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Preparation and investigation of nanostructured carbonaceous composites from the high-ash biomass

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Abstract

The various pathways of high-ash biomass processing to the valuable carbonaceous composites are considered. From the rice husk carbon–silica composites and supermicroporous carbon materials (SMC) were prepared. In the new SMCs, the specific surface area A_{BET} reaches 3460 m^2/g while micropore volume V_μ is up to 1.9 cm^3/g at the total of pore volume, V_Σ, as large as 3.0 cm^3/g. These carbons were shown to absorb up to 41 wt% of methane at room temperature and 60 atm and more than 6 wt% of hydrogen under mild cryogenic conditions (at 77 K). Also methods for the synthesis of carbon–silica composites with A_{BET} up to 710 m^2/g and with average size of SiO_2 particles less 5 nm are proposed. The expected practical application of the obtained carbon–silica composites may be first of all reinforcing rubber extenders and bi-functional sorbents for the gas and liquid purification.

Keywords: Rice husk; Carbon–silica; Composite; Supermicroporous; Carbons; Hydrogen adsorption

1. Introduction

Enormous potentialities of biomass as the main renewable energy resource and feedstock for production of valuable materials and chemicals are commonly recognized worldwide [1]. The ever-increased importance of biomass as the energy and materials resource has been lately accounted for by the rising prices for exhaustible fossil fuels.

At the same time, the bioenergy sources appear to be more expensive than fossil fuels today. However, this problem may be solved by applying of comprehensive biomass processing methods not only to generate heat or electricity but also to convert biomass into valuable products, such as synthesis gas, chemicals and valuable activated carbons [1–15]. This approach raises sufficiently the profitability of the renewable energetic.

High-ash biomass seems to be most appropriate for profitable biomass processing to produce valuable carbonaceous materials [16–26]. Rice husk represents an example of high-ash biomass waste. On the one hand, inorganic ash is a sufficient constituent of the rice husk (up to 20 wt%), on the other hand, rice husk is a large-capacity agricultural waste. Rice husk, a by-product of the rice milling industry, is produced in amount of approximately 100 million tonnes in the world, while only a little part of it are utilized efficiently [20]. Despite the increasing trend of the rice husk production, at present proper methods of rice husk processing are only developing because of its processing problems and specific properties (low apparent density, abrasiveness, high ash, etc.).

So, the aim of this work was to develop comprehensive pathways of biomass processing with the emphasis on production of valuable carbonaceous materials from high-ash biomass by the example of rice husk.

The development of high-ash biomass processing processes was focused on three directions, which are:

1. simple method of carbon–silica composites preparation from rice husk via its carbonization in the fluidized catalyst bed (FCB);
2. the development of nanostructural carbon–silica composites via rice husk carbonization followed by silica reprecipitation with or without separation of individual products;
3. the development of nanostructural supermicroporous carbons (SMC) via biomass carbonization followed by alkali activation of the carbonized agricultural waste, such as rice and oat husk, wheat straw.

Every type of obtained carbonaceous materials has great potential for various applications, such as catalysts supports, inexpensive bi-functional sorbents for liquid and gas purification, accumulators of power gases, reinforcing rubber extenders,

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as well as feedstock for the production of silicon compounds (Si, SiC, $SiCl_4$ and its derivatives, liquid glass) [19–37].

2. Experimental

2.1. Materials

The substrates used for studying the biomass carbonization were rice husk (RH, from Krasnodar Region, Russia), oats husk (OH) and wheat straw (WS, from Novosibirsk Region, Russia). The commercial catalyst BIC-12-73 (10–15 wt% $CuO + MgO + Cr_2O_3$ supported on γ-Al_2O_3; mass ratio of $CuCr_2O_4$:$MgCr_2O_4$ = 1:1; particles size, 1–2 mm) was used for carbonization of the rice and oats husk in a fluidized bed reactor.

2.2. Carbon–silica composites preparation via carbonization in FCB

Rice husk (Krasnodar Region) was disintegrated to obtain submillimeter particles and subjected to carbonization in a vertical cylinder steel reactor (i.d. = 40 mm) with a fluidized bed of IC-12-73 at 450, 500, 550 and 600 °C at α (molar O_2/C ratio) being not higher than 2.5 and contact time (τ) of RH in the carbonization zone no longer than 1 s. Solid products of carbonization were separated using a cyclone and accumulated in a tank. Elemental analysis of carbon–silica composites shown that the composites consist of carbonaceous phase and silica (summary about 98 wt%) with ash impurities of K_2O, CaO, Na_2O, MgO, Fe_2O_3, Al_2O_3, Mn_2O_3 (in decreasing order).

2.3. Carbon–silica composites preparation via silica reprecipitation

Carbon–silica composites (C/SiO_2) were synthesized by fluidized bed carbonization of RH at 450–600 °C, then treated with alkali metal carbonates (K_2CO_3, Na_2CO_3) taken in the amount corresponding to the formula $Me_2O \cdot nSiO_2$ (Me = Na, K) where $n = 0.67$–2 with respect to the molar content of SiO_2 in the composite. The resulting mixture was fused in an inert atmosphere (in nitrogen flowing at the rate of 5 l/h) for 2 h.

The fused sample was dissolved in water under stirring at 40–50 °C, cooled and acidified either by adding of solution of a 20% mineral acid (HCl, H_2SO_4) or by passing gaseous CO_2 through the solution. After SiO_2 was gelated, the stirring was stopped and the gel was allowed to stay for 24 h to age it. Then the gel was washed with distilled water using a Buchner funnel, dried under an infrared lamp and calcined at 150 °C up to the constancy of weight.

