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Porous Carbon Materials Produced by the Chemical Activation of Birch Wood

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Abstract—It was established that the main factors responsible for the yield and specific surface area of porous carbon materials obtained by the chemical activation of the wood of birch are the nature of a modifying agent and the temperature of pyrolysis. The additional opening of the porous structure of the product of the chemical activation of wood occurs at the stage of its water treatment as a result of the removal of water-soluble compounds. The conditions of the carbonization of birch wood modified with H_3PO_4, KOH, and $ZnCl_2$ were chosen in order to provide the significant development of the porous structure of carbon materials. The porous carbon material with the highest specific surface area (more than 2560 m^2/g) was obtained by the water washing of the product of the carbonization of birch wood modified H_3PO_4 at 400°C.

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INTRODUCTION

The production of porous carbon materials is a reasonable line in the utilization of raw waste lumber and waste wood. Interest is currently growing in the production of microporous sorbents capable of effectively adsorbing low-molecular-weight gases and exhibiting molecular-sieve properties in the separation of gas mixture [1–4].

The use of the chemical activation of raw materials based on the introduction of chemical additives into the source material with the subsequent heat treatment in an inert or oxidizing atmosphere is effective for the production of porous carbon materials. Compounds such as $ZnCl_2$, Al_2O_3, H_3PO_4, and alkali metal carbonates or oxides are used as chemical promoters [5–8]. At an elevated temperature, the promoters facilitate the removal of oxygen and other heteroatoms from the raw material and the development of the porous structure of the carbon material.

As compared with traditional methods used for the activation of a preliminarily carbonized product by gaseous reagents (water vapor, CO_2, and oxygen) [9, 10], chemical activation makes it possible to decrease power consumption for the activation of raw materials and to increase the specific surface areas and, in a number of cases, the yield of the porous carbon materials obtained.

Various factors, such as the nature and quantity of a chemical reagent, the final temperature, the rate of heating, and the process time, affect the formation of the porous structure of a carbon material in the course of chemical activation. By now, only limited data on the influence of the above factors on the yield and the structure of porous carbon materials obtained by the chemical activation of wood raw materials are available [11–13].

The aim of this work was to study the influence of the nature of chemical reagents and the conditions of the thermal activation and water treatment of birch wood on the yield and textural characteristics of the porous carbon material obtained on its basis.

EXPERIMENTAL

Air-dry sawdust of the wood of birch (fraction, 0.25–0.5 mm) was used as a source material for the preparation of porous carbon materials.

The modification of the sawdust was carried out by their impregnation with the aqueous solutions of KOH, phosphoric acid, or $ZnCl_2$ for 24 h followed by drying at a temperature of 102–105°C for two or three days to constant weight. The KOH and H_3PO_4 contents of the wood of birch were 50 wt %, and the concentrations of $ZnCl_2$ were 5 and 10 wt %.

The pyrolysis of the samples was carried out in a system with a horizontal flow reactor in a flow of argon supplied at a rate of 130 cm^3/min. The heating rate was 10 K/min; the final temperatures of heating were 200, 300, 400, 500, 600, 700, and 800°Cwith an exposure

Table 1. Textural characteristics of porous carbon materials obtained by the heat treatment of a mixture of the wood of birch with KOH at 800°C

Sample number	Wood/KOH weight ratio	Specific surface area S_{sp}, m^2/g	Total pore volume V_{pore}, cm^3/g	Micropore volume V_{micro}, cm^3/g	Average pore width, nm
1	1:1	880	0.42	0.31	2.19
2	1:2	963	0.48	0.33	2.14
3	1:3	1338	0.69	0.40	2.08

of 30 min at a final temperature. The carbon material obtained was washed with water at a temperature of 60°C to a neutral value of pH and dried at a temperature of 105°C.

The FTIR spectra of the samples were measured on a Vector 22 Fourier transform IR spectrometer from Bruker. The test samples were prepared as pressed pellets containing 2 mg of a porous carbon material in a matrix of potassium bromide.

