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Conditions and features of matrix and bulk carbonization of the organic precursors

Nataliya D. Lysenko · Pavel S. Yaremov ·
Vladimir G. Ilyin · Mariya V. Ovcharova

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Abstract Comparative research of matrix and bulk carbonization of some organic precursors (sucrose, acetonitrile) in silica mesoporous materials SBA-15 and KIT-6 was conducted. X-ray diffraction, nitrogen adsorption analysis, Raman spectroscopy were used for determination of the structural-sorption characteristics of the obtained materials. It was shown that the carbon mesoporous materials CMK-8 obtained in the mesopores of KIT-6 had higher adsorption characteristics because of features of three-dimensional cubic structure, larger pore volume and framework's wall thickness. It was established that partially graphitized spatially well-organized carbon materials were formed as a result of pyrolysis of acetonitrile in the silica matrices SBA-15 and KIT-6. It was conditioned by the absence of considerable spatial limitations for growth of graphite structures on the initial stage of the synthesis when the pores of the matrix were not filled up with the organic precursor. Product of bulk carbonization of sucrose is compact carbon microporous framework with low sorption characteristics (micropore volume is 0.09 cm^3/g).

Introduction

Porous carbon materials are widely used in the sorption processes of water and air purification, separation of gases, in chromatography, catalysis, etc., [1, 2]. It's due to their properties, in particular, high surface area, large pore volume, chemical inertness, high mechanical stability. Carbon mesoporous materials [3, 4], as a rule, are obtained by carbonization of the organic substances of natural or synthetic origin with subsequent activation of the samples. One of the most promising ways for obtaining of mesoporous carbon materials is the method of matrix synthesis [5–11], which consists in the fact that the organic precursor is subjected to carbonization in the pores of inorganic mesoporous matrix (in particular, silica). Obtained carbon is evolved by the treatment of carbon–silica composite with hydrofluoric acid or alkali. Method of matrix carbonization allows adjusting the porosity of the carbon material by varying of the structure, composition and pore size of the initial matrix (exotemplate), the nature of the organic precursor and the degree of pores filling of the matrix with it, the conditions of pyrolysis, etc. The method of chemical vapor deposition (CVD-method) of volatile organic compounds in the pores of inorganic matrices, especially zeolites, is the kind of matrix synthesis. Microporous carbon materials were obtained [12] as a result of pyrolysis of acetonitrile in template containing BEA zeolite. It was seemed interesting to find out the possibility of using of CVD-method for receiving of mesoporous carbon materials and determine their structural and sorption characteristics.

The aim of the article is to clarify the conditions and features of the matrix (silica exotemplates), including the CVD method, and bulk carbonization of the organic precursors.

Two types of silica mesoporous molecular sieves (MMS): SBA-15 (hexagonal symmetry) and KIT-6 (cubic symmetry) were chosen as the matrices. They have uniform relatively large mesopores (D $\sim$ 6.5–7.5 nm) and a high degree of spatial ordering. Sucrose was used as the organic precursor, since it allows obtaining materials with the most uniform porous structure. Vapor deposition of acetonitrile [12] and its subsequent pyrolysis were used to compare this

N. D. Lysenko (✉) · P. S. Yaremov · V. G. Ilyin ·
M. V. Ovcharova
L.V. Pisarzhevsky Institute of Physical Chemistry,
NAS of Ukraine, 31 pr. Nauky, Kyiv 03028, Ukraine
e-mail: natalka112@bigmir.net

method with regard to MMS, with a classical matrix synthesis, in which adsorption and polymerization of the organic substance occurred before the stage of high temperature treatment.

Experimental

Synthesis procedure

Synthesis of the initial inorganic matrices

Initial matrices—Si-MMS SBA-15 and KIT-6 were synthesized by standard methods [13, 14]. Molar ratio of reagents in the initial reaction mixture for synthesis of SBA-15 was: 1 TEOS:0.016 P-123:5.5 HCl:152 H_2O. 0.8 g Pluronic P-123 was dissolved in 24 mL of water and 4 mL of concentrated HCl (37%) at 40 °C. 2 mL of TEOS was added to the obtained solution and the reaction mixture was stirred for 20 h at 40 °C. The obtained mixture was subjected to hydrothermal treatment for 24 h at 100 °C. Solid product was filtered, washed with water and dried at 100 °C. Surface active substance was removed by the calcination of the samples in air for 4–5 h at the temperature 550 °C. (Heating rate was 2 °C/min.).

