Shape-selective catalysts: quasi-two-dimensional Pd-particles encapsulated in graphite

Ágnes Mastalir [a],*, Zoltán Király [b], Jürgen Walter [c], Ferenc Notheisz [a], Mihály Bartók [a]

[a] *Department of Organic Chemistry, University of Szeged, Dóm tér 8, H-6720 Szeged, Hungary*
[b] *Department of Colloid Chemistry, University of Szeged, Aradi vt. 1, H-6720 Szeged, Hungary*
[c] *Department of Materials Science and Processing, Osaka University, 2-1 Yamada-oka, Suita 565-0871, Japan*

Abstract

Pd–graphites were prepared by reduction of $PdCl_2$–graphite intercalation compounds ($PdCl_2$–GICs). Transmission electron microscope (TEM) measurements on the samples indicated that Pd nanoparticles with a wide size distribution were formed, mostly encapsulated inside the graphite host. The quasi-two-dimensional character of the Pd nanoparticles was confirmed by H_2 sorption studies, which revealed the absence of β-hydride formation over a broad range of pressure. Although the structures of the three Pd–graphites studied were very similar, differences were found between them in terms of their catalytic performance in the gas-phase reactions of 1-butene, *cis*-2-pentene and cyclohexene. It was established that the transformations of both 1-butene and *cis*-2-pentene took place in the interlamellar space of the graphite, whereas, in consequence of the the non-planar character of the substrate, the diffusion of cyclohexene between the graphite layers was sterically hindered. This molecular sieving effect implies that the Pd–graphites may be regarded as shape-selective catalysts. Pretreatment at 473 K was found to lower the catalytic activities considerably. The experimental evidence indicated that restructuring of the Pd crystallites resulted in a moderate aggregation of the active Pd-particles available for the reactant molecules. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Graphite intercalation compounds (GICs) are formed by inserting layers of atoms or molecules of a guest species between layers of the graphite host [1,2]. Graphite may be intercalated by a variety of compounds, including metal halides [3]. GICs containing metal halides as intercalates may be used as catalysts, organic reagents or precursor materials of finely dispersed metal particles intercalated in graphite [4–8]. Transition metal–GICs (graphimets)

prepared via the reduction of transition metal chlorides intercalated in graphite [9,10] have been found to be efficient catalysts in a number of organic reactions [11–14]. The reduction of metal halide GICs may also result in the formation of metal–graphite systems containing low-dimensional metal nanoparticles [15]. Alternatively, metal–graphites have also been prepared by the addition of metal halides to C_8K [16,17]. A recent paper reported on the formation of platinum nanosheets intercalated in graphite, obtained by the reduction of $PtCl_4$–GICs [18]. Carbon- and graphite-nanofiber supported noble metal catalysts were found to be efficient for alkene hydrogenation and *n*-hexane isomerization, respectively [19,20]. The

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* Corresponding author. Fax: +36-62-544200.
E-mail address: mastalir@chem.u-szeged.hu (Á. Mastalir).

transition metal–graphite systems are of particular interest because of their potential as hydrogenation catalysts [21–23].

It was previously assumed that Pd–graphite compounds prepared via the reduction of a $PdCl_2$–GIC precursor [23] may be suitable for H_2 storage. In order to clarify this point, H_2 sorption measurements were carried out and evaluated in the present study. Further, the catalytic activities of Pd–graphites were studied in the gas-phase reactions of 1-butene, cis-2-pentene and cyclohexene. The effects of thermal treatment on the catalytic performance were additionally investigated.

2. Experimental

$PdCl_2$ was mixed in an ampoule with crystallized natural graphite flakes from Kropfmühl, Germany. After evacuation, Cl_2 gas was introduced and the mixture was heated at 773 K for 7 days. The reduction of $PdCl_2$–GIC was performed in a H_2 stream of $300 \, cm^3$/min for 24 h [23]. Three Pd–graphite samples were used for further investigations: Pd1, Pd2 and Pd3, reduced at 623, 673 and 873 K, respectively. The Pd loading of each sample was 37%.

The Pd–graphite samples were characterized by means of transmission electron microscope (TEM) measurements, by using a Philips C-10 TEM operated with a LaB_6 cathode at 100 kV. The samples were dispersed in hexane and mounted on a Cu grid. The mean particle diameters d were calculated as number average values $(\sum n_i d_i / \sum n_i)$ from the magnified TEM images, for 200 particles on average.