Thermogravimetric analysis was carried out with the use of a Netzsch STA 449F1 instrument in a temperature range from 30 to 800°C at a sample heating rate of 5 K/min in an atmosphere of argon.

The textural characteristics of the samples were determined from the isotherms of nitrogen adsorption at 77 K with the use of an ASAP 2420 Micrometrics instrument in the range of the relative pressures $P/P_0 = 0.005–0.995$. Before the measurement, the samples were exposed in a vacuum at 300°C for 12 h.

RESULTS AND DISCUSSION

Preparation of porous carbon materials from birch wood modified with KOH. It is well known that the treatment of carbon-containing materials, for example, coal and lignin, with alkalis significantly contributes to the development of the porous structure of carbon products obtained by the pyrolysis of chemically modified raw materials at elevated temperatures [14–16].

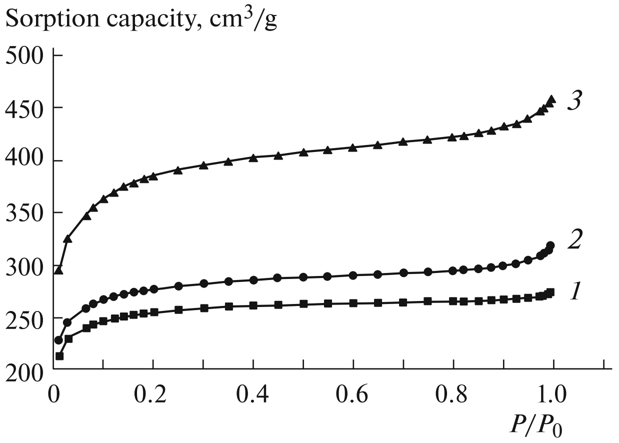

Fig. 1. Isotherms of nitrogen adsorption (77 K) on the samples of porous carbon materials obtained by the pyrolysis of birch wood–KOH mixtures with different component ratios: (*1*) 1 : 1, (*2*) 1 : 2, and (*3*) 1 : 3.

We studied the influence of the wood/KOH ratio, the temperature of the heat treatment of a mixture, and the stage of the washing of carbon products for the removal of water-soluble substances on the yield and the textural characteristics of the resulting porous carbon materials.

As a result of the experimental studies, we found that, in the pyrolysis of KOH–birch wood mixtures, an increase in the alkali content of the mixture from 1 : 1 to 1 : 3 led to an increase in the specific surface area of the porous carbon material from 880 to 1338 m^2/g and in the total pore volume from 0.42 to 0.69 cm^3/g (Table 1). In the absence of an alkali, the specific surface area of the sample of porous carbon material obtained by the pyrolysis of birch wood at 800°C was 378 m^2/g.

The isotherms of nitrogen adsorption at 77 K on the samples of porous carbon materials obtained by the pyrolysis of KOH mixtures with birch wood (Fig. 1) correspond to the type I isotherms in terms of shape and form; this fact is indicative of the developed microporous the texture of the resulting carbon materials [17].

The impregnation of the wood of birch with an aqueous solution of KOH was used for decreasing the consumption of alkali in the process of chemical activation. The sample obtained contained 50 wt % KOH. We studied the effect of the pyrolysis temperature of this sample on the yield and the specific surface area of the resulting solid product (Figs. 2 and 3). As follows from the data given in Fig. 2, the introduction of 50 wt % KOH into the wood increases the yield of solid products by a factor of 2–2.5 at pyrolysis temperatures higher than 300°C.

The specific surface area of the solid products of the pyrolysis of the initial wood and wood containing 50 wt % KOH weakly depends on treatment temperature and varies from 1 to 30 m^2/g.

