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CARBON IN CATALYSIS

# Carbon Supports from Natural Organic Materials and Carbon-Supported Palladium Catalysts

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**Abstract**—Experimental data are presented concerning the influence of preparation conditions on the pore structure of carbon supports obtained from different types of plant biomass, thermally expanded graphites, and chemically modified anthracites, on the distribution and particle size of supported palladium, and on the activity of the supported catalyst in the liquid-phase hydrogenation of hex-1-ene and cyclohexene.

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## INTRODUCTION

Carbon-supported catalysts are finding progressively increasing application [1]. They could be used still more widely if simple and efficient methods of preparing carbon supports from cheap natural raw materials were developed. These cheap materials are different types of natural biomass (wood, bark, and cellulose), natural graphites, and anthracites [2].

Birch wood is a traditional plant raw material for the preparation of porous carbon materials (PCMs) [3]. The low yield of the final product (at most 12% of the weight of the initial material) has stimulated studies aimed at widening the variety of raw materials by including wood waste and at improving the methods for raw material pyrolysis and activation.

The low reactivity of anthracites toward activating reagents (steam and carbon dioxide) complicates the preparation of related PCMs [4]. The present-day methods for their activation are inefficient and cannot afford a sufficiently wide variety of PCMs [5, 6]. The preparation of carbon supports with good adsorption characteristics by conventional methods of physical adsorption requires a long time and high temperatures. In this case, the burnout loss of the initial anthracite is above 50%. The high-temperature chemical modification of anthracite (for example, using $HClO_4$ or $HNO_3$) followed by physical activation enhances its reactivity [7–9].

Graphites are even more difficult to activate than anthracites. However, graphites can react with various chemicals to form intercalation compounds that increase their volume by a factor of several tens or hundreds times upon heating [10, 11]. The great variety of graphite intercalation compounds and their preparation methods provide the possibility of their synthesis from graphitized PCMs characterized by a high thermal stability and chemical inertness [12, 13].

Here, we describe our studies of the influence of preparation conditions on the pore structure of PCMs obtained from different types of natural organic raw materials and on the properties of PCM-supported palladium catalysts.

## RESULTS AND DISCUSSION

### *1. Carbon Supports from Plant Biomass*

Let us compare the pyrolysis of different types of wood (larch, asp, and beech) and the activation of the resulting charcoals. Pyrolysis was carried out in flowing nitrogen at atmospheric pressure, $T = 500$ or 800°C, and a heating rate of 3 or 12 K/min. Activation was performed in flowing $CO_2$ at 850°C. The texture of the resulting charcoals was studied by electron microscopy, mercury porosimetry, and the Brunauer–Emmett–Teller (BET) method. It turned out that the wood nature and pyrolysis conditions exert a substantial effect on the yields of solid, liquid, and gaseous products and on the pore structure of the resulting carbon.

The reactivity of crude charcoal gasified in a $CO_2$ flow is determined by both the nature of the initial material and the pyrolysis conditions. Aspen charcoal, whose extent of burnout after 30-min-long heat treatment at 800°C exceeds 50%, is activated most readily. Under the same conditions, the extent of burnout of beech charcoal is 26% and that of larch charcoal is only 14%.

The difference between the reactivities of the carbons can stem from the textural features of the initial wood. The wood density increases in the order aspen < beech < larch, whereas the reactivity of the charcoals obtained from these materials by gasification in flowing $CO_2$ increases in the opposite order, namely, larch < aspen < beech. Perhaps the charcoal produced from less dense wood has a looser structure, which favors its

**Table 1.** Influence of the duration of activation in flowing $CO_2$ at 850°C on the extent of burnout and the specific surface area of charcoal obtained by wood pyrolysis

| Initial wood | Activation time, min | Extent of burnout, wt % | Specific surface area, $m^2/g$ |
|---|---|---|---|
| Larch | 10 | 4 | 380 |
| | 20 | 9 | 462 |
| | 30 | 14 | 490 |
| | 40 | 18 | 545 |
| | 50 | 22 | 563 |
| | 60 | 26 | 600 |
| Beech | 10 | 9 | 200 |
| | 20 | 17 | 410 |
| | 30 | 26 | 493 |
| | 40 | 34 | 550 |
| | 50 | 43 | 533 |
| Aspen | 10 | 19 | 220 |
| | 20 | 35 | 480 |
| | 30 | 53 | 593 |

Note: Pyrolysis was carried out at 800°C at a heating rate of 3 K/min.

intensive gasification. Indeed, according to electron microscopic data, as compared to beech and larch charcoals, aspen charcoal is characterized by a more open pore structure dominated by larger pores.

