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HYBRID TEMPLATE-DIRECTED HYDROTHERMAL SYNTHESIS OF MCM-41 SILICAS WITH SURFACE SILANOL AND 3-CHLOROPROPYL GROUPS

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Silicas of MCM-41-type with reactive functional groups are widely used as starting substrates in large variety of post-synthetic chemical modification pathways. Therefore, variation of their structural characteristics in the process of templated sol-gel synthesis or post-synthetic treatment is of great importance. The aim of this work was to elucidate the influence of template agent selection on structural features of MCM-41-type materials with surface silanol and 3-chloropropyl groups. For this purpose, template-assisted sol-gel condensation of structure forming silanes (tetraethyl orthosilicate and 3-chloropropyltriethoxysilane) was carried out in the presence of decyltrimethylammonium bromide as structure-directing agent. The capability of cyclic oligosaccharide (β-cyclodextrin) to interact with surfactant micelles in the process of hydrothermal sol-gel synthesis and to influence the formation of mesoporous structure of silica materials was studied. The IR spectroscopy was applied to carry out control under the complete removal of template moieties from pores by extraction procedure and to confirm introduction of 3-chloropropyl groups into the surface layer of synthesized silicas. Arrangement of mesoscale pores and structural parameters were estimated from the results of X-ray diffraction and low-temperature adsorption-desorption of nitrogen. It has been found that β-cyclodextrin as component of hybrid template has positive effect on porous structure of 3-chloropropyl-functionalized MCM-41-type silica causing increase of surface area accompanied with preservation of pore ordering. Moreover, both ionic surfactant and oligosaccharide components of hybrid template act as porogens during sol-gel condensation of structure forming silanes enable to prepare silica materials with micro-mesoporosity. Proposed approach can be useful in synthesis of MCM-41-type silicas with surface linker groups and controlled structural characteristics (pore size, geometry and ordering), which have great potential as substrates in design of sophisticated materials.

***Keywords**: MCM-41-type silica, sol-gel synthesis, β-cyclodextrin, decyltrimethylammonium bromide, 3-chloropropyltriethoxysilane, IR spectroscopy, X-ray diffraction, low-temperature adsorption-desorption of nitrogen*

INTRODUCTION

Mesoporous silica materials of MCM-41 type have a honeycomb structure formed as the result of hexagonal packing of unidimensional cylindrical pores, high surface area, and large pore volume. Since the discovery by the Mobil group in 1992 [1], they have attracted great attention as sorbents, catalysts, sensors, and carriers of biologically active compounds [2–5]. Design of new MCM-41-type materials with excellent performance requires precise control of structural characteristics and chemical properties that can be realized in the process of templated sol-gel synthesis or post-synthetic treatment. Chemical composition of reaction mixture (silica precursor, template, catalyst, and solvent) along with sol-gel reaction conditions (temperature, stirring rate, aging time, microwave or hydrothermal treatment) play crucial role in mesoporous silica particles (MSPs) synthesis. It was demonstrated that geometrical parameters of pores can be regulated according to the size of analyte molecules by selection of proper templating agents [7–9] or post-synthetic activation [10, 11]. Chemical features of surface layer can be designed by addition of functional structure-forming silanes at sol-gel synthesis or involvement of surface groups of already formed MSPs into the chemical reactions with appropriate modifiers [12, 13].

Post-synthetic chemical modification of MSPs is widely employed approach for creation of new materials for specific applications. It opens up possibilities for directed changes of chemical properties by covalent attachment of organic moieties to silica surface. MCM-41-type silicas with highly reactive chloroalkyl groups are commonly used starting substrates in large variety of post-synthetic chemical modification pathways [3, 14–19]. Their structural characteristics lay in the basis and predetermine quality of resulting chemically modified materials. Therefore, experimental studies clarifying the influence of synthesis parameters variation on the structure of MSPs with surface linker groups attract considerable attention. Addition of functional silane with definite structure at the sol-gel synthesis changes reaction mixture composition and can be considered as one of the factors determining structural characteristics of organosilica. One-pot sol-gel synthesis of ordered silica materials with surface 3-cloropropyl groups was realized in the presence of cetyltrimethylammonium bromide (CTAB) as template [20−22]. Analysis of experimental results confirms that tetraethyl orthosilicate (TEOS) to 3-chloropropyltriethoxysilane (CPTES) ratio has noticeable influence on modification process and structure of final products. Along with the change in pore size, the ordering of the mesoporous structure decreases gradually with increasing of organosilane concentration in the reaction mixture [20–22]. Formation of hexagonally arranged mesoporous structure is less pronounced in the case of quaternary ammonium salts with shorter chain length like decyltrimethylammonium bromide (DTAB) [20, 23]. Therefore, synthesis of MCM-41-type chloropropylsilica with highly ordered pore channels in the range 2–2.5 nm is of great interest.

