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Effects of annealing and gas treatment on the morphology of platinum cluster size on highly oriented pyrolytic graphite by scanning tunneling microscopy

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We have used STM to examine the effects of annealing time in the presence of different gaseous species (Ar, H_2 and N_2) on the morphological transformation of vacuum-vapor deposited Pt clusters on highly oriented pyrolytic graphite (HOPG). This study shows that the morphological transformation of the Pt clusters on HOPG is a function of both gaseous species and annealing time. Without annealing, the as-deposited platinum consists of an aggregation of smaller clusters. These clusters become more uniform and spherical after annealing for 4 h in the presence of Ar and H_2. Further annealing shows a morphological transformation from spherical to elongated shape. Small amounts of hydrocarbon impurities in Ar or hydrogen might possibly explain the shape transformation of the Pt clusters. However, the morphological transformation of the Pt clusters is totally different when the sample is annealed in low sticking coefficient gas, N_2, suggesting adsorbed gases (hydrocarbon or hydrogen) have profound effects on the shape transformation. These results indicate that pretreatment conditions are important factors in the shape transformation, which may have significant influence on catalytic activity and selectivity.

Keywords: STM; Pt/HOPG; shape transformation; pretreatment effect

1. Introduction

The morphology of metal clusters plays an important role in determining the catalytic activity and selectivity of many structure-sensitive reactions. Thus a fundamental understanding of the particle size and shape of supported metal clusters is essential, and has been the focus of a number of studies, mainly by TEM and SEM [1–4]. Recently, with the development of non-destructive scanning tunneling microscopy (STM) [5], small clusters and surface structures can be observed in real three-dimensional space with atomic resolution. Ganz et al. [6] were among the pioneers in demonstrating STM as a very promising tool for the study of metal clus-

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ters supported on highly oriented pyrolytic graphite (HOPG). Their work was followed by a number of STM investigations into the characterization of the microstructure of surfaces such as statistical analysis of bond length and bond angle of Pt clusters and the morphology of small clusters on HOPG surface structure [7–10]. Also, Yeung and Wolf [11] reported the effect of substrate functionalization on crystal size, distribution, morphology, and surface structure. Although STM can help in elucidating the phenomenological effect of catalyst microstructure, correlations among the degree of aggregation of Pt on substrate, pretreatment conditions, and the transformation of cluster shapes have not been fully investigated. The objective of our STM work is to investigate the effects of annealing time in the presence of different gaseous species on the morphological transformation of vacuum vapor-deposited Pt clusters on HOPG. We will show that different gaseous environments have profound influences on the transformation of shapes of the Pt clusters as a function of annealing time.

2. Experimental

Samples of platinum clusters on HOPG were prepared by vacuum-vapor deposition technique. Platinum was deposited onto a newly cleaved HOPG surface by heating a platinum wire (Johnson Matthey, 99.99% pure) in a tungsten boat at about 1000°C for 10 s in a vacuum of 7×10^{-7} Torr. The HOPG substrate was rotated at different angles to control the amount of Pt deposited. It should be noted that all Pt samples used in this study were prepared under identical conditions. The deposited samples were then annealed in a quartz tube furnace under three different flowing gases (Ar, H_2 or N_2) at 600°C and 760 Torr. The gases used are ultra-high purity (Ar: 99.99%, H_2: 99.999%, N_2: 99.999%, all from Air Products). Three different samples were treated under different gases, and each sample was subjected to different annealing times of 0, 4, 12, or 24 h. The samples were then imaged with STM (Omicron) under ambient conditions without further treatment. All of the STM images were obtained in a constant current mode, with a current of 1.5 nA and a sample bias of −15 mV. Typical scanning time was about 140 s for each image. The results shown are selected from a number of STM images obtained, and they are representative of a particular treatment and annealing time. In addition, we have previously reported that no cluster-like bumps were observed on HOPG before deposition of Pt clusters [12].