Data characterizing the variation of the specific surface area of the carbons during their activation in flowing $CO_2$ at 850°C are presented in Table 1. At a given extent of burnout (25 wt %), the specific surface area of the larch active carbons is ~600 $m^2/g$ and that of the beech carbons is ~500 $m^2/g$. The aspen active carbons also have a large specific surface area (~600 $m^2/g$) at an extent of burnout larger than 50%.

Use of a mixture of steam and flue gas from power stations as an activating agent reduces the energy expenses for activation and enhances the process [14, 15]. The iodine sorption capacity of the aspen active carbons remained virtually unchanged upon activation for 30 min and decreased sharply upon a longer activation (the oxygen content of the activating agent was below 2 vol %, and the activation temperature was 850°C).

The steam activation of carbonized cedar nutshells at 850°C yielded a PCM with a developed system of micropores and mesopores [16]. The maximum yield of active carbon with a developed porous structure was achieved when the activating agent contained 25–80% steam and 0–2% oxygen (the balance was nitrogen). The iodine adsorption capacity of the PCM obtained from cedar nutshells in 40–70% yield was comparable with that of the commercial sorbents obtained from birch wood (50–80%).

Modification of plant polymers with different chemical reagents makes it possible to control the yield and texture of the carbon product. The modification of plant polymers with transition metal compounds is a promising approach [17–19]. The pyrolysis of metal-substituted plant materials is accompanied by their carbonization and chemical activation.

We studied the thermochemical transformations of birch wood modified with zinc chloride and the properties of the resulting PCMs. The $ZnCl_2$ content of the samples was 5 or 10 wt %.

Carbonization was carried out in a setup with a horizontal flow reactor by heating the samples in flowing argon to 800°C at a rate of 10 K/min. The samples were held for 30 min at the final temperature. The specific surface area of the carbon products was measured by the thermal desorption of nitrogen on a Gazometr-1 analyzer. Elemental composition was determined with a Flash EA 1112 instrument. Thermogravimetric studies were carried out on a Q-1500D thermoanalytical system (Paulik-Paulik-Erdey). IR spectra were recorded on a Vector 22 FTIR spectrophotometer.

The modification of birch wood with zinc chloride increased the yield of the carbon product by 10 wt % and the specific surface area by a factor of 10–25. Zinc chloride promotes the deoxygenation and condensation of the components of the organic mass of wood during pyrolysis and reduces the onset temperature of the intensive thermochemical transformations of wood by 100°C.

A promising way of producing high-quality active carbons is by activating crude wood charcoal in small fluidized-bed reactors [20]. Fluidized-bed activation proceeds at a high rate owing to the high heat- and mass-transfer rates.

The activation of crude charcoal produced from birch wood in a UVP-5B commercial apparatus (steam–gas mixture temperature, 500–1200°C; oxygen concentration in the activating agent, 0.5–8 vol %; steam concentration, 0–40 vol %) was studied in a fluidized-bed reactor. Active carbon with a total pore volume up to 2.1 $cm^3/g$ and an iodine sorption capacity up to 98% was obtained by optimizing the activation parameters [21]. The iodine adsorption capacity of the carbon products obtained under similar conditions in a fixed-bed reactor was 1.5–2 times lower, and their total pore volume was 1.2–1.5 times lower. It is noteworthy that the treatment time is 1.5–2 times shorter in a fluidized bed than in a fixed bed.