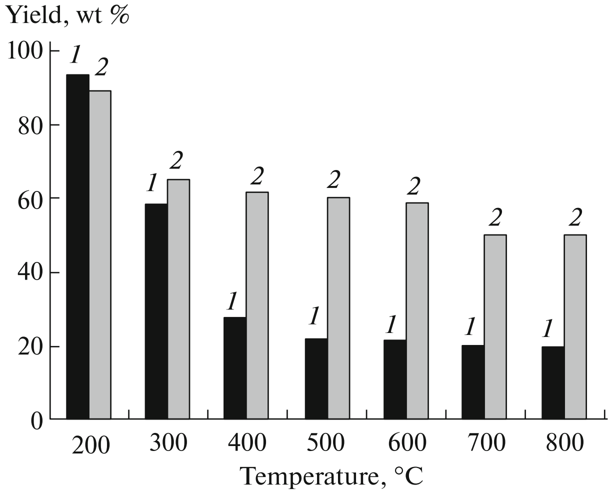

Fig. 2. Effect of the temperature of pyrolysis on the yield of solid product from (*1*) the initial wood of birch and (*2*) the wood modified with 50 wt % KOH.

The water treatment of the pyrolyzed samples was used for the removal of water-soluble substances and the opening of the porous structure of solid products. Figure 3 shows data on the influence of the washing of the solid pyrolysis products of birch wood modified with KOH on the yield and the specific surface area of the porous materials.

As follows from the experimental data, the greatest amount of water-soluble substances was present in the samples pyrolyzed at temperatures of 200 and 300°C (Fig. 3). An increase in the pyrolysis temperature above 300°C leads to an increase in the yield of porous carbon materials, obviously, because of a decrease in the concentration of water-soluble products in the samples.

The porous carbon materials obtained by the pyrolysis of the wood birch samples modified with KOH at temperatures of 600–800°Cexhibited the highest specific surface areas (750–1200 m^2/g) (Fig. 3).

Thus, the water treatment of the pyrolyzed birch wood samples modified with KOH facilitates the additional opening of their porous structure as a result of the removal of water-soluble substances.

The IR spectra of the samples of birch wood modified with KOH exhibited a decrease of the intensities of the absorption bands of aliphatic CH_2 and CH_3 groups (3000–2800 cm^{-1}) with the temperature of heat treatment (Fig. 4). Intense bands in the region of 1450–850 cm^{-1} and at 1584 cm^{-1}, which were observed in the spectra of all of the samples (regardless of the carbonization temperature), obviously, correspond to the vibrations of carbonates and the potassium salts of carboxylic acids [18].

