General and Inorganic Chemistry

Physicochemical features of the formation of siliceous porous mesophases

3.* Conditions of formation and properties of mesoporous silica

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Data on the optimization of alkalinity of the reaction mixture and the reaction temperature in the formation of the siliceous porous mesophase material C_{16}—SiO_2—MMM are presented. A criterion for the evaluation of the level of structure optimization for mesoporous mesophases is formulated. Measurements of the texture parameters of the materials treated in acidic media led to the assumption that the walls in the pure siliceous C_{16}—SiO_2—MMM system consist of separate blocks, which, apparently, are not bound completely to one another by chemical interactions.

Key words: mesophase mesoporous materials, structural and textural parameters, MAS ^{29}Si NMR spectroscopy.

Previously, we described[1,2] the main stages of formation of silicate mesoporous mesophase materials (C_n—SiO_2—MMM) of the MCM-41 type[3,4] prepared by homogeneous precipitation of soluble forms of SiO_2 in the presence of ionic surfactants (alkyltrimethylammonium cations $C_nH_{2n+1}TMA^+$, where n = 12, 14, 16, and 18 is the number of carbon atoms in the alkyl chain).

Here we studied the influence of the alkali concentration in the initial mixture and the temperature of the synthesis on the formation of the mesoporous mesophase material C_{16}—SiO_2—MMM. Pure SiO_2 in the presence of a cationic surfactant ($C_{16}H_{33}N(CH_3)_3{}^+Br^-$) was used in the synthesis aimed at optimizing reaction parameters and analyzing the main characteristics of the mesophase silicate material.

Experimental

The initial forms of the C_{16}—SiO_2—MMM samples were synthesized[1—7] by hydrothermal treatment (HTT) of reaction mixtures with the following molar compositions: $SiO_2 \cdot 0.25\ C_{16}H_{33}N(CH_3)_3Br \cdot x\ NaOH \cdot 150\ H_2O$, with x (OH : SiO_2) varying from 0.1 to 0.5. The synthesis was carried out for 40—50 h under static conditions in the temperature range of 20—165 °C and was followed by filtration, washing, and drying (at 30—40 °C). Sodium silicate was used as the source of SiO_2. The required concentration of NaOH was

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attained by neutralizing the mixture with a calculated amount of H_2SO_4.

The removal of the surfactant by heat treatment and the calculation of the compositions of the initial samples as $[C_{16}H_{33}NMe_3^+ : SiO_2]$ = N : Si molar ratios were carried out as described previously.[2]

Extraction of the surfactant from a sample included hydrothermal treatment of a suspension of the sample in aqueous acetic acid under static conditions for 4—23 h at 80—150 °C and subsequent filtration, washing, drying, and oxidative heat treatment (as described in Ref. 2). The amount of acetic acid needed for extraction was found as the molar ratio $[HOAc : C_{16}H_{33}NMe_3^+] = 5$, depending on the surfactant concentration in the sample. The pH of the mixtures was ~6.

The X-ray diffraction patterns were recorded using (Cu-Kα) radiation as described previously.[2] The relative intensity of the [100] reflection was calculated as the ratio of its integral intensity (equal to its height multiplied by the half-width) to the integral intensity of the [100] reflection of the reference sample determined under identical conditions. The C_{16}—SiO_2—MMM sample characterized by the greatest integral intensity of all the materials studied was used as the reference sample. The as-synthesized materials were analyzed using an as-synthesized reference sample, while calcined forms were studied with respect to the calcined form of the reference sample.

Some experiments were carried out using a high-resolution precision diffractometer at the Siberian Center of Synchrotron Radiation. High instrumental resolution of the diffractometer was provided by using a Ge(111) plane perfect crystal analyzer, which was adjusted for a diffracted beam, as well as a plane parallel collimator, which restricts the azimuth divergence of the diffracted beam to 5 mrad. As a result, the instrumental half-width of reflections did not exceed 0.04° 2θ in the low-angle region of 1—7° 2θ.

