

Single-step template synthesis of mesoporous silicas containing thiourea functional groups

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Mesoporous adsorbents containing mono- $(-(\text{CH}_2)_3\text{NHC}(=\text{S})\text{NHC}_2\text{H}_5)$ or bi- $(-(\text{CH}_2)_3\text{NHC}(=\text{S})\text{NHC}_2\text{H}_5/\text{amino})$ functional surface layer have been synthesized in a single-step process using bi- or tricomponent (with respect to alkoxy silanes) systems and 1-dodecylamine as a template. The studied systems have been shown to have a disordered lattice similar to hexagonal one, a developed porous structure (S_{sp} 409 to 718 m^2/g ; V_s 0.26 to 0.82 cm^3/g ; d 2.4 to 2.5 nm) and a relatively high content of functional groups ($C_{\text{C}=\text{S}}$ from 0.7 mmol/g to 2.2 mmol/g). It has been found that hydrothermal treatment of mesophases in a mother liquor for 24 hours at 80°C does not result in an enhanced structure ordering but even in worsened structure-adsorption characteristic of the final products.

Мезопористые адсорбенты, содержащие моно- $(-(\text{CH}_2)_3\text{NHC}(=\text{S})\text{NHC}_2\text{H}_5)$ или би- $(-(\text{CH}_2)_3\text{NHC}(=\text{S})\text{NHC}_2\text{H}_5/\text{амин})$ функциональный поверхностный слой, одностадийно синтезированы с использованием двух- или трёхкомпонентных (по алкоксициланам) систем и 1-додeciламина как темплата. Показано, что они имеют неупорядоченную решётку, близкую к гексагональной, развитую пористую структуру ($S_{уд}$ 409–718 $\text{м}^2/\text{г}$, V_c 0.26–0.82 $\text{см}^3/\text{г}$, d 2.4–2.5 нм) и относительно высокое содержание функциональных групп ($C_{\text{C}=\text{S}}$ — от 0.7 ммоль/г до 2.2 ммоль/г). Установлено, что гидротермальная обработка мезофаз в маточном растворе в течение 24 ч при 80°C не только не ведёт к более упорядоченной структуре, но даже несколько ухудшает структурно-адсорбционные характеристики конечных продуктов.

Ions of heavy metals, particularly mercury (II), being very dangerous for human organism, often are carried over the environment with water [1]. Thus, water purification from these ions pays a special attention. From this point of view, silicas modified with ligand groups imparting selectivity in sorption processes [2] are very attractive compounds. As a rule, thiol and thiourea groups are used to adsorb selectively Hg(II) ions. It is to note that the functionalization of silica matrix should not worsen its kinetic characteristics. Thus, in [3], the MCM-48 functionalized with 1-benzoyl-3-propylurea groups was chosen as a

matrix. The material so obtained appeared to be a good adsorbent for Hg(II) ions. The maximum sorption capacity was 6.7 mmol/g (at the functional group concentration 1.55 mmol/g). Thiourea group and its derivatives are very interesting complexing agents [4]. The use thereof provides effective silica sorbents. These materials are effective in extracting not only metals such as Ag(I), Hg(II), Pd(II), Pt(IV), etc., but also halogen anions (F^- , Br^-). However, mesoporous adsorption materials are usually synthesized in two-step synthesis. Recently, [5–7] the opportunity of one-step synthesis of selective mesoporous thiol-containing sorbents

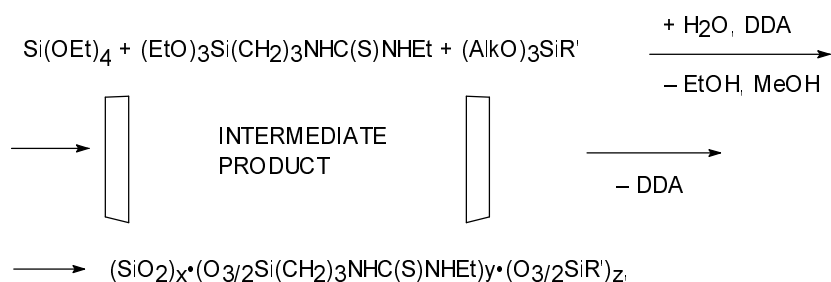
Table 1. Composition and functional groups content of obtained functionalized mesoporous silicas

