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Scanning tunneling microscopy and spectroscopy of silver and platinum catalysts

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Scanning tunneling microscopic studies of silver catalysts dispersed on highly oriented pyrolitic graphite (HOPG) with 2, 5 and 10 wt% metal loading prepared by wet impregnation and hydrogen reduction show spherical crystallites, with the 2 wt% catalysts having an average crystallite size of ~ 2 nm and the 5 and 10 wt% catalysts with size distributions of 2–5 and 4–12 nm respectively. The Ag catalysts prepared by $NaBH_4$ reduction show a narrower size distribution. Pt/HOPG catalysts with 2 and 5 wt% metal loading prepared by wet-impregnation and hydrogen reduction show large (2–11 nm) raft-like crystallites; small crystallites (~ 1 nm) could be obtained by $NaBH_4$ reduction. Tunneling spectroscopic measurements reveal the non-metallic nature of crystallites on the surface of Ag(2 wt%)/HOPG as well as Pt/HOPG prepared by $NaBH_4$ reduction.

Keywords: Scanning tunneling microscopy (STM); scanning tunneling spectroscopy (STS); silver catalysts; Pt catalysts; STM study of Ag and Pt catalysts

1. Introduction

Scanning tunneling microscopy (STM) has enabled studies of the structure of solid surfaces with atomic resolution. The technique has been employed to investigate surfaces of graphite, metals and semiconductors in recent years. Clearly, STM would be an ideal tool to study the nature of metal crystallites or clusters on the surfaces of supported metal catalysts. There have been very few STM studies of such catalyst systems hitherto [1–3]. We, therefore, considered it most worthwhile to study typical supported metal catalysts with varying metal loadings, prepared under conditions normally employed for carrying out catalytic reactions. For this purpose, we have investigated reduced Ag and Pt catalysts supported on highly

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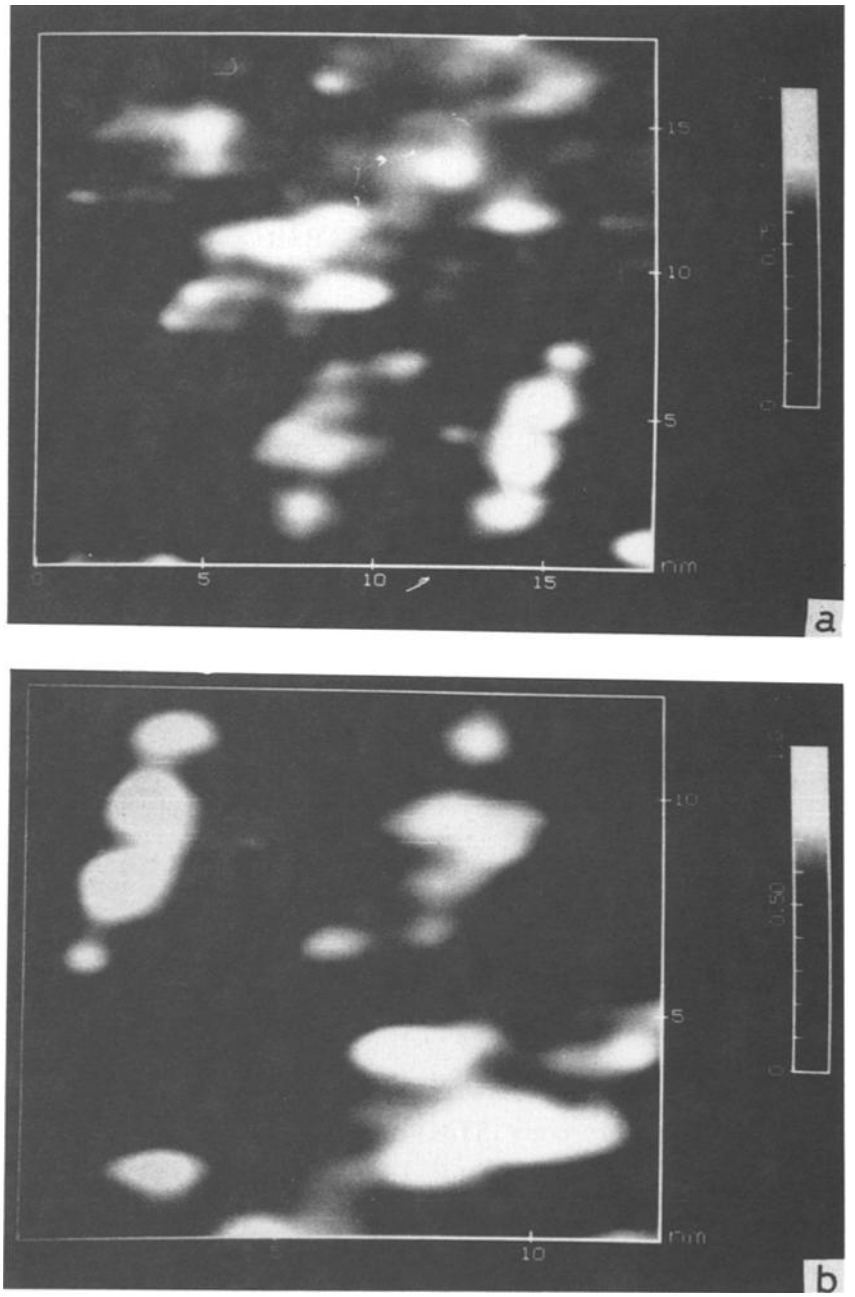