3. Results and discussion

Table 1 summarizes the effects of gas treatment and annealing time on the particle size and shapes of the Pt/HOPG sample. Fig. 1a shows a three-dimensional image of an as-deposited Pt cluster adsorbed on HOPG without annealing pretreat-

Table 1
Summary of the effects of gas treatment and annealing time on the particle size and shapes of the Pt/HOPG sample

Gas treatment	Annealing time (h)	Particle size (Å)	Particle shape
Ar	0	~ 160	oval
	4	~ 150	spherical
	12	120–150	spherical
	24	length: ~ 200 width: ~ 75	polyhedral elongated
H_2	0	~ 160	oval
	4	20–70	spherical
	12	length: ~ 90 width: ~ 30	polyhedral elongated
N_2	0	~ 160	oval
	4	length:~ 100 width: ~ 50	polyhedral elongated
	12	~ 80	cubo-octahedron
	24	~ 70	spherical

ment. The cluster appears as a bright spot in the upper left of the picture, and has a diameter of about 160 Å. The morphology of the Pt cluster shows both large elongated clusters and aggregations of smaller particles. In fact, the cross section profile of the cluster in fig. 1b clearly shows that it is formed from aggregations of smaller clusters. The sizes and heights of the clusters range from 20 to 50 Å, and 10 to 40 Å, respectively.

When the sample was annealed with Ar at 600°C for 4 h, clusters of about 150 Å were observed (fig. 2a). The heights of the clusters are about 12 Å. Interestingly, the Pt clusters are no longer aggregations of smaller clusters, and their shapes have become more uniform and spherical, as shown in the cross section profile (fig. 2b). This observation is consistent with those of Wang et al. [13] and of Chojnacki and Schmidt [14] using TEM. They suggested that the catalyst morphology is influenced by the presence of gaseous species, and by annealing time and temperature. In their study, the particles were found to transform from cubes to spheres, and in the case of heating in H_2, the spherical particles can transform back to cubes because of a significant anisotropy in surface energy produced [13].

The effects of annealing time on the transformation of the shapes of the Pt clusters were further illustrated when the sample was annealed for 12 and 24 h at 600°C. Fig. 2c is a scan of a 2000 Å×1500 Å area of the surface of a sample after annealing in Ar at 600°C for 12 h. The diameters and the heights of Pt clusters range from 100 to 150 Å and 10 to 15 Å, respectively. The Pt clusters are still quite spherical. However, some clusters (shown in the bottom right of the picture) now appear to have rounded corners. This shape transformation is more pronounced when