Molar ratio of reagents in the initial reaction mixture for the synthesis of KIT-6 was: 1 TEOS:0.017 P-123:1.83 HCl:195 H_2O:1.31 n-C_4H_9OH. 0.62 g of Pluronic P-123 was dissolved in 22.7 mL of water and 1.06 mL of concentrated HCl (37%) at 35 °C. 0.77 mL n-C_4H_9OH and after 1 h 1.5 mL of TEOS were added to the obtained solution, reaction mixture was stirred for 24 h at 35 °C. Hydrothermal treatment and calcination were performed similarly.

The chart of these syntheses looks as follow:

$$\text{P123} \xrightarrow[(+n\text{–C4H9OH})]{+\text{HCl},+\text{TEOS}} \text{gel} \xrightarrow{\text{aging}} \text{silica-organic mesophase}$$
$$\xrightarrow{\text{hydrothermaltreatment}} \text{silica matrix}$$

Synthesis of the porous carbon materials

A weighted amount of the initial silica MMS was stirred with water solution, containing some amounts of sucrose and concentrated sulfuric acid (out of account 1.25 and 0.14 g, respectively, for 1 g MMS with pore volume 1.3 cm^3/g). The obtained slurry was dried at first for 6 h at 100 °C, and then it was heated for the same time at 160 °C. Then the obtained composite containing partially decomposed after heating sucrose, was mixed again with water solution of sucrose and sulfuric acid (0.8 and 0.08 g, respectively, for 1 g MMS with pore volume 1.3 cm^3/g). After re-processing under identical conditions obtained dark brown powder was heated (heating rate 5 °C/min) in an inert atmosphere (argon) to 900 °C and kept at the indicated temperature for 2.5 h. Silica component was removed by the treatment of carbon–silica composite with 15% HF solution or 1 M aqueous-alcohol (1:1 by volume) NaOH solution at 80 °C with mixing on a magnetic stirrer. Carbon product was filtered, washed with ethanol and dried at 100 °C.

For synthesis of mesoporous carbons from acetonitrile the samples of template containing MMS were heated (heating rate 3 °C/min.) in an inert atmosphere (argon) up to 800 °C, then in an argon saturated with vapor of acetonitrile for 3 h, another 1 h they were heated in an inert atmosphere. Silica component was removed via the treatment of carbon–silica composite with 15% HF solution. Carbon product was filtered, washed with ethanol and dried at 100 °C. For the bulk carbonization aqueous solution of sulfuric acid (out of account 0.112 g of H_2SO_4 per 1 g of sucrose) was added to sucrose, then the mixture was stirred and dried at 100 °C. The obtained product was heated in a flow of argon for 2.5 h at 900 °C.

The scheme of matrix syntheses looks as follow:

$$\text{Silica matrix} \xrightarrow[+\text{heattreatment}]{+\text{organicprecursor}} \text{carbon-silica composite}$$
$$\xrightarrow{+\text{HF}} \text{carbon mesoporous material}$$

Characterization

The phase composition of the samples was analyzed using X-ray diffractometer Bruker D8 Advance with monochromated CuK_α-radiation. Adsorption of nitrogen was measured by volumetric method (77 K, up to 1 atm) on the analyzer of porous materials Sorptomatic 1990. Specific surface area S_{BET} was estimated by the BET equation [15]. Mesopore size was determined by BJH and DH [16]. Mesopore size was determined by the adsorption branch in the cases where the ad(de)sorption hysteresis on the isotherms ended in the ultimate strength of the meniscus of liquid adsorbate (nitrogen) to break (at $p/p_o \sim 0{,}45$–$0{,}50$). Micropore size was calculated from Horvath Kavazoe equation [17]. The values of micropore volume were refined with comparative t-plot method [15] for porous materials which containing micro-and mesopores in the one structure. Raman spectroscopy measurements were made on T6400 Jobin–Yvon spectrometer using He–Ne laser with a wavelength of 633 nm.

