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PECULIARITIES OF THE POROUS STRUCTURE OF ALUMINOSILICATE MESOPOROUS SUBSTANCES OBTAINED IN THE PRESENCE OF BIOTEMPLATES

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Abstract

Supramolecular structures of lecithin occurred to be the template in the synthesis of mesoporous aluminosilicates; using of various combinations of lecithin and cetyltrimethyl-ammonium bromide or octadecylamine as templating agents allowed to obtain mesoporous substances with pores up to 100 Å, as well as biporous materials in aluminosilicate system. In the presence of glucose oxidase and cetyltrimethyl-ammonium bromide combinations aluminosilicate substances with complex porous structure were shown to be formed (pore size distributions exhibited 3 peaks, corresponding 3 effective size of mesopores in the 30–100 Å range). The investigation of sorption of glucose oxidase on obtained aluminosilicate mesoporous substances was carried out, the results obtained allow us to consider such materials as prospect for creation high capable and selective sorbents for biomolecules sorption, as well as active elements of chemical and biosensors.

Keywords: biomimetic chemistry, biomineralization, glucose oxidase, Kelvin equation, lecithin, mesoporous aluminosilicates, methanol ad(de)sorption isotherm, porous structure

Introduction

The recent investigations indicate, that a biomimetic approach based on the main constructional processes of biomineralization results in the development of new strategies in controlled synthesis of high-ordered inorganic materials [1–6]. The significant advantages of such methods are relatively low processing temperature involved, using of biomolecules as template rather than toxic surfactants and using of water rather than organic solvents [1–3]. These factors render such synthetic routes and resulting materials as environmentally friendly [6].

The synthesis of the periodic mesoporous silica material [7] based on interface interactions between inorganic units and supramolecular assemblies of surfactant molecules is of vital to many areas including biomineralization and biomimetic chemistry. Although the exact mechanism for this type of mineralization is still controversial, this technique holds great promise as a synthetic scheme to form nanostructured materials with novel properties [8].

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Synthesized in the presence of biomolecules silica materials have specific affinity (specific adsorption sites with complementary structures) to the template molecules. Such materials are particularly attractive for sorption of biomolecules and uniquely supports for immobilized enzymes [9].

The objective of this work was to investigate porous structure of aluminosilicate materials prepared in presence of biotemplates (glucose oxidase (GO) or lecithin (L)) and their combinations with surfactants (cetyltrimethyl-ammonium bromide (CTMAB) or octadecylamine (ODA)) by methanol ad(de)sorption measurements.

Experimental

For synthesis of the materials in the reaction mixture $16.2SiO_2:Al_2O_3:5.4Na_2O:13.8CTMAB:1767H_2O$ (sample 1) lecithin or its combinations with CTMAB or ODA, or combination GO with CTMAB was added instead of CTMAB, thus that L:CTMAB (molar ratio) was 0.47 or 1.40 and L:ODA=0.34, 1.04 and GO:CTMAB (mass ratio)=0.5, 0.25. The hydrothermal synthesis was carried out at 353 K for 72 h. The obtained products were washed with water, dried and calcined at 823 K for 6 h in air. To investigate of reaction mixture pH and Si:Al ratio influence on the products structure, similar synthesis were carried out from a reaction mixture $116SiO_2:Al_2O_3:38Na_2O:49CTMAB:9101H_2O$ for combination L-CTMAB and L-ODA and from $SiO_2:0.33Na_2O:0.85CTMAB:100H_2O$ for combination GO-CTMAB. Numbers of samples are specified in Tables 1 and 2.