The H_2 sorption isotherms of the Pd–graphites were determined at 298.15 ± 0.04 K in the range 0–106 kPa by using a Micromeritics Gemini 2375 automated gas sorption apparatus. For comparative investigations, Pd–graphimet (1% Pd in graphite, a product of Alfa Chemical Co.) was employed. Before use, ca. 0.5 g of the sample was pretreated in the sorption vessel in static H_2 at 353 K for 1 h, followed by evacuation for 2 h ($p < 0.1$ Pa), and then for a further period of 2 h at 298.15 K. H_2 dosing was performed by sequential increase of the pressure with small pressure increments. The stepwise (cumulative) measurements, made in the scan mode, were controlled by Gemini software. More experimental details on the study of H_2 sorption on Pd–graphimet and carbon-supported

Pd, including microcalorimetry, have been published previously [24–26].

The catalytic test reactions were performed in a static recirculation reactor system operated at 298 K. The mass of catalyst was 5 mg. Before reactions, the samples were pretreated in 13 kPa of H_2 at 298 K for 1 h. For comparative measurements, pretreatments at 473 K were also applied, under otherwise the same conditions. The reaction mixture contained 2 kPa of alkene, 2 kPa of H_2 and 66 kPa of argon. The product distribution was determined by using a Hewlett-Packard gas chromatograph (GS-Al_2O_3 capillary column, $l = 50$ m, i.d. = 0.53 mm, $T = 380$ K).

3. Results and discussion

Previously reported XRD measurements revealed that the precursor $PdCl_2$–GIC was fully intercalated and the Pd nanoparticles formed after reduction were encapsulated inside the graphite host [23].

TEM bright field images demonstrated Pd nanoparticles apparently randomly distributed between the graphite layers (Fig. 1a,b). For all Pd–graphites, broad size distributions were observed and the particle diameters were in the range 5–540 nm (Fig. 2). Although more than 50% of all the Pd-particles had sizes in the relatively small interval 20–100 nm, a few particles with extremely high diameter also appeared. As reported previously, the thickness of the Pd nanoparticles did not exceed a few atomic diameters, in contrast with their extended lateral dimension. Accordingly, it was suggested that the Pd content of the reduced samples may be present as quasi-two-dimensional nanoparticles encapsulated inside the graphite host. In earlier studies, the presence of surface Pd-particles was unambiguously excluded [23,27].

The H_2 sorption isotherms of Pd1 and Pd–graphimet are displayed in Fig. 3. It should be noted that all the Pd–graphites furnished essentially the same H_2 sorption isotherms. Therefore, the representative sample Pd1 was chosen for demonstration. For better comparison, the amounts of sorbed H_2 were given per unit mass (left-hand scale) and per unit mole (right-hand scale) of Pd. Similarly to carbon-supported Pd [25], Pd–graphimet exhibited regular behavior with regard to H_2 sorption: the isotherm started with a pronounced chemisorption at a H/Pd ratio of ca. 0.20, followed
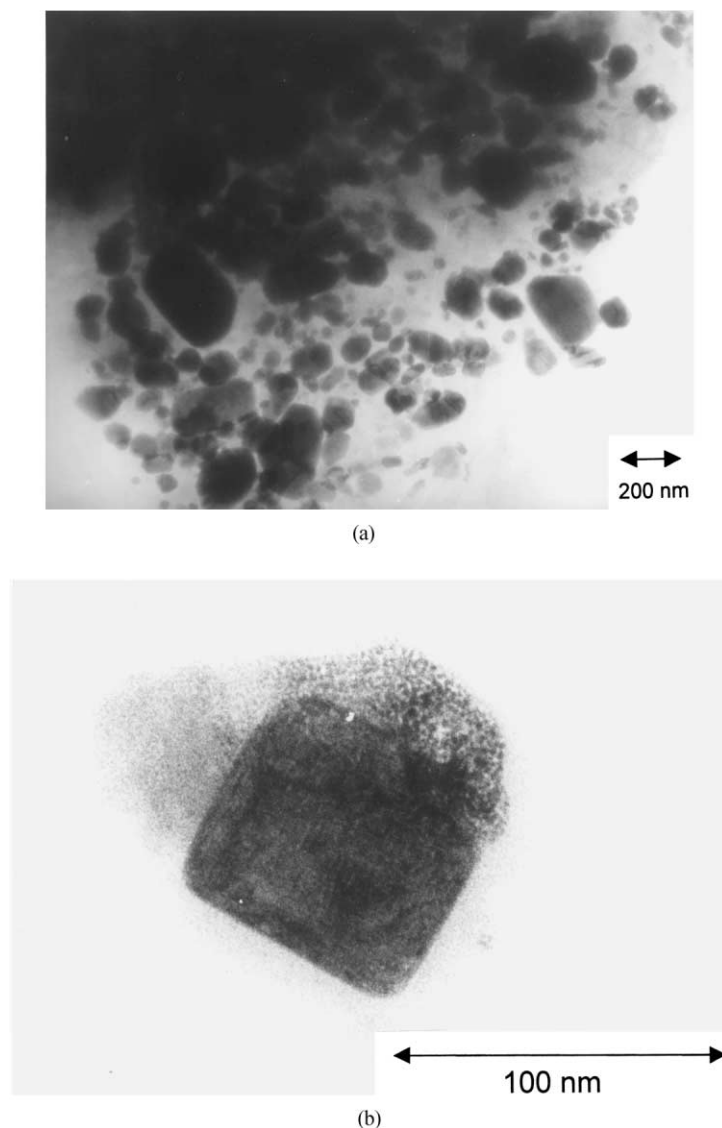
(a)

