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Preparation of mesoporous aluminosilicates in the presence of lecithin: a simulation of biomineralization processes

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Various combinations of lecithin with cetyltrimethylammonium bromide or octadecylamine were used as template agents in the preparation of biporous materials (pore size up to 100 Å) in the aluminosilicate system.

Recent studies indicate that a biomimetic approach based on the main constructional processes of biomineralization results in the development of new strategies in the controlled synthesis of high-ordered inorganic materials.[1-6] Considerable advantages of these methods consist in rather low process temperatures, the use of biomolecules rather than toxic surfactants as templates and the use of water in place of organic solvents.[1–3] Thus, these synthetic routes and the resulting materials can be considered to be environmentally friendly.[6] Aluminosilicate materials prepared in the presence of organic template molecules are of particular interest as appropriate supports for immobilised enzymes because of specific affinities to templates.[7] One of the problems arising with the use of biomolecules in the synthesis of inorganic substances is the sensitivity of biomolecules to reaction conditions.

We optimised the composition of reaction mixtures used for preparing MCM-41 aluminosilicate materials in order to attain near-neutral pH values of the reaction mixtures. These pH values are important for the retention of the physico-chemical properties and reactivity of biomolecules. The synthesis of MCM-41 aluminosilicate materials in the presence of cetyltrimethylammonium bromide (CTAB) was carried out using a reaction mixture of the following composition (pH was close to neutral): $16.2SiO_2\times$ $\times Al_2O_3\cdot 5.4Na_2O\cdot 13.8CTAB\cdot 1767H_2O$ (sample 1), sodium silicate and aluminium sulfate served as sources of silica and aluminium, respectively. The hydrothermal synthesis was performed at 423 K for 48 h. The product obtained was washed with water, dried and calcined at 823 K in air for 6 h.

The X-ray diffraction data (DRON-3M instrument, CuK radiation) and the adsorption (desorption) isotherms (methanol, 293 K, activation at 373 K) of sample 1 (Figure 1, Table 1) indicate that the material exhibits a hexagonal array of uniform mesopores with diameter $D = 34$ Å. The Si:Al ratio in sample 1 (7.8) is close to that in the reaction mixture. Thus, at neutral pH of the reaction mixture, a highly ordered aluminosilicate MCM-41 material with high aluminium content was obtained. This fact is important both for the preparation of mesoporous substances in the presence of biotemplates and for the synthesis of various inclusion compounds.[8]

This work was devoted to examining the applicability of supramolecular structures of lecithin (L) molecules as templates to the synthesis of mesoporous aluminosilicates. For this purpose, lecithin (17% of L- -phosphatidylcholine, Sigma) or its combinations with CTAB or octadecylamine (ODA) were added instead of CTAB to the reaction mixture, so that the L:CTAB and L:ODA molar ratios in the reaction mixture were 0.47 or 1.40 and 0.34 or 1.04, respectively. The hydrothermal synthesis was performed at 353 K for 72 h. The products obtained were washed with water, dried and calcined in air at 823 K for 6 h. To examine the effects of pH and the Si:Al ratio in the reaction mixture on the structure of the products, similar syntheses were carried out using the reaction mixture (pH ~ 9) $116SiO_2\cdot Al_2O_3\cdot 38Na_2O\cdot 49CTAB\cdot 9101H_2O$ (Table 1). The Kelvin equation (assuming a hemispherical meniscus shape and a zero contact angle) with the multilayer thickness correction was used for determining the pore size distribution.[9] The mesopore volume V_{mes} of the samples was estimated from the isotherms (Figures 1 and 2) at $p/p_s = 0.89$.

The X-ray diffraction patterns of samples 3–6 and 9 exhibited a single peak at low angles (Table 1 summarises the corresponding interplanar distances d).

