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SYNTHESIS OF SILICAS WITH CARBOXYL FUNCTIONALITY USING TEMPLATE METHOD

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A one-step method of synthesis of new materials with acidic carboxylic groups, based on the template method, has been developed. It was found that the postsynthetic treatment of silicas in boiling HCl leads to changes in structural parameters and changes the nature of functional groups. Efficiency of the methods was demonstrated by powder X-ray diffraction, infrared spectroscopy, and thermal analysis.

INTRODUCTION

Immobilization of acid functional groups into the superficial layer of silica is still a complex problem while the synthesis of organosilicas with different functional groups of another nature is presently a routine method [1–3]. Modification of silica surface by alkoxy(chlorine)silanes, as the simplest way of obtaining of stable superficial functional layers, is inapplicable in this case as obtaining of such modifiers is problematic in presence of mobile protons. Therefore multistage syntheses are used, as a rule, for creation of a superficial layer with acid groups. For example, to obtain silicas with residues of carboxylic acids, silica surface is at first modified by nitrile groups saponificated later on to carboxylic ones under these or those conditions [3, 4].

A similar situation is observed in case of a one-stage synthesis of mesoporous silicas by a template method [5]. Meanwhile appearance of water solutions of sodium salts of some carboxylic acids for sale [6] allows simplifying of the synthesis methods – using of a template method – mesoporous silicas containing carboxylic functional groups in the superficial layer. The one-stage way of synthesis of mesoporous silicas of SBA-15 type containing residues of propionic and ethylenediaminetriacetic acids is considered in this work as an example.

EXPERIMENTAL

We used carboxyethylsilanetriol, sodium salt (CST, 25% in water, Aldrich) and N-(trimethoxysilylpropyl)ethylenediamine triacetic acid,

trisodium salt (TEDA, 50% in water, Gelest) as a source of carboxylic groups during the template method. Tetraethoxysilane (TEOS) was applied as a structural agent and P123 – as a template. The details of the methods of synthesis of mesoporous samples are presented below.

Synthesis of SBA-15 (C0) [5]. 8 g Pluronic 123 was dissolved in 60 cm³ of water and 232 cm³ HCl (2N). The mixture was stirred for 30 min in a water bath at 40°C. Thereafter, 18.2 cm³ TEOS was added to the homogeneous solution under stirring. Precipitate fell down within 20 min. Obtained heterogeneous system shuffled for 6 hours in a water bath at 40°C. Further hydrothermal treatment in a teflonlined autoclave (HTT) was carried out for 24 hours at 100°C. After HTT white precipitation was filtered and dried in air overnight. Template was removed by calcination. It was carried out by slowly increasing temperature from room one to 500°C in 3 h and heating at 500°C for 6 h. Yield was 4.6 g.

Synthesis C1 TEOS/CST=10:1 (mol.) 2 g P123 was dissolved in 50 cm³ HCl (1.9 M) with constant stirring in a water bath at 40°C. 1.34 cm³ (0.0012 M) CST was added to homogenous mixture under magnetic stirring. Further mixing was conducted without heating. Then 4.4 cm³ (0.012 M) TEOS was added to the reaction mixture and homogeneous mixture was stirred for a few minutes. The mixture left standing after stirring for 0.5 h. Precipitate fell down. After HTT (24 h at 100°C), white precipitation was filtered and dried in air for 48 h. Template was extracted by boiling in

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methanol 4 times per 3 h. (1 g of sample – 30 cm³ methanol). Drying was conducted in a vacuum (0.5 h without heating, 0.5 h at 50°C, 3 hours at 110°C). Yield – 1.1 g.

Synthesis C2 TEOS/CST=10:2. It was carried out like C1.

Synthesis CN1 TEOS/TEDA=20:1. 6 g P123 was dissolved in 150 cm³ HCl (1.9 M) with constant stirring in a water bath at 40°C. 4.35 cm³ (0.003 mol) TEDA was added by mixing at room temperature. Separately, 13.35 cm³ (0.06 M) TEOS was dissolved in 15 cm³ HCl (1.9 M) with constant stirring at room temperature. Two solutions were mixed above 15 min, precipitation fell was observed throughout the volume, it still mixed at room temperature for 30 min. White precipitation after HTT (72 h at 100°C) was filtered and dried in air (48 h). After drying sample was washed in ethanol and was dried in vacuum as the sample C1. Yield – 3.86 g.

The samples C1a and CN1a were obtained after treatment of initial samples (C1 and CN1, respectively) by boiling in concentrated hydrochloric acid (10 cm³ acid for 1 g sample), washing to the neutral reaction of filtrate and drying in a vacuum at 110°C.

