GISAXS Studies of Model Nanocatalysts Synthesized by Cluster Deposition

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Introduction

Small nanoparticles possess unique, strongly size-dependent chemical and physical properties that make these particles ideal candidates for a number of applications, including catalysts or sensors due to their significantly higher activity and selectivity than their more bulk-like analogs [1]. In the smallest size regime, nanocluster catalytic activity changes by orders of magnitude with the addition or removal of a single atom, thus allowing a tuning of the properties of these particles atom by atom [2]. Equally effective tuning knobs for these model catalysts are the composition and morphology of the support, which can dramatically change the electronic structure of these particles, leading to drastic changes in both activity and specificity. However, the Achilles heal of these particles remains their sintering at elevated temperatures or when exposed to mixtures of reactive gases [3]. In the presented paper, the issues of thermal stability, isomerization and growth of models of catalytic active sites - atomic gold and platinum clusters and nanoparticles produced by cluster deposition on technologically relevan oxide surfaces – is addressed by employing synchrotron X-ray radiation techniques [4].

Methods and Materials

Support Materials. As support, naturally oxidized silicon wafers (SiO_2/Si) and thin alumina films prepared by atomic layer deposition (ALD) technique (Al_2O_3 /SiO_2/Si) were used.

Cluster deposition. The continuous beam of metal clusters was generated in a new high-flux laser vaporization cluster source. Narrow cluster distributions in the size range Au_n^+ or Pt_n^+, n=2,..10, with two to five dominant sizes can be generated. After the desired cluster distribution is produced, the cluster cations were deflected into an ion lense setup placed in front of the substrate mounted on a translation stage.

Grazing incidence small angle X-ray scattering (GISAXS). The X-ray scattering experiments were performed at the BESSRC 12-ID beam-line of the Advance Photon Source of ANL. This setup allows acquisition of two-dimensional scattering patterns in real time. The analysis of the data gives information about the average size and shape of supported nanoparticles, (see Figure 1). In order to improve the signal to noise ratio, anomalous GISAXS was used for samples with very low surface coverages.

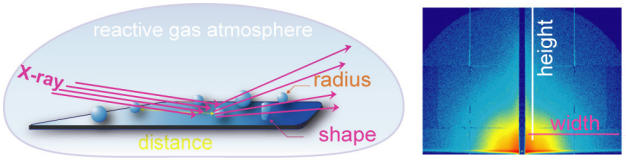

Fig. 1 Left: Schematic of GISAXS; right: 2-D GISAXS pattern.

Results

Au_n clusters in vacuum and in the presence of hydrogen. In the absence of hydrogen the increase in temperature did not induce any noticeable change in particle size in the temperature range up to 400 °C and a slow increase in the lateral dimension was observed after waiting two more hours at 400 °C. The height of the particles remained practically unchanged during the 8 hour heat treatment, thus indicating a two-dimensional nanoparticle growth. In the presence of hydrogen, a clear three-dimensional growth with an onset at around 350 °C is observed [5].

Structural transformation of Au_n clusters. Our results show no change in particle height in the low temperature region. At 140 °C, a sudden drop in height, indicative of a transition from tall particles to flat lateral structures. Further increase in temperature yields higher 3D structures. To our knowledge, our experimental results provide the first experimental evidence of "flipping" of such two-dimensional cluster structures from vertical into horizontal orientations [5] (which, in the case of MgO, have comparable stabilities[6]); further diffusion and aggregation of clusters results in an increase of particle height.

Pt_n clusters in vacuum and in the presence of hydrogen. Unprecedented thermal stability of Pt_{7-10} clusters supported on six cycle Al_2O_3 film on SiO_2/Si was observed [7]. The clusters did not undergo aggregation during the lengthy heat treatment reaching 400 ^oC in vacuum and when exposed to hydrogen. Our X-ray studies of the alumina support show that the stabilizing effect of the alumina films is caused by the film structure.

Results on growing nm-size particles of various shapes and an example of a catalytic reaction will be presented as well.

Discussion

The results demonstrate the powerful combination of controlled size-selected cluster deposition, synchrotron and atomic layer deposition techniques, which can aid in the design of new stable models of catalysts for detailed structure-function studies.

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References

[1] M. Haruta, Catalysis Today **36,** 153 (1997).
[2] H Hakkinen, S. Abbet, A. Sanchez, U. Heiz and U. Landman, Angew. Chemie **42,** 1297 (2003).
[3] B. K. Min, A. K. Santra, D. W. Goodman, Catalysis Today **85,** 113 (2003).
[4] B. Lee, S. Seifert, S. J. Riley, G.Y. Tikhonov, N. Tomczyk, S. Vajda, and R. E. Winans, J. Chem. Phys. **123**, 074701 (2005).
[5] S. Vajda, R.E. Winans, J.W. Elam, B. Lee, M.J. Pellin, S. Seifert, G.Y. Tikhonov and N.A. Tomczyk, Topics in Catalysis*, in Press* (2006)
[6] L. Molina, B. Hammer, J. Chem. Phys. **123**, 161104 (2005).
[7] R.E. Winans, S. Vajda, G.E. Ballentine, J.W. Elam, B. Lee, M.J. Pellin, S. Seifert, G.Y. Tikhonov and N. A. Tomczyk, Topics in Catalysis*, in Press* (2006)