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Scanning tunneling microscopy study of porous carbon impregnated with palladium chloride

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Mesoporous carbon "Sibunit" impregnated with aqueous solutions of H_2PdCl_4 has been studied with STM. The spontaneous reduction of Pd during the impregnation was confirmed by AES. The surface topography depends on the Pd surface coverage. When the Pd content on the surface is small, particles with an average diameter of ca. 2 nm are frequently observed, which are never imaged on the clean carbon support. When the Pd content is high, the surface still consists of small ca. 3–5 nm particles.

Keywords: carbon supports; Pd / C catalyst; scanning tunneling microscopy

1. Introduction

Scanning tunneling microscopy (STM) has been applied as a powerful tool to many systems modeling catalysts [1,2]. Although many authors underlined the wide potential of this method with regard to catalytic systems, STM investigations of real catalysts are at the starting point [2]. Recently, a few STM studies of model metal catalysts supported on graphite [3,4], oxide and carbide [5–7] and unsupported commercial metal catalysts [8,9] have been published. Nevertheless, as yet real catalysts consisting of highly dispersed metal supported on carbon have not been investigated with STM. The main problem arises from the identification of surface features on the STM images. We believe that much more studies are needed to determine the value of the STM technique for real catalyst systems.

In this paper, STM was applied to the study of the surface morphology of the mesoporous carbon Sibunit impregnated with palladium chloride and used for preparation of Pd/C catalysts.

2. Experimental

Mesoporous carbon Sibunit ($\sim 350\ m^2/g$) [10] was used as the support in granules with an average diameter of 3 mm. Two slightly different pretreatments of supports were used before impregnation. For sample I, the carbon supports were purified by boiling in 17% HCl and 5% HF, washing in boiling distilled water with a small additive of H_2O_2 to remove ferrum admixtures and drying in vacuo at 60°C. For sample II, H_2O_2 was not added. The impregnation with palladium chloride (~ 2 wt% Pd/C) was the same for both samples and performed with aqueous solutions of H_2PdCl_4 for 3 h at room temperature. After the impregnation the samples were washed in distilled water and dried in vacuo at 60°C.

STM images were obtained with a home built microscope based on a UHV chamber (Hochvakuum, Germany) equipped with an Auger spectrometer, mass spectrometer, electron beam or IR-radiation heater, ion guns and sample transfer facilities (for details see ref. [11]). Tungsten tips were prepared from 0.5 mm wire by electrochemical etching in 2 M KOH or NaOH solutions. The calibration of images was performed on graphite (HOPG) and step-like gold foil surfaces. The STM images were obtained in constant current mode on a few granules and cover an area of more than 5 μm^2 on each of them to be representative. Some images were subjected to low-pass filtering.

The surface composition of each granule under study was determined with an AES-spectrometer ESO-03 (S.-Petersburg, Russia) after STM study to prevent possible surface modification by the electron beam. The primary energy and intensity were 3 keV and ca. 10 $\mu A/cm^2$, respectively. AES and STM data were obtained in a vacuum of ca. 10^{-7} Pa. Samples were loaded in a vacuum chamber after several days of storage in dry air, but the Auger spectra were not changed with storage time. No additional surface treatments were done in a vacuum chamber.

3. Results and discussion

Our STM study of some carbon supports [11,12] had shown that the STM working mode was characterized by some peculiarities which were determined by the microstructure of the carbons. A stable tunnel current was obtained after a field desorption procedure only in front of the same carbon sample. Then reproducible STM images were obtained with a higher bias (ca. 5 V) as compared to those commonly used for massive foils and crystals. We had attributed these effects to the adherence to the tip apex of carbon particles which were loosely bound to the carbon surface [12].

The large scale STM images of porous carbon Sibunit show their surface to be very rough and of fractal type. Fig. 1 shows that it is produced by some kind of particles with an average size of ca. 5 nm. We did not succeed to achieve a more detailed structure. Since the samples were granular, the probability of finding an area with the plane perpendicular to the STM tip to investigate the structure with atomic resolution in the manner of, e.g., HOPG was rather small. So, it is still unclear whether these features are produced by graphite-like crystallites or by their amorphous carbon sheet [10,13].

