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Behavior of Pt Atoms on Oxide Supports During Reduction Treatments at Elevated Temperatures, Characterized by Aberration Corrected Stem Imaging

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Abstract Aberration-corrected scanning transmission electron microscopy at the sub-Ångström resolution allows imaging the structure of catalytic materials at the single atom level and permits fundamental studies of the behavior of heavy metal catalytic species as a result of elevated temperature gas-treatments. The present study is aimed at understanding the development of clusters and nanoparticles of Pt on γ-alumina during reduction treatments of a pre-oxidized highly dispersed catalyst. A special built ex situ reactor and a specimen holder allowing cyclic anaerobic transfer between the reactor and microscope were used for the study. The number of atoms in a nascent cluster can be determined along with the general shape of the cluster. Reduction experiments without air exposure of the sample showed that although clusters are formed at 500 °C, many Pt atoms are not associated with the cluster and are still dispersed on the catalyst support. After a 700 °C reduction, all of the Pt atoms are associated with the clusters. Movement of the clusters on the catalyst support is different depending upon the catalyst support.

Keywords Aberration-corrected electron microscopy · High-angle annular dark-field microscopy · Scanning transmission electron microscopy · Metal support interaction

1 Introduction

Supported metals on an oxide or graphitic support are important commercial catalysts and are used for refining of petroleum, conversion of automobile exhaust, fuel cells and many other processes. Since catalytic activity and selectivity can be impacted by the size of the clusters, many workers have investigated these materials using a variety of techniques. Electron microscopy has the advantage of being able to observe supported metals at specific locations as opposed to an averaging or bulk analysis.

Imaging of metal clusters on a catalyst support is most often conducted using high-angle annular dark-field (HAADF) imaging in the scanning transmission electron microscope (STEM). The primary advantage of the HAADF-STEM technique is that imaging is by Rutherford scattering where the image intensity for a given atom is roughly proportional to the square of the atomic number. Thus heavy metal nanoclusters produce high contrast compared to the low background of an oxide support and a small Pt or Pd cluster appears as a bright spot on the lower contrast oxide support. This was first demonstrated by Treacy et al. [1], who imaged 2 nm Pt crystallites on a high surface area γ-Al_2O_3. As the instrumentation improved smaller metal clusters were observed [2–4] Rice et al. [5]

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reported imaging of a single Pt atom in a zeolite cage while Nellist and Pennycook [6] observed individual Pt atoms dispersed on γ-Al_2O_3.

With the advent of aberration-corrected scanning transmission electron microscopy, it is now possible to form imaging probes of less than 0.1 nm diameter and with this higher resolution to be able to image individual atoms in a cluster. Using this type of microscope Blom et al. [7] reported imaging individual Pt atoms in a 1 nm cluster decorating both γ-Al_2O_3 and SiO_2 catalyst supports. Other systems have been examined and new insights into the surface chemistry of these clusters have been reported [8–11]. In this paper we characterize cluster development during reduction of Pt on γ-alumina, and also examine the behavior of Pt species on silica and titania supports in order to gain some initial insight into the effects of the support composition on cluster development.

2 Experimental

2.1 Instruments

Two different aberration-corrected electron microscopes were used for this study, a JEOL 2200FS and a FEI Titan 80-300. Both were operated at 200 kV accelerating voltage and both were equipped with a hexapole aberration corrector for the incident illumination (CEOS GmbH, Heidelberg, Ger.). The JEOL 2200FS was operated with a nominal STEM resolution of 0.07 nm at an illumination acceptance semi-angle of 26.5 mrad. The Titan 80-300 was operated at a probe convergence semi-angle of 24.5 mrad. For imaging experiments, the probe current was about 25 pA and the STEM resolution is approximately 0.08 nm. The inner and outer HAADF collection angles for imaging were 110–470 mrad for the JEOL instrument and 54–270 mrad for the FEI instrument. For EELS experiments, a Gatan GIF Tridiem 86ER was used in the Titan and the probe current was increased to about 100 pA at a STEM resolution of 0.12 nm. The energy resolution for the gun conditions used was 0.73 eV. The EELS collection semi-angle was 32 mrad, selected to be just larger than the probe convergence semi-angle. The ADF signal acquired simultaneously with the EELS spectrum images had collection angles of 32–70 mrad. The FEI Titan electron microscope was only used to examine the spent catalyst.

