EFFECT OF PRECURSOR AND SURFACTANT NATURE ON GEOMETRICAL CHARACTERISTICS OF MESOPOROUS SILICAS

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Abstract

Bimodal mesoporous silicas and materials MCM-41 type were synthesized with the use as a template cationic surfactants distinguished by a length of the alkyl chain. Fumed silica, tetraethyl orthosilicate as well as of mixture these compounds were applied as a silicate precursor. Obtained samples have been characterized by the powder X-ray diffraction technique and adsorption measurements. Specific surface area, pore diameter, pore size distribution was determined from nitrogen ad(de)sorption isotherms at 77 K for the silicas prepared. The products with bimodal pore distribution have not ordered structure and contain macropores and mesopores, whose sizes are typical for MCM-41 materials. Effect of surfactant and precursor nature on the geometrical features of the ordered structure of MCM-41 type and bimodal porous materials was studied.

Introduction

The synthesis of periodic mesoporous materials of the M41S type had become available with the use of different surfactants as micellar templates. They play a role of the structure-directing agents [1] in an assembly process of the periodic mesoporous materials because surfactants have ability to self-organize into mesophases with the different dimensional structure: hexagonal, cubic or lamellar.

For preparation of the MCM-41 type silica materials a series of the surfactants $C_nH_{2n+1}(CH_3)_3N^+A^-$, where A^- - counterion, n=14, 16 or 18, were mostly used as a micellar template and sodium silicate, tetraethyl orthosilicate (TEOS), fumed silica were applied as a silica source. Synthesis of the material with a hexagonal array of pores is usually carried out for a few hours as well as some days [2]. It is conceivable that the formation of the silica framework can come from both as a result of monomeric silicate ions adsorption on the micelle surface and at the expense of using of the more bulky oligomeric silicate species. In the most cases the synthesis of mesoporous silicas was performed under the conditions of hydrothermal treatment, while the use of the condensed silicate species allows one to avoid this stage. The some differences in the structure of surfactant, nature of counterion A^-, value of the surfactant/silica molar ratio, contents of water lead to obtain of the porous materials with the bimodal pore size distribution, where the product obtained contains of mesopores, their sizes being typical for the MCM-41 material and the larger ones [3].

In this work we have continued a systematic research in the field of synthesis of the bimodal mesoporous materials with the purpose of study of an effect of the cationic surfactant chain length on geometrical parameters of the mesoporous silicas.

Experimental

For preparation of the mesoporous silica matrices the fumed silica (Aerosil, 300 m^2/g) and tetraethoxysilane were used as a silicate precursor. Quaternary ammonium salts hexadecyltrimethylammonium bromide (CTMABr), octadecyltrimethylammonium chloride (ODTMACl) and tetramethylammonium bromide (TMABr) were applied as micellar templates. These short- and long-chain surfactants were transformed into hydroxyl form with the use of the ion-exchange column filled by the AB-17-8 anionite in hydroxyl form.

Synthesis of aerosilogel – Sample 1. Fumed silica (280 g; 4.67 mol) was suspended in water (1250 ml; 69.44 mol) at the intensive stirring. Obtained suspension is allowed to stand for 24-28 hrs at room temperature, then it was dried up at 150ºC and calcined at 540ºC for 6 h on air.

Synthesis of mesoporous silicas with the use of the short- and long-chain surfactants: with TMABr/OH – Sample 2; with ODTMACl/OH – Sample 3; with CTMABr/OH – Sample 4. Weighed portion of the fumed silica (6.4 g, 0.11 mol – for Sample 2; 14.6g, 0.24 mol – for Samples 3 and 4) was dissolved in an aqueous solution of the appropriate quaternary amine hydroxide (15.4 wt % solution TMABr/OH; 8.7% solution ODTMACl/OH; and 9.1% solution CTMABrOH) at stirring. Surfactant/silica molar ratios are indicated in the Table. Obtained homogeneous milk-white mixtures were dried on air at room temperature up to formation of the gel-like products. Finally the samples were calcined at 540ºC for 6 h on air.

Synthesis of mesoporous silica with the use of mixture of the fumed silica and TEOS as a silicate precursor – Sample 5. 8.7 wt % aqueous solution ODTMACl/OH was added to the mixture of the fumed silica (7.4 g, 0.123 mol) and TEOS (24 ml, 0.107 mol) at stirring. The obtained caseous suspension is allowed to age on air up to formation of the solid product. The sample prepared was calcined at 540ºC for 6 h on air.

