

**Partial oxidation reactions on size-selected clusters:
Towards the understanding of the size/shape & function relationship in catalysis**

S. Vajda^{1,2}, L. A. Curtiss^{1,2,3}, S. Lee¹, B. Lee⁴, Y. Lei^{1,5}, J. W. Elam⁵, J. P. Greeley²,
C. L. Marshall¹, S. Mucherie¹, M. J. Pellin⁷, P. C. Redfern³, M. G. Sternberg², S. Seifert⁴,
R. E. Winans⁴, P. Zapol^{1,2,3}, I. Barke⁷, A. Kleibert⁷, K. Sell⁷, V. von Oeynhausen⁷,
K.-H. Meiwes-Broer⁷, A. Fraile-Rodriguez⁸, D. Teschner⁹, R. Schlögl⁹, R. J. Meyer⁶,
J. Alonso¹⁰, M. Lopez¹⁰, L. Molina¹⁰

¹*Chemical Sciences and Engineering*, ²*Center for Nanoscale Materials*, ³*Materials Science*,

⁴*X-ray Science*, and ⁵*Energy Systems Division*, Argonne National Laboratory, USA

⁶*Chemical Engineering Department*, The University of Illinois at Chicago, USA

⁷*Institut für Physik*, Universität Rostock, Germany

⁸*Swiss Light Source*, Paul-Scherrer Institut, Switzerland

⁹*Abteilung Anorganische Chemie*, Fritz-Haber-Institut der Max-Planck-Gesellschaft,
Berlin, Germany

¹⁰*Departamento de Física Teórica*, Universidad de Valladolid, Spain

vajda@anl.gov

This paper focuses on the catalytic properties of size-selected clusters supported on technologically relevant oxide films with the goal to understand the effect of size and composition in complex reactions of high industrial relevance. In particular, partial oxidation reactions of alkanes and alkenes on supported size-selected atomic clusters and up to 20 nm particles are investigated, to our knowledge for the first time, under realistic reaction conditions (at atmospheric pressure and elevated temperatures). The size and shape of the nanocatalysts at work is monitored *in situ* by synchrotron X-ray scattering. The simultaneous detection of reaction products allows to elucidate the correlation between the size&shape and catalytic properties. High-resolution SEM was employed to image the supported clusters before and after the catalytic test; XPS to detect the catalytically relevant states.

Synthesis. The applied synthesis techniques allow for the ultimate control of both: surface composition, as well as cluster size and composition – prerequisites for producing highly uniform active sites on technologically relevant supports for basic catalysis studies. The atomic and several nm size clusters were produced in a laser ablation cluster source and ACIS source, respectively and deposited on thin amorphous alumina films prepared by atomic layer deposition technique on flat as well as nanoporous supports.

Reactions studied. *Epoxidation of propene (C=C bond activation).* The direct oxidation of propene to propylene oxide was studied on size-selected Ag nanoparticles as well as atomic Ag and Au clusters. Pronounced size-dependent reactivity was observed on Ag clusters; the performance of the atomic Au clusters was strongly dependent on additives to the gas mixture. XPS studies found metallic silver; there was no indication of any subsurface chemistry and no surface silver oxide formation. Gold is found metallic (Au⁰) under reaction conditions as well. Theoretical modeling performed on atomic Au and Ag clusters reveals the details of the catalytic steps taking place at the interface of the clusters with the support.

Dehydrogenation of propane (C-H bond activation). It was found that Pt clusters stabilized on high surface area nanoporous supports were highly active in the oxidative dehydrogenation of propane. The subnanometer clusters were by up to two orders of magnitude more active than previously reported platinum and vanadia catalysts, while at the same time maintaining high selectivity towards the formation of propylene. The results of theoretical calculations show that the extraordinary activity and selectivity of the subnanometer clusters is determined by the under-coordination of the Pt atoms.