MAS ^{29}Si NMR spectra were recorded as described previously.[2]

Adsorption characteristics were measured for calcined samples using a previously reported procedure.[2] The texture parameters of mesophases were calculated from recorded nitrogen adsorption isotherms using a known method.[8]

Results and Discussion

Intensity and half-width of X-ray reflections. As in the previous studies,[9—11] the general X-ray diffraction patterns of all the materials studied exhibit up to four reflections in the low-angle region of 2—7° 2θ. The reflections are well assigned as [*hk0*] in the approximation of *p6mm* hexagonal symmetry. The variation of the relative intensity of the [100] reflection (I_{100}) *vs.* the synthesis temperature (T_{HTT}) for reaction mixtures with different initial concentrations of the alkali for all the C_{16}—SiO_2—MMM systems studied are shown in Fig. 1. It can be seen that an increase in T_{HTT} in the 20—165 °C temperature range for any fixed OH : SiO_2 ratio does not result in substantial changes in I_{100}, except for the mixture with the lowest alkali content, OH : SiO_2 = 0.1 (see Fig. 1, curve *8*). Meanwhile, the change in the OH : SiO_2 ratio at any constant T_{HTT} crucially affects the I_{100} value, the highest intensity of the [100] reflection being observed for C_{16}—SiO_2—MMM prepared from reaction mixtures with OH : SiO_2 = 0.2 at T_{HTT} = 100—140 °C.

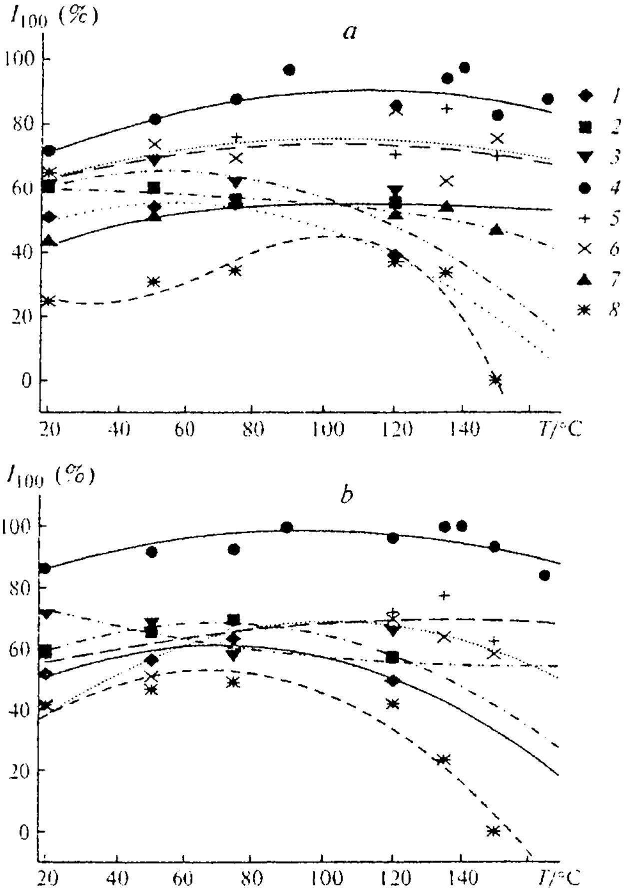

Fig. 1. Relative intensities of the [100] reflection (*I*) in the X-ray diffraction patterns of the initial (*a*) and calcined (*b*) samples of C_{16}—SiO_2—MMM depending on the temperature of the synthesis (hydrothermal treatment) for reaction mixtures with different alkali concentrations. The initial OH : SiO_2 molar ratio was 0.5 (*1*); 0.4 (*2*); 0.3 (*3*); 0.2 (*4*); 0.175 (*5*); 0.15 (*6*); 0.125 (*7*); and 0.1 (*8*).

The dependence of I_{100} on alkalinity of the initial reaction mixture, OH : SiO_2, for isothermal conditions of the synthesis is presented in Fig. 2, *a*. A sharp maximum of the intensity of the [100] reflection is noted in the region of OH : SiO_2 = 0.2—0.25. These initial reaction mixtures with the optimum alkalinity are nearly pH-neutral (pH ~ 8), which fully confirms earlier observations.[7] Thus, the C_{16}—SiO_2—MMM product obtained from these mixtures contains the highest concentration of the material with hexagonal packing. It can be seen in Fig. 2, *b* that the minimum half-width of the [100] reflection, equal to 0.18—0.22° 2θ in the X-ray diffraction patterns based on (Cu-Kα) radiation, corresponds to the greatest content of material with this type of structure in the solid product.

