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Texture and Adsorptive Properties of Microporous Amorphous Carbon Materials Prepared by the Chemical Activation of Carbonized High-Ash Biomass

P. M. Eletskii, V. A. Yakovlev, V. B. Fenelonov, and V. N. Parmon

Boreskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia
e-mail: yeletsky@catalysis.ru

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Abstract—Samples of microporous amorphous carbon materials with calculated BET specific surface areas of up to 3500 m^2/g, pore volumes of up to 3.0 cm^3/g, and micropore volumes of up to 1.9 cm^3/g were prepared using the chemical activation of rice hulls carbonized in a fluidized-bed reactor with a copper–chromium catalyst for deep oxidation. The effects of various activation parameters (temperature, activating agents, etc.) were studied, and optimum parameters were chosen. The resulting materials exhibited sorption capacities of up to 6.3 and 41 wt % for hydrogen at liquid nitrogen temperature and 50 atm and for methane at 0°C and 60 atm, respectively. Because of this, they are promising for use in the purification, storage, and transportation of fuel gases. Moreover, some aspects of the mechanism of the interaction of an activating agent with a carbon-containing precursor are proposed.

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INTRODUCTION

The most commonly used methods for the preparation of amorphous carbon materials with developed specific surface areas are based on so-called physical or chemical activation of coke, which is prepared by the preliminary carbonization of a carbon-containing precursor in an inert atmosphere at temperatures to 700–800°C [1–3]. In this case, physical activation usually implies thermooxidative treatment in the presence of CO_2, water vapor, air, etc., whereas chemical activation implies thermocatalytic treatment in an inert atmosphere in the presence of chemical catalysts: (a) acid–base catalysts ($ZnCl_2$, $AlCl_3$, H_3PO_4, etc.) or (b) redox catalysts (alkali metal hydroxides, carbonates, etc.), which can be reduced with hydrogen and oxidized with oxygen.

In spite of its obvious disadvantages (the consumption of relatively expensive catalyst components and problems related to the washing and utilization of these components), considerable recent attention has been focused on thermocatalytic activation because of the possibility of preparing carbon adsorbents with extremely high specific surface areas and microporosities [3–29].

The most effective chemical activating agent developing the specific surface area of the carbon precursor is molten KOH, which allows one to obtain microporous amorphous carbon materials with BET specific surface areas (A_{BET}) higher than 3000 m^2/g, pore volumes V_Σ to 2.0 cm^3/g, and micropore volumes V_μ to 1.6 cm^3/g [8–29]. For example, this activation has been used in the synthesis of well-known AX-21 carbon materials; these materials (initially referred to as PX-21 or Maxsorb) were developed in the 1970s by the Amoco Corporation (United States). Carbon materials of this kind are manufactured by the oxidative treatment of petroleum coke or pitch in nitric acid followed by activating in molten KOH at 700–800°C and washing the final product [13, 15]. Late in the 1970s, Anderson Development Company (United States) started the production of this material under the name AX-21, whereas Kansai Coke and Chemicals Co (Japan) has manufactured it since the 1980s under the name Maxsorb with various serial indices [20]. According to published data [20], the average specific surface area of AX-21 is $A_{BET} = 2670 \pm 600$ m^2/g, the micropore volume is 1.2 cm^3/g, and the average pore size is about 1 nm.

An alternative way of manufacturing microporous amorphous carbon materials referred to as Kemerit with analogous properties was proposed in [21]. The distingtions of this method consist in the replacement of the oxidizing agent (HNO_3) by the H_2SO_4–$NaNO_2$ system and in the use of a wider range of precursors. The specific surface areas and micropore volumes of the resulting materials varied over the ranges of 3000–4000 m^2/g and 1.0–1.2 cm^3/g, respectively [21]. Unfortunately, the procedure for the preparation of Kemerit materials does not exclude the formation of toxic sulfur and nitrogen oxides.

The correctness of the use of the standard BET method in determining the specific surface areas of microporous carbon and other adsorbents, the correspondence of the resulting values of A_{BET} to the really accessible geometric surface area A_0, etc., are beyond the scope of this work. These problems were discussed, for example, in [4–6]. Note that Dubinin et al. [4] classified carbon materials with the above specific characteristics as active carbons with a maximally developed micropore volume and estimated the true specific surface area A_0 at 1120 m^2/g. At the same time, Kaneko et al. [5] classified such materials with active carbons with an ultrahigh specific surface area and substantiated the occurrence of these systems. The consistency of the above approaches is due to the fact that the anomalously high adsorption properties of these materials can be expressed in terms of both formal specific surface areas and micropore volumes. In our case, we used both of these approaches.

In this work, we demonstrate the possibility of preparing microporous amorphous carbon materials with unique structural characteristics from inexpensive carbon-containing precursors, such as lignocellulose biomass, which are usually considered as, for example, crop production wastes. The main advantage of the new procedure for preparing microporous amorphous carbon materials is that the pretreatment of the precursor with oxidizing agents like nitric acid is not required. This considerably simplifies the manufacturing technology of these materials and excludes the formation of toxic gaseous and liquid wastes. High-ash biomass should be distinguished from other kinds of vegetable biomass for it contains considerable amounts of silica. It is likely that silica has a certain effect on the texture characteristics of the resulting materials. The SiO_2 content of rice hulls is 18–22 wt %; according to published data [23–25], rice hulls can be used to prepare microporous amorphous carbon materials with high texture characteristics ($A_{\text{BET}} \leq 3000$ m^2/g, $V_\Sigma \leq$ 1.9 cm^3/g, and $V_\mu \leq 0.8$ cm^3/g).

The aim of this work was to study the effects of various reaction conditions on the texture characteristics of the resulting microporous amorphous carbon materials and the adsorption properties of these materials using hydrogen and methane sorption as an example. In this case, the following activation parameters were varied: the physicochemical properties of a carbon-containing precursor prepared by the carbonization of vegetable biomass, the activating agent (sodium and potassium hydroxides and carbonates), and the activation temperature (700–900°C). Pyrolysis in an inert atmosphere at 450°C and catalytic partial oxidation in a fluidized bed at reduced temperatures (450–600°C) and a contact time (τ) shorter than 2 s were used in the preliminary carbonization of the lignocellulose biomass. This carbonization procedure allowed us to easily vary the composition of the resulting carbon precursors by changing temperature and contact time. In the partial oxidation of biomass in a fluidized bed, an excess amount of oxygen-containing organic substances was removed for alkaline activation; this is a prerequisite because the oxygen component lignocellulose reacts with an alkali to convert it into an inactive carbonate phase.

