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## Palladium Catalysts on Carbon Supports Prepared from a Natural Graphite and Anthracite

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*Influence of the conditions of the carbon supports preparation from an expanded natural graphite and chemically modified anthracites on the formation of carbon porous structure, on the distribution and sizes of supported palladium particles and their catalytic activity in liquid phase reactions of hexene-1 and cyclohexene hydrogenation has been studied. At the same reaction parameters and Pd content the catalytic activity of different samples varies by more than 100 times. Besides, the activity of some catalysts in hexene hydrogenation is much higher (up to 20 times) than that in cyclohexene hydrogenation reaction. The possible reasons for observed differences in Pd catalyst behavior are analysed.*

*Keywords: palladium catalyst, carbon support, expanded graphite, anthracites, chemical modification, hexene and cyclohexene hydrogenation.*

### Introduction

Rather high cost of synthetic active carbons can restrict the scale of carbon supports application in the industrial catalysis. At the same time the significant resources of inexpensive raw materials, presented by natural graphites and anthracite are not sufficiently used for the catalyst supports manufacture.

Relatively low reaction ability of natural graphites towards the activation agents (steam, oxygen, carbon dioxide) can make problems in the preparation of porous carbon supports on their basis. But graphites are able to form graphite

intercalated compounds which can sufficiently (by hundreds times) increase their volume after a high temperature treatment [1]. This unique property of intercalated graphites was used for manufacturing thermally expanded graphites. The latter have found an application in the production of various non-porous carbon products. The expanded graphites also have good prospects for their use in the preparation of carbon sorbents [2, 3] and catalyst supports [4-7]. At present a wide variety of graphite intercalated compounds is known and different methods are used for their synthesis. These conditions are favorable for

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producing porous carbon supports with demanded specific surface area and porosity on their basis.

The anthracites, like graphites have rather low reaction ability in the processes of steam and carbon dioxide activation, used for carbon sorbent manufacture [8]. In some cases the two-stage activation methods are used. They include the preliminary pyrolysis of anthracite [9, 10] or its pre-oxidation by air [11]. As a rule, it takes high temperatures and long time in order to obtain high quality carbon sorbents or supports by physical activation of the anthracites. Moreover, the burn-off taking place during the conventional activation process can result in significant loss of the anthracite mass (more than 50%).

There are some published data which demonstrate that the preliminary chemical activation of anthracites at room temperatures (for example, by  $\text{HClO}_4$  or  $\text{HNO}_3$ ) can sufficiently increase its reactivity for physical activation process [12, 13].

This paper describes how the methods of carbon support preparation from natural graphite and chemically modified anthracites influence on the formation of carbon porous structure, on the state of supported palladium and its catalytic activity in liquid-phase hydrogenation reactions.

### Experimental

Natural graphite from Zavalevsky pit (Ukraine) and anthracites from coal mine Ilovaiskaya (Ukraine) were used as initial raw materials for the preparation of porous carbon supports. All initial samples were demineralized before using for the residual ash content 0.08 wt.% (for graphite) and 0.1-0.4 wt.% (for anthracite) as described in [14].

The intercalation procedure included the treatment of demineralized graphite samples by oxidants and acids according to methods described in [15]. At selected parameters of treatment (Table 1) a formation of graphite intercalation

compounds takes place. The samples of expanded graphite were obtained by a fast heating of intercalated graphite. Depending on the conditions of intercalation and thermal treatment the volume of expanded graphite samples exceeds by tens and hundreds time a volume of intercalated graphite.

The chemically modified anthracite was obtained by the demineralized sample treatment by a mixture of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ , with the following air high-rate heating at the temperature up to 1173K and keeping at this temperature during 3 min. The methods of 5-7 samples preparation included the anthracite activation by water-steam or carbon dioxide. The activation of the samples was conducted by their fast heating (during 10 min) up to 1123K in the flow of activating agent (steam or  $\text{CO}_2$ ) with the following keeping at this temperature from 2.5 to 8 hours.

