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Physicochemical features of the formation of siliceous porous mesophases
4.* Effect of duration and temperature of the hydrothermal treatment on the structural and textural properties

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The results of investigation of mesoporous mesophase materials C12—SiO_2—MMM and C16—SiO_2—MMM prepared at the optimized composition of the reaction mixture and different durations of hydrothermal treatment (HTT) at 120 °C and 140 °C are presented. Hydrothermal treatment at 120 °C influences slightly the specific surface area and the volume of the mesopores but gives a more ordered structure. Prolonged HTT at 140 °C results in irreversible structure degradation. The samples obtained with the optimal HTT duration are characterized by the minimum width of X-ray reflections, the maximum surface and volume of mesopores, and the minimum external surface.

Key words: mesoporous mesophase materials, structural and textural parameters, optimization of synthesis conditions.

Previously,[1—3] we established the main stages, mechanisms, and parameters of the reaction medium stipulating the formation of highly ordered silicate mesoporous mesophase materials of the MCM-41 type,[4—7] prepared by homogeneous precipitation of soluble forms of SiO_2 at ~20 °C in the presence of ionic surfactants (alkyltrimethylammonium cations C_nTMA^+, where n = 12—18 is the number of C atoms in the alkyl chain) followed by hydrothermal treatment (HTT) at elevated temperatures. The criteria for an "ideal" structure organization were formulated; they include the presence in the X-ray diffraction patterns of at least four reflections with a half-width close to the experimental error of measurements, a narrow range corresponding to the mesopore filling in the corresponding adsorption isotherms, and the minimum "external" surface (A_{ext}) on which adsorption still continues after the mesopores in the mesophase bulk have been filled.[1] For an optimized composition of the initial reaction medium, the primary ordered mesophase is formed even at the stage of interaction between the components at ~20 °C. Hydrothermal treatment of the primary mesophase is accompanied by enhancement of the structural ordering. Irreversible structure degradation caused by hydrolysis of the surfactant—SiO_2 ionic bond is also possible at this stage. The optimal temperature of HTT is 100—140 °C. At lower

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temperatures, the rate of the ordering processes is too low, while at higher temperatures, the processes resulting in mesophase disorganization become too fast.

This work is a systematic study of the silicate mesoporous mesophase materials (MMM) synthesized in the presence of C_nTMA^+ (n = 12 and 16) at an optimized composition of the reaction mixture.

Experimental

Synthesis of MMM was performed using the optimum compositions of the initial reaction mixture, established previously,[3] which corresponds to the following molar ratios of the components: SiO_2 : 0.2 $C_nH_{2n+1}NMe_3Br$: 0.2 NaOH : 50 H_2O and at pH 8.0—8.5. Sodium silicate was used as the source of SiO_2. The general scheme of the synthesis was similar to that reported previously.[1–3] HTT was carried out for 40—400 h at 120±5 °C or at 140±5 °C and was followed by filtration, washing, preliminary drying at 30—40 °C, further drying at 120 °C, and calcination in an air stream at 550—580 °C.

The samples synthesized in the presence of surfactants with a length of the hydrocarbon chain in the molecule of n = 12 were designated as series C12, those prepared with n = 16 were called series C16. The sample designations used below include the number of the series and the temperature and time of HTT, for example, C16-120-40 implies a sample of the C16 series, which was subjected to the HTT at 120±5 °C for 40 h.

Investigation methods. X-Ray diffraction experiments were performed on a high-resolution precision diffractometer at the Siberian Center of Synchrotron Radiation with the instrumental broadening of the ≤0.04° 2θ reflections in the 1—7° 2θ range. These measurements were used to calculate the parameter a_0 of the hexagonal lattice of the MMM and the full-width half-maximum (FWHM) of the first reflection (001). The a_0 values were averaged using the results of calculations for the first four peaks in the X-ray diffraction pattern.

Adsorption isotherms were measured on an ASAP-2400 Micromeritics bulk adsorption setup using the standard procedure. From adsorption isotherms, the mesopore volume (V_{me}), the internal surface area of mesopores (A_{me}), and the external surface area of the mesoporous blocks (A_{ext}) were determined by the comparison method (see Refs. 2, 3).