The aim of this work was also to determine the main chemical activation processes that facilitate the formation of the micropore structure of the given carbon materials because it is unclear from published data how the structure of such materials is formed [13].

EXPERIMENTAL

Preliminary Carbonization of Biomass to Produce a Carbon-Containing Precursor

Rice hulls (5% moisture content and 19.5% ash content), oat hulls (5% moisture content and 8.3% ash content), and wheat straw (6% moisture content and 8.6% ash content) were used as starting materials for fluidized-bed carbonization. According to published data [30], the lignin, cellulose, and hemicellulose contents of rice hulls are ~20, ~40, and ~20 wt %, respectively.

Precarbonization was performed using the following two procedures: (1) treatment in a catalytic fluidized-bed reactor in the presence of air and (2) pyrolysis in an inert atmosphere.

In the course of fluidized-bed carbonization, ground biomass was supplied to the reactor with a flow of air (the molar ratio between atmospheric oxygen and carbon α was ~2). The contact time τ with a catalyst was ~1 s. Carbonization was performed at 450, 500, 550, and 600°C. The reactor temperature was regulated with external electric heaters; in this case, carbonization occurred in an autothermal regime at 600°C. The product as a carbon–silica composite (C/SiO_2) was separated in a cyclone and accumulated in a tank.

The pyrolysis of ground biomass was performed in an atmosphere of nitrogen (5 l/h) at 450°C for 2 h; the reactor temperature was also maintained using an external heater. Table 1 summarizes the main physicochemical properties of the resulting carbon–silica composites prepared from rice hulls.

Preparation of Microporous Amorphous Carbon Materials

The resulting carbonized material was treated with a solution of KOH or NaOH in a ratio of 1 g of C/SiO_2 per 72 mmol of an alkali hydroxide. An equimolar mixture of K_2CO_3 and Na_2CO_3 in a ratio of 18 mmol of each carbonate per gram precursor was also used in this study; it was mechanically mixed with carbonization products in order to prevent hydrolysis with the formation of an alkali.

After drying at 120°C overnight, the resulting mixture was placed in a thermostated reactor as a unit of an automated kinetic system (Fig. 1). The mixture was heated to the specified temperature at a rate of 15 K/min and kept at this temperature for 2 h in an atmosphere of nitrogen (5 l/h).

Table 1. Texture characteristics of carbon–silica composites prepared by the carbonization of rice hulls using pyrolysis (P) in an inert atmosphere (450°C) and in a fluidized-bed (FB) reactor (450–600°C) according to BET data

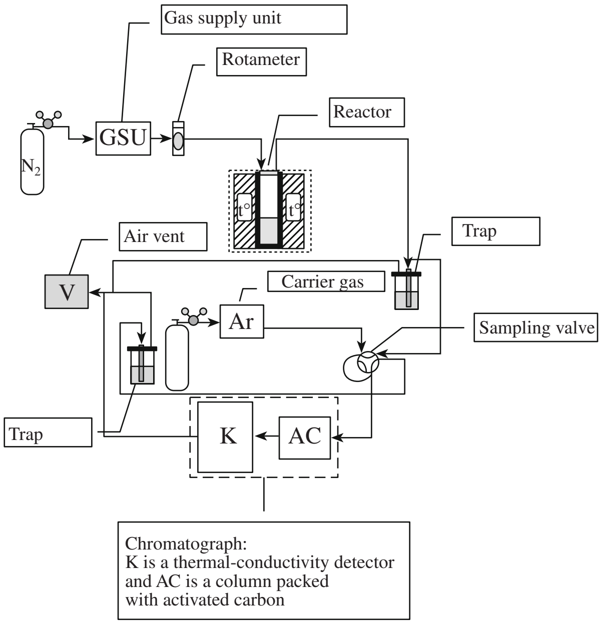
Temperature, °C; carbonization procedure	A_{BET}, m^2/g	V_Σ, cm^3/g	V_μ, cm^3/g	Surface ash content (XPS)	Bulk ash content, %
450, P	56	0.05	0.01	–	46
450, FB	32	0.04	~0	40	35
500, FB	176	0.15	0.03	59	56
550, FB	246	0.21	0.05	70	69
600, FB	233	0.22	0.04	74	76

After activation, the product was washed in distilled water to a neutral reaction. Then, the product was washed with a 3 N HCl solution to remove mineral impurities followed by washing with distilled water to a neutral reaction. The resulting samples were dried to constant weight at 120°C in air.

In the course of activation, gaseous activation products were analyzed using an automated system (Fig. 1) with a Chromos 1100 gas chromatograph. An AG-5 chromatographic column packed with active carbon was used in the experiments (3.0 m × 0.2 mm; $T = 50$°C; carrier gas (Ar) flow rate, 50 ml/min). This column allowed us to separate and identify CH_4, H_2, CO, and CO_2 with the use of a thermal-conductivity detector.

Physical Investigation Techniques

The texture characteristics of samples were measured based on the physical adsorption of N_2 at liquid nitrogen temperature with the use of an ASAP-2400 automated volumetric adsorption instrument (Micromeritics, United States). Before analysis, the samples were calcined at 150°C for 4 h at a pressure of 1×10^{-3} Torr. The analysis time was varied depending on particular samples. The resulting adsorption isotherms were used to calculate the specific surface area (A_{BET}), total pore volume (V_Σ) (from limiting saturation at the relative pressure $P/P_0 = 1$), micropore volume (V_μ), and surface remaining after pore filling (A_{ext}).



Chromatograph:
K is a thermal-conductivity detector
and AC is a column packed
with activated carbon

Fig. 1. Schematic diagram of the system for the analysis of gaseous products in the production of microporous amorphous carbon materials.

The electron microscopic studies of samples were performed using a JEM-2010 transmission electron microscope (JEOL, Japan) with an accelerating voltage of 200 kV and a resolution of 0.14 nm.

Studies on the adsorption of H_2 were performed at liquid nitrogen temperature, which was maintained using a thermoregulating system at a constant level of liquid nitrogen. The values of adsorption were calculated as the difference between the actual hydrogen content of the adsorber and the hydrogen content of a model system whose gas volume was equal to the total porosity of the adsorber, as measured with helium as a nonsorbed gas at the same pressure and temperature. In the case of methane, measurements were performed analogously at 0°C.

