

# MESOPOROUS SILICAS: MORPHOLOGY CONTROL AND TEMPLATE SYNTHESIS INSIDE LARGE PORES OF SILICA GEL

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**Abstract.** The influence of pH, nature of alcohol and initial components concentrations in micellar solution on the structural-adsorption characteristics of spherical mesoporous silicas has been investigated. The peculiarities of template synthesis of mesoporous silicas inside large pores of silica gel were also studied. Synthesized silicas were characterized by low-temperature nitrogen adsorption-desorption, X-ray diffraction and scanning electronic microscopy.

**Keywords:** Mesoporous silica, template synthesis, spherical particles, MCM-41, nanoporous reactor.

## 1. Introduction

The use of supramolecular micellar templates for synthesis of ordered mesoporous materials is considered as one of the most important discoveries in the field of materials science. The ability of this approach to design nanoscale pore structure is being intensively investigated with the aim to create new type of catalysts and adsorbents.<sup>1,2</sup> Pore structure control and regulation of macroscopical shape of mesoporous silicas are the current trends in the template synthesis of ordered porous materials.<sup>3-5</sup> Besides, the improvement of MCM-41 silicas mechanical stability is a significant parameter for MCM-41 application. In the present paper the optimal conditions for synthesis of mesoporous silicas with spherical morphology of particles were determined. It was also proposed an approach for improvement of mechanical properties of the nano-materials by carrying out template synthesis of mesoporous silicas inside pore volume of silicas with more stable porous structure.

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## 2. Experimental

### 2.1. SYNTHESIS OF MESOPOROUS SILICAS WITH SPHERICAL MORPHOLOGY OF PARTICLES

Syntheses were carried out in the alcohol-ammonia media by the modified Stöber method<sup>6</sup> in ethanol and isopropanol using tetraethoxysilane (TEOS) as a silica precursor and cetyltrimethylammonium bromide (CTAB) as supra-molecular template with the molar ratio of components 1TEOS:  $x$ CTAB: 11NH<sub>3</sub>: 144H<sub>2</sub>O : 58ROH, where  $X = 0.1, 0.2$  and  $0.3$ . Synthesis in the acidic media was held using TEOS and CTAB with the molar ratio of components 1TEOS: 0.1CTAB: 0.45HCl: 100H<sub>2</sub>O.

### 2.2. SYNTHESIS OF MESOPOROUS SILICAS IN NANOREACTORS BASED ON LARGE PORES OF SILICA GEL

Step-by-step incorporations of micellar solutions inside pore volume of silica gel with the surface area about 115 m<sup>2</sup>/g and the average pore diameter about 24 nm were made. Micellar solution with molar ratio of components 1TEOS: 0.18CTAB: 5NH<sub>3</sub>: 75H<sub>2</sub>O was prepared according to procedure.<sup>7</sup>

After template elimination the synthesized materials were characterized by low-temperature adsorption-desorption of nitrogen (ASAP-2000) to estimate surface area (BET equation), pore size distribution (BJH method). Structure of samples was determined by X-ray diffraction at small angles. Scanning electronic microscopy was used to investigate particle size and morphology of the synthesized silica materials.

## 3. Results and Discussions

### 3.1. SYNTHESIS OF MESOPOROUS SILICAS WITH SPHERICAL MORPHOLOGY OF PARTICLES

Nitrogen adsorption-desorption isotherms for silicas synthesized in the alcohol-ammonia media using ethanol at different molar ratios to CTAB/TEOS are type IV in the IUPAC classification.<sup>8</sup> In the interval of relative pressures  $p/p_0 = 0.15-0.27$  the range of capillary condensation with steep increase in the adsorbed nitrogen is observed. Surface areas of the synthesized silicas were 700–1,200 m<sup>2</sup>/g, pore sizes determined by the BJH-method are 2.5–3.0 nm. Nitrogen adsorption-desorption isotherms for the silicas synthesized in the alkaline media with use of isopropanol with molar ratio of CTAB/TEOS = 0.2 and 0.3 are also the type IV in the IUPAC classification, surface areas of synthesized

samples are 400–500 m<sup>2</sup>/g. Nitrogen adsorption isotherm for silicas synthesized in acidic media is the type I in IUPAC classification, surface area of synthesized sample is 600 m<sup>2</sup>/g (Figure 1).

