

O 28: Symposium: Size-Selected Clusters at Surfaces II (Invited Speakers: Steven Buratto, Stefan Vajda, Matthias Arenz)

Time: Tuesday 11:15–13:00

Location: MA 005

Invited Talk O 28.1 Tue 11:15 MA 005
Size-selected Au and Ag nanoclusters on rutile TiO₂ (110) (1x1) surfaces probed by UHV-STM — XIAO TONG, LAUREN BENZ, STEEVE CHRETIEN, PAUL KEMPER, MICHAEL BOWERS, HORIA METIU, and •STEVEN BURATTO — University of California, Santa Barbara, CA USA

Catalysis of the oxidation of CO and small olefins by Au and Ag nanoclusters on oxide supports is known to be strongly dependent on the size of the cluster and its interaction with the oxide surface. In our group we have probed this size dependence by depositing size-selected clusters of Ag_n⁺ and Au_n⁺ (n = 1-7) from the gas phase onto single crystal rutile TiO₂ (110) (1x1) surfaces at room temperature under soft-landing (< 2 eV/atom) conditions. We analyze the clusters on the surface using ultra-high vacuum scanning tunneling microscopy (UHV-STM) and compare the resulting structures with theory. In the case of Au_n⁺, Ag_n⁺ and Ag₂⁺ clusters deposited under soft-landing conditions we observe large, sintered clusters indicating high mobility for these species on the surface. For Au_n⁺ (n > 1) and Ag_n⁺ (n > 2) clusters deposited under soft-landing conditions, however, we observe a high density of intact clusters bound to the surface indicating that these species have very limited mobility on the surface. We have also shown that the sintering of Au⁺ soft-landed on TiO₂ (110) occurs only for a surface covered with hydroxyl groups. On a pristine surface with an oxygen vacancy density near 10%, Au atoms remain intact on the surface.

Invited Talk O 28.2 Tue 11:45 MA 005
Towards the understanding of size/shape and function relationship in catalysis of complex reactions — •STEFAN VAJDA¹, SUNGSIK LEE¹, LARRY A. CURTISS¹, JEFFREY P. GREELEY¹, PAUL C. REDFERN¹, PETER ZAPOL¹, MICHAEL J. PELLIN¹, JEFFREY W. ELAM¹, BYEONGDU LEE¹, SÖNKE SEIFERT¹, RANDALL E. WINANS¹, YU LEI^{1,2}, RANDALL J. MEYER², ARANTXA FRAILE-RODRÍGUEZ³, LUIS M. MOLINA⁴, MARIA J. LÓPEZ⁴, JULIO M. ALONSO⁴, KRISTIAN SELL⁵, INGO BARKE⁵, ARMIN KLEIBERT⁵, VIOLA VON OEYNHAUSEN⁵, and KARL-HEINZ MEIWES-BROER⁵ — ¹Argonne National Laboratory, Argonne, USA — ²University of Illinois at Chicago, USA — ³Swiss Light Source, Paul Scherrer Institut, Villigen, Switzerland — ⁴Universidad de Valladolid, Valladolid, Spain — ⁵Institut für Physik, Universität Rostock, Rostock, Germany

This contribution focuses on partial oxidation reactions catalyzed by sub-nanometer to several ten nanometer large size-selected clusters. Catalytic performance and changes in cluster shape are studied under realistic reaction conditions, allowing to elucidate the size/shape/composition and function relationship in catalysis. Here we show 1) gold and silver clusters which promote with high selectivity the direct oxidation of propylene to propylene oxide, and 2) sub-nanometer platinum clusters catalyzing the oxidative dehydrogenation of propane with high selectivity and activity. Theoretical calculations and modeling provide a detailed insight of the catalytic process. The findings stress the important role of small clusters in promoting reactions with high selectivity and activity.

Invited Talk O 28.3 Tue 12:15 MA 005
Cluster Catalysis: Size dependent reactivity induced by reverse spill-over — •MATTHIAS ARENZ, MARTIN RÖTTGEN, CHRISTOPHER HARDING, SEBASTIAN KUNZ, VAHIDEH HABIBOUR, VIKTORIA TESLENKO, and ULRICH HEIZ — Technische Universität München, München, Germany

In heterogeneous, the routes whereby molecules come and go from active sites can substantially affect their reactivity. In the presented work, the CO oxidation rate on size selected Pd clusters supported on thin MgO films is investigated in pulsed molecular beam experiments. By varying the cluster coverage independent of the cluster size, we were able to change the ratio of direct and diffusion flux (reverse spill over) of CO onto the cluster catalyst and thus probe the influence of reverse spill-over on the reaction rate for different cluster sizes (Pd8 and Pd30). The experimental results show, that the change in reaction rate as a function of cluster coverage is different for Pd8 and Pd30. In order to explain these findings, the CO flux onto the clusters is modeled utilizing the collection zone model for the given experimental conditions. The results indicate that for small clusters (Pd8), the reaction probability of an impinging CO molecule is independent of whether it is supplied by diffusion or direct flux. By contrast, for larger clusters (Pd30) a reduced reaction probability is found for CO supplied by reverse spill over compared to CO supplied by direct flux.

O 28.4 Tue 12:45 MA 005
Deuteration of mass-selected C_n clusters deposited on HOPG — •ARTUR BÖTTCHER, DANIEL LÖFFLER, PATRICK WEIS, MANFRED KAPPES, ANGELA BIHLMEIER, and WILHELM KLOPPER — Institut für Physikalische Chemie, Universität Karlsruhe (TH), D-76128 Karlsruhe, Germany

We studied the size-selectivity in the deuteration of carbon clusters, C_n (n=48-70) deposited on HOPG. In contrast to the weakly stabilized molecular solids of classical fullerenes, the non-IPR fullerenes form strongly bound [C_n]_m oligomers stabilized by covalent bonds between the non-IPR sites in C_n cages. The deuteration procedure has been performed under ultra high vacuum conditions by exposing the deposited layers to atomic deuterium. The adoption of deuterium atoms raises the inter-cage cohesion of the C₆₀ and C₇₀ films what has been attributed to the formation of D-induced polymeric chains likely comprising covalently interlinked cages. Deuteration of non-IPR films results in considerable weakening of the inter-cage bonds as revealed by lower sublimation enthalpies found for all C_nD_x films [1]. DFT calculations indicate a considerable reduction of the inter-cage bonds accompanying the progressing D-adoption. This process ends with D-induced scission of oligomers and formation of weakly interacting C_nD_x cages. The contrary reaction trends are triggered by the presence of the non-IPR sites which act as decisive reaction centers. The size of the C_n cages appears of minor relevance for the reaction path.

[1] D. Löffler et al. J. Chem. Phys. Smalley Issue(2007)