Adsorption measurements were accomplished with a vacuum static volumetric technique on Sorptomatic-190 ("Fisons"). Nitrogen adsorption was studied at 77K in the range of relative pressures  $10^{-3}$ -0.999. The isotherms of carbon dioxide adsorption were obtained at 273K and relative pressures  $4 \cdot 10^{-5}$ -0.03. The comparison of these two gases adsorption gives the more detailed information about porous structure of the sample [16]. The microporosity of the samples was analysed from the isotherms of  $\text{N}_2$  and  $\text{CO}_2$  adsorption, using the TVFMP method [17]. It is known that the micropores with a diameter less than 0.7 nm are practically inaccessible for  $\text{N}_2$  molecules at 77K due the diffusion limitations. However, the use of  $\text{CO}_2$  as an adsorbate at 273-298K and  $P/P_0 < 0.03$  makes it possible to detect such small micropores [18, 19].

The specific surface area of the carbon samples was estimated by BET method, based on the measurement of equilibrium nitrogen adsorption at 77K [20]. This method gives the reliable results in the absence of significant amount of small micropores in the sample.

The calculation of BET surface area of the carbon samples was carried out in the range of equilibrium pressures of the nitrogen vapors  $P/P_0 = 0.005-0.020$ , using the value of nitrogen molecular area in the occupied monolayer  $W_m = 0.162 \text{ nm}^2$  [21]. The error of measurements of the specific surface area of standard samples on "Sorpomatic-1900" was near  $\pm 2.8 \text{ rel.}\%$  [22]. The total adsorption volume of the pores in carbon samples was determined from the value of adsorbed nitrogen at  $P/P_0 = 0.996$  and 77K. In fact, this value corresponds to the total volume of pores with diameter less 100 nm. Before adsorption experiments all samples were treated in vacuum at 573-623 during 24 hours.

Palladium catalysts were prepared by the carbon supports impregnation with a water-alcohol solution of  $\text{H}_2\text{PdCl}_4$  and subsequent drying at 373K. The catalysts were reduced in a hydrogen flow at 423K before catalytic experiments. The concentration of palladium in all catalysts was about 1 wt.%. The size of catalyst particles varied in the range 0.25-0.50  $\mu\text{m}$ .

The information about the state of supported palladium was obtained with the use of a transmission electron microscope JEM-100C (resolution 0.45 nm, acceleration voltage 100 kV) and with a high-resolution electron microscope JEM-2010 (resolution 0.14 nm, accelerating voltage 200 kV). Before the measurements, the alcohol suspensions of samples were dispersed by ultrasound treatment with the frequency 35 KHz and then supported on the perforated carbon films. The latter were fasten on the copper wire netting and placed under the electronic beam [23].

Activity of palladium catalysts was studied in reactions of liquid-phase hydrogenation of hexene-1 and cyclohexene, using a stirred static reactor (60  $\text{cm}^3$  volume) which was made from a glass. The charge of catalyst varied between 0.2-0.3 g depending on its activity. Catalytic experiments were conducted at 323K, atmospheric

pressure and the stirring rate prevented the diffusion limitations, connected with the reagent transport to catalyst particles. The catalytic activity of different catalysts was compared according to the initial rates of the hydrogen uptake.

## Results and discussion

### 1. Textural characteristics of carbon supports

#### *Supports from the expanded graphite*

Depending on the intercalation method used for preparation of the samples of thermally expanded graphite, the BET surface area, calculated from the isotherms of  $\text{N}_2$  adsorption at 77K (Fig. 1) varies from 53  $\text{m}^2/\text{g}$  to 12  $\text{m}^2/\text{g}$  and the total pore volume – from 0.241 to 0.083  $\text{cm}^3/\text{g}$  (Table 1).