(b)

Fig. 1. (a) TEM bright field image of Pd1. (b) TEM bright field image of a typical Pd-particle encapsulated in graphite.

by an S-shaped absorption curve, attributed to the successive formation of two interstitial solid solutions, the α- and β-hydride phases [28]. The α/β breakthrough pressure was situated at ca. $p_{\alpha/\beta} = 1.5\,\text{kPa}$. In the co-existence region (along the ascending section of the isotherm) the β-phase developed at the expense of the α-phase until the absorption of H_2 levelled off beyond 4 kPa at a plateau of ca. $H/Pd = 0.96$. As compared with the pressure range

of the adsorption path, the desorption path was shifted to a lower pressure range, ultimately leading to the appearance of a hysteresis loop in the isotherm. The descending branch of the isotherm was steeper than the ascending branch, and the β/α decomposition pressure, which is considered to be the equilibrium pressure [24], was located at $p_{\beta/\alpha} = 0.8\,\text{kPa}$.

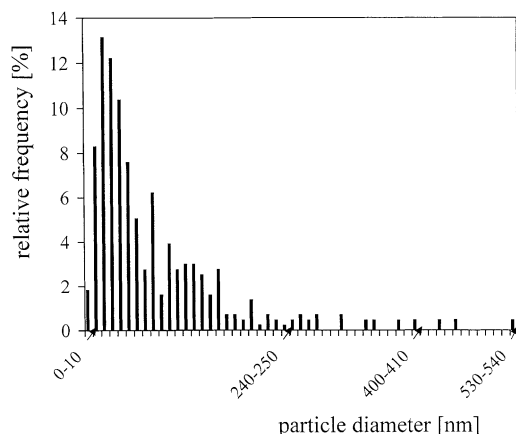The isotherm of Pd1 displayed a marked difference from that obtained for Pd–graphimet. The

Fig. 2. Particle size distribution of Pd1.

chemisorption capacity of Pd1 at 0 kPa was H/Pd = 0.015, which is one order of magnitude smaller than that for Pd–graphimet. It is noteworthy that no β-hydride formation was observed for Pd1, and the H/Pd ratio remained apparently constant throughout a wide pressure range (0–100 kPa, see inset in Fig. 3).

The significant difference in H_2 sorption behavior between the two samples can be explained in terms of their different structures. As reported previously, Pd–graphimet contains a considerable amount of surface metal, which, similarly as for carbon-supported Pd catalysts, is of crucial importance in catalytic transformations. Further, the Pd content of Pd–graphimet consists of three-dimensional particles, and the
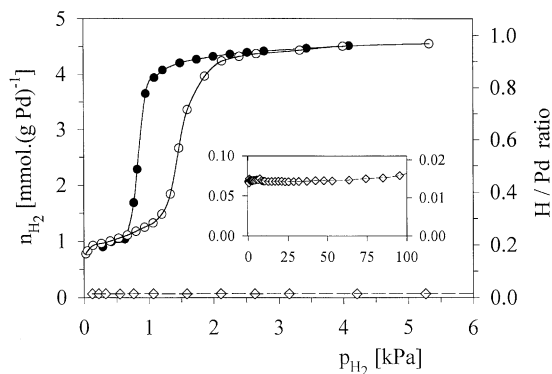

