

Mesoporous SBA-15 silica modified with calix[4]arene and β -cyclodextrin

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Mesoporous SBA-15 type silica with covalently fixed β -cyclodextrin (0.56 mmol/g) and calix[4]arene (0.40 mmol/g) functional groups and with specific surface areas of 384 to 723 m²/g have been obtained.

Получены мезопористые кремнеземы типа SBA-15 с ковалентно привитыми циклодекстриновыми (0.56 ммоль/г) и каликс[4]ареновыми (0.40 ммоль/г) функциональными группами, обладающие развитой пористой структурой ($S_{y\delta} = 384\text{--}723 \text{ м}^2/\text{г}$).

The development of hybrid organic-inorganic materials with a supramolecular surface layer is a rather complicated task [1, 2]. Two different preparation routes have been usually used. The first one is based on the surface modification of already obtained carriers [3] and as the second way, the sol-gel method is used where the matrix and its surface layer are formed simultaneously [4]. Each of those methods includes some advantages and some drawbacks. Thus, the sol-gel method allows to obtain polysiloxane materials in one stage with both embedded [5] and covalently bounded calixarene and cyclodextrin molecules [6, 7] having a well developed porous structure. However, the synthesis of such hybrid materials by the sol-gel method with the contents of functional groups close to 1.0 mmol/g and above is problematic. This is due first of all to geometrical sizes of molecules together with low solubility thereof in water and/or nonaqueous solvents. Besides, a part of fixed molecules remains unavailable for substrates. Application of chemical modification method, for example, of silica sur-

face provides matrixes with covalently fixed supramolecular layer, where practically all functional groups are available [8, 9]. However, the content thereof is usually about one order lower than in the case of polysiloxane matrices obtained by sol-gel method. On the other hand, the materials obtained in this way are characterized by good adsorption kinetics.

A compromise could be provided by the template method [10] that can be realized in two variants. The first one is the one-stage production of functionalized mesoporous silicas, when the structure-forming and functionalizing agents are introduced simultaneously [11] into the initial reaction solution. After the surfactant removal (usually by extraction with a nonaqueous solvent), the nanoporous silica matrix contains required functional groups in the surface layer. The second possibility is the two-step method. First, the mesoporous silica is prepared (the surfactant being removed from mesophase by calcination) with consequent chemical modification of its surface containing silanol groups using known ap-

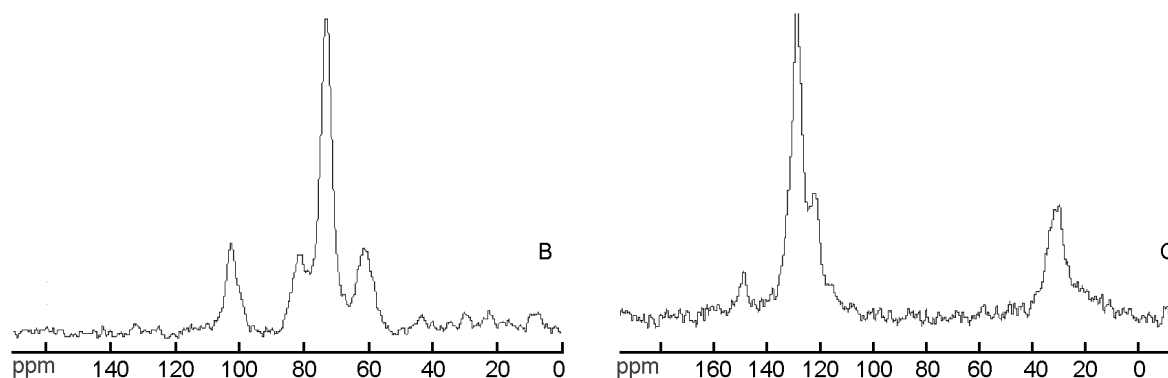


Fig. 1. ^{13}C CP/MAS NMR spectra of samples **B** and **C**.

proaches [3, 12]. Development of these two variants of the template method for formation of supramolecular layers and comparison of properties of obtained materials (among themselves and with materials obtained by the sol-gel method and method resulting in amorphous silica surface modification) is no doubt of a great practical importance. Nowadays, similar materials are recommended for application in chromatography [13] and adsorption processes [14]. The aim of this work is to develop the techniques of mesoporous silica modification by calix[4]arene and β -cyclodextrin groups, to obtain samples of such hybrid materials and investigate their structure.

The initial mesoporous SBA-15 silica (sample **A**) was synthesized as described in [15]. After preliminary hydroxylation of SBA-15 with hydrochloric acid and drying in vacuum, this material was modified with macrocyclic compounds β -cyclodextrin (β CD) from water-ethanol solution (sample **B**) and calix[4]arene from toluene solution (sample **C**). In the last case, the technique was close to that described by S. Shiraishi et al. [16], where the silica surface was preliminarily treated with SiCl_4 .