The texture and sorption properties of the PCMs obtained from larch and silver fir bark in a fluidized-bed reactor were also studied [22, 23]. The pore structure and sorption properties of these active carbons are determined by the conditions of the preliminary extraction treatment of bark, which is performed to extract valuable substances. As the number of extraction stages is increased, the specific surface area of the PCM increases, the mesopore volume becomes larger due to

micropore "etching," and the mesopores burn to macropore sizes. The preliminary extraction treatment of bark with hexane and alcohol enhances the iodine and methylene blue sorption capacities of the resulting active carbons. The powder materials produced from bark are similar to the commercial cleaning active carbons and their foreign analogues.

An efficient method for preparation of PCM powders from various solid organic raw materials is oxidative treatment in fluidized catalyst bed reactors [24]. By blowing raw material particles into a fluidized bed of larger catalyst particles with a nitrogen flow containing small amounts of oxygen and steam, it is possible to combine the pyrolysis of the raw material and the activation of the resulting carbon products and to obtain a wide variety of PCMs. The role of the catalyst is to speed up the oxidation of the volatile organic pyrolysis products in the fluidized bed. The heat being released maintains the autothermal regime of the process.

Short (several-seconds-long) thermal treatment of powdered hydrolyzed lignin in a fluidized bed of the Al–Cu–Cr oxide catalyst at 670–820°C afforded a PCM with a developed pore structure [25]. The iodine sorption capacity of the carbon products and their reactivity in steam activation depend on the regime of thermal treatment. The optimum conditions were found for the carbonization of hydrolyzed lignin and for the activation of the carbon product. This enabled us to produce quality PCMs (pore volume 2.9 $cm^3/g$, specific surface 750–800 $m^2/g$) in 15–19% yield in terms of the dry lignin weight.

Fibrous supports open up new possibilities in controlling the hydrodynamic regimes of catalytic reactors. Fibrous carbon materials can be obtained by the carbonization of cellulose-containing materials.

The thermal transformations of copper-containing celluloses were studied by IR spectroscopy, ESR, and DTA during their pyrolysis at 250 to 700°C [26]. The cellulose modification conditions and the pyrolysis parameters for the modified materials were optimized to obtain PCMa with a specific surface area up to 600 $m^2/g$. As found by scanning electron microscopy, the carbonized copper-containing materials retain the fibrous structure of the starting cellulose [27].

The texture of porous carbon fiber obtained by the carbonization of woven cellulose [28] was studied by transmission electron microscopy. The carbon fiber had a nanoporous structure formed by short bent layers of graphite-like carbon. The spacing between the (002) graphite layers in fibrous carbon is 0.35–0.40 nm. The material surface contained circular structures with a characteristic size of ~1 nm consisting of graphite-like layers. As found by adsorption measurements, the carbon fiber has a developed nanoporous structure. Its BET specific surface area is as large as 1000 $m^2/g$, and its total pore volume is 0.56 $cm^3/g$. The mesopore size ranges from 4.5 to 10.0 nm, and the mesopore volume is 0.227 $cm^3/g$. The volume of the micropores smaller than 1.0 nm is 0.297 $cm^3/g$.

### *2. Carbon Supports from Solid Fossil Materials*

**Carbonization and activation of brown coals.** The conventional methods of PCM production from brown coals include two stages: coal carbonization and the partial gasification (activation) of the carbon product. We developed a single-stage brown coal carbonization–activation process according to which coal particles are transported with flowing air through a fluidized bed of larger particles of catalytically active open-hearth slag [24]. The solid products obtained under the optimum conditions are nanoporous carbon materials with a predominant pose size of 3–6 nm and a specific surface area above 400 $m^2/g$. These PCMs have a higher reactivity in steam activation than the brown coal carbonization products obtained by conventional methods. Their activation at 650°C until 50–60% burnout produces a PCM with a specific surface area of ~1000 $m^2/g$ [29].

Powdered brown coal carbonization products in combination with coking coal or petroleum pitch can be used in the production of molded sorbents, which have a small specific surface area and a low sorption capacity though. However, the latter can be considerably increased by short-term treatment of the sorbent with steam at 800°C. The optimum duration of the steam activation of the materials obtained from brown coal semicoke and coking coal as a binder is 20 min. The sorbents obtained under these conditions have a specific surface area up to 460 $m^2/g$, a total pore volume up to 0.44 $cm^3/g$, and a mechanical strength of ~32 $kg/cm^2$ [30].