Synthesis of mesoporous silica with the use of TEOS as a silica source – Sample 6. TEOS (22.4 ml, 0.1 mol) was added at stirring to 3.48 wt % aqueous solution ODTMACl/OH. Obtained homogeneous milk-white mixture was subjected to aging on air up to the gel-like product formation and then was calcined at 540ºC for 6 h on air.

Synthesis of the MCM-41 materials with the use of CTMABr (Sample 7) and ODTMACl (Sample 8) as a micellar template. Samples were synthesized according to the following procedure. Weighed portion of the surfactant CTMABr (8.3 g, 0.023 mol) or ODTMACl (7.9 g, 0.023 mol) was dissolved in 43 ml of concentrated ammonia solution and intermixed to homogeneous milk-white mixture. After addition TEOS (9.67 ml, 0.043 mol) the mixture obtained was stirred up to gelation. The resulting products were dried up at air with following calcination at 540ºC for 6 h on air.

Characterization of the synthesized samples was performed by the powder X-ray diffraction (XRD) data (automated diffractometer DRON-3M, CuK_α radiation) and nitrogen adsorption isotherm measurements at 77K on ASAP-2000 Micromeritics equipment. Average pore diameter was estimated by Gurvich method (d=4V/S). The specific surface area, S_{BET}, was determined from the linear part of the BET equation (at p/p_s=0.05-0.35). Pore volume distribution was calculated from desorption branch of an isotherm of nitrogen adsorption using the Barrett-Joyner-Halenda (BJH) formula [4-6].

Results and discussion

It has been known that XRD technique allows one to reveal a presence of a dimensional self-organization in the mesoporous materials. The X-ray diffraction patterns of the Samples 7 and 8 exhibit distinct small-angle peaks in the range $2\theta=2\text{-}6^{o}$, which can be attributed to different *hkl* reflections and are characteristic of the well-ordered hexagonal structure. The XRD patterns for MCM-41 samples are shown in Fig.1. The XRD diffractograms for the rest synthesized mesoporous silicas are depicted in Fig.2.

The most complete and reliable information about mesoporous structure comes from the low-temperature N_2 ad(de)sorption isotherms [7]. Adsorption data for the synthesized samples are represented in Table.

Table. Geometrical characteristics of the synthesized mesoporous silicas.

Sample	Micellar template	Silicate precursor, mol		Medium, mol	Surfac-tant/ silica molar ratio	Pore diameter Å	BET surface area, m^2/g
		Fumed silica	TEOS				
1	-	1.0		H_2O, 14.9	-	208	253
2	TMABr/OH	1.0		H_2O, 12.0	0.22	209	205
3	ODTMACl/OH	1.0		H_2O, 23.2	0.10	98	388
4	CTMABr/OH	1.0		H_2O, 22.9	0.10	136	416
5	ODTMACl/OH	1.0	1.2	H_2O, 48.3	0.10	93	463
6	ODTMACl/OH		1.0	H_2O, 55.6	0.10	63	784
7	CTMABr		1.0	NH_4OH, 27.7	0.52	36	1171
8	ODTMACl		1.0	NH_4OH, 27.7	0.52	49	977

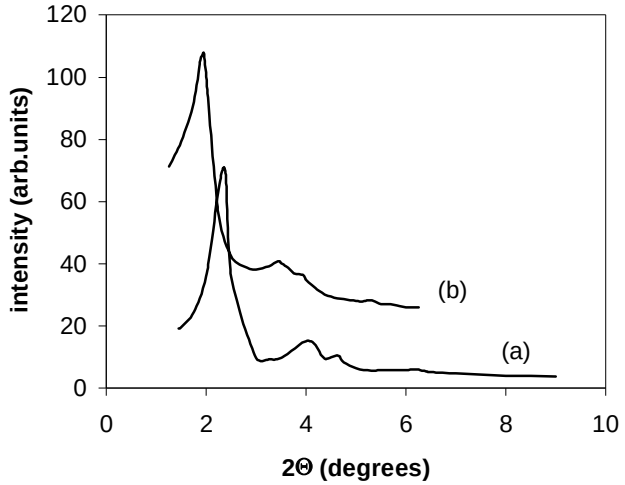

Fig. 1. X-ray diffraction patterns of the MCM-41 type silicas:
(*a*) – Sample 7; (*b*) – Sample 8.

