

MCM-41 SILICAS WITH HIGH CONTENT OF SURFACE 3-AMINOPROPYL GROUPS

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In recent years, organosilica materials of MCM-41-type with high specific surface area, large pore volume, size-tunable mesopores, and low toxicity have attracted a great interest for a variety of applications such as adsorption, catalysis, sensing, and drug delivery. Among them, nanoparticles of aminofunctionalized MCM-41 have gained considerable research attention due to several attractive features like relatively straightforward preparation, easy regulation of amino groups coverage, and ability to undergo a wide range of reactions. Postsynthetic modification of MCM-41 by (3-aminopropyl)triethoxysilane leads to the preferable immobilization of functional groups on external surface and near by pore orificies of carrier. It causes the decrease of pore diameter, surface area and pore volume of resulting material. Contrariwise, direct co-condensation of structure forming silanes around template aggregates in the process of sol-gel synthesis circumvents the problem of pores accessibility. However, materials with high content of organic functionalities prepared via this method possess less ordered mesoporous structure. This is caused by the necessity for addition of increasing amounts of organosilane precursor into the synthesized gel to attain high density of surface 3-aminopropyl groups that, as consequence, significantly disrupt the process of synthesis. As high surface area, large pore volume, hexagonally ordered uniform pores and controllable density of functional groups are crucial parameters of structurally stable silica matrix required for its successful application, the development of improved one-pot co-condensation strategy is of grate importance.

In the present work, we propose simple method of synthesis of mesoporous silica nanoparticles (MSN) with high content of surface 3-aminopropyl groups and well-defined hexagonally ordered mesoporous structure by hydrothermal sol-gel condensation of tetraethyl orthosilicate and (3-aminopropyl)triethoxysilane in the presence of cetyltrimethylammonium bromide as pore generating agent and azo dye, alizarin yellow (AY), as cosurfactant. In accordance with the analysis of low-temperature adsorption-desorption of nitrogen, addition of increasing amounts of (3-aminopropyl)triethoxysilane in sol-gel process causes drastic decrease of surface area and pore volume of synthesized material (Table). At the same time, results of x-ray powder diffraction analysis prove that partial loss of long-range ordering of porous structure takes place. Introduction of azo dye in sol-gel reaction mixture contributes into the formation of highly ordered arrays of cylindrical mesopores, and strongly affects specific surface area, pore volume and pore size of synthesized aminosilica nanoparticles (Table).

Table. Parameters of porous structure and content of surface 3-aminopropyl groups of organosilica materials

Silica	S, m ² /g	V, cm ³ /g	D, nm	[–NH ₂],	
				mmol/g	μmol/m ²
4%-NH ₂ -MSN-C ₁₆	515	0.91	3.93; 5.09	0.28	0.54
10%-NH ₂ -MSN-C ₁₆	343	0.65	3.66; 5.09	0.76	2.22
4%-NH ₂ -AY-MSN-C ₁₆	622	1.06	3.93; 5.29	0.22	0.35
10%-NH ₂ -AY-MSN-C ₁₆	339	0.75	3.66; 5.09	0.70	2.06
50%-NH ₂ -AY-MSN-C ₁₆	406	0.72	5.09	1.17	2.88