Sample	Functional group	Ratio of alkoxy-silanes	Elemental analysis, % (mass.)					Content of functional groups, mmol/g	
			C	H	N	S	C/N/S	C _{C=S}	C _{NH}
FMS-1.1A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅)	10:2	14.5	3.3	5.4	6.4	6/1.9/1	2.2	-
FMS-2A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) -(CH ₂) ₃ NH ₂	10:1:1	11.1	3.6	4.0	2.2	13/4/1	0.7	1.6
FMS-2.1A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) -(CH ₂) ₃ NH ₂	10:1:1	12.1	3.4	4.3	3.3	9.7/3/1	1.1	1.1
FMS-3A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) = [(CH ₂) ₃] ₂ NH	10:0.67:0.67	14.9	3.4	3.3	2.2	18/3.5/1	0.7	1.1
FMS-3.1A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) = [(CH ₂) ₃] ₂ NH	10:0.67:0.67	12.9	3.3	3.4	2.32	14.8/3.4/1	0.7	1.1
FMS 4A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) -(CH ₂) ₃ NHCH ₂ CH ₂ NH ₂	10:1.33:0.67	13.4	3.5	5.1	3.4	13.8/4.5/1.33	1.1	0.8
FMS-4.1A	-(CH ₂) ₃ NHC(S)NH(C ₂ H ₅) -(CH ₂) ₃ NHCH ₂ CH ₂ NH ₂	10:1.33:0.67	14.5	3.5	5.4	4.2	12.4/3.9/1.33	1.4	0.7

for Hg(II) using different types of templates: cetyltrimethylammonium bromide [5], *n*-octylamine [6], triblock surfactant [7] has been demonstrated. In this connection, the main goal of our investigations is to synthesize mesoporous sorbents with thiourea group selective to Hg(II) ions in one-step template process. In this paper, the synthesis of mesoporous adsorbents (1-dodecylamine as template) functionalized with 1-ethyl-3-propylthiourea group, their structure-adsorption characteristics and the influence of the hydrothermal treatment (HTT) is described. It is expected that the HTT of the mesophases provides more ordered adsorbents and, consequently, an improvement of the pore structure parameters.

Tetraethoxysilane, Si(OC₂H₅)₄ (TEOS, 98 %); 3-aminopropyltriethoxysilane, (C₂H₅O)₃Si(CH₂)₃NH₂ (APTES, 99 %); bis-[(3-trimethoxysilyl)-propyl]amine, [(CH₃O)₃Si(CH₂)₃]₂NH (BTMPA, 97 %, Fluka); N-[3-trimethoxysilyl]-propyl]ethylenediamine, (CH₃O)₃Si(CH₂)₃NH(CH₂)₂NH₂ (TMPEA, 97 %); 1-dodecylamine, CH₃(CH₂)₁₁NH₂ (DDA); anhydrous acetonitrile and ethanol were used as initial materials (all reagents from Aldrich, if no otherwise specified). The trifunctional silane with thiourea groups ((C₂H₅O)₃Si(CH₂)₃NHC(S)NHC₂H₅, ETUS) was synthesized according to [8]. The samples were synthesized using the following technique. FMS-2A (TEOS/ETUS/APTES = 10:1:1): to the DDA (0.015 mol) solution in ethanol (30 cm³), first ETUS (0.005 mol), then TEOS (0.05 mol) and APTES

(0.005 mol) were added under stirring. Then, under continuous stirring, water (25 cm³) was added dropwise. During about two minutes, a precipitate was formed from the clear solution, which was left to stand at ambient temperature for 48 h. Then it was filtered off and dried in air during 48 h. The FMS-3A (TEOS/ETUS/BTMPA = 10:0.67:0.67) and FMS-4A (TEOS/ETUS/TMPED = 1.33:0.67) samples were synthesized in the same way. Thus, the molar ratio of reactants as follows: 0.1 TEOS:0.02 (RO)₃SiR' (total quantity trifunctional silanes): 0.03 DDA: 2.8 H₂O. When using BTMPA, the presence of two (CH₃O)₃Si(CH₂)₃-chains in its molecule was taken into account, i.e. the molar ratio of trifunctional silanes (BTMPA/ETUS) in the initial solution for the FMS-3A sample was 0.67:0.67. When using TMPED, the presence in its molecule of two amino centers was taken into account, i.e. the molar ratio of trifunctional silanes in the initial solution for the FMS-4A sample was 1.33:0.67. The surfactant was washed out from all obtained white powdery substances with acetonitrile under boiling for 3 h (60 cm³ CH₃CN per 2 g of sample); the operation was repeated thrice. Then the samples were dried in vacuum at 100°C for 4 h. The FMS-1.1A (TEOS/ETUS = 10:2), FMS-2.1A, FMS-3.1A and FMS-4.1A samples were synthesized from white precipitates in mother liquor using HTT at 80±2°C for 24 hours. The further treatment of the samples was analogous to that mentioned above.



where Alk = CH₃ or C₂H₅; R' = - (CH₂)₃NH₂, 1/2 = (CH₂)₃½NH or - CH₂)₃NHCH₂CH₂NH₂.