RESULTS AND DISCUSSION

Earlier [7] we tried to obtain xerogels with such functional groups as $\equiv\text{Si}(\text{CH}_2)_2\text{COOH}$ and $\equiv\text{Si}(\text{CH}_2)_3\text{COOH}$ using the approach suggested by O. Chuiko with co-authors as early as in 1964 [8]. It turned out, however, that after saponification of nitrile groups in an acid medium almost half of them were transformed not in carboxylic but in esteric groups. It was clearly shown with assistance of IR and solid state ¹³C NMR spectroscopy [7]. Taking into consideration this fact, as well as shortcomings characteristic of functionalized polysiloxane xerogels obtained by sol-gel method [9], the other method that is the template method was applied in this work for synthesis of carboxyl-containing silica. Trifunctional silanes containing already sodium salts of carbonic acids (nature of their spacers is schematically represented in the Fig. 1) were used as source materials.

P123 was used as a surfactant in the template synthesis. In this case mechanical stability of the obtained mesoporous silicas substantially

increases as a result of increase in thickness of walls between pores [5]. Template was extracted from mesophase with the acidified alcohol at its boiling temperature.

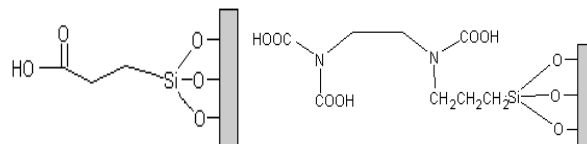


Fig. 1. The nature of the active functional surface layer

To transfer the fastened functional groups in acidic ones, the samples obtained were post-synthesized by boiling concentrated hydrochloric acid (C1a and CN1a samples). It was assumed that analogically to phosphorus-containing xerogels [11] such treatment would lead to ion exchange and improvement of parameters of the porous structure of final materials.

The results of powder X-ray diffraction of some synthesized samples are presented (Fig. 2, Table 1).

Table 1 Sizes of interfacial distance (d_{100}) and distance between the centers of pores (a_0)

Sample	The washed form	
	d_{100}^1 , nm	a_0 , nm
C0	1.85	2.14
	1.11	1.28
	0.99	1.14
C1	1.54	1.78
C1a	1.65	1.91
CN1	1.81	2.09
CN1a	1.81	2.09

¹for sample C2 wasn't recorded reflex, so the calculations were not conducted

Unlike initial SBA-15, diffraction patterns for samples containing sodium salts of carbonic acids, after extraction of template contain only one clear but less intensive and a bit spread reflex at $2\theta \approx 1^\circ$. After treatment of samples by boiling acid, an increase in intensity and some narrowing of this reflex in case of CN1 is observed; while in case of C1 the picture is just the opposite (Fig. 2). Moreover, diffraction pattern of C1a sample has a wide halo in the area of angles $2\theta \approx 3-4^\circ$ that can testify to appearance of some part of amorphous silica. It is not excluded that such a difference is determined by ratio of TEOS / trifunctional silane for C1a sample equal to 10:1, while in case of CN1a sample – only 20:1.