RESULTS AND DISCUSSION

As follows from published data [3, 5, 8–29], the most important factors affecting the development of the micropore structure of amorphous carbon materials in the course of chemical activation are the nature of the carbon precursor, the temperature profile of thermal treatment, the nature and amount of the activating agent, and the method of mixture preparation. Studies on the preparation of microporous amorphous carbon materials by the chemical activation of carbonized rice hulls were started in the past decade. Guo et al. [23–25] prepared these materials from rice hulls that were precarbonized by pyrolysis in an inert atmosphere at 400°C for 2 h followed by activation with sodium and potassium hydroxides and carbonates at 650–800°C. They found that KOH was the best activating agent, and the weight ratio between KOH and the carbon-containing precursor should be about 4 : 1 or 72 mmol of KOH per gram precursor. In the case of NaOH, the optimum

Table 2. Texture characteristics of microporous carbon materials prepared by the interaction of various carbon precursors with KOH (N_2, 2 h)

Starting material	Treatment conditions	A_{BET}, m^2/g	Sample*	A_{BET}/A_{μ}^{**}, m^2/g	V_{Σ}/V_{μ}, cm^3/g	Fraction of micropores, %
Rice hulls	P450	56	MPC 45P802K	2940/2840	1.46/1.33	91.1
	FB450	32	MPC 45802K	2960/2780	1.80/1.62	90.0
	FB500	176	MPC 50802K	3360/3100	2.18/1.87	85.8
	FB550	246	MPC 55802K	2970/2880	1.60/1.49	93.1
	FB600	233	MPC 60802K	2910/2440	2.12/1.57	74.0
Oat hulls (OH)	FB500	80	MPC OH45802K	2930/2770	1.83/1.57	85.8
Wheat straw (WS)	P500	21	MPC WS50P802K	3270/3254	1.58/1.54	97.5

* In the sample designation, the first two figures refer to the precarbonization temperature (e.g., 50 corresponds to 500°C); P indicates the carbonization of biomass by pyrolysis; the second two figures refer to the activation temperature (e.g., 80 corresponds to 800°C); 2 is the activation time, h; and K refers to the activating agent (KOH).

** Specific surface area of micropores.

alkali-to-precursor weight ratio was about 3 : 1. They also found that the optimum activation temperature was 750–800°C. At 800°C, the optimum activation time was 2 h [25]. However, Guo and his colleagues did not systematically study the effect of activation temperature on the texture properties of the resulting materials, or the effect of the nature of the carbon precursor. Moreover, they insufficiently elucidated the mechanism of interactions between the activating agent and the precursor.

In this work, we studied the effects of the following factors on the texture characteristics of the resulting materials: (1) the nature of carbon-containing precursors, namely, carbon–silica composites prepared by the carbonization of rice hulls using two procedures; (2) the nature of the activating agents KOH and NaOH and equimolar mixtures of KOH + NaOH and K_2CO_3 + Na_2CO_3; and (3) the temperature of activation.

Effect of the Nature of a Carbon Precursor on the Texture Characteristics of the Resulting Microporous Amorphous Carbon Materials

As mentioned above, the nature of a carbon-containing precursor is of considerable importance in the production of microporous carbon. The occurrence of oxygen both as incompletely decomposed organic compounds in the bulk of the carbon phase and as oxygen-containing functional groups on the precursor surface is a necessary condition for the formation of the micropore structure of these materials. Treatment with mineral acids like HNO_3 is commonly used for the modification of the carbon phase [13, 15, 21]. With the use of carbonized lignocellulose materials, a sufficient amount of oxygen occurs in the carbon phase from the outset and additional treatment is not required.

We used rice hulls, oat hulls, and wheat straw, which were carbonized in a fluidized bed of a catalyst or by pyrolysis in an inert atmosphere, as precursors for the preparation of microporous amorphous carbon materials.

To study the effect of the nature of the carbon-containing precursor, the other parameters of the preparation of microporous carbon remained constant: activating agent, KOH; activation at 800°C in an atmosphere of nitrogen for 2 h. Table 2 summarizes the experimental results.

In Table 2, it can be seen that all of the samples except for a microporous amorphous carbon material prepared from rice hulls carbonized in a fluidized bed (FB) at 500°C exhibited approximately the same characteristics: A_{BET} = 2900–3000 m^2/g, V_{Σ} = 1.6–2.1 cm^3/g, and the volume fraction of micropores was mainly greater than 80%.

The sample prepared from rice hulls carbonized in a fluidized bed at 500°C exhibited the most developed micropore structure. This is likely due to the physicochemical properties of the carbon precursor (C/SiO_2 FB500), namely, a combination of a sufficiently high specific surface area (176 m^2/g), ash content, and concentration of oxygen-containing organic substances. The high specific surface area of this composite is responsible for the high degree of contact with the activating agent.

Note that, as compared with pyrolysis, carbonization in a fluidized-bed reactor occurs much more rapidly; it does not require an inert atmosphere and is much more environmentally friendly; the autothermal regime can occur under certain conditions. Therefore, this procedure is considered more promising; it was mainly used in this work for the carbonization of biomass.

As noted above, the bulk and surface concentrations of oxygen in the carbon phase of a precursor are of crucial importance for the formation of the micropore structure in alkaline activation. Previous data on the thermogravimetric analysis of rice hulls [32] indicated that a decrease in the fluidized-bed carbonization temperature of rice hulls resulted in an increase in the con-

Table 3. Texture characteristics of microporous carbon materials prepared by the interaction of rice hulls carbonized in a fluidized-bed reactor at 500°C with various activating agents (N_2, 2 h)

Sample	Agent and activation temperature, °C	A_{BET}/A_{μ}, m^2/g	V_{Σ}/V_{μ}, cm^3/g	Fraction of micropores, %
MPC 50802K	KOH, 800	3360/3100	2.18/1.87	85.8
MPC 50802N	NaOH, 800	1130/1040	0.64/0.49	76.6
MPC 50802KCNC11	$K_2CO_3 + Na_2CO_3$ 1 : 1, 800	1430/620	1.36/0.27	19.8
MPC 50802KN11	NaOH + KOH 1 : 1, 800	3330/3220	1.71/1.58	92.4

centration of volatile organic compounds. Therefore, the high values of texture characteristics found in rice hulls carbonized at reduced temperatures seem reasonable.

The use of raw materials other than rice hulls (precarbonized oat hulls and wheat straw) also allowed us to prepare materials whose characteristics were highly competitive with those of the carbon materials prepared from carbonized rice hulls. This fact suggests that microporous amorphous carbon materials with highly developed micropore structures can be prepared from almost any type of vegetable biomass.

The apparent density of the resulting materials was 0.07 ± 0.01 g/cm^3 in all of the samples. Nevertheless, the apparent density can be increased by vacuum pressing with the use of binders.

Thus, a carbon–silica composite prepared in a fluidized bed at 500°C is an optimum precursor for the production of microporous amorphous carbon materials with the best characteristics from the carbonization products of rice hulls. This precursor was used in the subsequent experiments for chemical activation under various conditions.