Fig. 1. STM images of Ag(2 wt%)/HOPG catalyst prepared by wet impregnation: (a) and (b) are top-views from different areas; (c) and (d) are the corresponding side-views.

oriented pyrolitic graphite (HOPG). The use of HOPG as a substrate was necessary for the STM study as it is a good conductor and can be easily cleaved providing atomically flat planes over a large area. In addition to reduced Ag and Pt catalysts

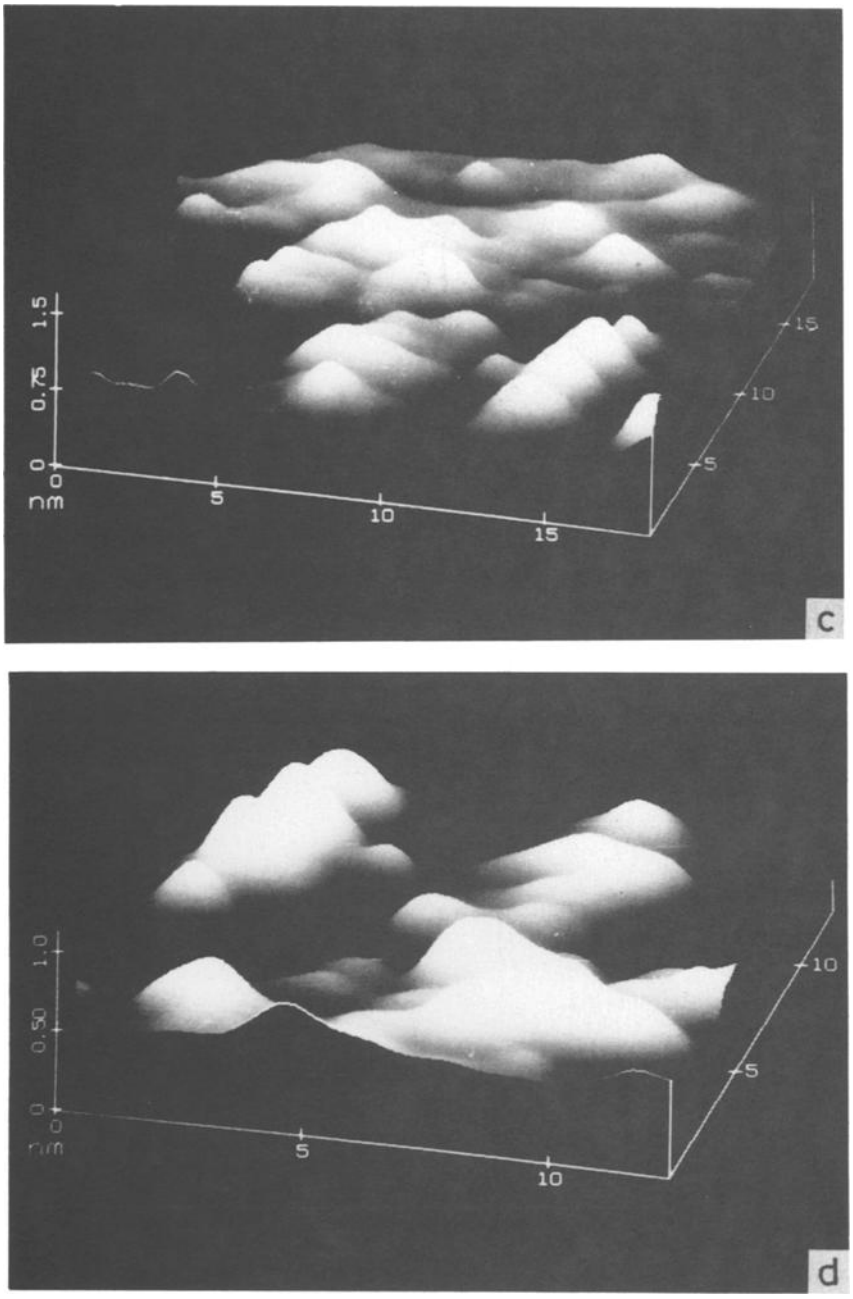

Fig. 1. (continued).

prepared by the wet-impregnation method, we have studied Ag and Pt catalysts prepared by chemical means wherein a reagent containing Ag or Pt was reduced in aqueous medium using sodium borohydride.