It is known that a spontaneous reduction of Pd adsorbed on activated carbons can occur (see, e.g., ref. [14]). The Auger spectrum of sample II shows (fig. 2) the

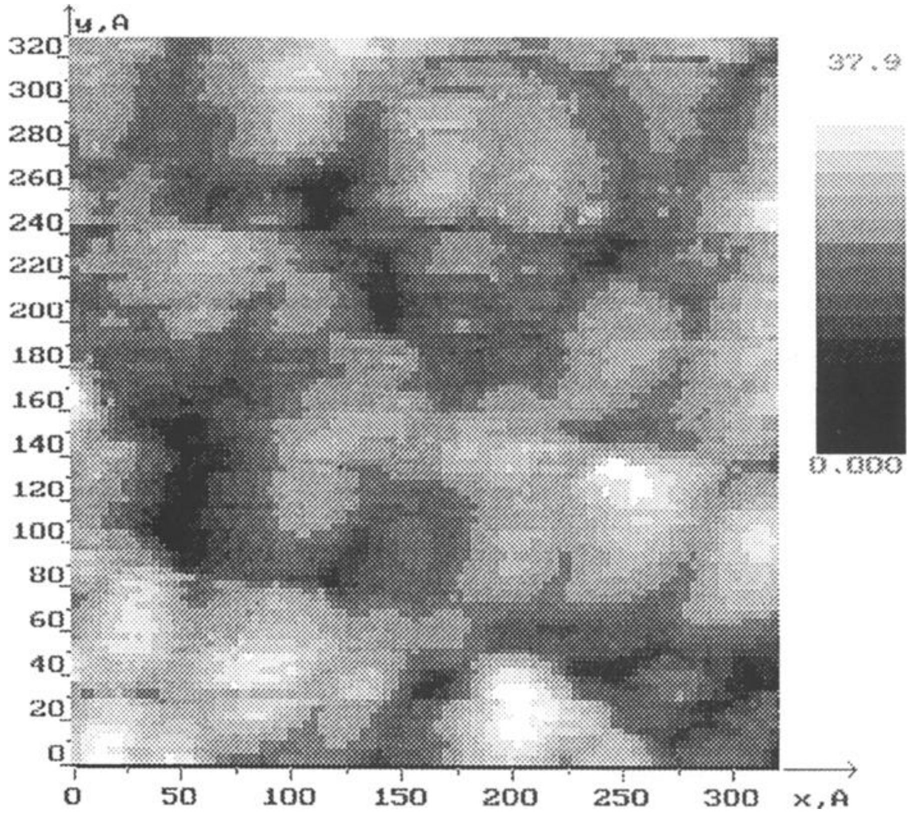

Fig. 1. The STM image of porous carbon support surface. Tunneling setpoints 5 V, 1 nA. The right column corresponds to dark-to-white z-gradation in angström (here and in the following images).

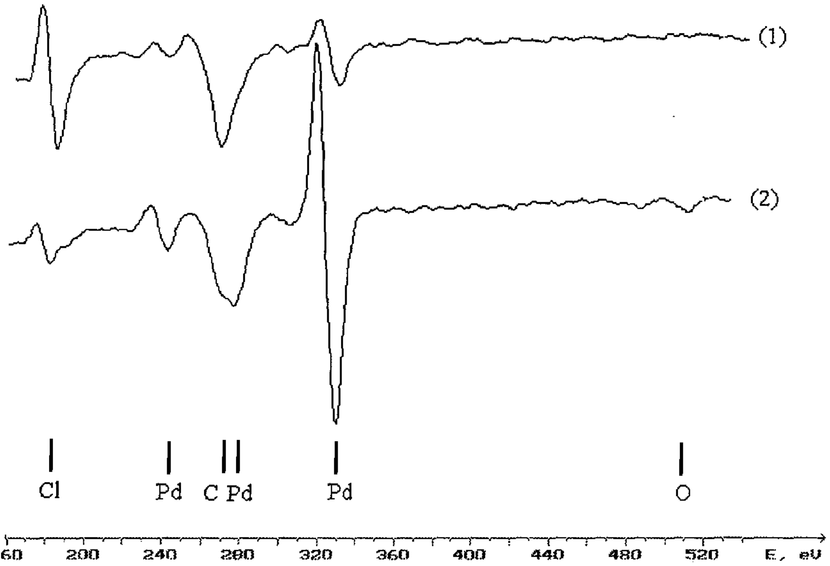

Fig. 2. Auger spectra of the $PdCl_2$ powder mixed with carbon (1) and impregnated sample II (2).