Importantly, a high concentration of amorphous silica facilitates the development of micropores. This is likely due to the removal of the silica phase as silicates from the carbon matrix during activation with the simultaneous activation of the released carbon surface. Evidently, for this reason, the pore and micropore volumes of the microporous amorphous carbon materials prepared in this study were, on average, greater than those of materials prepared from low-ash feedstock, for example, AX-21 [15].

Effect of the Nature of an Activating Agent on the Properties of Microporous Amorphous Carbon Materials

The nature of the activating agent is also a key parameter of chemical activation. The most effective agent that allowed us to prepare microporous amorphous carbon materials with a maximally developed micropore structure is KOH. However, because it is expensive, it should be replaced with a less expensive agent with analogous properties. In this context, we used sodium hydroxide and its equimolar mixture with KOH in a proportion of 1 g of precursor per 72 mmol of alkali metal cations (i.e., 72 mmol of NaOH or a mixture of 36 mmol of sodium and potassium hydroxides) in this study.

In addition, we also used an equimolar mixture of sodium and potassium carbonates (T_m = 730°C [31]) with the above proportion of Na and K cations to the precursor (i.e., 18 mmol of each of the carbonates per gram composite) for activation. To prevent hydrolysis, the carbonates and C/SiO_2 FB500 were mechanically mixed. All other activation conditions remained constant: $T = 800$°C; activation time, 2 h; and nitrogen flow rate, 5 l/h. The mixtures of alkalis with the precursor after stirring in an aqueous solution were dried to constant weight.

Table 3 summarizes the texture characteristics of the resulting products. As can be seen in Table 3, activating agents other than KOH cannot form carbon materials with high specific surface areas and large micropore volumes. In this case, the use of an equimolar mixture of K_2CO_3 and Na_2CO_3 as an activating agent resulted in the production of a mesoporous carbon material. This fact suggests that the mechanism of pore structure formation was different from that in the case of KOH (see below). In the case of a carbonate mixture, it is likely that pores are mainly formed by the physical activation of the carbon component with carbon dioxide, which is formed by the interaction of carbonate with SiO_2, and by the removal of the latter as sodium and potassium silicates. The resulting mesoporous carbon material with a specific surface area of higher than 1430 cm^3/g and a total pore volume of 1.35 cm^3/g (mesopores constitute the major portion of total pores) is promising for use as a catalyst support, and it invites further investigation.

The use of an equimolar mixture of NaOH and KOH allowed us to obtain a microporous amorphous carbon material with texture characteristics that compare well with those of carbon materials prepared by activation with KOH. It is likely that this result is due to ion-exchange equilibrium between the reaction products of alkalis with carbon and starting agents. Sodium and potassium hydroxides interact with carbon in accordance with the following reaction scheme [8]:

$$6MeOH + 2C \longrightarrow 2Me + 3H_2 + 2Me_2CO_3. \qquad (I)$$

Table 4. Texture characteristics of microporous carbon materials prepared by the interaction of rice hulls carbonized in a fluidized-bed reactor at 500°C with KOH at 700–900°C (N_2, 2 h) and their sorption capacities for hydrogen and methane

Sample	T, °C	A_{BET}/A_{μ}, m^2/g	V_{Σ}/V_{μ}, cm^3/g	Fraction of micropores, %	Hydrogen adsorption*, wt %	Methane adsorption**, wt %
MPC 50702K	700	3170/3060	1.77/1.45	81.9	4.7	28
MPC 50752K	750	3450/3270	2.01/1.68	83.6	5.7	27
MPC 50802K	800	3360/3100	2.18/1.87	85.8	6.3	33
MPC 50852K	850	3170/2680	2.26/1.74	77.0	5.8	34
MPC 50902K	900	3210/1730	2.97/1.48	49.8	6.2	41

* Hydrogen adsorption at –196°C and 50 atm.

** Methane adsorption at 0°C and 60 atm.

In the case of KOH, the above interaction occurs more intensely because of the thermodynamic characteristics of the process ($\Delta G^0(\mathrm{M} = \mathrm{Na}, T = 830°\mathrm{C}) = -31.3$ kJ/mol, $\Delta G^0(\mathrm{M} = \mathrm{K}, T = 830°\mathrm{C}) = -47.0$ kJ/mol). It is likely that for this reason KOH is consumed more rapidly in reaction (I) with the formation of carbonate, which, probably, interacts with NaOH by the following reaction:

$$K_2CO_3 + 2NaOH \rightleftharpoons 2KOH + Na_2CO_3. \qquad \text{(II)}$$

It is likely that KOH is recycled in this manner at the expense of sodium hydroxide; because of this, an equimolar mixture of KOH and NaOH is competitive with potassium hydroxide in terms of efficiency.

Thus, potassium hydroxide or its equimolar mixture with NaOH was the most efficient activating agent, which allowed us to prepare microporous amorphous carbon materials with maximum specific surface areas and developed micropore structures. The use of an anhydrous mixture of sodium and potassium carbonates resulted in the production of mesoporous carbon materials with sufficiently developed specific surface areas and mesopore volumes. These materials are promising for use as catalyst supports. Evidently, the mechanisms of the development of pore structures in microporous amorphous carbon materials were different in the above cases.

Effect of Activation Temperature on the Properties of Microporous Carbon Materials

The temperature of the interaction of molten alkali with a carbon precursor is also an important factor, the effect of which on the texture characteristics of the resulting carbon materials was studied in this work.

To correctly study the effect of activation temperature, we performed experiments in which all of the other activation conditions remained fixed: the carbon precursor was a carbon–silica composite prepared by the fluidized-bed carbonization of rice hulls at 500°C, and the activating agent was KOH. The temperature was varied from 700 to 900°C at a step of 50°C, and the activation time was 2 h. Table 4 summarizes the results of these experiments.

Data given in Table 4 indicate that microporous amorphous carbon material samples prepared in the above temperature range exhibited the specific surface area A_{BET} over 3000 m^2/g. However, the micropore volume and fraction in the total pore volume essentially depended on the thermal treatment temperature.

It can be seen that materials with the greatest volume and fraction of micropores were formed by activation over the temperature range of 750–800°C. In this case, as the temperature was increased to 800°C, the total pore volume mainly increased because of an increase in the micropore volume. At higher temperatures, the fraction of micropores decreased with the formation of mesopores. The total pore volume increased with activation temperature, but the volume fraction of micropores decreased. It is believed that high activation temperature facilitates the graphitization of the micropore structure by ordering with an increase in the number of graphite layers in pore walls and by mesopore formation. Thus, varying only the given parameter (temperature) allowed us to vary the texture characteristics of the resulting materials over a wide range.