2.4. Preparation of nanostructural supermicroporous carbons via alkali activation of carbonized rice husk

Carbon–silica composites (C/SiO_2) used as carbon-containing precursors of supermicroporous carbons (SMC) were synthesized by fluidized bed carbonization of rice and oats husk, wheat straw.

The carbon-containing precursors were impregnated with the aqueous solution of an activating agent (KOH, K_2CO_3 and NaOH) at the activating agent to carbon precursor ratio equal to 72 mmol/g [18].

After water removal, the resulting mixture was heated in flowing nitrogen up to the activation temperature. The activation time was no longer than 2 h at the stationary temperature. The reactor was cooled, the carbon material washed and dried at 120 °C for 24 h.

2.5. Materials characterization

Fourier transform infrared (FT-IR) studies were carried out using MB–102 (Bomem, Canada) with KBr method [39]. X-ray diffraction (XRD) studies were carried out using HZG-Y with Cu Kα radiation. The size and shape of nanoparticles were determined using a high-resolution transmission electron microscope (HRTEM, JEM-2010, JEOL, Japan) at the resolution of 0.14 nm. X-ray photoelectron spectra (XPS) of synthesized C/SiO_2 were acquired with reference to the Al Kα line as the excitation source ($h\nu = 1486.6$ eV) using a VG ESCALAB HP ("Vacuum Generators", Great Britain) at the background pressure lower than 2.1–9.0 Torr. The binding energies were referenced to the Au $4f_{7/2}$ (84.0 eV) and Cu $2p_{3/2}$ (932.67 eV) with an uncertainty of ± 0.2 eV. A Derivatograph-Q-1500 D (MOM, Hungary) was used for thermogravimetric studies at the sample heating rate of 10°/min from room temperature to 800 °C (with samples weighing 50 mg). TGA studies were carried out using platinum labyrinth-crucibles in inert atmosphere and platinum disc crucibles in air-containing atmosphere.

3. Results and discussion

Methods under development in this work for processing the high-ash biomass as well as basic parameters of the target products are illustrated in Fig. 1. Common stages are seen to be inherent in these methods, while varying their sequence and reaction parameters makes it possible to produce carbon materials with essentially different properties.

3.1. Carbon–silica composites from rice husk via carbonization in FCB

The literature analysis shows that a aim of lot of reports devoted rice husk processing is amorphous silica preparation via the incineration by different methods or an using of rice husk as fuel in the fluidized bed reactors, e.g. [24–26]. However, there are some articles devoted carbon–silica composites preparation from the rice husk. These composites planed to apply as precursor of some silicon compounds—Si_3N_4, SiC, as inexpensive adsorbents and fillers in the cements, elastomer, etc. The main method of its production is pyrolysis in inert atmosphere during few hours at high temperature [21–23]. As a result the specific surface areas of these composites do not exceed 450 m^2/g [23].

In our case, for carbon–silica composites preparation was employed different method—the carbonization in fluidized cat-

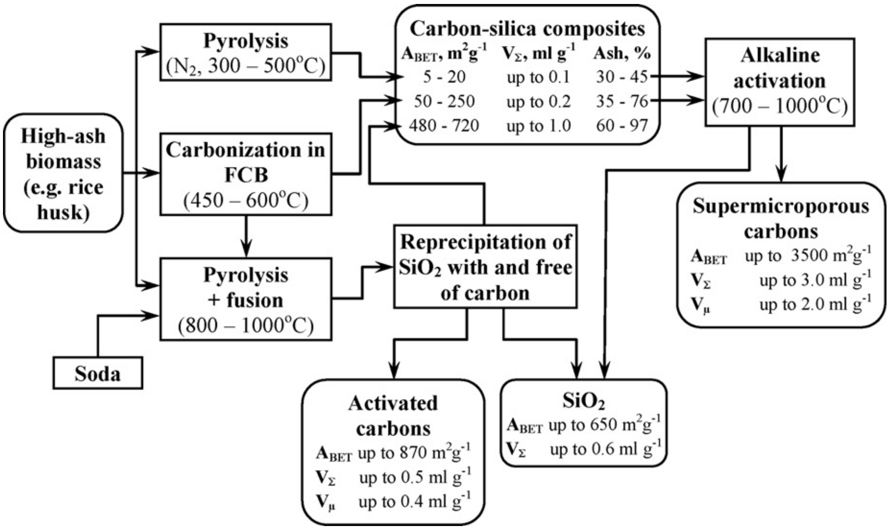


Fig. 1. Scheme of high-ash biomass processing to carbonaceous composites.

alyst bed reactor. This approach allows to reduce process time from several hours to few seconds, decrease treatment temperature and raise unit capacity.

Table 1 shows texture parameters of carbonized carbon–silica composites synthesized in a fluidized bed of the IC-12-73 catalyst at various temperatures.

The tabulated data show that the burning degree (the ash content) of the carbon phase increases with the carbonization temperature while, on the other hand, A_{BET}, V_{Σ}, V_{μ} are maximal at 550 °C. Evidently, the composite surface area increases due to the fast gasification of the initial biomass, while the gasification temperature affects the process intensity. The low textural parameters of the composite synthesized at 450 °C are thought to indicate that the gasification and carbonization processes are incomplete and the sample contains volatile compounds in considerable mounts.

To understand how the FCB temperature influences the processes of gasification and carbonization of rice husk during the short residence time (<1 s) of biomass in the reactor, the synthesized samples were studied using TGA in air and inert media.

