STM and TEM investigation of a technical platinum/graphite catalyst

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A technical, powder, platinum-on-graphite catalyst has been investigated up to atomic scale by transmission electron microscopy (TEM) and scanning tunneling microscopy (STM). The catalyst had been prepared from a colloidal platinum sol. STM confirms, in addition to spherical particles, the presence of raft structures on the support surface, which had been suggested by the TEM images. The height of these raft structures varies from one to ten atomic layers.

Keywords: platinum/graphite; STM; TEM

1. Introduction

The microstructure and morphology of supported metal particles play an important role in determining the catalytic activity and selectivity of structure sensitive reactions. Much work has been carried out on the characterization of the microstructure of supported metal particles by different techniques, such as transmission electron microscopy (TEM) and scanning electron microscopy (SEM) [1]. The application of scanning tunneling microscopy (STM) to heterogeneous catalysts has increased in recent years, not only due to its capability to image three-dimensional small clusters, or even isolated atoms [2], but also due to the possibility of working under a variety of conditions (air, liquid, UHV and high temperature [3]) and to investigate the surface structure of powder materials such as carbon black [4] and graphite powder [5].

In situ measurements under conditions of high reaction temperatures and pressures have been demonstrated by McIntyre et al. [3]. They investigated the stability of Pt(110) as a function of oxygen and hydrogen pressure and temperature. Recently Somorjai and co-workers [6] published a study dealing with the use of a platinum–rhodium (Pt/Rh) STM tip for local rehydrogenation of carbonaceous

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fragments deposited on a platinum (111) surface. Asakura et al. [7] studied the local geometric and electronic structure of model metal-supported dispersed metal oxide, ZrO_2, on Pd(100) with STM and scanning tunneling spectroscopy (STS) as a function of chemical treatments. STM studies on model systems of metal particles supported on graphite have already been reported [8–14]. Yeung and Wolf [13] published STM work in which Pt and Pd particles were prepared by chemical impregnation from a precursor and physical deposition by vacuum evaporation of Pt metal on highly oriented pyrolytic graphite (HOPG). Sarte et al. [14] studied a model system in which palladium particles were deposited by ion-exchange on HOPG. Although STM studies on the Pt/graphite system have already been reported, previous investigators have mostly used flat substrates such as HOPG with relative low surface area (1–3 m^2/g). In this work we have investigated a technical platinum/graphite catalyst prepared from a colloidal Pt precursor. The platinum is supported on a fine pyrolytic graphite powder (Lonza AG) with 75 m^2/g BET surface area. A characterization of both the graphite substrate and the deposited platinum down to an atomic scale is described.

2. Experimental

STM images were obtained using a commercial STM (Topometrix, TMX2000) working in air at room temperature. All the images were taken with a one micron scanner in constant current mode. The sample was investigated at several different locations to ensure representative data. Images reported here were recorded using a bias voltage of 100 mV and a set-point current of 2 nA. STM tips were made by mechanically cutting Pt/Ir (80/20%) wire. The STM was calibrated by measuring atomic steps on graphite and gold as well as by atomic resolution on graphite.

Industrial graphite powder HSAG 300 (Lonza) with 75 m^2/g surface area was used as a support. The preparation method for the platinum on graphite catalyst consisted of the preparation of a platinum colloid by reduction of $PtCl_2$ with tetraalkylammonium hydrotriethylborate in THF and subsequent adsorption of the platinum particles onto the graphite [15]. For STM measurements the powder sample was pressed to make tablets.

High resolution transmission electron micrographs were recorded using a Philips CM30ST (300 kV) instrument. The sample was loaded dry onto perforated, thin carbon film supported on copper grids. Transmission electron microscopy was carried out using a Hitachi H-600 instrument.

3. Results and discussion

The two techniques, STM and TEM, have been used for comparison. TEM is an established method which has very often been applied to the investigation of

powder catalysts. In contrast STM is relatively a new technique with an important advantage, namely that of three-dimensional imaging in real space.

Fig. 1 is a representative transmission electron micrograph of the Pt/graphite catalyst showing mainly two different structures: isolated islands and labyrinth structure. A statistical average among several images showed that the platinum covered ca. 40% of the graphite surface. Varying thickness of the platinum aggregates was deduced from markedly differing contrast at small particle dimensions (i.e. the Bragg effect should be negligible).