The prepared series of microporous carbon materials with various volume ratios between micro- and mesopores was tested for sorption capacity toward hydrogen and methane. These gases were chosen as test sorptives because they are promising chemical energy carriers; efficient storage techniques, particularly, onboard facilities, should be chosen for these gases. Therefore, in the case of the high adsorption capacity of the resulting microporous amorphous carbon materials for these gases, these materials could be widely used in hydrogen power engineering and in transportation.

It is well known (e.g., see [35–38]) that hydrogen exhibits a noticeable adsorbability only at elevated pressure and under cryogenic conditions. Methane can be adsorbed in considerable amounts under pressure even at 0°C [39–41].

Table 4 summarizes the sorption capacities of the test carbon materials for hydrogen (at liquid nitrogen temperature and 50 atm) and methane (at 0°C and

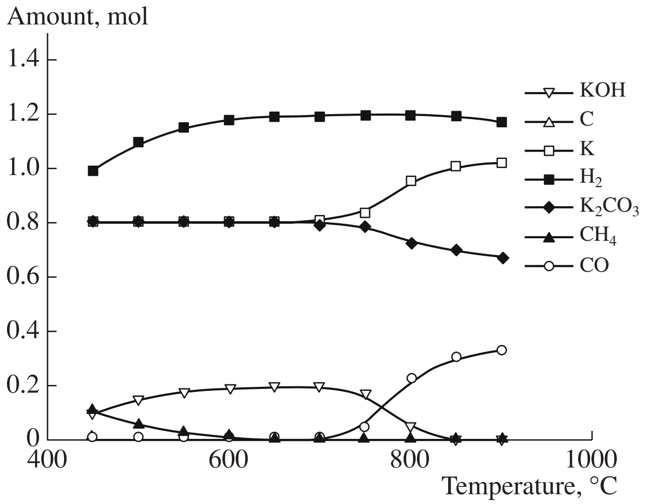


Fig. 2. The calculated temperature dependence of the composition of an equilibrium reaction mixture of KOH + C (in a molar ratio of 2.4 : 1).

60 atm). It can be seen that the sorption capacities of the prepared materials for hydrogen varied from 4.7 to 6.3 wt % regardless of the texture characteristics of the samples. In the case of methane adsorption, a correlation between the amount of sorbed CH_4 and the total pore volume was observed; this fact suggests a polymolecular mechanism of methane adsorption. Note that sample MPC 50902K with the maximum pore volume exhibited a maximum sorption capacity for CH_4 (more than 40 wt %); evidently, this fact also suggests polymolecular adsorption of methane in meso- and macropores.

Thus, the microporous amorphous carbon material samples exhibited very high adsorption characteristics toward hydrogen and methane. Because of this, they are promising for use as effective adsorbents of fuel gases. In this case, materials with a great fraction of micropores are required for hydrogen adsorption, whereas it is obvious that more mesoporous amorphous carbon materials are required for gases with bulkier molecules.

Formation of Microporous Amorphous Carbon Materials under Conditions of Chemical Activation by KOH

Interaction of activating reagents with a carbon-containing precursor. As noted above, an analysis of published data suggested that the formation of the micropore structure of carbon materials with the maximally possible surface area (~3500 m^2/g, BET) in the course of the alkaline activation of carbon precursors was covered insufficiently [13]. Thermodynamic calculations [8, 18] indicated that the products of the interaction of MOH (where M = Na or K) with a carbon precursor are hydrogen, potassium or sodium metal, and potassium or sodium carbonate (see reaction scheme (I)). In the case of M = Na, this interaction is thermodynamically possible at $T \geq 700°C$ ($\Delta G^0 \sim 0$), whereas for M = K this process is possible even at $T \geq 580°C$. Lillo-Rodenas et al. [8] believed that this interaction is crucial for the formation of the micropore structure by the burning of carbon layers with the formation of micropores. Moreover, Halpin and Jenkins [19], who used KOH for activation, noted that the micropore structure can be formed in the course of thermal treatment at temperatures lower than 1000°C by the intercalation of potassium compounds into the interplanar space of a graphite-like structure to considerably increase distances between the planar fragments of graphite layers. After cooling the fusion products and washing out potassium salts, the extended texture of these fragments was retained to form thus the microporosity of these materials.

To confirm this mechanism of micropore formation and the possible activating effect of potassium carbonate, we performed thermodynamic calculations for chemical activation products at various temperatures using the NASA program [34].

Figures 2 and 3 show the calculated temperature dependence of interaction products in the KOH–C and K_2CO_3–C systems, respectively. In these calculations, carbon and potassium hydroxide or carbonate were used as the initial reagents in molar ratios of 1 : 2.4 (KOH) and 1 : 2 (K_2CO_3), which correspond to the experimental conditions. The composition of a product mixture in thermodynamic equilibrium was calculated for a specified temperature and atmospheric pressure; in this case, the kinetics of reactions was ignored.

Data given in Fig. 2 demonstrate that reaction (I) can occur because potassium metal, hydrogen, and potassium carbonate are the main reaction products of KOH with carbon. Because carbon was taken in excess in the calculations, it was present in the final reaction products.

We experimentally found potassium metal deposits on the walls of the top part (colder) of the reactor in the course of the alkaline activation of a carbon substrate; this fact also suggests the occurrence of reaction (I).

The thermodynamic calculations also demonstrated that methane can be formed at low temperatures by carbon hydrogenation with hydrogen formed in reaction (I). As the temperature is increased, the thermodynamic equilibrium shifts toward carbon and hydrogen. It is obvious that the reaction of carbon hydrogenation does not actually occur at 400–500°C because of kinetic hindrances. Note that, at temperatures higher than 800°C, the resulting K_2CO_3 can interact with carbon by reaction (III), as supported by data in Fig. 3:

$$K_2CO_3 + 2C \longrightarrow 2K + 3CO. \qquad \text{(III)}$$

In Fig. 3, it can be seen that potassium carbonate can be reduced with the formation of potassium metal.