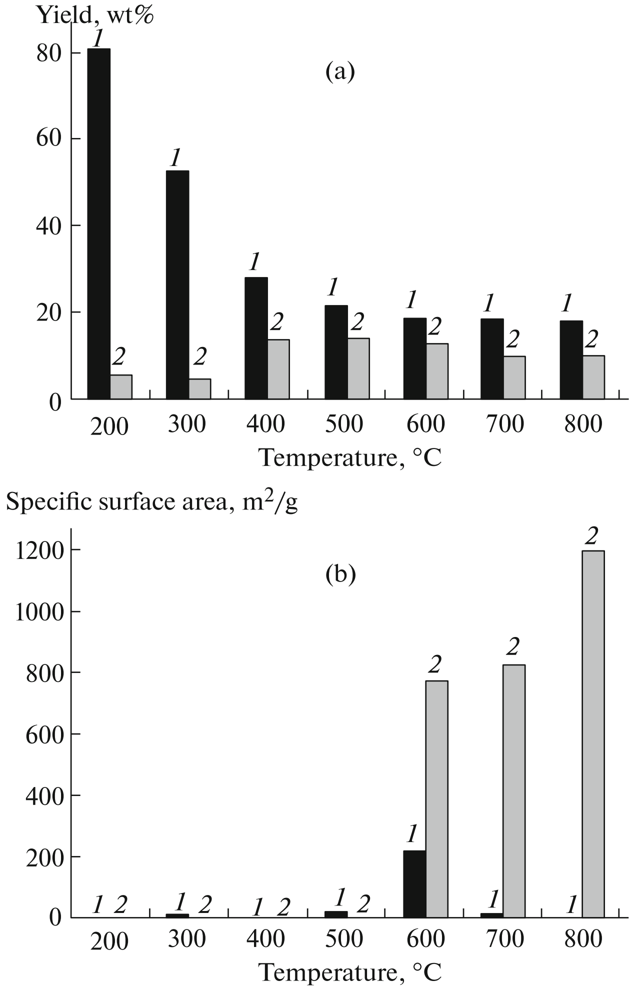

Fig. 3. Effect of the temperature of pyrolysis of (*1*) the initial wood of birch and (*2*) the wood containing 50 wt % KOH on (a) the yield and (b) the specific surface area of the porous materials washed with water.

After the washing of the pyrolyzed samples with water, there were no absorption bands due to the vibrations of potassium compounds in their IR spectra (Fig. 4), and the intensities of all absorption bands decreased with the temperature of heat treatment. The presence of absorption bands at 1700 and 1300–1040 cm^{-1} is indicative of the presence keto ether compounds in the samples; the concentration of these compounds noticeably decreased in the samples pyrolyzed at temperatures higher than 500°C [18, 19].

Modification of the birch wood with H_3PO_4. As in the case of porous carbon materials obtained from the birch wood modified with KOH, an increase in the yield of the carbon product in the presence of phosphoric acid was observed at carbonization temperatures higher than 300°C (Fig. 5a). However, in the samples modified with H_3PO_4, a considerable increase in the specific surface areas (500–700 m^2/g) was

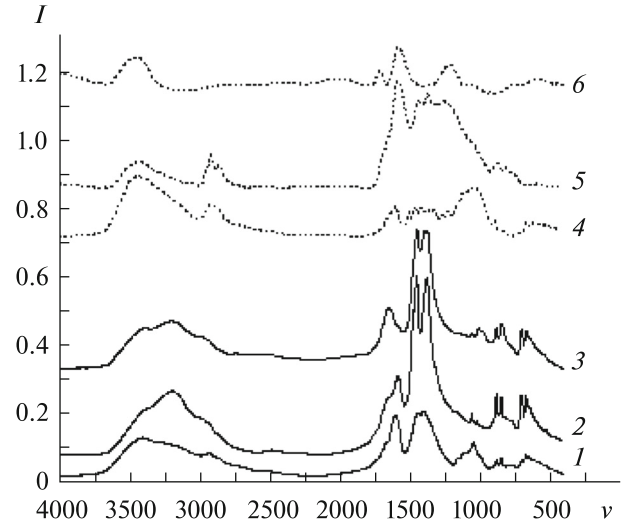

Fig. 4. IR spectra of the solid products obtained by the pyrolysis of birch wood containing 50% KOH (*1–3*) before and (*4–6*) after water treatment. Temperature of pyrolysis: (*1*, *4*) 25, (*2*, *5*) 400, or (*3*, *6*) 800°C.

observed only at pyrolysis temperatures of 700–800°C (Fig. 5b).

The X-ray fluorescence analysis of the samples showed that the phosphorus content of the obtained carbon materials noticeably decreased with the temperature of carbonization. Thus, after pyrolysis at 800°C, the phosphorus content of the porous carbon material was lower by an order of magnitude than that in the initial sample. This suggests the thermal instability of phosphorus-containing compounds and the removal of them as volatile products upon heat treatment. This, obviously, facilitates the formation of a developed porous structure of carbon materials upon the high-temperature treatment. Thus, the modification of wood with phosphoric acid increases the yield and specific surface area of the obtained carbon materials.

The water treatment of the pyrolyzed samples was used for the removal of water-soluble compounds and the opening of the porous structure of solid products obtained by the pyrolysis of the birch wood modified with H_3PO_4. It was found that, with an increase in the pyrolysis temperature of these samples from 200 to 800°C, an increase in the yield of water-washed porous carbon materials was observed, whereas the yield of a solid product dramatically decreased with the pyrolysis temperature in the case of the initial wood (Fig. 6). At pyrolysis temperatures of 600–800°C, the yield of porous carbon materials from the modified wood of birch was higher than that from the parent wood (Fig. 6a).