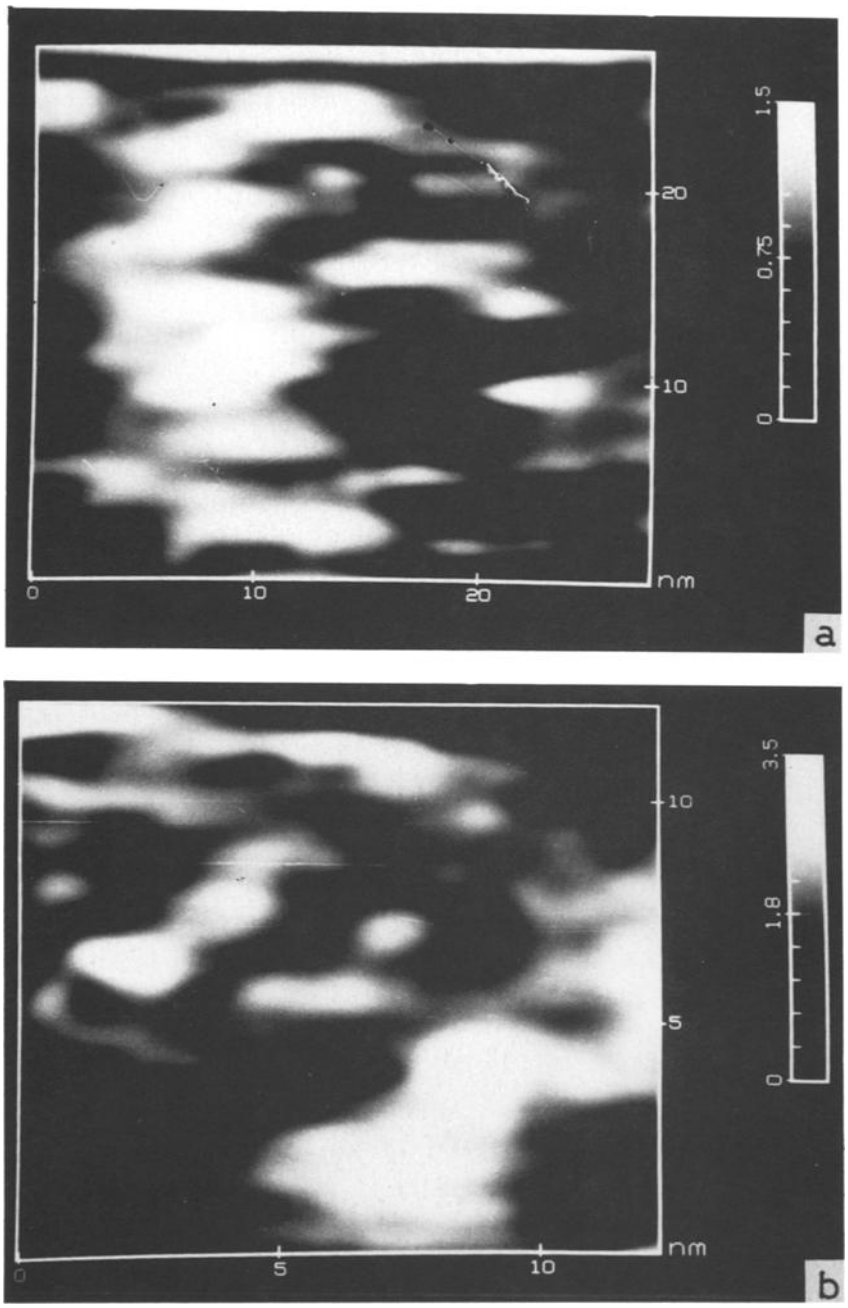

Fig. 2. STM images of Ag(5 wt%)/HOPG catalyst prepared by wet impregnation: (a) and (b) are top-views from different areas; (c) and (d) are the corresponding side-views.

A particularly interesting aspect of the present investigation is the use of scanning tunneling spectroscopy (STS) to explore whether the crystallites of Ag and Pt were metallic or not. It is noteworthy that in the STS technique [4], one establishes