Fig. 3. H_2 sorption isotherms of Pd1 (◇) and Pd–graphimet: (○) adsorption path; (●) desorption path; $m = 0.5$ g, $T = 298.15 \pm 0.04$ K.

average particle size of the quasi-spherical Pd-particles was 4.5 nm [14]. The experimental evidence indicated that most of the surface sites and some of the interlayer sites were accessible for H_2 chemisorption and the interstitial sites were accessible for H_2 absorption. In contrast, the Pd-particles detected in the Pd–graphites were found to be quasi-two-dimensional, with an average diameter of 92 nm and a thickness of less than 2 nm, corresponding to 2–5 layers of Pd atoms [23]. The Pd sheets are sandwiched between two neighboring graphite layers so that H_2 chemisorption may occur on the edges only (along the circumference of the Pd platelets). On the other hand, since the thickness of the Pd film is very low, there are no bulk Pd atoms in this quasi-two-dimensional structure in the classical sense, so that H_2 is not absorbed by the Pd species and, thus, the formation of β-hydride does not take place, at least in the pressure range 0–100 kPa. Accordingly, it is unlikely that the Pd–graphites can be used as H_2 storage materials.

As may be seen in Fig. 4a–c, markedly high catalytic activities were observed for the transformation of 1-butene on all Pd–graphites. For each sample, complete transformation took place, with the formation of butane as the main reaction product, which indicated a pronounced hydrogenation activity. The selectivities for the formation of the isomerization products were also significant, and the production of trans-2-butene predominated over that of the cis-isomer. As the reaction progressed, both 2-butene isomers were hydrogenated to butane and this reaction was more pronounced for the cis-isomer. This was particularly noticeable for Pd3, for which the selectivity of trans-2-butene formation remained practically unchanged, whereas the decrease in the selectivity of cis-2-butene formation was similar in extent to the increase observed for the selectivity of butane production. Although the structural properties of all Pd–graphites proved to be very similar, differences were found between them in terms of catalytic performance. The catalytic activity of Pd3 was lower than those of Pd1 and Pd2. It is assumed that the high temperature of reduction applied for Pd3 resulted in a moderate aggregation of the Pd-particles, although no direct evidence of this was revealed by the TEM measurements. The activities may be more readily distinguished in Fig. 5, which also displays the conversions obtained after pretreatment at 473 K.
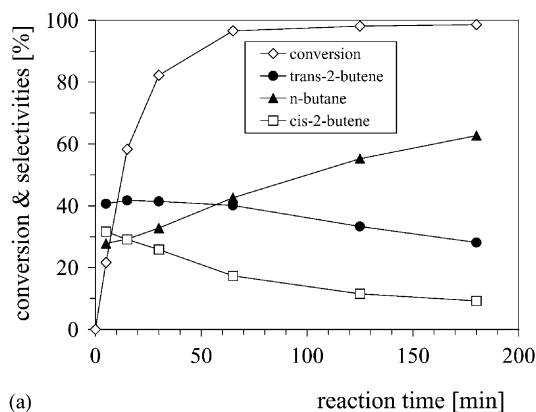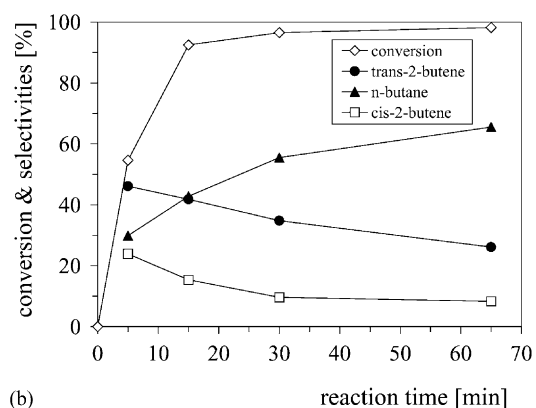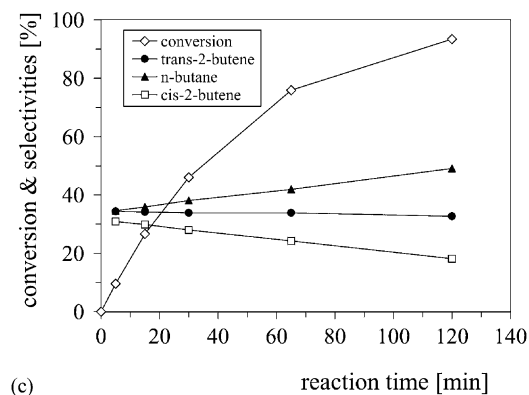
(a)