The isotherms of  $\text{N}_2$  adsorption at 77K appeared to be reversible with the shape corresponding to the mono-layer and multi-layer adsorption on non-porous or macroporous solids. These isotherms show no saturation in the scope of relatively high pressures ( $P/P_0 \rightarrow 1$ ). This fact makes it difficult to calculate the total adsorption volume of the pores. The values of total adsorption volume were defined at  $P/P_0 = 0.996$ . They correspond to the total volume of pores with diameter less 50 nm. Total volume of pores varies for different carbon samples from 0.083 to 0.319  $\text{cm}^3/\text{g}$ . The values of micropores volume, calculated from the isotherms of  $\text{N}_2$  adsorption are very small.

Since the nitrogen molecules cannot penetrate to the most narrow pores owing to the activation diffusion at 77K [18], the  $\text{CO}_2$  adsorption at 273K [24] was used in order to obtain the information about the microporous characteristics of the samples.

According to obtained data the amount of carbon dioxide adsorbed at 273K on the samples of thermally expanded graphite varies in the same order as in the case of  $\text{N}_2$  adsorption at 77K.

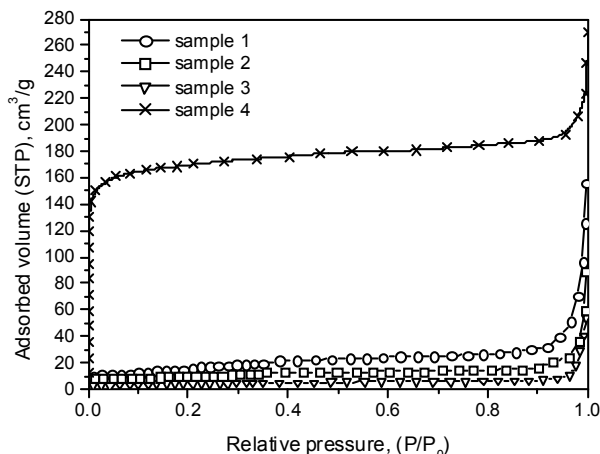


Fig.1. Isotherms of nitrogen adsorption at 77 K on the samples of expanded graphite and chemically modified anthracite (sample numbers correspond to that in table 1)

Table 1. Some characteristics of the initial and treated natural graphite and anthracites

N	Sample	Characteristics of the samples				Method of treatment
		Ahs content		BET surface area, * m <sup>2</sup> /g		
		Initial	Demineralized **	Initial	Treated	
1	Graphite	0.1	0.08	1.0	53	CrO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> , heating at 1173 K, 30 c
2	Graphite	0.1	0.08	1.0	33	Consecutive treatment by HNO <sub>3</sub> and CH <sub>3</sub> COOH, heating at 1173K, 30 c
3	Graphite	0.1	0.08	1.0	12	HNO <sub>3</sub> , heating at 1173 K, 30 c
4	Anthracite	3.3	0.14	1.5	653	HNO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub> , heating at 1173 K, 3 min
5	Anthracite	3.3	0.14	1.5	288	HClO <sub>4</sub> , activation by CO <sub>2</sub> at 1123 K, 24 h
6	Anthracite	3.3	0.14	1.5	868	Activation by H <sub>2</sub> O at 1123 K, 6 h
7	Anthracite	3.3	0.14	1.5	410	Activation by CO <sub>2</sub> at 1123 K, 8 h
8	Anthracite	3.3	0.14	1.5	1150	Activation by H <sub>2</sub> O at 1123 K, 2,5 h

\* calculated from N<sub>2</sub> adsorption at 77K

\*\* demineralized by mixture of HCl and HF

The maximum adsorption of the both gases was observed for the sample of expanded graphite obtained with the use CrO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture. The minimum adsorption corresponds to the sample prepared by the consecutive treatment with HNO<sub>3</sub> and CH<sub>3</sub>COOH. The first sample has the volume of micropores and specific surface area 0.330 cm<sup>3</sup>/g and 850 m<sup>2</sup>/g, respectively. This sample differs from the other samples of thermally expanded graphite by the lesser diameter of the micropores (0.77 nm).

Electrochemical intercalation provides the expanded graphite samples with the higher total

pore volume (from 0.216 cm<sup>3</sup>/g to 0.544 cm<sup>3</sup>/g and BET surface area 40-70 m<sup>2</sup>/g.