To elucidate real processes occurring in the chemical activation of carbon precursors, we performed a

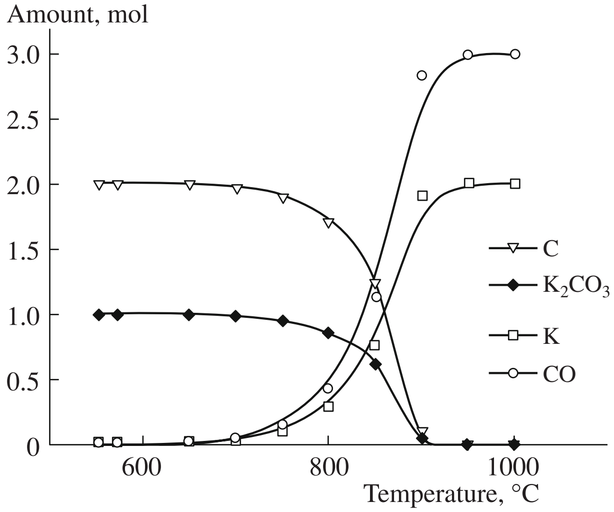


Fig. 3. The calculated temperature dependence of the composition of an equilibrium reaction mixture of K_2CO_3 + C (in a molar ratio of 2 : 1).

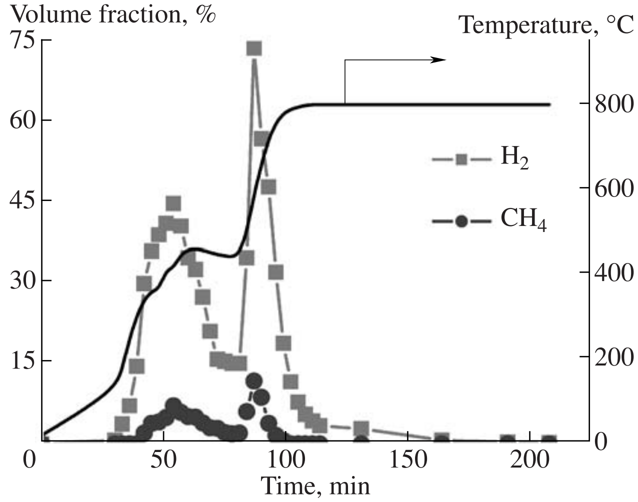


Fig. 4. Composition of gaseous products in the activation of a C/SiO_2 sample (FB500) with potassium hydroxide at 800°C.

number of experiments on the analysis of gaseous products in the chemical activation of carbonized high-ash biomass.

We performed test experiments on the activation of rice hulls carbonized in a fluidized bed at 500°C with potassium hydroxide and an equimolar mixture of sodium and potassium carbonates at 800°C (Figs. 4 and 5, respectively) with the corresponding temperature profiles. Throughout the entire thermal treatment, gaseous activation products were analyzed.

In the latter case, we used an equimolar mixture of sodium and potassium carbonates in order to decrease the melting temperature of the carbonate mixture to 730°C [31] (whereas $T_m(Na_2CO_3)$ = 854°C and $T_m(K_2CO_3)$ = 901°C [31]) for more effective interaction with SiO_2.

In Fig. 4, it can be seen that carbon and methane are the main gaseous products of the interaction of KOH and carbonized rice hulls. In this case, correlation between the volume concentration of gases and the temperature profile of the reaction was observed up to a steady-state temperature of 800°C. Then, gas evolution almost disappeared; this was likely due to the termination of main reaction (I) because of the complete consumption of KOH, which was taken in an insufficient amount. Evidently, the further genesis of the carbon phase occurred without noticeable formation of gaseous products. A correlation between the yield of methane and the concentration of H_2 was also observed; this correlation indirectly suggests the hydrogenation of various carbon-containing functional groups in the precursor. As found previously [32], rice hulls carbonized in a fluidized bed at 500°C contained an amount of undecomposed lignocellulose fragments (4 wt % volatile substances), which decompose in the course of pyrolysis to release CO, CO_2, H_2O, and light hydrocarbons. Considerable amounts of CO and CO_2 were not detected in the gas mixture; this was likely due to the methanolysis of CO and the binding of CO_2 to potassium hydroxide to form carbonate.

The analysis of a gas atmosphere in the course of the thermal treatment of carbonized rice hulls (C/SiO_2) with the Na_2CO_3–K_2CO_3 system in an inert atmosphere demonstrated (Fig. 5) that the gas mixture at low temperatures (to 400°C) mainly consisted of CO_2. Over the temperature range of 400–750°C, the release of methane, hydrogen, and CO was observed along with the formation of CO_2. At 800°C, a decrease in the concentration of hydrogen in the gas phase and a smoother decrease in the concentration of CO_2 were observed.

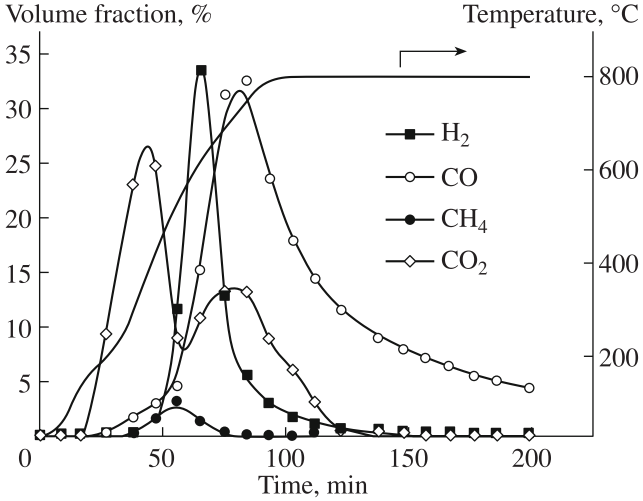


Fig. 5. Composition of gaseous products in the activation of a C/SiO_2 sample (FB500) with the K_2CO_3–Na_2CO_3 system (in a molar ratio of 1 : 1) at 800°C.

The concentration of CO decreased less rapidly; in this case, the release of CO did not terminate even after treating the mixture at 800°C for 2 h.

Thus, the interaction of an equimolar mixture of $K_2CO_3 + Na_2CO_3$ with C/SiO_2 FB500 can be represented by the following set of chemical reactions:

$$\text{carbon-containing precursor phase} \longrightarrow CO_2 + CO + H_2 + CH_4 + \text{volatile organic substances}, \quad (IV)$$

$$M_2CO_3 + SiO_2 \longrightarrow M_2SiO_3 + CO_2 \ (M = K, Na), \quad (V)$$

$$CO_2 + C \rightleftharpoons 2CO, \quad (VI)$$

$$CO + 2H_2 \rightleftharpoons CH_4 + H_2O, \quad (VII)$$

$$H_2O + C \rightleftharpoons CO + H_2. \quad (VIII)$$

As follows from the above reaction equations, the presence of CO, H_2, CH_4, and CO_2 in the gas phase at low temperature can be explained by the decomposition of surface functional groups of the carbon precursor and organic compounds of the carbon phase, which were formed upon the carbonization of rice hulls. For example, methane can also be formed by the interaction of CO with hydrogen in accordance with reactions (VII) and (VIII). Note that the curve of CO_2 concentration changes exhibited two peaks, which suggest two sources of CO_2 formation (reactions (IV) and (V)). Thermodynamic analysis of reaction (VI) indicated that equilibrium was shifted to the right starting with 650°C. This fact explains the decrease in the CO_2 concentration and the increase in the CO concentration at elevated temperatures.

