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Hexagonal or Quasi Two-Dimensional Palladium Nanoparticles—Tested at the Heck Reaction

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This paper deals with the occurrence of quasi two-dimensional palladium nanoparticles (hcp structure, 53 nm in average lateral dimension, approx. 37 wt% Pd) encapsulated into graphite. Microphotographs showed that the nanoparticles occurred in the interlayer spacing of graphite. Raman spectroscopy of Pd–graphite showed absolutely no charge-transfer interaction between Pd nanoparticles and the carbon lattice. The Pd nanoparticles proved to be active catalysts for the Heck reaction. In this test reaction a halobenzene reacts with styrene to form diphenylethene (stilbene). Although no interaction between nanoparticles and the carbon lattice occurs, the nanoparticles remain inside the carbon lattice after the Heck reaction. They could be not washed out; therefore, the catalyst is stable.

Key Words: **graphite intercalation compounds; palladium; nanoparticles; low-dimensional compounds; Heck reaction C–C coupling reaction; stilbene synthesis; stability of catalysts; quasi two-dimensional; transmission electron microscopy; Raman spectroscopy.**

INTRODUCTION

Palladium is a well-known catalytically active metal, e.g., (1–5). Only the face-centered cubic (fcc) modification exists, and this type of palladium is paramagnetic. Theoretically it has been predicted that ultrathin palladium or clusters of well-defined sizes should be ferromagnetic (6–8).

Graphite can be intercalated by several metal chlorides [e.g., $TaCl_5$ (9), $PdCl_2$ (10), $SeCl_4$ (11), or $NiCl_2$ (12)]. The formed graphite intercalation compounds (GICs) are layered materials with alternating graphene (IUPAC nomenclature of a single carbon layer with graphitic character) and guest layers. Such metal chloride GICs can be reduced by hydrogen gas (13, 14) to form metallic nanoparticles encapsulated into graphite. Palladium nanoparticles have been produced by reduction of a $PdCl_2$–GIC precursor (15–20). All of these palladium nanoparticles showed the common fcc structure of palladium and they were too thick to have the theoretically predicted size for ferromagnetism. However, such palladium nanoparticles are still in use as catalysts for hydrogenation and isomerization reactions (15–20).

Recently, quasi two-dimensional palladium nanoparticles (average lateral dimension 53 nm, thickness of a few layers) were prepared by reduction of a $PdCl_2$–GIC precursor by hydrogen gas at 400°C (20). The sample showed hexagonal, cubic, and intermediate bodies (20). The selected-area electron diffraction (SAED) pattern showed mixed cubic and hexagonal reflection (20).

A magnetic study on the sample with the encapsulated quasi two-dimensional nanoparticles (20) showed for the first time the theoretically predicted ferromagnetic offset in palladium (21). This study supports the conclusion that the observed particles are quasi two-dimensional and the axis ratio of lateral dimension to thickness is 24–70 (20). Hexagonal close-packed (hcp) palladium is not a new modification; it is an abnormal state, kinetically conditioned by the reduced dimension of the bodies. The hcp particles transform into fcc particles by growing in thickness (20). Recently, hcp Ni nanoparticles (<4 nm) have been observed; all larger Ni nanoparticles occurred in the common fcc structure, while the SAED pattern showed mixed hcp and fcc reflections (22).

Support–metal interactions are important for several catalytic reactions. The current work applied Raman spectroscopy to investigate a possible charge-transfer interaction between carbon and palladium in the precursor compound as well as in the case of encapsulated quasi two-dimensional nanoparticles. Transmission electron microscopy (TEM) is applied to demonstrate where the nanoparticles are localized before and after the interaction by using the flakes as catalyst. The question is whether the nanoparticles are immobilized or could be washed out, which would destroy the catalyst. Common GICs tend to deintercalate by contact with a humid environment (e.g., 23,

