

ROLE OF IONENE IN COMPOSITION OF POROUS STRUCTURE OF TEMPLATE-SYNTHESIZED SILICAS

I. S. Berezovska^{1*}, V. V. Yanishpolskii¹, V. A. Tertykh¹, M. V. Burmistr² and K. M. Sukhyi²

¹Institute of Surface Chemistry of National Academy of Sciences of Ukraine, Gen. Naumov Str. 17, 03164 Kyiv, Ukraine

²Ukrainian Technical University of Chemical Technologies, Dnipropetrovsk, Ukraine

Effect of the presence of I-4 Me-Ph ionene in the supramolecular template (cetyltrimethylammonium bromide) on formation of porous structure of silicas has been studied. As-synthesized nanocomposites were characterized by using thermal analysis. Nitrogen adsorption-desorption measurements, X-ray diffraction and scanning electronic microscopy were applied to determine adsorption-structural characteristics and morphology of particles of the mesoporous templated silicas prepared in basic media.

Keywords: ionene, mesoporous silica, micellar template, particle morphology, porous structure

Introduction

Template synthesis of silicas with controlled porosity and adjusted morphology of particles has been intensively investigated because of their applications in separation processes, catalysis and sensor technologies [1, 2]. A variety of micellar templates have been used for porous structure design in silicas synthesized by the hydrolytic sol-gel route [3]. Ionic surfactants with different lengths of hydrocarbon chain are the most widely applied to form mesoporous structure because of the possibility of their self-assembly into the charged micelles. The bonding of silica on the micelle surface is realized due to complementary electrostatic interactions between inorganic ions and charged head groups of surfactants. Ordered porous structure of silicas is formed after template elimination by calcination of sol-gel products. At the same time for the solving of some practical questions it is important to control of silica synthesis at a macroscopic level. In particular, the method of preparation of MCM-41 silica with high specific surface area and spherical morphology of particles was offered [4–6] based on the modified Stober synthesis [7] using tetraalkoxysilane hydrolysis in alcohol-ammonia media in the presence of cationic surfactant – cetyltrimethylammonium bromide.

There has been considerable interest in studying the influence of polymers with high charge density, especially organic polymers with a quaternary nitrogen atom (polycations, ionenes), on the composition of the porous structure of template-synthesized silicas. Recently silica-polyviologen hybrids have been prepared [8–11] by hydrolytic sol-gel synthesis.

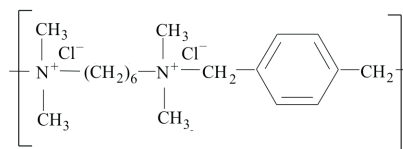
After calcinations, silicas with specific surface area of 240–400 m² g⁻¹ and disordered mesoporous structure were obtained.

The aim of the present work is to study the effect of pure ionene and ionene incorporated into a micellar template on the porous structure and particle morphology of silicas obtained by calcination of sol-gel products.

Experimental

Tetraethoxysilane (TEOS) was applied as a silica precursor. Hydrolysis was carried out according to the modified Stober method in alcohol-ammonia media with application of different structure-directing reagents with the following molar ratio of components: 1TEOS:0.3X:11NH₃:144H₂O:58C₂H₅OH, where X is the structure-directing reagent.

The following structure-directing reagents were used: (a) cetyltrimethylammonium bromide (CTAB); (b) mixtures of CTAB with various amounts of I-4 Me-Ph ionene; (c) pure ionene of the general formula:



Constant molar silica/template ratio of 0.3 was kept for all syntheses. The template synthesis is governed by Coulombic interactions between silicate anions and positively charged nitrogen atoms on

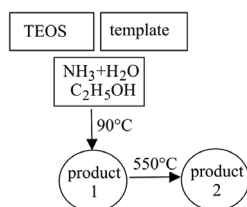
* Author for correspondence: berinna2003@rambler.ru

micelle surface. Therefore, we have taken into account the fact that the CTAB molecule contains one quaternary atom of nitrogen and that one monomer link of the used ionene includes two positively charged nitrogen atoms. Compositions of the applied templates are represented in Table 1.