reaction time [min]
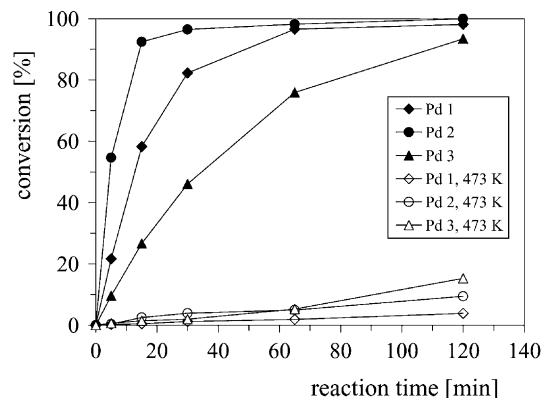
Fig. 5. Catalytic performance of Pd–graphites after pretreatments at 298 and 473 K: $m = 5 \times 10^{-3}$ g, $T = 298$ K, reaction mixture 2 kPa of 1-butene, 2 kPa of H_2, 66 kPa of Ar.

As seen in Fig. 5, thermal treatment resulted in a dramatic activity loss for all Pd–graphite samples. A similar observation was earlier made for Pd–graphimet, and was attributed in part to the migration of interlayer Pd atoms onto the surface of graphite [14]. Nevertheless, as a result of the large particle size of the intercalated species, migration is unlikely for Pd–graphites. Instead, the deactivation may be attributed to Pd agglomeration inside the graphite layers, i.e. to encapsulation of the active Pd atoms available for the reactant molecules at ambient temperature. The encapsulated Pd content of Pd–graphites offers more shape-selectivity as compared with Pd–graphimet, the latter being similar in many respects to carbon-supported Pd [14].

Fig. 6a–c demonstrate that the conversions observed for the transformation of *cis*-2-pentene were considerably lower than those for 1-butene. For all samples, predominantly *trans*-2-pentene was formed, with a selectivity of 60% or more. Hydrogenation was less significant, but pentane still comprised a substantial proportion of the product mixture. The production of a small amount of 1-pentene was also observed, formed by double bond isomerization of the reactant. For all the samples, the experimental evidence indicated that the product selectivities displayed hardly any difference throughout the reaction time interval investigated. Further, the product distributions obtained for Pd1 and Pd3 were very close, which suggested that their active site distributions must have been similar. The

(b)

reaction time [min]

(c)

reaction time [min]

Fig. 4. (a) Transformation of 1-butene on Pd1. (b) Transformation of 1-butene on Pd2. (c) Transformation of 1-butene on Pd3: $m = 5 \times 10^{-3}$ g, $T = 298$ K, reaction mixture: 2 kPa of 1-butene, 2 kPa of H_2, 66 kPa of Ar.
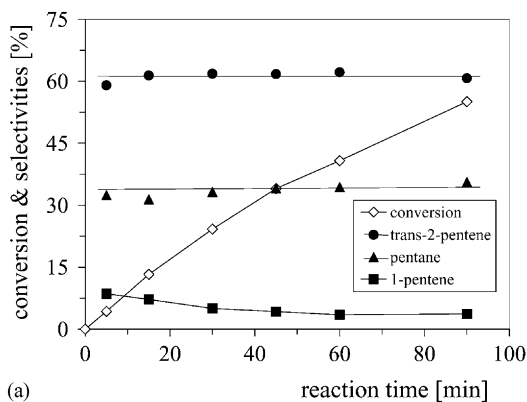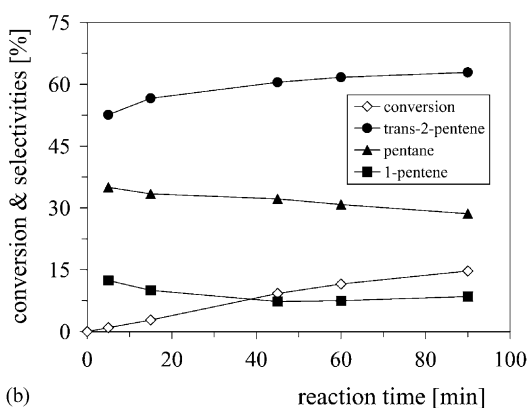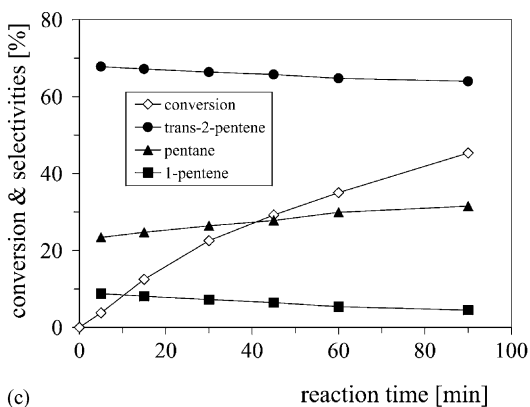
(a)