The ^{13}C CP/MAS NMR spectra were recorded with Bruker AC-300 spectrometer at $f=75.5$ MHz. The ^{29}Si CP/MAS NMR spectra were recorded at $f=59.7$ MHz. Tetramethylsilane was used as a reference standard. The small-angle X-ray powder diffraction (XRD) data were taken on a DRON-4-07 using $\text{CuK}\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$). The scanning was carried out within $0.4\text{--}10.0$ 2θ , deg. The transmission electron microscopic (TEM) measurements were performed using a JEM 2010 (JEOL). Structural-adsorption characteristics were calculated from low-temperature nitrogen adsorption isotherms (Kelvin-1042, Costech

Microanalytical). Prior to the adsorption measurements, each sample was degassed at 120°C in vacuum. The specific surface area was determined by the BET method [17] and the effective pore diameter by the BJH method [18].

As follows from the elemental analysis data, the content of functional groups in Sample **B** was 0.57 mmol/g (nitrogen) (or 0.56 mmol/g carbon), while in Sample **C**, 0.40 mmol/g (carbon). The presence of functional groups in the synthesized samples was also confirmed by IR spectroscopy data (Nicolet NEXUS FTIR spectrometer) and confirmed by solid-state NMR spectroscopy data. Thus, the ^{13}C CP/MAS NMR spectrum of sample **B** (Fig. 1) contains three low-intensity signals at 9.1 , 23.3 , and 43.7 ppm typical for carbon atoms of propyl chain ($=\text{SiCH}_2-$, $-\text{C}[\text{CH}_2]\text{C}-$ and $-\text{CH}_2\text{NH}-$, respectively). The low-intensity signals at 30.1 and 34.8 ppm that can be assigned to the $\text{N,N}'$ -dimethylformamide (DMF) carbonyl carbon atom (in DMF spectrum they are at 31.5 and 36.5 ppm [20]) which was used as a solvent for alkoxy-silyl derivative of β CD are also presented in this spectrum. Three intense signals at 61.0 ; 73.1 , and 80.9 ppm are characteristic for carbon atoms of glucopyranose cycles bounded to oxygen atoms. The medium-intensity signal at 103.6 ppm belongs to anomeric carbon atom, $\text{O}-\text{C}-\text{O}$.

In the ^{13}C CP/MAS NMR spectrum of sample **C** (Fig. 1), two signals at 122.2 and 128.9 ppm characteristic for carbon atoms of phenolic rings of calixarene [20] have been identified. There is also a medium-intensity signal at 30.6 ppm in the spectrum which is typical of carbon atom of methylene groups binding these rings. The medium intensity signal at 148.5 ppm can be assigned to carbon atoms of phenolic

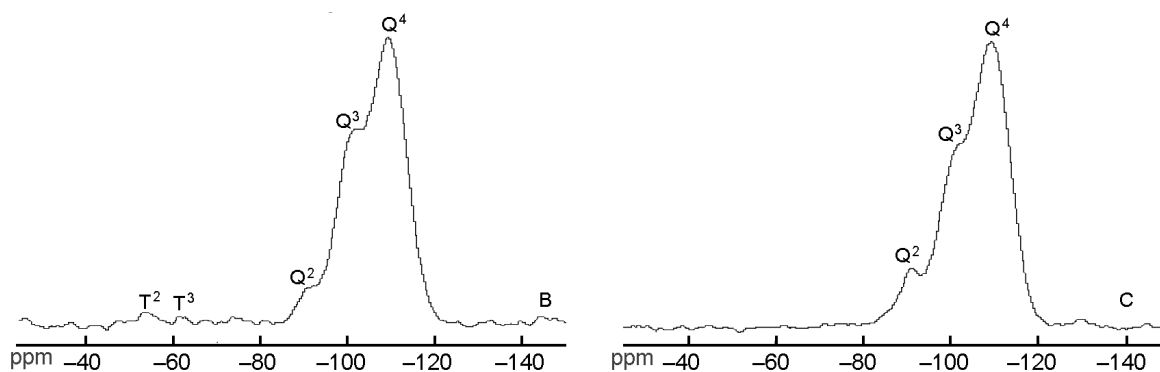


Fig. 2. ^{29}Si CP/MAS NMR spectra of samples **B** and **C**.

