

Effect of Reaction Medium on Hydrothermal Stability of Mesostructured Silicate Material MCM-41

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Abstract

For the example of sequential replacement of equivalent reagents, the effect of the reaction medium on the formation of mesostructured silicates of MCM-41 type is studied. It is shown that the reagents providing pH of the medium, solubility of the main interacting reagents can substantially affect the rates of hydrolysis and polymerization of silica, as well as enhance or weaken osmosis in the pores thus affecting the formation of the structure of a substance and finally its hydrothermal stability.

INTRODUCTION

A ten year history of the investigations of silicate mesostructured materials has demonstrated a powerful potential of the method of liquid crystal templating for the formation of new inorganic materials [1–9]. These materials are of interest for many areas of chemistry because of their unique properties based on large, regularly arranged internal surface. The interaction of the molecules of a surfactant with inorganic poly-anions leads under definite conditions to the formation of supramolecular particles which are condensed from solution and form a mesostructured mesophase arranged according to the laws of a liquid crystal medium. After hydrothermal treatment in autoclave and subsequent calcination in air for removing of organic template, a mesostructured porous material is formed; its composition corresponds to silicon oxide with a surface arranged in regular geometry; the surface reaches 1000 m²/g and more.

A broad range of combinations, ratios of components, mixing modes, stages and conditions of synthesis have been already described. In the recent years, the problem concerning

the accuracy of reproducibility of the substance becomes urgent because research area develops toward the application of mesoporous mesostructured materials. The most important problem is that involving the stability of a material in rigid reaction media, in particular the problem of thermohydrostability [2, 5, 12–16]. It was revealed that the samples of MCM-41 material [10, 11] lose their mesostructure under exposure to boiling water [13, 14] and pass into the amorphous state. Some works were published the goal of which was to search for a recipe for eliminating this drawback. In particular, among the items under investigation were the so-called salt effect [15, 17–20], processes involving the growth of organosilicon fragments on pore walls [16, 21], increase in pore wall thickness during hydrothermal treatment [22].

Variety of results and published considerations concerning the reasons of low thermohydrostability of materials was probably induced by a complexity of their formation processes, insufficient knowledge of the substance molecular structure and the lack of clear ideas of the role of reaction components.

TABLE 1

Molar ratios of the reagents used to synthesize the materials of 1–6 series, and some radiographic structural characteristics of the obtained samples at each stage of treatment

Series	Molar ratio	$a/d(100)$, Å			
		1	2	3	4
1	1TEOS/21.75NH ₃ /52EtOH/0.2CTABr/475H ₂ O	42.30/36.80	43.72/37.97	42.48/36.79	42.22/36.71
2	1TEOS/21.75NH ₃ /0EtOH/0.2CTABr/475H ₂ O	44.02/38.17	47.42/41.34	43.82/38.14	–/37.33
3	1TEOS/0.78NaOH/52EtOH/0.2CTABr/475H ₂ O	41.40/35.04	–/34.53	–/–	–/–
4	1TEOS/0.43NaOH/0EtOH/0.2CTABr/475H ₂ O	–/49.87	–/43.66	–/38.05	–/–
5	1SiO ₂ /1.5NaOH/52EtOH/0.2CTABr/475H ₂ O	42.22/36.83	44.02/38.17	–/32.84	–/–
6	1SiO ₂ /1.5NaOH/0EtOH/0.2CTABr/475H ₂ O	43.18/37.56	45.48/39.62	–/31.12	–/–

Notes. 1. a is the lattice parameter, Å; $d(100)$ is the interplanar space (100), Å. 2. Materials: 1 – obtained at the stage of synthesis at room temperature; 2 – subjected to HTT at 110 °C; 3 – calcinated at $T = 550$ °C; 4 – subjected to stability test.

The present investigation is aimed at more detailed examination of the roles of different synthesis-involved components in the formation of material's properties. The initial information included our preliminary experimental data on hydrothermal stability of MCM-41 samples obtained alcohol-ammonia and aqueous-alkaline media. The products are comparable in geometric perfection the silica framework; however, in the first case we obtained a material presenting rather high stability in boiling water, while in the second case the material was unstable. The plan of investigation involved sequential replacement of the corresponding components, so that a transition from alcohol-ammonia medium to aqueous alkaline one could be carried out. It is evident that a simple replacement of one component for another cannot lead to obtaining a material with optimal properties. However, such a goal was not put forward. The problem was to fix qualitative changes arising when a component was replaced, thus revealing the role of this component. The state of the materials at each stage of their formation was characterized with the help of X-ray diffraction patterns. At the final stage, the substances were subjected to testing for stability in boiling water.

