

## O 76: Poster Session VI: Supported nanoclusters: structure, reactions, catalysis

Time: Wednesday 13:30–15:30

Location: P

O 76.1 Wed 13:30 P

**Cu nanoparticle morphology and growth behavior on the vicinal ZnO(10-14) surface** — ●ROBERT GLEISSNER<sup>1,2</sup>, HESHMAT NOEI<sup>1</sup>, VEDRAN VONK<sup>1</sup>, SIMON CHUNG<sup>1</sup>, GUILHERME D. L. SEMIONE<sup>1</sup>, E. ERIK BECK<sup>1,2</sup>, GÖKHAN GIZER<sup>3</sup>, and ANDREAS STIERLE<sup>1,2</sup> — <sup>1</sup>Deutsches Elektronen-Synchrotron DESY, Hamburg, Germany — <sup>2</sup>Universität Hamburg, Hamburg, Germany — <sup>3</sup>Helmholtz Zentrum Geesthacht, Geesthacht, Germany

The ZnO(10-14) surface raised recent scientific interest for its outstanding stability despite its high indexed orientation, which results in a stepped mixed-terminated surface. In this study, copper nanoparticles were grown via physical vapor deposition onto a ZnO(10-14) single crystalline surface and the structure and morphology was investigated using low energy electron diffraction, high energy grazing incidence x-ray diffraction, scanning electron microscopy and scanning tunneling microscopy.

Caused by anisotropic diffusion, elongated Cu particles are formed parallel to the surface steps of the substrate. They show a unique tilt of their (111) planes parallel to the (0001) terraces of the vicinal surface. This causes the generation of large, high indexed Cu facets in which their atomic steps could act as reaction sites in catalytic reactions such as methanol synthesis and CO<sub>2</sub> activation.

O 76.2 Wed 13:30 P

**Metastability of Palladium Carbide Nanoparticles during Hydrogen Release from Liquid Organic Hydrogen Carriers** — ●RALF SCHUSTER<sup>1</sup>, MANON BERTRAM<sup>1</sup>, HENNING RUNGE<sup>2</sup>, SIMON CHUNG<sup>2</sup>, VEDRAN VONK<sup>2</sup>, HESHMAT NOEI<sup>2</sup>, YAROSLAVA LYKHACH<sup>1</sup>, ANDREAS STIERLE<sup>2</sup>, and JÖRG LIBUDA<sup>1</sup> — <sup>1</sup>Interface Research and Catalysis, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, D-91058 Erlangen — <sup>2</sup>Deutsches Elektronen-Synchrotron DESY, Notkestr. 85, D-22607 Hamburg

Surface carbon species can be formed by unselective decomposition during heterogeneously catalyzed dehydrogenation of liquid organic hydrogen carriers (LOHCs). These species may diffuse into the bulk of the catalyst, forming metal carbide phases and, thus, influence the activity and selectivity of the catalyst. For palladium, however, the carbide phase is metastable with respect to palladium and graphite. Therefore, we studied the formation and stability of palladium carbide phases on well-defined Pd/Al<sub>2</sub>O<sub>3</sub> model catalysts. The phase composition of the nanoparticles was investigated as a function of particle size and gas flow rate under reaction conditions (500 K, 1 bar) by high-energy grazing incidence X-ray diffraction. We showed that the stability of palladium carbide critically depends on both nanoparticle size and gas flow rate. For small nanoparticles under low gas flow rate the Pd<sub>6</sub>C phase is stable, while a high gas flow rate results in immediate decomposition of the carbide after formation. For bigger particles at a low gas flow rate, however, the carbide is stable for an incubation period, after which the growth of graphene triggers its decomposition.

O 76.3 Wed 13:30 P

**Reactivity and Passivation of Fe Nanoclusters on h-BN/Rh(111)** — ●NATALIE JESSICA WALESKA, FABIAN DÜLL, PHILIPP BACHMANN, FELIX HEMAUER, JOHANN STEINHÄUER, HANSPETER STEINRÜCK, and CHRISTIAN PAPP — Friedrich-Alexander-Universität, Erlangen, Germany

Iron is a nontoxic and affordable element, which shows high catalytic activity. Iron containing catalysts are used in important industrial reactions, such as the Fischer-Tropsch synthesis and the Haber-Bosch process. Especially, iron nanoclusters are of interest because of their potential utilization in electrochemical devices or high-density data storage applications due to their magnetic properties.