Results and discussion

As follows from XRD data (Fig. 1), XRD-pattern of carbon material obtained by carbonization of sucrose in matrix

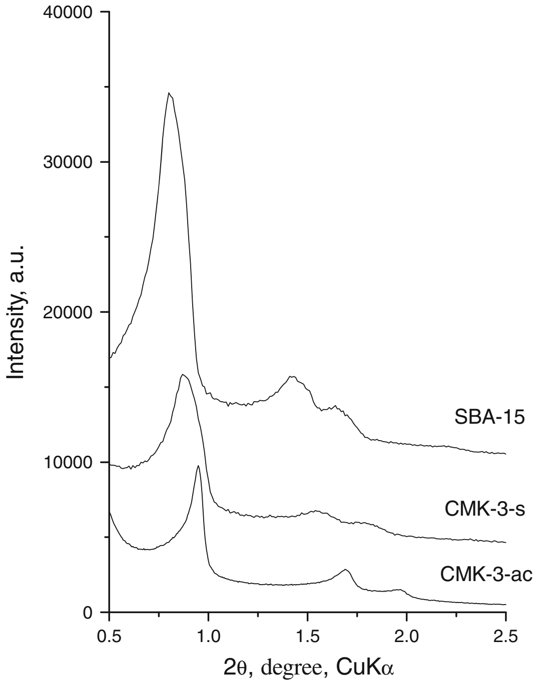

Fig. 1 XRD patterns for SBA-15, CMK-3-s, CMK-3-ac

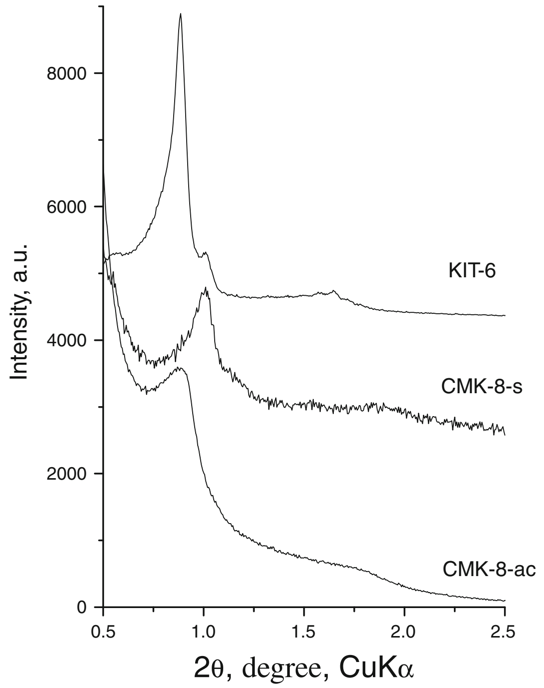

Fig. 2 XRD patterns for KIT-6, CMK-8-s, CMK-8-ac

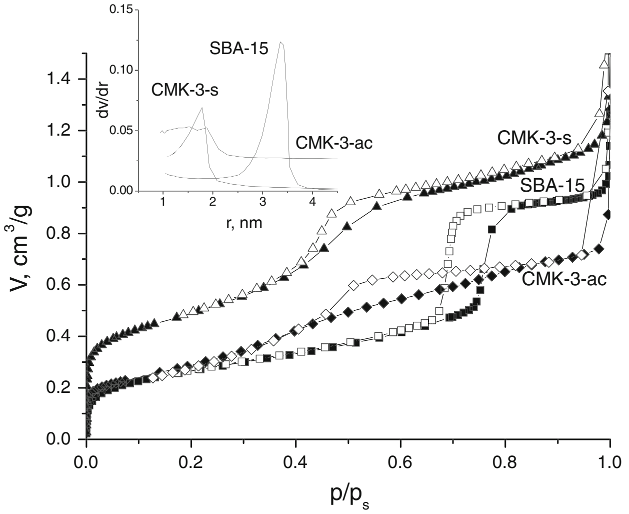

Fig. 3 Nitrogen adsorption isotherms and corresponding pore size distributions for SBA-15, CMK-3-s, CMK-3-ac

SBA-15 (CMK-3-s), is identical with the XRD-pattern of the initial exotemplate (three small angled peaks are characteristic for hexagonal structure).

Carbonization of sucrose in MMS KIT-6 (cubic symmetry Ia $\bar{3}$d) leads to the formation of replica (CMK-8-s) of the initial silica matrix, with three-dimensional organization of carbon particles (as a rods) that are packed in two enantiomeric interpenetrative systems [14]. XRD pattern of CMK-8-s (Fig. 2) contains one well-resolved small angle peak, slightly shifted to region of larger 2θ angles due to compression of the unit cell during the heat treatment of organic-silica composite.