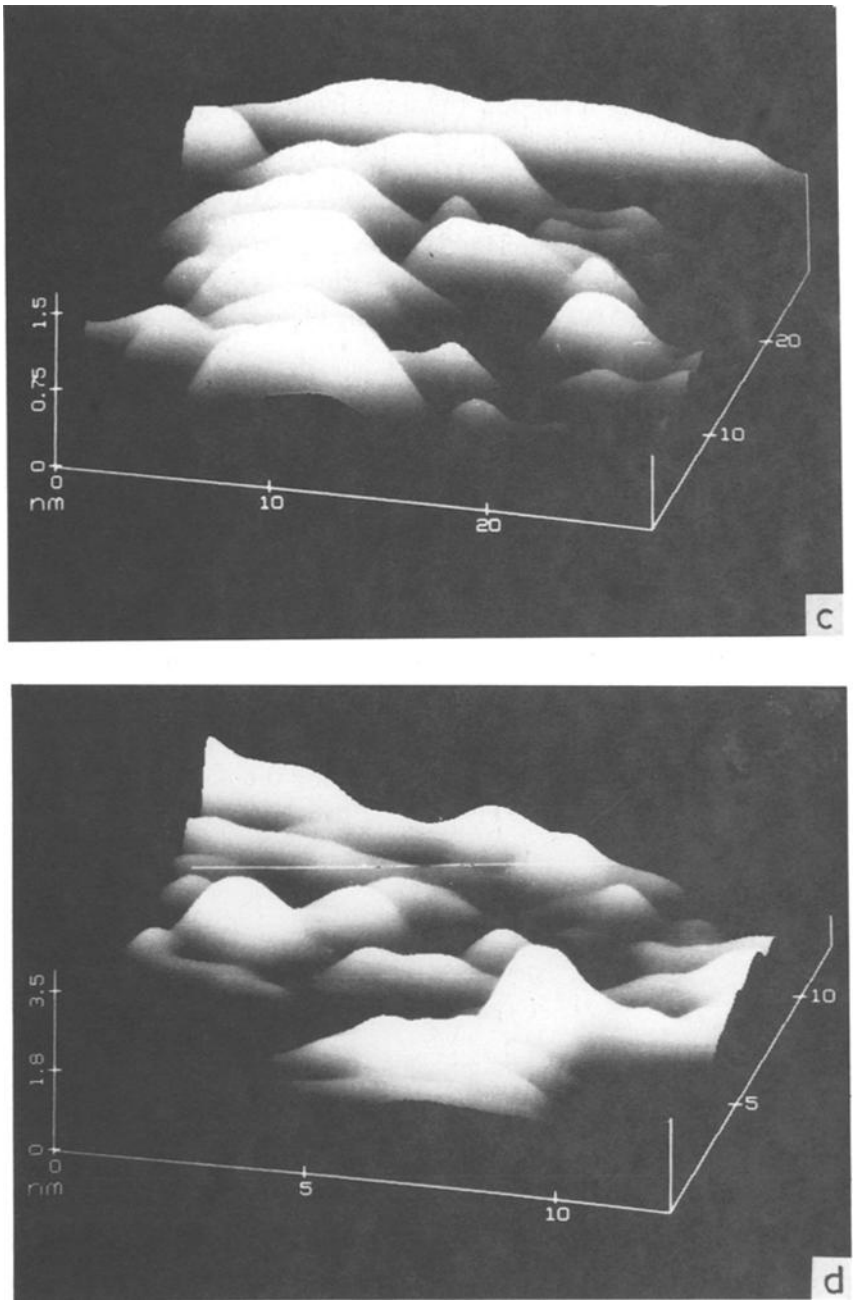

Fig. 2. (continued).

point contacts to obtain current–voltage (I–V) characteristics for very small crystallites unlike in the usual four-probe resistivity measurements where only bulk samples can be studied.

2. Experimental

The HOPG employed as a support obtained from Union Carbide (courtesy of Dr. Arthur Moore), was characterized by STM prior to catalyst preparation. In the wet-impregnation method, a piece of HOPG ($\sim$ 100 mg) was cut into small flakes ($\sim$ 1 mm $\times$ 1 mm) and soaked in an aqueous solution of $AgNO_3$ (or H_2PtCl_6) containing the desired amount of Ag or Pt. These samples were subjected to reduction at 773 K in a stream of pure, dry hydrogen without prior calcination. Catalysts with Ag loading of 2, 5 and 10 wt% and Pt loading of 2 and 5 wt% were prepared by this procedure.

In the chemical reduction method, an aqueous solution (0.015 M) of $AgNO_3$ (or H_2PtCl_6) was treated with a solution of $NaBH_4$ (6.6×10^{-3} M) at room temperature. A few drops of the resulting fresh sol were deposited on cleaved HOPG (metal loading $\leqslant 1$ wt%).

STM imaging was carried out under ambient conditions using a Nanoscope II scanning tunneling microscope provided with Pt–Ir tips. The catalyst sample was glued to the specimen platform using conductive silver paint. STM was operated in constant current imaging mode with bias voltages of 10–225 mV and tunneling currents of 0.3–1 nA. Scanning frequency was maintained at 78 Hz with 400 lines per scan. The reproducibility of images was confirmed by changing the tip frequently.

Spectroscopy using STM was performed at selected points on the topographic scans by opening the feedback loop and monitoring the normalized conductance ($d \ln(I)/d \ln(V)$) while sweeping the bias voltage over a range.

3. Results and discussion

3.1. STM STUDIES

In figs. 1 and 2 we show STM images of Ag/HOPG catalysts with metal loadings of 2, 5 and 10 wt% respectively, both in top and side views. We see in figs. 1a and 2a aggregates of metal crystallites or clusters on the surfaces of the catalysts. On a closer view (figs. 1b, 2b and 3b), however, loosely packed spherical particles of different sizes can be delineated. Side views corresponding to these images establish the essential sphericity of the particles. From figs. 1 and 2, it is seen that the size distribution of the crystallites or clusters depends on the metal loading. Accordingly, the Ag(2 wt%)/HOPG catalyst has crystallites in the 1–3 nm range whereas the Ag(5 wt%)/HOPG catalyst shows slightly bigger crystallites in the 2–5 nm range. The Ag(10 wt%)/HOPG catalyst has crystallites extending upto 10 nm. This trend in the size variation is, however, as expected. In order to quantitatively describe the size distribution of the crystallites with different silver loadings, we have prepared histograms (fig. 3) by measuring the sizes of 50 particles or more