3.1.1. TGA analysis of carbon–silica composites after FCB carbonization of rice husk

TG, DTG and DTA data obtained with samples in air are processed and summarized in Table 2 in comparison with the TGA data of the initial rice husk. The tabulated data show that the initial rice husk contains at least three main types of carbon-

Table 1
Textural parameters of carbon–silica composites synthesized from rice husk in FCB at 450–600 °C

FCB temperature (°C)	A_{BET} (m^2/g)	V_{Σ} (cm^3/g)	V_{μ} (cm^3/g)	Average pore size (Å)	Ash content (%)
450	32	0.04	∼0	53	35
500	176	0.15	0.03	26	56
550	246	0.21	0.05	26	69
600	233	0.22	0.04	28	76

Table 2
TGA data (in air; temperature region, from ambient up to 800 °C; heating rate, 10 °C/min) on carbon–silica composites produced by carbonization of RH at various temperatures

Parameter	Initial RH	FCB carbonization temperature of RH (°C)			
		450	500	550	600
Temperature region of weight loss (°C)	Up to 510	Up to 450	Up to 505	Up to 475	Up to 470
Constituents (wt%), including:					
H_2O_{ads}	4 (85 °C[a])	3 (60 °C)	4 (70 °C)	4 (65 °C)	4 (65 °C)
Volatiles	44 (330 °C) 4 (340 °C)	33 (325 °C)	6 (325 °C)	–	–
Soot	32 (440 °C)	36 (415 °C)	40 (400 °C)	31 (395 °C)	22 (400 °C)
SiO_2 (ash)	16	28	51	65	74

[a] In parentheses are temperatures of the maximal weight losses of the C/SiO_2 components and, correspondingly, of the maximal exothermic effects.

Table 3
TGA data (in nitrogen; temperature region, from ambient up to 800 °C; heating rate, 10 °C/min) on carbon–silica composites produced by carbonization of RH at various temperatures

Parameter	Initial RH	FCB carbonization temperature of RH (°C)			
		450	500	550	600
Temperature region of weight loss (°C)	Up to 600	Up to 700	Up to 700	Up to 600	Up to 600
Constituents (wt%), including:					
H_2O_{ads}	7 (125 °C[a])	4 (125 °C)	6 (120 °C)	5,4 (120 °C)	4 (125 °C)
Volatiles	14 (280 °C) 31 (335 °C)	18 (335 °C)	4 (420 °C)	–	–
Soot[b]	32	50	39	29.6	22
SiO_2 (ash)[b]	16	28	51	65	74

[a] In parentheses are temperatures of the maximal weight losses of the C/SiO_2 components and, correspondingly, of the maximal endothermic effects.
[b] Data from ash content definition of TGA analysis residua.

containing species to be oxidized with the maximal weight loss at 330, 340 and 440 °C. There are two types of carbonaceous species in the samples carbonized at 450 and 500 °C, which are identified as volatile compounds (primarily CO_2 and H_2O [1]) and soot, respectively. Note that the content of volatile compounds in the composites decreases with a rise of the FCB temperature; the samples synthesized at 550 and 600 °C are free of them but characterized by uniform burning of carbon with the maximal weight loss at 400–140 °C. In the case of uniform heating (10 °C/min) of the sample up to 500 °C, the further temperature elevation results in neither changes in the sample weight nor thermal effects, the ash being grey colored in all the cases to indicate, probably, the presence of carbon traces in the form, e.g. of a solid solution.

TGA data also were obtained in an inert atmosphere (Table 3) in order to study the pyrolysis processes during the thermal treatment of rice husk. The TGA data summarized in Table 3 demonstrate that the temperature of water evolution from the samples is higher (above 40–60 °C) in the inert atmosphere than in air, while a total quantity of evolved volatiles (primarily levoglucosan [38]) decreases and the sample weight loses more uniformly. Generally, the inert atmosphere experiments indicate once again the absence of volatile components in the samples carbonized at above 550 °C. The TGA data obtained are useful to understand regularities of these materials processing into carbon-containing composites.

In addition, it seemed reasonable of apply FT-IR and XPS techniques for studying the surface composition of carbon–silica composites.

3.1.2. *FT-IR-analysis of carbon–silica composites after FCB carbonization of rice husk*

Fig. 2 shows IR spectra of carbonized SiO_2 prepared by FCB carbonization of rice husk at 450–600 °C. In all the spectra, there are four main absorption regions at 3400, 1650, 1100 and 460 cm^{-1}. The region at 3400 cm^{-1} relates to the surface hydroxyl groups and chemisorbed water [39]. An intense peak at 1080 cm^{-1}, as well as a peak at 1200 cm^{-1}, are assigned to siloxane groups, such as Si–O–Si. A peak at 2930 cm^{-1} argues for the presence of C–H groups in certain amountg on the carbon surface. As the carbonization temperature rises, the intensity of the peak at 2930 cm^{-1} decreases to indicate elimination of these surface carbon species. Oxidized carbon species (absorption at 1710, 1620 and 1450 cm^{-1}) are in more considerable amounts on the surface. Absorption bands at 1710 and 1620 cm^{-1} are assigned to vibrations of the C=O bands in ketone and aldehyde groups, respectively. A low intense broad peak at 1450 cm^{-1} relates to vibrations of the C–O bond in a carboxyl group. The intensity ratio of these peaks does not change with elevated carbonization temperature.

3.1.3. *XPS analysis of carbon–silica composites after FCB carbonization of rice husk*

XPS technique was used to characterize the chemical composition of the sample surface; an overview XPS spectrum is shown in Fig. 3. In the spectrum, there are silicon lines Si 2p and Si 2s along with intense lines of oxygen and carbon. For example, an intense line at 285 eV relates to electron photoemission from C 1s level, and a peak at 533 eV to electron photoemission from O 1s level.