The mesopore size (d_{me}) and the thickness (h_w) of the wall between them were calculated in terms of the texture approaches described previously.[1–3] A simulation of the electron density distribution in the inorganic mesophase[8] showed that the pores are nearly hexagonal (the honeycomb model). Within the framework of this model, the equations for calculation[1–3] can be written as follows

$$d_{me} = a_0\sqrt{\varepsilon_{me}},$$
$$h_w = a_0 - d_{me} = a_0(1 - \sqrt{\varepsilon_{me}}), \quad (1)$$

where a_0 is the hexagonal lattice parameter, determined from X-ray diffraction data, ε_{me} is the porosity of the mesoporous phase, which can be calculated from the formula

$$\varepsilon_{me} = \frac{\rho V_{me}}{\rho V_{me} + 1}. \quad (2)$$

Here, ρ is the true density of the inorganic phase, which was taken to be 2.2 $cm^3\ g^{-1}$, V_{me} is the mesopore volume, determined from adsorption measurements.[1–3]

Results and Discussion

X-Ray diffraction patterns of the samples studied are normal for systems of this type; in most cases, they contain at least four narrow reflections. The variation of the lattice parameter and FWHM as functions of the HTT duration τ_{HTT} (Fig. 1) indicates that the parameter a_0 increases with an increase in τ_{HTT} in all cases. At a temperature of 120 °C, this increase is slight (4.33—4.45 nm for the C16-120 series and 3.72—3.81 nm for the C12-120 series); at 140 °C, it is much greater (4.69—5.50 nm for the C16-140 series and 3.71—4.79 nm for the C12-140 series).

The variation of FWHM, which was shown previously[1–3] to be an important characteristics of the degree of ordering of a mesostructure, together with the number of peaks recorded, is more specific. It follows from

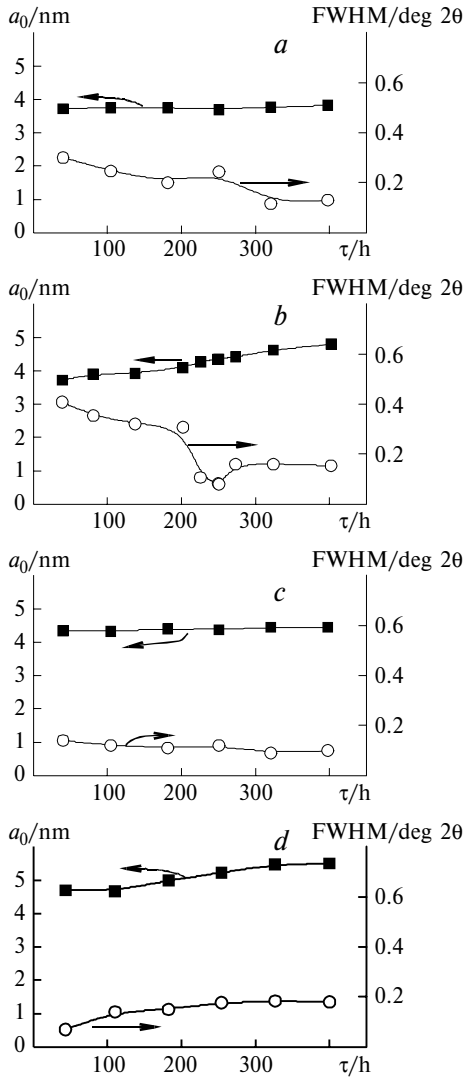

Fig. 1. Lattice parameter (a_0) and FWHM *vs.* HTT duration for the samples: C12-120 (*a*); C12-140 (*b*); C16-120 (*c*); and C16-140 (*d*).