2.2 Ex-situ Reactor

For the JEOL 2200FS a specially designed single-tilt sample holder with retractable sealing mechanism that allowed for sample exchange without air exposure was used for the ex-situ reduction in H_2 studies. This specimen rod had been previously demonstrated to eliminate air exposure during sample transfer between the ex-situ reactor and microscope [12]. The reactor was flushed several times with ultrapure H_2 and N_2 before increasing the temperature in N_2 to the desired reduction temperature. Since a holey C TEM grid was used to support the sample, any trace O_2 at elevated temperature would be obvious because the C that was acting as a platform for the sample would be removed by oxidation.

2.3 Catalyst Samples

All samples were prepared by impregnation techniques known to produce well-dispersed metal species as well as uniform metals distribution on an oxide support [13]. Reductions were conducted in 4% H_2/Ar at the temperatures specified.

3 Results and Discussion

3.1 Pt on Alumina

A 0.35 weight percent Pt on γ-Al_2O_3 that had been oxidized at 500 °C showed individual Pt atoms dispersed on the alumina catalyst support as shown in Fig. 1. A few Pt dimers and an occasional Pt trimer were observed. Of the many locations examined only a couple of Pt clusters of 10–15 atoms were observed. Such clusters were particularly rare. The Pt atoms appeared to be rather uniformly distributed on the oxide and there did not appear to be any regions of higher concentration of these atoms. The image in Fig. 1b has been processed using a high pass filter in order to make the Pt atoms more easily observable.

No attempt was made to correlate Pt atom position with respect to the alumina lattice since there was some movement of the Pt atoms by the electron beam. There did not, however, appear to be any unusual defect sites in the alumina associated with the Pt atoms. It should be noted that in this microscope mode, O atoms would not be visible either for alumina or for any oxygen that might be associated with the Pt.

When the oxidized catalyst was reduced at 500 °C for 2 h and air exposed during transfer into the microscope, 0.6–1 nm Pt clusters were observed decorating the catalyst support as has been reported by others [3] using a traditional dedicated STEM. Examination at higher magnification revealed the individual Pt atoms in the clusters (Fig. 2). In addition to these clusters there were still isolated Pt atoms and dimers on the catalyst support that were distant from the clusters and did not appear to be associated with any cluster. These isolated Pt atoms tended to move less under the electron beam than those in the cluster,