The characterization of samples was carried out by the powder X-ray diffraction (XRD) data (automated diffractometer DRON-3M, CuK_α radiation) and methanol ad(de)sorption measurements at 293 K on standard vacuum set-up based on the McBain-Backr quartz spring balance (prior to measurements samples were degassed at 390 K). The Kelvin equation (assuming hemispherical meniscus and zero contact angle) with the multilayer thickness correction was applied to determine the pore diameter distribution [10]. The BET surface area S_{BET} was calculated in the usual manner [11], the methanol molecule area was accepted to be 21.3 $Å^2$. Mesopore volume V_{MES} and total volume V_Σ of the samples was estimated from the volume adsorbed at $p/p_s = 0.89$ and 0.95 respectively assuming that the pores have been filled with condensed liquid adsorptive. The framework wall thickness t of hexagonal mesopores is determined by substracting the Kelvin mesopore size from repeat distance a_0 between pore centers ($a_0=2d_{100}/3^{1/2}$).

The sorption of glucose oxidase on obtained aluminosilicate mesoporous substances was carried out from acetate buffer of pH=4 and pH=5 (0.02 g GO per 1 ml of buffer; 0.08 g of sorbent per 1 ml of solution) at 35°C over a period of 2 h. The samples produced were washed by water, 0.5 M NaCl solution, then by acetate buffer of corresponding pH and by water, and dried in air.

Results and discussion

Type IV (in the IUPAC classification [10]) isotherm (Fig. 1) of silicate sample 4 (Table 1) obtained in the presence of combination GO:CTMAB=0.5 is similar to that for MCM-41, but exhibits less sharp inflection characteristic of capillary condensation within uniform pores in the p/p_s=0.4–0.5 region and more distinctive hysteresis loop in the p/p_s=0–0.5 region.

Table 1 Some characteristics of the samples obtained in the presence of glucose oxidase (GO)

No.	Si:Al[a]	Template/ mass ratio	d/	D/	t/	V_{MES}/	V_{Σ}/	S_{BET}/
				Å		cm^3 g^{-1}		m^2 g^{-1}
1	8.1	CTMAB	39	34	11	0.48	0.64	662
2	8.1	GO:CTMAB = 1:2	40	31 45 81	15	0.52 0.06 0.04	0.84	660
3	8.1	GO:CTMAB = 1:4	38	27 42 68	17	0.29 0.09 0.09	0.63	476
4	∞	GO:CTMAB = 1:4	53	31	30	0.19	0.30	207

[a] Si:Al ratio in reaction mixture

Table 2 Some characteristics of the samples obtained in the presence of lecithin (L)

No.	Si:Al[a]	Template	d/	D/	V_{MES}/	V_{Σ}/	S_{BET}/
			Å		cm^3 g^{-1}		m^2 g^{-1}
1	8.1	CTMAB	39	34	0.48	0.64	662
2	8.1	L	–	38 44	0.28 0.15	0.57	513
3	8.1	L:CTMAB=0.47	54	36 98	0.36 0.37	0.77	588
4	8.1	L:CTMAB=1.40	54	31 40	0.29 0.15	0.70	596
5	8.1	L:ODA=0.34	57	41 65	0.61 0.23	0.95	420
6	8.1	L:ODA=1.04	59	42	0.37	0.52	483
7	58	CTMAB	39	34	0.92	1.44	943
8	58	L	–	46 66	0.19 0.17	1.07	259
9	58	L:CTMAB=0.47	59	91	1.50	1.58	401
10	58	L:CTMAB=1.40	–	80	1.28	1.33	342
11	58	L:ODA=1.04	–	58 114	0.19 0.56	1.23	256

[a] Si:Al ratio in reaction mixture

The XRD pattern exhibits a single diffraction peak corresponding to 53 Å. So this material display somewhat less regular, yet essentially uniform hexagonal pore arrangements. The effective size of these pores, as determined from pore size distribution curves is 31 Å. The framework wall thickness of these mesostructures (≥30 Å) are consistently larger than those of MCM-41 materials prepared in the presence of only CTMAB.