According to the electron microscopy data the structure of initial graphite consists of the thin plates with a cross size near 1 mkm and with a thickness from a few nm to tens nm. The plates lie on each other and form crystalline polytypes as a consequence of an erroneous superposition of the graphite layers. The electron diffraction spectra show a high degree of plate crystallinity. The morphology of intercalated graphite samples was the same as that of the initial ones. But in the case of intercalated graphite the strengthening of

periodical background connected with the Moire effects was observed. Such an effect is known to take place as a consequence of the crystalline plate superposition with a small divergence of their orientation. Besides, on the electron microscopy images of intercalated graphites the splitting of graphite plates is observed. The electron diffraction pictures also indicate the splitting effect.

Thermally expanded graphites have more dispersed and imperfect structure as compared to the intercalated samples. EM data show the more pronounced effects connected with an erroneous superposition of the graphite layers. The latter results in the appearance of the crystalline polytypes which are observed on the microdiffraction image. The most pronounced effects were observed in the case of thermally expanded graphite produced with the use of  $\text{CrO}_3/\text{H}_2\text{SO}_4$  mixture. It is worth to note that this sample has the most developed microporous structure.

#### *Supports from anthracite*

BET surface area of the porous anthracites was defined from isotherms of nitrogen adsorption at 77K. Their microtextural characteristics were calculated, predominantly from the isotherms of  $\text{CO}_2$  adsorption at 273K. Presented in Table 2 data show that BET surface area of the studied anthracites varies from 288  $\text{m}^2/\text{g}$  to 1150  $\text{m}^2/\text{g}$  depending on the anthracite activation treatment.

Analysis of  $\text{CO}_2$  adsorption isotherms has shown that all studied anthracite samples have the developed microporous structure. Calculated values of the micropore volumes and micropore surface area vary for studied samples from 0.133  $\text{cm}^3/\text{g}$  to 0.259  $\text{cm}^3/\text{g}$  and from 162  $\text{m}^2/\text{g}$  to 345  $\text{m}^2/\text{g}$ , respectively. Estimated diameters of the micropores were in the range of 1.50-1.89 nm. The sample, obtained by anthracite treatment with the mixture of nitric and sulphuric acids has the

most developed microstructure. For this sample the main microtextural characteristics estimated from isotherms of  $\text{N}_2$  and  $\text{CO}_2$  adsorption were compared using TVFMP method [17]. Isotherm of  $\text{CO}_2$  adsorption at 273K is shown on Fig. 2. The equation of Dubinin-Radushkevich was used for calculating micropore volume and surface area. The affinity coefficients were taken 0.3 for nitrogen and 0.46 for carbon dioxide, their density being 0.808  $\text{g}/\text{cm}^3$  for  $\text{N}_2$  and 1.023  $\text{g}/\text{cm}^3$  for  $\text{CO}_2$ .

The comparison of nitrogen and carbon dioxide adsorption data indicates that activated anthracite is basically microporous material. The total volume of pores (0.319  $\text{cm}^3/\text{g}$ ) in this sample is presented predominantly by micropores (volume of micropores 0.259  $\text{cm}^3/\text{g}$ ). In order to study the uniformity of micropores distribution in this sample the DFT-method was used [25].

Presented on Fig. 3 the histogram indicates that in the sample 4 micropores width varies from 0.7 to 2.5 nm. The average size of micropores is 0.94 nm.

Results of the electron microscopy study testify the differences in the state of anthracite surfaces in porous samples prepared by different methods. The samples of anthracites activated by  $\text{H}_2\text{O}$  and  $\text{CO}_2$  have a rough surface and the disordered structure. According to electron microdiffraction and HREM data their structure is formed by distorted fragments of the graphite plane 002.

For the porous carbon obtained by high-rate heating of the anthracite treated by nitric acid and sulphuric acid mixture the spotted contrast was detected on some graphite plates. The electron diffraction pattern of these plates corresponds to the polycrystalline graphite from thermally expanded natural graphite [26].