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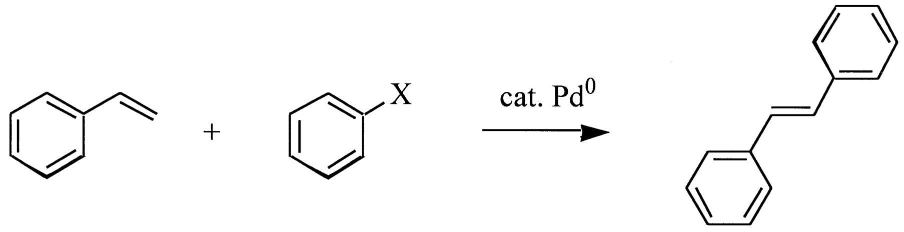


1 **2a**: X = I **2b**: X = Cl **3**

SCHEME 1. Heck reaction of styrene (**1**) with halobenzenes (**2**).

24). In order to test the catalytic activity of this special type of nanoparticles we chose the Heck reaction (1), shown in Scheme 1.

Styrene (**1**) reacts with a halobenzene (**2a**, **2b**) to form stilbene (diphenylethene) (**3**). This is the most intensely studied Pd-catalyzed process. Until now, the Heck reaction has not been an important industrial process, because an active and cheap catalyst is not available, but the Heck reaction has some technical interest. Normally this important C–C coupling process is performed as a homogeneously catalyzed reaction, but it is well known that palladium on graphite is also a suitable catalyst (2). However, it is still a matter of debate whether the latter case is indeed a heterogeneously catalyzed reaction or the active catalyst results from partial solubilization. Recently, palladium clusters were found to be especially active catalysts for the Heck reaction, even suitable for notoriously unreactive aryl chlorides as coupling components (3–5). With regard to the topical interest in catalysts for the Heck reaction, we assume that testing quasi two-dimensional Pd nanoparticles is important as a way to gain insight into the special case of a heterogeneously catalyzed Heck reaction.

METHODS

$PdCl_2$ was mixed with natural graphite (grade RFL 99.9-S) from Graphitwerke Kropfmühl, Hauzenberg, Germany, or highly oriented pyrolytic graphite (HOPG) (grade ZYA) from Advanced Ceramics Corp., Cleveland, OH. The ampoules with the mixtures were evacuated and chlorine gas was condensed in each ampoule, 500 mbar measured at room temperature. After the ampoules were sealed, the mixtures were heated at 500°C for 1 week. The success of intercalation was proved by X-ray diffraction (XRD) as well as by Raman microscopy. The $PdCl_2$–GICs were reduced at 400°C in a hydrogen atmosphere. The reduction was proved by XRD and SAED and nanoparticles were observed by TEM. Scanning tunneling microscopy (STM) was used to detect whether palladium nanoparticles are located at the surface of the flakes.

A Hitachi H-9000 transmission electron microscope was operated at 300 kV accelerating voltage (LaB_6 cathode). Raman measurements were performed by using a T64000 Raman microscope from Jobin Yvon. Measurement conditions were laser power 20 mW ($\lambda = 514.5$ nm) and sample collection time 30 s (every spectrum is the average of 10 scans at 30 s collection time). All investigations were done at room temperature in air, with a lateral resolution of 1 μm. Reference material was pristine HOPG; E_{2g} mode of HOPG, 1582 cm^{-1}. A Nanoscope III STM was operated in air, and commercially available Pt–Ir tips were used. Scan ranges varied between 11 μm and 5 nm.

The Heck reaction was performed with RFL 99.9-S natural graphite flakes from Graphitwerke Kropfmühl; the Pd content was approximately 37 wt%. We tried the Heck reaction of styrene (**1**) with iodobenzene (**2a**) on a 1-mmol scale [1 mmol of styrene, 2 mmol of iodobenzene, 4 mmol of potassium carbonate, 2 mmol of tetra-*N*-butylammonium bromide, 10.2 mg of the quasi two-dimensional palladium particles encapsulated in graphite (37%), 10 ml of dry dimethylformamide, sealed tube, 100°C, 4 days]. The catalyst was recovered from the reaction mixture by filtration and rinsed with dichloromethane, water, and acetone.

