocluster arrays supported on two-dimensional templates are intriguing systems for the investigation of catalytic processes. We report on the reactivity of Pt nanoparticles deposited on h-BN/Rh(111). In our model study we employ high-resolution XPS to investigate the interaction of such nanoclusters with CO. Three CO-induced species are observed in the C 1s core level spectra. These are assigned to CO adsorbed in on-top and bridge terrace sites and step sites in comparison with single crystal data. The step sites are occupied first during adsorption and show the highest desorption temperature, indicating that these are the most stable adsorption sites for CO. Also a temperature induced site change of CO from terrace to step sites is observed. The first adsorption/desorption cycle differs from later cycles, due to sintering. This behavior is explained by a change of the shape of the nanoparticles during the first adsorption/desorption cycle. Furthermore, we will discuss similarities and differences to platinum nanoclusters supported on graphene.

O 61.8 Tue 18:30 P2-OG2

Surface assisted synthesis of a porphyrin fragment on Cu(111) and its FM-AFM characterization — ●FELIX BISCHOFF, JACOB DUCKE, ALEXANDER RISS, JOHANNES V. BARTH, and WILLI AUWÄRTER — Physik-Department E20, TUM, James-Franck-Str. 1, 85748 Garching

In-vacuo heterogeneous nano-chemistry bares the potential for creating compounds not achievable with other approaches due to the reactivity of intermediate or final products. For example, the thermal instability of porphyrin fragments such as oligopyrroles often renders them inapplicable for standard UHV preparation techniques. Therefore di- or tripyrrins and related species are scarce in vacuum based surface science and these classes of molecules remain nearly unstudied despite their promising properties as metal-complexing agents in functional organo-metallic compounds or as fluorescent sensors. In this combined low-temperature scanning tunneling microscopy (LT-STM) and frequency modulated atomic force microscopy (FM-AFM) study we will demonstrate the formation of a hitherto unreported porphyrin fragment synthesized through pyrrole cleaving from free-base tetraphenylporphyrins (2H-TPP) on Cu(111). The novel copper metalated tripyrrin derivative is structurally characterized by visualizing its chemical structure via FM-AFM with CO-functionalized tips and via tip manipulations. We will furthermore suggest a possible reaction pathway by identifying reaction intermediates. Additionally, the products of the thermally activated flattening reaction of 2H-TPP on Cu(111) will be structurally determined by FM-AFM.