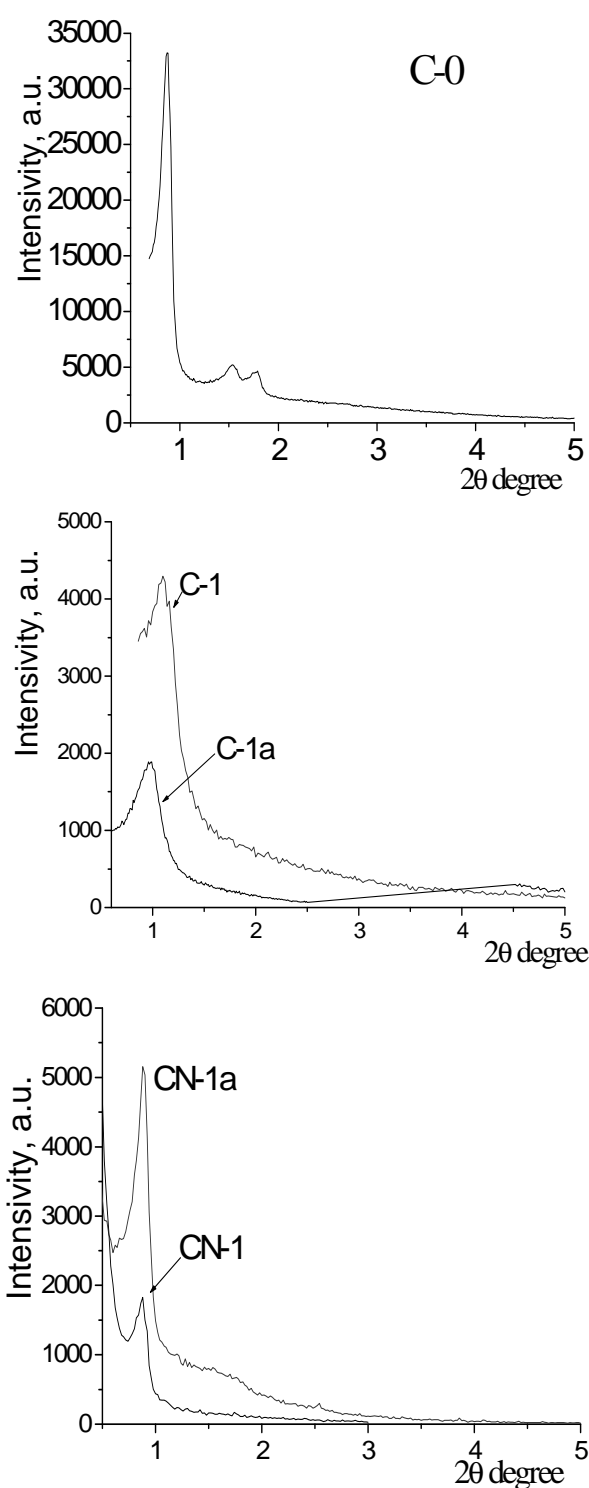


Fig. 2. Powder X-ray diffraction patterns for SBA-15 mesoporous silicas

Presence of functional groups of input tri-functional silanes in the samples is confirmed by IR spectroscopy.

Thus, the IR spectra of all carboxylic-containing silica (Fig. 3) contain an intensive band

in the area of $1715\text{--}1730\text{ cm}^{-1}$ attributed to vibrations of $-\text{CO}$ groups (ν_{as}). A weak band reflection is identified in the area of $1630\text{--}1650\text{ cm}^{-1}$ attributed to vibrations $\nu_{\text{s}}(\text{CO})$ for CN1 and CN1a [11]. Presence of methylene groups of the spacers is identified by IR spectra of low intensive reflection bands in the area of $1350\text{--}1485\text{ cm}^{-1}$ and $2850\text{--}3000\text{ cm}^{-1}$.

Note that the most intensive absorption band is identified in spectra of all samples in the area of $1050\text{--}1180\text{ cm}^{-1}$ testifying to presence of a three-dimensional framework of siloxane bonds [12]. Finally, an intensive band (Fig. 3) related to vibrations $\nu(\text{OH})$ of silanol groups is observed in the range of $3655\text{--}3675\text{ cm}^{-1}$ [12].

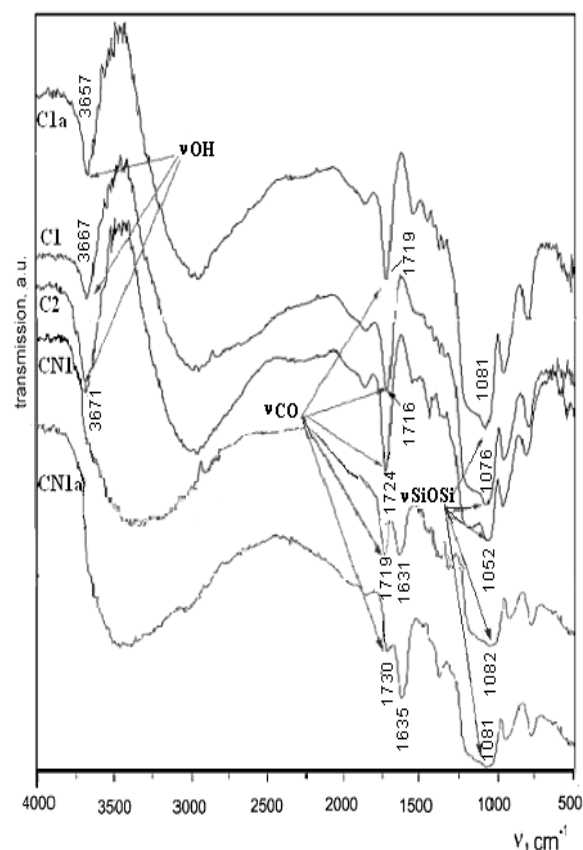


Fig. 3. IR spectra of the synthesized silicas

Analysis of the thermograms (Fig. 4, presented for CN1 and CN1a samples only) testifies to thermal stability of the synthesized samples.