Lattice parameter and texture characteristics. As was to be expected in view of the data published previously,[12—15] an increase in the temperature of synthesis should result in a larger lattice parameter for

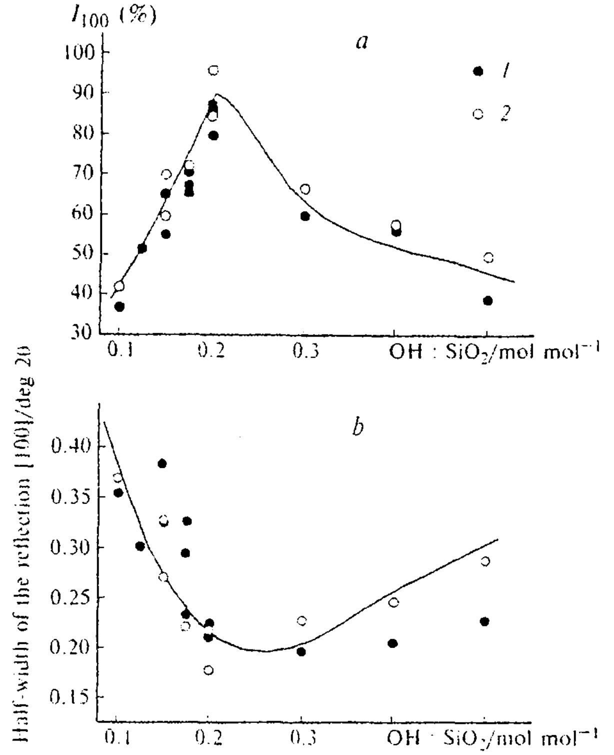

Fig. 2. Relative intensity (*a*) and half-width (*b*) of the [100] reflection in the general X-ray diffraction patterns of the initial (*1*) and calcined (*2*) C_{16}—SiO_2—MMM samples *vs.* the OH : SiO_2 molar ratio in the initial reaction mixtures for hydrothermal treatment at 120 °C.

C_{16}—SiO_2—MMM (a_0), which was assumed[2] to be a consequence of the thermal expansion of the hydrocarbon fraction of the mesophase. For hexagonal packing, it is known[8] that $a_0 = d_c + h_w$, where d_c is the mesopore diameter, and h_w is the thickness of the wall formed by an inorganic material (silicate, in this particular case). Evidently, an increase in a_0 upon the above-mentioned thermal expansion should be mainly due to an increase in the first addend, *i.e.*, d_c.

Indeed (Fig. 3, *a*), in the case of reaction mixtures with optimum alkalinity, an increase in the synthesis temperature results in a monotonic increase in a_0. The calculation of the corresponding texture parameters according to a known method[8] using data on nitrogen adsorption shows (see Fig. 3, *c*) that an increase in the temperature of the synthesis from 20 to 165 °C (for a constant time equal to 40—44 h) leads to an increase in d_c by a factor of about 1.5. The wall thickness h_w remains virtually constant ($h_w \approx 0.75$—0.8 nm) for $T_{HTT} \le 140$ °C and rapidly grows for $T_{HTT} > 140$ °C. This fact is not related directly to the thermal expansion of the hydrocarbon fraction of the mesophase. The wall thickening observed at high temperatures is due most likely to secondary restructurization processes in C_{16}—SiO_2—MMM, proceeding, for example, *via* the hydrolysis mechanism described in our previous publication.[2]