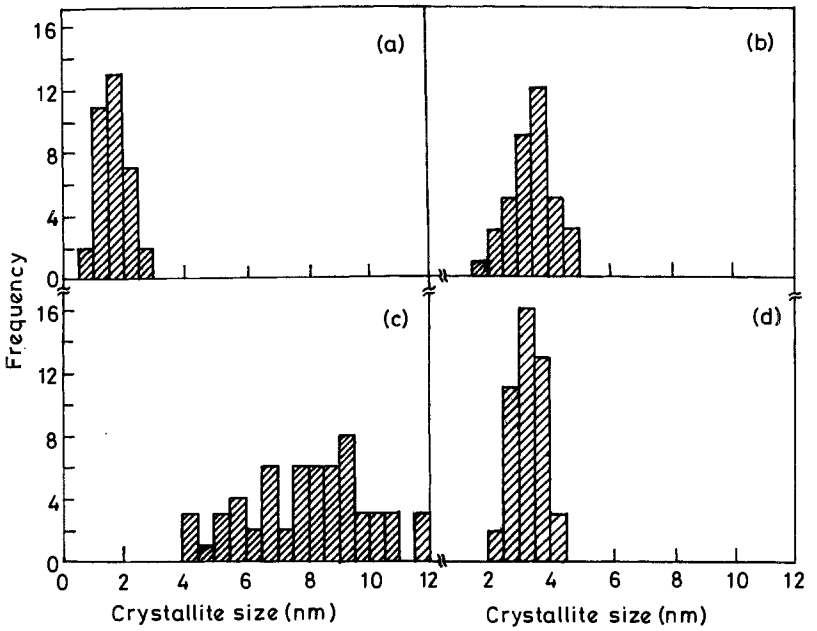

Fig. 3. Size distribution of crystallites in Ag(x wt%)/HOPG catalysts prepared by wet impregnation: (a) 2%, (b) 5%, (c) 10%, (d) chemically reduced Ag/HOPG catalyst.

from different areas of the micrographs. As seen from the figure, the average crystallite size (diameter) is around 2 nm for 2 wt% catalyst. The diameter increases to around 4 nm in the 5 wt% catalyst. Unlike the 2 and 5 wt% samples, (figs. 3a and 3b), the 10 wt% catalyst exhibits a broad distribution (fig. 3c) with an average size of around 9 nm.

STM images of Ag/HOPG catalyst prepared by $NaBH_4$ reduction in aqueous medium showed distinct particles without any agglomeration and the particles seem to be more spherical than those obtained by the wet impregnation method. The particles show a distribution in size in the 2–4 nm range (fig. 3d) with an average size of around 3.5 nm. Interestingly, this distribution is much narrower than in the catalysts prepared by wet impregnation and hydrogen reduction.

We have carried out STM studies on Pt/HOPG catalysts prepared by wet impregnation as well as by $NaBH_4$ reduction in aqueous medium. The crystallites on the surface of these catalysts are more irregular in contrast to the spherical nature of Ag crystallites. The side views indicate raft-like nature of the crystallites protruding out of the surface. The crystallites in the 2 wt% catalyst are in the 2–8 nm range while in the 5 wt% catalyst, they occur in the 5–11 nm range. The histograms in figs. 4a and 4b give an average size of 4.5 and 8 nm respectively for the 2 and 5 wt% catalysts. It is noteworthy that there is a wider size distribution in the Pt catalysts compared to that in the Ag catalysts for a given metal loading.