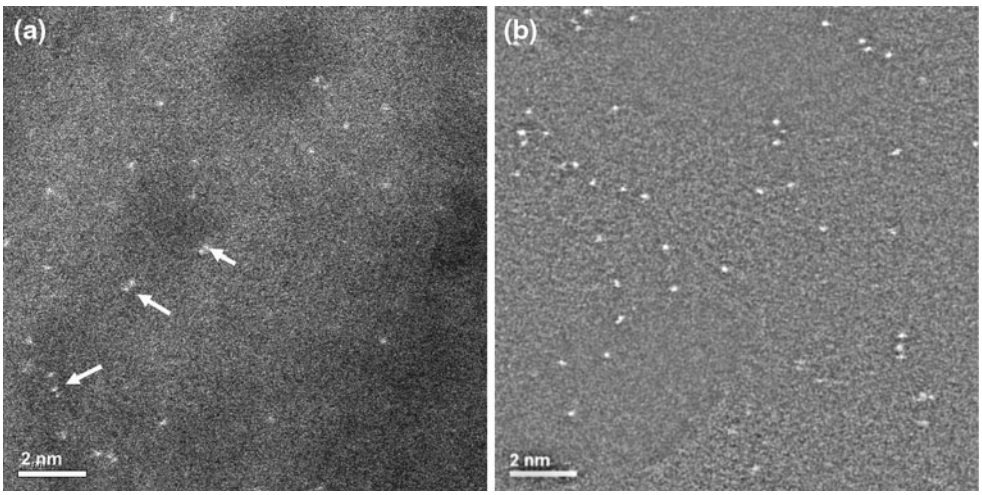

Fig. 1 Oxidized 0.35 wt% Pt on γ-Al_2O_3 showing individual Pt atoms decorating the oxide support. The Pt atoms are the white spots. *Arrows* point to a few of the dimer and trimer Pt atoms. **a** Non-processed image. **b** Different image of the same sample after processed using a high pass filter in order to make the Pt atoms more visible

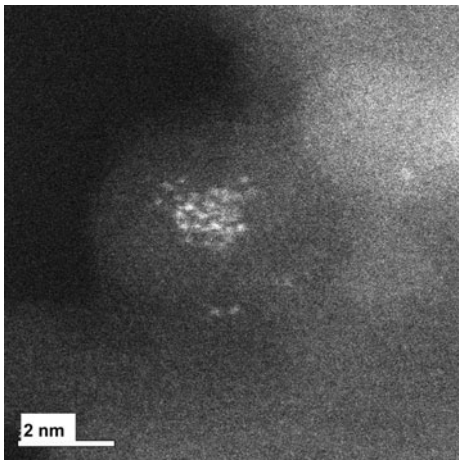

Fig. 2 Pt atoms that form 0.6 to 1 nm cluster. A couple of Pt atoms are isolated and not part of the cluster

suggesting that they have greater bonding to the oxide support (Fig. 3). The clusters had a "raft-like" appearance with the relative brightness of the individual species in the cluster varying by a factor of about 2 (i.e. some of the "spots" in the cluster were twice as bright as others). Those spots that were twice the brightness would be consistent with a 2-atom stack along the beam direction. Unfortunately because the Pt atoms move and rearrange under the electron beam, it is not possible to reliably determine any information with respect to bonding to the alumina or definitive shape of a cluster.

Although the shape changed under the electron beam, the number of atoms in the cluster appeared to remain the same, varying from about 15 to 25. Many models have been proposed for clusters of this size based on crystallites having the symmetries of bulk metals. Poltorak and Boronin [14] modeled such clusters and reported for a crystal edge of 0.895 nm that there would be 19 atoms in the cluster. The fraction of surface atoms would be 0.95. Their model is in very excellent agreement with our observations. EXAFS studies [15] have also suggested that the clusters have a raft-like morphology.

Vila et al. [16] have theorized based on DFT/MD simulations that 10-atom Pt clusters are tethered to the catalyst support by transient fluctuating surface bonds. The Pt atom movements observed here seem to mimic those simulations. However, much of the movement of the cluster may be a result of the interaction of the electron beam with the atoms. In principle beam-activated trajectories could be used to study available states for the atoms on the surface at elevated energy without raising the temperature of the entire sample.

Samples were also reduced in the ex-situ reactor and transferred under inert atmosphere conditions into the microscope. As shown in Fig. 4 for various reduction temperatures, at 300 °C Pt clusters are just starting to form. At 350 °C reduction the clusters are quite small and consist of only about 6–12 atoms with many individual Pt atoms still present. At 700 °C reduction all of the Pt atoms are found in the metal clusters. These clusters have about 15–25 atoms.

3.2 Pt on Silica and Titania

Since 0.35 wt% Pt on SiO_2 readily agglomerates during reduction in H_2, the oxidized catalyst was examined. In contrast to the oxidized Pt on alumina, Pt clusters were very apparent on the SiO_2 and were present everywhere. These clusters ranged in size from about 0.6 to 2 nm. The number of atoms in the cluster was also quite varied but the cluster still seemed to have a raft-like morphology.