RESULTS AND DISCUSSION

Figures 1a–1c show bright field TEM images of an as-prepared sample with Pd nanoparticles encapsulated into graphite. Figure 1a is an overview; the image shows that the flake is heavily loaded with nanoparticles, and most of them are encapsulated into the flake. Figure 1b shows a detail of the prismatic edge. Nanoparticles are located directly at the edge of the flake; they are mostly encapsulated, but some smaller parts remain outside. Figure 1c is a detail photograph of totally encapsulated particles. By arrows two particles are marked; one of them is quite perfectly cubic and the second is more hexagonal. The cubic body shows no transparency; therefore, these particles should be thicker. The hexagonal body shows high transparency and an underlying particle can be clearly distinguished. All three TEM images show that larger cavities exist between the nanoparticles; in most cases particles are separated with respect to each other. Additionally, the surfaces of several flakes were

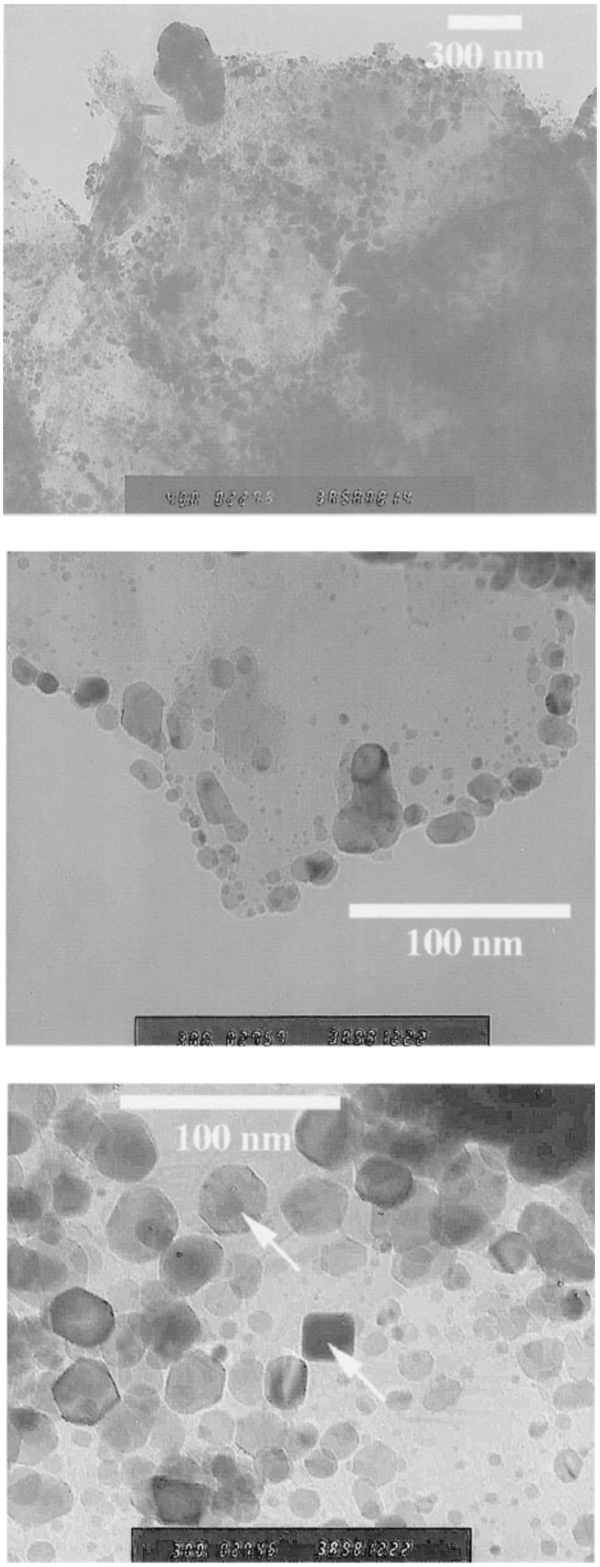


FIG. 1. All images were obtained on as-prepared catalysts. (a) Overview TEM bright field image. (b) Detail photograph of a prismatic edge. (c) Totally encapsulated nanoparticles. Arrows refer to an almost perfect cubic crystal and to a hexagonal particle. The contrast and therefore the thicknesses are different. The cubic particle occurs almost dark (thick); the hexagonal particle is transparent (thin).

investigated by STM to detect nonencapsulated nanoparticles or palladium atoms on the basal face. It was not possible to observe palladium nanoparticles or atoms by STM. On the other hand, atomic resolution of graphite could be obtained. This leads to the conclusion that the particles observed by TEM are really encapsulated inside the graphite lattice. Of course, not all surface areas could be investigated by STM, but a high surface contamination can be ruled out.

