JOURNAL OF CATALYSIS **163,** 492–495 (1996)
ARTICLE NO. 0351

NOTE

Electrochemical Deposition of Platinum Hydrosol on Graphite Observed by Scanning Tunneling Microscopy

Ligand stabilized metal colloids are discussed as promising candidates for metal catalyst precursors or even supported catalysts (for a review, see Refs. (1, 2)). The protective shell around the metal particles prevents their agglomeration and leads to a highly dispersed metal phase. A narrow metal particle size distribution, as revealed by transmission electron microscopy, is achieved by specific reduction techniques (1, 2). These catalysts are generally prepared by adsorption, i.e., by adding the support material to the colloidal solution, followed by a drying step. Another way to prepare supported catalysts is electrophoretic deposition, which was recently demonstrated for a gold colloid (3). For conductive supports, such as carbon, an electrochemical deposition of colloids can be envisioned also. To our knowledge this has not been investigated yet.

In this note we present, first, the results of a combined scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) study on the electrochemical deposition of platinum nanocolloids with an organic shell (hydrosol) onto highly oriented pyrolytic graphite (HOPG).

STM measurements, both in colloidal solution and in air, were performed with a home-built microscope (4). The sample potential was controlled by a potentiostat; a saturated calomel electrode (SCE) was used as reference (for details, see the figure captions). STM images were obtained with a tungsten tip, in the constant current mode, and the tip was kept at a fixed potential. The platinum colloid, with N(Dodecyl)Methyl$_2$(CH$_2$)$_3$SO$_3$ molecules (denoted SB12) as the protective shell, was synthesized following the procedure described in Ref. (2). An elemental analysis of the colloid powder gave a platinum content of 15 wt%. The colloidal solution was prepared by dissolving the colloid powder (0.5 g/liter) in deoxygenated Millipore® water. HOPG samples were cut with a razor blade directly before being mounted into the electrochemical cell.

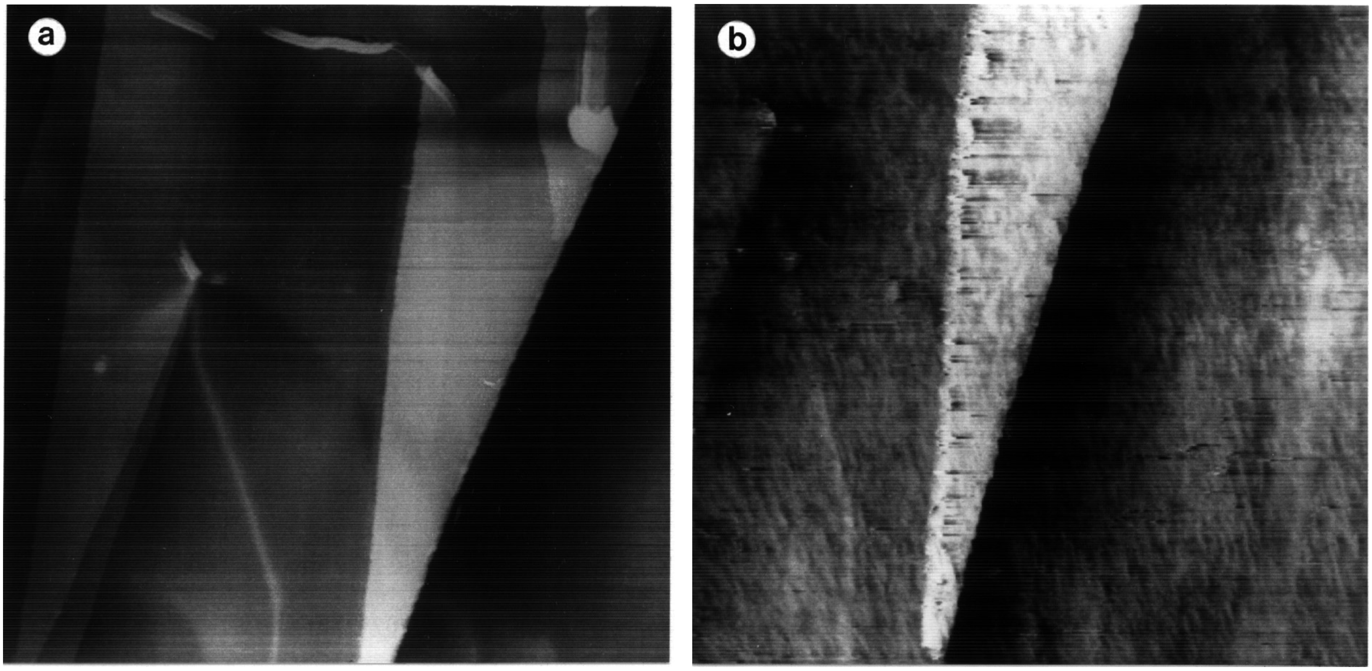

FIG. 1. STM image of the HOPG substrate recorded *in situ* in 10^{-2} *M* Na_2SO_4 and Pt sol solution (see text) (2000×2000 Å^2, $U_{tip} = 0.6$ V, $I_t = 2$ *n*A): (a) at a potential of 1000 mV$_{SCE}$; (b) at 500 mV$_{SCE}$, after a short potential excursion to 1300 mV$_{SCE}$.