The concentration of water-soluble substances in the samples of porous carbon materials from birch wood modified with H_3PO_4 decreased with the temperature of pyrolysis, and the solid product obtained after treatment at 800°C was almost insoluble in water.

The water washing of porous carbon material samples from the birch wood modified with H_3PO_4 led to a considerable increase in their specific surface areas. A maximum specific surface area (2560 m^2/g) was observed in the sample obtained at 400°C (Fig. 6b). One of the reasons for the high specific surface area of this sample can be the removal of water-soluble phosphorus-containing compounds in the process of water washing, as evidenced by data obtained by the X-ray fluorescence and IR-spectral (Fig. 7) analysis of the sample. A decrease in the specific surface area of the samples of porous carbon materials obtained at pyrolysis temperatures higher than 500°C can be caused by the formation of water-insoluble products, which block their pores.

The IR spectra of the samples obtained by the heat treatment of birch wood containing H_3PO_4 in a temperature range of 25–500°C are similarly shaped (Fig. 7). Intense absorption in the region of 3600–2000 cm^{-1} suggests the presence of OH groups, including P–OH groups, and a small quantity of aliphatic methyl and methylene groups. An absorption at 1714 cm^{-1} band indicates the presence of C=O bonds. Absorption in the region of 1400–980 cm^{-1} is, probably, caused by the stretching vibrations of C–O, C–C, and P–O–C bonds or alkyl-substituted and aryl-substituted phosphate groups and by the deformation vibrations of CH_2 and CH_3 groups [19, 20]. In the spectra of samples 6–8, which were obtained at treatment temperatures of 600, 700, and 800°C, the intensity of absorption bands noticeably decreased. In general, the results of an infrared-spectroscopic study indicate the progressive removal of different functional groups as the temperature of pyrolysis is increased.

The intensity of the absorption bands of different functional groups in the IR spectra also sharply decreased after the water washing of the heat-treated samples (Fig. 7); this fact indicates the removal of water-soluble compounds containing P–OH, P–O–C, etc., groups. The presence of the absorption bands of phosphorus-containing groups in the IR spectra of the water extracts indirectly confirms the assumption that an increase in the specific surface area of the water-washed porous carbon materials is caused by the additional opening of their porous structure as a result of the removal of phosphorus-containing substances.

Modification of birch wood with $ZnCl_2$. We studied the influence of the concentration of $ZnCl_2$ introduced into the birch wood and the temperature of