EXPERIMENTAL

The initial reagents were: cetyltrimethylammonium bromide (CTABr) C₁₆H₃₃(CH₃)₃NBr – Aldrich (Cat.:85.582-0); tetraethoxy silane

Si(C₂H₅O)₄ (TEOS) of “ch.d.a.” grade (pure for analysis) (TU 6-09-3687-74); Na₂SiO₃·9H₂O (Reakhim 130 159, GOST 4239-77); NH₃ – 13.4 mol/l, $\rho = 0.905$ g/cm³ (ch.d.a.); NaOH (ch.d.a.); EtOH rectificate 96 % by vol.; concentrated H₂SO₄ (ch.d.a.). Stoichiometric ratios of the components taken for synthesis are listed in Table 1.

CTABr was dissolved in water or water-ethanol solution at room temperature under intensive stirring. In order to make up the desirable medium, ammonia or NaOH were added to the surfactant solution. Either TEOS or preliminarily prepared sodium silicate solution were added dropwise to the solution under vigorous stirring with a magnetic mixer. Hydrolysis, turbidity and the formation of a suspension were observed almost immediately after adding the source of silica. The medium exhibited pH 12.5 before introducing TEOS and 11.5 after its introduction (after 10 min). In this investigation, the time for the formation of the product was restricted by 2 h, which is considered to be optimal formation time in ethanol-ammonia medium. In two hours after having poured the solutions together, the suspension is either filtered, washed with water till the washing water exhibits neutral pH and dried in air, or is transferred into a Teflon autoclave for hydrothermal treatment (HTT) at the temperature of 110 °C for 2 h. After filtration, washing and drying at room temperature, the material is subjected to calcination in the air at 550 °C. The rate of tempera-

ture rise during calcination was 3 °C/min. After having achieved the final calcination temperature, the sample stayed in the furnace for 3 h. No corrections for changes in the volume of the mixture due to the removal of ethanol were made (see Table 1, series 2, 4 and 6). Sodium silicate was the source of silicon in the 5th and 6th series of experiments. The necessary pH was achieved in these experiments by acidifying with sulphuric acid solution.

Tests for stability were carried out exposing the substance in boiling water for 2 h, with subsequent qualitative analysis of changes in the X-ray diffraction patterns.

After the stages of precipitation (1), HTT (2), calcination (3), boiling in water (4) the materials were sampled for diffraction patterns. They were recorded with an automatic diffractometer DRON-4 (CuK_α radiation, graphite monochromator in a reflected beam). For recording at small angles, a standard optical scheme of the diffractometer was supplemented by the collimation slit (0.25 mm) at the primary beam at a distance of 90 mm from the tube focus; in addition, a modified Soller slit was mounted (the distance between plates was 0.2 mm). Scanning was carried out within the angle range 1–7° 2θ with a step of 0.04° and time of accumulation in a point 10 s.

RESULTS AND DISCUSSION

The X-ray diffraction patterns of the synthesized products at different stages of formation are shown in Fig. 1, *a–f*.

The evolution of the product with the optimal set of components for the ethanol-ammonia synthesis (see Fig. 1, *a*, curves 1–4) is not accompanied by strong changes in the lattice parameter. The largest change (by about 1.5 Å) occurs after HTT in autoclave; however, after calcination the framework returns practically to the initial state. No noticeable changes in the lattice parameter occur during boiling the product in water. The diffraction patterns contain up to five peaks. Immediately after condensation the product has a perfect structure; however, some insignificant details are present in the diffraction patterns evidencing non-uniformity of the framework: a weakly

noticeable shoulder of (100) line, planarity of the summits of (110) and (200) peaks. Hydrothermal treatment renders uniformity to the material. Boiling leads to hardly noticeable degradation which is exhibited in small broadening of the peaks and a decrease in the intensity of far-off lines.