Fig. 2 depicts a high resolution micrograph (HRTEM) of the same sample showing lattice resolution. The weakly resolved background fringes represent the lattice of graphite with a distance of 0.14 nm. The resolution of the platinum aggregates also suggests that their thickness varies. Some of the platinum aggregates show

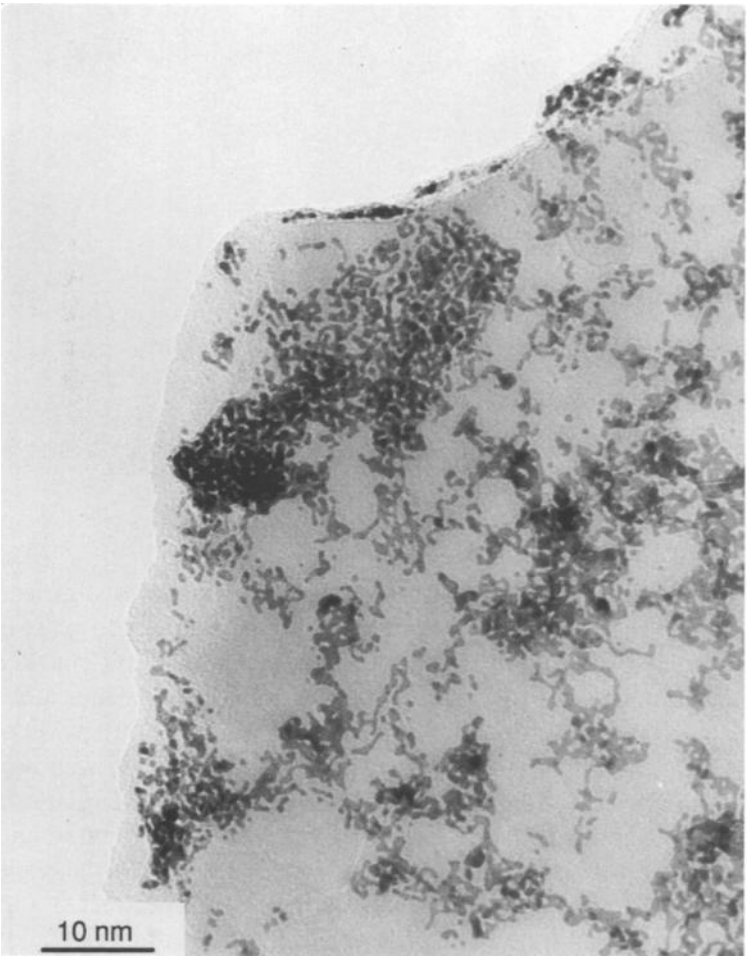

Fig. 1. TEM micrograph of Pt/graphite catalyst.

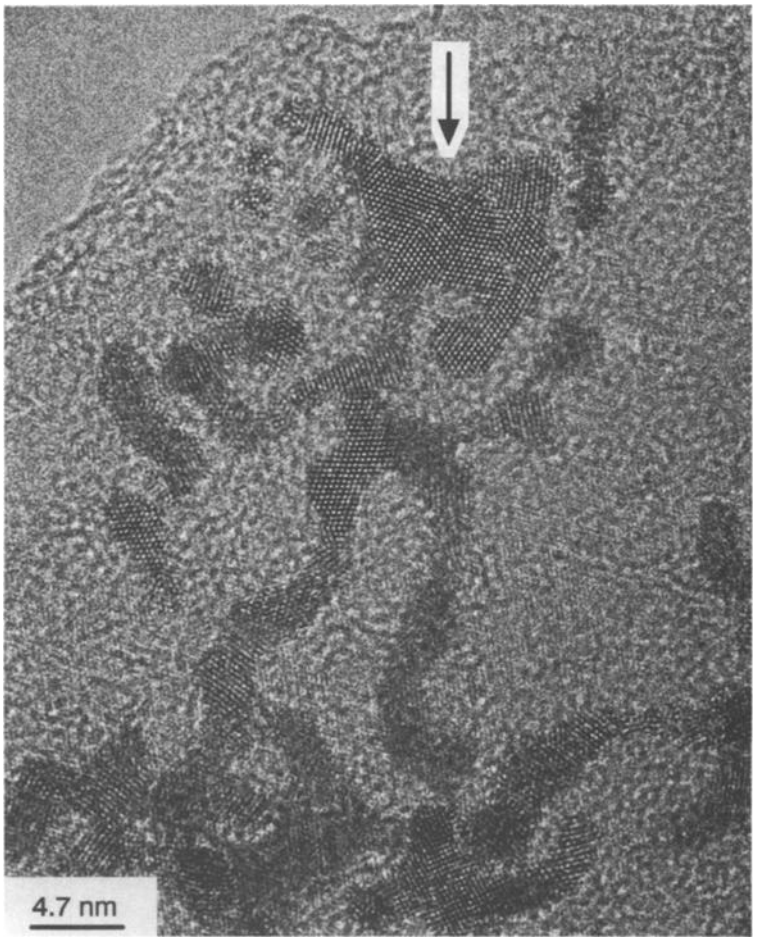

Fig. 2. HRTEM micrograph of Pt/graphite catalyst.