Brown coal bioprocessing products are another cheap binder usable in the preparation of stable carbon pellets from brown coal [31]. As the pyrolysis temperature is raised from 450 to 550°C, the strength of the brown coal pellets grows and their shrinkage increases approximately from 20 to 30%. As the duration of steam activation and the extent of burnout of the pyrolyzed pellets at 800°C increase, their abrasion resistance decreases and their specific surface area and total pore volume increase.

Optimization of the pyrolysis and activation conditions makes it possible to obtain, from brown coal, using 30% burnout and a biological binder content of 15%, carbon sorbent pellets with an abrasion resistance of 76–77%, a specific surface area of 460–480 $m^2/g$, and a pore volume of 0.46 $cm^3/g$ (Table 2).

**Thermal and chemical activation of anthracites.** PCM powders can be obtained from anthracites by two different methods, namely, rapid heating of powdered anthracite in a fluidized bed of an oxidation catalyst or open-hearth slag and thermal treatment of chemically modified anthracite in a fixed bed under heat shock conditions [32].

Rapid heating enhances the reactivity of anthracite toward gasifying agents. The sorption capacity of the

**Table 2.** Influence of the extent of burnout during the activation of carbonized brown coal pellets on selected characteristics of the resulting PCM

| Extent of burnout, % | Abrasion resistance, % | Specific surface area, $m^2/g$ | Total pore volume, $cm^3/g$ |
|---|---|---|---|
| 10 | 83 | 240 | 0.24 |
| 20 | 80 | 360 | 0.39 |
| 30 | 76.5 | 460 | 0.46 |
| 40 | 50 | 480 | 0.54 |
| 50 | 33 | 460 | 0.69 |

Note: Carbonization was carried out at 550°C, and subsequent activation was performed at 800°C. The biological binder content was 15 wt %.

thermally treated and then activated anthracite is two times higher than that of anthracite activated without thermal pretreatment. For heat-treated anthracite, the activation time is shorter by a factor larger than 3 and the consumption of the starting material is lower.

Pretreatment of demineralized anthracite with a mixture of nitric and sulfuric acids at room temperature considerably changes its chemical composition and structure. Subsequent short-term thermal treatment of thus modified anthracite by rapidly heating it to 900°C favors a significant development of its microporous structure. As can be seen from the pore size distribution histogram presented in Fig. 1, the pore width varies from 0.7 to 2.5 nm. The resulting PCM exhibits a high iodine sorption capacity (~70%). The PCM yield is 84% of the initial anthracite weight, which is twice as large as the PCM yield in the conventional steam–gas activation process, and the thermal treatment time is only a few minutes.

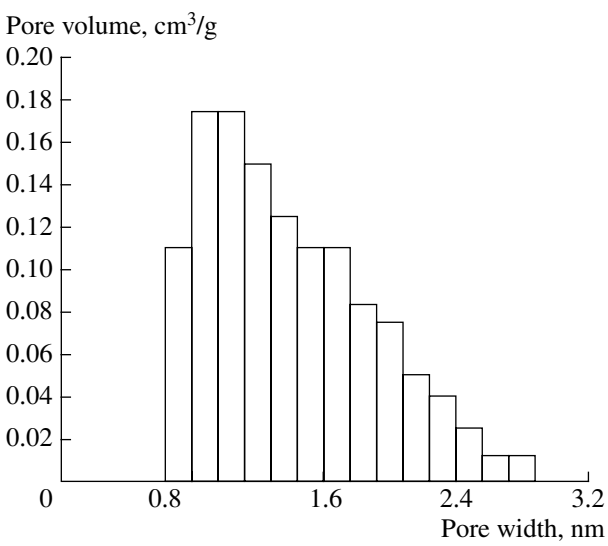


**Fig. 1.** Micropores size distribution in the PCM obtained from chemically modified anthracite (determined by nitrogen adsorption at 77 K).