The composition of the silicate mesophase can be formally described[2] as $\{(\alpha)[NR_4]^+[OSi(OH)_3]^-, (1\text{-}\alpha)[Si(OH)_4]\}$. This formula includes both ionized (bound to the surfactant cation by electrostatic forces) and electrically neutral SiO_2 forms. This description corresponds to polysilicate anions having a single negative charge. An increase in the synthesis temperature induces hydrolytic decomposition and, hence, results in a lower N : Si ratio in C_{16}—SiO_2—MMM (*i.e*, in a lower concentration of the surfactant cations in the material, Fig. 4, *a*). This should be accompanied by an increase in the proportion of electrically neutral forms of silica, which ensures the possibility of condensation of the silicate tetrahedra. Indeed (see Fig. 4, *a*), the Q_4 : Q_3 ratio, *i.e.*, the ratio of integral intensities of the MAS ^{29}Si NMR signals due to Si atoms with 4 and 3 silicon atoms in the second coordination sphere, respectively,[2] markedly increases with an increase in the synthesis temperature.

The deviation of alkalinity of the initial reaction mixture (OH : SiO_2) from the optimum value for isothermal conditions of synthesis results in a substantial decrease in the lattice parameter a_0 (see Fig. 3, *b*). Calculation of the textural contributions of the lattice parameter shows (see Fig. 3, *d*) that, whereas the wall thickness h_w decreases monotonically with increase in the alkali concentration, the d_c value passes through a maximum located in the region of the optimum alkalinity of the reaction mixture (OH : $SiO_2 \approx 0.20$—0.25). An increase in the OH : SiO_2 molar ratio in the reaction mixture means evidently an increase in the concentration of surfactant cations linked to ionized forms of SiO_2 in the initial C_{16}—SiO_2—MMM samples. Conversely, a decrease in the alkalinity should result in a higher proportion of the electrically neutral forms of silica, which are not linked to the surfactant cations. Indeed (see Fig. 4, *b*), an increase in the OH : SiO_2 ratio leads to an increase in the concentration of the surfactant cations in C_{16}—SiO_2—MMM (an increase in the N : Si ratio) and, simultaneously, to a decrease in the degree of condensation of the silicate tetrahedra (a decrease in the Q_4 : Q_3 ratio). It is significant that the above-described changes in the C_{16}—SiO_2—MMM system are monotonic in the range of OH : SiO_2 ratios studied and do not reflect the presence of any specific (or optimal) regions of alkalinity. Meanwhile, the decrease in the OH : SiO_2 ratio from 0.20—0.25 to 0.1 (*i.e.*, from optimum alkalinity toward lower OH : SiO_2 values, see Fig. 3, *d*) results, on the one hand, in a greater contribution of electrically neutral SiO_2 forms not bound to surfactant cations and, on the other hand, in a higher degree of compaction of the silicate particles during the formation of C_{16}—SiO_2—MMM (see Fig. 4, *b*). As a consequence, the average wall thickness h_w increases (see Fig. 3, *d*) and the average mesopore diameter d_c decreases.

When the OH : SiO_2 ratio increases (from the optimum value of 0.20—0.25 to higher values), the propor-