Thus, we can conclude that the interaction of KOH with a carbon precursor occurred with the formation of H_2, K, and K_2CO_3. In this case, the interaction of the resulting potassium carbonate with carbon was not observed experimentally, probably for kinetic reasons. According to Lillo-Rodenas et al. [8], the interaction of NaOH with carbon is thermodynamically less favorable; however, generally, it is analogous to that of KOH.

The activation of C/SiO_2 FB500 with an equimolar mixture of $K_2CO_3 + Na_2CO_3$, which was mechanically mixed with the precursor, mainly took place by the removal of SiO_2 as silicates and by the physical activation of the carbon phase with CO_2, which was formed in the interaction of silicon dioxide with carbonates.

At the same time, reactions (I)–(VIII) cannot completely explain the formation of the micropore structure of the given carbon materials because the above processes mainly led to the formation of pores larger than 2 nm.

Formation of the micropore structure of amorphous carbon materials. It is well known from published data that the texture characteristics of microporous amorphous carbon materials depend on the presence of oxygen and other heteroatoms, such as Cl, in the precursor. These heteroatoms can occur as either surface functional groups or bulk phase constituents in the form of various chemical compounds. In particular, as mentioned above, the AX-21 carbon materials were prepared from petroleum coke, which was pretreated in concentrated nitric acid in order to increase the degree of precursor oxidation. In this work, we performed experiments on the activation of graphite and fibrous carbon, which was prepared by the pyrolysis of hydrocarbons on highly disperse nickel-containing catalysts [42].

It is well known that graphite has a highly ordered structure and a minimum amount of surface functional groups [33]. Catalytic fibrous carbon also has a surface almost unmodified with oxygen-containing groups. In this case, the activation parameters did not differ from the following parameters used for the activation of carbonized rice hulls: $T = 800°C$; activating agent, KOH at a KOH/C weight ratio of 4 : 1; and activation time, 2 h.

The alkaline activation of graphite did almost not affected its texture characteristics (A_{BET} of the starting graphite was 2 m^2/g and $V_\Sigma = 0$ cm^3/g; A_{BET} of the graphite activation product was 2 m^2/g and $V_\Sigma =$ 0.01 cm^3/g). The activation of catalytic fibrous carbon ($A_{BET} = 130$ m^2/g and $V_\Sigma = 0.3$ cm^3/g) with potassium hydroxide resulted in an increase in its texture properties ($A_{BET} = 350$ m^2/g, $V_\Sigma = 0.64$ cm^3/g, and $V_\mu =$ 0.03 cm^3/g); however, this increase was insignificant as compared with that in carbon–silica composites from rice hulls.

Thus, it can be seen that the use of unmodified catalytic fibrous carbon and graphite did not cause the development of a micropore structure. An increase in the specific surface area of catalytic fibrous carbon after alkaline activation took place due to the development of mesopores, which resulted from the burning of graphite layers in accordance with mechanism (I). In this case, we experimentally found the formation of a much larger amount of potassium metal as in the case of carbonized rice hulls whose oxygen-containing compounds interact with potassium metal to form potassium oxides and carbonate. Note that, after the activation of graphite, it should be washed to a neutral reaction several times because the solution became strongly alkaline (pH ~12) as a result of the removal of

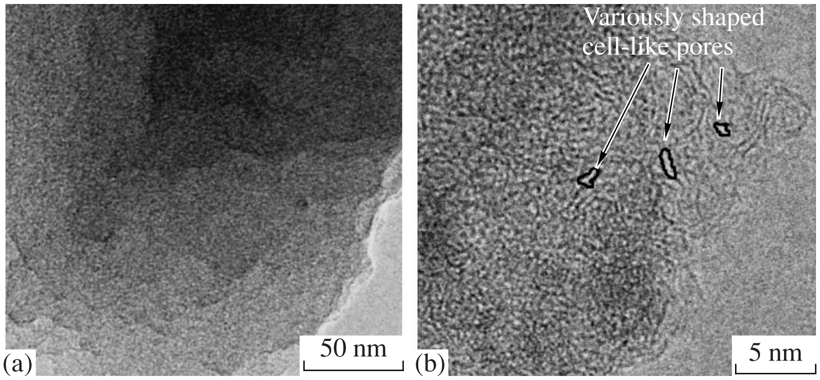


Fig. 6. TEM micrographs of MPC 50802K ($A_{\text{BET}} = 3360$ m^2/g; $V_\Sigma = 2.18$ cm^3/g; $V_\mu = 1.87$ cm^3/g).

potassium from graphite after keeping a washed sample in water. It is likely that potassium was intercalated into the carbon matrix in the course of alkaline activation. However, as believed by Halpin and Jenkins [19], we did not observe experimentally the development of a micropore structure; this is indicative of a crucially different mechanism of micropore structure formation. We believe that the presence of oxygen-containing compounds as functional groups on the surface of a carbon precursor and oxygen-containing fragments in the bulk is a governing factor directly responsible for the formation of the micropore structure.

Marsh et al. [13, 14] also demonstrated the importance of oxygen-containing functional groups for the preparation of microporous carbon materials with a maximum specific surface area. However, they suggested the formation of an alcoholate or phenolate fragment like –OK; both oxygen from the carbon precursor and potassium hydroxide can serve as an oxygen source in these species. It is likely that the latter statement is incorrect because it implies the formation of microporous amorphous carbon materials with the use of oxidant-unmodified precursors like graphite or catalytic fibrous carbon.

To understand the genesis of the micropore texture, we studied the resulting materials using transmission electron microscopy (TEM). Figure 6a shows a survey micrograph of microporous carbon prepared by the interaction of rice hulls carbonized in a fluidized bed at 500°C with KOH at 800°C. The tested carbon material had a specific surface area $A_{\text{BET}} = 3400$ m^2/g, a total pore volume $V_\Sigma = 2.2$ cm^3/g, and a micropore volume $V_\mu = 1.9$ cm^3/g.

