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LETTERS

Thermal Stability of Supported Platinum Clusters Studied by in Situ GISAXS

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Sintering of supported nanocatalysts often leads to the loss of the catalytic activity and selectivity. This paper reports on synchrotron X-ray studies of the thermal stability of supported platinum nanoparticles produced by cluster deposition on the naturally oxidized surface of a silicon wafer (SiO_2/Si(111)). The temperature region of aggregation was determined by gradually heating the samples up to above 400 °C, and recording two-dimensional in situ X-ray scattering images during the heat treatment. The data analysis reveals an unexpectedly high stability of the supported particles, which preserve their original size up to about 320 °C, at which an abrupt onset of the agglomeration takes place.

Introduction

Sintering of supported catalytically active nanoparticles during chemical reactions at elevated temperatures often leads to the loss of the catalytic activity and selectivity of these particles.[1−3] This paper is devoted to the study of the thermal stability of deposited platinum nanoparticles by employing grazing incidence small-angle X-ray scattering technique (GISAXS).

GISAXS can provide the same type of information as regular SAXS, but in addition, it can give depth profile information. It is ideal for in situ studies because it is very sensitive to surface species and there is less parasitic scattering resulting from the substrate compared to a direct transmission scattering experiment. GISAXS was first demonstrated using a lab X-ray source for studying gold films.[4] More recently the technique has become popular for studying quantum dots and clusters on and imbedded into surfaces. For instance, CdS quantum dots prepared from ion implantation of S and Cd in SiO_2 followed by annealing were characterized by GISAXS.[5] Variation of the size of the quantum dots (on the order of 4−5 nm) was determined as a function of depth. In a study of gold aggregates and carbon−platinum clusters, Naudon et al.[6] make an important point that this method samples a large area, yielding good statistics which is difficult to do with microscopy. They noted that clusters as small as 40 atoms were observed for the C−Pt clusters, and the anisotropy of the aggregates can be clearly resolved as well. Recent work of Renaud et al.[7] demonstrated the high sensitivity of the GISAXS technique to monitor in real time the growth of Pd clusters on MgO(100) and of Co on Au(111) during metal vapor deposition and this work has been extended to a quantitative study of the growth of Pd particles on MgO.[8] Also, GISAXS was used to characterize Au clusters deposited on a Si wafer, which was covered by a C sublayer to make a comparison with TEM.[9] With the clusters sitting on the surface and not embedded, it is possible to process the horizontal and vertical slices of the data using the reflected main beam as the reference and use the classical SAXS approaches for analyzing the data.[9] This is done for data taken at the critical angle of the substrate, in this case, silicon, $\alpha_c = 0.15°$.

Experimental Methods

Cluster Production and Deposition. The experimental setup and the design of the cluster source has been described in details

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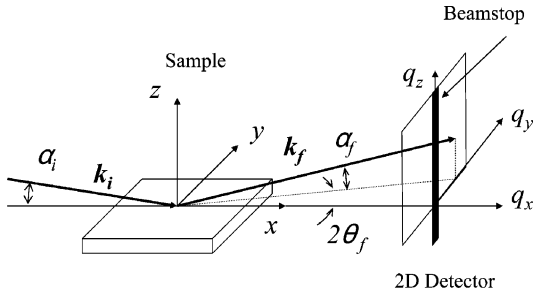

Figure 1. Schematic GISAXS experiment. Incident X-ray beam (k_i) angle and scattered beam (k_f) are α_i and α_f respectively. Scattering vectors q are calculated from $(4\pi/\lambda)$ sin θ_f, where θ_f is the scattering half angle and λ is the wavelength of the X-rays.

elsewhere[10,11] and only details concerning the cluster deposition are given here. An oxidized surface of a silicon wafer (SiO_2/Si(111)) was used as the substrate for cluster deposition. The beam of platinum clusters was produced in a cluster source with 1 cm channel length by vaporizing the metal from a platinum rod with a frequency doubled YAG laser operating at a repetition rate of 50 Hz, and helium was used as a carrier gas. A substrate holder, capable of holding up to six substrates was mounted on a translation stage and positioned at a distance of 5 cm from the nozzle of the source. Using a mask placed in front of the substrate, a 5.2 mm diameter area of the substrate was exposed to the cluster beam. In this arrangement, the full distribution of clusters produced in the source was used for deposition.

GISAXS. The GISAXS experiments were performed in a vacuum chamber equipped with a sample holder mounted on a goniometer. The sample holder is made of a brass rod with a milled flat surface on its end and with built-in (remote controlled) heaters, allowing heating of the sample up to 500 °C. The samples were heated stepwise in 20 °C increments with a 10 min wait time between steps. During heat treatment, scattering data can be collected as a function of time and temperature. X-rays produced in an undulator (12.0 keV) pass through a double-crystal monochromator ($\Delta E/E \sim 10^{-4}$) and a focusing mirror. The beam was scattered off the surface of the sample at and near the critical angle of the silicon substrate. The scattered X-rays are detected by a nine-element mosaic CCD detector (150 × 150 mm) with a maximum resolution of 3000 × 3000 pixels.[12] The data are analyzed by taking cuts in the q_{xy} direction for horizontal information and in the q_z direction for vertical information (see Figure 1). From these data the radius of gyration (R_g) was calculated using a Guinier analysis. Silver behenate is used to calibrate both horizontal and vertical q values.