In addition, Auger lines O KVV and C KVV appear at 980 and 1230 eV, respectively, in the spectra [40]. Less intense lines at 104 and 155 eV relate to electron photoemission from levels Si 2p and Si 2s, respectively. No other element impurities are detected. The XPS data are used to determine relative concen-

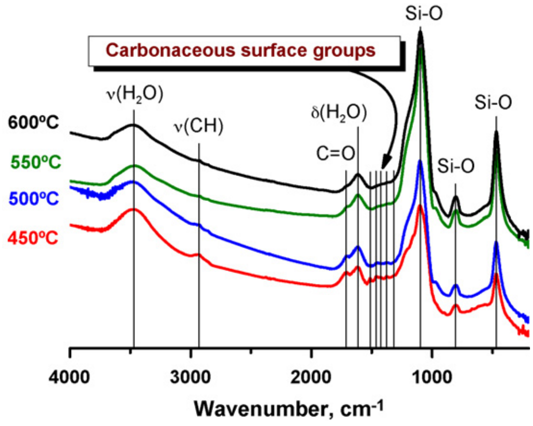


Fig. 2. FT-IR spectra of C/SiO_2 produced by burning rice husk at 450–600 °C.

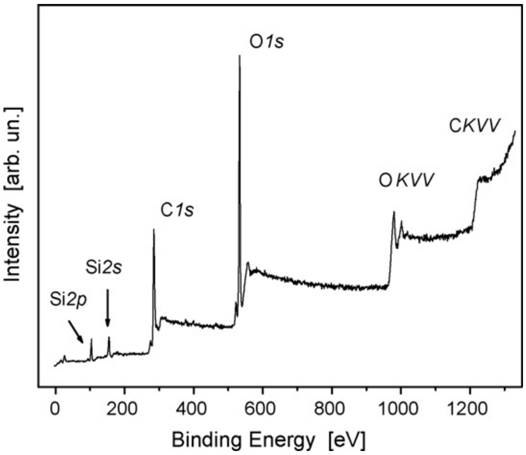


Fig. 3. Overview XPS spectrum of sample C/SiO_2 (450 °C).

trations of elements (atomic ratios) in the surface region and to calculate the surface ash content (see Table 4 for the results).

Elevation of the burning temperature results, on one hand, in elimination of a part of carbon to increase the ash content in the samples and, on the other hand, in a decrease in the atomic ratio of [O]/[Si]. For example, the [O]/[Si] atomic ratio equals 3.9 in the sample produced at 450 °C that indicates a considerable oxygen content in the surface carbonaceous phase. When RH is carbonized at a fluidized bed at 600 °C, the [O]/[Si] atomic ratio is close to the stoichiometry of SiO_2, i.e. [O]/[Si] = 2.1 (Table 4). One can also see that the bulk ash content is almost identical to the XPS data on the surface ash content. Hence, the carbon and silica phases are homogeneously distributed through the resulting composites to provide a large interaction surface for both phases. Elemental analysis of carbon–silica composites shown that the composites consist completely of carbon and silica (99.5 wt%).

Thus, the carbon–silica composites produced by low temperature (450–600 °C) FCB carbonization of rice husk at subsecond contact times are composites with the homogeneously distributed carbon and silica phases. The textural characteristics of the composites and concentrations of their carbonaceous constituents including volatile components can easily be varied depending on the fluidized bed temperature. That is why these materials are promising for such applications as bi-functional sorbents for the liquids and gases purification, reinforcing rubber extenders, and also as initial materials for production of H_2, syngas, microporous carbons and liquid glass, amorphous silica, other silicon compounds and nanostructural carbon–silica composites. Development and characterization of two type carbon-containing materials will be described below.

Table 4
Relative atomic concentrations of oxygen, carbon and silicon at the surface region of samples C/SiO_2 prepared at different temperatures (T) of carbonization of rice husk

T (°C)	[O]/[Si]	[C]/[Si]	Bulk ash (%)	Surface ash (by XPS) (%)
450	3.9	6.1	35	37
500	2.6	3.1	56	56
550	2.3	1.9	69	69
600	2.1	1.7	76	73

3.2. Nanostructural carbon–silica composites via rice husk carbonization followed by silica reprecipitation

In some applications, a high-surface nanostructure of silica composites (with primary globules no more than 5–10 nm in size) is necessary. One of them is the application of amorphous silica as a reinforcing rubber extender. Traditionally, these silica materials are produced using the sol–gel method by preparation of a silicate-block from sand followed of melting at 1500 °C with Na_2CO_3. Then the silica phase is reprecipitated by acidifying the liquid glass with mineral acids.

This is a very material and energy consuming process. However, there are available data on the use of rice husk as a silica source to produce liquid glass. When so, rice husk is burnt different ways and the ash (amorphous SiO_2) is dissolved in alkalis. The resulting liquid glass is acidified with mineral acids (H_2SO_4, HCl) and the reprecipitated SiO_2 is produced by the traditional sol–gel method.

In the present paper, we suggest to employ a simpler and cheaper method for preparation of reprecipitated silica from rice husk.

This is a two-step process:

Step 1 Fusing of the carbonized rice husk with alkali metal carbonates by the following main reactions:

$$Me_2CO_3 + SiO_2 \rightarrow Me_2SiO_3 + CO_2 \quad (Me = K, Na)$$

$$CO_2 + C \leftrightarrows 2CO$$

The materials are fused at a lower temperature (900 °C) in comparison to the traditional process for preparation of silicate-block (1500 °C) through sand melting with K_2CO_3. In the process under consideration, silica is leached from the composite (C/SiO_2) to form silicates while the carbon surface is enlarged due to carbon dioxide activation.

