

BILE ACID-ASSISTED SOL-GEL SYNTHESIS OF MESOPOROUS SILICA MATERIALS

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Mesoporous silicas of MCM-41 type belong to the most studied inorganic materials due to their beneficial properties. High specific surface area, large pore volume, narrow pore size distribution, well-defined hexagonal structural ordering of homogeneous pore channels along with high thermal stability, biocompatibility, easy morphology control and surface functionalization open up great perspectives of MCM-41 application in the field of catalysis, adsorption, separation, sensing, and biomedicine. Structural parameters of MCM-41 can be easily optimized in accordance with the assigned tasks by variation of synthetic conditions and chemical composition of reaction mixture. As condensation of structure-forming silanes proceeds around supramolecular surfactant assemblies, template plays extremely important role in directing the formation of arranged MCM-41 framework.

In the present study, the ability of organic additives incorporated into the micelles of long-chain quaternary ammonium template, cetyltrimethylammonium bromide, to affect structural parameters of MCM-41 was studied on example of cholic acid (CA) as structure-directing and CA-silane (CAS) as structure-forming agent. Solubilization of amphiphilic additives like bile acids by surfactant micelles causes changes in composition, critical micelle concentration, and geometry configuration of supramolecular aggregates. Molecules of CA and CAS introduced in surfactant solution integrate into the micelles of surfactant due to the electrostatic and hydrophobic forces and interact simultaneously with micellar and extra-micellar environment at sol-gel synthesis. Structural characteristics of CA-NH₂-MCM-41 and CAS-NH₂-MCM-41 obtained by sol-gel condensation of tetraethyl orthosilicate and (3-aminopropyl)triethoxysilane in the presence of CA and CAS, correspondingly, were studied by low-temperature nitrogen adsorption-desorption and x-ray diffraction analysis.

As can be seen from Figure 1, introduction of CA and CAS in sol-gel synthesis results in transformation of isotherm profiles from type II with hysteresis loop of the type H3 for NH₂-MCM-41 to the type IV with hysteresis loop of the type H3 for CA-NH₂-MCM-41 and CAS-NH₂-MCM-41.