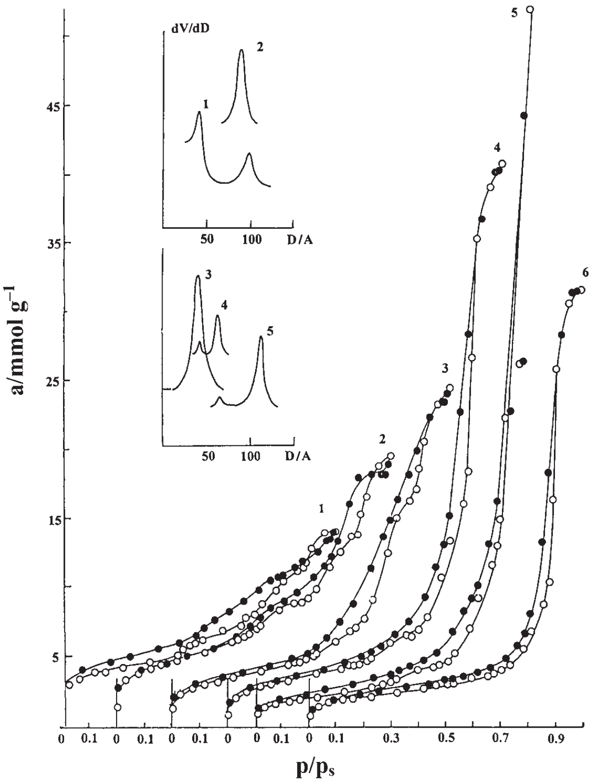

Fig. 1 Methanol ad(de)sorption isotherm obtained for samples 2 (1), 3 (2), 4 (3) synthesized in the presence of glucose oxidase. (Inset) Pore size distribution of samples 2 (1), 3 (2), 4 (3) calculated from methanol-desorption branch;
• – adsorption, o – desorption

In aluminosilicate system (Si:Al=8) in the presence of combination GO:CTMAB= 0.5 and 0.25 mesoporous substances with complex porous structure were obtained. Both samples exhibit similar isotherms (Fig. 1) with four hysteresis loops, which begin and end at similar values of p/p_s and pore size distributions exhibited 3 peaks, corresponding 3 effective sizes of mesopores in the 30–100 Å range (Table 1), but the sample obtained in the presence of GO:CTMAB=0.25 exhibits a wider pore size distribution. Both adsorption and desorption branches are steep from p/p_s=0.4 to p/p_s=0.5, such hysteresis loop may be given by cylindrically shaped capillaries which are open at both ends. The hexagonal structure of mesopores of such sizes (D=31 and 27 Å respectively) is confined by XRD pattern which are nearly identical, with both materials exhibiting three peaks which can be indexed on a hexagonal lattice is typical of MCM-41 materials. The first XRD line is d_{100}=40 and 38 Å respectively. Silicate and aluminosilicate mesoporous substances obtained as in the presence of only CTMAB so in the presence of its combinations with GO possess hexagonal array of uniform mesopores with D near 30 Å. The occurring of such pores is related to the templating role of CTMAB. It is confined by the fact that MCM-41 material obtained in the presence of the same quantity of CTMAB as in the case of combination GO:CTMAB=0.5 but without GO have the same V_{MES} and surface areas. When the quantity of CTMAB is smaller (GO:CTMAB=0.25) the pore volume and surface areas are also smaller. The form of another size pores is not clear. According to the form of hysteresis loops, corresponding these pores it may be assumed ink-bottles form of the capillaries.

The XRD-patterns of the samples 3–6, 9, obtained in the presence of combination L–CTMAB, L–ODA exhibited single peak at low angles (corresponding d-spacing are specified in Table 2).

It was shown (Fig. 2, Table 2), that in presence of only lecithin mesoporous substances are formed, that is supramolecular structures of lecithin molecules are a template in aluminosilicate framework formation. The self-assembly of L amphiphilic molecules in spheres, cylinders, bilayers and bicontinuous phase in a free solution is well investigated (under such reaction conditions L molecules form lamellar bilayer structures such as flat layers or closed vesicles) [12], but it is not absolutely clear how these aggregates are affected by presence of inorganic particles, and what structure have supramolecular vesicles, participating in templating process.