Figure 2 shows the Raman spectra of the $PdCl_2$–GIC (host material, HOPG) precursor, the Pd–graphite (carbon material, HOPG) sample, and as reference pristine HOPG. An ordinary intercalation compound is characterized by a host–guest interaction. Therefore, graphene layers directly adjacent to an intercalate layer (charge-transfer interaction between the layers) show bands upshifted with respect to those of pristine graphite (25). In the case of third or higher stages, two distinguishable graphene sheets exist. Sheets with an adjacent guest layer show a pronounced upshift with respect to the bands for graphite. Graphene layers with no adjacent guest layer generate a second band near 1582 cm^{-1}; a small upshift is possible (25). As one can see from Fig. 2 and Table 1, the $PdCl_2$–GIC precursor shows such bands. The upshift of the upper band is 26 cm^{-1} (Table 1); this is relatively low for metal chloride GICs (25, 26). On the other hand, Pd–graphite shows only one band in this region and its position is shifted back to that of the band for pristine HOPG. The second band in the spectrum of Pd–graphite occurs at 1360 cm^{-1} (Table 1); this is the so-called D-band. These bands are due to disorder in carbon materials. The formation of nanoparticles in the interlayer space produces some stress and cracks in the carbon lattice. It should be noted that regions without a D-band could be observed by Raman microscopy also. Due to the shift back to graphite (the so-called G-band), it was apparent that the Pd–graphite sample no longer showed a charge-transfer interaction between Pd and carbon (Table 1). From this point of view, the material can no longer be described as an ordinary graphite intercalation compound. Normally it is expected that nanoparticles are only encapsulated into graphite, without any interaction with the carbon

TABLE 1

Raman Data Obtained from Fig. 2

Substance	Position (cm^{-1})	Explanation
$PdCl_2$–GIC	1608	graphene layer adjacent to guest layer, CT
	1589	graphene layer adjacent to another graphene layer
Pd–graphite	1583	shift back to the carbon position, no CT
	1360	D-band due to increasing disorder (cracks)
Pristine HOPG	1582	reference material

Note. CT = charge transfer.

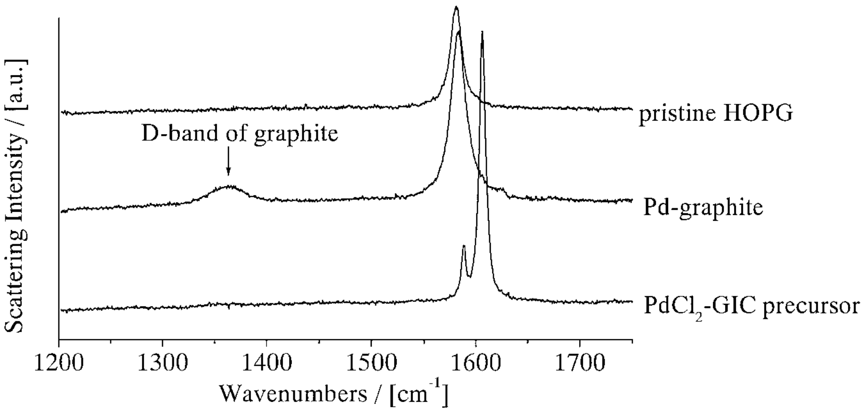


FIG. 2. Raman spectra of a $PdCl_2$–GIC precursor, Pd–graphite (nanoparticles), and pristine HOPG. The Pd–graphite sample shows definitely no charge-transfer interaction between palladium and carbon (see text). The D-band is due to increasing disorder in carbon.