0021-9517/96 $18.00

FIG. 2. STM image of the electrochemically treated sample after annealing in vacuum at 500°C for 15 min, recorded in air (2000×2000 Å^2, $U_{tip} = -0.6$ V, $I_t = 4$ *n*A).

Prior to the STM characterization, cyclic voltammograms were recorded in the respective solutions. The obtained curves did not display any specific adsorption peaks, independent of the presence of SB12 or Pt/SB12. The onset of hydrogen evolution shifted towards more positive values, similar to those observed on pure Pt, after an excursion to 1300 mV_{SCE} in Pt/SB12 containing solutions. Similar shifts were not observed in Pt-free solutions. The positive shift of the H_2 evolution is interpreted in terms of hydrogen evolution at deposited Pt/SB12. The cyclovoltammograms did not indicate any additional charge transfer through the double layer. Similarly, no decrease of the double layer capacitance was observed, which is explained by the dielectrical properties of the organic shell molecules.

For the STM measurements, the samples were mounted in the electrochemical STM cell and covered with 3 ml of 10^{-2} *M* Na_2SO_4 solution, at a potential of $+400$ mV_{SCE}. In the entire potential range from -400 mV_{SCE} to $+700$ mV_{SCE} the smooth surface topography characteristic of clean graphite was observed, with large flat terraces of about 200 nm width and monoatomic steps. Addition of 1 ml Pt colloidal solution at a potential of -400 mV_{SCE} into the cell did not cause any changes in the STM images, up to potentials around 1000 mV_{SCE} (Fig. 1a). When the potential was increased up to 1300 mV_{SCE}, the STM images became unstable. After returning to lower potentials, the surface had changed significantly. This is demonstrated in Fig. 1b, which shows a distinct roughening of the

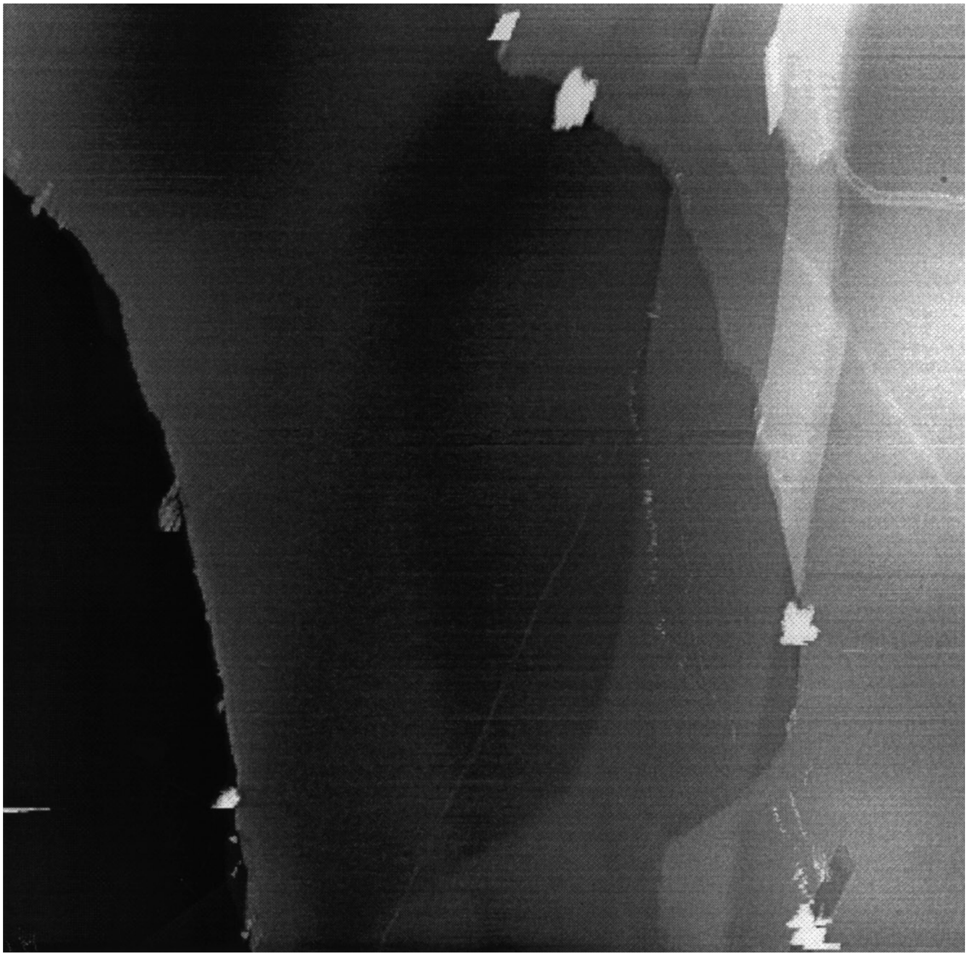

FIG. 3. STM image of "dipped" sample after anealing in vacuum at 500°C for 15 min, recorded in air (2000×2000 Å^2, $U_{tip} = -0.6$ V, $I_t = 4$ *n*A).