Combination of a cationic surfactant template with substances capable to incorporate into the micellar aggregates opens up new opportunities for regulation of mesoporous silica matrix structural characteristics [24–28]. Solubilization of organic additives causes changes in critical micelle concentration as well as configuration of surfactant micelles and, as a result, has substantial influence on mesoporous structure of silica materials prepared by template-assisted sol-gel synthesis. In our previous work [29] we utilized the capability of some amphiphilic organic compounds and related alkoxysilanes derivatives to participate in CTAB micelles formation and influence structure formation in mesoporous silica materials. It was found that choose of proper amphiphilic additive have positive impact on structural characteristics of synthesized MCM-41 materials. Among the variety of organic moieties that can be used as the components of hybrid template, cyclodextrins belong to the promising ones due to their capability to form inclusion complexes with long-chain quaternary ammonium salts [30−34], compatibility with silica matrix [35–38], and narrow high temperature decomposition interval [39]. So, in this study, sol-gel synthesis of MCM-41 silicas with surface silanol and 3-chloropropyl groups was carried out in the presence of decyltrimethylammonium bromide (DTAB). The effect of β-cyclodextin (β-CD) as component of hybrid template on structural characteristics of resulting silica materials was studied by IR spectroscopy, X-ray diffraction, and low-temperature adsorption-desorption of nitrogen.

EXPERIMENTAL

Tetraethyl orthosilicate (≥99 %, Merck) and 3-chloropropyltriethoxysilane (≥95 %, Aldrich) were used as silica source. Decyltrimethylammonium bromide (≥97 %, Merck) and β-cyclodextrin hydrate (≥99 %, Acros Organics) were applied as templates. Aqueous ammonia 25 % (analytical grade, Reakhim) was used as catalyst in sol-gel synthesis. Ethanol 96 % and hydrochloric acid 37 % (analytical grade, Reakhim) were employed for template extraction procedure. All chemicals were used without additional purification.

Synthesis of MCM-41-type silicas. In order to obtain MSPs with surface silanol and 3-chloropropyl groups (MSP-C_{10} and Cl-MSP-C_{10}), sol-gel condensation procedure was realized in water-ethanol-ammonia solution with DTAB as template. Briefly, the batch of DTAB was placed into a conical vessel, dissolved in mixture of deionized water and ethanol. After that, 25 % aqueous ammonium solution was poured into the reaction vessel and TEOS or its mixture with CPTES was slowly added to the solution under vigorous mixing. The resultant reaction slurry was stirred at 293 K for 2 h, then transferred to a polypropylene bottle and aged at 373 K for 24 h.

Synthesis of MSPs with incorporated β-CD moieties (CD_{inc}-MSP-C_{10} and CD_{inc}-Cl-MSP-C_{10}) was realized by base catalyzed hydrothermal-assisted sol-gel condensation of TEOS or its mixture with CPTES in the presence of micellar system containing long-chain quaternary ammonium salt and cyclic oligosaccharide. In particular, appropriate quantities of DTAB and β-CD were dissolved in water-ethanol solution with stirring at room temperature. Then, 25 % aqueous ammonium was poured to provide alkaline condition of the reaction mixture, and TEOS or its blend with CPTES was added to the solution dropwise under continuous stirring. The subsequent step of synthesis procedure was the same as for MSP-C_{10} and Cl-MSP-C_{10} silicas.

The final molar compositions of the reaction mixtures used for MCM-41-type silicas synthesis are listed in Table 1. After hydrothermal treatment synthesized silicas were filtered, washed with small quantities of deionized water, and dried in air at 273 K for 2 h. Then long-chain quaternary ammonium salt as well as β-CD physically sorbed on the pore walls of mesoporous silicas were removed by solvent extraction in acid-ethanol solution for 24 h. For successful elimination of templates, the extraction was repeated three times. After extraction procedure, the samples were washed with deionized water until the negative test for chloride ions with $AgNO_3$.