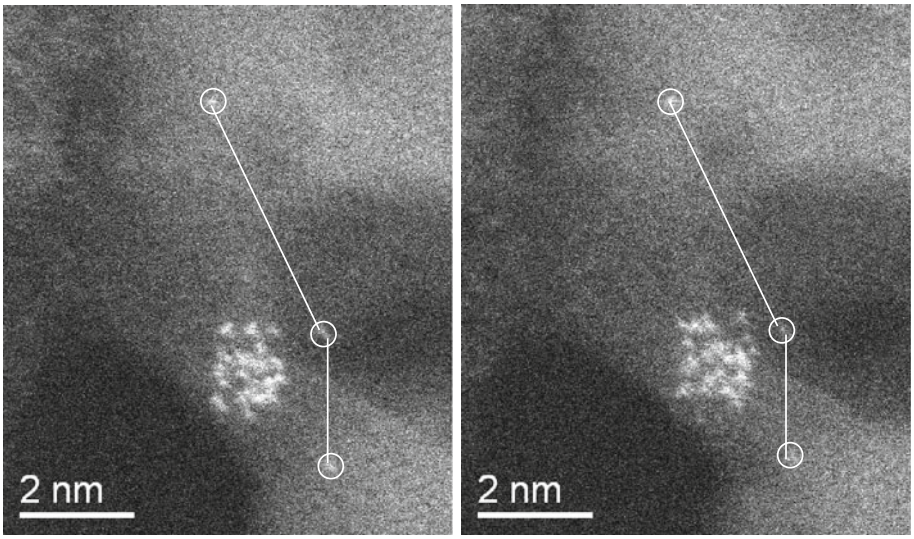

Fig. 3 Pt atoms in cluster rearrange during exposure to the electron beam. Pt atoms not associated with the cluster tend to move less

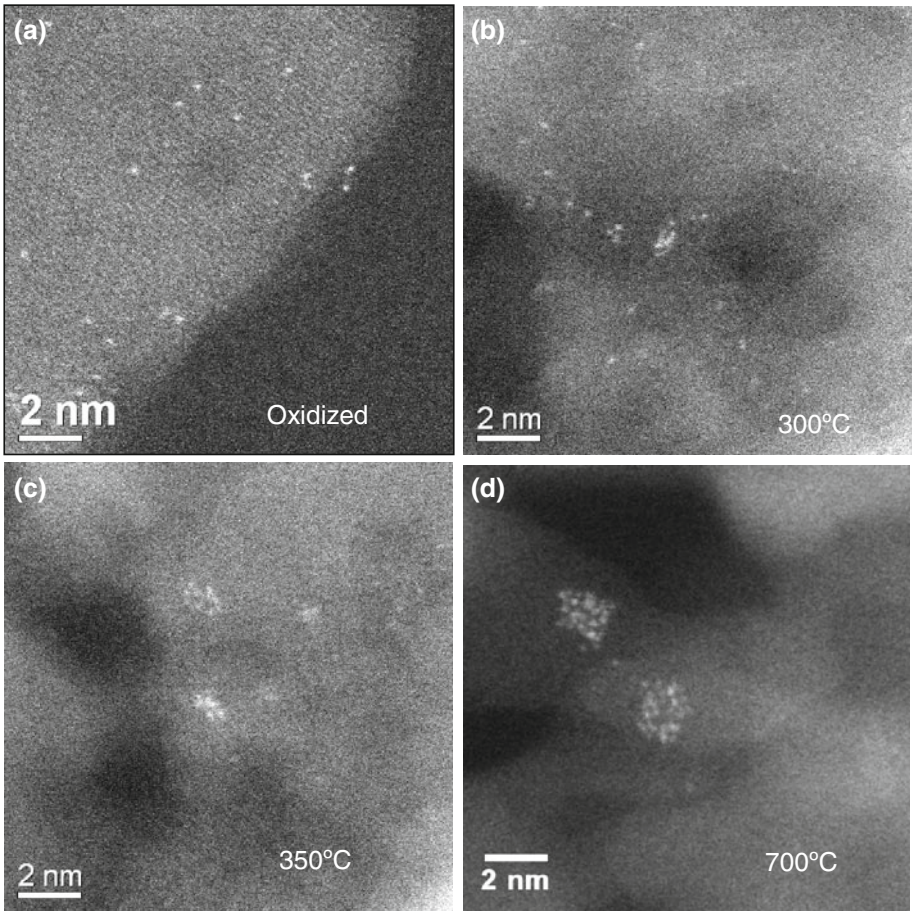

Fig. 4 Ex-situ reduction of oxidized Pt on alumina. Increasing reduction temperatures resulted in greater number of Pt atoms in the cluster