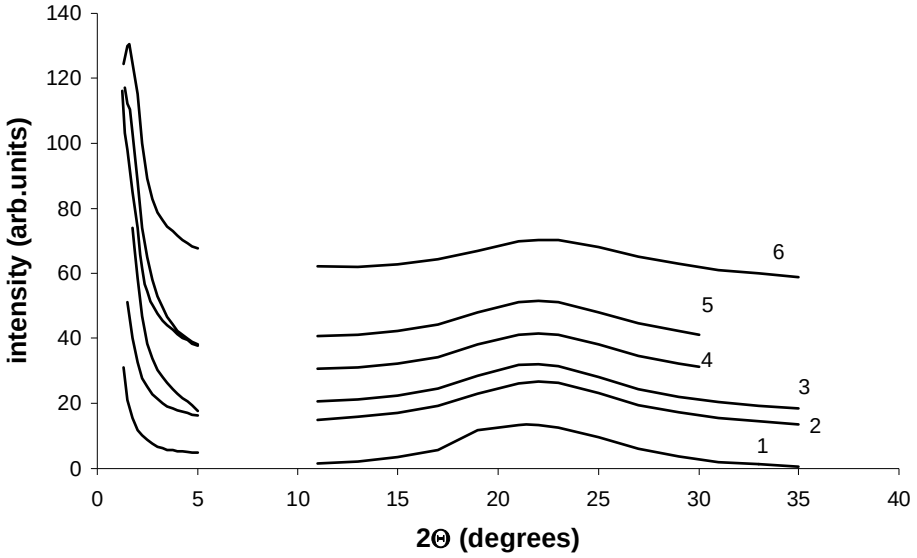

Fig. 2. X-ray diffraction patterns of the porous silicas (Samples 1-6).

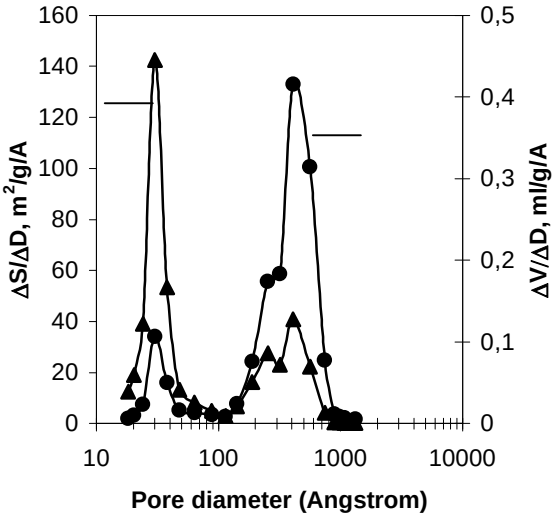

Fig. 3. Pore volume and pore surface area distributions for the Sample 3.

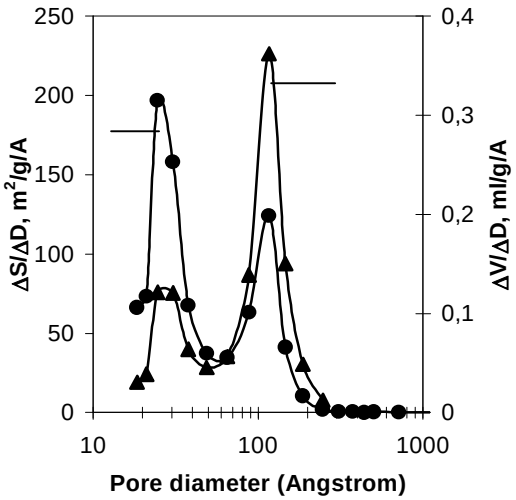

Fig. 4. Pore volume and pore surface area distributions for the Sample 6.

From the adsorption measurements and XRD data it follows that the carrying out of syntheses with the use of the fumed silica, TEOS, mixture of the fumed silica and TEOS as a silicate precursor and the cationic long-chain surfactants as a micellar template permits one to obtain mesoporous materials. These samples have specific surface areas, which exceed in different extent of S_{BET} for the aerosilogel.

At the use of the short-chain surfactant (TMABr) the amorphous macroporous silicas with low specific surface area are formed (Sample 2). In fact, in line with the data [8, 9] surfactant molecules with a number of carbon atoms in alkyl chain less 7 do not form micelles

in aqueous solutions, and consequently, supramolecular templates are absent under these synthetic conditions.

Bimodal pore distribution and an increase of specific surface area approximately up to 400 m^2/g were observed for the Sample 3 (Fig. 3) and Sample 4 (see previous our work [6]), prepared with the use of the long-chain surfactants ODTMACl/OH, CTMABr/OH and the fumed silica as a silicate precursor. For the Sample 3 there are two maxima on a curve of pore distribution at 33 and 434Å. The pore diameter 33Å in this sample corresponds to the pore size of the MCM-41 type materials, however in XRD pattern of this sample we do not find a presence of the reflections at small angles, which are characteristics of the well-ordered hexagonal structure. At the same time the most considerable increase of surface is attributed to these pores. The curve of pore distribution for Sample 4 reveals two maxima at 30 and 300Å and hexagonal dimensional packing is also absent. In view of the fact that mesopore sizes for the Sample 4 are smaller compared with those for the Sample 3, consequently the increment of surface attributed to these mesopores for the former sample is larger as compared with the Sample 3. The difference in mesopore sizes can be related to an effect of the alkyl chain length in the molecules of applied cationic surfactants. Other authors [9, 10, 11] have also detected a similar influence of a chain length in the template molecule on the pore size.