Table 1. Molar composition of reaction mixtures at synthesis of MSPs in the presence of DTAB

Silica	Molar composition of reaction mixture	Surface groups
MSP-C_{10}	0.1 TEOS : 0.02 DTAB : 0.47 NH_4OH : 0.47 C_2H_5OH : 13.6 H_2O	≡SiOH
CD_{inc}-MSP-C_{10}	0.096 TEOS : 0.001 β-CD : 0.02 DTAB : 0.47 NH_4OH : 0.47 C_2H_5OH : 13.6 H_2O	≡SiOH
Cl-MSP-C_{10}	0.09 TEOS : 0.01 CPTES : 0.02 DTAB : 0.47 NH_4OH :0.47 C_2H_5OH : 13.6 H_2O	≡SiOH $-(CH_2)_3Cl$
CD_{inc}-Cl-MSP-C_{10}	0.09 TEOS : 0.01 CPTES : 0.001 β-CD : 0.02 DTAB : 0.47 NH_4OH : 0.47 C_2H_5OH : 13.6 H_2O	≡SiOH $-(CH_2)_3Cl$

Characterization of MCM-41 silicas. Transmission IR spectra were registered on a Thermo Nicollet NEXUS FT-IR spectrophotometer in the range from 4000 to 400 cm^{-1} for solid pellets of synthesized silicas. Along with IR spectroscopy, chemical analysis on β-CD retaining in silicas after extraction procedure was used to control oligosaccharide removal. The content of β-CD in CD_{inc}-MSP-C_{10} and CD_{inc}-Cl-MSP-C_{10} was determined by acid hydrolysis of β-cyclodextrin up to glucose. The concentration of glucose after the reaction with potassium ferricyanide was defined by spectrophotometry using a Specord M-40 equipment (Germany, Carl Zeiss, Jena) at $\lambda = 420$ nm [40].

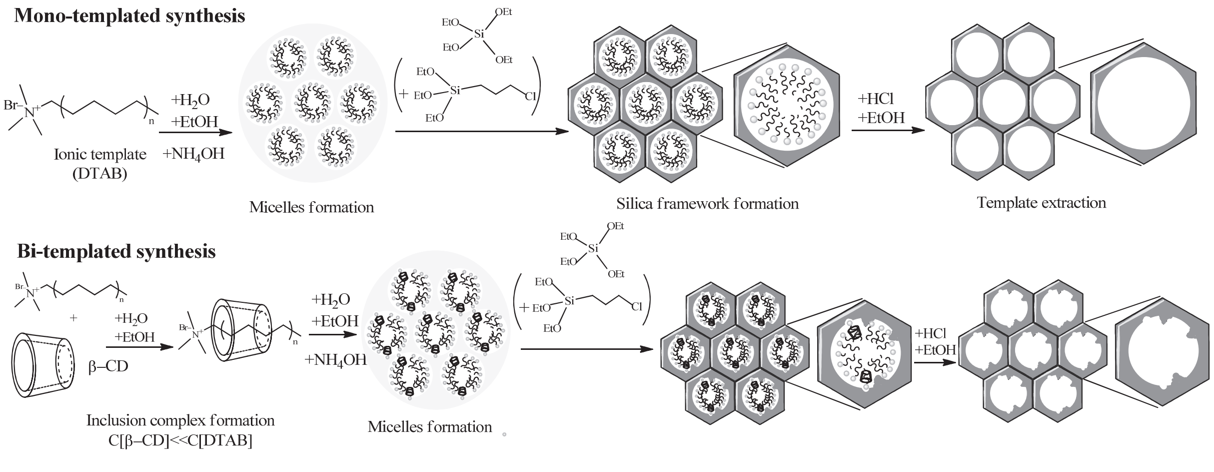
Powder X-ray diffraction patterns of synthesized MSPs were registered on a DRON-4-02 diffractometer with monochromatic CuK_α emission ($\lambda = 0.15418$ nm) and a nickel filter.

Low-temperature adsorption-desorption of nitrogen was performed with a Kelvin-1042 Sorptometer. Prior to the measurements, all samples were outgased at 413 K for 20 h. Specific surface area S_{BET} of silica materials was determined using the BET method in the relative pressure p/p_o range up to 0.30. The pore size distributions were calculated by applying the non-local density functional theory (NLDFT) from the adsorption branch or both adsorption and desorption branches analysis (equilibrium model). The total pore volume V_{total} was rated from the amount of nitrogen adsorbed at $p/p_o = 0.99$.