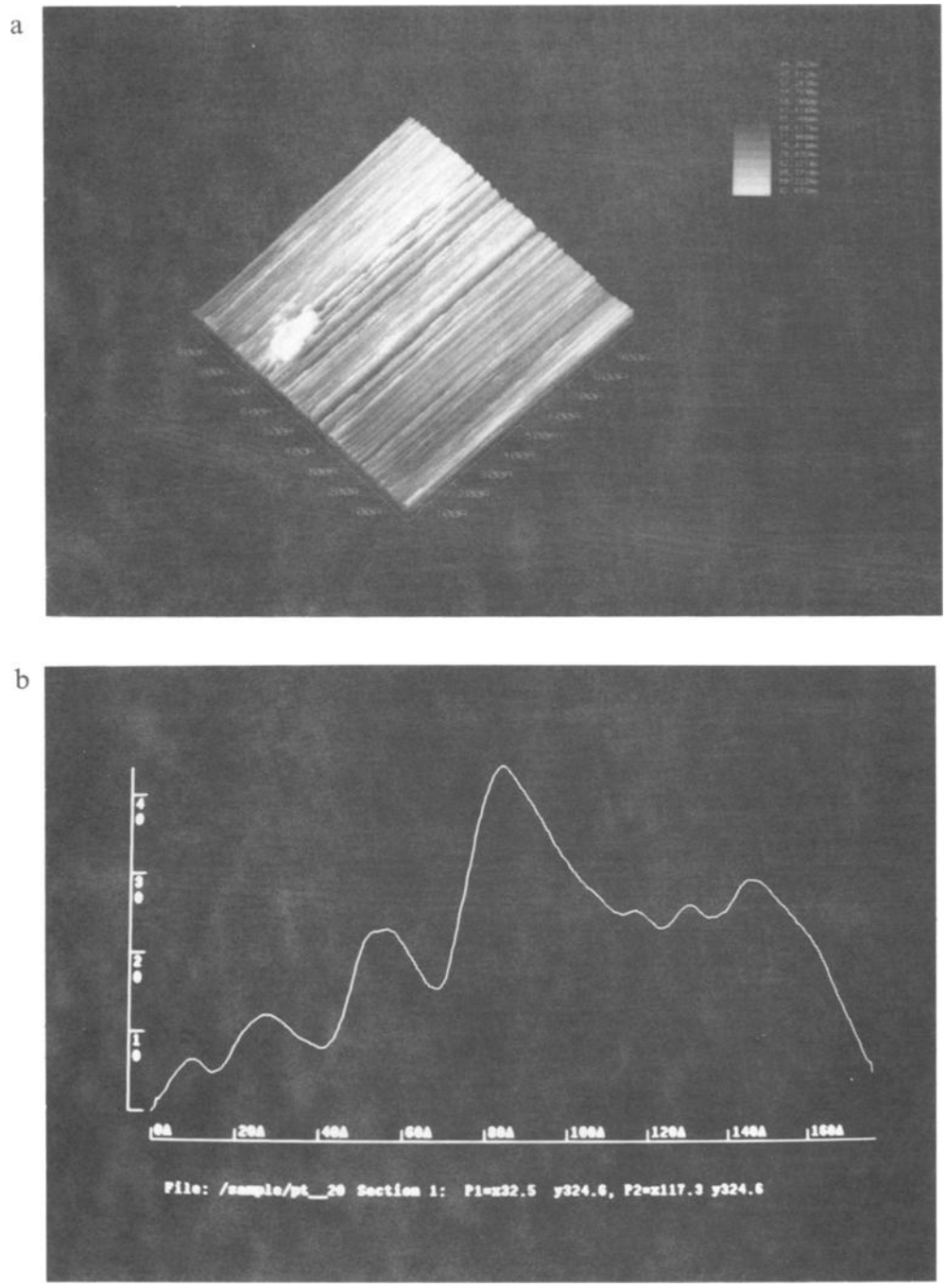

Fig. 1. (a) Three-dimensional STM image of vacuum vapor-deposited Pt clusters formed on HOPG without annealing. (b) Cross section profile of Pt cluster showing that the Pt cluster is an aggregation of smaller clusters.

the sample is annealed for a longer time (24 h), as shown in fig. 2d. In this sample the spherical shape of the Pt clusters no longer appears, and the clusters have become elongated. These elongated clusters are roughly 200 Å long, 75 Å wide and 15 Å high. The average volume of these elongated clusters is within 15% of the average volume of spherical clusters, indicating that the elongated clusters are indeed the result of transformation of spherical clusters.

After 24 h of annealing, it is reasonable to assume that the clusters have attained their equilibrium shape at 600°C. However, there is still no general agreement on the equilibrium shape of small clusters. Based on experimental and theoretical considerations, Drechsler [15] concludes that the equilibrium shape of small particles should be nearly spherical, but with the formation of carbon and oxygen species on the surface, polyhedra are observed. On the other hand, Wang et al. [13] suggest that for clean surface the equilibrium shape is polyhedral, while for adsorbate-covered surface, the equilibrium shape is spherical. In this study, we observed the transformation of irregular clusters (as-deposited) to uniform sphere (4 h), to polyhedra with rounded corners (12 h), and to elongated polyhedra (24 h). Though high purity argon (99.99%) was used during the annealing, it is possible that with a long annealing time a small amount of hydrocarbon impurities was decomposed and adsorbed onto the surface. This may explain the transformation of spherical shapes (relatively clean) to polyhedral shapes (with adsorbates), according to Drechsler [15].