small amounts of carbon and oxygen (the C 272 eV peak overlaps partly with the Pd 279 eV peak). So the AES data indicate that most of the surface (ca. 95% in sample II) is covered by Pd and its derivatives, e.g. $PdCl_2$. To roughly calculate the ratio of the reduced and oxidized Pd on the surface, the AES spectra of pure $PdCl_2$ powder mixed with carbon have been recorded for comparison. Regarding the Pd : Cl intensity ratio in these samples one can suppose that in sample II almost 90% of the surface Pd is in the reduced state. The similar AES spectra of sample I show a low Pd surface coverage (ca. 80% of granule surface consisted of carbon) and a lower content of reduced Pd, ca. 60–80%. (The mechanism of Pd reduction in the impregnation will be discussed elsewhere [16].)

It was surprising, that the adherence effects revealed on the pure carbon supports [12] were also observed in the impregnated samples. Sometimes, the apparent lengthenings of the tip due to a possible sticking of carbon particles to the tip occurred during scanning. Moreover, they occurred more often with sample II than with sample I and pure support. This fact could indicate that the impregnation "glued" somehow the loosely bound particles on the surface. For comparison, STM images were obtained with the same bias and current set points as for unsupported carbon (5 V and ca. 1 nA, respectively).

In general, the impregnation did not change dramatically the large scale surface

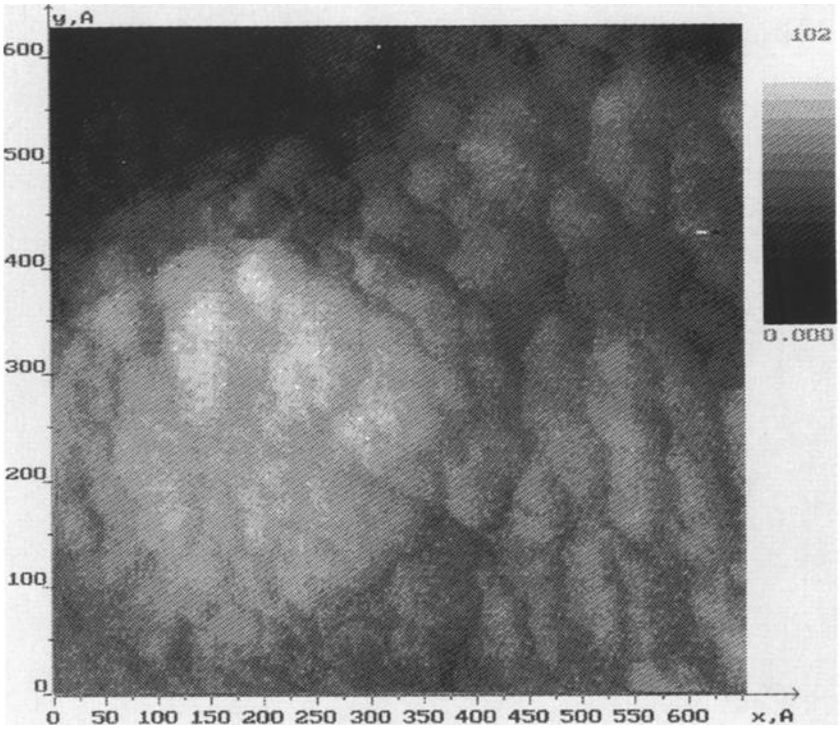

Fig. 3. Typical large scale STM image of the granule surface of the porous carbon Sibunit, impregnated with palladium chloride (sample II).

morphology of both impregnated samples in comparison to the carbon support. Large globules with "snake skin" type structure (fig. 3) were similar to those observed on the carbon support [12]. However, in sample I we could often observe particles of 2 nm in diameter (fig. 4), which we never observed in the pure support (see fig. 1). We believe that this topographic features may be attributed to Pd particles or particles of its derivatives.

