Study of Morphology Changes in Reacting Nano Catalysts using Grazing Incidence Small-Angle X-ray Scattering

Randall E. Winans[1*], Byeongdu Lee[1], Soenke Seifert[1], Sungsik Lee[2], Jeffrey W. Elam[3], Michael J. Pellin[4], Ingo Barke[5], Armin Kleiber[5], K. Sell[5], Viola von Oeynhause[5], Karl-Heinz Meiwes-Broer[5], and Stefan Vajda [6,7]

[1]X-ray Science Division [2]Chemical Sciences and Engineering Division [3]Energy Systems Division [4]Material Science Division, [6]Chemical Sciences and Engineering Division & Center for Nanoscale Materials, Argonne National Laboratory, Argonne, IL; [5]Institut für Physik, Universität Rostock, 18051 Rostock, Germany [7]Department of Chemical Engineering, School of Engineering & Applied Science, Yale University, New Haven, CT

*rewinans@anl.gov

Introduction

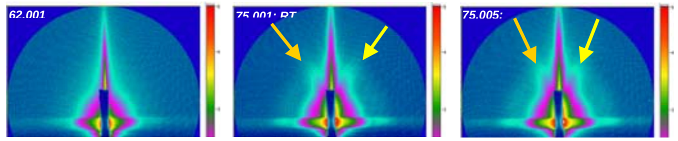
In the study of catalytic reactions, grazing incidence SAXS (GISAXS) experiments on flat catalytic support substrates with size-selected metal clusters can provide both *ex-situ* and *in-situ* information on cluster size, shape, and inter-particle distance (Advanced Photon Source (APS) beamline 12-ID). GISAXS can also give depth profile information, and the aspect ratio (height/diameter) of a cluster can be calculated from the GISAXS data to obtain the interfacial energy. GISAXS is ideal for *in-situ* studies since it is very sensitive to surface species and there is less parasitic scattering resulting from the substrate compared to a conventional direct-transmission SAXS experiment. GISAXS has been used to study the thermal stability and reactivity of Pt, Au, and Ag clusters (6 – 12 atoms) deposited on a variety of surfaces with insightful results.[1] One example is the partial oxidation of olefins to alkyl oxides where it has been found that the size and shape of catalytic size-selected nanoparticles is important. ASAXS refers to the extension of standard SAXS experiments in which the energy of the probing X-rays is tuned near the absorption edge of an element in the sample. This method overcomes the problem of separating the scattering of clusters from that of the support. For the first time anomalous GISAXS has been obtained on metal clusters on surfaces and has provided significant insight into the structure of very small metal clusters on surfaces.[2]

Materials and Methods

The size selected metal particles were prepared by laser vaporization followed by separation in a quadrupole mass spectrometer prior to deposition on the surface. The GISAXS experiments were performed in a vacuum chamber equipped with a heated sample holder mounted on a goniometer at APS beamline 12-ID-C. During heat treatment, scattering data can be collected as a function of time and temperature. The beam was scattered off the surface of the sample at and near the critical angle (α_c=0.15) of the silicon substrate. The scattered X-rays are detected by a nine-element mosaic CCD detector. The data is analyzed by taking cuts in the q_{xy} direction for horizontal information and in the q_z direction for vertical information.[3]

Results and Discussion.

The partial oxidation of propylene to propylene oxide has been studied using silver nanoclusters on an atomic layer deposition (ALD) prepared alumina surface. The original particles are oblate and upon exposure to propylene the particles begin to flatten. The arrows point out the change in scattering which reflects the change in the wetting angle at the nanoparticle support interface. The effect is due to the propylene since these particles have been exposed to air. Upon heating the surface, the wetting angle changes along with the aspect ratio of the particles. At 200 °C the particles become spherical and do not change over 4 hrs of the reaction. After cooling back to 23 °C the shape and of the particles does not change remaining spherical.



a **b** **c**

Figure 3. GISAXS data on changes in shape of silver nanoparticles on alumina exposed to 1 atm of 1% propylene and 0.5% oxygen in helium: (a) 23 °C at time zero, (b) 23 °C at 30 min and (c) 23°C at 60 min.

Significance

GISAXS has been demonstrated as a powerful tool for studying the changes of catalytic metal nanoparticles on flat surfaces under realistic reaction conditions.

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References

(1)Winans, R. E.; Vajda, S.; Ballentine, G. E.; Elam, J. W.; Lee, B.; Pellin, M. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A. *Topics in Catalysis* **2006**, *39*, 145-149.

(2)Lee, B.; Seifert, S.; Riley, S. J.; Tikhonov, G.; Tomczyk, N. A.; Vajda, S.; Winans, R. E. *Journal of Chemical Physics* **2005**, *123*, 074701/1-074701/7.

(3)Winans, R. E.; Vajda, S.; Lee, B.; Riley, S. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A. *Journal of Physical Chemistry B* **2004**, *108*, 18105-18107.