It was shown that using various combinations of lecithin and cetyltrimethylammonium bromide or octadecylamine as templating agents allowed to obtain mesoporous substances with pores up to 100 Å, as well as biporous materials in aluminosilicate system. The biporous materials obtaining indicates, that together with mixed micelles [13] in a reaction mixture other types of micelles (for example, micelles, consisting CTMAB or ODA, and also liposomes or disk-type structures of lecithin with small inclusion of CTMAB or ODA) will be formed.

It was known, that the structure of organic-inorganic composites is determined by organic-organic (OO) interactions forming array of organic molecules, organic-inorganic (OI) interactions on the appropriate interfaces, and inorganic-inorganic (II) interactions causing polymerization of inorganic particles [14]. It is clear that the role of each interaction types in porous structure formation depends on synthesis conditions, and also template nature. As the process of mesoporous substances obtaining includes a stage of OI composites formation, our data can be considered as confirmation of such representations.

The structure of preorganized lecithin and CTMAB or ODA molecule array forming aluminosilicate framework depends on a Si:Al ratio and pH of a reaction mixture (Fig. 2).

Important trends are revealed by a comparison of ad(de)sorption isotherms and the corresponding Kelvin pore size distributions for samples obtained at different

Si:Al ratio and pH in reaction mixture. The ad(de)sorption isotherms of mesoporous substances obtained when Si:Al=58 in reaction mixture have sharp increase at $p/p_{s}=0.8$, associated with large pores (up to 100 Å) and large adsorption pore volume. On ad(de)sorption isotherms of samples 8, 9, 11 with Si:Al=58 there is small riser at $p/p_{s}=0.5$–0.65 region appropriate to pores up to 55 Å. The ad(de)sorption isotherms of samples with Si:Al=8 exhibit several less sharp steps and therefore more irregular pore arrangement that indicating a wider pore size distribution and smaller total adsorption volume V_{Σ}. So the samples with Si:Al=58 have larger and more homogeneous pores, than sample with Si:Al=8. These distinctions are explained, on our sight, to that at Si:Al=58 and more basic pH the original array of lecithin molecules is disrupted upon strong ionic interactions with highly negatively charged aluminosilicate particles and then reorganized to a new configuration which is similar to cylindrical homogeneous on the size structures of CTMAB [8], formed at the basic synthesis of MCM-41 materials.

The reduction of structure ordering when Si:Al=8 may be explained not only by the increase of aluminium content, but also by that the slightly negatively charged

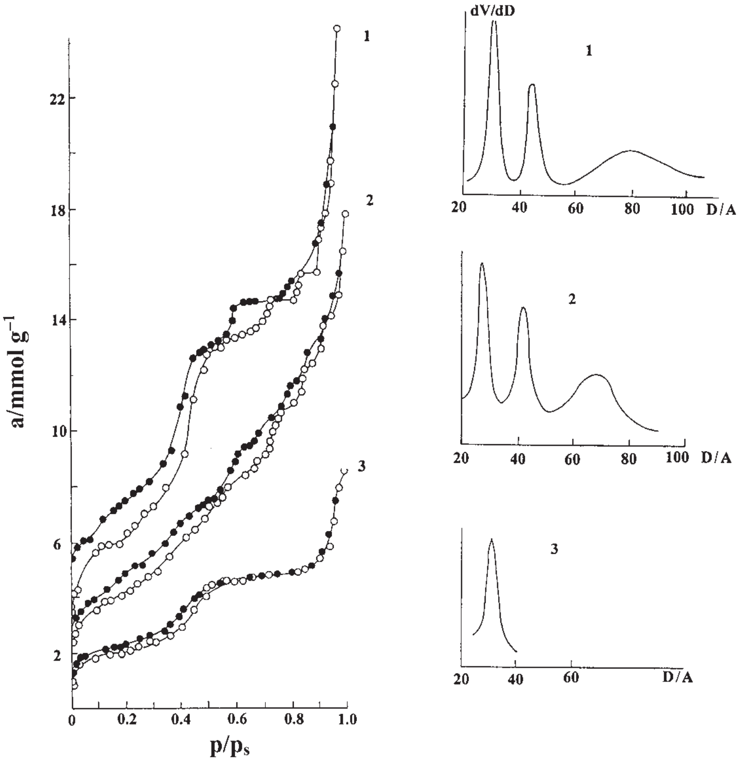

Fig. 2 Methanol ad(de)sorption isotherms obtained for samples 2(1), 3(2), 5(3), 9(4), 8(5), 11(6), prepared in the presence of lecithin. (Inset) Pore size distribution of samples 3(1), 9(2), 6(3), 5(4), 11(5) calculated from methanol-desorption branch