In order to verify the effect of adsorbed gases on morphological transformation of Pt clusters on HOPG, H_2 was used as an annealing agent. Hydrogen may produce small amounts of hydrocarbon (such as CH_4) when it reacts with graphite substrate. Evidence for this has been found from Yang's [16] work by using TEM. He observed the formation of circular etch pits when the basal plane was reacted with H_2 at above 800°C. He also found that the hexagonal shape of the etch pits was formed by H_2O in the temperature range from 600 to 900°C. His study suggested that the hydrocarbon species was formed by the dissociative chemisorption of H_2 on the active sites of the basal plane in this temperature range. However, Baker et al. [17] noted that in the Pt/graphite/H_2 system, H_2 reduction to CH_4 required a very high temperature ($\sim$ 1000°C), except with lattice vacancies and steps.

Fig. 3a shows a three-dimensional STM image of Pt clusters on a HOPG sample annealed in H_2 at 600°C for 4 h. The diameters and heights of Pt clusters range from 20 to 70 Å and from 4 to 6 Å, respectively. Interestingly, the shapes of the Pt clusters are quite uniform and spherical. This observation is consistent with that observed in Ar annealed samples. Thus, one possible explanation of our observation is that hydrogen reacts with carbon to produce the hydrocarbon species initially, and then these impurities affect the transformation of the shapes of the Pt clusters, as proposed by Drechsler [15]. In contrast, however, Wang et al. [13] and Chojnacki and Schmidt [14] found that the shape of Al_2O_3 and SiO_2 supported Pt particles appeared to be cubic in the case of heating in H_2.