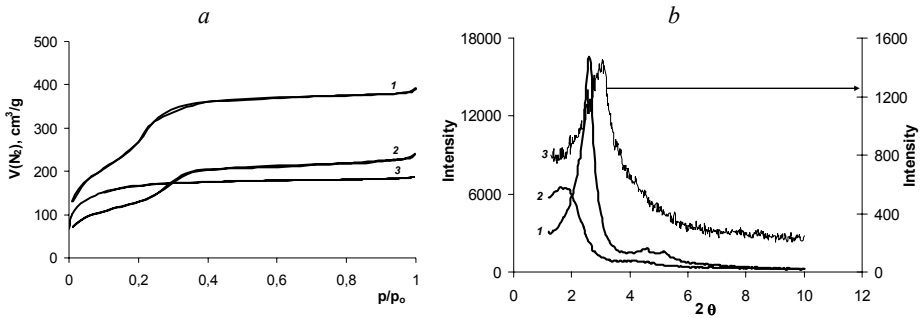


Figure 1. Nitrogen adsorption-desorption isotherms (a) and diffractograms (b) for silicas synthesized in the alkaline media using ethanol (1) or isopropanol (2) in acidic media (3).

X-ray powder patterns of silicas synthesized in ethanol with ratio of TEOS/CTAB = 0.3 and 0.2 show three Bragg peaks in the range of  $2\theta = 2.5\text{--}7.0$  with (100), (110) and (200) indexes, characterizing the periodic structures with the hexagonal pore orientation. X-ray powder patterns of silicas synthesized in isopropanol with molar ratio of CTAB/TEOS = 0.2 and 0.3 have only one marked peak. Lattice parameter  $a_o$  (a distance between cylindrical pore centers) is estimated by  $a_o = 2d_{100}/3^{0.5}$ . Pore thickness is determined according to the formula  $h = a_o - d_p$ , where  $d_p$  – a pore diameter determined by the BJH-method; and the values of  $h$  are 1.4–2.0 nm that are typical for the MCM-41 silicas.<sup>9</sup> X-ray powder patterns of silicas synthesized in acidic media have only one peak characterizing a weakly ordered pore structure (Figure 2). Structural-adsorption characteristics of the materials synthesized in the alcohol-ammonia media are presented in the Table 1.

TABLE 1. Structural-adsorption characteristics of materials synthesized in the alcohol-ammonia media.

CTAB/TEOS molar ratio	Alcohol	Structure	$a_o$ (nm)	$d_p$ (nm)	Surface area (m <sup>2</sup> /g)
0.1	Isopropanol	Disordered	–	3.4	166
0.2	Isopropanol	Disordered	–	3.0	505
0.3	Isopropanol	Disordered	–	3.1	458
0.1	Ethanol	Weakly ordered	5.2	3.0	701
0.2	Ethanol	Hexagonal ordered	4.0	2.7	1,227
0.3	Ethanol	Hexagonal ordered	3.9	2.5	946

Scanning electronic microscopy results for silicas synthesized with molar ratio of CTAB/TEOS = 0.3 testify the unimodal spherical particles of 0.5 $\mu$  size. The silicas synthesized in hydrochloride acid, unlike the alkaline media samples, have larger particle diameter and SEM-photos show spherical particles of 10 $\mu$  size (Figure 3). The final particles size depends on the rates of precursor silica hydrolysis and further polycondensation of hydrolysis products. In the alkaline media fast hydrolysis and polycondensation provide the formation spherical particles after two-hours stirring. On the contrary, slow condensation rate in the acidic media is favor for the larger size particles growth. Mesophase formation in the acidic media is possible due to halide anions coordination of positive charged micellar aggregates and silica surface. Such weak interactions are considered to provide the organization of weakly ordered pore structure. In the alkaline media pore structure formation is a result of direct interaction between silica macroanions and positive charged CTAB micelles. Thus, in the alcohol-ammonia media mesoporous silicas with the ordered hexagonal pore structure and high specific surface area have been synthesized.