Step 2 Preparation of reprecipitated silica. The silica–carbon fusion is dissolved in hot water, the solution was acidified under stirring by passing carbon dioxide. Then the standard sol–gel procedures are used for the gel ageing, washing and drying of SiO_2.

Generally, the second step can be presented as the overall reaction:

$$Me_2SiO_3 + H_2O + 2CO_2 \rightarrow 2MeHCO_3 + SiO_2\downarrow$$
$$(Me = K, Na)$$

Thus, a specific feature of the suggested method is the use of carbon dioxide as the acidifying agent to allow the recycle of carbonate of alkali metals. Carbon dioxide can be obtained either during the first stage through oxidation of CO or during the FCB carbonization of rice husk. At the second stage, carbon particles undergoes

Table 5
Textural characteristics of carbon–silica composites produced by fusing with sodium and potassium carbonates followed by reprecipitation of the silica phase

Precursor	Ash of precursor (%)	Product	Ash of product (%)	A_{BET} (m^2/g)	V_Σ (cm^3/g)	V_μ (cm^3/g)	$\langle d_{pore} \rangle$ (Å)
RH	19	C/SiO_2	44.7	662	0.54	0.16	24.5
RH	19	C[a]	7.0	872	0.47	0.40	16.3
RH	19	SiO_2[b]	~100	645	0.57	0.33	35.1
C/SiO_2 FCB500	60	C/SiO_2	49	479	0.58	0.16	36.4
C/SiO_2 FCB550	65	C/SiO_2	44	620	372	0.71	34.0

Conditions: K_2CO_3 as an activating agent, taken in the ratio 1:1 to SiO_2; fusion temperature 900 °C; fusion time 2 h. CO_2 is used for precipitation of SiO_2.

[a] Obtained through washing from SiO_2.

[b] Reprecipitated without C.

no transformation but behave as centers for nucleation of the silica phase.

The nanostructure of the resulting carbon–silica composites is essentially different from that of the traditionally produced materials.

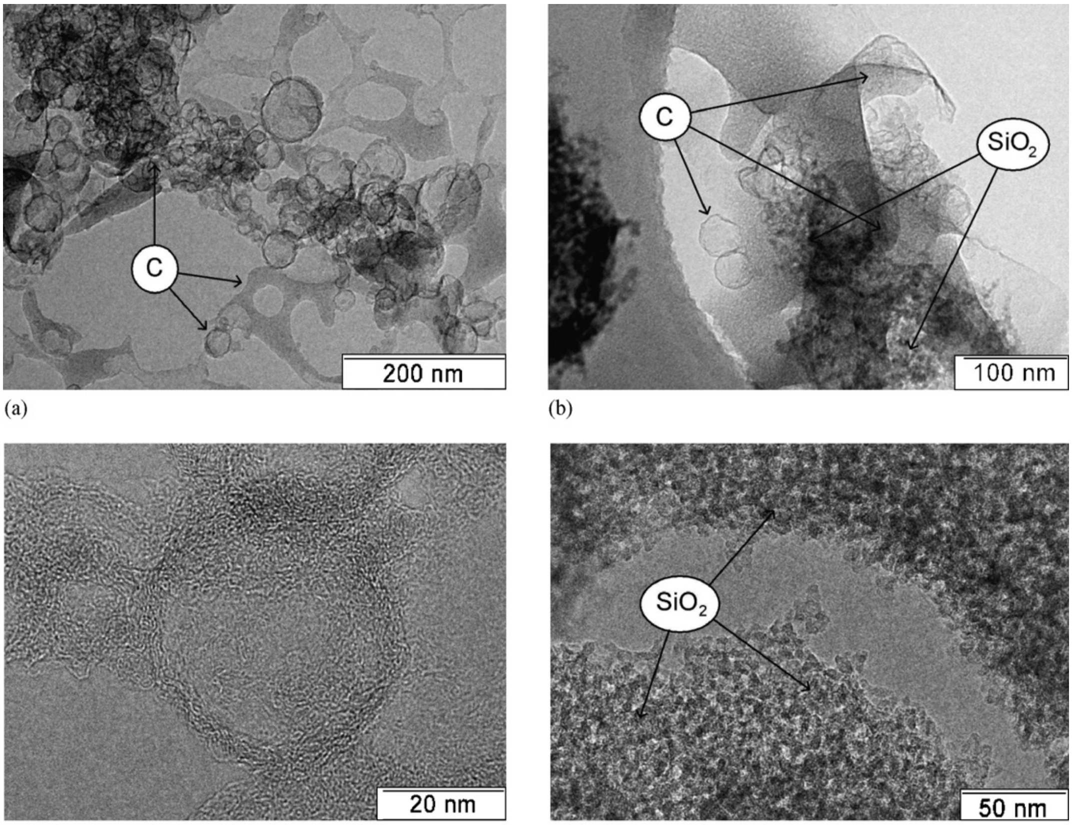
Table 5 demonstrates textural and some other characteristics of the produced materials.

The tabulated data show a more extended texture is characteristic of the composites produced by the suggested method. In addition, this method allows rice husk to be used as a carbon-containing precursor to simplify considerably the process for production of carbon–silica composites. HRTEM technique was used to characterize the composite nanostructure.