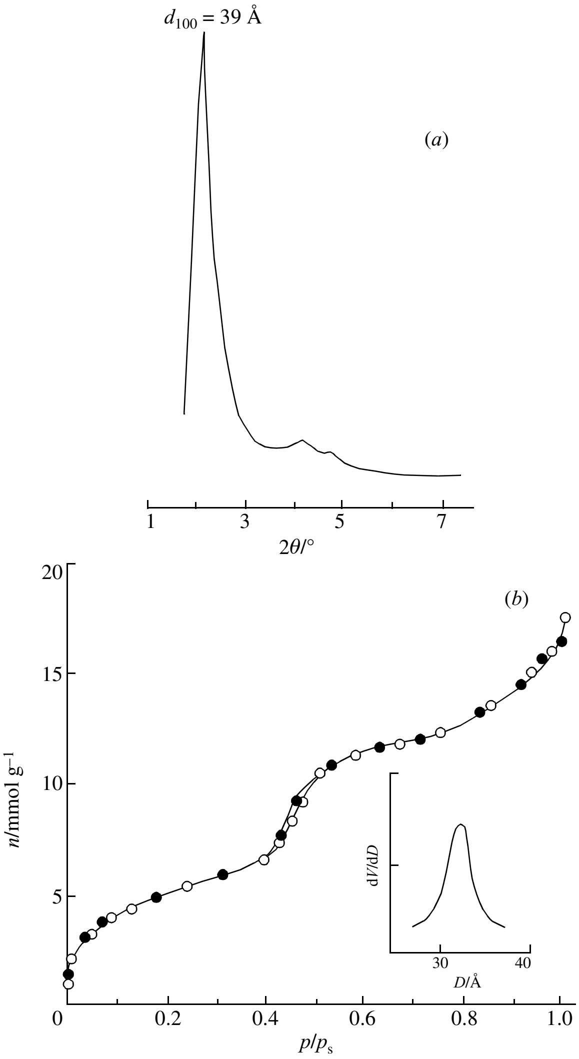

Figure 1 (*a*) X-ray diffraction pattern and (*b*) methanol adsorption (desorption) isotherm for sample 1. Insert: Pore size distribution of sample 1, calculated from the methanol desorption branch.

It was found (Figure 2, Table 1) that mesoporous substances are formed in the presence of only lecithin; that is, the supramolecular structures of lecithin molecules are a template in the formation of an aluminosilicate framework. The self-assembly of amphiphilic lecithin molecules in spherical, cylindrical and bilayer structures and two-dimensional phases in a free solution is well studied (under the reaction conditions, lecithin molecules form lamellar bilayer structures such as flat layers or closed vesicles).[10] However, it is unknown how the presence of inorganic species affects these aggregates, and which is the structure of supramolecular vesicles participating in the templating process.

The structure of organic–inorganic composites is determined by the organic–organic interactions to form arrays of organic molecules, organic–inorganic interactions at the appropriate interfaces, and inorganic–inorganic interactions resulting in the polymerization of inorganic species.[11] It is obvious that the role of each type of these interactions in the formation of porous structures depends on the synthesis conditions and the nature of the template.

The structure of pre-organised lecithin molecule arrays that form an aluminosilicate framework depends on the Si:Al ratio and the pH of the reaction mixture (Figure 2). The alkalinity of the reaction mixture controls the geometry and charge density of aluminosilicate species and template head groups (Me_3N^+ groups of lecithin and CTAB and NH_2 groups of ODA). Sample 8 (Si:Al = 58) has larger and more homogeneous pores than sample 2 (Si:Al = 8). In our opinion, this difference can be explained by the fact that at Si:Al = 58 in alkaline media the initial arrangement of lecithin molecules is disrupted upon strong ionic interactions with negatively charged aluminosilicate particles. Next, they undergo reorganisation to form new configurations uniform in size, which are similar to cylindrical CTAB structures[11] formed in the alkaline synthesis of MCM-41 materials.

The disordering of the structure at Si:Al = 8 can be explained not only by an increase in the aluminium content but also by the fact that the slightly negatively charged aluminosilicate particles insignificantly perturb the self-organisation of lecithin vesicles, which exhibit a spread in size. It is our opinion that the structure formation processes in the above systems are similar to naturally occurring biomineralization processes because the supramolecular structures of lecithin participate in the templating process, and the interaction between aluminosilicate oligomers and the template surface depends on the Si:Al ratio and the pH of the reaction mixture.

It is likely that the bilayer structures of lecithin molecules (the thickness is approximately equal to 40 Å)[10] play a templating role in the formation of 40 Å diameter pores in samples 2 and 8. The fact that pores of this size in sample 8 exhibit a small adsorption volume indicates that bilayer structures are also formed in a reaction mixture with Si:Al = 58, however, the amount of these structures is insignificant because of strong organic–inorganic interactions.