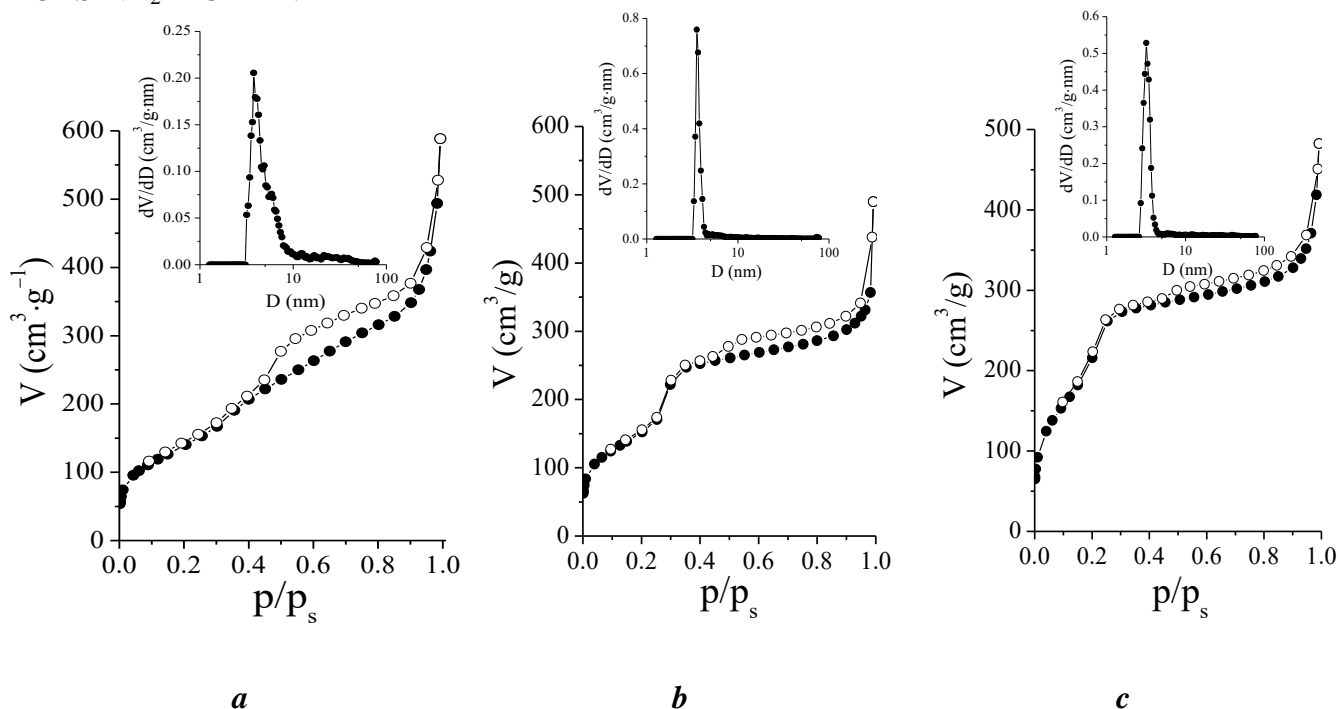


Fig. 1 Low-temperature nitrogen adsorption-desorption isotherms and pore size distributions (inserts) for NH₂-MCM-41 (a), CA-NH₂-MCM-41 (b), and CAS-NH₂-MCM-41 (c)

Such changes confirm improvement of hexagonally arranged mesoporous structure typical for MCM-41 due to addition of amphiphilic substances in sol-gel synthesis. Linear increase in nitrogen adsorption on isotherms obtained for CA-NH₂-MCM-41 and CAS-NH₂-MCM-41 is followed by its sharp rise at relative pressures from 0.25 to 0.35, which is characteristic of capillary condensation proceeding within uniform mesopores. Structural parameters calculated from the results of low-temperature nitrogen adsorption-desorption (Table) prove that introduction of CA as co-temple or CAS as structure-forming agent in sol-gel synthesis causes substantial increase of surface area and narrowing of pore diameter, which is more pronounced in the case of CAS.

The x-ray diffraction analysis of synthesized silica materials confirms that introduction of CA and CAS in sol-gel synthesis results in CA-NH₂-MCM-41 and CAS-NH₂-MCM-41 silicas with improved hexagonally ordered mesoporous structure. The position of (100) reflexes are registered at 2.15 and 2.25 deg, whereas, their intensities are increased as compared to NH₂-MCM-41 (Fig. 2). Moreover, in the case of CAS-NH₂-MCM-41 intensities of higher-angle reflections belonging to the (110), and (200) planes are noticeably enhanced to. This fact indicates that CAS-NH₂-MCM-41 organosilica has more uniform hexagonally ordered mesoporous structure in comparison with parent amino silica and synthesized in the presence of CA one.

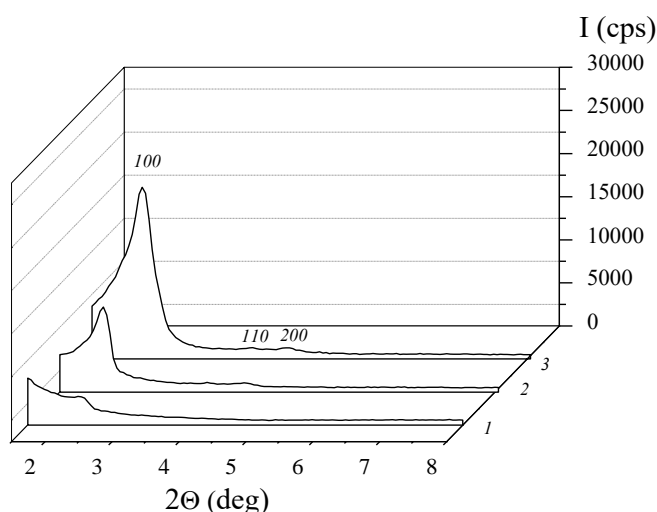


Fig. 2 X-ray diffraction patterns of NH₂-MCM-41 (curve 1), CA-NH₂-MCM-41 (curve 2), and CAS-NH₂-MCM-41 (curve 3)

Table

Structural parameters of mesoporous silica materials.

Silica	Low-temperature nitrogen adsorption-desorption			X-ray diffraction analysis			
	S _{BET} (m ² /g)	V (cm ³ /g)	D (nm)	d ₁₀₀ (nm)	a (nm)	D (nm)	B (nm)
NH ₂ -MCM-41	515	0.91	3.78	3.93	4.53	3.89	0.64
CA-NH ₂ -MCM-41	550	0.76	3.54	4.11	4.75	3.94	0.81
CAS-NH ₂ -MCM-41	740	0.75	3.18	3.93	4.53	3.76	0.77

The results of low-temperature nitrogen adsorption-desorption and x-ray diffraction analysis confirm that CA additive as component of structure-directing micelles and CA-containing silane as structure-forming agent have positive impact on formation of hexagonally ordered mesoporous structure of MCM-41-type silicas. This fact can be explained by tight interactions arising between hydrophobic parts of introduced compounds and long alkyl chains of cationic surfactant on the one side and between hydrophilic groups of additives and growing anionic oligomers of orthosilicic acid on the other side. Synthesized silica materials have hexagonally arranged porous structure with relatively narrow distribution of cylindrical channels and can be considered as promising adsorbents and carriers of biologically active compounds.