extremely low contrast suggesting they may be too thin to show lattice resolution, others are thick enough for achieving lattice resolution. Present are (111) faces with a lattice distance of 0.28 nm. In the upper part of the micrograph (marked by arrow) one can see domains with different orientations as well as defects such as dislocations and grain boundary between two crystallites. For determination of the thickness of the particles and as a complementary technique STM was used. Figs. 3a and 3b show similar structures as present in fig. 2. The STM images represent a small selection from a large data base containing images of treated and untreated graphite samples. Spherical shaped platinum particles (fig. 3a) as well as "rafts" (fig. 3b) can be seen. The height of such structures varies between 1 and 10 atomic layers. Fig. 3c shows a high resolution STM image of platinum particle and graphite substrate. The distance between two spots (atoms) on the right-hand side of the figure (graphite) is 0.24 nm corresponding to the distance between two carbon

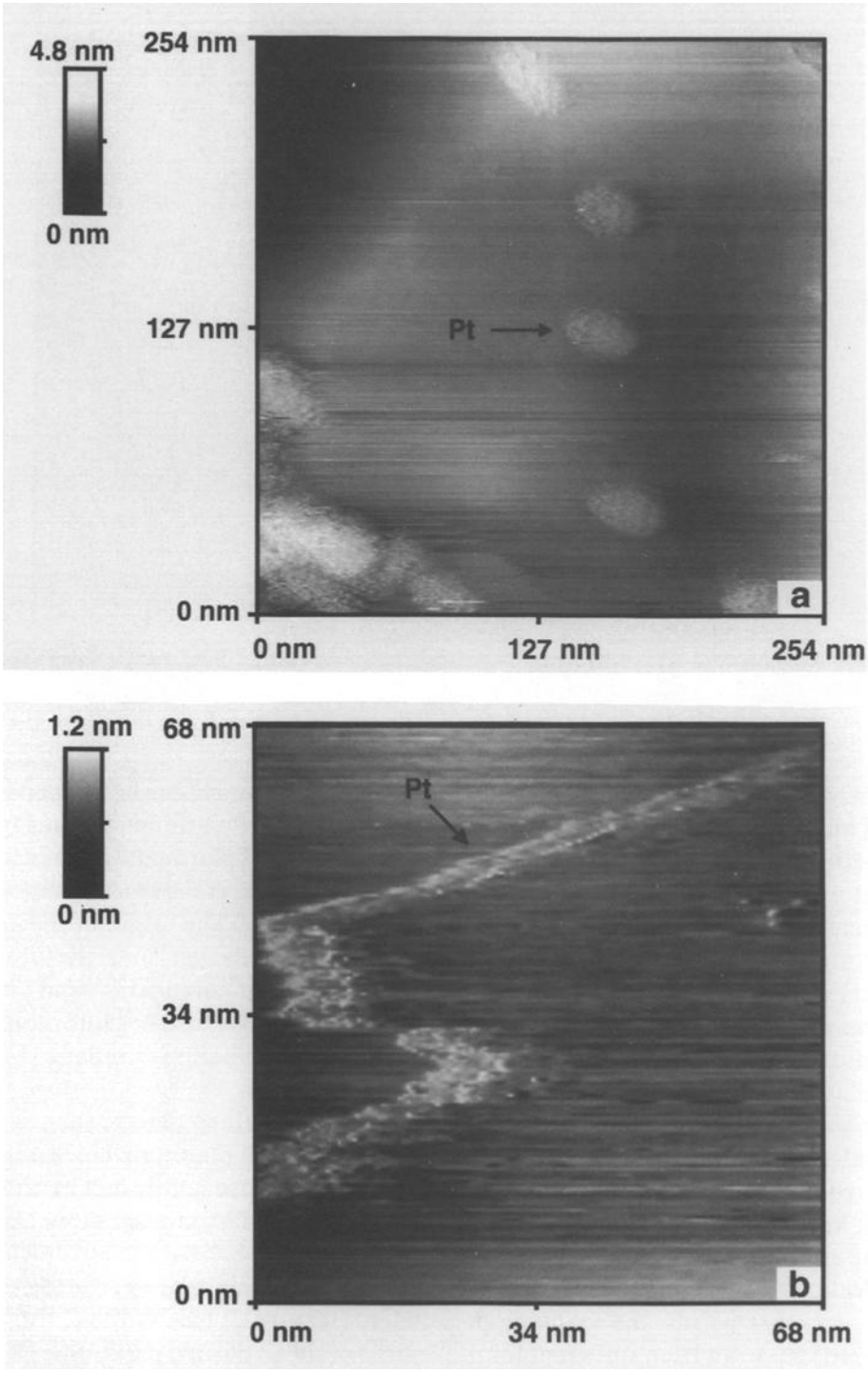

Fig. 3. STM images showing main morphologies of platinum deposited on graphite: (a) spherical Pt particles; (b) "rafts" of Pt; (c) atomic resolution of Pt and graphite.