3.2.1. HRTEM studies of nanostructural carbon–silica composites

Fig. 4 shows HRTEM images of a typical carbon–silica composite produced by the suggested method. HRTEM studies demonstrated that at least three carbon species are comprised in the carbon phase, which are:

- Leaflike carbon with particles of 2000 nm × 200 nm × 5 nm in size. This carbon species seem to form at carbonization of the cellulose at the preserved initial macrostructure.
- A variety of coral-like carbons formed, probably, upon decomposition of volatile products of lignocellulose.
- Hollow carbonaceous spheres of 5–80 nm in diameter. This is most likely that this carbon species results from decompo-



(a) (b) (c) (d)

Fig. 4. TEM-EDX analysis of nanostructured carbon–silica composite prepared from rice husk by silica reprecipitation. Fragments of the composite: (a) coral-, leaflike carbonaceous particles and hollow spheres (predominantly); (b) leaf- and sphere-like carbon and SiO_2 globules in the composite; (c) detailed hollow carbonaceous sphere; (d) SiO_2 globules in the composite.

sition of volatile products of pyrolysis on the surface of the silicate template. When so, the silicate template is covered by an amorphous carbon layer less than 5 nm in thickness (Fig. 4c). When dissolved in hot water, the silicate template diffuses through the crust carbon layer and escapes the sphere cavity to produce hollow spheres of amorphous carbon. The sphere size depends on the size of primary templates formed upon interaction between alkali metal carbonates and the silica phase of the carbon–silica composite.

The reprecipitated silica phase in the composites consists of SiO_2 nanospheres of ca. 5 nm in size, the SiO_2 nanosphere being distributed uniformly enough through the surface of carbon particles. The latter is a favorable feature to homogenize the silica phase during preparation of rubber mixtures.

A variety of carbon species in the nanostructured composites may be partly caused by transformations of the non-decomposed (during FCB carbonization) lignocellulose fragments subjected to catalytic pyrolysis at the fusion stage (first step). Therefore, it seems interesting to characterize the composition of gaseous products formed at the fusion stage.

3.2.2. Analysis of gaseous products of fusion step

Fig. 5 illustrates the gas phase composition at the fusion stage in the heating mode during the production of nanostructural carbon–silica composites. The rice husk carbonized in the fluidized bed at 450, 500, 550 and 600 °C was used as precursor. The initial rice husk was not analyzed because of a considerable amount of tar formed during the mixture heating to 600 °C.

One can see in Fig. 5 that CO_2 and CH_4 are detected among the reaction products in all low-temperature experiments, the amount of fusion evolved methane being decreased with the rise of temperature of rice husk pre-carbonization. When rice husk is pre-carbonized at 600 °C, methane is not formed at any temperature. It is most likely that methane is formed upon catalytic pyrolysis of lignocellulose fragments of the carbonaceous precursor; these fragments decrease in amount with the rise of temperature of FCB pre-carbonization.

The formation of CO and H_2 in considerable amounts is observed in all experiments. The content of carbon monoxide in the gas mixture increases with the temperature elevation due to CO_2 gasification of carbon by reaction: $CO_2 + C \leftrightarrows 2CO$.

The presence of hydrogen in the gas mixture is surprising. However, the hydrogen formation may be accounted for by the interaction of carbon with adsorbed water and KOH generated upon hydrolysis of the carbonate at the impregnation stage:

$$2H_2O + C \rightarrow CO_2 + 2H_2$$

$$H_2O + C \rightarrow CO + H_2$$

$$3KOH + C \rightarrow K_2CO_3 + K + \tfrac{3}{2}H_2$$

This is the authors' opinion that these gases, i.e. CO, CO_2 and H_2, also are formed upon decomposition of the lignocellulose fragments after FCB carbonization when the fluidized bed temperature is elevated up to 600 °C.

Thus, thorough characterization of the prepared samples using, among others, a number of physicochemical methods (FT-IR, XRD, XPS) has led to conclude that rice husk carbonized in the fluidized bed at low temperatures (450–500 °C) is most appropriate to obtain a large-surface texture of the carbon phase in nanostructural carbon–silica composites produced through fusion of C/SiO_2 composites with alkali metal carbonates. Again, when such a precursor is used, the gaseous product mixture has the maximal calorific value (up to 18 MJ/m^3). Calorific value of pyrolysis gases is a very important param-

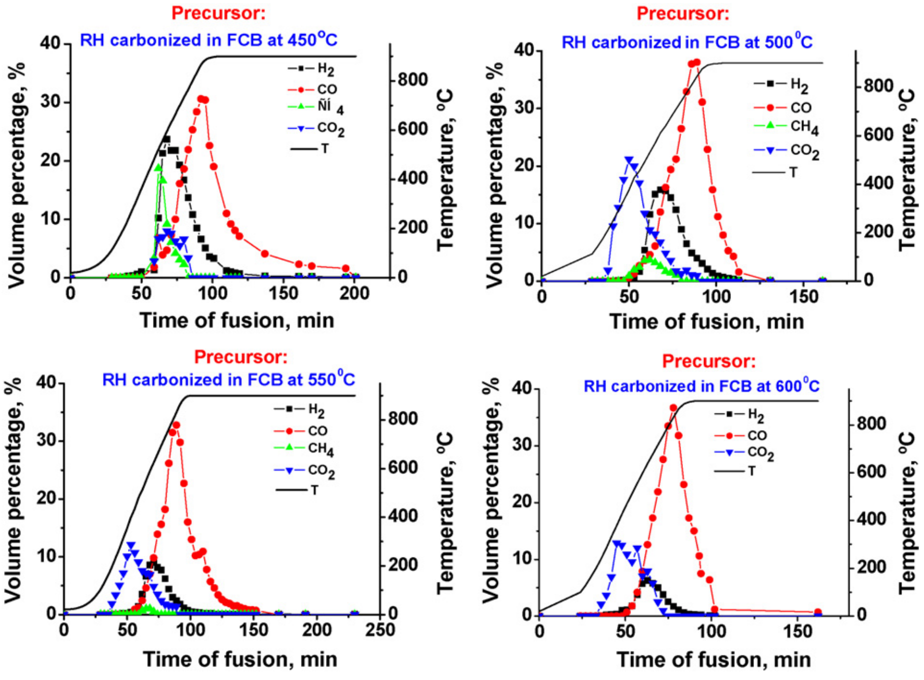


Fig. 5. Gas phase composition during fusion of K_2CO_3 and carbonaceous precursors depending on the heating temperature and time.

eter because these gases can be used for heat supply to the fusion stage and to other endothermic stages of the process.