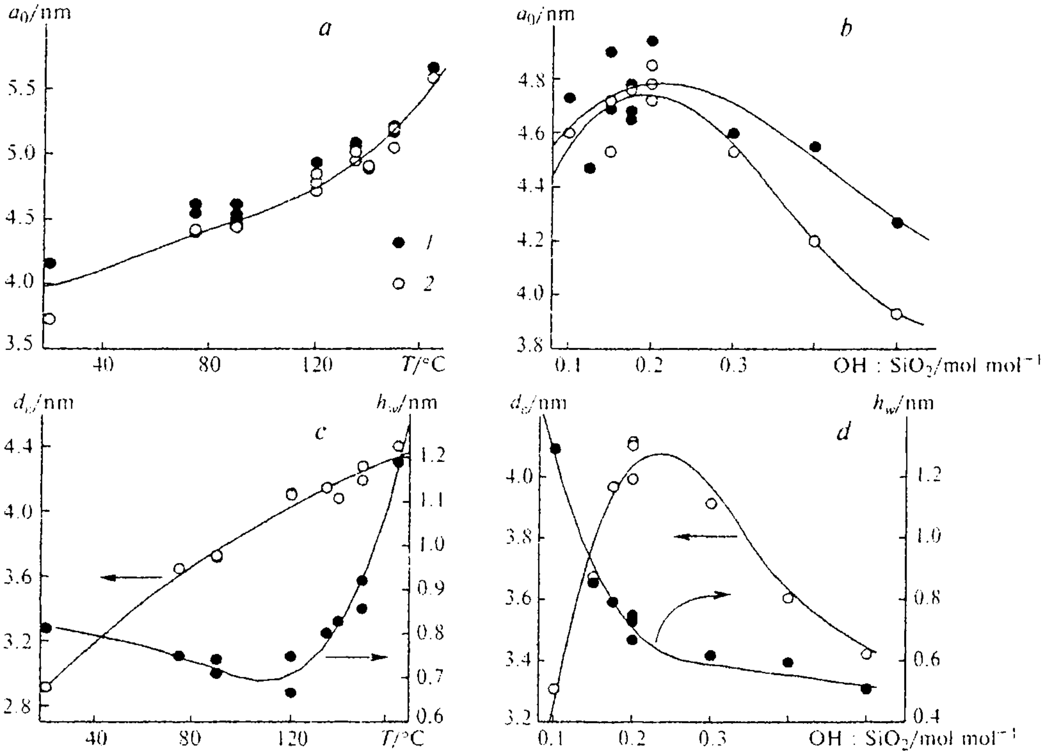

Fig. 3. Lattice parameter a_0 (*a, b*), mesopore diameter d_p, and wall thickness h_w (*c, d*) in the C_{16}—SiO_2—MMM systems *vs.* temperature of the synthesis for reaction mixtures with an initial OH : SiO_2 molar ratio of 0.2 (*a, c*) and *vs.* the OH : SiO_2 molar ratio for a hydrothermal treatment temperature of 120 °C (*b, d*). (*1*) Initial and (*2*) calcined C_{16}—SiO_2—MMM samples.

tion of ionized forms of SiO_2 in the system increases; therefore, the average wall thickness h_w does not change significantly (or somewhat decreases, see Fig. 3, *d*) in this region of alkalinity. However, despite the simultaneous increase in the concentration of the surfactant cations in the material (see Fig. 4, *b*), the average mesopore diameter also substantially decreases with an increase in the OH : SiO_2 ratio in this region (see Fig. 3, *d*). Apparently, unlike the conditions with relatively low alkalinity, in this case, polycondensation processes in the silicate wall during the synthesis are complicated by a high degree of ionization of SiO_2 (see Fig. 4, *b*). As long as such a C_{16}—SiO_2—MMM system occurs in the initial state and contains surfactant cations, the low degree of condensation of the wall material does not manifest itself anyhow. Investigation of calcined materials showed that C_{16}—SiO_2—MMM samples prepared under highly alkaline conditions are characterized by a substantial decrease in the lattice parameter (see Fig. 3, *b*), due to additional condensation of the wall material. Apparently, it is this decrease that accounts for the smaller mesopore diameters for C_{16}—SiO_2—MMM samples synthesized under highly alkaline conditions.

Thus, there exists a certain optimum region of the alkali concentration for the formation of C_{16}—SiO_2—MMM, which ensures the maximum concentration of the material with a hexagonal packing in the products of a synthesis (see Fig. 2) carried out at 100—140 °C (see Fig. 1). The lattice parameter for such material virtually does not change upon removal of the surfactant cations by oxidative heat treatment (see Fig. 3, *a, b*); it corresponds to the maximum mesopore diameter d_p and the minimum wall thickness h_w (see Fig. 3, *d*). Since the optimum structure corresponds to the atomic ratio N : Si ≈ 0.15—0.17 (see Fig. 4), it can be suggested that silicate anions of a particular type are involved in its formation. Specifically, if these are single-charged anions, they incorporate six Si atoms. The degree of polycondensation of the silicate tetrahedra in the wall of the C_{16}—SiO_2—MMM structure corresponds to $Q_4 : Q_3 \approx 1.7\pm0.1$ (for the initial form of the material before calcination, see Fig. 4), which is close to published values.[5]