aluminosilicate particles insignificantly perturb self-organizing lecithin vesicles, having large disorder on the size. So hydrogen bonding, van der Waals and dipole interactions at the organic-inorganic interface rather than ionic form material structure. As supramolecular structures of lecithin participate in templating process, and interaction between aluminosilicate oligomers and template surface depends on the Si:Al ratio and pH of a reaction mixture, thus processes occurring in investigated substances structure formation are similar to biomineralization processes in the nature.

In general, lipid-based architectures are often labile, dynamic construction, compared with polypeptide assembles in which strong intersubunit interactions tend to give rise to rigid compact structures. It is that to allow us to obtained three narrow pore size distributions in the presence of glucose oxidase and wider distributions in the presence of lecithin.

The investigation of sorption of glucose oxidase on obtained aluminosilicate mesoporous substances was carried out (Table 3).

Table 3 Sorption of glucose oxidase on obtained aluminosilicate mesoporous substances

No.	Si:Al[a]	Template	*D*/ Å	V_{MES}/	V_{Σ}	*a*/ mg m^{-1}
				cm^3 g^{-1}		
1	8.1	–	up 60	0.26	1.07	27
			60–150	0.76		
2	58	–	up 60	0.14	1.07	43
			60–150	0.27		
3	8.1	CTMAB	34	0.48	0.64	130
4	58	CTMAB	34	0.92	1.44	64
5	8.1	L:CTMAB=0.47	36	0.36	0.77	66
			98	0.37		
6	58	L:CTMAB=1.40	80	1.28	1.33	151
7	58	:ODA=1.04	58	0.19	1.23	130
			114	0.56		
8	8.1	GO:CTMAB=1:2	31	0.52	0.84	42
			45	0.06		
			81	0.04		
9	8.1	GO:CTMAB=1:4	27	0.29	0.63	69
			42	0.09		
			68	0.09		

[a] Si:Al ratio in reaction mixture

In the case of mesoporous substances obtained in the presence of L–CTMAB and L–ODA combinations the greatest capacity (more than 100 mg g^{-1}) was exhibited by samples 10, 11 possessing the large pores with great adsorption volume. The samples 3 (Si:Al=8) obtained in the presence of lecithin and samples obtained in the presence of glucose oxidase (Si:Al=8) are characterized by low sorption capacity in spite of the high content of Al and presence of large pores, because of small adsorption volume of such pores.

Conclusions

It was established that mesoporous aluminosilicate materials have been prepared in the presence of supramolecular assembly of lecithin molecules and the formation of the porous structure materials occur in a manner similar to natural biomineralization processes. In the presence of various combinations of lecithin and cetyltrimethyl-ammonium bromide or octadecylamine as templating agents in aluminosilicate system mesoporous substances with a pore diameter up to 100 Å, and also biporous materials were obtained. This new, low-cost, environmentally friendly templating pathway leads to mesoporous materials with large pore volume and hybrid porous structure.

In the presence of glucose oxidase and cetyltrimethyl-ammonium bromide combinations aluminosilicate substances with complex porous structure were shown to be formed (pore size distributions exhibited 3 peaks, corresponding 3 effective size of mesopores in the 30–100 Å range).

The investigation of sorption of glucose oxidase on obtained aluminosilicate mesoporous substances was carried out, the results obtained allow us to consider such materials as prospect for creation high capable and selective sorbents for biomolecules sorption, as well as active elements of chemical and biosensors.

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