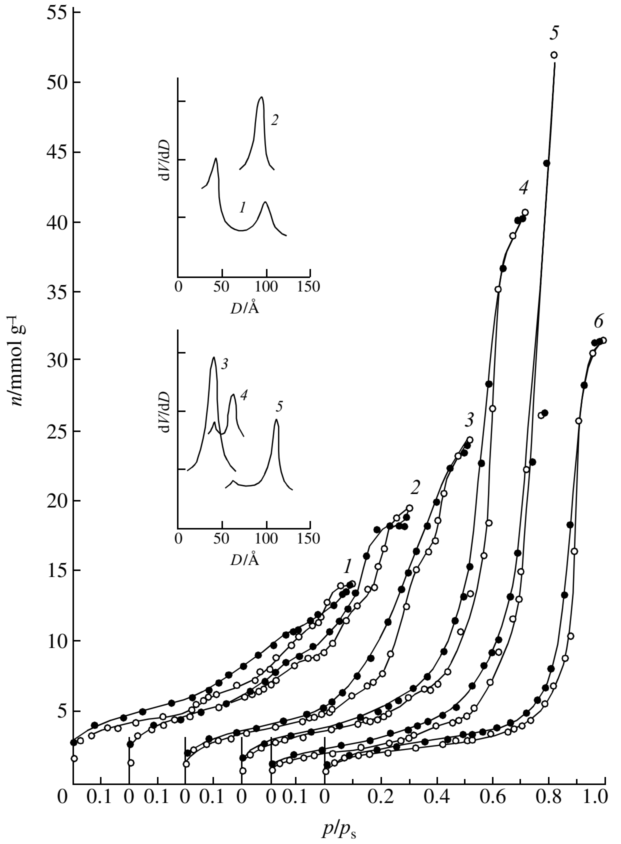

Figure 2 Methanol adsorption (desorption) isotherms for samples (*1*) 2, (*2*) 3, (*3*) 5, (*4*) 9, (*5*) 8 and (*6*) 11. Insert: Pore size distribution of samples (*1*) 3, (*2*) 9, (*3*) 6, (*4*) 5, and (*5*) 11, calculated from the methanol desorption branch.

Table 1 Characteristics of the materials obtained.

Sample no.	Si:Al^a	Template	D/Å	d/Å	V_{mes}/cm^3 g^{-1}
1	8.1	CTAB	34	39	0.58
2^b	8.1	L	38; 44	—	0.48
3^b	8.1	L:CTAB = 0.47	36; 98	54	0.62
4^b	8.1	L:CTAB = 1.40	31; 40	54	0.61
5^b	8.1	L:ODA = 0.34	41; 65	57	0.76
6	8.1	L:ODA = 1.04	42	59	0.47
7	58	CTAB	34	39	1.00
8^b	58	L	46; 66	—	0.47
9	58	L:CTAB = 0.47	91	59	1.07
10	58	L:CTAB = 1.40	80	—	0.92
11^b	58	L:ODA = 1.04	58; 114	—	0.66

^{a}The Si:Al ratio in the reaction mixture. ^{b}Materials with a bimodal mesopore size distribution.

These assumptions concerning a key role of organic–inorganic and organic–organic interactions in the formation of aluminosilicate frameworks were also supported by the data on the porous structure of substances obtained in the presence of lecithin mixtures with CTAB or ODA (Figure 2, Table 1). We found that mesoporous substances with pore diameters up to 100 Å and biporous materials which have bimodal mesopore size distribution can be prepared in the presence of the above combinations as template agents in the aluminosilicate system. The formation of biporous materials indicates that along with mixed micelles[12] other types of micelles (for example, micelles that consist of CTAB or ODA and also liposomes or disc-shaped lecithin structures with small inclusions of CTAB or ODA) can occur in the reaction mixture. The participation of such structures in the framework formation depends upon the pH of the reaction mixture. The adsorption (desorption) isotherms of samples with Si:Al = = 8 (pH close to neutral) exhibit well-defined steps due to various types of the templating agents (Figure 2), whereas the shape of the isotherms of samples with Si:Al = 58 (pH ~ 9) is independent of the template and is characterised by a sharp rise at $p/p_s > 0.8$ and by a larger mesopore volume (for samples obtained in the presence of the same template).

Thus, the inexpensive and environmentally benign template procedure described leads to mesoporous materials with large pore volumes and hybrid porous structures.

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