3.3. Nanostructural supermicroporous carbons via biomass carbonization and subsequent alkali activation

In Fig. 1, we demonstrate a possibility to produce supermicroporous carbons (SMC) with large surface areas from carbonized rice husk. Traditionally, SMC with the specific surface area up to 2000–3500 m^2/g and pore volume up to 2.0 cm^3/g and micropore volume up to 1.5 cm^3/g are synthesized through chemical activation of various carbon-containing precursors (pyridine, PVC, oil coke, activated carbons, etc.) by alkali metal hydroxides at 700–1000 °C [42–44].

The principal advantage of our proprietary method for synthesis of SMC in comparison to the analogues (AX-21, MAXSORB) is no need in the pretreatment of the carbon precursors with concentrated nitric acid in order to oxidize the carbon surface. For this reason, toxic wastes are not evolved. The biomass (rice husk) carbonized at low temperatures comprises, initially, oxygen-containing functional groups in considerable quantities. Earlier in Refs. [17,18], it was shown that pyrolyzed rice husk was used for the supermicroporous carbons preparation. However, obtained coals had the texture characteristics no more than $A_{\mathrm{BET}} = 3000\ m^2/g$, $V_{\Sigma} = 1.9\ cm^3/g$ and $V_{\mu} = 0.8\ cm^3/g$.

Hence, the basic stage of SMC synthesis is alkali activation of a carbon-containing precursor. When the carbon–silica precursor is used, the activation is described by the following equations:

with SiO_2

$$KOH + SiO_2 \rightarrow K_2SiO_3 + H_2O$$

$$K_2SiO_3 + SiO_2 \rightarrow K_2Si_2O_5$$

with carbon

$$6KOH + 2C \rightarrow 2K + 3H_2 + 2K_2CO_3$$

Even though these reaction equations agree with literature data [41], we think them inappropriate to describe the mechanism of the formation of the microporous SMC structure because they neglect the role of surface functional groups. The mechanism of SMC genesis is not as yet understood in detail and not discussed in this paper. However, some preliminary data indicate the redox nature of the mechanism and, probably, the key role of potassium in this process.

Note that a number of factors influence the genesis of SMC. These are:

- nature of carbonaceous precursor;
- type of activation agent;
- temperature of activation, heating procedure;
- time of activation;
- molar ratio of activation agent and carbonaceous material;
- method of preliminary preparation of mixture, etc.

Our studies have revealed that the most important factors are nature of the carbonaceous precursor, activation agent and activation temperature.

3.3.1. Influence of the nature of the carbonaceous precursor on the microporous carbons genesis

Data on the influence of the nature of carbonaceous precursor on the final textural parameters of microporous carbons activated with KOH at 800 °C are given in Table 6. The carbon-mineral materials used for the activation were synthesized through carbonization of agricultural wastes, such as rice husk, oats husk and wheat straw. The ash content in the carbonized products was 35–75% depending on the treatment temperature. It is seen from the tabulated data that all these carbonaceous precursors are appropriate for synthesis of supermicroporous carbons with a large surface areas and high micropore proportions. This is mostly accounted for by similar compositions and textures of the precursors used, namely by the presence of oxygen-containing groups, large surface area and high-ash content, the latter also is though to affect the formation of the microporous structure. In a test experiment, graphite, which does not reveal the enumerated properties, was used as the precursor. The porous structure was not formed while A_{BET} of the graphite was 2–4 m^2/g both before and after the alkali activation. Elemental analysis of supermicroporous carbons shown that the materials content ash impurities (about 4 wt%).

The results obtained led to conclude that the optimal carbonaceous precursor for production of supermicroporous carbons is rice husk carbonized in a fluidized catalyst bed at 500 °C. The conclusion is based on the comparatively high content of oxygen-containing fragments the conclusion is based on the

Table 6
Textural characteristics of SMC prepared from various carbonaceous precursors

Initial biomass	Preliminary treatment	Precursor A_{BET} (m^2/g)	Product[a] A_{BET}/A_{μ} (m^2/g)	V_{Σ}/V_{μ} (cm^3/g)	%Micropores
Rice husk	Pyrolysis 400	4	2600/2460	1.53/1.24	89.5
	FCB 450	32	2960/2780	1.80/1.62	94.1
	FCB 500	176	3360/3100	2.18/1.87	92.3
	FCB 550	246	2970/2880	1.60/1.49	93.1
	FCB 600	233	2910/2440	2.12/1.57	84.0
Oats husk	FCB 500	80	2930/2770	1.83/1.57	94.6
Wheat straw	pyrolysis 500	21	3270/3254	1.58/1.54	99.5

[a] Activating agent is KOH, activation temperature 800 °C, rest conditions are identical to those described in Section 2.4.