To obtain monodisperse, ordered Fe nanocluster arrays, h-BN was used as a template on the Rh(111) surface. Due to the lattice mis-

match, differences in the strength of interaction between the h-BN sheet and the Rh(111) surface occur, leading to corrugation of the nanosheet and the formation of pores and wires.

We studied Fe nanocluster arrays formed in the pores of h-BN/Rh(111) using in situ high-resolution X-ray photoelectron spectroscopy. CO was used as a probe molecule to investigate the morphology, such as the available adsorption sites and the reactivity of the nanoclusters. On the as prepared Fe clusters, CO was adsorbed at on-top and hollow/edge sites and dissociated at 300 K. For the C and O pre-covered Fe nanoclusters we found a passivation of the catalytic activity as a result of adsorption site blocking, allowing for the determination of the most active sites of the Fe clusters.

O 76.4 Wed 13:30 P

**Systematic first-principles investigation of support effects for coinage metals on alkaline earth oxides** — ●KYEONGHYEON NAM<sup>1</sup>, JULIUS HORNUNG<sup>2</sup>, CHRISTOPH SCHEURER<sup>1</sup>, and KARSTEN REUTER<sup>1</sup> — <sup>1</sup>Fritz Haber Institute of the Max Planck Society — <sup>2</sup>Technical University of Munich

Reaching an atomic-scale understanding of metal-support effects is a long-standing and still elusive goal of catalysis research. One avenue to disentangle the intricate interference of geometric and electronic effects is to engage in trend studies over structurally similar systems. To this end, we perform a systematic density-functional theory study of alkaline earth oxide (MgO, CaO, SrO, BaO) supported Cu and Ag thin films. Considering CO and hydroxyl adsorption at various surface sites, we compute adsorption energies with and without geometric optimization and correlate this data with electronic structure properties like Löwdin charges and interfacial energetics like adhesion energies. Metal doping of the oxide supports with Mo in varying positions was analyzed in an effort to expand our understanding of metal-support interactions and the critical parameters that determine catalyst activity and stability [1]. Our results indicate that oxide supports with heavier cations (SrO, BaO) favor the formation of Cu agglomerates in the presence of CO adsorbates, while such drastic rearrangements are not observed for oxides with lighter cations (MgO, CaO).

[1] X. Shao *et al.*, Angew. Chem. Int. Ed. **50**, 11525 (2011).

O 76.5 Wed 13:30 P

**Structure and Chemical Properties of CeO<sub>2</sub> on a Curved Cu(111) Crystal** — ●LORENA GLATTHAAR<sup>1,2</sup>, KHADIZA ALI<sup>2</sup>, J. ENRIQUE ORTEGA<sup>2</sup>, and FREDERIK SCHILLER<sup>2</sup> — <sup>1</sup>Physikalisch-Chemisches Institut, Justus Liebig University, D-35392 Giessen, Germany — <sup>2</sup>Centro de Física de Materiales, E-20018 San Sebastián, Spain

The system CeO<sub>x</sub>/Cu has attracted interest as an inverse catalyst for CO oxidation, water-gas shift and CO<sub>2</sub> hydrogenation. While previous work focused on characterizing this system and the named reactions on Cu(111) or with powdered samples, we investigated this system on the vicinal surfaces of Cu(111), which are shown to be much closer to a nanostructured catalysts compared to the low index surfaces. We grew CeO<sub>2</sub> on a curved Cu(111) single crystal with well defined vicinal surfaces and a continuous variation of step density depending on the vicinal angle. We characterized the CeO<sub>x</sub>/Cu system with LEED, STM and XPS. XPS analysis indicates only Ce(IV) oxide formed regardless of the position on the curved crystal. On the Cu(111) part of the curved sample, CeO<sub>2</sub> nanostructures seems to grown on Cu-oxide areas, leaving the remaining Cu(111) surface uncovered. On both A- and B-step vicinal surfaces of the curved crystal, facets build up after CeO<sub>2</sub> deposition. The stable facets of the B-step vicinals are (111) and (110). At the A-step side three stable facets have been observed, namely the (111), (223) and an additional one at 22° with respect to (111). STM measurements reveal that the CeO<sub>2</sub> structures mainly cover the Cu(111), leaving the (223) facet CeO<sub>2</sub> free.