The concept of "ideal" structure of a mesoporous material and criteria of closeness to this state for the synthesis products. According to published data,[9] the structure of C_{16}—SiO_2—MMM contains a system of hexagonally packed mesopores with either cylindrical or hexagonal configurations. If investigation of the product shows that cross sections of all mesopores are equal and do not vary along the mesopore length, the structure of this material can be regarded ideal. The closer the structure characteristics of the synthesis product to those

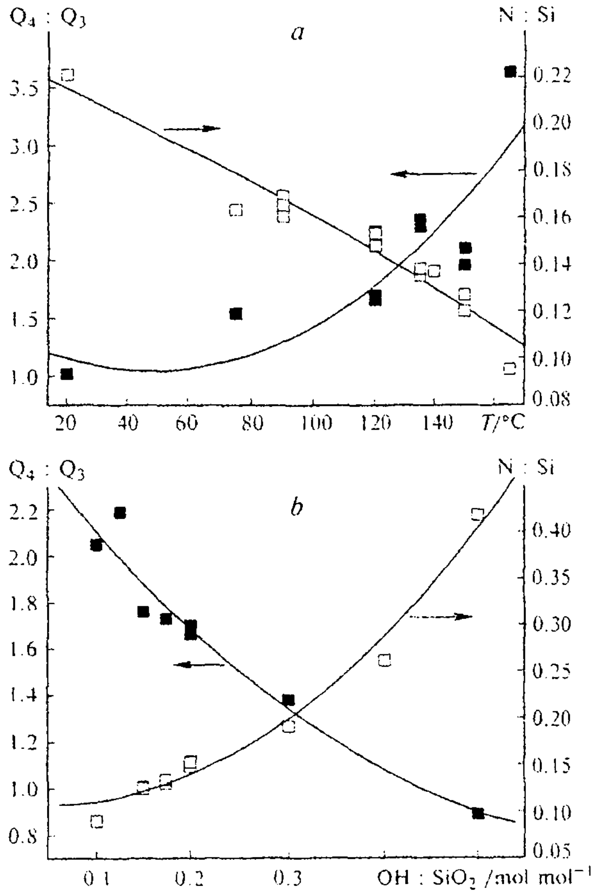

Fig. 4. $Q_4 : Q_3$ ratio and the N : Si atomic ratio in the initial forms of C_{16}—SiO_2—MMM *vs.* temperature of the synthesis for reaction mixtures with the initial molar ratio OH : SiO_2 = 0.2 (*a*) and *vs.* the OH : SiO_2 molar ratio for a hydrothermal treatment temperature of 120 °C (*b*): (*1*) adsorption, (*2*) desorption.

of the perfect structure, the higher the degree of structural organization in this sample. Several criteria can be formulated in order to determine the degree to which the structure of the material prepared resembles the ideal structure.

First, a high degree of structural organization means that the lattice parameter a_0 is constant; for mesophase systems, this, in turn, implies that the half-width of reflections observed in X-ray diffraction patterns is close to the experimental error. Since the reflection half-width is mainly determined by the angle of divergence of the initial beam, it should be 0.03—0.04° 2θ for X-ray diffraction patterns recorded using synchrotron radiation.

Second, the strictly constant diameter of all mesopores along the full length of the cylinder means that the adsorption and desorption branches of the isotherm for low-temperature nitrogen adsorption coincide, at least, for pore sizes not exceeding 4.5 nm.

Third, the absence of diameter spread between the mesopores (*i.e.*, the strictly constant mesopore diameter throughout the system) indicates that the range of variation of the relative pressure $\Delta(p/p_0)$ in which the capil-

