

O 75: Particles and clusters

Time: Thursday 16:00–17:45

Location: MA 041

O 75.1 Thu 16:00 MA 041

Towards Catalysis by Gold Clusters: reaction cycles and poisons — ELIZABETH C. BERET, ●LUCA M. GHIRINGHELLI, and MATTHIAS SCHEFFLER — Fritz Haber Institute, D-14195, Berlin

Nanosized gold particles are good catalysts in a variety of oxidation reactions. These reactions, for which oxidation of CO to CO₂ serves as a paradigm, imply a transition in the total spin and therefore do not occur spontaneously in the gas phase. In the catalytic process, the catalyst clusters are exposed to an atmosphere of gas-phase O₂ and CO reactants at finite temperature and pressure. We have thus modeled free gold clusters in contact with an atmosphere composed of O₂ and CO by means of DFT calculations (PBE functional), and accounted for both temperature and pressure effects employing *ab initio* atomistic thermodynamics. On the basis of this analysis, we could recognize the thermodynamic driving force of the catalytic CO oxidation process and single out the possible (*p, T*)-dependent reaction cycles and those paths leading to stable structures that poison the catalytic process. This as a useful (exploratory) theoretical step, before taking chemical reaction kinetics into consideration. In the proposed reaction paths, the total spin is conserved in each elementary step, and it is the adsorption of an incoming O₂ molecule that drives the catalyst cluster from the singlet to the triplet spin state, and *vice versa*

O 75.2 Thu 16:15 MA 041

Endohedral doping of hydrogenated Si fullerenes: A route to magnetic Si building blocks? — ●DENNIS PALAGIN and KARSTEN REUTER — TU München

Metal encapsulation was found to produce fullerene and other polyhedral cage structures of silicon and therewith provides an intriguing novel nanoform of Si for device applications. In these structures the cage geometry is stabilized through a strong interaction with the endohedral dopant atom. The recent suggestion that also hydrogen termination of Si₁₆ could yield an empty fullerene configuration has raised hopes that metal-doping corresponding Si₁₆H₁₆ fullerenes would yield cage structures with minimized *M*-Si interaction [1]. With the atomic character of e.g. magnetic dopants then likely conserved, this would offer a route to develop Si fullerene species with large magnetic moments. We scrutinize this proposition through density-functional theory based global geometry optimization. While we can confirm that the fullerene is indeed the ground-state structure of Si₁₆H₁₆, this is unfortunately not the case for Ti or Cr dopant atoms. Strongly distorted or even broken cages are instead significantly more stable. We therefore screen a larger range of dopant atoms and critically discuss the resulting *M*-Si interaction in all of these cases.

[1] V. Kumar and Y. Kawazoe, Phys. Rev. Lett. 90, 055502 (2003).

O 75.3 Thu 16:30 MA 041

The size-dependent agglomeration of nanoparticles in solvents — GEDIMINAS GALINIS, GAUTHIER TORRICELLI, HANIEH YAZDANFAR, ATEA AKRAIAM, MARK WATKINS, and ●KLAUS VON HAEFTEN — Department of Physics and Astronomy, University of Leicester, Leicester, LE1 7RH, United Kingdom

Nanoparticles suspended in solvents usually tend to agglomerate by mutual physisorption. We have investigated this phenomenon by depositing silicon clusters with a broad size distribution (peak size 40 to 60 nm) into water. Drops of the cluster-water suspension were then placed on highly oriented pyrolytic graphite (HOPG) and dried in vacuum. AFM measurements in UHV revealed a height distribution peaking at 1 to 2 nanometers, which was much smaller than the original size distribution. We explain this observation as being due to size-dependent agglomeration in water caused by the balance of thermal energy and van der Waals attraction. The maximum height of 3 nm diameter was consistent with the prediction of the Hamaker theory [1]. While single clusters where identified most clusters were laterally agglomerated and for high densities a distinct second layer was identified. In addition, the clusters showed various forms of self-organisation such as rings or gratings depending on the wetting behaviour of the solvents.

[1] G. Torricelli, A. Akraiam, K. von Haeften, Nanotechnology 22, 315711 (2011).

O 75.4 Thu 16:45 MA 041

Traceable size determination of spherical nanoparticles via Small Angle X-ray Scattering (SAXS) — ●GUDRUN GLEBER¹, MICHAEL KRUMREY¹, ARMIN HOELL², LEVENT CIBIK¹, STEFANIE MARGGRAF¹, and PETER MÜLLER¹ — ¹Physikalisch-Technische Bundesanstalt, Abbestr. 2-12, 10587 Berlin — ²Helmholtz-Zentrum Berlin, Albert-Einstein-Str. 15, 12489 Berlin

Although various methods to measure the size of nanoparticles are available, the results of different methods often do not agree. In the framework of an European metrology project, several methods were used for traceable size determination and their results were compared.