As can be seen in the micrograph, the outer surface of a carbon material particle is homogeneous and microporous without an expressed mesopore structure. Such a homogeneous morphology of microporous amorphous carbon materials is typical of the entire sample. At a higher resolution (Fig. 6b), it can be seen that the microporous amorphous carbon material has a disordered cell-like structure with cell-like pore walls consisting of only a single graphite plane fragment. Figure 6b shows the characteristic shapes of cell-like pores, which were recognized only at the peripheral regions of carbon particles; this suggests an anisotropic spatial orientation of pores. As can be seen in Fig. 6b, the fragments of graphite-like layers that form the structure of the carbon material have a rounded shape, and they are occasionally crosslinked at an angle of less than 90°. The cell shapes varied from spherical to slit-like; however, the cell size was no greater than 3 nm. The above-described texture of this sample is typical of all of the microporous amorphous carbon materials; generally, it corresponds to the description of carbon materials of this kind prepared by the KOH activation of modified petroleum pitch [13–17]. Marsh et al. [17] made analogous conclusions on the structure of PX-21 and PX-22 materials based on CO_2 adsorption and high-resolution electron-microscopic data without conclusions concerning the mechanism of micropore structure formation.

However, earlier, Marsh et al. [14] noted that the anisotropic cell-like structure of such materials can be formed through the growth of layered nematic liquid crystals consisting of ordered graphite-like layer fragments. According to Marsh et al. [14], coking coal softened and melted upon carbonization with the formation of anisotropic carbon fragments, which retained their individuality rather than agglomerated during the subsequent growth to impart a nanomosaic character to the texture. On the other hand, the plasticity of liquid crystals allows the growing anisotropic fragments of graphite-like layers to agglomerate. In this situation, Marsh et al. [14] believed that the addition of potassium salts initially decreased the fluidity of the carbon precursor under conditions of activation because of the increase in the number of bonds that usually occur between aromatic and nonaromatic units in coal. A decrease in the mobility of planar fragments prevents their ordering and stabilizes the anisotropic cell-like structure. However, the nature of the formation of these stabilizing bonds with the participation of potassium compounds was not elucidated, likely due to the nonobviousness of the interaction of aromatic and nonaromatic fragments in the presence of potassium compounds as a catalyst.

At the same time, it is evident that the above stabilizing bonds, which appear upon alkaline activation, are responsible for the formation of bent micropore walls and the micropore structure as a whole. It is likely that the formation of crosslinking bonds between graphite-like fragments at various angles occurs with the participation of oxygen-containing groups like R–OH, R^1–O–R^2, and R–COOH. According to Marsh et al. [13], at the stage of primary treatment with KOH, protonated groups form corresponding salt species, which participate in the subsequent transformations.

It is our opinion that potassium metal, which is formed by the interaction of carbon with KOH, plays a key role in the genesis of a micropore structure. Potassium metal reacts with oxygen-containing groups by a redox mechanism to form aromatic radicals ($R^{\bullet}$) followed by a rearrangement of these radicals with the formation of oxygen compounds of potassium (K_2O, K_2O_2). The occurrence of these oxygen compounds in the thermal treatment products of the carbon precursor with KOH was detected by XPS [27]. In this case, aromatic graphite-like fragments can connect to each other not only at end faces to form a single plane but also through carbon-containing bridges like –CH_2–, –CO–, and –C=C–. In the latter case, the connecting bridges allow these fragments to rotate with respect to each other to finally form the cell-like structure of the carbon material. Evidently, electron transfer from an alkali metal to a carbon fragment is required for initiating these processes. In this context, note that the ionization potentials of alkali metals are arranged in the following order: Li (5.39 eV) > Na (5.14 eV) > K (4.34 eV). Except for Rb and Cs, potassium possesses the lowest ionization potential. This fact may explain its higher efficiency compared to Na in the production of microporous amorphous carbon materials.

Thus, the genesis of the micropore structure of a carbon material with a maximum specific surface area formed by the alkaline activation of a carbon precursor exhibits the following special features:

- the formation of a microporous texture occurs only in the presence of oxygen as a constituent of chemical compounds in the bulk of the carbon phase or as surface functional groups;
- potassium hydroxide is the best activating agent;
- the anisotropic cell-like structure of microporous carbon is formed through the growth of layered nematic liquid crystals, which consist of ordered layered graphite-like fragments;
- the formation of additional stabilizing bonds between the layered graphite-like fragments prevents the possible fusion and ordering of liquid crystals to a graphite-like structure;
- stabilizing bonds between graphite-like fragments are formed by the interaction of oxygen-containing compounds and functional groups of the carbon precursor with potassium metal, which, in turn, is formed by the interaction of carbon with KOH;
- the interaction of functional groups with potassium metal implies a radical mechanism with electron transfer from the alkali metal to a functional group of the carbon fragment (graphene);
- stabilizing bonds between graphenes can be not only end contacts, which result in the growth of graphene, but also carbon-containing bridges like –CH_2–, –CO–, and –C=C–, which are responsible for the formation of cell-like microporosity due to the nonplanar orientation of joined graphenes.

CONCLUSIONS

Thus, in this work, we determined optimum conditions for the alkaline activation of carbonized high-ash biomass. These conditions allowed us to prepare microporous carbon materials with maximum specific surface areas to 3500 m^2/g, total pore volumes to 3.0 cm^3/g, and micropore volumes to 1.9 cm^3/g.

We found that the conditions of the precarbonization of the carbon precursor are a crucial factor for the production of microporous amorphous carbon materials because carbonization conditions are responsible for the amount and type of oxygen-containing functional groups, which participate in the genesis of the microporous texture. We found that the optimum conditions of precarbonization include the thermal treatment of the starting raw material in the fluidized bed of the catalyst at 500°C with a contact time shorter than 1 s.

It is reasonable to perform alkaline activation in the presence of potassium hydroxide at 750–800°C. A higher activation temperature resulted in a decrease in the fraction of micropores, probably because of the graphitization of the micropore structure by ordering with an increase in the number of graphite layers in pore walls and mesopore formation.

Tests for the adsorption capacity of carbon materials prepared at different temperatures demonstrated their high capacities for hydrogen (to 6.3 wt % at liquid nitrogen temperature at 50 atm) and methane (to 41 wt % at 0°C and 60 atm). Thus, these materials are promising for use as transport accumulators of H_2 or CH_4 for fuel cells and as membranes for the separation of various gas mixtures.

The resulting carbon materials have an anisotropic cell-like microporous structure. According to Marsh et al. [14], this structure is formed through the growth of layered nematic liquid crystals consisting of ordered layered graphite-like fragments. The crosslinking of structure-forming layered fragments by various bonds is responsible for pore structure anisotropy. These bonds are formed by the interaction of oxygen-containing functional groups of graphite-like fragments with potassium metal, which, in turn, is formed by the interaction of carbon with KOH.

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