Figure 3 shows nitrogen adsorption isotherms for the carbon replicas CMK-3-s. The porous structure of the samples is characterized by increased level of specific surface area (1120 m^2/g) and pore volume (1.2 cm^3/g) and smaller mesopore size (up to 3.6 nm due to the replication process) than the initial exotemplate SBA-15 (600 m^2/g, 1.0 cm^3/g, and 6.8 nm, respectively).

Obtained carbon materials respond to high ordered uniform mesoporous structures with relatively narrow mesopore size distribution. It can be explained by a high mesopore filling degree of matrix with indicated precursor and the formation of homogeneous (dense) carbon framework in the conditions of two-stage impregnation of the matrix with aqueous solutions of sucrose and sulfuric acid. In addition, filling of mesopore space (voids) is happen as a result. Analysis of nitrogen adsorption isotherms (Fig. 4, Table 1) shows that the synthesized carbon replicas CMK-8-s are characterized by high-specific surface area (1550 m^2/g), pore volume (2.0 cm^3/g), substantial reduction in size (up to 3.8 nm), and some decrease of uniformity of mesopores. It's due to the process of inversion replication of the matrix porous structure. Thus, according to the data of comparative method (*t*-plot), micropore formation or occurrence is not happening ($V_{\mathrm{micro}} = 0.05$ cm^3/g) during dissolution of silica framework of the initial matrix, which indicates its relatively high homogeneity (monolithic).

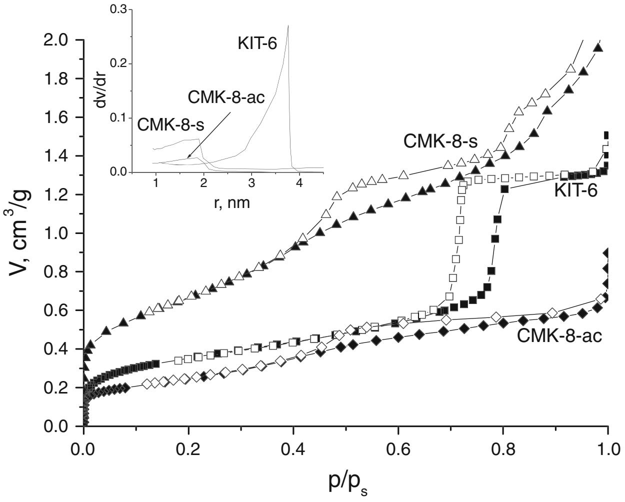

Fig. 4 Nitrogen adsorption isotherms and corresponding pore size distributions for KIT-6, CMK-8-s, CMK-8-ac

The feature of carbonization of investigated precursors in matrix KIT-6 which is characterized by 3-dimensional cubic structure, is increasing of micro- and mesopore free volume comparatively with SBA-15 (V_{micro}—from 0.05 to 0.10 cm^3/g, D_{mezo}—from 6.6 to 7.4 nm, V_{mezo}—from 0.95 to 1.23 cm^3/g) (Table 1) and accordingly their accessibility for adsorption, polymerization, and carbonization of precursor's molecules. In addition, increasing of the volume occupied by the walls of mesopores in the initial matrix KIT-6, comparatively with SBA-15, leads to the corresponding growth of the volume and mesopore specific surface area of the products of carbonization CMK-8-s—$V_{\mathrm{mezo}} = 1.53$ cm^3/g, $S_{\mathrm{mezo}} = 1390$ m^2/g, $S_{\mathrm{BET}} = 1560$ m^2/g. Here D_{mezo} slightly decreases that testifies to the decreasing of density of the filling with indicated precursor of the mesopores of matrix KIT-6.

Bulk carbonization of sucrose in the same experimental conditions leads to the obtaining of compact carbon material with low sorption characteristics, in particular, pore volume (they are micropores) of the obtained sample is 0.09 cm^3/g. So during pyrolysis pores are generated as a result of dehydration of sucrose and subsequent formation of the dense microporous framework from obtained carbon fragments. Carbon mesoporous replicas except such micropores (approximately in the same volume) have mesopores instead of silica walls after the removal of inorganic matrix.

Replication of the porous structure (Fig. 1, 2, Table 1) of the initial exotemplates SBA-15 and KIT-6 takes place in the case of vapor deposition and subsequent carbonization of acetonitrile in the pores of the matrices as well as in the case of matrix carbonization of sucrose. Position of small-angle peaks (particularly, the ratio of squares of sines angle θ), testifies to the presence of, hexagonal and cubic structures, respectively.