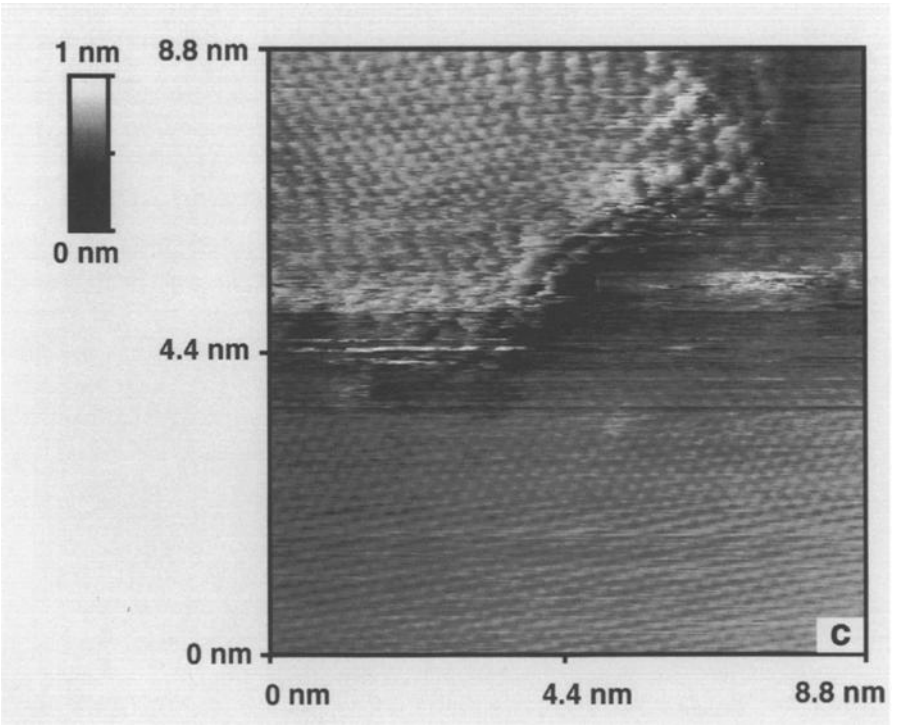

Fig. 3. (Continued).

atoms as seen by STM [5]. The distance between the spots on the left upper side is 0.28 nm. This value is equivalent to the lattice distance of platinum. 2D hexagonal structure on both sides of the image is seen. In the case of platinum this is in agreement with a surface of a (111) close packed structure. Reference measurements of untreated graphite samples showed no similar structures. The origin of the apparent "atomic resolution" of the platinum particles is not clear yet, since the measurements were performed in air (contamination). The height corrugation and "huge" atoms near the edge of the particle can be attributed to adsorbed organic molecules (impurities originating from solution) giving periodic oscillations similar to Friedel oscillations [16].

It was observed using TEM that platinum deposited along defects such as steps but also on the flat graphite surface. Fig. 1 shows rows of platinum which could be interpreted as atoms situated along steps. This can be also confirmed by the contrast variation in the support either side of this line. STM images show also the same effect.

We have not observed any movement of the deposited platinum during operation. In other words, the scanning parameters (scan-rate, bias voltage, tunneling current) have not been sufficient for movement of the deposited platinum. This can be explained either by a stronger interaction between Pt and substrate than between tip and Pt or by an epitaxial arrangement of the platinum on the surface, which

can prevent the motion of the islands. Furthermore, in the case of the thinner platinum aggregates (one up to two atomic layers) the influence of the crystal structure and surface states of the support must be considered.

4. Conclusions

TEM and STM have been used to resolve the morphology of a technical Pt/graphite catalyst. The combined use of these methods indicates that the deposited platinum exists in two morphologically different forms, as spherical particles and as rafts with various heights. Platinum and support (graphite) have been characterized up to atomic scale by STM and TEM. The study demonstrates that STM is a suitable technique even for the investigation of certain technical catalysts, with inherently large surface area and inhomogeneity.

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