Our suggestion becomes more certain when we consider the data obtained in samples II with a high Pd surface coverage. From fig. 5 one can see the highly dispersed surface structure which consists of 3–5 nm hemispherical particles. Since according to AES the surface is mostly covered by reduced Pd, it is reasonable to attribute these features to metal particles.

For sample II X-ray powder diffraction data show the presence of numerous crystallites with average size of ca. 30 nm. However, we have not succeeded to find anywhere large well faceted particles. Moreover, the STM data show clearly that the surface consists mostly of small nanoscale particles. Only once we observed the step-like surface (fig. 6) with step heights of ca. 0.3 nm, but it was unclear whether this feature belonged to the large Pd particle or to the area of the free carbon support surface, since the heights were not measured with sufficient accuracy to assign them an interatomic distance.

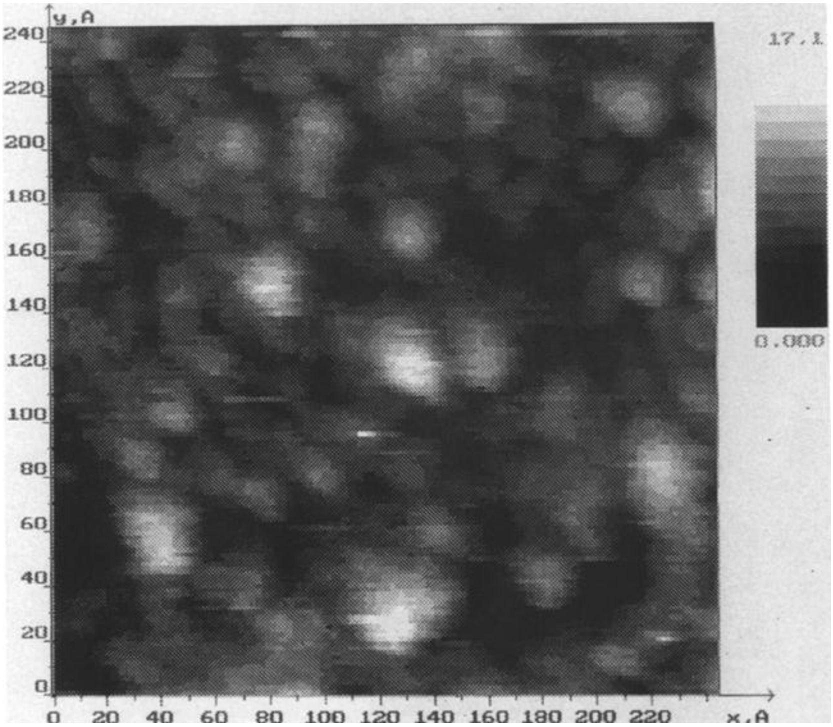

Fig. 4. The STM image of sample I with low Pd surface coverage. Small, ca. 2 nm, features are observed which are absent on the clean support of fig. 1.