**Thermal expansion of intercalated natural graphites.** Natural graphites available from the Zaval'evskii and Kyshtymskii Graphite Industrial Complexes were used to obtain graphitized PCMs. The specific surface area of the starting graphite samples was ~1 $m^2/g$. Demineralized samples were intercalated by chemical and electrochemical means.

In the former case, the starting graphite was treated with oxidizers and acids [33]. The GKhA sample was prepared by the oxidation of graphite with chromic anhydride in concentrated sulfuric acid, the GAK sample was obtained by treating graphite with concentrated nitric acid, and the GAUK sample was prepared by successive treatment of graphite with concentrated nitric and glacial acetic acids.

Electrochemical intercalation was carried out using nitric acid (GAK-AK and GT-AK samples) or sulfuric acid (GAK-SK and GT-SK samples). In addition, we studied the texture of the PCM prepared from commercial graphite intercalated with nitric acid (GO-4/4.5).

Thermally expanded graphite (TEG) was prepared by heat-treating intercalated samples at 900°C for 60 s.

As follows from the data presented in Table 3, TEG samples differ noticeably in texture, which depends most strongly on the nature of the intercalating agent. The samples obtained by electrochemical intercalation with nitric acid have a larger specific surface area and a larger pore volume than the samples intercalated with sulfuric acid.

The changes in the appearance of the graphite samples upon intercalation and thermal treatment are illustrated in Fig. 2. The graphite particles from the Zaval'evskoe deposit are flat flakes with rounded edges (Fig. 2a), and the same particles intercalated with perchloric acid take a vermicular shape upon thermal treatment (Fig. 2b).

The thermal expansion coefficient of chemically modified natural graphite from the Kyshtymskoe deposit was substantially larger if, after nitric acid intercalation, it was additionally treated with different organic compounds, petroleum bitumen, and coal tar pitch. As the bitumen content of the batch was raised from 10 to 40 wt %, the BET specific surface area of TEG increased from 20 to 170 $m^2/g$. For treatment with charcoal tar pitch, the maximum specific surface area (~110 $m^2/g$) was achieved with a batch containing 20 wt % pitch.

A drawback of TEG is its low mechanical strength, which limits the use of TEG-based carbon supports. However, TEG can easily be molded without additives of binders and the resulting molded products have high strength.

We studied the effect of the molding conditions on the texture of TEG obtained by thermal treatment of GO-4/4.5 commercial intercalated graphite at 900°C.

**Table 3.** TEG texture parameters determined by $N_2$ adsorption at 77 K

| Sample | Specific surface area, $m^2/g$ | Pore volume, $cm^3/g$ | Average pore diameter, nm | Micropore volume, $cm^3/g$ |
|---|---|---|---|---|
| | | Chemical intercalation | | |
| GKhA | 53.0 | 0.241 | 18.2 | 0.028 |
| GAK | 12.3 | 0.083 | 27.0 | 0.006 |
| GAUK | 33.3 | 0.138 | 16.6 | 0.013 |
| GO-4/4.5 | 41.1 | 0.140 | 13.7 | 0.006 |
| | | Electrochemical intercalation | | |
| GAK-AK | 70.0 | 0.407 | 23.1 | 0.020 |
| GAK-SK | 45.7 | 0.244 | 21.3 | 0.013 |
| GT-AK | 68.5 | 0.554 | 32.3 | 0.007 |
| GT-SK | 40.6 | 0.216 | 21.3 | 0.012 |

Molding decreased the specific surface area and porosity of the initial sample. The most pronounced (more than twofold) decrease in the specific surface area was observed at a specific molding pressure of 0.5 atm/cm$^2$. Increasing the molding pressure to 2.5 atm/cm$^2$ exerted only a weak effect on the TEG texture.

### *3. Palladium Catalysts on Carbon Supports Produced from Natural Raw Materials*

**State of supported palladium.** The distribution and particle size of supported palladium depend on the method by which the carbon support was prepared from a plant polymer, natural graphite, or anthracite. Different procedures are used to load carbon supports with palladium. We impregnated the carbon support with a water–ethanol solution of $H_2PdCl_4$ [34]. The supported palladium content of all catalysts was 1 wt %.