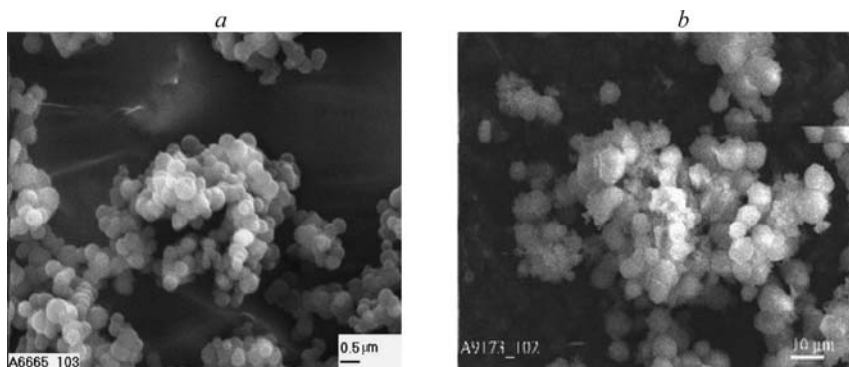


Figure 2. SEM-photos of silicas synthesized in the ethanol-ammonia media with molar ratio of CTAB/TEOS = 0.3 (a) and in the acidic media with molar ratio of CTAB/TEOS = 0.1 (b).

Particles of unimodal spherical granulation have been obtained in ethanol using molar ratio of CTAB/TEOS = 0.2 and 0.3. Porous silicas with weakly ordered pore structure and spherical particles of 10  $\mu$  size have been synthesized in the acidic media.

### 3.2. SYNTHESIS OF MESOPOROUS SILICAS INSIDE NANOREACTORS BASED ON LARGE PORES OF SILICA GEL

Nitrogen adsorption-desorption isotherm for silica gel is a type III in the IUPAC classification,<sup>8</sup> has a hysteresis loop at high relative pressure and reveals the existence of large pores in the sample. Nitrogen adsorption-desorption isotherms

of silica gel after template syntheses inside nanopores are characterized by appearance of capillary condensation ranges ( $0.3 < p/p_0 < 0.4$ ) and testify the mesopores presence. The sharpness of these sections was increased after each template synthesis and accompanied with decreasing of hysteresis loop that can be explained by filling of silica gel pore volume with mesoporous silicas.

Specific surface area of the initial silica gel is  $115 \text{ m}^2/\text{g}$  (by the BET-equation) and the BJH pore size distribution curve for silica gel has a broad peak in the range of pore size 30–50 nm (Figure 3, curve 1). Samples with incorporated mesoporous silicas are characterized by increase in specific surface area from 115 up to  $377 \text{ m}^2/\text{g}$  (Figure 3a). Pore size distributions curves exhibit the presence of peaks corresponding to pores of 2.5 nm size (Figure 3c).

Absence of any peaks in the X-ray powder patterns of initial silica gel confirms its amorphous nature (Figure 3b, curve 1). It is clear from X-ray diffraction patterns that introduction of micellar solution increases the reflections' intensity in the low-angle region (Figure 3b, curves 2–7). Broad low angle diffraction peak should result from the formation of wormlike pore structure and weak intensity of reflection can be explained by small quantity of incorporated silicas (20% of sample total weight after the sixth introduction of