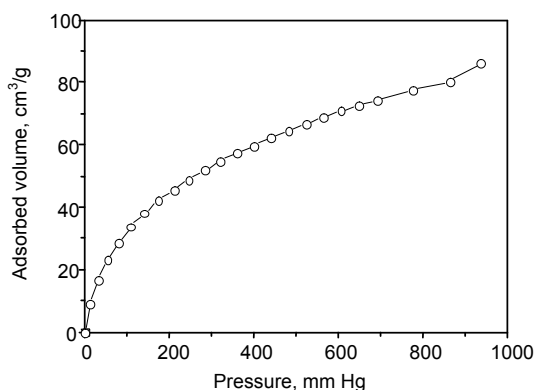


Fig. 2. Isotherm of carbon dioxide adsorption at 273 K on the sample of activated anthracite (prepared by treatment with  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture)

## 2. State of the supported palladium

### *Palladium on the thermally expanded graphite*

The initial catalysts and those reduced by  $\text{H}_2$  palladium both prepared by  $\text{H}_2\text{PdCl}_4$  supporting on porous materials from thermally expanded graphite were X-ray amorphous. Therefore, the main information concerning the state of supported palladium was obtained by transmission electron microscopy method.

It has been found earlier [5] that the size, morphology of palladium particles and their distribution over the support surface differ significantly for all three types of expanded graphite used. During the deposition of  $\text{H}_2\text{PdCl}_4$  onto the graphite surface, the reduction of  $\text{Pd}^{2+}$  ions takes place. This results in the partial or complete reduction of supported  $\text{H}_2\text{PdCl}_4$  with the formation of the metallic palladium particles.

The most homogeneous distribution of nanosized palladium particles (2-4 nm) was observed for the support from expanded graphite prepared by intercalation with  $\text{HNO}_3$ . Besides, this sample has the highest stability against sintering in hydrogen atmosphere. Fig. 4 demonstrates the electron microscopy image of this sample.

In the non-reduced sample of expanded graphite prepared by intercalation with nitric acid

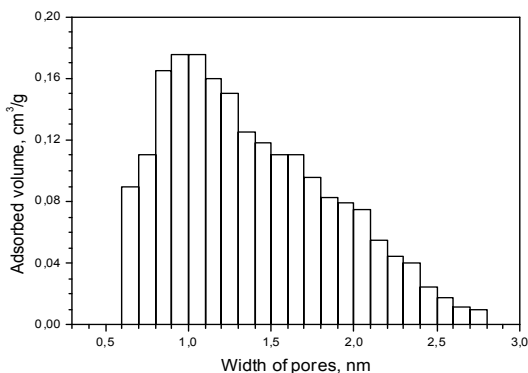


Fig. 3. Pore size distribution histogram in sample of chemically modified anthracite, calculated from nitrogen adsorption at 77 K

and acetic acid the small palladium particles (1-4 nm) form clusters with the sizes up to 20 nm. These palladium clusters are homogeneously distributed over the support surface. For this sample the most intensive sintering of supported palladium with the formation of metallic particles of a dendrite type was observed after its reduction at 423K in hydrogen atmosphere.

The less homogeneous distribution of supported palladium particles was detected for expanded graphite prepared by intercalation with  $\text{CrO}_3$  and  $\text{H}_2\text{SO}_4$  mixture. Along with nanosized palladium particles (1-3 nm) this sample contains metal particles with sizes of tens nm.

### *Palladium on the anthracite supports*

All palladium catalysts prepared by  $\text{H}_2\text{PdCl}_4$  supporting on the porous anthracites are X-ray amorphous at Pd content 1 wt.%. Results of electron microscopy study show that the method of porous support preparation influences significantly on the size of supported palladium particles and on their distribution over the carbon surface.