Table 7
Texture characteristics of SMC prepared in the presence of various activation agents

Activation agent	A_{BET}/A_{μ} (m^2/g)	V_{Σ}/V_{μ} (cm^3/g)	%Micropores
KOH	3360/3100	2.18/1.87	92.3
NaOH	1130/1040	0.64/0.49	92.0
K_2CO_3[a]	1490/1330	0.95/0.63	89.3
KOH/NaOH = 1:1	3330/3220	1.93/1.63	96.7

[a] The activation temperature was 900 °C.

Table 8
Texture characteristics of SMCs prepared at the various activation temperature

Activation temperature (°C)	A_{BET}/A_{μ} (m^2/g)	V_{Σ}/V_{μ} (cm^3/g)	%Micropores
700	3170/3060	1.77/1.45	96.5
750	3450/3270	2.01/1.68	94.8
800	3360/3100	2.18/1.87	92.3
850	3170/2680	2.26/1.74	84.5
900	3210/1730	2.97/1.48	53.9

comparatively high content of oxygen-containing fragments (TGA data, Table 2) due to the presence of volatile components in the sample. On the other hand, a large-surface texture is characteristic of this sample (Table 1) to provide better interaction with the activating agent. In addition, the inherent low ash content allows higher yields of the target product – SMC – to be obtained.

3.3.2. Influence of the nature of activation agent on the microporous carbons genesis

Another factor affecting the genesis of the microporous structure is the nature of the activating agent. This is commonly accepted that the best agent for chemical activation is KOH. Indeed, the use of KOH allowed supermicroporous carbon to be synthesized with the maximal surface area. At the same time, literature data [17] indicate only slightly lower activity of NaOH. However, the data obtained (Table 7) show that NaOH is ineffective in the case under consideration and allows SMCs to be prepared with comparatively low A_{BET} and V_{μ}. The studies of K_2CO_3 and a KOH/NaOH mixture as activating agents demonstrated the key role of the alkali cation, namely K^+, in the process. A probable reason for different activities of K and Na is their different intercalating ability in the carbon materials. For example, the use of sodium–potassium alloy allowed only potassium intercalates to be synthesized [45] but no introduction of sodium in graphite was observed. From the authors' opinion, the sodium reductive potential is insufficient for introduction in the graphite lattice. Besides, sodium features a higher energy of the crystal lattice and ionization potential but lower atomic compressibility than potassium, rubidium and cesium.

While discussing experimental data obtained with K_2CO_3, it should be emphasized that the real activating agent is KOH in this case which is formed upon hydrolysis of potassium carbonate during impregnation of the carbonaceous material with the K_2CO_3 solution. The comparatively low A_{BET} and V_{μ} are inevitable due to the low KOH concentration in the mixture to be fused because KOH is partly consumed for the interaction with SiO_2 in the carbon–silica composite.

3.3.3. Influence of the activation temperature on the microporous carbons genesis

The third important factor affecting the genesis of SMCs is the activation temperature. To ensure the correct determination of the influence of activation temperature, all the other conditions were identical; FCB carbonized (500 °C) rice husk as the carbonaceous precursor, KOH as the activating agent. The results are summarized in Table 8.

The largest specific surface area and the highest micropore proportion are seen to achieve at 750–800 °C. As the temperature rises, a total of pore volume increases, the increase being provided by an increase in the micropore volume at below 800 °C. Above 800 °C, the micropore volume decreases but a total of pore volume increases, probably due to burning-out of the micropores to form meso- and macropores. Thus, a variation in only one parameter, the activation temperature, allows the textural characteristics (pore size distribution) to be controlled over a wide range at identical total surface area of SMCs. Methodical investigation of SMCs preparation conditions allowed to obtain carbonaceous materials with higher values of A_{BET}, V_{Σ}, V_{μ} and quota of micropores, than carbons prepared by Chinese authors [17,18].

4. Conclusions

Unique properties of high-ash biomass, with rice husk as a typical example, allow the production of a variety of valuable carbon-containing composites. Such composites can have different characteristics:

- Carbonization of rice husk in the fluidized catalyst bed at $\alpha = 1–2.5$ and $\tau \sim 1$ s produces carbon–silica composites with advanced textural characteristics: A_{BET} up to 250 m^2/g, V_{pore} up to 0.22 cm^3/g at the conditions of homogeneously distributed carbonaceous and silica phases. It is shown that the variation in the carbonization temperature in the range of 450–600 °C allows variations of not only textural parameters but also the ash content (from 35 to 80%) in the composites.
- Fusion of rice husk or its carbonization products with alkali metal carbonates followed by reprecipitation of the silica phase allows production of nanostructured carbon–silica composites with A_{BET} up to 710 m^2/g and V_{pore} up to 0.7 cm^3/g, while the carbon phase of the composite comprises several types of carbon particles including leaflike carbon (>2000 nm × 200 nm × 5 nm) and hollow carbonaceous spheres with diameter 10–80 nm. The silica phase consists of 5 nm nanospheres.
- Alkali activation of carbonized biomass (rice husk, oats husk and wheat straw) produces supermicroporous carbons with the maximal surface area and micropore volume: A_{BET} up to 3400 m^2/g; V_{μ} up to 1.9 cm^3/g and V_{pore} up to 3.0 cm^3/g. The basic process parameters, such as nature of the carbona-

ceous precursor and activating agent, which affect the textural parameters of target carbons and pore size distribution, are identified.

- The synthesized carbon-containing composites are promising in numerous applications including cleaning of gaseous and liquid media, adsorptive storage of gases (including hardly sorbable hydrogen), reinforcing rubber extenders, feedstock for synthesis of silicon-containing compounds.

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