Table 1 Compositions of micellar templates in sol–gel syntheses of silicas

| Template | Molar ratio of template/TEOS | I-4 Me-Ph/mol% |
|----------------|------------------------------|----------------|
| CTAB | 0.3 | – |
| CTAB+I-4 Me-Ph | 0.3 | 1 |
| CTAB+I-4 Me-Ph | 0.3 | 10 |
| CTAB+I-4 Me-Ph | 0.3 | 33 |
| I-4 Me-Ph | 0.3 | 100 |

The synthetic procedures used are represented by the following general scheme:



Synthesis of silica with the use of CTAB as a template

CTAB (2.5 g, 0.007 mol) was dissolved in distilled water (50 cm³), then 25% ammonia (20 cm³, 0.2 mol) and 96% ethanol (80 cm³, 1.3 mol) were added. The solution obtained was stirred for 15 min and TEOS (5 cm³, 0.22 mol) was introduced. The gel was stirred for 2 h at room temperature and the white precipitate formed was filtered and washed with water (100 cm³) and ethanol (100 cm³). To evaporate residual water, the washed sample was dried for 5 h at 90°C and calcined in air at 550°C for 5 h to completely remove organic compounds.

Synthesis of silica with use of mixtures of CTAB with the different amounts of I-4 Me-Ph ionene as a template

Weighed portions of polymer (0.012, 0.12 and 0.4 g) and CTAB (2.47, 2.3 and 1.74 g; 0.0069, 0.0063 and 0.0047 mol) were dissolved in distilled water (50 cm³). 25% ammonia (20 cm³, 0.2 mol) and 96% ethanol (80 cm³, 1.3 mol) were added to each solution and stirred for 15 min. After addition of TEOS (5 cm³, 0.022 mol) the mixtures were stirred for 2 h at room temperature, filtered and washed with water (100 cm³) and ethanol (100 cm³). The resulting products were dried for 5 h at 90°C and followed by calcination for 5 h at 550°C.

Synthesis of silica with the use of ionene as a template

Ionene (1.2 g) was dissolved in distilled water (50 cm³). After adding 25% ammonia (20 cm³, 0.2 mol) and 96% ethanol (80 cm³, 1.3 mol) the solution was stirred at room temperature for 15 min. Then TEOS (5 cm³, 0.022 mol) was added and the resulting gel was stirred for 2 h. The filtered precipitate was washed with water (100 cm³) and ethanol (100 cm³) and dried for 5 h at 90°C. Finally the synthesized material was calcined at 550°C for 5 h.

The characteristics of silica–template composites have been studied by thermogravimetric analysis (TG) using Derivatograph Q-1500 (Hungary), the heating rate was 5°C min⁻¹. The synthesized silicas were investigated by adsorption–desorption of nitrogen at 77 K (ASAP-2000). From isotherms of nitrogen adsorption, the specific surface area, pore volume and pore size distribution were determined. The structure of samples was investigated using small-angle X-ray diffraction (XRD) (automated diffractometer DRON-4-07, CuK_α-radiation). Scanning electronic microscopy (X-ray micro-analyzer Superprobe-733, JEOL) was applied to study the form and size of the obtained silica particles.

Results and discussion

Results of thermal analysis of the as-synthesized nanocomposites, containing as templates 67% CTAB +33% ionene or only pure ionene are presented in Fig. 1.