Since fibrous carbon from cellulose has a developed nanoporous structure consisting of pores almost uniform in size, palladium is uniformly distributed when $H_2PdCl_4$ is supported on this material [28]. Raising the temperature of reduction of palladium supported on fibrous carbon in flowing hydrogen to 423 K does not change the sizes or distribution of the metal particles. The supported metal particles are mainly localized in mesopores, and their predominant size is 4–5 nm. Larger palladium particles are present in insignificant amounts.

Palladium particles supported on the carbon supports obtained by the carbonization of microcrystalline cellulose are mainly 1–2 nm in size and are uniformly distributed on the carbon surface [35]. Palladium aggregates consisting of metal particles ~5 nm in size are also observed, and the size of the aggregates themselves is about 50 nm. The nanosized palladium particles are

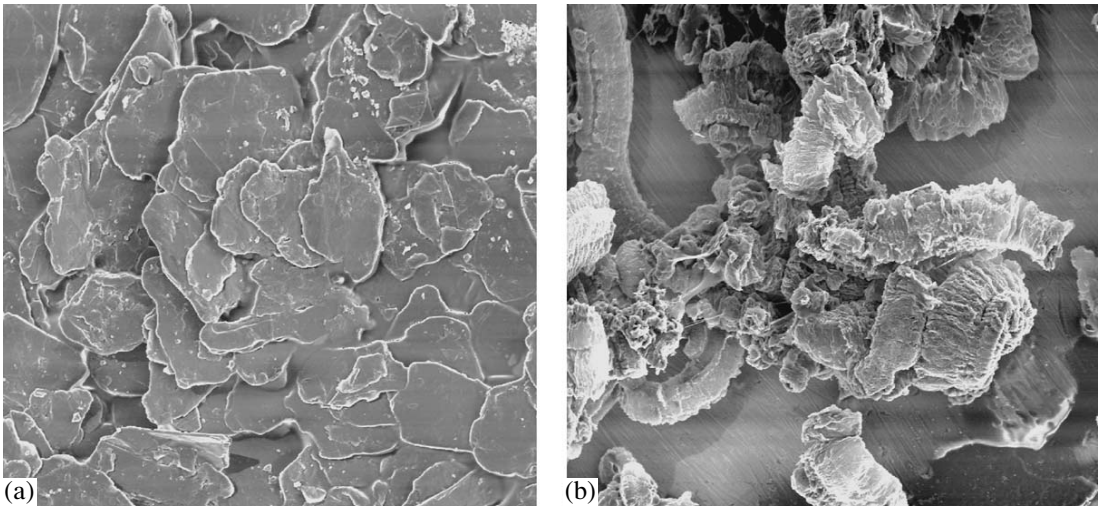


**Fig. 2.** Electron micrographs of the initial and thermally expanded graphite samples (×250): (a) graphite from the Zaval'evskoe deposit and (b) the same graphite intercalated with nitric acid after the thermal treatment under stationary conditions at 900°C.