In the case of porous anthracite supports prepared without chemical modification before activation treatment the supported palladium particles are distributed heterogeneously over the support surface. In these samples along with the



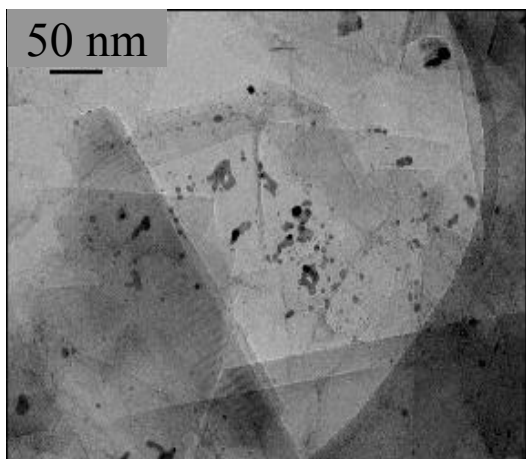


Fig. 4. EM image of 1 % Pd/expanded graphite after reduction by  $H_2$  at 423 K (expanded graphite was prepared by  $HNO_3$  intercalation)

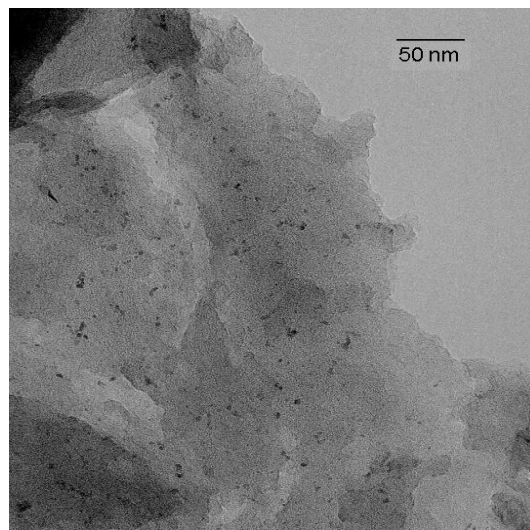


Fig. 5. EM image of 1% Pd/anthracite after reduction by  $H_2$  at 423 K (anthracite support was modified by  $HClO_4$  and activated by  $CO_2$  at 1123 K)

small particles (up to 10 nm) the larger clusters of these particles were also detected. The formation of nano-particles of metallic palladium takes place in non-reduced catalysts. The amount of metallic particles is defined by the nature of anthracite supports and the conditions of their activation treatment.

The distinctive feature of carbon supports from chemically modified anthracites is the homogeneous distribution of nanosized particles of  $H_2PdCl_4$  and metallic palladium over the carbon surface (Fig. 5).

The distribution of supported palladium was changed only slightly after the catalysts reduction at 423K in the hydrogen flow at atmospheric pressure. For porous supports from non-modified anthracites the formation, along with the small metal particles, some amount of the bigger palladium particles took place. The most dispersed and uniform distribution of supported palladium particles with an average size near 2 nm was observed for the carbon supports prepared from the chemically modified anthracites. In some cases the reduction treatment increases the number of superdispersed metal particles and non-reduced

palladium compounds localized into the small micropores of the anthracite support.

### 3. Catalytic activity of supported palladium

The catalytic activity of palladium supported on porous carbons from thermally expanded graphites and activated anthracites was compared in the reactions of hexene-1 and cyclohexene liquid phase hydrogenation. The significant influence of the method of carbon supports preparation on catalytic properties of palladium catalysts was detected (Fig. 6). The possible reason responsible for this effect is connected with the specific character of interaction of supported  $H_2PdCl_4$  with the surface of carbon supports prepared by different methods [27]. The formation of different amount of metallic palladium in non-reduced catalysts serves as an indirect evidence of the difference in the nature and number of reactive surface centers in porous carbons used.