Under the electron beam, the Pt atoms were extremely mobile for the Pt on SiO_2. While the Pt atoms in the clusters on the alumina rearranged, the clusters themselves remained fairly coherent. That was not the case for either the Pt atoms or the clusters in the case of the silica support. As depicted in Fig. 5, the clusters tended to move more as a group to form a larger cluster. It sometimes appeared as if the clusters move towards each other in a non-random fashion. On the other hand, the small cluster in the lower part of each image of Fig. 5 did not appear to be moving and seems to be anchored to the catalyst support.

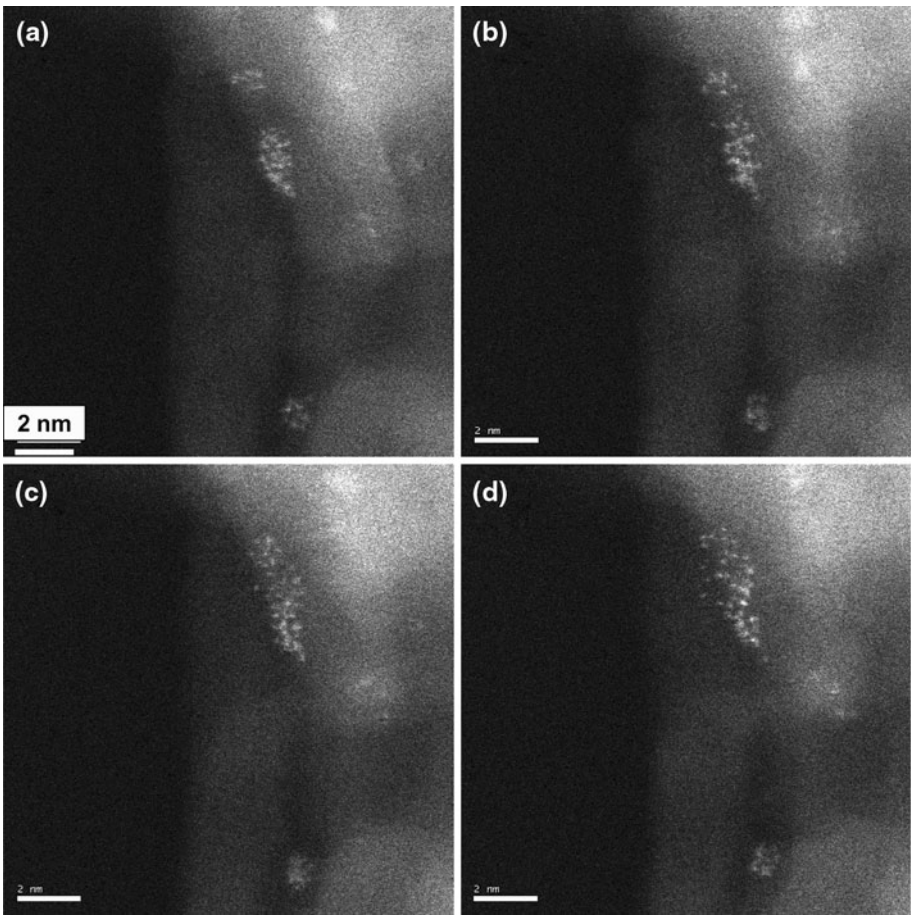

Fig. 5 A series of images of the same sample region, **a**–**c**, then **d** showing movement of Pt on SiO_2 as a function of electron beam exposure. The two clusters near the top of each image merge together while the cluster in the bottom has hardly moved

A 1 wt% Pt on TiO_2 (anatase) had 1 nm clusters decorating the catalyst support. The individual Pt atoms in the cluster tended not to rearrange, as shown in Fig. 6 and seemed constrained by the underlying structure of the TiO_2. In addition to the clusters some individual Pt atoms are present. With this study the presence of a Ti–O overlayer could not be verified as has been observed by others [17].