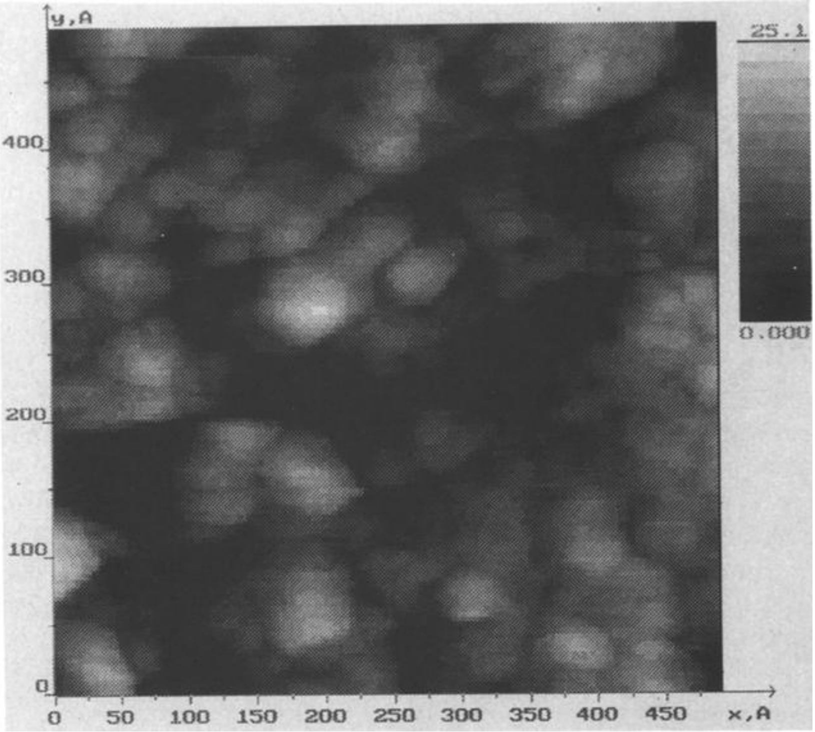

Fig. 5. The STM image of sample II with high Pd surface coverage.

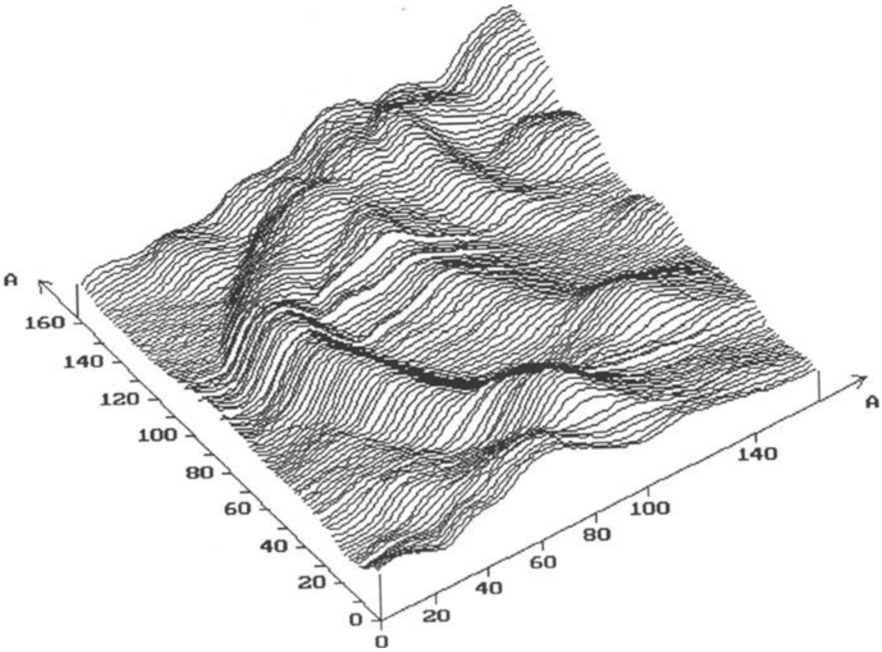

Fig. 6. A step-like surface structure in sample II. Isometry view. The step heights are ca. 0.3 nm.

4. Conclusions

Our results demonstrate that STM images of heterogeneous catalysts are really hard to interpret with regard to the chemical identification of STM image features. However, when the sample surface is partially covered by a supported component, its STM visualization is based on the different size or roughness of component and support. When the surface coverage is high, it is reasonable to attribute the observed features to the supported phase.

The spontaneous reduction of Pd during the impregnation of the mesoporous carbon Sibunit by H_2PdCl_4 is confirmed by AES. The surface topography revealed by STM depends on the surface content. When the Pd content on the sample surface is small, particles with an average diameter of 2 nm are frequently observed, which are never imaged on the clean carbon support. When the Pd content is high, the surface structure still consists of the small $\sim$ 3–5 nm particles. So, in both cases the metal surface area in the impregnated samples is likely to be determined by small particles.

Thus, STM studies really can provide useful information about the surface structure of the catalyst and can be used for its characterization, especially in combination with other surface techniques.

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