RESULTS AND DISCUSSIONS

This work is devoted to study the influence both silica source and template agent selection on structural features of MCM-41-type materials. Two synthetic pathways were employed to obtain MSPs with surface silanol and 3-chloropropyl groups. It was realized commonly reported in the literature mono-templated hydrothermal sol-gel synthesis of MSP-C_{10} and Cl-MSP-C_{10} silica materials in the presence of ionic surfactant (DTAB). Also, bi-templated synthesis of CD_{inc}-MSP-C_{10} and CD_{inc}-Cl-MSP-C_{10} was performed with hybrid template consisting of DTAB and β-CD (Scheme 1).

The IR spectroscopy was applied to carry out control under the complete removal of template moieties from the pore volume of MSPs by extraction procedure and confirm introduction of 3-chloropropyl groups into the surface layer of Cl-MSP-C_{10} and CD_{inc}-Cl-MSP-C_{10} silicas (Fig. 1).



Scheme 1. The representation of two synthetic pathways for MSPs obtaining

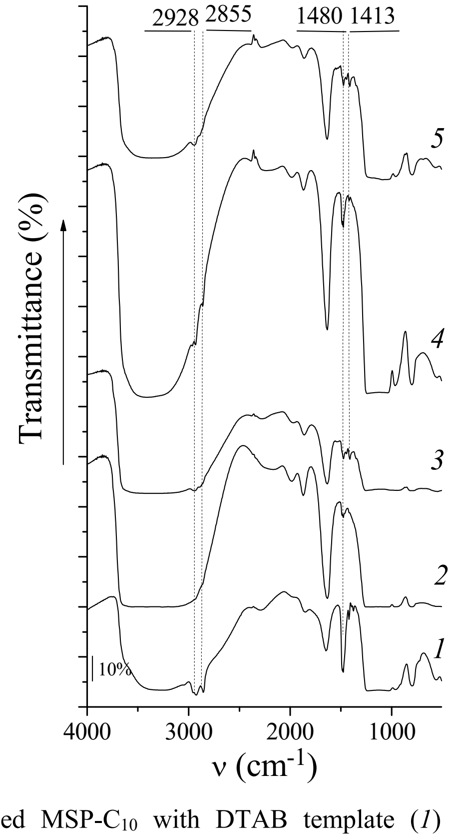


Fig. 1. IR spectra of as-synthesized MSP-C_{10} with DTAB template (*1*) and MSP-C_{10} (*2*), Cl-MSP-C_{10} (*3*), CD_{inc}-MSP-C_{10} (*4*), CD_{inc}-Cl-MSP-C_{10} (*5*) after template extraction

In the IR spectrum of as-synthesized MSP-C_{10} the absorption bands in the regions 2800–3000 and 1300–1500 cm^{-1} belonging to the valence and deformation vibrations of the C–H bonds in the alkyl groups of DTAB template, respectively, are registered (Fig. 1, curve *1*). The broad band at 3650–3800 cm^{-1} is attributed to the valence vibrations of the O–H bonds in the surface silanol groups and adsorbed water molecules. The band at 960 cm^{-1} is caused by the stretching vibrations of the Si–OH bonds in the silanol groups of mesoporous silica. It is followed by the band at 1640 cm^{-1} belonging to the deformation vibrations of the H–O–H bonds in adsorbed water molecules. Extraction procedure leads to the disappearance of the absorption bands at 2800–3000 cm^{-1} in the spectrum of MSP-C$_{10}$ due to the complete removal of template from mesopores (Fig. 1, curve *2*). In the case of CD$_{inc}$-MSP-C$_{10}$ these bands became slightly visible (Fig. 1, curve *4*).

In the IR spectra of Cl-MSP-C$_{10}$ and CD$_{inc}$-Cl-MSP-C$_{10}$ silicas after template extraction, the absorption bands at 2928 and 2855 cm^{-1} corresponding to the valence vibrations of the C–H bonds in the 3-chloropropyl groups are registered (Fig. 1, curves *3, 5*). Moreover, the absorption bands in the region 1300–1500 cm^{-1} belonging to the deformation vibrations of these bonds are also observed. Obtained results confirm introduction of 3-chloropropyl groups into the silica framework as the result of sol-gel condensation of TEOS and CPTES.