Mobility of reduced Pt atoms in the clusters was greatest for the SiO_2 catalyst, less so for the Al_2O_3 catalyst and virtually non-existent for the TiO_2 catalyst. This observation is consistent with metal support interaction calculations and studies [18] where TiO_2 catalyst support had the strongest metal support interaction while SiO_2 catalyst support had the weakest.

3.3 Spent Pt Catalysts

Deactivation of Pt catalysts is often attributed to coke formation. The 0.35 wt% Pt on alumina catalyst after reduction in H_2 at 550 °C for 1 h and then reacted with *n*-heptane for $2^1/_2$ h at 500 °C resulted in 0.7% C on the catalyst sample as measured by combustion carbon. Cluster size did not appear to change as the clusters remained in the 0.6–1 nm in size. At higher magnification the individual Pt atoms in the cluster could be imaged as well as Pt atoms that were not associated with any clusters (Fig. 7). During the sample preparation using isopropanol some of the clusters came off of the alumina catalyst support and were found on the thin silicon film of the TEM grid (Fig. 8). These Pt clusters were attached to a graphite sheet that was about 3–5 nm in length and width. When a dry sample procedure was used, all of the clusters and Pt atoms remained on the alumina catalyst support. An EELS map depicting the graphite sheets was not feasible because of the beam damage to the alumina catalyst support while collecting the data although new high-speed spectrometers [19] may make this experiment possible.

The presence of sheets of graphite patches surrounding the Pt particles and extending onto the alumina catalyst support has been reported by Gallezot et al. [20]. They noted that the carbon sheets extended no more than 20 nm from the Pt particle. Their results for Pt crystallites of 3–6 nm in size are very consistent with those reported here for much smaller clusters.