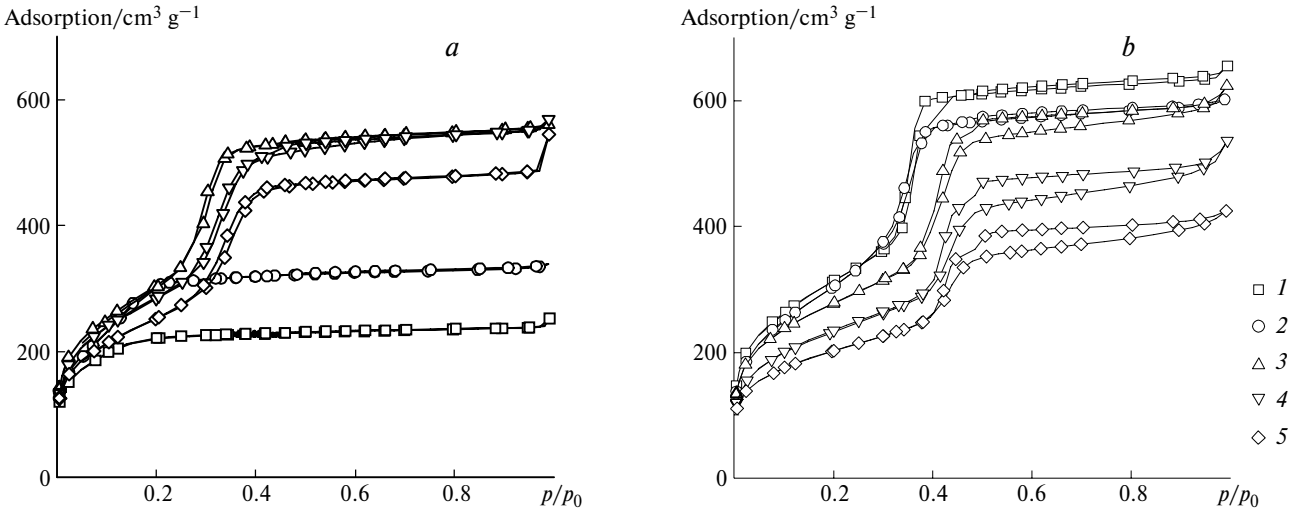

Fig. 2. Adsorption isotherms for samples obtained with different HTT durations at 140 °C. (*a*) C12-140-series: -39 (*1*), -81 (*2*), -249 (*3*), -324 (*4*), -402 (*5*); (*b*) C16-140-series: -43 (*1*), -110 (*2*), -254 (*3*), -326 (*4*), -400 (*5*).

Fig. 1 that, in the C16-120 series, FWHM decreases monotonically with an increase in τ_{HTT}, indicating an increase in the degree of ordering. However, in the C16-140 series, the C16-140-43 sample prepared with the shortest HTT (for this series) was found to be the most ordered. An increase in τ_{HTT} results in greater FWHM, *i.e.* in a lower degree of ordering.

In the C12-120 series, a more or less monotonic decrease in FWHM is observed, while in the C12-140 series, FWHM passes through a clear-cut minimum at τ_{HTT} ~225—250 h. The certainty of this minimum is confirmed by characteristics of the samples synthesized at τ_{HTT} = 249 and 250 h. The results suggest that in this series, structure ordering occurs at $\tau_{HTT} < 225$—250 h, while for $\tau_{HTT} > 250$ h, partial disorganization of the structure begins.

The X-ray diffraction data are confirmed by the results of adsorption measurements.

It follows from Fig. 2, *a* that the pattern of the adsorption isotherm of the C16-140-43 sample is typical of highly organized MMM with a hexagonal structure. The initial section of this isotherm corresponds to adsorption on the whole surface, the region of steep ascend corresponds to the filling of mesopores in the mesophase; after they have been filled, adsorption takes place on the remaining "external" surface.

An increase in the duration of HTT in this series leads to a decrease in the amount adsorbed, extends the