A sharp decrease in ethanol concentration in the reaction medium causes noticeable non-uniformity of the primary product (see Fig. 1, *b*, curve 1). The (100) line acquires a shoulder from the side of smaller angles. Correspondingly, the (110) and (200) lines somewhat broaden and lose intensity. It is likely that a phase with larger cell size and possibly with larger pore size is present along with the main mesophase. The size of unit cell of the main product is larger by 1.5 Å than that of the reference product (see Fig. 1, *a*, curve 1). Hydrothermal treatment improves the hexagonal structure; the unit cell parameter increases by 4 Å. The obtained result is in contradiction with the existing notions about the role of ethanol and other organic additives as swelling agents leading to an increase in volume (swelling) of the main component. After calcination, the lattice parameter sharply decreases, too, almost reaching its initial value. The stability of the material in boiling water decreases substantially. The X-ray diffraction patterns of the product after boiling (see Fig. 1, *b*, curve 4) exhibits noticeable broadening of the primary beam of the diffractometer (the background of the patterns in the region of the primary beam), which is an evidence of the formation of the small-sized particles. So, boiling is accompanied by fragmentation of the primary particles into smaller ones.

The result of replacement of ammonia as a pH-forming agent by an equivalent amount of NaOH (according to the initial pH 12.5) is shown in Fig. 1, *c*, curves 1–4. As early as the stage of condensation, we observe the start of the conversion of the product into a state which is intermediate between MCM-41 and MCM-48 with cubic symmetry. This is evidenced by a decrease in the interplanar spacing for the main diffraction line and its splitting during HTT. A perfect product of cubic symmetry was not observed in this case, which is likely to be due to insufficient HTT time or some