The successful removal of β-CD template from mesopores of MSPs was proved via chemical analysis. It was shown that after the second extraction cycle the residual quantity of β-CD in CD$_{inc}$-MSP-C$_{10}$ and CD$_{inc}$-Cl-MSP-C$_{10}$ silicas was 3.5–6 μmol·g^{-1}, whereas after the third extraction cycle the complete removing of β-CD was observed.

The X-ray diffraction and low-temperature nitrogen adsorption-desorption studies were carried out to confirm long-range porous order and estimate structural parameters of synthesized MSPs. The X-ray diffraction pattern of MSP-C$_{10}$ silica contains only one well-resolved diffraction peak at 2θ equal to 2.88 deg. assigned to the (100) plane (Fig. 2 *a*, curve *1*). In the case of Cl-MSP-C$_{10}$, position of the peak is slightly shifted to the high-angle region and registered at 2θ equal to 2.9 deg. (Fig. 2 *a*, curve *2*). This fact indicates decrease in distance between reflecting planes in Cl-MSP-C$_{10}$ as the result of smaller pores formation due to the addition of CPTES into the sol-gel reaction mixture (Table 2). Also, the intensity of diffraction peak assigned to the (100) plane on the diffractogram of Cl-MSP-C$_{10}$ is lower in comparison with MSP-C$_{10}$.

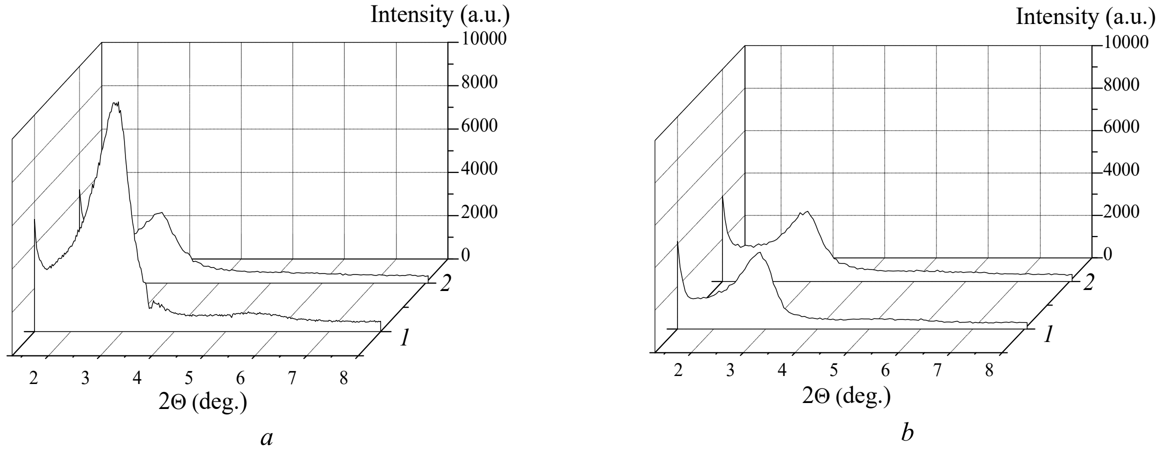


Fig. 2. X-ray diffraction patterns of MSPs: *a*–MSP-C$_{10}$ (*1*) and Cl-MSP-C$_{10}$ (*2*); *b*–CD$_{inc}$-MSP-C$_{10}$ (*1*) and CD$_{inc}$-Cl-MSP-C$_{10}$ (*2*)

Table 2. Structural parameters of MSPs calculated from X-ray diffraction analysis

Silica	d_{100}, nm	a, nm	V_{total}, cm^3·g^{-1}	D, nm	B, nm
MSP-C$_{10}$	3.07	3.54	0.70	2.90	0.64
CD$_{inc}$-MSP-C$_{10}$	3.05	3.52	0.58	2.77	0.75
Cl-MSP-C$_{10}$	3.05	3.52	0.55	2.73	0.78
CD$_{inc}$-Cl-MSP-C$_{10}$	2.99	3.46	0.56	2.70	0.76

Structural parameters of silica materials synthesized in the presence of DTAB as template were calculated and listed in Table 2. The Bragg equation was used to evaluate the distance between lattice planes *d* from the diffraction peak position [41]:

$$n\lambda = 2d\sin\theta,$$

where *n* is the integer number of wavelengths or order of diffraction, λ is the wavelength of the X-ray radiation, and θ is the diffraction angle.