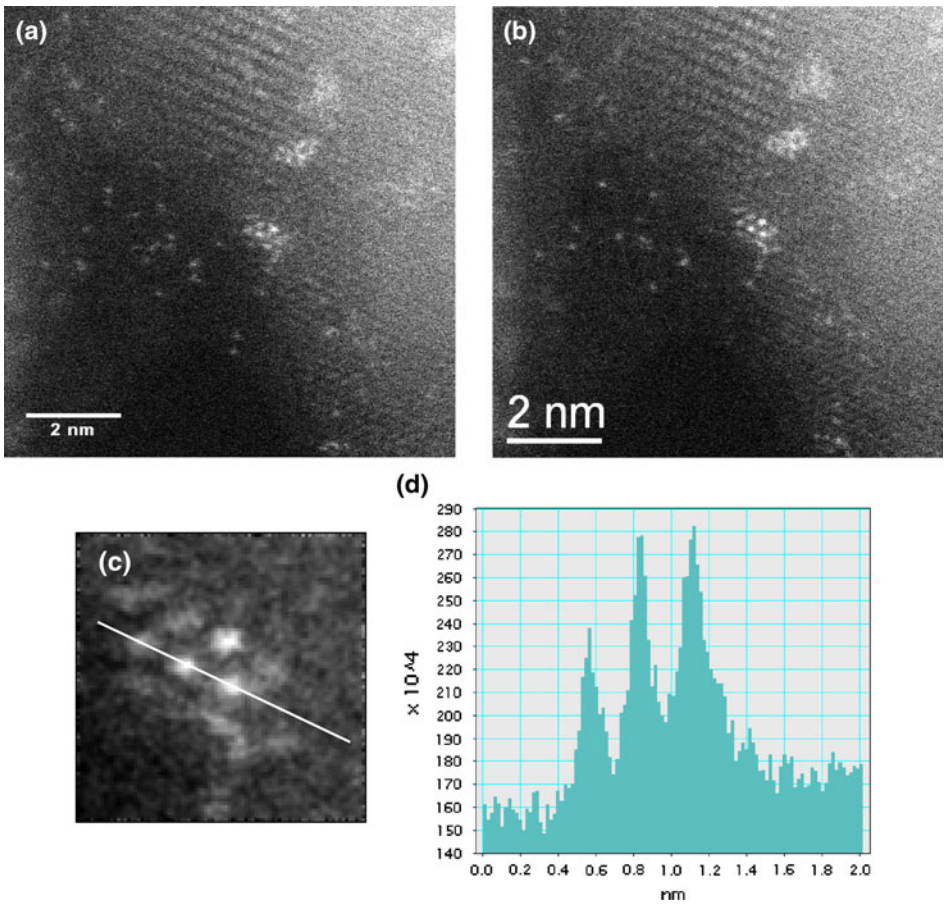

Fig. 6 Successive images **a, b** showing virtually no movement of atoms for Pt on TiO_2. A couple of Pt atoms are on *top* of each other as shown by the intensity of the *spots*. **c** shows one such cluster and **d** shows a profile along a *line* of atoms which is 1 atom, 2 atoms and 2 atoms tall

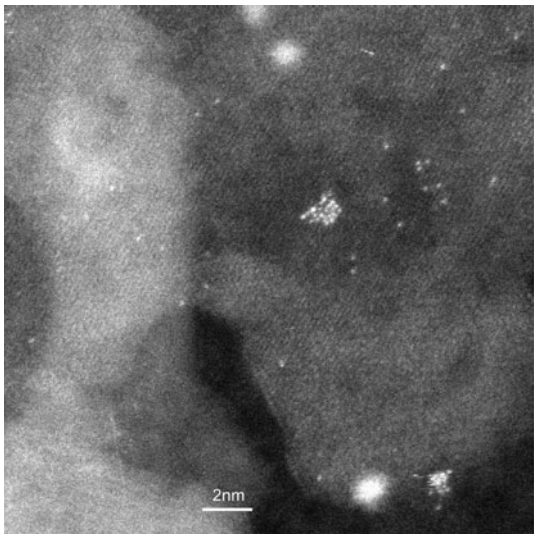

Fig. 7 Pt atoms in cluster after exposure to *n*-heptane at 500°C for $2^1/_2$ h. Some Pt atoms are not associated with any clusters

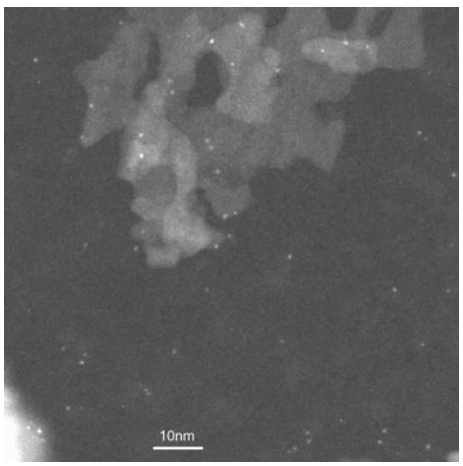

Fig. 8 Some Pt clusters and associated graphite was removed from the alumina during the sample preparation. In bright-field mode the C can be observed associated with these Pt clusters that have come from the catalyst

4 Conclusions

As demonstrated here the aberration corrected scanning transmission electron microscope can provide unique insights into catalysis and provide fundamental information about metal catalyst systems. The number of atoms in a metal cluster can be determined and the shape of the Pt clusters tends to be "raft-like". For lower temperature

reductions not all of the Pt atoms are associated with clusters. There is virtually no change in cluster size after reaction with hydrocarbons.

Care must be exercised in conducting structural studies of metal clusters on an oxide support because of the interaction of the electron beam with the metal atoms. Thus being able to image the active site in a hydrogenation or dehydrogenation reaction may not be feasible with current instrumental capabilities.

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