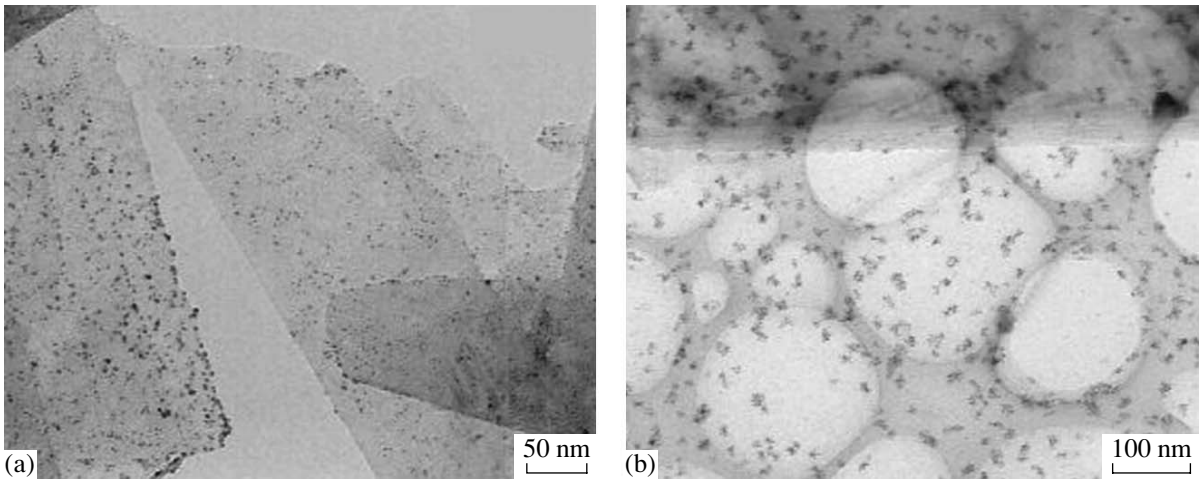


**Fig. 3.** Electron micrographs of the 1% Pd/TEG catalyst whose support was obtained from graphite intercalated with (a) $HNO_3$ and (b) $HNO_3$ and then $CH_3COOH$.

resistant to sintering in a hydrogen atmosphere at 423 K.

Depending on the method of preparation of the carbon support, palladium underwent partial or almost complete reduction while TEG or anthracite was loaded with $H_2PdCl_4$. By changing the conditions of synthesis of the carbon support from graphite or anthracite, one can ensure the domination of 1- to 2-nm palladium particles or their aggregates or the localization of the metal inside narrow micropores.

When no chemical modification was used in the preparation of activated anthracite, the supported palladium compound was distributed nonuniformly and large aggregates formed along with particles smaller than 10 nm. Smaller and uniformly distributed supported palladium particles with an average size of about 2 nm formed on chemically modified anthracite supports [36].

The method of preparation of TEG has a substantial effect on the size of the supported palladium particles, their morphology, and their distribution on the carbon support [37]. The most uniform distribution of nanosized (2–4 nm) palladium particles is achieved on the TEG support obtained using nitric acid intercalation. An electron micrograph of this material is shown in Fig. 3a. This catalyst is the most resistant to sintering under conditions of hydrogen reduction. On the TEG sample prepared by successive treatment of graphite with nitric and acetic acids, most of the 1- to 4-nm palladium particles are grouped into clusters rather uniformly distributed on the carbon surface (Fig. 3b). The reduction of this sample with hydrogen at 150°C is accompanied by noticeable sintering of the supported palladium into aggregates with a dendrite structure.

**Catalytic activity of supported palladium in hydrogenation.** The activities of the palladium catalysts prepared by supporting $H_2PdCl_4$ on different PCMs were compared in the liquid-phase hydrogenation of hex-1-ene and cyclohexene. It turned out that the method of preparation of the carbon support has a substantial effect on the catalytic properties of the catalysts (Table 4). To a certain extent, this is due to the fact that supported $H_2PdCl_4$ interacts differently with carbon supports prepared by different methods. Considerable amounts of palladium particles were found in some unreduced $H_2PdCl_4$/PCM catalysts.

No well-defined correlation was observed between the specific surface area of the carbon support and catalytic activity. The catalysts containing aggregates of nanosized metal particles are the most active in hex-1-ene and cyclohexene hydrogenation. The catalysts in which a considerable part of ultrafine palladium particles are localized in micropores of the carbon support exhibit low hydrogenating activity.

The low catalytic activity of the ultrafine particles of supported palladium can be explained by the strong interaction of the metal localized in the micropores with the carbon support. This strong interaction can substantially affect the electronic state of the metal and its adsorption properties [38]. In addition, the impeded diffusion of the reactant and product molecules in the micropores also contributes to the decrease in catalytic activity.

In each particular case, any of these factors can play the main role, depending on the method of preparation of the carbon support.

On the catalysts examined, hex-1-ene is hydrogenated more rapidly than cyclohexene (Table 4). This effect is most pronounced when a considerable part of the ultrafine palladium particles are localized in narrow micropores of the carbon support. It can be assumed that the linear molecules of hex-1-ene diffuse into narrow slitlike pores more rapidly than cyclohexene molecules because of the larger effective radius of the latter.