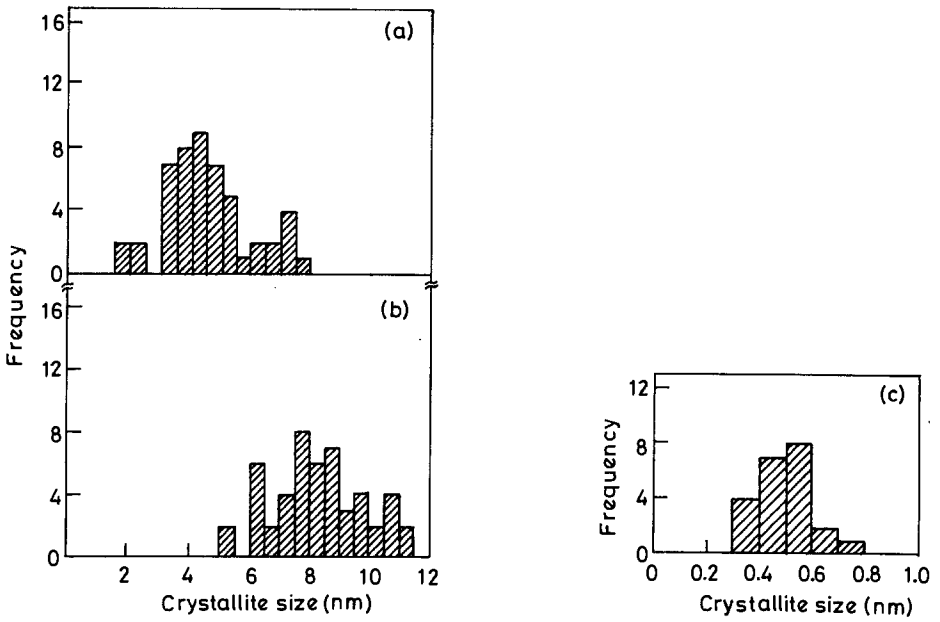

Fig. 4. Size distribution of crystallites in Pt(x wt%)/HOPG catalysts prepared by wet impregnation: (a) 2%, (b) 5%, (c) chemically reduced Pt/HOPG catalyst.

In fig. 5, we show STM images of the Pt/HOPG catalyst obtained by chemical reduction method (soon after the addition of reducing agent). We observe very small crystallites or clusters in the 0.3–1 nm range. The crystallites are spherical in nature unlike those prepared by the wet-impregnation method followed by hydrogen reduction. The histogram in fig. 4c, shows the average particle size to be 0.6 nm.

3.2. STS STUDIES

We have carried out tunneling spectroscopic measurements on metal crystallites pre-selected from the microscopic images of the catalysts. In fig. 6, typical STS data of Ag/HOPG catalysts with 2, 5 and 10 wt% metal loading are presented. In the case of the 2 wt% catalyst, crystallites of $\sim$ 1.4 nm size were chosen for STS measurements. The normalized conductance of such a crystallite showed a reproducible change in slope for a bias voltage of $\sim$ +45 mV. From this plot (fig. 6a), we conclude that there is an energy gap and estimate the gap to be $\sim$ 90 meV, indicating the nonmetallic nature of the metal cluster. On the other hand, the normalized conductance varied monotonically with the bias voltage in the case of the 5 and 10 wt% catalysts, where the measurements were carried out on crystallites of 2.4 and 9.4 nm size, respectively. We therefore note that under reaction conditions, a