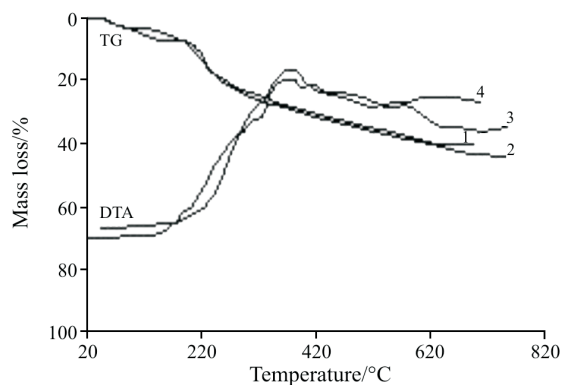


Fig. 1 TG and DTA curves of the as-synthesized nanocomposites, containing as a template 1, 3 – 67% CTAB +33% ionene and 2, 4 – pure I-4 Me-Ph ionene

TG and DTA curves show a typical decomposition profile with initial mass loss (about 5%) at less than 100°C that can be attributed to evaporation of residual water, alcohol and ammonia. The main mass losses (about 35%) with exothermal effects (DTA curves), which are observed in the temperature range from 200 to 700°C are connected with the template

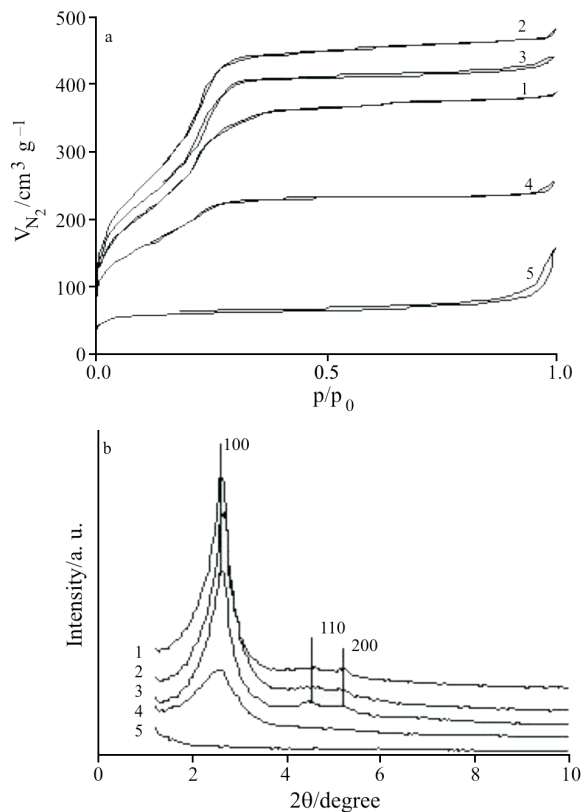


Fig. 2 a – Nitrogen adsorption isotherms and b – X-ray diffractograms of silicas synthesized with different amounts of I-4 Me-Ph ionene in the template: 1 – 0, 2 – 1, 3 – 10, 4 – 33 and 5 – 100%

decomposition. TG curves show a sharp drop at 180–250°C (20 mass%) and smooth mass losses in the range from 250 to 700°C, which can be explained by strong interaction between silica surface and the organic template molecules.

Nitrogen adsorption isotherms (Fig. 2) of silicas, synthesized with CTAB, and of mixtures of CTAB with small amounts of ionene (1–10%) as templates, show typical type IV isotherms. A sharp rise in nitrogen adsorption was observed over a narrow range of relative pressures ($p/p_0=0.15-0.27$) due to capillary condensation inside mesopores. At higher values of p/p_0 , the isotherms have a long plateau, which indicate an overall pore filling. The desorption curves of the isotherms almost coincide with the adsorption ones. Specific surface areas, determined by the BET method, were 1200–800 $\text{m}^2 \text{g}^{-1}$ and pore sizes calculated by the BJH-method are 2.3–2.5 nm. Further increase of polymer concentration (up to 33%) led to decrease in surface areas of up to 700 $\text{m}^2 \text{g}^{-1}$; pore diameter is 2.1 nm with appearance of peaks on the pore size distribution curves in the range of 50–100 nm. The region of capillary condensation became weakly expressed and it can be explained by a decrease of mesopores. The adsorption isotherm of silica synthesized with the use of