Results and Discussion

The degree of the coverage of the substrate surface with clusters was controlled by the number of shots of the 50 Hz vaporization laser applied on the metal target rod. In the case of applying 50 laser shots, the surface coverage was 6.8×10^{14} (±10%) Pt atoms per cm^2, which corresponds to 34% of one atomic monolayer. Such high surface coverage can lead to the agglomeration of the clusters landing on the support during the deposition process. Also, the exposure of the sample to air during transport to the beam-line may cause additional agglomeration as well. However, it has been shown that Pt clusters deposited onto a γ-Al_2O_3(111)/NiAl(110) substrate under high vacuum were not changed when transferred in air for TEM analysis.[13,14] Pt clusters prepared from dendrimers and deposited onto silica were found to show only limited sintering at 425 °C under oxidation.[15]

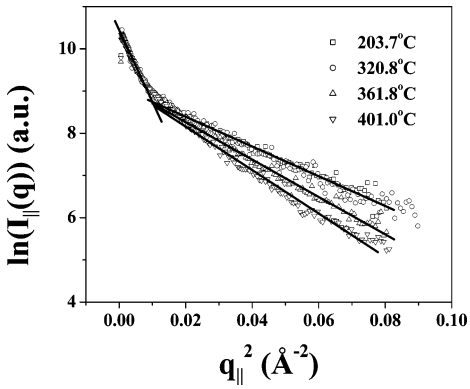

Figure 2. Data are shown for horizontal slices at selected temperatures and fits are derived from Guinier analysis. The low q section, which does not change with temperature, is likely to result from scattering of the substrate.

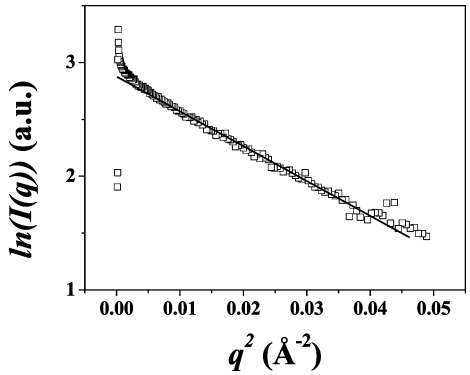

Figure 3. Data for Guiner analysis of vertical slices for all temperatures. Only one region is found that results from the height of the clusters on the surface.

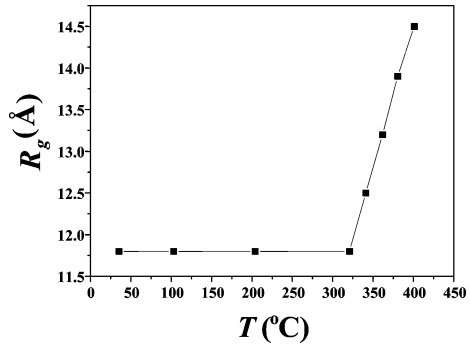

Figure 4. Change in radius of gyration calculated from horizontal slices.

Guinier analysis of the vertical slice of the data at room temperature gives an $R_g = 11.1$ Å, whereas the horizontal slice yields $R_g = 11.6$ Å. Within the deviation of the measurements the clusters are roughly spherical with a diameter of $d = 29.7$ Å ($d = 2 \times 1.29 \times R_g$). This size corresponds to a cluster of approximately 900 Pt atoms, and 7.5×10^{11} clusters/cm^2. As the sample was heated, the cluster size in the horizontal (Figure 2) and vertical direction (Figure 3) did not change until the temperature reached 320 °C. At this temperature the clusters began to grow gradually along the surface of the substrate in a fairly linear fashion as is shown in Figure 4. There was no growth observed in the vertical direction. Thus, the agglomeration leads to the formation of oblate spheroids with the minor axis being equal to the original spheroids. Gan et al.[16] performed STM studies of the nucleation and growth of Pt clusters on TiO_2(110), and observed highly asymmetric size distributions

suggesting clusters grew by Ostwald ripening rather than by coalescence. However, the apparent height of the clusters seemed to be dependent on the bias used for STM. The Pt clusters in vacuo on the SiO_2/Si(111) support appear to be very thermally stable. For comparison, when 4.5 nm gold particles dispersed in silica (SBA-15) were heated to 160 °C in CO atmosphere, the clusters agglomerated into 10−50 nm particles and moved outside of the channels where they originally resided.[17] Exposure of gold clusters with an average diameter of ∼2.6 nm supported on TiO_2(110) surface to a mixture of CO/O_2 at room temperature leads to a formation of both smaller and larger clusters, and the average height of the particles changes as well.[18] The stability of the Pt particles may be due in part to the fact that they are dilute on the surface at the given surface coverage. In addition, strong cluster−surface interactions between the platinum clusters and the silicon-oxide surface may contribute to their stability as well.[1]

Conclusions

Platinum clusters were generated in a laser vaporization source and deposited on the naturally oxidized surface of a silicon wafer (SiO_2/Si(111)). To determine the temperature region of nanoparticle stability, the samples were gradually heated in vacuo from room temperature up to above 400 °C, and X-ray scattering images were collected during the heat treatment. The analysis of the GISAXS data shows that the supported particles preserve their original size in a very broad temperature range, before an abrupt onset of the agglomeration takes place. These experiments demonstrate the powerful combination of cluster deposition technique with synchrotron X-ray techniques, which can aid in characterization and design of novel nanoparticle-support combinations with potential use in catalysis. Work on the kinetics of cluster aggregation and the effect of initial cluster size and the material of the support on the size of the nanoparticles formed on the support is currently under investigation.[19]

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