**Table 4.** Catalytic activity of palladium catalysts (1 wt % Pd) on carbon supports in the liquid-phase hydrogenation of hex-1-ene and cyclohexene at 323 K

| Starting material for the carbon support | Specific surface area, $m^2/g$ | Reduction* | Reaction rate (mol $H_2$) (mol Pd)$^{-1}$ min$^{-1}$ | | Hex-1-ene/cyclohexene reaction rate ratio |
|---|---|---|---|---|---|
| | | | hex-1-ene | cyclohexene | |
| Graphite | 53 | – | <0.1 | <0.1 | ~1 |
| | | + | 0.53 | 0.30 | 1.77 |
| ″ | 33 | – | 11.12 | 10.70 | 1.05 |
| | | + | 36.25 | 21.80 | 1.66 |
| ″ | 12 | – | 6.18 | <0.1 | >60 |
| | | + | 26.10 | 7.10 | 3.68 |
| Anthracite | 868 | – | 21.22 | 13.90 | 1.53 |
| | | + | 32.21 | 29.50 | 1.10 |
| ″ | 549 | – | 16.90 | 6.45 | 2.62 |
| | | + | 16.66 | 17.31 | 0.96 |
| ″ | 425 | – | 9.94 | 2.23 | 4.46 |
| | | + | 10.11 | 1.96 | 5.16 |
| ″ | 410 | – | 15.60 | 0.92 | 16.96 |
| | | + | 26.13 | 1.22 | 21.41 |
| Cellulose fiber | 1000 | + | – | 61.2 | – |
| Microcrystalline cellulose | 520 | + | – | 47.3 | – |

* The catalysts were reduced in flowing hydrogen at 423 K.

In addition, the chemical modification of graphites and anthracites changes the chemical composition of the surface. It is known that the treatment of a carbon material with an oxidizer (for instance, nitric or perchloric acid) increases the concentration of surface electron-withdrawing functional groups [9, 39, 40] and decreases the fraction of electron-donating sites, including π-conjugated systems on the carbon surface.

## CONCLUSIONS

The above results suggest that various types of cheap natural organic raw materials (plant biomass, fossil coal, and natural graphites) are promising for the production of carbon supports and carbon-supported catalysts.

Improved methods were proposed for the preparation of powder, granular, fibrous, and molded PCMs with a developed micropore and mesopore surface from various woods, cellulose, bark, cedar nutshell, and hydrolyzed lignin.

The process conditions for the simultaneous carbonization and activation of powdered brown coal in a fluidized bed of an oxidation catalyst were optimized so as to obtain a PCM with a specific surface area of at least 400 $m^2/g$ by single-stage thermal treatment no longer than a few seconds. Activation of the resulting PCM with water vapor increases its specific surface area to 1000 $m^2/g$. Molding the PCM powder from brown coal with binders (such as petroleum pitch, coking coal, and brown coal biological treatment products) followed by activation affords stable molded supports with a specific surface area of 460–480 $m^2/g$.

The influence of the synthesis conditions on the porous structure of carbon supports from thermally expanded natural graphite and chemically modified anthracites was studied. Thermally expanded graphite from the Zaval'evskoe and Kyshtymskoe deposits was found to be largely microporous. Depending on the intercalation and thermal expansion conditions, the average width of the slitlike pores of graphite ranges from 0.77 to 0.92 nm and the BET specific surface area lies between 12 and 70 $m^2/g$.

The carbon supports prepared by thermal treatment of anthracites modified with $HClO_4$ or an $HNO_3$–$H_2SO_4$ mixture also have a developed micropore structure. Their total specific surface area is 280–1150 $m^2/g$, their specific micropore surface area is 162–345 $m^2/g$, their micropore volume is 0.133–0.253 $cm^3/g$, and their average pore width is 1.5–1.9 nm.

The methods for preparation of finely dispersed palladium catalysts on carbon supports from cellulose, activated anthracites, and TEG are described.

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