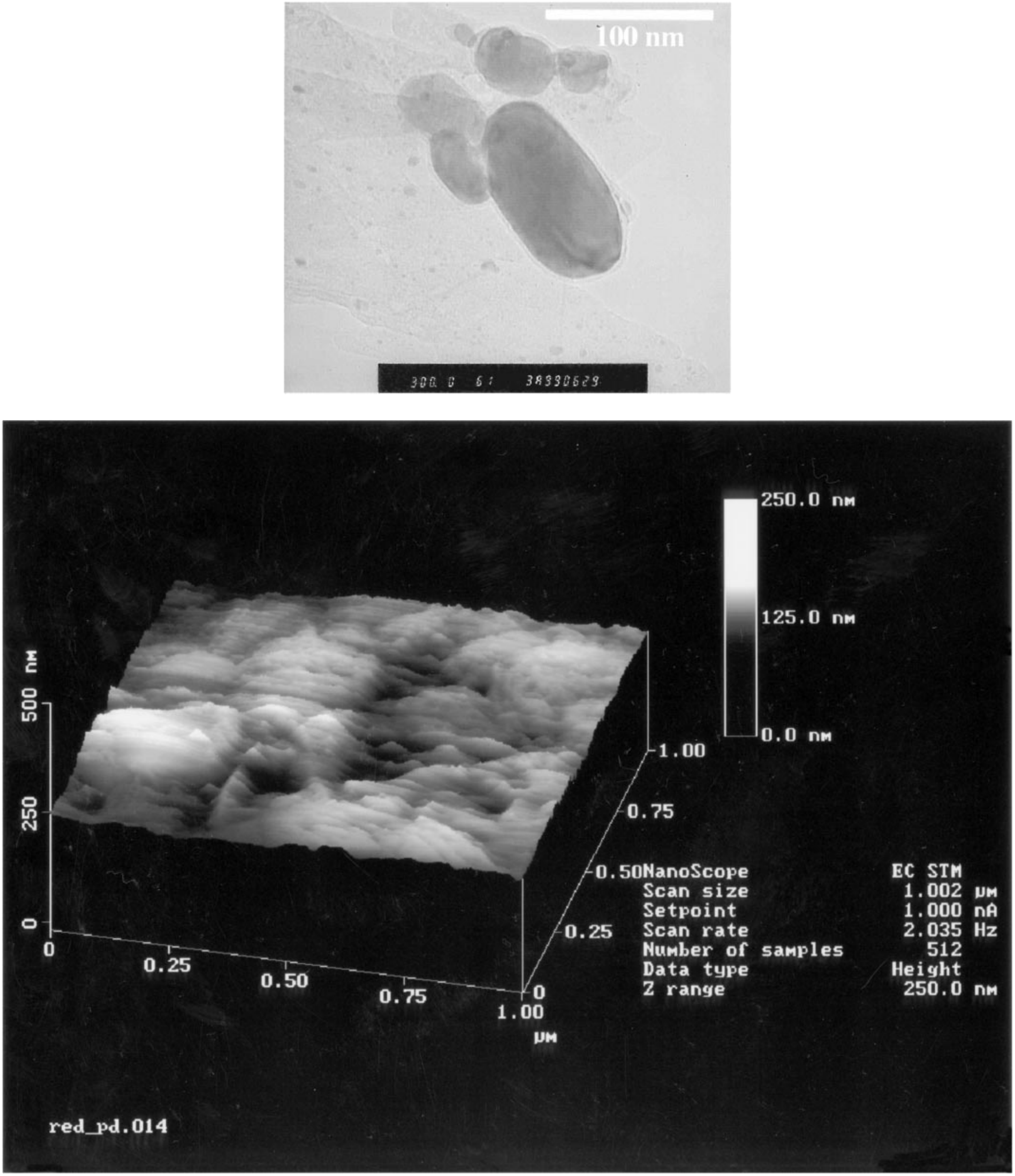
material; for this reason such compounds are also called "graphimets" or metal graphites to distinguish them from ordinary GICs. However, low-dimensional Pd in a hcp form has never been observed before. The question remains whether this phase is still separated from the carbon (stable for itself), as in the case of fcc Pd nanoparticles, or experiences a charge-transfer interaction with the carbon. This finding is supported by STM measurements. It was not possible to observe palladium nanoparticles or palladium atoms on the basal plane by STM; no signals even from particles beneath the first graphene sheet could be gathered. Therefore, the particles should be electronically separated from the carbon. On the other hand, with common GICs it is possible to observe the superstructures of guest with respect to the carbon host lattice (27, 28).