The elemental analysis was carried out at Analytical Laboratory, the Institute of Organic Chemistry (NASU, Kyiv). X-ray diffraction powder examinations were done using a DRON-4-07 diffractometer in Cu K_α radiation. The DRIFT spectra were recorded on the Thermo Nicolet Nexus FT-IR at 8 cm⁻¹ resolution using the Spectra Tech collector diffuse reflectance accessory at room temperature. The samples were mixed with KBr (1:30) and were used to fill the DRIFT sample cup before measurements. The nitrogen adsorption isotherms for all the samples were measured by a Kelvin-1042 adsorption analyzer. Before the measurements, the samples were outgassed at 383 K in helium. The BET specific surface area [9] was calculated in the relative pressure range between 0.05 and 0.35. The total pore volume (V_s) was determined from the amount adsorbed at the relative pressure 0.99 [9]. The pore size distributions were determined using the Barrett, Joyner and Halenda (BJH) approach [10].

Multicomponent systems were used for synthesis of functionalized mesoporous silica (FMS) (see schema).

The elemental analysis data for the samples obtained (after extraction the template using boiling acetonitrile) are presented in Table 1. These data show indirectly that the nature of functional groups remains unchanged after the HTT of mesophases as well as after template removal. The somewhat higher carbon content in FMS samples extracted from template can testify to the presence of a small quantity of non-hydrolyzed alkoxy groups [11] and probably DDA traces.

IR spectra of some synthesized samples (after template extraction) are shown in Fig. 1. All the spectra contain an intense absorption band with high-frequency shoulder in the 1050–1200 cm⁻¹ region. Its presence can be attributed to formation of three-dimensional siloxane network with carbon-containing functional groups [12]. The IR spectra of all samples show also a sharp moderate intensity adsorption band at about

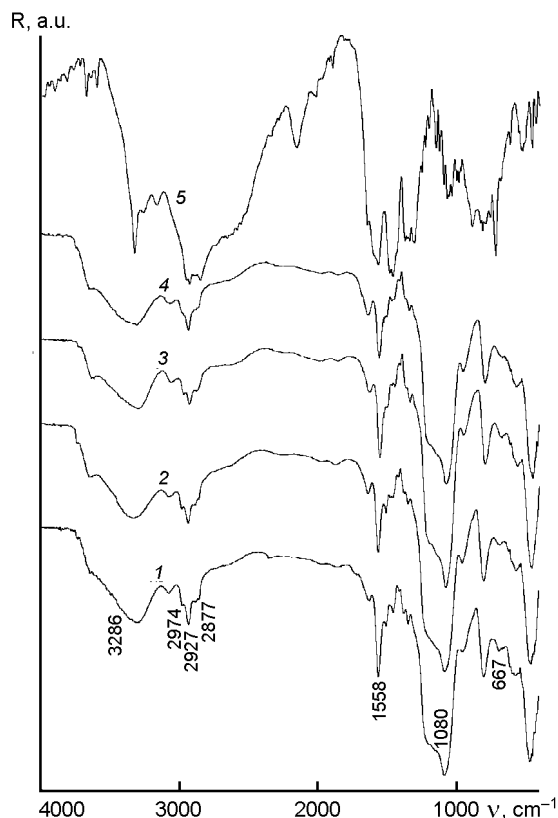


Fig. 1. IR spectrum of FMS-4.1A (1), FMS-3.1A (2), FMS-2.1A (3), FMS-2A (4), and ETUS (5).

1560 cm⁻¹, which can be attributed to $\nu_{as}(\text{NCN})$ vibration of thiourea fragment -NH-C(S)-NH- [13]. This fact is also confirmed by the presence of an intense and broad absorption band at about 3300 cm⁻¹, which can be masked by absorption band of water $\nu(\text{OH})$ vibration. Furthermore, in the 2800–3000 cm⁻¹ region, there is a well-defined adsorption band of C-H bonds valence vibrations in an alkyl chain. There is no absorption bands that are typical for DDA in the IR spectra.