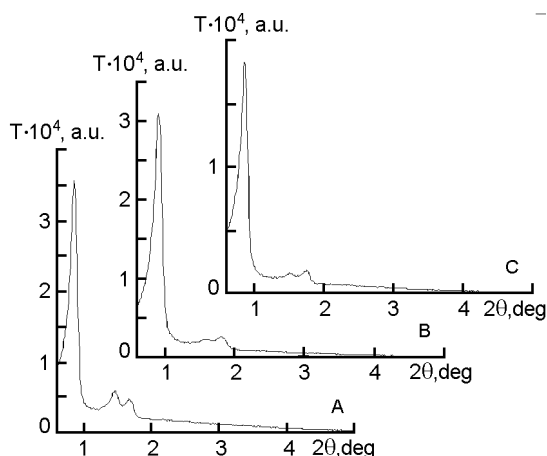


Fig. 3. Powder XRD patterns for the initial and modified SBA-15.

ring bound with hydroxyl group (C–OH) that is not involved in covalent binding of macrocycle to the SBA-15 surface. Thus, the ^{13}C CP/MAS NMR spectra evidence the presence of calixarene and cyclodextrin functional groups bound to silica SBA-15 surface by spacers $\equiv\text{Si}(\text{CH}_2)_3\text{NHC}(\text{O})\text{O}-$ (sample **B**) and $\equiv\text{Si}-\text{O}-\text{Si}(\text{OC})_3$ (**C**).

The ^{29}Si CP/MAS NMR spectra of these samples (Fig. 2) contain a weak signal at -90 ppm and two intense resonance signals at -100 and -109 ppm. These signals correspond to Q^2 , $[(\equiv\text{SiO})_2\text{Si}(\text{OR})_2]$, Q^3 , $[(\equiv\text{SiO})_3\text{SiOR}]$ and Q^4 , $[(\equiv\text{SiO})_4\text{Si}]$ structural units, respectively ($\text{R} = \text{H}$ and/or $-$ in the

case of sample **B** — ethoxy group) [21]. Moreover, in the spectrum of sample **B**, there are two weak signals at -54 and -62 ppm which are characteristic for structural units T^2 , $[(\equiv\text{SiO})_2\text{Si}(\text{OR})\text{R}']$ and T^3 , $[(\equiv\text{SiO})_3\text{SiR}']$, respectively ($\text{R}' =$ organic functional group). The absence of those structural units in the ^{29}Si CP/MAS spectrum of sample **C** (Fig. 2) was expected depending on the chosen way of calix[4]arene fixing.

The powder XRD patterns of all samples show one narrow intense ($2\theta = 0.85\text{--}0.9$) and two moderate intensity peaks at $2\theta = 1.2\text{--}2$ (Fig. 3). The presence of these reflections — (100), (110) and (200) — is associated with the $p6mm$ hexagonal symmetry [22].

In Table, the structural parameters of obtained samples calculated from the XRD patterns data are presented. As is obvious, the fixing of macrocycles causes increase in thickness of pore walls (h_w) that, in turn, results in reduced mesopore diameter (d_{me}). It is also to note that modification of SBA-15 silica (sample **A**) by bulk organic groups does not affect the structural ordering degree of the obtained materials (samples **B** and **C**). The XRD results are in a good agreement with the TEM images. The TEM images presented in Fig. 4 show the highly ordered pore structure of sample **A** (Fig. 4a) that is kept at its modification by bulk calix[4]arene molecules (sample **C**) (Fig. 4b).

Nitrogen adsorption-desorption isotherms of synthesized materials are presented in Fig. 5.

Table. Structural properties of synthesized samples

Sample	Determined from nitrogen adsorption			Determined from XRD data			
	S_{sp} , m^2/g	V_s , cm^3/g	d , nm	d_{100} , nm	a_0 , nm	d_{me} , nm	h_w , nm
A	723	0.92	6.62	10.4	12.0	10.3	1.7
B	420	0.51	5.53	9.8	11.3	8.7	2.7
C	384	0.45	5.5	10.3	11.9	8.8	3.1