As one can see, these particles are electronically totally separated; no force exists to keep them inside the interlayer spacing of graphite. This raises the next question. How stable are such materials in liquids at higher temperatures? Common graphimets were in use for gas-phase reactions (17) only. It is well known that GICs hydrolyze by contact with humidity and deintercalate (e.g., 23, 24). In other words, if the CT interaction breaks down, the deintercalation of hydrolysis products starts. As a catalyst for the Heck reaction the flakes with the encapsulated particles are exposed to several liquids (including water by washing). It is important to test how environmentally stable such encapsulated nanoparticles are during such treatment. If the nanoparticles remain stable inside the carbon lattice, they can be used as a catalyst. If they can be washed out, the catalyst would be destroyed by the treatment.

For this reason we performed the Heck reaction to test (i) how chemically active the sample is and (ii) how stable the catalyst is. After two runs (chlorobenzene and iodobenzene) the flakes were investigated by TEM again. The exposure time (see below) was long enough, compared to GICs (23, 24, 26), to detect possible decomposition.

Figure 3a shows a bright field TEM image of the catalyst after it was used in two runs. Of course, the observed areas after use of the flakes are not identical with the thin slices from the as-prepared compounds. However, we have many more TEM images than could be shown here. All of our images show that the nanoparticles remain stable inside the graphite interlayer space, to an overwhelming extent. They were not washed out by the high-temperature treatment in dimethylformamide at 100°C for 95 h nor by washing of the flakes with water and various organic solvents. No significant differences between thin slices of as-prepared and exposed catalysts could be observed. The reason for the different stabilities of GICs and metal graphites is likely that the hydrolysis products of GICs are monomers or oligomers (9, 23), which gives them the possibility of diffusing out of the host material. On the other hand, nanoparticles are too large to move by diffusion; this could explain their immobile behavior. Figure 3b shows an STM image; the basal plane is highly affected by partly swelling and groove formations, and no palladium particles or atoms can be observed at different scan sizes (5 nm–11 μm).

In order to test the catalytic activity of the sample we tested the Heck reaction with iodobenzene (**2a**). By flash chromatography an 82% yield of the coupling product stilbene (**3**) was isolated; in contrast, with chlorobenzene (**2b**) no coupling product at all was observed. Clearly, our sample is an active catalyst for the Heck reaction, but it is somewhat less reactive than the palladium cluster introduced by Reetz and Lohmer (3). Most importantly, TEM investigation of the recovered catalyst revealed that it was unchanged and therefore completely stable under the relatively vigorous reaction conditions applied. No Pd particles or atoms could be detected on the surface by STM. Of course not all of the surface area, especially at the prismatic edges, could be observed. It is worth mentioning that the flakes showed catalytic activity after two runs, in which the treatment was quite harsh. However, we cannot give conlusive evidence that the reaction occurs in the interlayer



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NanoScope                 EC STM
Scan size                 1.002 µm
Setpoint                  1.000 nA
Scan rate                 2.035 Hz
Number of samples           512
Data type                 Height
Z range                   250.0 nm
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FIG. 3. (a) Particles at the prismatic edge after two runs as catalyst, TEM bright field image. (b) A STM image of the basal plane. Palladium cannot be detected by STM; the carbon lattice is hardly affected (mountain-like topograhy). Different scan sizes (5 nm–11 μm) gave no hint of surface contamination by Pd atoms or particles.