The phenomenon of a metallic palladium formation in non-reduced catalysts was detected by electron-microscopy methods. Also, this phenomenon was indirectly confirmed by the appearance of catalytic activity of non-reduced

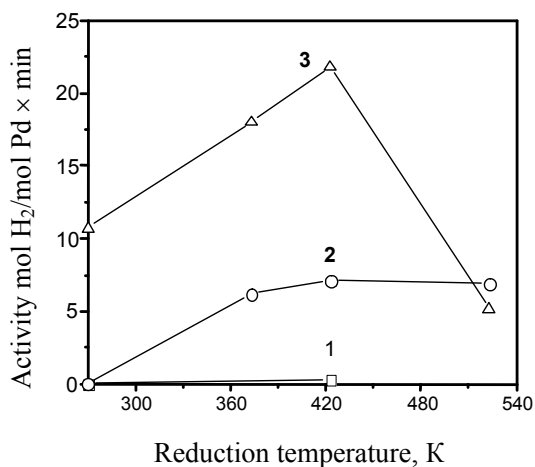


Fig. 6. Catalytic activity of 1 % Pd/expanded graphite in cyclohexene hydrogenation at 323 K (expanded graphite supports were prepared by intercalation  $\text{CrO}_3/\text{H}_2\text{SO}_4$  (1),  $\text{HNO}_3$  (2) and  $\text{HNO}_3$  and  $\text{CH}_3\text{COOH}$  (3))

samples in the hydrogenation reactions. No direct correlation between the specific surface area of carbon support and catalytic activity was observed. The catalysts containing the clusters of nanosized palladium particles exhibited the highest activity in reactions of hexene-1 and cyclohexene hydrogenation.

The hydrogenation activity of catalysts with a predominant localization of small palladium particles inside the carbon support micropores was very low. The decreased catalytic activity of superdispersed palladium particles localized in the smallest micropores can be explained in the context of a strong interaction between the metal and carbon support [28]. This interaction can change the electronic state of supported palladium and its adsorption properties [29]. Furthermore, a limited diffusion of the reagents and products in the micropores should result in the decreased activity of such catalysts.

Either of these two factors can predominate for a specific carbon support depending on the method of its preparation.

The activity of some catalysts Pd/carbon in hexene-1 hydrogenation exceeds in some cases

their activity in cyclohexene hydrogenation reaction (Table 2). The observed effect is more pronounced for catalysts with a predominant localization of superdispersed palladium particles in the smallest micropores of the carbon support. Probably, the rate of diffusion of linear hexene-1 molecule in the narrow slit-like micropores is higher than that of cyclohexene molecule, which has the higher effective radius. Taking this assumption into account, the observed difference in catalytic properties of palladium on porous supports from graphite and anthracites can be explained by the different number of narrow slit-like micropores formed in the carbon supports prepared by different methods.

Besides, the chemical treatment of graphites and anthracites used for porous supports preparation changes the composition of the functional groups on their surface. It is known that the treatment of carbon material by oxidative reagents (for example, by nitric or chloric acids) results in the increase of concentration of surface electron-acceptor groups [13]. The simultaneous reduction of the concentration of electron-donor surface centers, in particular presented by  $\pi$ -conjugative systems of the carbon surface takes place.

Some results of the accomplished study indicate that the concentration of electron-donor centers is higher on the surface of supports from expanded graphites as compared to carbon supports, obtained from anthracites. In the case of graphite-origin supports the predominant part of  $\text{H}_2\text{PdCl}_4$  was reduced to metallic palladium during supporting at room temperature.

Carbon supports from anthracites have a high concentration of electron-acceptor surface groups. The presence of  $\text{Cl}^-$  was proved by XPS method in the anthracites modified by  $\text{HClO}_4$  [12]. In the case of anthracites modified by  $\text{HNO}_3/\text{H}_2\text{SO}_4$  mixture, the nitrogen-containing groups were detected by FTIR spectroscopy method. Nevertheless, the



Table 2. The comparison of catalytic activity of palladium on supports from expanded graphite and activated anthracite in reactions of hexene-1 and cyclohexene hydrogenation at 323 K