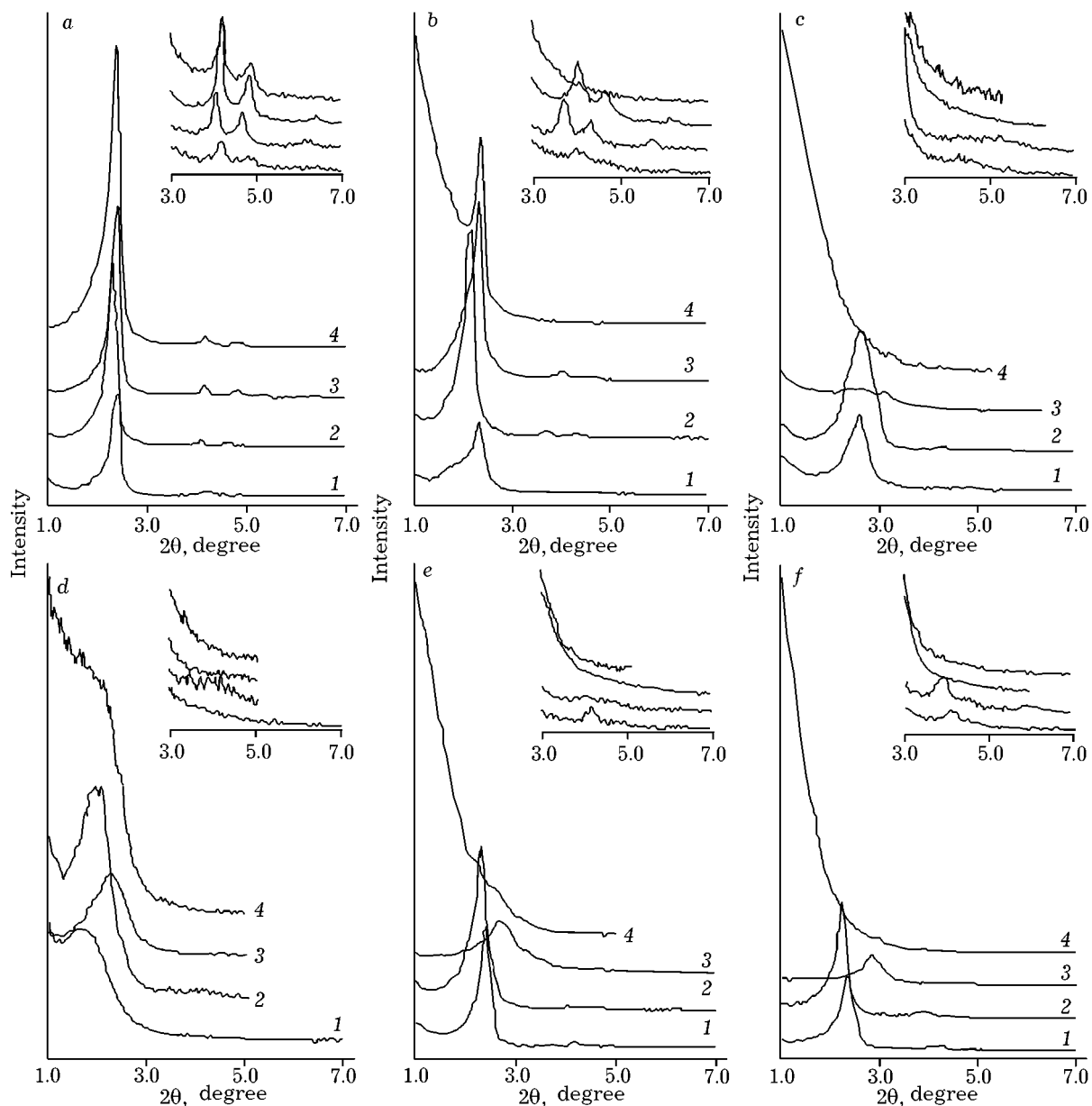


Fig. 1. Diffraction patterns of the synthesized materials (see Table 1): *a-f* – series 1–6, respectively.

other kinetic reasons. Further calcination does not lead to the formation of a perfect product, however, the formed structure approaches a cubic type. The obtained material is not stable toward boiling in water.

Further on, changes in the medium are followed in series 4 by replacing ethanol with water (see Fig. 1, *d*, curves 1–4). The effect is to a definite extent similar to that observed in the 2nd series: the arrangement of the primary product worsened due to insufficient readiness of the surfactant for the reaction. As suggested by the interplanar space of the basic

reflection ($d/n = 49.9 \text{ \AA}$), the condensed substance can be referred to the hexagonal form. A decrease in the interplanar distance of this reflection till $d/n = 43.7 \text{ \AA}$ during HTT is most likely caused by the start of transformation of the product's structure into the cubic form. Calcination is accompanied by further very strong decrease in the interplanar spacing ($d/n = 38.1 \text{ \AA}$). The final product is unstable toward boiling in water.

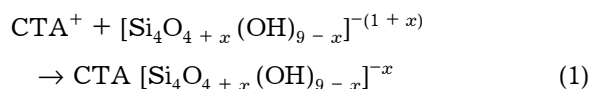
The effect of replacement of the silica source was studied in series 5 and 6. In these experiments, sodium silicate was used instead of tetra-

ethylorthosilicate. The indicated series (see Fig. 1, *e*, and *f*) differ by the presence of ethanol. In series 5, rather well structured product with hexagonal symmetry is formed. The lattice parameter ($a = 42.2 \text{ \AA}$) corresponds to the reference version (series 1). The result of HTT (see Fig. 1, *e*) can be interpreted as a start of the structural rearrangement: the (110) and (200) lines disappear almost completely, and the basic reflection shifts toward larger angles. The starting changes enhance during calcination (see Fig. 1, *e*, curve 3). The formed product, which is unstable in boiling water, cannot be related to any definite structural type.

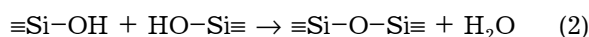
A similar behaviour is observed in the 6th series. A difference from the 5th series is some lag in time. After HTT, the product achieves a more perfect state characterized by the hexagonal symmetry. An increase in the lattice parameter from 43.2 to 45.4 \AA can be stressed, which is typical for the application of rigid (weakly polarizable) alkaline agents. However, during calcination, an active rearrangement, presumably to the cubic phase, starts. The product is similarly unstable to boiling in water.

So, noticeable changes in the quality of the formed product are observed under replacement of the reagents. Since chemical composition of the final substance is the same in all cases, the changes are to be due to the changes in kinetic characteristics of separate processes, which causes their mutual deregulation and finally results in the products with imperfect structure. The obtained results, and especially the role of separate components, can be explained on the basis of building up an hierarchy of the basic processes taking place during the formation of the substance.