Again, the effects of annealing time on the shape change of the Pt clusters were

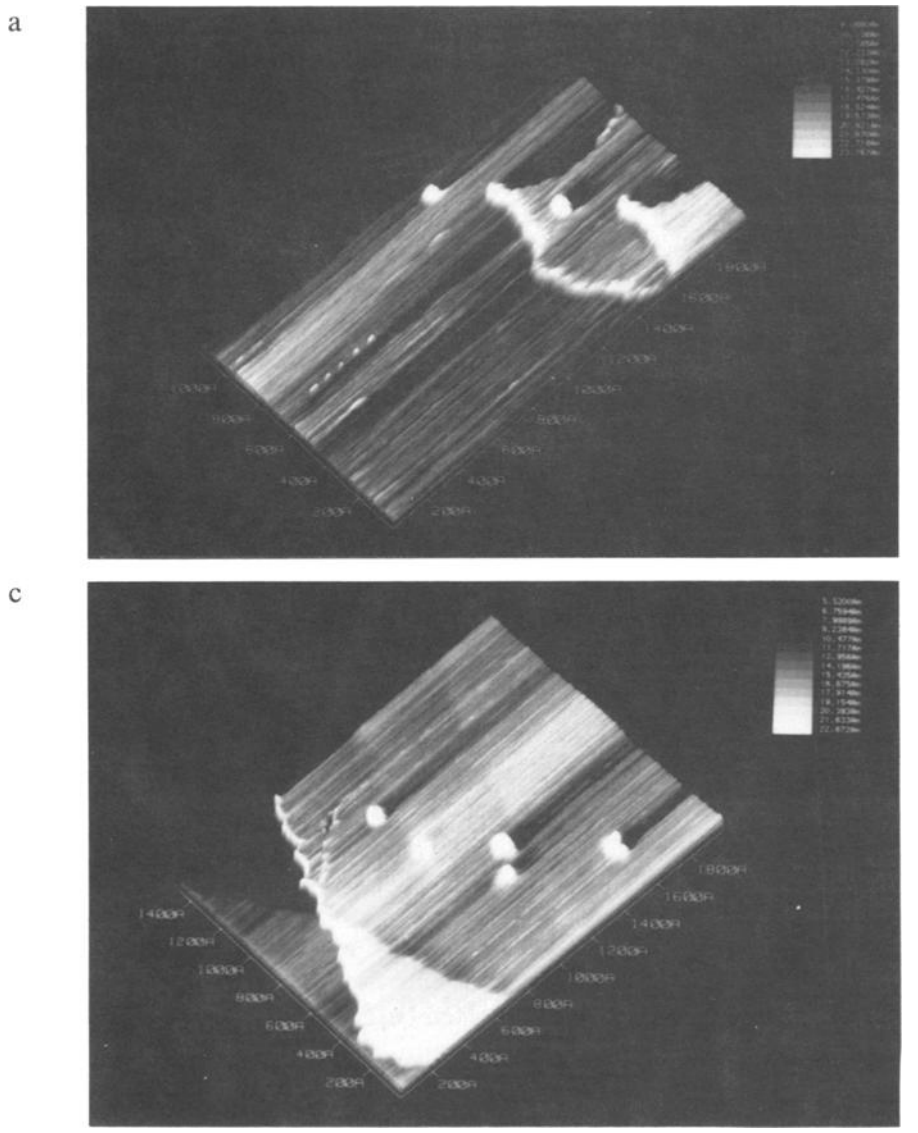

Fig. 2. (a) Three-dimensional STM image of Pt clusters on HOPG annealed in Ar at 600°C for 4 h. (b) Cross section profile of Pt cluster (left cluster in (a)). (c) Annealing for 12 h. (d) Annealing for 24 h.

investigated when the sample was annealed for longer time at 600°C. The scan of a 1000 Å × 900 Å area of the sample surface after annealing in H_2 at 600°C for 12 h is shown in fig. 3b. The Pt clusters appear to be roughly spherical, or they have already transformed to elongated shape. Evidence of complete transformation from spherical to elongated is also found in a different area of the same sample. Fig. 3c shows the polyhedral elongated shape of the Pt clusters in a 200 Å × 200 Å

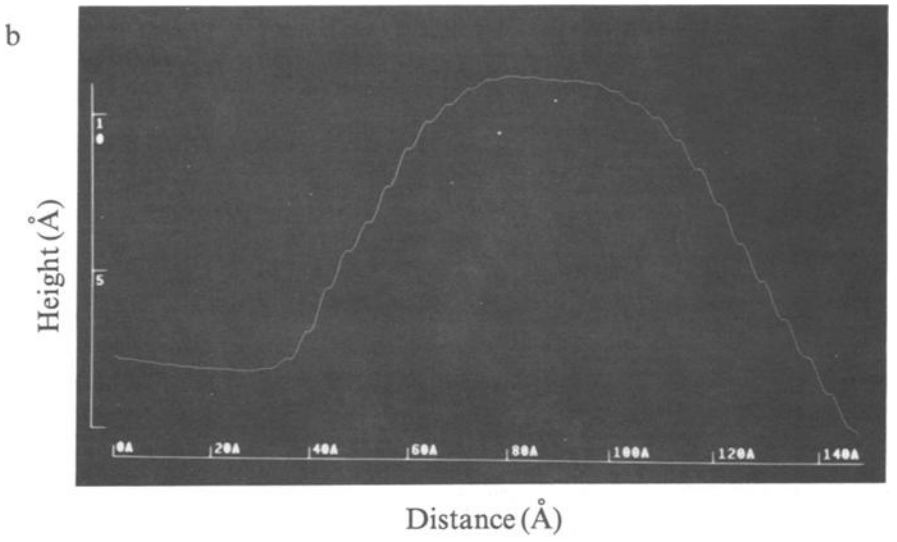

Fig 2. Continued

area on the same sample surface. The elongated clusters are about 90 Å long, 30 Å wide, and 6 Å high. The transformation from spherical to elongated shape is more pronounced with even a shorter annealing time with H_2 replacing Ar. This observation shows that adsorbates (H_2 or hydrocarbon impurities) cause the shape transformation of the Pt clusters.