Support nature	Activation method	BET m <sup>2</sup> /g	Activity mol H <sub>2</sub> /mol Pd × min		Ratio of activities hexene-1 /cyclohexene
			hexene-1	cyclohexene	
Graphite	Intercalation with CrO <sub>3</sub> /H <sub>2</sub> SO <sub>4</sub>	0.53	0.53	0.30	1.77
Graphite	Intercalation with HNO <sub>3</sub> and CH <sub>3</sub> COOH	33	36.25	21.80	1.66
Graphite	Intercalation with HNO <sub>3</sub>	12	26.10	7.10	3.68
Anthracite	Treatment with HNO <sub>3</sub> / H <sub>2</sub> SO <sub>4</sub> , heating at 1173 K, 3 min	653		15.16	
Anthracite	Treatment with HClO <sub>4</sub> and activation by CO <sub>2</sub> at 1123K, 24 h	288	9.94	2.23	4.46
Anthracite	Activation by H <sub>2</sub> O at 1123K, 6 h	868	32.21	29.50	1.10
Anthracite	Activation by CO <sub>2</sub> at 1123K, 8 h	410	26.13	1.22	24.41

surface of these modified anthracites contains some amount of electron-donor centers which are able to reduce the supported H<sub>2</sub>PdCl<sub>4</sub> with the formation of metallic palladium particles.

### Conclusion

Results of the accomplished study show that it is possible to prepare the carbon supports with the developed pores structure using the method of natural graphites intercalation and anthracites chemical modification.

The samples of expanded natural graphite have the predominantly microporous structure. Depending on the conditions of graphite intercalation and thermal expansion the average width of slit-like pores in carbon supports prepared on their basis varies from 0.77 to 0.92 nm, the volume of micropores from 0.144 to 0.330 cm<sup>3</sup>/g, the surface of micropores from 300 to 850 m<sup>2</sup>/g.

Carbon supports prepared from anthracites, using their preliminary modification by HClO<sub>4</sub> or HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> mixture and subsequent activation by CO<sub>2</sub> or steam have also the

developed microporosity. The specific surface area of anthracite samples varies from 288 to 1150 m<sup>2</sup>/g, the volume of micropores from 0.133 to 0.253 m<sup>3</sup>/g, the surface of micropores from 162 to 345 m<sup>2</sup>/g, the average diameter of pores from 1.50 to 1.89 nm.

The state of palladium in the catalysts prepared by supporting of H<sub>2</sub>PdCl<sub>4</sub> on porous carbons from graphite and anthracite is defined predominantly by the nature of initial material and by the method of porous structure development. During supporting H<sub>2</sub>PdCl<sub>4</sub> on carbon surface the formation of metallic palladium takes place. The degree of H<sub>2</sub>PdCl<sub>4</sub> reduction, the size of palladium particles and their distribution over surface are varied depending on the method of carbon support preparation.

The most uniform distribution of nanosized palladium particles was observed on carbon supports from thermally expanded graphite. The optimized conditions of carbon supports preparation were selected which supply the predominant formation of metallic palladium

particles with sizes 1-2 nm, or clusters of these particles or small metal particles localized into narrow micropores.

The hydrogenation activity of such palladium catalysts varied in the wide limits depending on the state of supported palladium. Catalysts containing the clusters from nanosized palladium particles have the highest activity in reactions of hexene-1 and cyclohexene hydrogenation.

The catalysts with small palladium particles localized in micropores of carbon support exhibit low hydrogenation activity. Besides, the activity of such catalysts in reaction of hexene-1 hydrogenation exceeds their activity in cyclohexene hydrogenation by the extent from a few times to several dozens. The observed effects can be explained in the context of a strong interaction between carbon support and small palladium particles localized in micropores along with a limited diffusion of reagents and products

in the micropores of carbon support. Either of these two factors can predominate in a specific carbon support, depending of the method of its preparation.

The obtained results make it possible to assume that the concentration of electron-donor centers, reducing  $\text{H}_2\text{PdCl}_4$  to metallic palladium is higher on the surface of supports prepared from graphite. Carbon supports from anthracites have higher concentration of electron-acceptor groups. Therefore, the strategy for synthesis porous supports from natural graphites and anthracites should include the increase of their mesoporosity along with the control over electron-donor and electron-acceptor properties of the carbon surface.

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