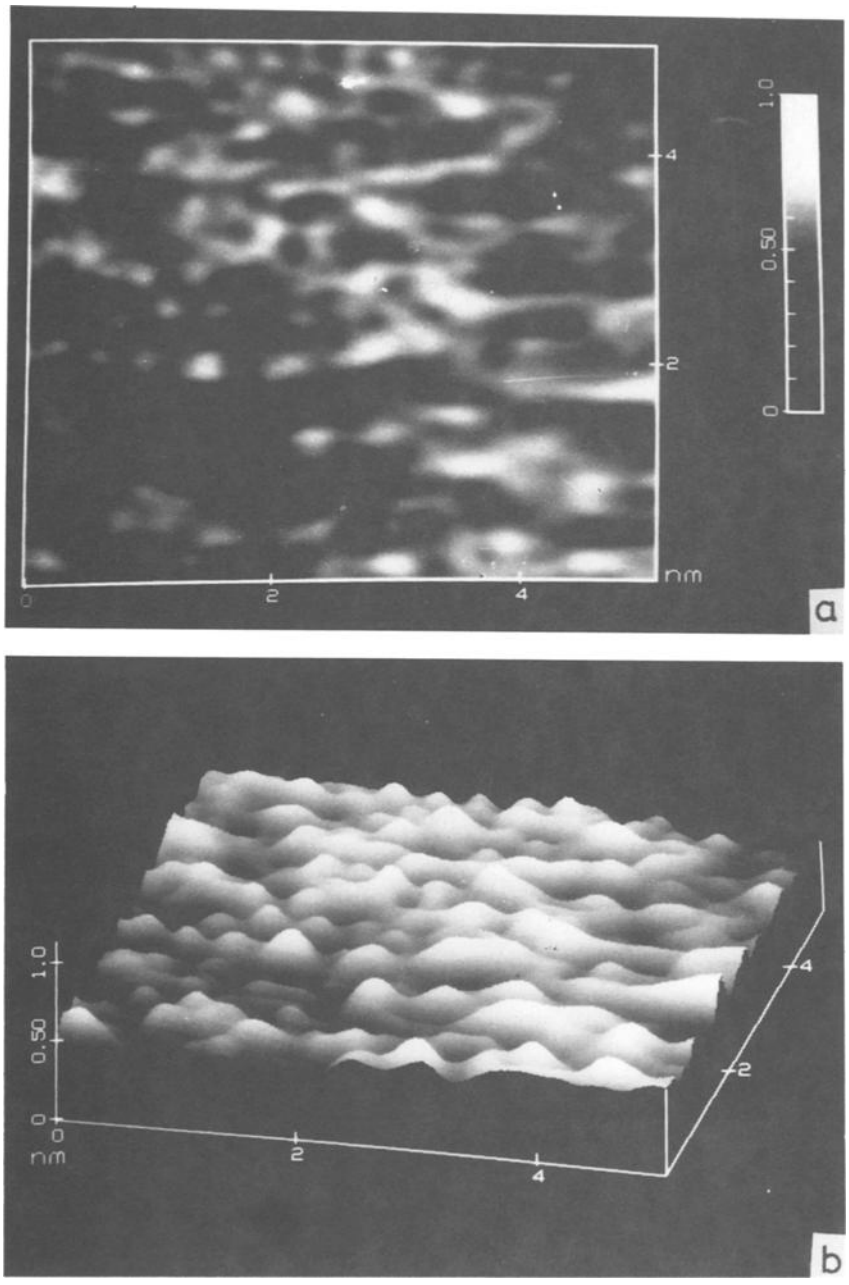

Fig. 5. STM images of chemically reduced Pt/HOPG catalyst: (a) top view, (b) side view.

high proportion of crystallites on the surfaces of the 5 and 10 wt% catalysts would be metallic.

In the case of Pt/HOPG catalysts, we observed earlier that even with 2 wt% load-

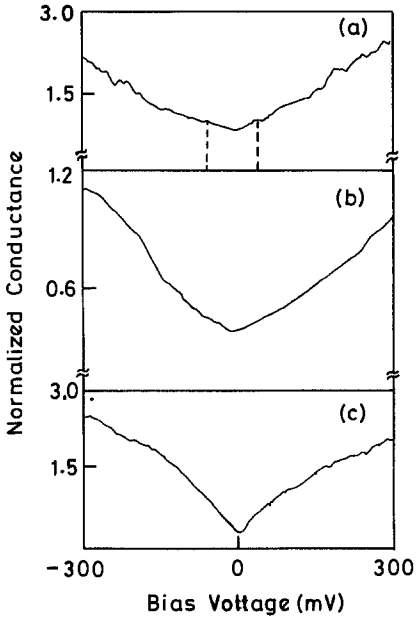

Fig. 6. Variation of the normalized conductance with bias voltage for Ag(x wt%)/HOPG catalysts prepared by wet impregnation: (a) 2%, (b) 5%, (c) 10%.

ing, the crystallites were substantially large. Accordingly, the normalized conductance versus bias voltage curves (fig. 7a) show no evidence of a gap indicating the crystallites to be metallic. On the other hand, a gap of 150 meV is found in the case of the Pt/HOPG catalyst prepared by chemical reduction method (fig. 7b). This is not surprising since the crystallites in this case are quite small ($\sim$ 1 nm).

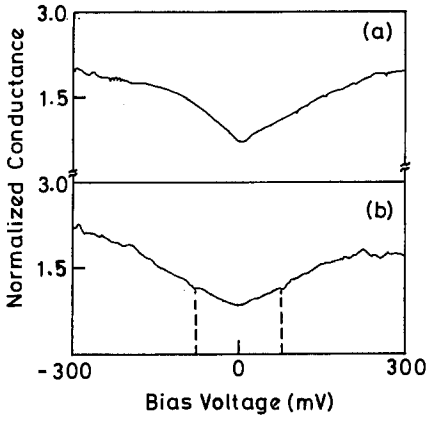

Fig. 7. Variation of the normalized conductance with bias voltage for Pt/HOPG catalysts: (a) catalyst with 2 wt% metal loading prepared by the wet impregnation method; (b) catalyst obtained by chemical reduction method.

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