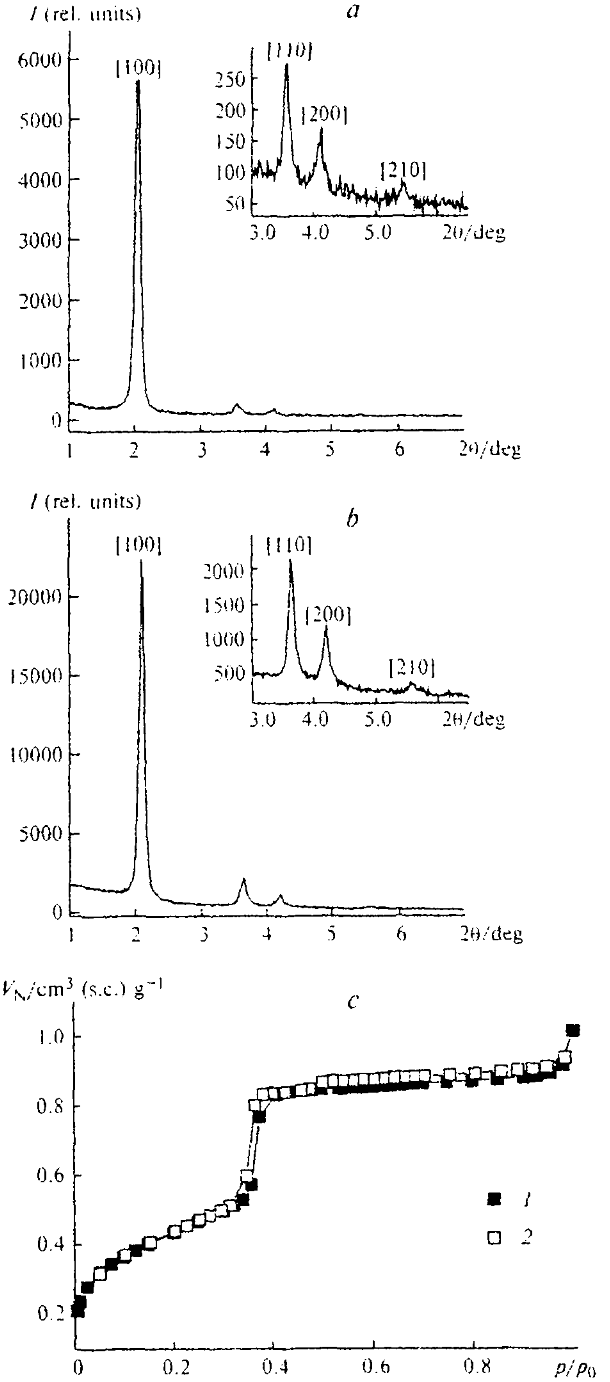

Fig. 5. X-ray diffraction patterns of the initial (*a*) and calcined (*b*) forms of the optimal C_{16}—SiO_2—MMM sample obtained using synchrotron radiation and isotherm of nitrogen adsorption on this system in the calcined form (*c*) (s.c. — standard conditions). Details of the XRD pattern for the angle range of 3—6.5° 2θ are shown in the insets.

lary condensation of nitrogen during the low-temperature adsorption occurs is very narrow and that its measurement is determined only by the minimum step of variation of p/p_0 in the adsorption measurements.

Let us consider the C_{16}—SiO_2—MMM system under study in terms of the criteria listed above. It can be seen from Fig. 5, *a* and *b* that the reflections present in the X-ray diffraction patterns of this sample in both the initial and calcined forms are symmetrical (the line contour is close to the Lorentzian curve) and the half-width of the [100] reflection is 0.07° 2θ, which is close to the instrumental broadening (0.04° 2θ) for this region of angles. The adsorption and desorption branches of the isotherm of nitrogen adsorption by the calcined sample virtually coincide (see Fig. 5, *c*) and the range of relative pressure in which capillary condensation of nitrogen takes place is ~0.01 p/p_0 units, which is close to the minimum possible experimental step of variation of the relative pressure during adsorption measurements. Thus, the optimum conditions of the formation of C_{16}—SiO_2—MMM found in this study ensure the formation of a structure similar in characteristics to a material with ideal hexagonal packing of mesopores.

Characteristic features of the structure of the silicate wall in C_{16}—SiO_2—MMM. It is known from a number of publications (see, for example Refs. 16—19) that the C_{16}—SiO_2—MMM structure is highly thermally stable; it does not change upon removal of the surfactant cations by oxidative heat treatment but is destroyed upon water adsorption at temperatures close to ~20 °C. This destruction has been attributed[4,18,19] to the hydrophilicity of the silicate mesophase. Hence, it has been proposed to enhance the hydrophobic properties of this material by modifying the surface of the silicate walls by various organosilicon compounds, in order to increase the stability of the calcined C_{16}—SiO_2—MMM form. However, only in a few papers, did the authors pay attention to the structural properties of the silicate mesoporous material under consideration. Therefore, it could be suggested that a low hydrolytic stability is peculiar only to materials with defective structure.