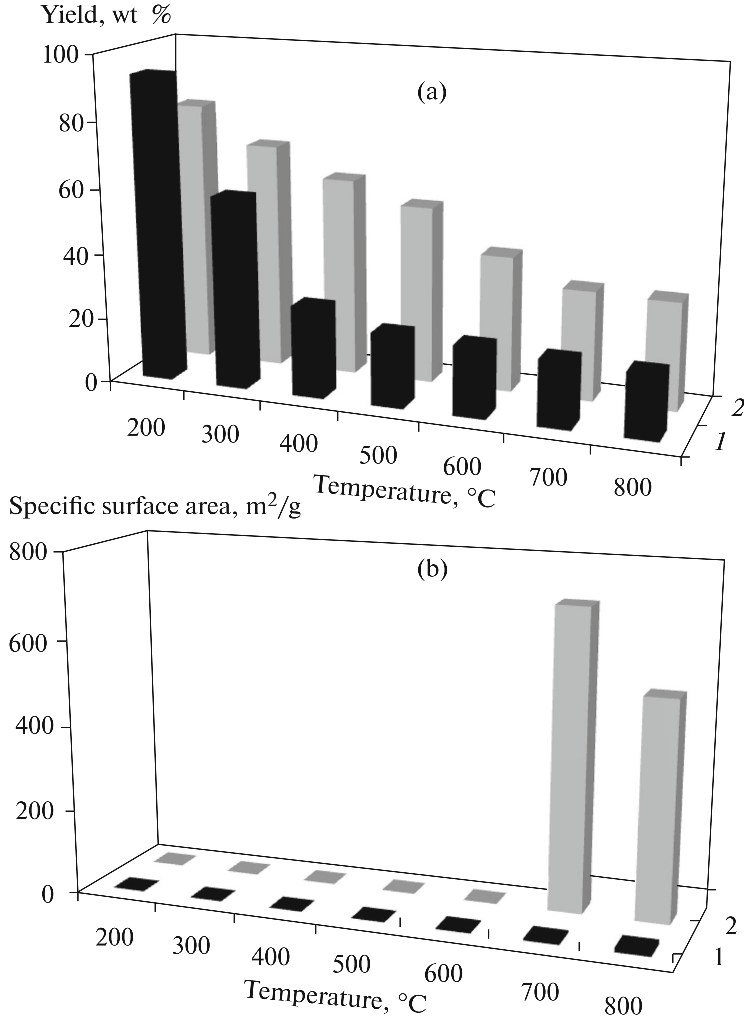

Fig. 5. Effect of the temperature of pyrolysis of (*1*) the initial birch wood and (*2*) the wood modified with H_3PO_4 on (a) the yield and (b) the specific surface area of the solid product.

pyrolysis on the yield and the specific surface area of the porous carbon materials obtained (Table 2).

The main decrease in the yield of porous carbon materials from the initial birch wood occurred in a temperature range of 200–400°C or in a narrower range of 200–300°C for the wood samples modified with zinc chloride. In the range of pyrolysis temperatures of 400–800°C, the yield of porous carbon materials from the birch wood containing $ZnCl_2$ was higher by a factor of about 1.5 than that from the initial wood. In this case, a variation in the zinc chloride content of the wood from 5 to 10 wt % had almost no effect on the yield of porous carbon materials.

The specific surface area of porous carbon materials substantially changes in the course of the pyrolysis of wood modified with $ZnCl_2$ (Table 2). For the porous carbon material from the initial wood, it was only 27 m^2/g at a pyrolysis temperature of 800°C, whereas the specific surface area of the porous carbon material obtained under analogous conditions from the wood containing 5 wt % $ZnCl_2$ was 300 m^2/g. The porous carbon material with a maximum specific surface area (670 m^2/g) was obtained by the pyrolysis of a wood sample containing 10 wt % $ZnCl_2$ at a temperature of 700°C.

Thus, the chemical activation of the birch wood with zinc chloride facilitates an increase in the yield and specific surface area of the resulting porous carbon materials. Moreover, with an increase in the zinc chloride content of the birch wood, the yield of a carbon residue remained almost unchanged, but the specific surface area increased by a factor of 1.5–2.

According to the results of a thermogravimetric study, in the presence $ZnCl_2$, the initial temperature