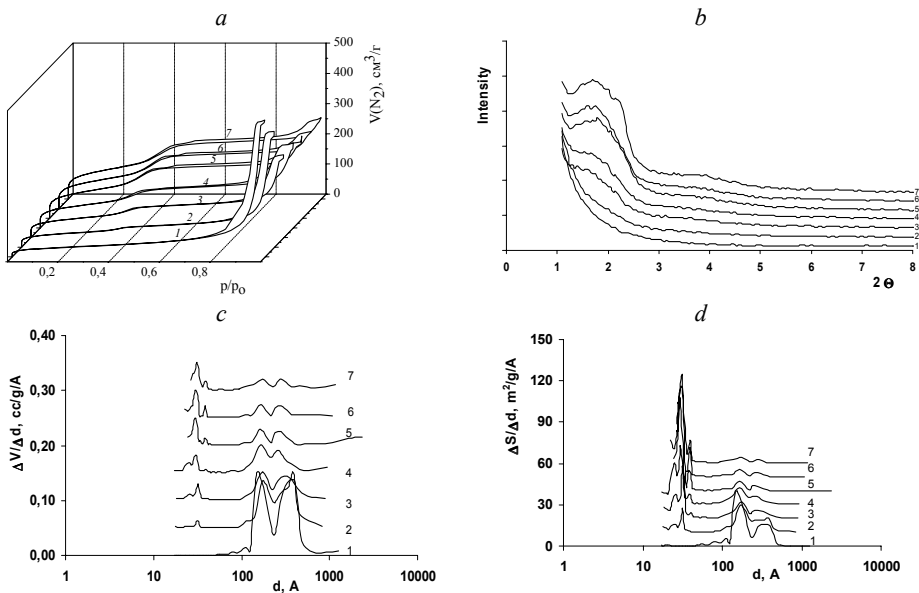


Figure 3. Nitrogen adsorption-desorption isotherms (a), diffractograms (b) and differential curves of dependence of pore size on pore volume (c) and surface area (d) for silicas synthesized inside large pores of silica gel: initial silica gel (1) and silica gels after the first (2), the second (3), the third (4), the fourth (5), the fifth (6), the sixth (7) introducing of MCM-41.

TABLE 2. Structural-adsorption characteristics of synthesized silicas (where  $S_{\text{BET}}$  – specific surface area by BET-equation;  $S_t$  – total surface area,  $S_{\text{ex}}$  – external surface area,  $S_p$  – pore surface area,  $V_p$  – pore volume,  $V_c$  – core volume and  $r_p$  – mesopore radius estimated by  $\alpha_s$ -analysis ).

N	Samples	$S_{\text{BET}}$ ( $\text{m}^2/\text{g}$ )	$\alpha_s$ -analysis					
			$S_t$ ( $\text{m}^2/\text{g}$ )	$S_{\text{ex}}$ ( $\text{m}^2/\text{g}$ )	$S_p$ ( $\text{m}^2/\text{g}$ )	$V_p$ ( $\text{cm}^3/\text{g}$ )	$V_c$ ( $\text{cm}^3/\text{g}$ )	$r_p$ (nm)
1	Initial silica gel	115	116	–	–	0.615	–	–
2	Silica gel after the first introduction of micellar solution	170	173	–	–	0.54	0.018	–
3	Silica gel after the second introduction of micellar solution	233	237	–	–	0.34	0.033	–
4	Silica gel after the third introduction of micellar solution	283	289	11.56	277	0.32	0.060	1.3
5	Silica gel after the fourth introduction of micellar solution	349	347	5.78	341	0.34	0.079	1.3
6	Silica gel after the fifth introduction of micellar solution	362	364	5.78	358	0.35	0.098	1.4
7	Silica gel after the sixth introduction of micellar solution	377	376	5.78	370	0.36	0.105	1.4

micellar solution). Structural-adsorption characteristics of synthesized silicas were estimated by  $\alpha_s$ -analysis.<sup>8,10</sup>

Elaborated synthetic procedures are systematic combination of template synthesis and conventional sol-gel process. Syntheses were realized via two stages: at the first stage silica gel was impregnated with micellar solution and at the second stage ammonia was added in order to catalyze hydrolysis and condensation of TEOS to provide mesoporous silicas formation. The main condition for successful template synthesis inside pores of silica gel matrix was a high value of TEOS/H<sub>2</sub>O molar ratio. Template synthesis of mesoporous silicas with pore diameter of 2.5 nm were carried out inside nanoreactors based on large pores of silica gel. Specific surface area of initial silica gel was 115 m<sup>2</sup>/g and after micellar solution introducing the calcined samples had surface area about 377 m<sup>2</sup>/g.

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