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A facile low-temperature approach for organics removal from SiO₂-CTAB mesoporous particles

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Abstract. A simple, fast and efficient method has been developed for removing pore-forming organic substances from MCM-41 type materials without affecting their shape, structural and adsorption characteristics. The method is based on express annealing of the synthesized silica materials in vacuum at low temperatures. It was shown that the synthesized particles do not sinter during annealing in vacuum and are monodisperse and aggregatively stable.

Keywords: Mesoporous silica, template method, organics removal, CTAB, vacuum annealing

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Материалы конференции

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Низкотемпературный метод удаления органических веществ из мезопористых частиц SiO₂-ЦТАБ

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Аннотация. Разработан простой, быстрый и эффективный способ удаления порообразующих органических веществ из материалов типа МСМ-41 без изменения их формы, структурных и адсорбционных характеристик. Метод основан на экспресс-отжиге синтезированных кремнеземных материалов в вакууме при низких температурах. Показано, что синтезированные частицы не спекаются в процессе отжига в вакууме, остаются монодисперсными и агрегативно устойчивыми.

Ключевые слова: мезопористый кремнезем, темплатный метод, удаление органики, ЦТАБ, отжиг в вакууме

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Introduction

MCM-41 type porous silica materials are actively studied owing to the wide range of their possible applications as adsorbents, in catalysis and biomedicine [1, 2]. A template method is applied to obtain such materials with the use of micelles of alkylamines as a template. Control over the internal structure, particle and pore size is carried out by varying the synthesis conditions and the structure of surfactant template. The elimination of these organic templates from the pores is a crucial step in the synthesis of mesoporous silica materials. Thermal calcination is a common method for template removal in the laboratory due to high efficiency, easy operation, and requirement of simple equipment. However, the significant reduction of silanol concentrations happens during calcination (which renders the sample unsuitable for post-modification), besides, the structural shrinkage is invariably detected following template removal. In addition to the removal of organics by calcination, various post synthetic methods are also used to wash particles from surfactant in organic solvents under the action of ultrasound or microwaves [3, 4]. As a rule, all of the above template removal methods include several successive stages, for example, washing, centrifugation, drying, etc., which significantly increases the time required to obtain the final product [3–5]. Thus, the development of a procedure for a fast, efficient, low-temperature and one-stage removal of the template from the pores of MCM-41 type particles is still a crucial task.

Materials and Methods

Materials. Cetyltrimethylammonium bromide (CTAB), C₁₆H₃₃N(CH₃)₃Br, 99+% (Acros); aqueous ammonia (NH₃), 24% wt., ≥99.99%; ethanol (C₂H₅OH), 95% wt.; deionized water (H₂O) 10 MΩ; tetraethoxysilane (TEOS), Si(OC₂H₅)₄, 99+% (Acros), hydrochloric acid (HCl), 37% wt., ACS reagent grade.

Methods. In the present study we used spherical mesoporous silica particles (MSP) with a diameter of 550 ± 25 nm. MSP were synthesized according to the method developed by us via hydrolysis of TEOS in a mixture of NH₃–H₂O–C₂H₅OH containing a pore-forming agent – CTAB [6]. The removal of organics from the pores of MSP-CTAB particles was carried out in three different ways and then the structural characteristics of the resulting particles were compared. The first way was a traditional calcination of MSP-CTAB at 550 °C in air for 6 h. In the second one organics were removed in two stages. The synthesized MSP-CTAB particles were first washed in an alcoholic solution of HCl (0.01 M) for 10 h. Then the washed particles were annealed at 400 °C in air for 5 h. The third way to remove pore-forming substance was fast (within 1 h) annealing of particles at 300 °C in dynamic vacuum under pressure of 0.1 Torr.

IR transmission spectra were measured using an IFS Bruker 113v Fourier spectrometer. Spectra were recorded in vacuum in the range of 450–4000 cm⁻¹ with the use of DTGS detector. Spectral resolution was 4 cm⁻¹. Spectra were obtained from the sample area of 1.25×1.25 mm. The nitrogen adsorption was performed using a Micromeritics 3FLEX at a temperature of 77 K. The specific surface area was calculated by the Brunauer–Emmett–Teller (BET) method, and the pore size distribution was found using the nonlocal density functional theory (NLDFT). Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm). The preparation of particles for TEM studies is described in Ref. [7]. Microscopic studies also were carried out using an NT-MDT SMENA atomic force microscope (AFM) in a tapping mode. Particle size distribution and the electrophoretic mobility of synthesized MSP were determined by dynamic light scattering (DLS) and electrophoretic light scattering methods, respectively, at 25 °C with the use of a Zetasizer Nano analyzer. The particle size distribution and the electrokinetic potential were calculated using the built-in analyzer software.

Results and Discussion

Monodisperse spherical MSP are synthesized via basic hydrolysis of TEOS in a $\text{NH}_3\text{-H}_2\text{O-C}_2\text{H}_5\text{OH-CTAB}$ medium [6]. CTAB molecules are present mainly in the form of cylindrical micelles in the chosen reaction medium. Negatively charged products of TEOS hydrolysis interact with positively charged trimethylammonium groups, which are located on the surface of CTAB micelles. As a result, the micelles are covered with a layer of amorphous SiO_2 [6,8]. Furthermore, these silica-coated micelles form clusters $\sim 10\text{--}15$ nm in size in the reaction mixture due to van der Waals forces. As the number of clusters grows, the aggregative stability of the system decreases and, as a result, the clusters coagulate to form submicrometer spherical aggregates.