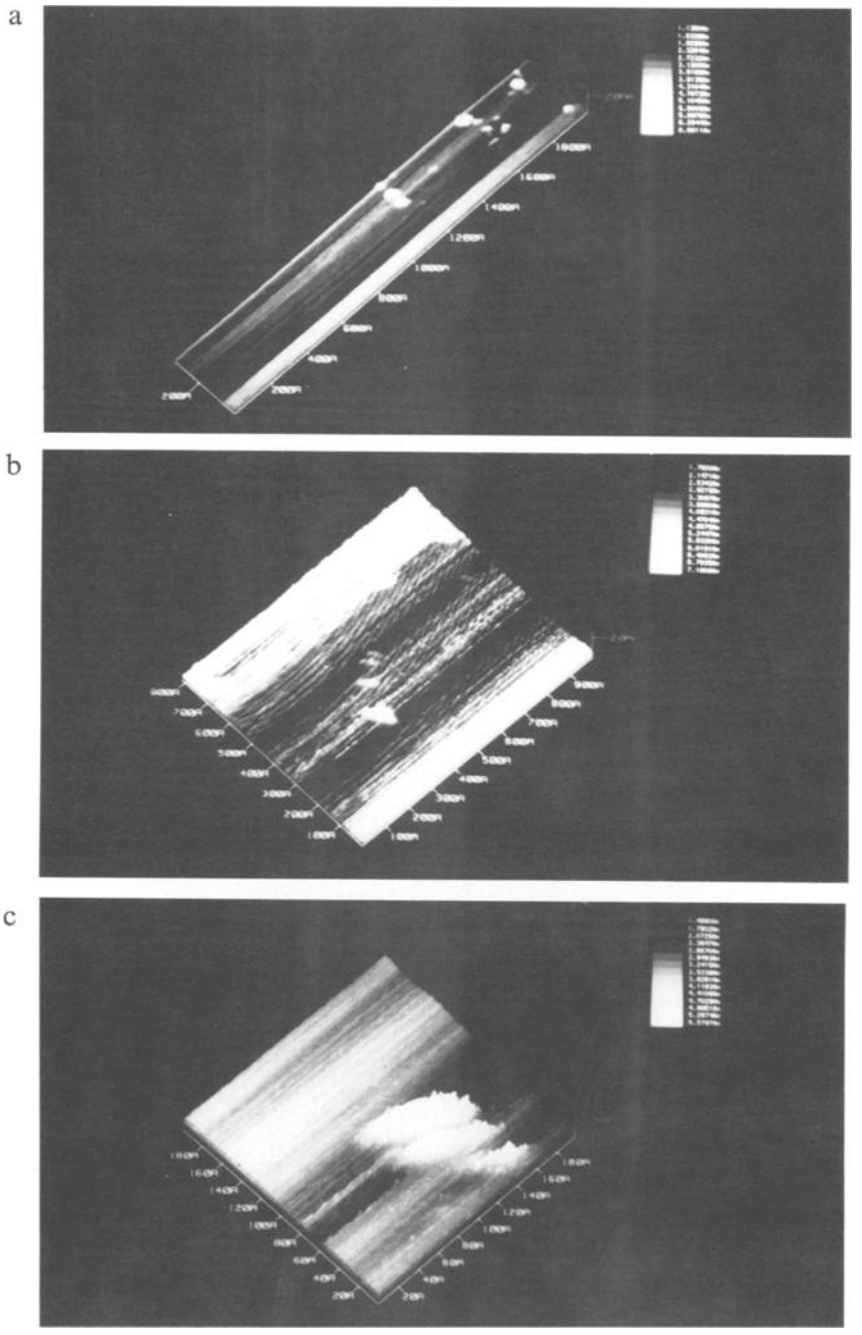

Fig. 3. (a) Three-dimensional STM image of Pt clusters on HOPG annealed in H_2 at 600°C for 4 h. The Pt clusters are quite uniform and spherical. The diameters and heights range from 20 to 70 Å and, from 4 to 6 Å, respectively. (b) Annealed for 12 h. The Pt clusters appear to be roughly spherical, or have already transformed to elongated shape. (c) Different area of the same condition as (b), showing complete transformation from spherical to elongated Pt clusters.

During our investigation we observed an interesting morphology transformation of the Pt clusters as a function of annealing time in Ar and H_2 treatments: irregular clusters became uniform spheres and elongated polyhedra. We were puzzled by the fact that this transformation is observable in the presence of gases (hydrocarbon impurities in Ar and H_2) that can adsorb on Pt surface. These observations raise a question: Is the gas treatment the primary cause affecting the morphology transformation of the Pt clusters? We addressed this question by using an ultra-high purity low sticking coefficient gas, N_2 at 600°C for 4, 12, and 24 h for the Pt/HOPG sample. Since nitrogen has been used as an inert gas in many catalytic reactions, and the ultra-high purity gas (99.999%) contains extremely small amounts of hydrocarbon impurities, this gas will be useful to clarify the above questions.