The unit cell parameter *a* (distances between the centers of the nearest pores) was calculated by equation represented in [42]:

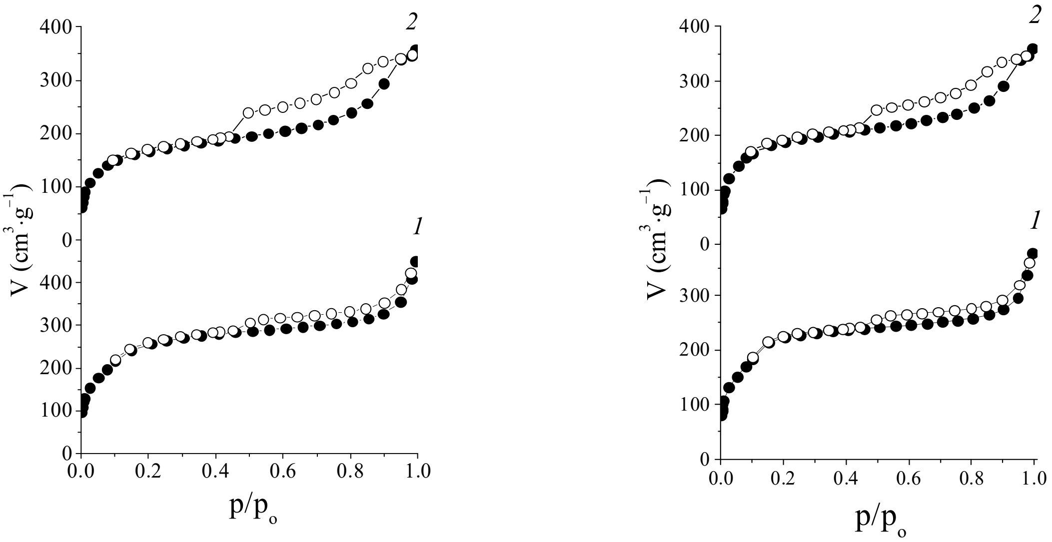
$$a = \frac{2d_{100}}{\sqrt{3}}.$$

Diameter of cylindrical pores *D* was estimated using interplanar distance *d* for (100) reflex and pore volume *V* (obtained from low-temperature adsorption-desorption of nitrogen at $p/p_o = 0.99$) for amorphous silica with pore density $\rho = 2.2$ g·cm^{-3} by the formula [43]:

$$D = cd\sqrt{\frac{\rho V_p}{1+\rho V_p}}.$$

The constant *c* for cylindrical pores is equal to $\sqrt{\frac{8}{\pi\sqrt{3}}}$. The pore wall thickness *B* was calculated as the difference between unit cell parameter and pore diameter.

Incorporation of β-CD macromolecules into the micelles of long-chain quaternary ammonium salt at sol-gel synthesis of silicas with surface silanol and 3-chloropropyl groups is accompanied by changes in mesoporous structure and, as consequence, in X-ray diffraction profiles of resulting materials. The effect of β-CD as component of hybrid template on structural characteristics of synthesized materials was analyzed by comparison the X-ray diffraction patterns of MSP-C$_{10}$ and Cl-MSP-C$_{10}$ silicas with those of CD$_{inc}$-MSP-C$_{10}$ and CD$_{inc}$-Cl-MSP-C$_{16}$, respectively (Fig. 2). As seen from the diffractogram of CD$_{inc}$-MSP-C$_{10}$, incorporation of β-CD into the DTAB micelles leads to the noticeable decrease of peak from the (100) plane (Fig. 2 *b*, curve *1*). At the same time, slight shift of reflex to the high-angle region is observed, confirming decrease of distance between reflecting planes. The same tendency was observed in our previous studies concerning influence of amphiphilic additives on the structural parameters of silica materials synthesized in the presence of CTAB as template [29], but β-CD caused much greater decrease of interplanar distances as component of hybrid template.



a *b*

Fig. 3. Isotherms of low-temperature nitrogen adsorption-desorption of MSPs: *a* – MSP-C$_{10}$ (*1*) and Cl-MSP-C$_{10}$ (*2*); *b* – CD$_{inc}$-MSP-C$_{10}$ (*1*) and CD$_{inc}$-Cl-MSP-C$_{10}$ (*2*)

The X-ray diffraction pattern of CD_{inc}-Cl-MSP-C_{10} has only one low-intensity reflex from the (100) plane at 2θ equal to 2.95 deg. (Fig. 2 *b*, curve *2*), that is shifted to the high-angle region in comparison with the position of diffraction peak on the diffractogram of parent Cl-MSP-C_{10}. Obviously, the incorporation of cyclic oligosaccharide in DTAB micelles causes changes in distances between the planes and the pore centers of synthesized CD_{inc}-Cl-MSP-C_{10} silica. Introduction of β-CD as additive in CTAB-assisted sol-gel synthesis had similar effect on the structure of resulting CD_{inc}-Cl-MSP-C_{16} silica [29]. The intensity of diffraction peaks for Cl-MSP-C_{10} and CD_{inc}-Cl-MSP-C_{10} is almost the same.