The powder X-ray diffraction patterns of all FMS samples obtained with and without HTT are shown in Fig. 2. Those comprise a

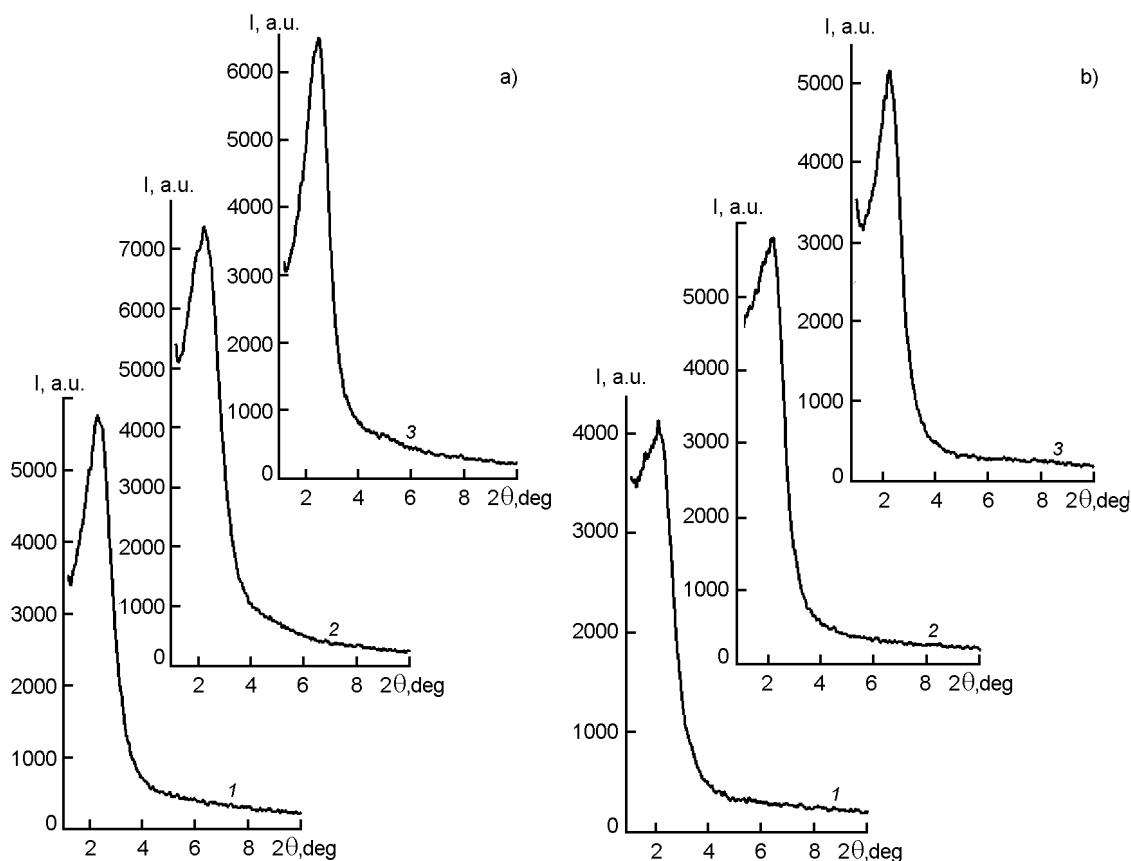


Fig. 2. Powder XRD patterns of materials prior to (a) and after HTT (b). 1–FMS-2A; 2–FMS-3A; 3–FMS-4A.

single broad reflex which is typical for the mesoporous silicas synthesized with DDA [14]. Interplanar spacing d_{100} constants for all obtained samples, as calculated from these patterns, are presented in Table 2.

The nitrogen adsorption isotherms of synthesized materials are shown in Fig. 3. As is seen, the isotherms for FMS-2A, FMS-2.1A, FMS-4A and FMS-4.1A samples belong to the Type I according to IUPAC classification [15]. Isotherms of FMS-1.1A and FMS-3.1A samples are similar to those described above, while the isotherm of FMS-3A sample belongs to the Type IV. The structure and adsorption parameters of all samples, as calculated from obtained isotherms, are displayed in Table 2.