space of graphite. Reactions in the interlayer space of graphite are controversial. Some papers reported that only small molecules such as oxygen diffuse quickly into the graphimet layers (29, 30). These authors assume in their work that the nanoparticles would form a monolayer with the thickness of Pt atoms (280 pm) (29). Considering theoretical calculations (6) which predict ferromagnetism in Pd for 2–5 layers and our experimental work which showed ferromagnetism (21), we assume a thickness of at least 2–5 layers for nanoparticles. If we assume that a Pd atom shows a van der Waals radius of 145 pm, the expansion of the interlayer space is between 580 and 1450 pm. On the other hand, stilbene shows a thickness of 335 pm (thickness of a graphene sheet), assuming that the molecule is not twisted. Even if the stilbene is twisted, there should be enough space in the interlayer space for all reactant molecules to move. The STM image (Fig. 3b) shows that the graphene surface is no longer smooth. Different thick nanoparticles beneath the surface lead to the mountain-like topography.

It is well known that lithium diphenylide reduces metal chloride GICs very quickly and LiCl goes out of the carbon lattice (10). Some papers reported oligomerization (e.g., benzene or ethylene) reactions in the interlayer space of graphite (31–35) or polymerization reactions (36). A general problem with GICs is that they decompose in a humid environment. In other words, hydrolysis products deintercalate out of the host lattice (9, 23), and molecules thick in comparison to stilbene can migrate into the interlayer space of graphite.

A second possibility is that some Pd atoms remained as surface contaminants, and they are the active sites. The concentration of such surface contamination should be not very high, and these contaminants should be at least partly removed by the treatment (washing). As noted before, after the second run we observed high reactivity.

A third possibility could be that particles near prismatic edges remain partly outside the graphite lattice; such uncovered areas could be the active sites. The surface area of such particles is certainly not very high. Currently, nobody knows the catalytic activity of hcp (ferromagnetic) palladium particles compared to that of fcc (paramagnetic) palladium. If the reactions were performed on these nonencapsulated areas the activity would be extremely high. However, the activity of this sample is really astonishing, and we cannot give conclusive evidence about which part of our sample is the active center. We believe that most likely it is the interlayer space, because the concentration of Pd(0) is much higher than in all other theoretically possible active centers.

CONCLUSION

The quasi two-dimensional encapsulation of palladium nanoparticles into carbon shows no charge-transfer interaction between the palladium and the carbon lattice. Therefore, this system can be described as palladium metal dispersed (encapsulated) in the interlayer spacing of graphite. The nanoparticles remain immobile because of their relatively large sizes and high masses. Such particles are not able to diffuse out from the carbon lattice. This behavior is an important difference from common GICs.

It could be concluded from the evidence obtained by STM and TEM that the particles are encapsulated into the carbon lattice. Only some particles near the prismatic edges remain partly outside. Currently, it is not possible to determine definitely whether the reaction occurs on the partly embedded particles, located at the prismatic face, or in the interlayer space of graphite, similar to zeolites. The catalytic activity was tested for the Heck reaction, confirming that these flakes can be classified as active and stable catalysts. The activity of the particles cannot be explained by a metal–support interaction because no charge transfer exists between carbon and palladium. Compared to common catalysts, the particle size [on average 53 nm in lateral dimension (20)] is very large and the surface could be relatively low. However, the occurrence of ferromagnetism in the sample (21) shows that the electronic states are different from those of common bulk (fcc) particles. The catalytic activity seems to be attributable to the low dimensionality of the metal particles.

Generally three distinguishable possible active centers could exist: (a) Pd(0) particles exist in the interlayer space, where the expansion of the interlayer space is larger than that in other graphimets (29, 30). Reactants could move between the lamellae. (b) Some flakes at the prismatic edge could remain partly outside of the graphite lattice. The surface area of such partly uncoated particles is low. If the active site is located there, the particles should show an astonishing activity. However, the activity of hcp (ferromagnetic) Pd compared to fcc (paramagnetic) Pd is unknown. (c) Some Pd atoms could remain as surface contaminants at the prismatic edges. Such Pd(0) atoms could be the active sites. Their concentration should be low, and they should be very likely washed out by the treatment. It was proved that the catalysts are active in the second run.

Once again, we cannot definitely locate the active site in our system, but we have shown that the flakes are active catalysts for the Heck reaction.

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