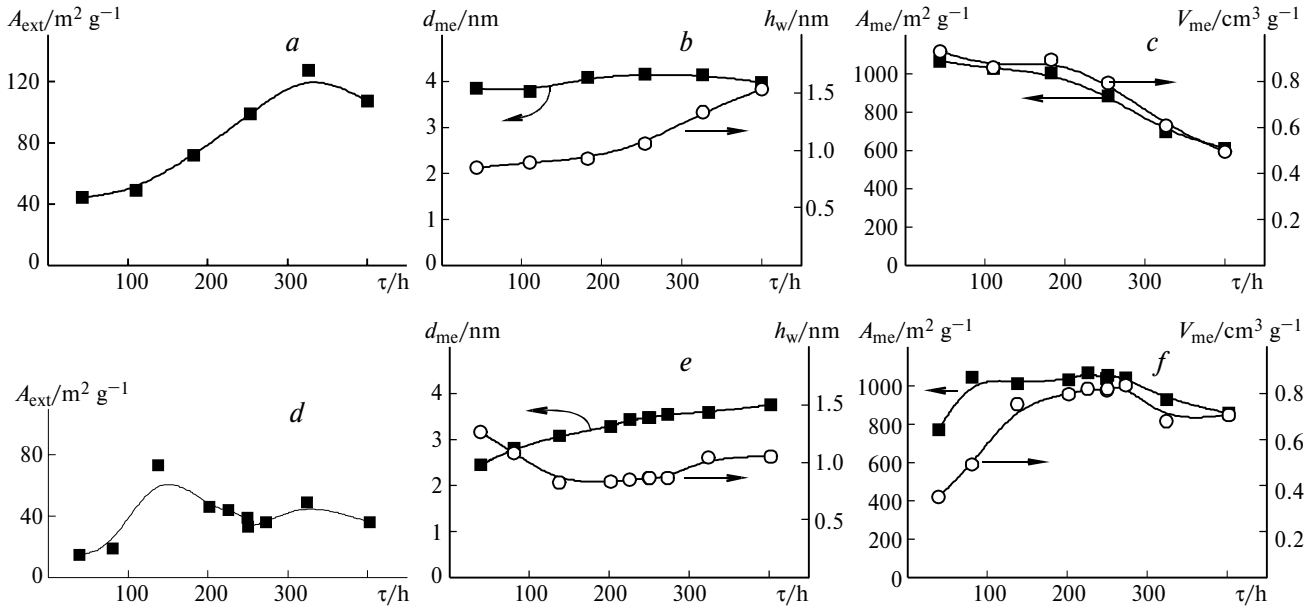

Fig. 3. Variation of the textural characteristics for samples of the C16-140 (*a*—*c*) and C12-140 (*d*—*f*) series *vs.* HTT duration. (*a*, *d*) The external surface A_{ext}; (*b*, *e*) pore diameter d_{me} and wall thickness h_w; (*c*, *f*) mesopore surface area A_{me} and volume V_{me}.

region of mesopore filling, and gives rise to hysteresis, first, in the region of adsorption on the external surface and subsequently in the region of mesopore filling. It can be seen from Fig. 3, *a* that the calculated external surface area (A_{ext}) increases, at the limit, virtually twice, while the volume V_{me} and the mesopore surface area A_{me} simultaneously decrease. These changes in the texture parameters point to a decrease in the degree of ordering, *i.e.*, they are in line with the observed increase in the structural parameter FWHM. This is accompanied by slight changes in the calculated mesopore diameter d_{me} (3.8—4.1 nm); the increase in the hexagonal lattice parameter a_0 is mainly due to an increase in the average thickness of the wall between mesopores h_w (0.85—1.53 nm).

The C16-140-43 sample having the most perfect structure for this series is characterized by the greatest V_{me} and A_{me} values and the smallest A_{ext}, h_w, and FWHM values. The structural (a_0 and FWHM) and textural (A_{me}, A_{ext}, V_{me}, d_{me}, h_w, and β) characteristics of this sample and the samples characterized by the minimum FWHM in the other series are listed in Table 1. The roughness factor β has been introduced previously[9] as the ratio of the really measured surface area of channels A_{me} to the model ideally smooth surface area of these channels A^*_{me}. This factor is calculated from the formula

$$\beta = A_{me}/A^*_{me} = d_{me}/d_{V/A}, \quad (3)$$

where d_{me} is determined from Eq. (1) and the volume-surface diameter $d_{V/A}$ is defined as

$$d_{V/A} = 4V_{me}/A_{me}. \quad (4)$$

In the model with hexagonal pores, the $d_{V/A}$ value is equal to the diameter of the cylinder inscribed in a hexagonal prism, V_{me} and A_{me} are the volume and the surface area of the corresponding hexagonal channels.

Figures 2, *b* and 3, *d—f* show the results of a study of samples of the C12-140 series. In this case, when $\tau_{HTT} < 100$ h, the adsorption isotherms exhibit no region of mesopore filling, typical of MMM. The pattern of the resulting curves corresponds to the adsorption isotherms obtained for supermicroporous systems. The calculated mesopore size in these samples is 2.5—2.8 nm, FWHM is > 0.350° 2θ. More prolonged HTT results in an increase in the calculated mesopore size d_{me} up to ≥3 nm, and the corresponding adsorption isotherms of N_2 assume the shape typical of mesophase systems with a clearly defined region of mesopore filling. This is accompanied by an increase in the volume V_{me} and the surface area A_{me} of the mesopores. Samples with the most perfect structure for this series were prepared at τ_{HTT} = 225—250 h (see Table 1). Further increase in the duration of HTT, as in the C16-140 series, is accompanied by a decrease in V_{me} and A_{me} and by an increase in A_{ext}, h_w, and FWHM.

In the C16-120 series, an increase in τ_{HTT} has little influence on the textural parameters such as the mesopore volume (V_{me}) and surface area (A_{me}) or the external surface area A_{ext}, although it is accompanied by a pronounced decrease in FWHM. Nitrogen adsorption isotherms for samples of this series virtually coincide, have a shape typical of MMM, and are not presented here. Characteristics of the sample having the minimum FWHM value over this series are listed in Table 1; the parameters of other samples within this series differ by no more than 3% (except for FWHM).