Now we consider the state of the wall in the initial form of the optimal C_{16}—SiO_2—MMM. To this end, we analyzed in this study the variation of the structure-textural parameters of C_{16}—SiO_2—MMM following the gradual extraction of the surfactant cations by acid treatment.

Hydrolysis (see above and Fig. 4) results in a decrease in the surfactant concentration in the material even at the HTT stage. In the case of extraction with an acid, it is reasonable to expect that equilibrium of hydrolysis would be shifted to the right and the surfactant cations would be removed more fully from the initial sample even when the material is treated at a lower temperature and for a shorter period than during synthesis. Indeed (Table 1), acid treatment results in a decrease in the (N : Si) atomic ratio in all the C_{16}—SiO_2—MMM samples synthesized at different temperatures. The removal of the surfactant is not accompanied by a change in the lattice parameter a_0 but decreases the relative intensity of the [100] reflection. It is clear that those fragments of the C_{16}—SiO_2—MMM structure from which the surfactant cations have been extracted are destroyed and, therefore, they cannot be observed in the X-ray diffraction patterns. For the rest of the structure, which has not lost the surfactant cations during the extraction, the lattice parameter remains unchanged. Therefore, the texture characteristics of C_{16}—SiO_2—MMM are expected to change upon extraction.

Measurements of the texture parameters of the extracted samples (see Table 1) show that the degree of removal of the surfactant can be increased by increasing the temperature of extraction to 120 °C, and the interior surface area and the specific volume of the mesopores can thus be diminished. Simultaneously, the outer surface area of the samples markedly increases. On further increase in the extraction temperature, the outer surface of the mesoporous material also decreases.

Table 1. Change in the structural-textural parameters of C_{16}—SiO_2—MMM prepared at the optimum alkalinity of the initial mixture after extraction treatment

T_{synth} /°C	Extraction conditions T/°C	t/h	The N : Si atomic ratio	I_{100} (%)	a /nm	S_{sp}/m^2 g^{-1} of mesopores	outer	V_{sp} /cm^3 g^{-1}
90	Without extraction		0.165	>95	4.5	907	130	0.775
	80	4	0.078	85—90	4.5	477	428	0.460
	100	4	0.054	50—60	4.5	311	493	0.330
	120	4	0.034	30—40	4.5	37	598	0.083
	140	4	0.023	<10	?	~0	217	~0
135	Without extraction		0.138	100	4.9	930	45	0.796
	120	23	0.058	50—60	4.9	302	200	0.242
140	Without extraction		0.137	100	4.9	848	63	0.762
	100	4	0.060	50—60	4.9	446	367	0.502
150	Without extraction		0.125	90	5.1	865	48	0.757
	120	23	0.058	40—50	5.0	233	243	0.202

The conditions used for the extraction treatment were milder than the synthesis conditions. Therefore, in the mixtures prepared at about neutral pH, the state of SiO_2 in the material of the walls has hardly changed after extraction. The changes in the texture parameters of C_{16}—SiO_2—MMM observed upon extraction of the surfactant (see Table 1) can be accounted for only by specific features of the structure of the silicate wall. Indeed, destruction of the hexagonal packing of mesopores should, evidently, be accompanied by a decrease in the relative intensity of the [100] reflection and by a decrease in the specific surface area and volume of the mesopores. The texture of the material formed after extraction would fully reproduce the structure of the silicate wall in the initial C_{16}—SiO_2—MMM form. As the initial form is destroyed during extraction, the outer surface substantially increases; therefore, the destroyed material consists apparently of silicate blocks whose number increases as the initial hexagonal packing collapses. Owing to the collapse, the outer surface increases. The destruction of the initial structure described here is possible only in the case where the silicate wall in the initial C_{16}—SiO_2—MMM sample is constructed from blocks not linked to one another by chemical bonds.

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