(b)

(c)

Fig. 6. (a) Reaction of *cis*-2-pentene on Pd1. (b) Reaction of *cis*-2-pentene on Pd2. (c) Reaction of *cis*-2-pentene on Pd3. $m = 5 \times 10^{-3}$ g, $T = 298$ K, reaction mixture: 2 kPa of *cis*-2-pentene, 2 kPa of H$_2$, 66 kPa of Ar.
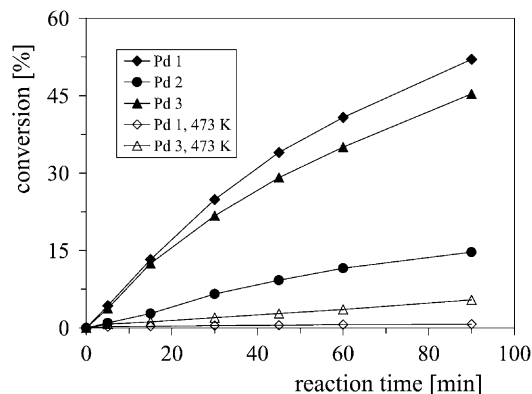

Fig. 7. Catalytic performance of Pd–graphites after pretreatments at 298 and 473 K: $m = 5 \times 10^{-3}$ g, $T = 298$ K, reaction mixture 2 kPa of *cis*-2-pentene, 2 kPa of H$_2$, 66 kPa of Ar.

catalytic activity of Pd2, however, was considerably lower, which suggested that only part of its Pd content was accessible for the reactant molecules. Despite the activity difference, no appreciable change in product distribution was observed, except for the selectivity of 1-pentene formation, which was somewhat higher than those observed for Pd1 and Pd3. On the whole, as compared with the reaction of 1-butene, limited access to the active Pd content of the Pd–graphites can be established for the transformation of *cis*-2-pentene.

This is also demonstrated in Fig. 7, which additionally presents the activities obtained after the pretreatment at 473 K. It is obvious that the effect of thermal treatment was very similar to that observed for the reaction of 1-butene: the activities of Pd1 and Pd3 were substantially lower than those of the pristine samples, whereas for Pd2, the sample with the lowest activity in this reaction, the activity even decreased to zero.

It is well known that unlike the above substrates, cyclohexene is a relatively large non-planar cyclic molecule. Accordingly, in its transformation on Pd–graphites, rather low activities were expected. In fact, cyclohexene underwent no conversion on any of the catalysts, even after prolonged reaction times. The conversions and the selectivities of the main reaction products, measured at a reaction time of 60 min, are listed in Table 1.

Since no surface Pd-particles were present on any of the samples [23], the high conversions obtained for the reaction of 1-butene, a terminal alkene, may be

Table 1
Transformations of alkenes on Pd–graphites

Sample	$C_{1\text{-butene}}$ (%)[a]	$C_{cis\text{-}2\text{-pentene}}$ (%)[a]	S_{butane} (%)[b]	$S_{trans\text{-}2\text{-pentene}}$ (%)[b]
Pd1	96	41	43	62
Pd2	97	12	65	62
Pd3	75	35	42	64

[a] Conversion at $t = 60$ min.
[b] Selectivity at $t = 60$ min.