The use of DDA as a neutral templating agent provides an easy synthesis mesoporous silicas with mono- and bifunctional surface layer containing thiourea groups, $\equiv\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$. The boiling acetonitrile has been found to be a very effective template-removing agent. The powder X-ray diffraction patterns of all FMS samples comprise a single reflex at $\sim 2.9^\circ 2\theta$, which is typical to the mesoporous silicas

synthesized with DDA [16]. It was demonstrated that such materials have small scattering domain sizes and can still exhibit local hexagonal symmetry [17]. The comparison of X-ray patterns of the samples synthesized using HTT (Fig. 2b) and without it (Fig. 2a) testifies that in case of the HTT use the corresponding X-ray patterns are worse than when HTT is not used. Furthermore, it is expected that the HTT will increase the lattice parameter (a_0), due to thermal expansion of the mesophase hydrocarbon fragments. That conclusion was confirmed before in the synthesis of silica mesoporous materials in the presence of alkyl trimethylammonium cations [18, 19]. However, it is seen from Table 2 that in FMS samples this effect is observed only after the template removal from the mesophase. Furthermore, after removing the template, the lattice parameter increase is practically observed for all samples. However, this increase is more significant in HTT treated samples (Table 2). Obviously, these effects are due to the presence of functional groups at the surface micelle/polysilox-

Table 2. Structural characteristics of obtained adsorbents

Sample	Initial form		Removed form		S_{sp} , m ² /g	V_s , cm ³ /g	d , nm
	d_{100} , nm	a_0 , nm	d_{100} , nm	a_0 , nm			
FMS-1.1A	3.61	4.16	3.84	4.44	593	0.34	2.4
FMS-2A	3.68	4.25	3.84	4.44	718	0.4	2.5
FMS-2.1A	3.68	4.25	4.02	4.64	409	0.26	2.4
FMS-3A	3.54	4.08	3.93	4.53	602	0.82	2.5
FMS-3.1A	3.61	4.16	4.42	5.10	508	0.34	2.4
FMS-4A	3.54	4.08	3.54	4.08	674	0.36	2.4

ane network interface in the mesophases. Negative influence of the HTT affects also the structure-adsorption characteristics (Table 2). In HTT treated samples, S_{sp} and V_s values are smaller. However, the pore diameter remains practically unchanged. It can be concluded that the mesoporous structure is partially destroyed during the HTT.

Thus, the use of DDA in di- or tricompound (with respect to alkoxy silanes) systems during template synthesis allows to obtain the mesophases easily from which the template can be removed using boiling acetonitrile. The elemental analysis and IR spectroscopy data indicate the presence of the surface layer in these samples which consists of either thiourea groups $\equiv\text{Si}(\text{CH}_2)_3\text{NHC}(\text{S})\text{NHC}_2\text{H}_5$ or a combination thereof with amino groups. The synthesized mesoporous silicas show a developed pore structure and relatively high content of functional groups ($C_{C=S}$ 0.7 to 2.2 mmol/g). Hydrothermal treatment of the mesophases in mother liquor causes neither an improvement of mesoporous structure nor structure-adsorption characteristics of the final products.

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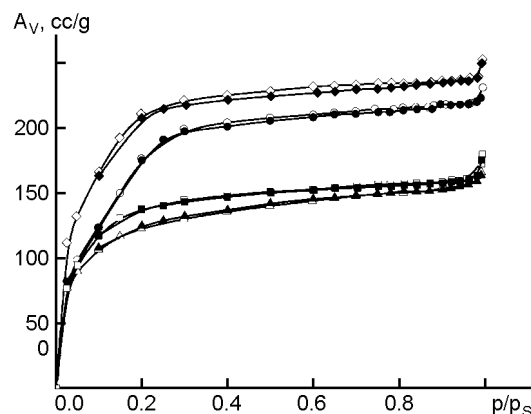


Fig. 3. N_2 adsorption-desorption isotherms of FMS-2A (1), FMS-2.1A (2), FMS-4A (3) and FMS-4.1A (4).

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Одностадійний темплатний синтез мезопористих кремнеземів з тіосечовинними функціональними групами

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Мезопористі адсорбенти, що містять моно-(-NHC(=S)NHC₂H₅) чи бі- (-NHC(=S)NHC₂H₅/амін) функціональний поверхневий шар, одностадійно синтезовано з використанням дво- чи трикомпонентних (за алкоксисиланами) систем і 1-додециламіна як темплату. Показано, що вони мають неупорядковану ґратку, близьку до гексагональної, розвинуту порувату структуру ($S_{num} = 409-718$ м²/г, $V_c = 0.26-0.82$ см³/г, $d = 2.4-2.5$ нм) та відносно високий вміст функціональних груп ($C_{C=S}$ від 0.7 ммоль/г до 2.2 ммоль/г). Встановлено, що гідротермальна обробка мезофаз у маточному розчині протягом 24 годин при 80°C не тільки не веде до більш впорядкованої структури, а навіть дещо погіршує структурно-адсорбційні характеристики кінцевих продуктів.