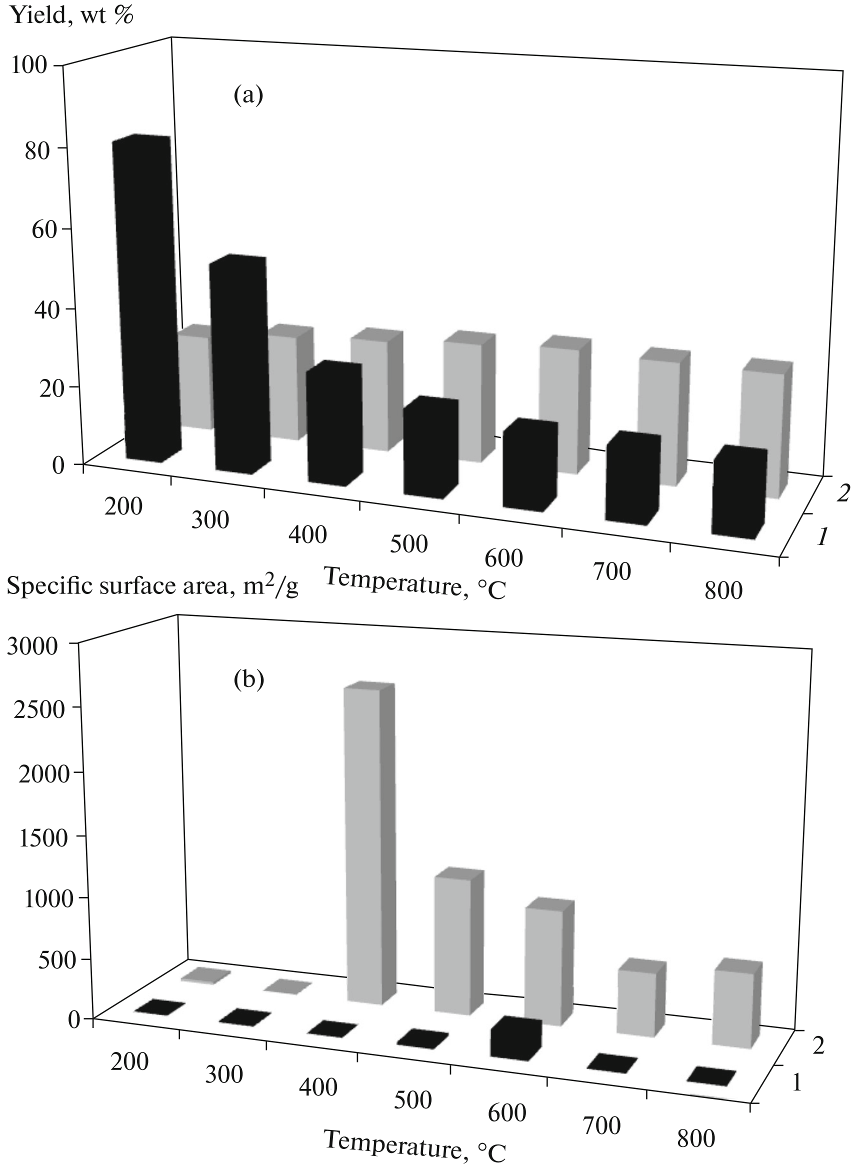

Fig. 6. Effect of the temperature of pyrolysis of (*1*) the initial birch wood and (*2*) the wood modified with H_3PO_4 on (a) the yield and (b) the specific surface area of the carbon material washed with water.

and intensity of the thermochemical conversion of birch wood noticeably decreased. The highest rate of the thermal destruction of the initial wood of birch was observed at 330°C or, in the case of modified wood samples, at 290 and 235°C for $ZnCl_2$ concentrations of 5 and 10 wt %, respectively.

The elemental analysis data and the results of the IR-spectroscopic study indicate that a noticeable change in the chemical composition of the initial wood of birch began to occur at a pyrolysis temperature of 300°C or at 200°C in the pyrolysis of wood modified with $ZnCl_2$. It is likely that the additives of $ZnCl_2$ intensify the processes of decarboxylation, decarbonylation, and aromatization at elevated temperatures. In this case, the C/O and C/H ratios noticeably increase and the porous structure of a carbon product is developed.

Thus, the modification of the wood of birch with zinc chloride leads to the displacement of the onset of intense thermochemical conversions of wood into the low-temperature region, a certain increase in the yield of a carbon product, and an increase in its specific surface area (by a factor of 10–25 in comparison with porous carbon materials from the initial birch wood).