Application of a mixture of the fumed silica and TEOS as an inorganic precursor at the molar ratio of surfactant/silica=0.1 does not improve of structural features of the Sample 5, though a small increase of specific surface area is observed. The Sample 6, synthesized from TEOS and ODTMACl/OH at the same molar ratio of surfactant/silica, reveals the bimodal pore distribution (Fig. 4) as well as high specific surface area (784 m^2/g). XRD pattern of this mesoporous silica exhibits only the small-angle peak because of the poorly ordered pore system [11]. It may well be that at the realization of the bimodal mesoporous materials synthesis at the lower molar ratio of surfactant/silica the primary particles are small and spherical in the shape due to insufficient silicate polymerization. Thereafter these particles coalesce to form a secondary porous structure.

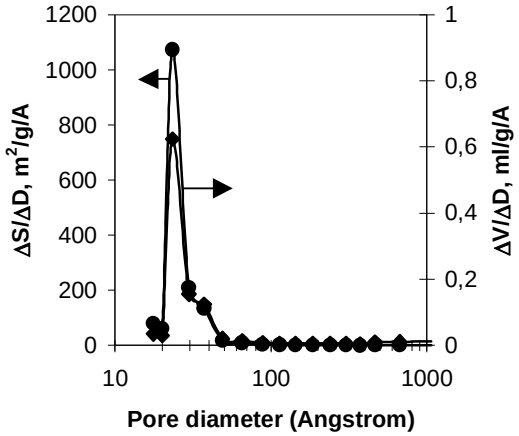

Fig. 5. Pore volume and pore surface area distributions for the Sample 7.

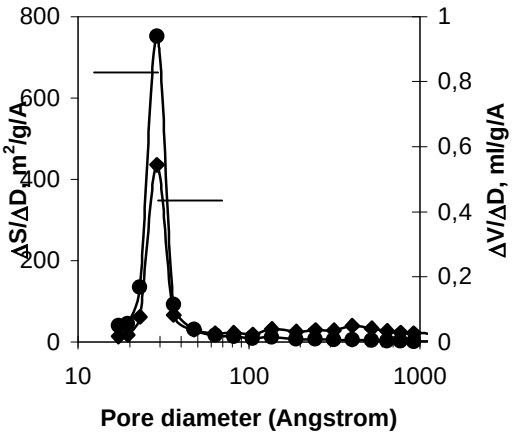

Fig. 6. Pore volume and pore surface area distributions for the Sample 8.

At an increase of a molar ratio of surfactant/silica to 0.52 the organic template molecules self-organize into micellar structures, which are optimum for preparation of the ordered mesopores materials in the basic media. From adsorption data and XRD results it appears that in this case the highly ordered MCM-41 materials, possessing by the uniform pore size structure (35-50Å) and extraordinary high specific surface area (980-1170 m^2/g), can be obtained. The curves of pore distributions for the Samples 7 and 8 are represented in Figs. 5 and 6 respectively. It is characteristically that an effect of the alkyl chain length of surfactant on pore size of the synthesized mesoporous materials is also observed.

Hence, it can be stated that in the systems ODTMACl-TEOS and CTMABr-TEOS in the NH_4OH media the optimum geometrical and energy accordance is realized for preparation MCM-41 products owing to the rigid silicate framework is formed around supramolecular structures of the cationic surfactant.

Conclusion

The obtained results testify about essential effect of the surfactant and silicate precursor nature on the geometrical parameters of mesoporous silicas. An use of tetraethyl orthosilicate and fumed silica as a silica precursor, hexadecyltrimethylammonium bromide and octadecyltrimethylammonium chloride as a micellar template at the molar ratio surfactant/silica is equal 0.10 results in the bimodal mesoporous materials involved macropores as well as mesopores and having non-ordered hexagonal structure. Synthesis of products exhibiting the typical highly-ordered MCM-41 materials structure with the exclusively narrow mesopore distribution, hexagonal symmetry of the porous framework and high specific surface was executed at an increase of the molar ratio surfactant/silica to 0.52.

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