The isotherms of low-temperature adsorption-desorption of nitrogen and pore size distributions for MSPs prepared by mono- or bi-templated sol-gel method are represented in Figures 3 and 4.

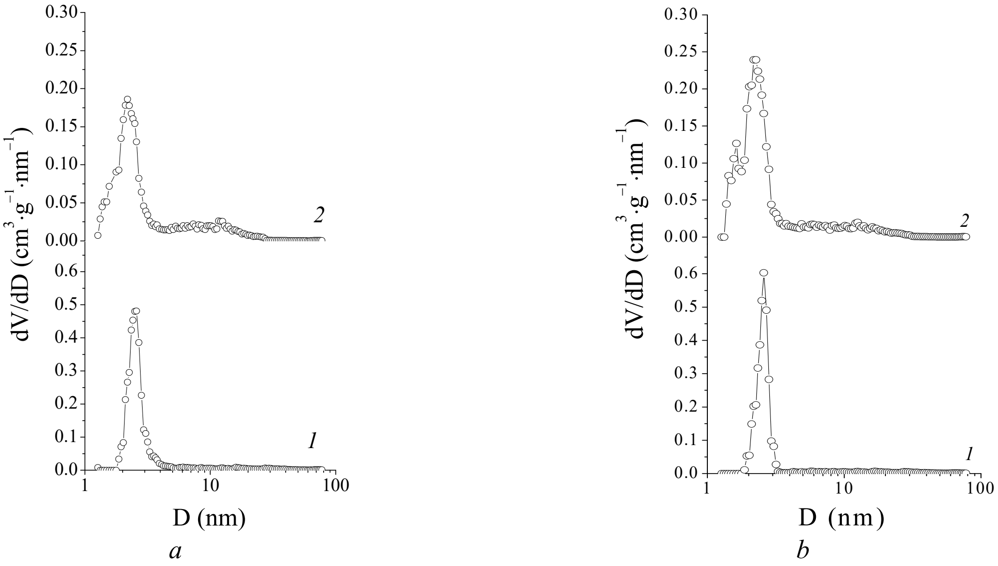


Fig. 4. Pore size distributions for MSPs: *a* – MSP-C_{10} (*1*) and Cl-MSP-C_{10} (*2*); *b* – CD_{inc}-MSP-C_{10} (*1*) and CD_{inc}-Cl-MSP-C_{10} (*2*)

It can be seen that the profiles of isotherms for synthesized silicas reveal the type II with reversible broad hysteresis loop of the type H3 according to the IUPAC classification [44]. Increase of the hysteresis loop evidences widening of pore size distributions for MSPs with functional 3-chloropropyl groups (Fig. 4). Since the average pore sizes of MSPs synthesized with DTAB are below the critical diameter for nitrogen at 77 K, the tensile strength effect is present as a distinct step on the desorption branch of hysteresis loop closure. Obviously, the removal of nitrogen from pores of silica materials takes place via cavitation process in porous system with narrowed pore entrances causing the appearance of artifact peaks on the pore size distribution curves at ~5 nm (correspond to the steep desorption step at $p/p_o \sim 0.4$) [44–47]. Indeed, the diameters of pores calculated by NLDFT from the adsorption branch and both adsorption and desorption branches analysis (equilibrium model) differ (Table 3).

The application of NLDFT to the adsorption branch of isotherm allows obtaining valid information about the structure of synthesized materials. Importantly, that analysis of isotherms by $NLDFT_{ads.}$ evidences the existence of pores with size 1.63 nm, which correlate nicely with the molecular diameter of β-CD (1.53 nm). Moreover, an increase was found in surface area and pore volume for CD_{inc}-Cl-MSP-C_{10} prepared with hybrid template system (Table 3). Apparently, both ionic surfactant and oligosaccharide act as porogens during sol-gel condensation of structure forming TEOS and CPTES silanes. Proposed approach could be applied for synthesis of micro-mesoporous silica with controlled pore size and geometry as well as well-ordered pore organization. Such materials have great potential as substrates in design of sophisticated materials.