The effects of annealing time on the morphology change of the Pt clusters were investigated using N_2 for 4, 12 and 24 h at 600°C. Fig. 4a shows a typical three-dimensional STM image of Pt clusters grown by annealing for 4 h at 600°C in N_2. Two clusters are observed in the area of 1000 Å in X and 400 Å in Y. The Pt clusters appear to be elongated polyhedral. No spherical particle is found during the initial annealing period. The elongated Pt clusters are roughly 100 Å long, 50 Å wide, and 6 Å high. This result shows that an originally aggregated large cluster (fig. 1a) breaks up into separate polyhedral elongated particles, which in turn decompose into smaller Pt clusters in the initial annealing stage under N_2. It should also be noted that the polyhedral elongated shape of the Pt clusters was observed after longer annealing times in Ar or H_2 atmospheres. This sample was further annealed for 12 and 24 h to determine whether any morphological transformation of the Pt clusters was enhanced with increasing annealing time.

The cuba-octahedron shape of the Pt clusters is observed in the sample annealed in the presence of N_2 for 12 h at 600°C, as shown in fig. 4b. In this sample, the polyhedral elongated shape of the Pt clusters no longer exists, and they have become cuba-octahedron in shape. The morphological transformation of the Pt clusters from elongated to cubo-octahedron is interesting because it shows the process of transformation from an initial to an intermediate annealing stage which is near equilibrium morphology. This shape transformation of the Pt clusters is more pronounced when the sample is annealed for 24 h, as shown in fig. 4c. The shape of the Pt particles is spherical, indicating that the morphology of the clusters has attained an equilibrium structure [15]. Thus, longer annealing time allows the Pt clusters to form a well developed phase and to approach equilibrium. It is well known that nitrogen does not chemisorb significantly on Pt [14]. Thus, one could speculate at length about the role of annealing temperature in affecting the shape transformation of the Pt clusters. It is possible, therefore, that longer annealing time is needed for adequate mobility for transformation from elongated polyhedral to spherical shape at this temperature.

During our STM investigation, we did not observe any apparent movements of the Pt clusters after annealing under different environments. Repeated scanning of a specific area consistently resulted in the same image. This finding is consistent

