

O 43: Oxides and Insulators: Adsorption II

Time: Wednesday 15:45–16:45

Location: H42

O 43.1 Wed 15:45 H42

Coadsorption of CO and CO₂ on zinc oxide: from single crystal to powder particles — •HENSHAN QIU¹, YUEMIN WANG^{1,2}, XINYU XIA², MARTIN MUHLER², and CHRISTOF WÖLL¹ — ¹Lehrstuhl für Physikalische Chemie I, Ruhr-Universität Bochum, D-44780 Bochum — ²Lehrstuhl für Technische Chemie, Ruhr-Universität Bochum, D-44780 Bochum

The interaction of CO and CO₂ with ZnO surfaces was studied using high resolution electron energy loss spectroscopy (HREELS), thermal desorption spectroscopy (TDS) and microcalorimetry. Exposing the non-polar ZnO(10-10) surface to CO₂ results in the formation of an unusual tridentate carbonate species with the two carbon dioxide O-atoms being almost equivalently bound to two different Zn surface atoms. Two stable carbonate phases are found: a full (1x1) monolayer with a binding energy of 52 kJ/mol and a half monolayer with (2x1) structure and binding energy of 86 kJ/mol. With regard to CO adsorption on ZnO(10-10), the precoverage of CO₂ leads to an increase of CO binding energy from 30 to 55 kJ/mol and a slight blue-shift of the $\nu(\text{C-O})$ peak by 1 meV. The amount of adsorbed CO increases first due to the existence of surface carbonates and then decreases because of site blocking effect. The co-adsorbed CO₂ leads also to stronger adsorption of CO on ZnO powder particles, giving rise to an adsorption energy distribution between 45-65 kJ/mol. The increase of interaction strength is attributed to the formation of tridentate carbonates on the most exposed ZnO(10-10) surfaces, which increases the Lewis acidity of the surface.

O 43.2 Wed 16:00 H42

Influence of Electronic Correlations on the Ground-State Properties of Cerium Dioxide Bulk and Surfaces — •ELENA VOLOSHINA¹, CARSTEN MUELLER², BEATE PAULUS¹, and KERSTI HERMANSSON² — ¹MPI fuer Physik komplexer Systeme, Noethnitzer Str. 38, 01187 Dresden, Germany — ²Department of Materials Chemistry, The Angstrom Laboratory, University of Uppsala, Box 538, Laegerhyddsvaegen 1, 75121 Uppsala, Schweden

Ceria plays an important role as a component in the active noble metal support in automotive three-way catalytic converters, where NO_x, CO, and hydrocarbons are simultaneously removed [1]. The electron-correlation effects on the ground-state properties of bulk CeO₂ are studied by ab initio quantum-chemical methods. For this purpose the method of increments is applied. It combines Hartree-Fock calculations for periodic systems with correlation calculations requiring only information of the corresponding finite-cluster calculations. After inclusion of correlations obtained at the CCSD(T) level the calculated values are in good agreement with experiment [2]. With this detailed description of the electronic correlations in bulk CeO₂, it is now possible to extend the work to CeO₂ surfaces and adsorbed molecules on them. Here we present absorption energies of CO and N₂O. Especially for these weakly bound molecules an explicitly correlated method is

necessary to describe accurately the van der Waals interaction.

- [1] J. Kaspar, P. Fornasiero, and M. Graziani, *Catal. Today* 50, 285 (1999).
- [2] E. Voloshina and B. Paulus, *J. Chem. Phys.* 124, 234711 (2006).

O 43.3 Wed 16:15 H42

Zero-bias conductance anomaly in single Au-CO complexes on a FeO thin film on Pt(111) — •NIKLAS NILIUS, EMILE RIENKS, HANS-PETER RUST, and HANS-JOACHIM FREUND — Fritz-Haber-Institut der MPG, Berlin

A thin film of FeO grown on Pt(111) forms a hexagonal Moiré pattern due to the 11% lattice mismatch with the metal support that is characterized by a modulated stacking sequence of the Fe ions with respect to the Pt(111) lattice. The spatial inhomogeneity of electronic and chemical properties within the Moiré unit cell stimulates a self-organization of Au adatoms into a hexagonal adatom network. Conductance spectra of the adatoms reveal an unoccupied resonance at +0.5 eV, but no features around the Fermi level, as measured by low-temperature STS. After CO adsorption onto the Au monomers, a pronounced zero-bias anomaly appears in the differential conductance of the species. The phenomenon is discussed in terms of the Kondo effect that might be induced by a change of the spin/charge distribution of the Au-CO complex after CO adsorption.

O 43.4 Wed 16:30 H42

Water on ZnO(11 $\bar{2}$ 0): An UPS Study — •JOACHIM WIDER and CHRISTIAN PETTENKOFER — Hahn-Meitner-Institut, Glienicker Strasse 100, 14109 Berlin

In order to understand the growth process of epitaxially grown MOMBE ZnO films on Al₂O₃, we have studied the adsorption of H₂O on a ZnO(11 $\bar{2}$ 0) single crystal. Furthermore it is controversially discussed, whether water adsorbs molecularly or dissociatively on oxide surfaces [1, 2]. Our UV photoemission experiments show that at 95 K water adsorbs both, molecularly and dissociatively on ZnO(11 $\bar{2}$ 0). At increasing exposures, the fraction of dissociatively adsorbed water remains constant, whereas the molecularly adsorbed water forms a ice multilayer. In a second experiment, we annealed the water exposed surface. Between 160 and 180 K, the ice multilayer desorbs, and a layer consisting of H₂O and OH remains on the surface. At 395 K, all adsorbates are desorbed. The adsorption of 20 L H₂O results in a band bending of 0.9 eV. Subsequent annealing decreases band bending. Upon adsorption, the workfunction is constant within 0.1 eV. Annealing the sample yields a sudden increase of the work function at 100 K of 0.2 eV, followed by decrease at 160, and a slow increase between 180 and 340 K of 0.3 eV. At 395 K, the work function has the same value as the clean cooled sample.

- [1] G. Zwicker, K. Jacobi, *Surf. Sci.* 131 (1983) 179.
- [2] B. Meyer, D. Marx, O. Dolub, U. Diebold, M. Kunat, D. Langenberg, C. Wöll, *Angew. Chem. Int. Ed.* 43 (2004) 6642.