terraces. We tentatively attribute this to a densely packed layer of Pt colloid particles/SB12 molecules adsorbed on the graphite surface. This interpretation is supported by XPS measurements (5, 6) which showed a large amount of platinum, equivalent to approximately one monolayer coverage (spectra not shown). In addition, also S, N, and O were detected with their atomic ratios close to the elemental composition of SB12 molecules. This indicates that these molecules adsorb intact. The XPS data also revealed that the Pt surface concentration after this electrochemical treatment is by one order of magnitude higher as compared to samples which have been prepared by dipping HOPG into the same aqueous colloidal solution for 15 min without the application of an external potential. Hence, the combined STM and XPS data clearly demonstrate that Pt colloid particles irreversibly adsorb on the graphite surface at potentials higher than 1000 mV_{SCE}.

After annealing these colloid covered samples in vacuum for 15 min at 500°C, only Pt and C signals were observed in the XP spectra. Apparently, the organic shell molecules had decomposed, and S, N, and O had formed volatile compounds. STM images of these annealed samples, recorded in air, also revealed drastic modifications of the surface morphology. A large number of small particles are detected which are randomly distributed over the surface (Fig. 2). Furthermore, small pits are clearly observed on the graphite surface. These pits, which are not observed without a preceding electrochemical treatment, were most likely created by oxidation of the graphite substrate in the aqueous Pt-sol/electrolyte solution in the very positive potential range (7). The oxidation reaction, which may be accompanied by the evolution of gaseous products such as CO_2, is likely to be responsible for the instability of the STM images under these conditions. The fact that these etch pits are not resolved in *in situ* STM images in solution (Fig. 1b) can be explained by the presence of the colloid adlayer.

As displayed in Fig. 2, the particles are imaged on average about 5 nm in diameter an 4 nm in height, which is close to the particle size of 3 nm observed by TEM (2). The irregular, elongated shape of the observed Pt particles, as well as their preferential orientation in this image, arises from a tip artefact; it reflects the shape of the tip. The comparable particle sizes observed in STM and TEM, indicate that the particles have not sintered after deposition and subsequent annealing; i.e., they are immobilized by the electrochemical deposition. We attribute this to an enhanced interaction between support and colloid particles due to graphite oxidation. Deposition by simply dipping HOPG into colloidal solution, on the other hand, results in significantly weaker interaction: STM images of a “dipped” sample, recorded after subsequent annealing in a vacuum, show much fewer particles, which are generally stabilized by steps (Fig. 3).

In summary, we have shown by direct STM observation that a stable and highly dispersed state of adsorbed platinum on graphite supports can be obtained by electrochemical deposition of platinum hydrosol. This process includes the electrochemical oxidation of the support. It leads to a high platinum surface coverage, much higher than obtained by dipping techniques. Further investigations to elucidate the mechanism of the deposition process are in progress.

ACKNOWLEDGMENTS

The authors gratefully acknowledge Professor H. Bönnemann for kindly providing the platinum colloid. Financial support came from the German Ministry of Education, Science, Research and Technology (BMBF). One of us (Sh. K. S.) thanks the Deutsche Forschungsgemeinschaft for supporting the visit at the University of Ulm by a travel grant (DFG 436 RUS 17/116/94).

REFERENCES

1. Schmid, G., *Chem. Rev.* **92**, 1709 (1992).
2. Bönnemann, H., Brijoux, W., Brinkmann, R., Frentzen, R., Joussen, T., Köppler, R., Korall, B., Neiteler, P., and Richter, J., *J. Mol. Catal.* **86**, 129 (1994).
3. Giersig, M., and Mulvaney, P., *Langmuir* **9**, 3408 (1993).
4. Wiechers, J., Twomey, T., Kolb, D. M., and Behm, R. J., *J. Electroanal. Chem.* **248**, 451 (1988).
5. The XPS spectra were recorded using Mg-K_α radiation and a pass energy of 50 eV.
6. Witek, G., Noeske, M., Mestl, G., Shaikhutdinov, Sh., and Behm, R. J., *Appl. Catal.*, in press.
7. Kinoshita, K., *in* “Carbon: Electrochemical and Physicochemical Properties,” p. 316. Wiley, New York, 1988.

Sh. K. Shaikhutdinov[1]
F. A. Möller
G. Mestl
R. J. Behm

Abtleilung Oberflächenchemie und Katalyse
Universität Ulm
D-89069 Ulm
Germany

Received April 5, 1995; revised April 4, 1996; accepted April 15, 1996

---

[1] Present address: Boreskov Institute of Catalysis, Novosibirsk 630090, Russia.