As samples, spherical particles made of gold, PMMA, Silica, and Latex of nominal sizes between 10 nm and 200 nm in aqueous solution were used. The Small Angle X-ray Scattering (SAXS) experiments were performed at the Four-Crystal Monochromator (FCM) beamline in the laboratory of Physikalisch-Technische Bundesanstalt (PTB) at BESSY II using the SAXS setup of the Helmholtz-Zentrum Berlin (HZB). Besides the setup based uncertainties such as the uncertainties of photon energy, of detector pixel size, and of the distance between sample and detector, those based on the analysis process as e.g. assumption of particle shape, size distribution function, and background contribution were investigated.

O 75.5 Thu 17:00 MA 041

Ultraviolet photoelectron spectroscopy of mass selected metal clusters on graphite (HOPG) — ●NATALIE MIROSLAWSKI¹, DAVID ENGEMANN¹, NIKLAS GRÖNHAGEN¹, BERND VON ISSENDORFF², and HEINZ HÖVEL¹ — ¹Experimentelle Physik I, Technische Universität Dortmund, Germany — ²Fakultät für Physik, Universität Freiburg, Germany

Mass selected silver and copper clusters between 34 and 923 atoms were deposited with less than 0.1 eV/atom kinetic energy on graphite (HOPG) and investigated with ultraviolet photoelectron spectroscopy (UPS) with a photon energy of 21.2 eV. The clusters were deposited with different coverage for each cluster size and measured at 125 K. For a better interpretation we subtracted normalized HOPG spectra from the measured cluster spectra to extract the d-band structure of the clusters. To investigate the cluster mobility and coalescence we varied the deposition temperature and the cluster coverage. Additionally we annealed the sample after deposition at different temperatures and observed changes in the UPS spectra depending on the cluster coverage.

O 75.6 Thu 17:15 MA 041

Ag clusters on SiO₂ and in matrices: UV-VIS absorption and XANES — ●STEFANIE DUFFE¹, SABRINA HOFFMANN¹, KAMIL LATUSSEK¹, DAVID ENGEMANN¹, CHRISTIAN STERNEMANN¹, CHRISTOPH J. SAHLE¹, HEINZ HÖVEL¹, RALPH WAGNER², and PIETER GLATZEL³ — ¹TU Dortmund, Experiment. Physik I/DELTA, Dortmund, Germany — ²BU Wuppertal, Fachgruppe Physik-Materialwiss., Wuppertal, Germany — ³ESRF, Grenoble, France

We produce Ag clusters by supersonic nozzle expansion using THECLA, a THERmal CLuster Apparatus [1,2] which was designed to enable optical spectroscopy of clusters in a free jet and deposited on silica glass (SiO₂) [2] or in matrices. The optical properties and the UV-VIS absorption band of Ag clusters alter significantly with size, shape, interparticle spacing and the properties of the local environment. We investigate the plasmon resonance of Ag clusters on SiO₂, in PDMS (polydimethylsiloxane) or aerogel before and after exposure to air by optical spectroscopy [3]. XANES measurements at the Ag L_{1,2,3}-edges [4] were carried out at the synchrotron radiation sources DELTA and ESRF. Embedding the clusters into PDMS [5] or aerogel enables the investigation of a much higher amount of separated clusters which is otherwise limited by coalescence and electromagnetic coupling.

[1] O. F. Hagen, Z. Phys. D 20, 425 (1991). [2] H. Hövel et al., Phys. Rev. B 48, 18178 (1993). [3] U. Kreibitz et al. In: Advances in Metal and Semiconductor Clusters Vol. 4, (ed. M.A. Duncan), JAI press Inc., 345 (1998). [4] P. Behrens et al., Z. anorg. allg. Chem. 625, 111 (1999). [5] L. Ravagnan et al., J. Phys. D 42, 082005 (2009).

O 75.7 Thu 17:30 MA 041

How do metal clusters split water? Towards a theoretical understanding of co-catalysts for water

oxidation — •HARALD OBERHOFER and KARSTEN REUTER — TU Munich, Garching, Germany

Efficient, sustainable production of molecular hydrogen—a promising alternative to batteries in terms of energy storage—is still an unsolved problem. Implementation of direct water splitting using only sunlight and suitable photo-catalysts so far has been hampered by poor photon absorption properties of the materials and low reaction efficiencies. One ansatz of overcoming the latter obstacle is the use of small metal clusters as co-catalysts, a method that yielded promising results in experiments. Yet, the actual effect of co-catalysts on the reaction is

poorly understood. In our contribution we discuss our DFT-based efforts towards a microscopic understanding of small metal clusters as co-catalysts. We present our studies, based on a thermodynamic approach pioneered by Nørskov and Rossmeisl [J. Phys. Chem. B **108**, 17886 (2004)], of the water oxidation reaction on various metal clusters in the non-scalable size regime (less than 20 atoms) and compare with the extended surface. On top of these results we discuss the influence of solvent on the reaction as well as the stabilisation of electron holes necessary for the reaction. Conclusions of the presented work will in the future be used to postulate micro-kinetic reaction pathways and determine reaction rates comparable with experiment.