

Metal nanoclusters – what are they good for?

Hannu Häkkinen

Department of Physics, Nanoscience Center, University of Jyväskylä, Finland

The discovery of “magic” (i.e. extraordinary abundant and stable) sizes in the mass-abundance spectra of clusters of alkali metals in early 1980’s triggered a surge of activities in a new interdisciplinary field that has been customarily called “cluster science”. [1] In the early days of cluster science much of the research was mainly focused on (i) the dependence of various properties on the size of clusters (in fact, clusters bridge the materials gap between atoms or molecules and bulk matter, offering an ideal “laboratory” to study size-dependent physical and chemical properties) and on (ii) the obvious analogies of the interplay between stability and shell structure to that found in nuclei (clusters of nucleons!) or in atoms. With the emerging widespread interest in nanoscale systems, the impetus of cluster research is now motivated by the question how the remarkable size-dependent properties of metal clusters could be best utilized *while the clusters are interacting with the environment*, e.g., bound or implanted in a support, or stabilized and surface-passivated by molecules. This type of research has then relevance regarding atomic-scale design of components that could be of potential use in future nanotechnologies.

In this talk I discuss large-scale density functional simulations where electronic, optical and chemical properties of gold and palladium nanoclusters are investigated. [2-6] It is shown that binding to MgO support is significantly enhanced by surface color centers (oxygen vacancies) that also act as electron donors to the metal cluster in the case of gold, making the supported cluster a reaction center of catalyzed CO oxidation. Supported Pd clusters also act as reaction centers for this reaction, but involving a profoundly different mechanism where the fully oxidized supported Pd_xO_y cluster is the active catalyst. Time permitting I will also discuss phosphine- and thiol-passivated WAu₁₂, Au₃₉ and Au₅₅ clusters. It is shown that the properties of the gold core can be controlled by changing the ligand from π -acidic to σ -donating, i.e., by “chemical charging”. Exchange of phosphine ligands to CO molecules is energetically possible for some of the clusters, making them interesting candidates for nanocatalysts for CO oxidation.

References

- [1] W.A. deHeer, Rev. Mod. Phys. **65**, 611 (1993).
- [2] A. Sanchez, S. Abbet, U. Heiz, W.-D. Schneider, H. Häkkinen, R. N. Barnett, and U. Landman, J. Phys. Chem. A **103**, 9573 (1999).
- [3] M. Moseler, H. Häkkinen and U. Landman, Phys. Rev. Lett. **89**, 176103 (2002).
- [4] H. Häkkinen, S. Abbet, A. Sanchez, U. Heiz and U. Landman, Angew. Chem. Int. Ed. **42**, 1297 (2003).
- [5] H. Häkkinen, M. Moseler, O. Kostko, N. Morgner, M. A. Hoffman, and B. v. Issendorff, Phys. Rev. Lett. **93**, 093401 (2004).
- [6] B. Yoon, H. Häkkinen, U. Landman, A. Wörz, J.-M. Antonietti, S. Abbet, K. Judai, U. Heiz, Science **307** in press (2005).