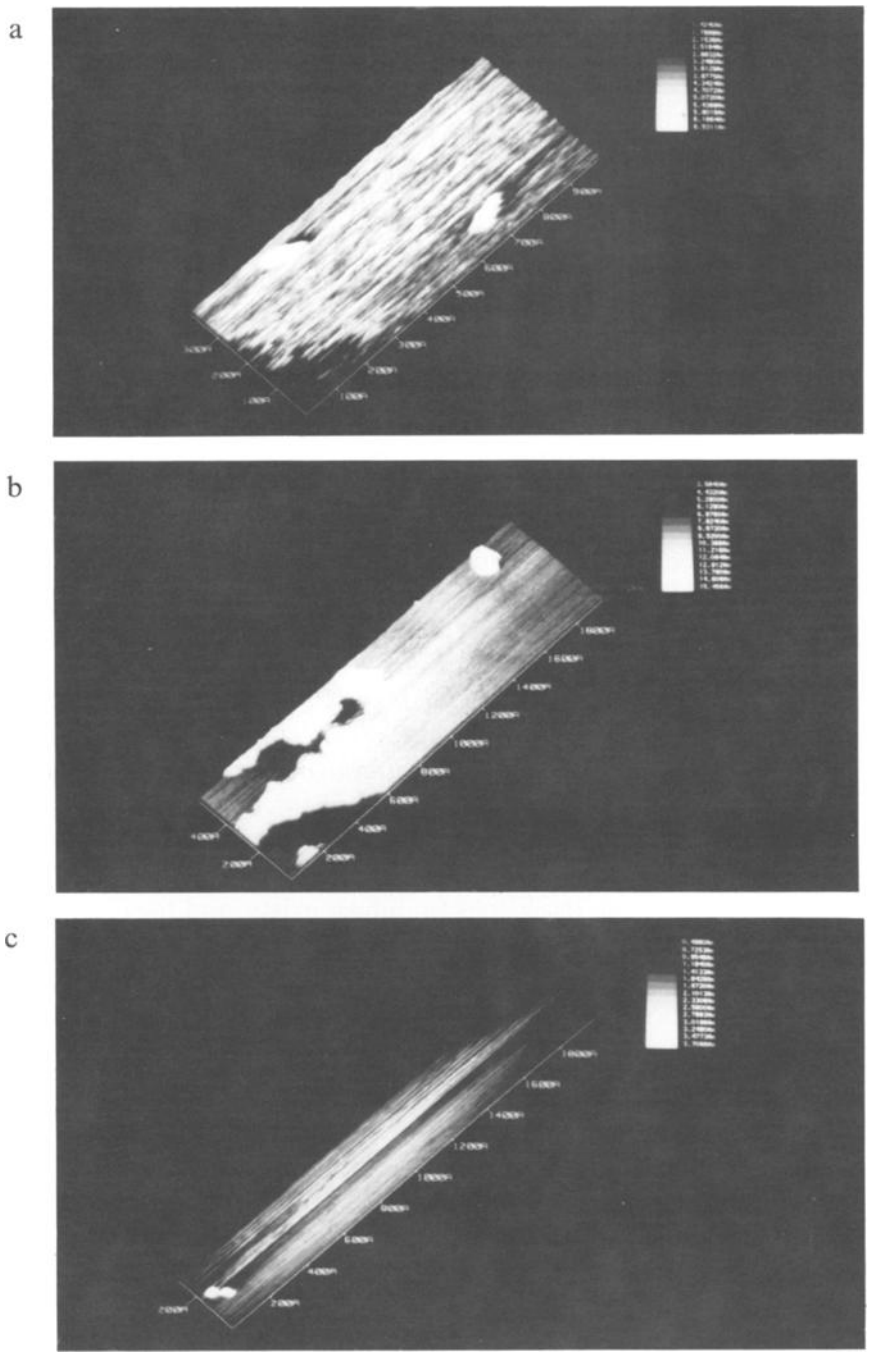

Fig. 4. (a) Three-dimensional STM image of Pt clusters grown by annealing in N_2 at 600°C for 4 h. (b) Annealed for 12 h. (c) Annealed for 24 h. Two spherical Pt clusters are observed.

with Zhou and Gulari's work on Pt film on HOPG [10], but mobile clusters of phosphotungstic acid [18], reduced Pt crystallites on nitric acid functionalized graphite [11], and gold particles [19] are also reported. It may be possible that our scanning conditions were optimal that no destructive tip-induced movement was observed. Chu et al. [20] observed formation of voids and/or channels after H_2 reduction at 900°C on Pt/HOPG. However, no gasification reaction of graphite was observed in this study because of the low reaction temperature (600°C) used.

4. Summary

The effects of annealing time in the presence of different gaseous species on the morphological transformation of vacuum-vapor deposited Pt clusters on HOPG were investigated by STM. We observed the transformation of irregular clusters (as deposited) to uniform spheres (4 h), to polyhedral with rounded corners (12 h), to elongated polyhedral (24 h) in the presence of Ar or H_2 annealed at 600°C. Small amounts of hydrocarbon impurities in Ar or hydrogen might possibly explain the shape transformation of the Pt clusters. However, the morphological transformation of the Pt clusters is totally different when the sample is annealed in N_2. This indicates that adsorbed gases have profound effects on the transformation of Pt clusters as described by Drechsler [15]. Finally, this study shows that the morphological transformation of the Pt clusters on HOPG is a function of both gaseous species and annealing time. Thus, pretreatment conditions are important factors in the shape transformation, which may have significant influence on catalytic activity and selectivity.

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