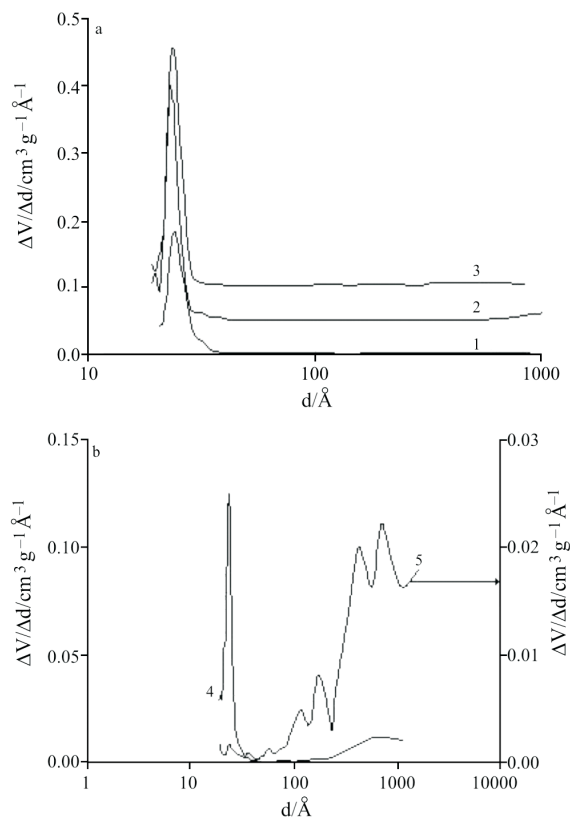


Fig. 3 Pore size distributions (by BJH) for silicas synthesized with the different amounts of I-4 Me-Ph ionene in the template: 1 – 0, 2 – 1, 3 – 10, 4 – 33 and 5 – 100%. Curves 2 and 3 were raised with the displacement magnitude 0.01, 0.05 and 0.10 $\text{cm}^3 \text{g}^{-1}$, respectively

ionene as a template gave a type I isotherm and the resulting material has a relatively low value of specific surface area (240 $\text{m}^2 \text{g}^{-1}$) and broad pore size distribution in the range (10–100 nm).

X-ray diffraction patterns (Fig. 2b) of silicas synthesized using pure CTAB as a template and in the presence of small amounts of ionene (up to 10%) show three low Bragg angle peaks in the range $2\theta=2.5-7.0^\circ$ which can be indexed as (100), (110) and (200) in the hexagonal system and are typical for MCM-41 materials [4, 6]. Diffractogram of silicas synthesized with ionene content of 33% has one weak peak; silicas synthesised with pure ionene as a template have no peaks and are characterized by the disordered structure of pores. The distances between pore centres (lattice parameter, a) were determined using a formula $a_0=2d_{100}/3^{0.5}$ (d_{100} – interplanar distance of (100) planes). Pore wall thickness of the samples can be calculated from a_0 by subtracting pore diameter determined by BJH method. Values obtained were 1.4–1.8 nm and they are acceptable for silicas [6].

Adsorption-structural characteristics of silicas synthesized with different ratios CTAB and ionene in the template are presented in Table 2.

Table 2 Adsorption-structural parameters of synthesized silicas

| I-4 Me-Ph ionene/% | Average pore diameter/nm (by BJH) | Surface area/m ² g ⁻¹ (from BET) | Parameter of lattice a_0 /nm (from X-ray data) | Structure of pores (from X-ray data) |
|--------------------|-----------------------------------|--|--|--------------------------------------|
| – | 2.5 | 800 | 3.9 | hexagonal ordered |
| 1 | 2.3 | 1234 | 3.8 | hexagonal ordered |
| 10 | 2.5 | 1055 | 3.9 | hexagonal ordered |
| 33 | 2.1 | 702 | 3.9 | slightly ordered |
| 100 | | 239 | – | disordered |