Virtually the same conclusions can be drawn from comparison of the results obtained for samples of the C12-120 series. The adsorption isotherms for samples of this series also almost coincide. Only for samples prepared with the shortest (40 h) and longest (~400 h) HTT, does noticeable (by 15—20%) relative decrease in the mesopore volume occur. The mesopore size d_{me} somewhat increases (2.82—3.00 nm) with an increase in τ_{HTT}, while the calculated wall thickness decreases (0.8—0.75 nm). In addition, as τ_{HTT} increases, the external surface area A_{ext} markedly decreases (by a factor of ~2). Characteristics of the most ordered sample in this series are alao listed in Table 1.

Apart from the minimum FWHM, the samples listed in Table 1 possess the most highly ordered structure and texture over each series because they are characterized by the maximum volume V_{me} and surface area A_{me} of mesopores and the minimum external surface A_{ext}. In addition, the roughness factors β of these samples are the lowest over the corresponding series. In the C16 series, the factor β varies over the range of 1.10—1.20, while in the C12 series, it amounts to 1.4—1.5 for samples with

Table 1. Structural and textural characteristics of samples from different series with the smallest full-width half-maximum (FWHM) of the first reflection

Sample	a_0	FWHM	A_{me}	A_{ext}	V_{me}	d_{me}	h_w	β*
	nm		$m^2\ g^{-1}$		$/cm^3\ g^{-1}$	nm		
C16-120-321	4.454	0.092	1127	37	0.930	3.65	0.80	1.10
C16-140-43	4.688	0.071	1065	44	0.930	3.84	0.85	1.10
C12-120-321	3.755	0.117	1226	29	0.802	3.00	0.75	1.14
C12-140-250	4.335	0.081	1053	33	0.818	3.47	0.86	1.12

* β is the parameter of the surface roughness (the explanations are in the text).

the shortest HTT; then it decreases to the values presented in Table 1 and increases again to 1.2—1.3.

The whole set of the experimental data obtained demonstrates that the systems prepared with HTT at 120 and 140 °C exhibit largely different types of behavior. At 120 °C, the system is obviously more stable and inert; an increase in τ_{HTT} has only a slight influence on the mesopore specific surface area A_{me} and volume V_{me} but results in a decrease in FWHM and a slight increase in the parameter a_0. The most highly organized structures in the C16-120 and C12-120 series are formed with $\tau_{HTT} \approx 300$ h. The main differences between these series show themselves in the texture parameters (see Table 1) and are related to the length of the hydrocarbon group of surfactant molecules. Hence, the HTT under these conditions leads to an enhancement in the structural ordering of the material.

At 140 °C, the system is less stable. When the HTT duration exceeds some optimum value τ^*_{HTT}, the FWHM and the outer surface area A_{ext} increase, whereas the mesophase volume and the surface area decrease, *i.e*,. signs of the irreversible structure degradation appear. In the C16-140 series, $\tau^*_{HTT} \leq 43$ h, while in the C12-140 series, $\tau^*_{HTT} \approx 250$ h. However, the decrease in the degree of ordering when $\tau_{HTT} > \tau^*_{HTT}$ results not only in a correlated decrease in the mesopore volume V_{me} and the surface area A_{me} but also in an increase in the calculated values for the average thickness of the wall between the mesopores h_w.

It can be demonstrated that an ideal honeycomb structure allows simultaneous decrease in V_{me} and A_{me} and an increase in h_w without degradation. Indeed, combined solution of Eqs. (1)—(4) gives a strict relation between the honeycomb structure parameters

$$A_{me} = \frac{4\beta}{h_w \rho} \cdot \frac{\sqrt{\varepsilon}}{(\sqrt{\varepsilon} + 1)}. \quad (5)$$

In the region of porosities $\varepsilon = 0.6$—0.8 typical of MMM of the MCM-41 type, the parameter $[\sqrt{\varepsilon} / (1 + \sqrt{\varepsilon})]$ varies only from 0.436 to 0.472 and can be taken to be ~0.45. Hence, when $\beta \approx$ const and ρ — const, the A_{me} value is inversely proportional to h_w.

A similar expression relating V_{me} to h_w can be written as follows

$$V_{me} = \frac{d_{me}\sqrt{\varepsilon}}{h_w \rho(\sqrt{\varepsilon} + 1)}. \quad (6)$$

Analysis of the experimental data shows that Eqs. (5) and (6) hold for all the series studied including the data for the C16-140 and C12-140 series. Therefore, the observed concerted decrease in V_{me} and A_{me} with an increase in h_w cannot point unambiguously to amorphization of the structure.

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