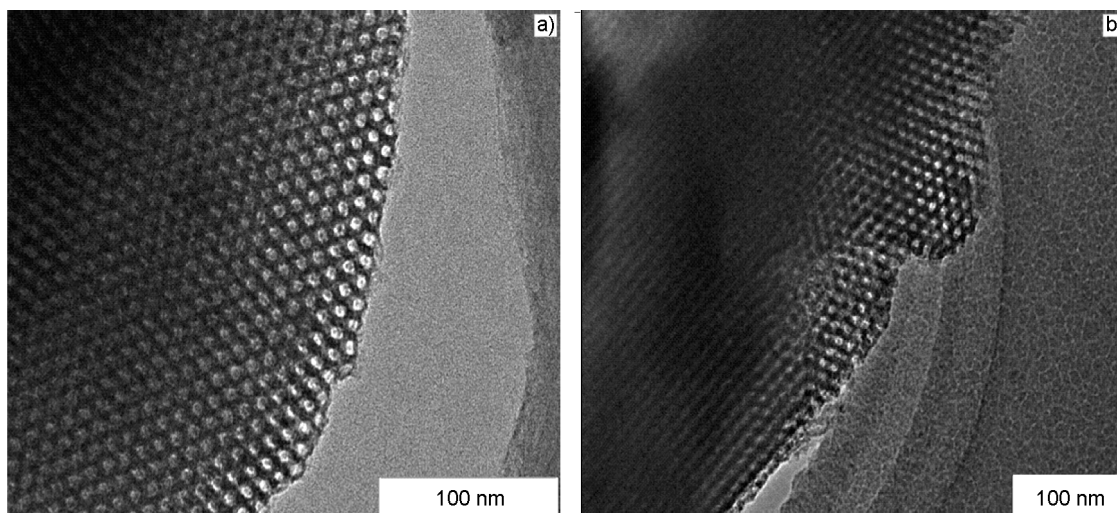


Fig. 4. TEM images of samples A (a) and C (b).

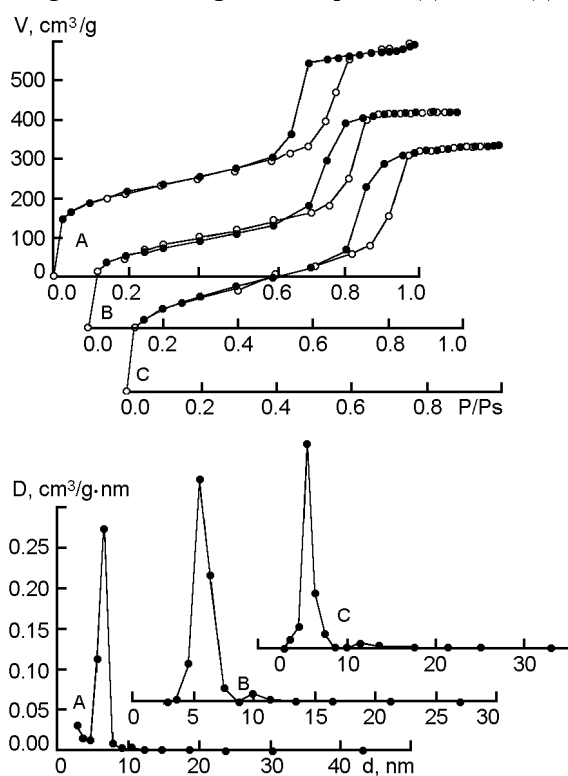


Fig. 5. Nitrogen adsorption-desorption isotherms for the synthesized materials and their PSDs.

The isotherms have S-like character with the clear hysteresis loop and belong to type IV (according to IUPAC classification [23]). This type of isotherm is typical for highly ordered mesoporous materials with hexagonal structure and relatively narrow region of mesopore filling that is in accordance with TEM images which indicated occurrence of the close size pores.

The analysis of structural-adsorption characteristics of the samples calculated from nitrogen adsorption-desorption isotherms (Table) testifies that the silica surface modification with by bulk organic groups causes a decrease of the specific surface area (S_{sp}) as well as of the pore volume (V_s). This fact is in a good agreement with conclusions made from powder XRD patterns (Table).

Thus, it has been shown that the proposed approaches allow to obtain mesoporous SBA-15 silica modified by bulk groups such as β -cyclodextrins and calix[4]arenes. According to the XRD data and TEM images, the modifying of SBA-15 by such bulk macrocyclic groups does not affect the structure organization degree of the synthesized materials. The presence of the introduced functional groups in the structure of the synthesized samples is confirmed by IR, ^{13}C and ^{29}Si CP/MAS NMR spectroscopy. The synthesized materials are characterized by a developed porous structure ($S_{sp} = 723\text{--}384\text{ m}^2/\text{g}$, $V_s = 0.92\text{--}0.45\text{ cm}^3/\text{g}$). The structural type of samples is kept at modifying of SBA-15 by β -cyclodextrin and calix[4]arene groups.

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Мезопористий кремнезем SBA-15, модифікований калікс[4]ареном та β -циклодекстрином

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Одержано мезопористі кремнеземи типу SBA-15 з ковалентно зафіксованими β -циклодекстриновими (0.56 ммоль/г) і калікс[4]ареновими (0.40 ммоль/г) функціональними групами, які характеризуються розвинутою пористою структурою ($S_{num} = 384-723 \text{ м}^2/\text{г}$).