The feature of replication of the porous structure of SBA-15 in the process of carbonization of acetonitrile (Fig. 1, Table 1) comparatively with sucrose, is significant decrease of micropore volume and ordering ($V_{\mathrm{micro}} = 0.05$ cm^3/g, slight maximum at $D_{\mathrm{micro}} = 0.62$ nm). It's probably because of unfavorable conditions for adsorption (accumulation) and subsequent carbonization of the molecules of acetonitrile in relatively large mesopores of SBA-15. Corresponding replication of KIT-6 deteriorates in the presence of the molecules of acetonitrile (Figs. 2, 4, Table 1). Decreasing of micro- and mesopore volume in the sample CMK-8-ac comparatively with CMK-3-ac may be associated with increasing of the mesopore size in KIT-6 and uneven pore filling of silica exotemplate.

The product of pyrolysis of acetonitrile (800 °C) in SBA-15 (sample CMK-3-ac) contains graphite domains unlike the sample CMK-3-s synthesized by matrix carbonization of sucrose. It's confirmed by the presence on XRD pattern of typical for graphite peak at $2\theta = 25.4°$, (interplanar distance is 3.51 Å), while sample is spatially ordered, as it is verified by intense, well separated small angle peaks (Fig. 5).

Graphite nature of the obtained carbon material CMK-3-ac was confirmed by Raman spectroscopy (Fig. 6): intensity of the band (G band) which corresponds to the bond of the carbon atoms in sp^2-hybrid state (1590 cm^{-1}) is about twice higher than for porous carbon from sucrose (CMK-3-s). D band (1340 cm^{-1}) indicates to the presence of disordered amorphous (non-graphitic) carbon material.

Table 1 Adsorption-structural characteristics (N_2, 77 K) of carbon mesoporous materials

Sample	a_0 (nm)	Wall thickness (nm)	V_{meso} (cm^3/g)	D_{meso} (nm)	S_{meso} (m^2/g)	V_{micro} (cm^3/g)	D_{micro} (nm)	S_{BET} (m^2/g)	V_{Σ} (cm^3/g)
SBA-15	10.97	4.25	0.95	6.72	440	0.05	1.16	620	1.00
CMK-3-s	10.09	6.55	1.10	3.54	940	0.12	0.48	1120	1.22
CMK-3-ac	9.34	6.44	0.70	2.90	515	0.05	0.61	670	0.75
KIT-6	24.45	4.17	1.23	7.48	470	0.10	1.04	830	1.33
CMK-8-s	21.64	5.30	1.53	3.40	1390	0.05	0.55	1560	1.93
CMK-8-ac	24.44	6.33	0.55	3.14	465	0.05	0.54	575	0.60

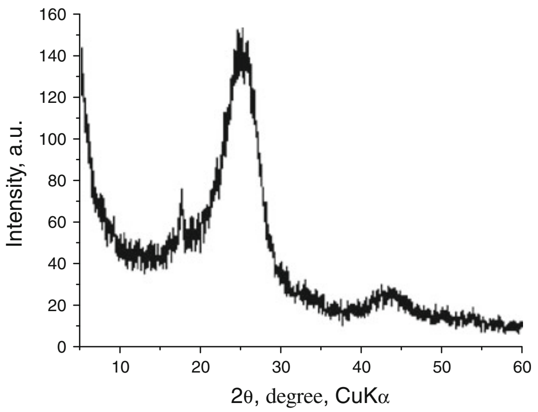

Fig. 5 XRD pattern for CMK-3-ac

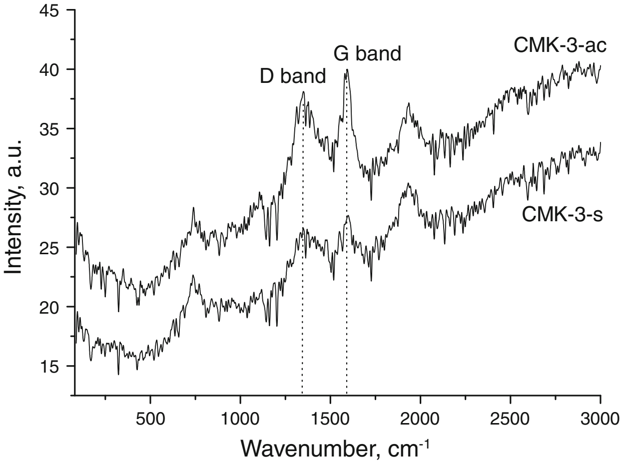

Fig. 6 Raman spectra for the carbon materials obtained by matrix carbonization of sucrose (CMK-3-s) and CVD of acetonitrile (CMK-3-ac)