explained by suggesting that the reaction took place in the interlamellar space of the graphite host. A similar observation was earlier made for the same reaction on Pd–graphimet, but the latter also contained surface Pd-particles, which affected its activity to an appreciable extent [14,26]. It is clear from Table 1 that the selectivities of butane formation for Pd1 and Pd3 were very close, but differed from that for Pd2, which displayed a more pronounced hydrogenation activity. The similar natures of Pd1 and Pd3 are also emphasized by the conversions obtained for the transformation of the non-terminal alkene *cis*-2-pentene, which, despite being considerably lower than those observed for 1-butene, equally point to the occurrence of interlamellar reactions. It is assumed that the longer carbon chain in *cis*-2-pentene as compared with that in 1-butene hampered its diffusion between the layers of graphite and the reaction rate was, therefore, lower. The evidence that the selectivities of *trans*-2-pentene formation were practically the same for all these catalysts indicated that the numbers of active sites responsible for *cis* → *trans* isomerization were very similar. Given that the selectivities of the other reaction products at 60 min were equally close, the lower activity of Pd2 for *cis*-2-pentene may be due to an enhanced amount of encapsulated Pd, as compared with those for Pd1 and Pd3. It is possible that for Pd2 certain active sites available for 1-butene are inaccessible for *cis*-2-pentene, whereas no such evidence was found for Pd1 and Pd3. Although the activity of Pd3 was considerably smaller than those of the other samples, the structural differences must have been rather subtle since they could not be detected by TEM measurements. A more thorough interpretation of the catalytic behavior of Pd–graphites would need further experiments, involving the single turnover method [29,30].

The fact that cyclohexene was not transformed on any of the Pd–graphites indicated that in consequence of the increased size and the non-planar character of the reactant, the occurrence of an interlamellar reaction is to be excluded. This is in accordance with previous results on Pd–graphimet, which suggested that cyclohexene was unable to penetrate between the graphite layers [14,26]. The complete lack of activity on Pd–graphites is also attributed to the absence of surface Pd-particles. Accordingly, a molecular sieving effect of the samples can be established and Pd–graphites may, therefore, be regarded as shape-selective catalysts.

The structures of these Pd–graphites were also investigated by TEM after pretreatment at 473 K, followed by the catalytic reaction. It was found that this thermal treatment increased the size of the Pd nanoparticles to a moderate extent. A more noteworthy change was observed in the particle shapes; this was mainly indicated by the appearance of Pd nanorods, as seen in Fig. 8a and b.

Nevertheless, Pd-particles with unchanged morphology were also detected. The elongated Pd-particles observed after reduction at 473 K indicated that the template effect of the graphite host caused the crystallites to grow more readily in the lateral direction [15]. It is clearly seen in Fig. 8a that the particles remained intercalated in the graphite after the thermal treatment and reaction. Moreover, the proportion of relatively small particles (30–100 nm) decreased, whereas that of large aggregates ($d > 200$ nm) increased (Fig. 9). That is also indicated by the average particle diameter for Pd1 (181 nm), which was twice as high as that for the pristine sample. Even pretreatment at the relatively low temperature of 473 K reduced the activities of all the Pd–graphites to an unexpectedly dramatic extent. When the catalysts were pretreated at room temperature, no evidence of restructuring was found by TEM. The rearrangement observed during pretreatment at 473 K was rather surprising since the
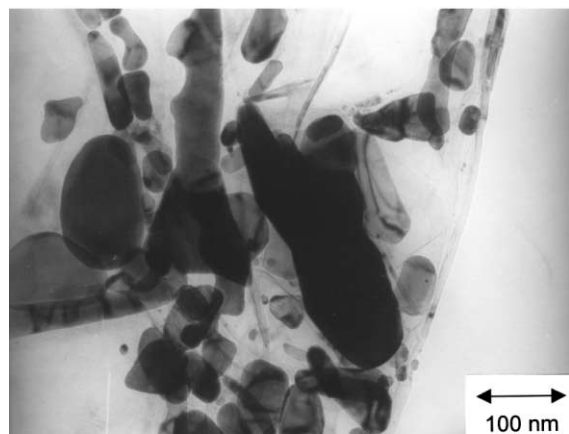
(a)
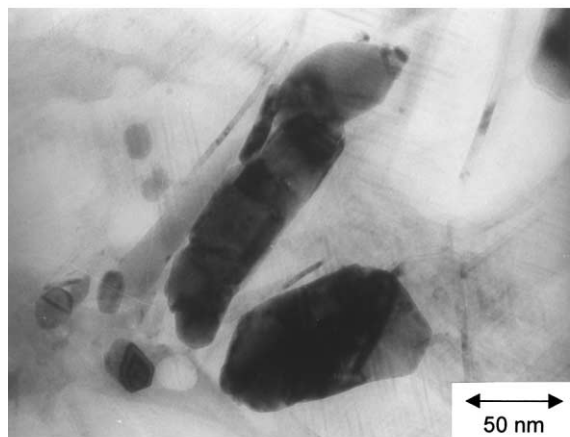
(b)