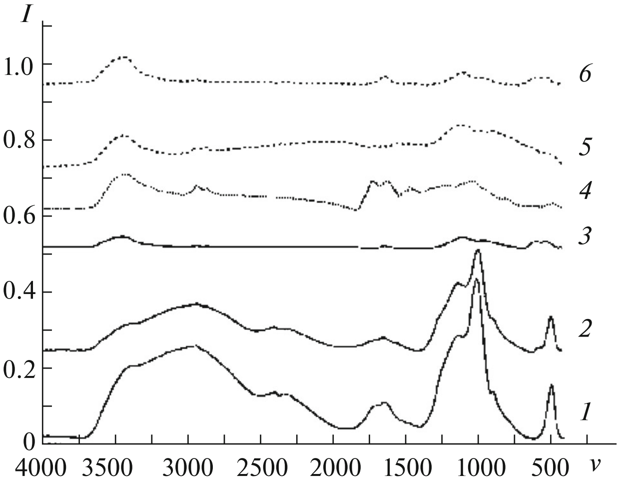

Fig. 7. IR spectra of the solid products obtained by the pyrolysis of the birch wood containing H_3PO_4 (*1–3*) before and (*4–6*) after water treatment. Temperature of pyrolysis: (*1*, *4*) 25, (*2*, *5*) 400, or (*3*, *6*) 800°C.

CONCLUSIONS

We found the influence of the nature of a chemical promoter, the process conditions of the pyrolysis of birch wood modified with H_3PO_4, KOH, and $ZnCl_2$, and the water treatment of the carbonization product of the chemically modified wood on the yield and the textural characteristics of the resulting porous carbon materials.

The specific surface areas and pore volumes of the porous carbon materials obtained by the pyrolysis of KOH–birch wood mixtures at 800°C increase with the alkali content of the mixture. The specific surface area of porous carbon materials increases from 880 to 1338 m^2/g, and the total pore volume increases from 0.42 to 0.69 cm^3/g as the wood/KOH weight ratio is increased from 1 : 1 to 1 : 3.

With a 50 wt % KOH content of the wood, the porous structure of the obtained porous carbon materials cannot be developed even at high pyrolysis temperatures (600–800°C). However, the removal of water-soluble compounds, which, probably, occur in the form of carbonates and the potassium salts of carboxylic acids, from them leads to an increase in the specific surface area of the porous carbon materials to 750–1200 m^2/g.

In the case of the porous carbon materials obtained from the wood of birch modified with 50 wt % H_3PO_4, a considerable increase in the specific surface area (500–700 m^2/g) was observed at pyrolysis temperatures of 700–800°C. The removal of soluble phosphorus-containing compounds after the treatment of these porous carbon materials with water led to a notable increase in their specific surface areas (to 2560 m^2/g for the sample pyrolyzed at 400°C).

The chemical activation of the wood of birch with 5 and 10 wt % $ZnCl_2$ facilitated an increase in the yield of the porous carbon materials obtained at pyrolysis temperatures of 400–800°C. In the presence of $ZnCl_2$, the initial temperature and intensity of the thermochemical processes of birch wood conversion noticeably (by approximately 90°C) decreased.

The specific surface area of the porous carbon materials from the wood containing 5 wt % $ZnCl_2$ was as high as 300 m^2/g at a pyrolysis temperature of 800°C, whereas it was 670 m^2/g at a $ZnCl_2$ content of 10 wt % and a pyrolysis temperature of 700°C.

Thus, the modification of the wood of birch with $ZnCl_2$ leads to the intensification of the thermochemical processes of wood conversion and an increase in the yield of porous carbon materials by a factor of 1.5 and in their specific surface areas by a factor of 10–25.

Table 2. Yield and specific surface area of the carbon products from the wood of birch

Pyrolysis temperatur, °C	Yield, wt %			Specific surface area, m^2/g		
	initial wood	modified with 5% $ZnCl_2$	modified with 10% $ZnCl_2$	initial wood	modified with 5% $ZnCl_2$	modified with 10% $ZnCl_2$
None	100.0	100.0	100.0	0	0	0
200	93.4	76.5	69.6	0.6	1.5	0.7
300	58.5	42.9	41.3	2.0	1.9	1.1
400	27.7	41.5	36.6	6.0	3.2	1.8
500	22.3	34.2	33.5	10.9	25.8	281.0
600	21.9	30.0	30.5	30.7	208.8	419.0
700	20.6	30.0	29.0	16.2	268.5	666.0
800	19.8	26.0	27.4	27.2	296.1	474.0

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