Thus, at the temperature below 180°C the mass loss up is observed (8.5% for CN1 and 10.6% for CN1a) due to water extraction. Decomposition of organic component begins at the temperature above 200°C . Heating in air at the temperature above 200°C caused a mass loss related to

full oxidation of organic groups. In this case, the mass loss for sample CN1 is of 19.8% (calculated theoretically – 15%) and for CN1a – 19.7% (calculated theoretically – 19%). In the first case the difference in weight loss can be attributed primarily to desorption and decomposition of the tracers of triblock copolymer.

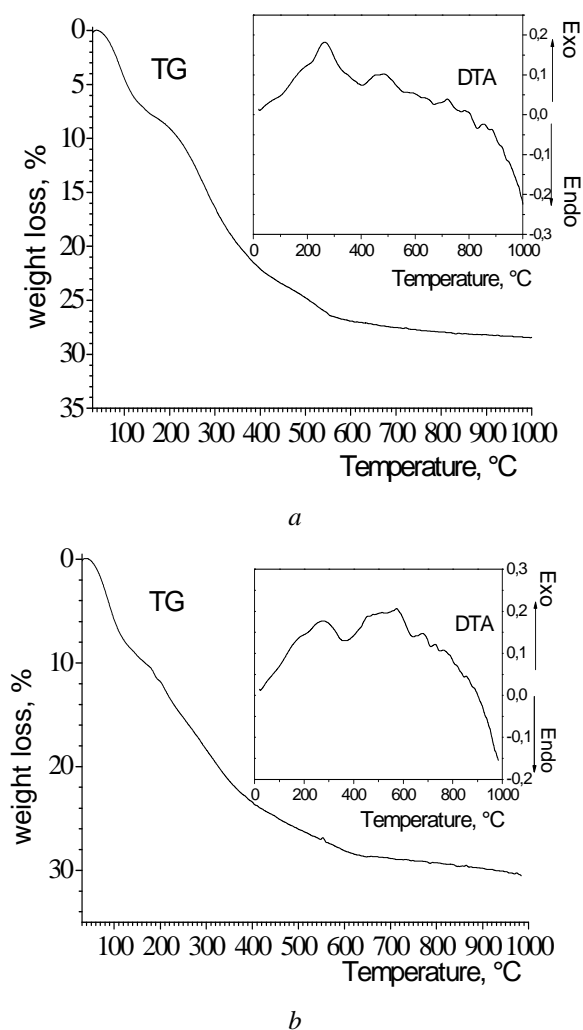


Fig. 4. Thermograms of samples: *a* – CN1, *b* – CN1a

The proposed method of obtaining mesoporous silica is an alternative for the approach based on saponification of nitrile groups. For example, the synthesis of SBA-15 with carboxyl groups by treatment of mesophases obtained using 4-(triethoxysilyl)butyronitrile with highly concentrated solution of sulfuric acid is described in [13]. Comparison of IR spectra of two samples obtained in this work with the IR spectrum of the sample C1a leads to the conclusion that the position of the absorption band of carboxyl groups is practically the same.

CONCLUSION

The methods of synthesis which allow one-stage obtaining of mesoporous silica of SBA-15 type functionalized by residues of propionic and ethylenediaminetriacetic acids have been developed. It has been shown that the ordered spatial hexagonal type structure of the samples obtained is preserved in case of extraction of template and its further treatment with concentrated hydrochloric acid.

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Синтез кремнеземів з карбоксильною функціональністю з використанням темплатного методу

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На основі темплатного методу розроблено методику одностадійного синтезу нових матеріалів з кислотними карбоксильними групами. Встановлено, що процедура постсинтетичної обробки зразків кремнеземів в киплячій соляній кислоті приводить до зміни структурних параметрів і природи функціональних груп. Ефективність розроблених методик була доведена за допомогою дифрактометрії, ІЧ-спектроскопії та термічного аналізу.

Синтез кремнеземов с карбоксильной функциональностью с использованием темплатного метода

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На основе темплатного метода разработана методика одностадийного синтеза новых материалов с кислотными карбоксильными группами. Установлено, что процедура постсинтетической обработки образцов кремнеземов в кипящей соляной кислоте приводит к изменению структурных параметров и природы функциональных групп. Эффективность разработанных методик была доказана с помощью дифрактометрии, ИК-спектроскопии и термического анализа.