Fig. 8. (a) TEM bright field image of Pd1 after reduction at 473 K. (b) Typical Pd particles formed on reduction at 473 K.
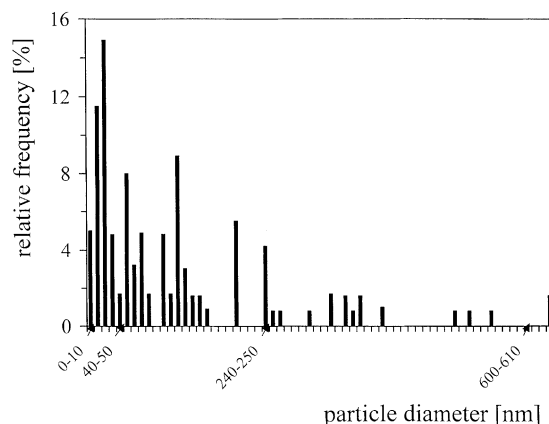

Fig. 9. Particle size distribution of Pd1 after pretreatment at 473 K.

restructuring model, the rates of surface reactions are determined by the rates of dynamic surface rearrangements [32–34]. That is, the flexibility of metal surfaces influences the rate of restructuring: the more open the surface, the more flexible the surface atoms. Metal atoms situated in a close-packed arrangement are fairly rigid because of the high coordination, and the thermodynamic driving force of their restructuring is, therefore, not very high. On the other hand, metal atoms that have fewer neighbors are more flexible and may restructure more readily [33]. According to the above considerations, the quasi-two-dimensional structure of the Pd–graphites may give rise to the facile redispersion of these catalysts. The activity loss observed for all the Pd–graphites reflects a long-term effect of rearrangement, similarly to that obtained for Pd–graphimet [14]. Nevertheless, the formation of a carbonaceous overlayer on the active centres cannot be completely excluded.

4. Conclusions

In the current study, the structure and catalytic performance of Pd–graphite compounds prepared by the reduction of $PdCl_2$–GICs were investigated. TEM images revealed that the majority of the Pd-particles formed were encapsulated inside the graphite host. Further, a broad size distribution of 5–540 nm was experienced for all samples. H_2 sorption measurements demonstrated no β-hydride formation for any of the Pd–graphites throughout a wide pressure range, which

temperature of reduction in the preparation method was considerably higher (673 K). However, it should be noted that towards the end of the reduction, a clean metal surface was heated in a H_2 atmosphere, whereas at the beginning of the pretreatment at 473 K, a sample oxidized by air was heated in H_2. Rearrangement of the metal particles may, therefore, be attributed to a strong local overheating, due to the reaction of H_2 with O_2 on the surface of the Pd. The redispersion of metal crystallites is generally regarded as a complex phenomenon, involving both crystallite and atomic migration [31]. According to the dynamic

confirmed the quasi-two-dimensional character of the Pd nanoparticles obtained upon reduction.

Although the same overall structural properties were observed for all Pd–graphites, differences were found between them at a molecular level. This was related in part to the preparation temperature and to the extent of Pd encapsulation. The conversions in the transformation of the terminal alkene 1-butene were considerably higher than those for the reaction of the non-terminal alkene *cis*-2-pentene. Since both the presence of the surface Pd particles and the migration of interlayer Pd on the surface of the graphite were excluded, it is most likely that the catalytic activities of the Pd–graphites were controlled by the diffusion of the reactants to the active centres. Accordingly, the size and structure of the reactant molecules were of crucial importance. This is also suggested by the lack of conversion for the non-planar cyclic alkene cyclohexene; due to steric hindrance, this molecule cannot diffuse into the interlamellar space of graphite. It follows that the Pd–graphites possess a molecular sieving effect and they may, therefore, be regarded as shape-selective catalysts.

The pretreatment of the samples at 473 K was found to result in a pronounced deactivation, which was attributed to restructuring of the active Pd atoms, also indicated by changes in particle morphology and aggregation.

Acknowledgements

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