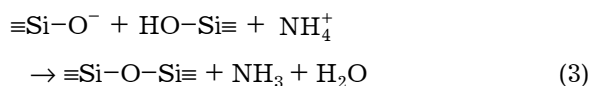
Many researchers agree at present in understanding the main process in the formation of a mesoporous substance as a supramolecular interaction between the cetyltrimethylammonium ions and the silicate polyanions [1, 4, 5, 9, 23]. No necessary specificity exists so far in the problem concerning the kinds and size of polyanions; nevertheless, the data are being accumulated which suggest that the interaction is fully or nearly stoichiometric in its character. This can be represented by the following equation:



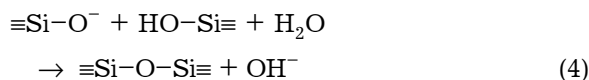
where CTA^+ is $\text{C}_{16}\text{H}_{33}(\text{CH}_3)_3\text{N}^+$. The formed supramolecular fragments condense. The principle that governs crystallization is the formation of a surface profitable from the energy viewpoint according to the liquid crystal principle. After that, cross-linking of polyanions in a wall occurs, or polymerization of silica, which is the most lengthy process occurring according to the reaction



The main reason hindering polymerization is the charge of the wall, which is larger than the charge compensated by the surfactant cation. In addition, large charge leads to the formation of defects in polyanion packing due to their repulsion. Additionally charged polyanions require neutralization, which is combined with the transport (diffusion) of a neutralizing agent. Besides water, ammonia can also act as a neutralizing agent. With ammonia, the products are neutral similarly, and the equilibrium is shifted to the right:



Hydrolysis of the silicon-oxygen wall by water is described by the equation



Sodium cations (or other counter-ions) near the wall compensate the charge of the wall. Since a strong base is formed in the reaction region, hydrolysis is reversible, and polymerization rate decreases. Hindered diffusion of sodium and hydroxide ions from the channels (pores) of a mesoporous body also helps deceleration.

The presence of sodium ions in the pores can also cause osmosis. The charge of the silicate skeleton of the material is located on its surface; since the inner surface is larger than the outer one (the difference reaching several times in some cases), the corresponding amount of compensating counter-ions is to be present

inside the pores. This is the reason of re-distribution of the ions inside the system. A definite part of the charge, in agreement with stoichiometry, is compensated by the surfactant, while the rest relates to ammonium or sodium cations. If the ratio of the initial reagents leads to the situation when the concentration of sodium ions (for example) inside the pores is larger than that in the external solution, osmotic pressure arises inside the pores; it is able not only to increase pore size but also to cause the transformation of the structure. A likely reason of osmotic pressure can be also an excess surfactant concentration. This phenomenon is known as swelling. The application of salt additives in order to improve the stability of the material to hydrothermal treatment has been already described [15, 17–20]. It was discovered that the introduction of additional sodium ions into the reaction solution after precipitation of the phase (but before HTT) causes improvement of the material's structure. The phenomenon receives a simple explanation on the basis of the hypothesis involving osmosis.

Sodium ions are very strong transformers of the structure. Their action is twofold: on the one hand, they prevent polymerization of the framework leaving it in a mobile state; on the other hand, they cause osmotic pressure inside the pores. A positive result of the action of osmosis is ordering and alignment of pores. In particular, this is exhibited by more perfect diffraction patterns of the products after HTT. A negative consequence is exhibited as too large broadening of the pores, when polysilicate ions in the walls move aside each other, so that polymerization becomes spatially hindered. The described behaviour accompanied to a substantial extent the experimental series 3–6.

CONCLUSION

The scheme of processes under consideration allows to give a reasonable explanation of the obtained results and of the role of each of the reagents used. The formation of mesostructured mesoporous material occurs as a result of a number of processes differing by their start time and rate. The formation of the necessary forms of silicate polyanions and dis-

solution of the surfactant with the formation of solitary anions occur at the preliminary stages. This is the basis for the formation of supramolecular particles (silicate polyanion – cation – surfactant). Then the formed particles condense and form a mesophase in which hydrolysis and polymerization of the wall material takes place. The role of an alcohol (ethanol) is just a solvent for the surfactant. Alkaline reagents provide hydrolysis, polymerization and osmosis.

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