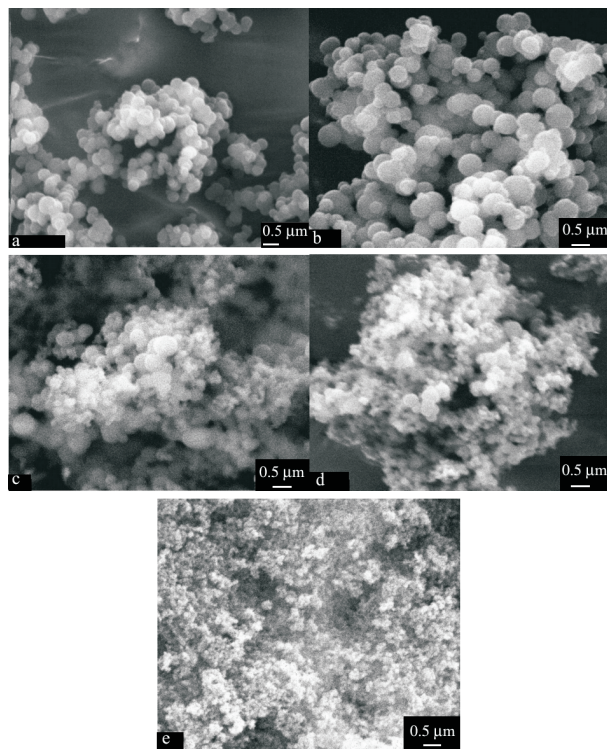


Fig. 4 SEM micrographs of silicas synthesized using as a template 1 – CTAB and CTAB with different amounts of I-4 Me-Ph ionene: b – 1, c – 10, d – 33 and e – 100%

Scanning electronic micrographs (Fig. 4) of silicas synthesized in alcohol–ammonia media using CTAB as a supramolecular template show that a majority of particles have almost perfect spherical granulation with average particle diameter about 0.5 μm . Addition of ionene into template leads to decrease of particles sizes from 0.5 to 0.1 μm and transformation of spherical particles to irregular agglomerates.

Conclusions

It was established that the introduction of small concentrations (up to 10 mol%) of ionene into micellar template has no significant effect on the porous structure of synthesized silicas; samples with specific surface area of 1230–800 $\text{m}^2 \text{g}^{-1}$, average pore size 2.3–2.5 nm and ordered hexagonal pore structure have been obtained. With increase in polymer content (33 and 100%), macropore formation and decrease in specific surface area of silicas has been observed. Diameter of the formed silica particles decreases in all ranges of polymer concentrations.

References

- 1 H. Chen and Y. Wang, *Ceramics International*, 28 (2002) 541.
- 2 D. Brunel, A. C. Blanc, A. Galarneau and F. Fajula, *Catal. Today*, 73 (2002) 139.
- 3 V. T. John, B. Simmons, G. L. McPherson and A. Bose, *Curr. Opin. Colloid Interface Sci.*, 7 (2002) 288.
- 4 M. Grun, K. K. Unger, A. Matsumoto and K. Tsutsumi, *Microporous Mesoporous Mater.*, 27 (1999) 207.
- 5 Y. Miyake, T. Yuomoto, H. Kitamura and T. Sugimoto, *Phys. Chem. Chem. Phys.*, 4 (2002) 2680.
- 6 A. Wang and T. Kabe, *Chem. Commun.*, N20 (1999) 2067.
- 7 W. Stober, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 26 (1968) 62.
- 8 M. J. Adeogun and J. N. Hay, *Polym. Int.*, 41 (1996) 123.
- 9 M. J. Adeogun and J. N. Hay, *J. Sol-Gel Sci. Technol.*, 20 (2001) 119.
- 10 M. J. Adeogun and J. N. Hay, *Chem. Mater.*, 12 (2000) 767.
- 11 M. J. Adeogun, J. P. A. Fairclough, J. N. Hay and A. J. Ryan, *J. Sol-Gel Sci. Technol.*, 13 (1998) 27.

DOI: 10.1007/s10973-006-7579-1