Table 3. Structural parameters of MSPs calculated from low-temperature adsorption-desorption of nitrogen

Silica	S_{BET}, $m^2 \cdot g^{-1}$	V_{total}, $cm^3 \cdot g^{-1}$	D, nm	
			$NLDFT_{eq}$, nm	$NLDFT_{ads}$, nm
MSP-C_{10}	1003	0.70	2.43; 5.29	2.58
CD_{inc}-MSP-C_{10}	896	0.58	2.50; 5.29	2.58
Cl-MSP-C_{10}	634	0.55	2.35; 5.09	2.19
CD_{inc}-Cl-MSP-C_{10}	719	0.56	2.35; 5.09	1.63; 2.19

CONCLUSIONS

In the present study, the influence of both silica source and template agent selection on structural features of MSPs was studied. Hydrothermal sol-gel synthesis of MCM-41-type silicas with silanol and 3-chloropropyl surface groups was carried out in the presence of DTAB as structure-directing agent and its mixture with β-CD. The effect of cyclic oligosaccharide additive on the structural parameters of silica materials was evaluated by X-ray diffraction as well as by low-temperature adsorption-desorption of nitrogen. According to the obtained results, using of β-CD as the component of hybrid template in synthesis of MCM-41-type material with surface 3-chloropropyl groups causes increase of specific surface area (from 634 to 719 $m^2 \cdot g^{-1}$) and formation of two types of pores (1.63 and 2.19 nm) along with preservation of ordered porous structure. These results show a principle possibility of MCM-41 porous structure regulation by introduction of organic additives into sol-gel synthesis and can be used in synthesis of functional silica materials with surface linker groups for sophisticated materials design.

Гідротермальний синтез кремнеземів МСМ-41 з поверхневими силанольними та 3-хлоропропільними групами за участі гібридного темплату

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Кремнеземи типу МСМ-41 з реакційноздатними функціональними групами широко використовуються як субстрати у великому розмаїтті напрямків пост-синтетичного модифікування. Тому дуже важливим є варіювання їхніх структурних характеристик у процесі темплатного золь-гель синтезу чи пост-синтетичної обробки. Метою даної роботи було визначення впливу темплатного агента на структуру матеріалів типу МСМ-41 з поверхневими силанольними та 3-хлоропропільними групами. Для цього було здійснено темплатну золь-гель конденсацію структуроутворюючих силанів (тетраетилортосилікату та 3-хлоропропілтриетоксисилану) у присутності децилтриметиламоній броміду як структуруючого агента. Було досліджено здатність циклічного олігосахариду (β-циклодекстрину) взаємодіяти з міцелами поверхнево-активної речовини в процесі гідротермального золь-гель синтезу та впливати на формування мезопористої структури кремнеземних матеріалів. Контроль повноти вилучення темплату з пор у результаті екстракції та підтвердження введення 3-хлоропропільних груп у поверхневий шар синтезованих кремнеземів здійснювали з використанням ІЧ спектроскопії. Впорядкування мезорозмірних пор та структурні параметри оцінювали за результатами рентгенівської дифракції та низькотемпературної адсорбції-десорбції азоту. Встановлено, що β-циклодекстрин як компонент гібридного темплату має позитивний вплив на пористу структуру 3-хлоропропілфункціоналізованого кремнезему типу МСМ-41, спричиняючи зростання питомої поверхні, що супроводжується збереженням впорядкування пор. Крім того, обидві складові гібридного темплату, йонна поверхнево-активна речовина та олігосахарид, діють як пороутворювачі впродовж золь-гель конденсації структуроутворюючих силанів, що дає змогу одержати мікро-мезопористі кремнеземні матеріали. Запропонований підхід може бути корисним у синтезі кремнеземів типу МСМ-41 з поверхневими лінкерними групами та контрольованими структурними *характеристиками (розмір пор, геометрія та впорядкування), які мають великі перспективи як субстрати в дизайні складних матеріалів.*

***Ключові слова**: кремнезем типу МСМ-41, золь-гель синтез, β-циклодекстрин, децилтриметиламоній бромід, (3-хлоропропіл)триетоксисилан, ІЧ спектроскопія, рентгенівська дифракція, низькотемпературна адсорбція-десорбція азоту*

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