There are obviously spatial limits of the processes of the formation of graphite like structures during the implementation of carbonization in the pores of the matrix, prefilled with organic precursors, particularly, with sucrose. It's displayed in the fact that the temperature of pyrolysis of acetonitrile and carbonization of sucrose in SBA-15 were 800 and 900 °C, respectively. Consistent, gradual filling of adsorption space with the molecules of acetonitrile takes place in the process of pyrolysis in the gas phase. It probably significantly reduces or even eliminates spatial restrictions during adsorption, pore filling, as well as in the process of growth of graphite structures, especially during the initial stage of synthesis, when the pores are not filled with carbon yet. In addition, sorption of acetonitrile may also occur on the outer surface, where the processes of graphitization are unlimited too. However, since the outer surface of SBA-15 is very small compared with the mesopore surface area (about 5%, it is 30 m^2/g), than it is likely that the main factors that cause, "allow" the formation of graphite structures (in the process of obtaining carbon materials by CVD method), are the large pore size of the matrix (about 7 nm) and the nature of adsorption of organic precursors (gradual pore filling).

Spatially ordered samples are generated in the result of pyrolysis of acetonitrile (CVD-method) in template containing MMS (SBA-15 and KIT-6). These materials are replicas of the initial matrices, they have relatively low absorption characteristics (probably due to large pore of the matrix, which can lead to their inhomogeneous filling with organic matter) and partially graphitized framework (because obviously absence of steric constraints for the formation and growth of graphite structures in relatively large (6.5–7.5 nm) pores on the surface of MMS).

Carbon mesoporous materials as activated carbon, have so-called turbostratic structure, which is characterized by the absence of 3-dimensional ordering of graphite layers. Flat 2-dimensional hexagonal grids in the carbon materials can be placed in parallel and equal, though different from graphite, distances from one another, but in a different way back to the normal axis [18].

Carbon atoms are mainly in the sp^2-hybrid state in some way oriented periodic graphite structures, the distance between the layers is 3.35 Å [18]. Structure and chemical texture differs from graphite in turbostratic (disordered layered) state, which is characterized for amorphous carbon materials. Specifically, there is no strict periodicity of elementary layers, distances between them are different and fluctuate around the average value of 3.44 Å (unlike equidistance structure of graphite, where flat layers are placed one another at equal distances 3.35 Å). According to work [18], carbon atoms do not occupy ideal positions in the networks of turbostratic structure, and shifted relative to the plane grid within 0.14–0.17 Å. This bias can be explained by the fact that in the turbostratic structure carbon atoms are in different valence state than in sp^2-hybridization which is characterized for graphite. Here the part of carbon atoms, especially peripheral is in sp-hybrid state.

Conclusions

Carbon mesoporous materials with uniform porous structure were obtained using the method of matrix synthesis (SBA-15 and KIT-6 were the hard inorganic templates; sucrose and acetonitrile were the organic precursors). Mesoporous carbon CMK-8-s which was synthesized in the pores of KIT-6 had higher adsorption characteristics than CMK-3-s which was obtained in the matrix SBA-15. It's due to the features of three-dimensional cubic structure of KIT-6, larger pore volume and framework's wall thickness. Partially graphitized spatially well-organized carbon materials were formed in the result of pyrolysis of acetonitrile in silica matrices SBA-15 and KIT-6. It's connected with the absence of considerable spatial limitations for growth of graphite structures on the initial stage of the synthesis when the pores of the matrix are not filled up with the organic precursor. Obtained carbon materials can find their application as electrode materials because of their graphite-like structure which was received during comparatively low-temperature synthesis. Product of bulk carbonization of sucrose is compact carbon microporous framework with low sorption characteristics (micropore volume is 0.09 cm^3/g). It's concerned with the processes of dehydratation of sucrose (in the presence of sulfuric acid) and subsequent formation of the dense microporous framework from obtained carbon fragments.

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