The organics removal from the pores of the synthesized particles was carried out by several methods (Fig. 1). In the first case organics are removed by a long-term (6 h) high-temperature (550°C) annealing of particles in air (the thus obtained particles were designated as MSP-a). During annealing an oxidation of CTAB molecules occurs followed by the formation of CO , CO_2 , and NO_x oxides, which are subsequently removed from the pores by surface diffusion. When calcination can affect the composition and/or structure of the material low-temperature methods are required to remove pore-forming substances. For example, multiple (2 to 5 times) washing of MSP from CTAB in an alcoholic HCl solution is applied. Then, the resulting particles are annealed at 400°C in air for 5 h (MSP-w) to remove water and CTAB molecules remaining after washing. In order to further reduce the annealing temperature and the number of stages required to remove organic pore-forming substances from MSP we propose a new low-temperature method for CTAB removing, which is annealing of particles at 300°C in vacuum for 1 h (MSP-vac).

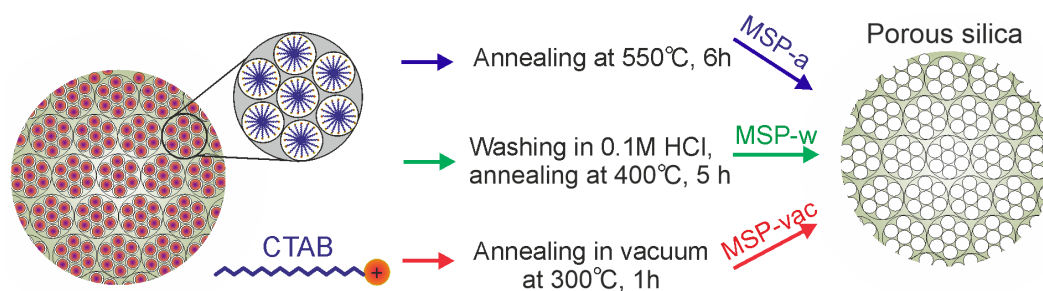


Fig. 1. Schematic representation of different approaches for CTAB removal from MSP

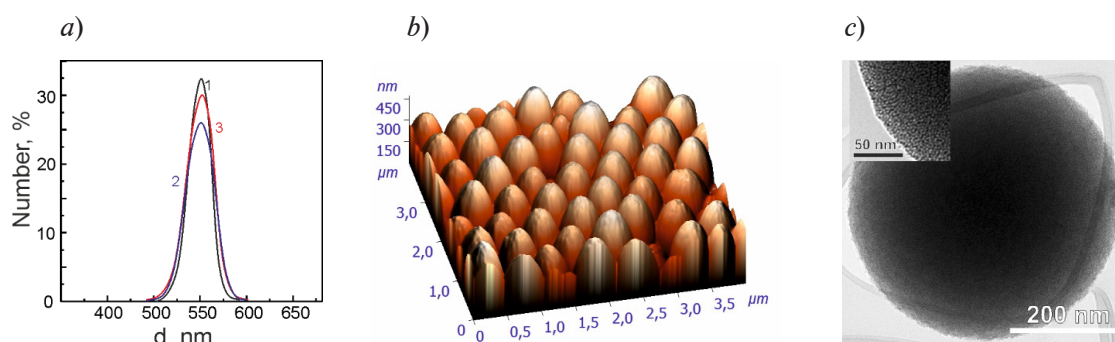


Fig. 2. Particle size distribution measured by DLS method: (1) MSP-w, (2) MSP-a, (3) MSP-vac (a). AFM image of MSP-vac (b). TEM image and its enlarged fragment (inset) of MSP-vac (c)

Fig. 2, a shows the size distributions measured by the DLS method for all synthesized particles. The average diameter of all obtained particles is the same and found to be 555 nm, the standard size deviation does not exceed 5%. The zeta potential value of MSP-vac was found to be -34 mV at $\text{pH} = 5.5$, which is close to the values obtained for MSP-a (-35 mV) and MSP-w (-38 mV). The results obtained indicate that all the particles are aggregatively stable in aqueous suspensions regardless the method of CTAB removal. AFM image of a monolayer of MSP-vac

(Fig. 2,*b*) shows that they form a hexagonal close packing similar to opal-like structure [6], which additionally confirms that the particles are monodisperse and not coalesced. The average particle diameter determined by AFM was found to be 545 ± 25 nm, which is consistent with the DLS data (Fig. 2,*a*). There are 3-nm pores visible on the TEM image of the particles (Fig. 2,*c*), besides, a roughness of ~ 10 nm can be seen on the surface of the particles, which is comparable to the size of the clusters forming the particles [6]. Apparently, during vacuum annealing CTAB is removed both from the pores and from the outer surface of the particles, otherwise the presence of organics decomposition products on the particle surface would lead to a decrease in roughness. Thus, according to the results of DLS, AFM and TEM (Fig. 2), the synthesized MSP-vac particles do not sinter during annealing in vacuum and are monodisperse and aggregatively stable.

Fig. 3,*a* shows the results of the FTIR study of silica particles right after the synthesis and after removal of CTAB by various methods. The spectral bands were identified based on the given in Ref. [9]. The band at 1630 cm^{-1} present in the spectra of all MSPs corresponds to bending vibrations of H–O–H. The transmission spectra of the particles also contain a broad band at 3450 cm^{-1} (Fig. 3,*a*, curves 2-5), to which OH stretching vibrations in hydrogen-bound molecules of physically adsorbed water mainly contribute. There is a weak broad band in the region $3650\text{--}3700 \text{ cm}^{-1}$ and the narrow band at 3745 cm^{-1} , which correspond to vibrations of terminal and single silanol groups, respectively. Thus, all types of particles contain surface hydroxyl groups, which allows for further functionalization. The absorption bands corresponding to the vibrations of carbon-containing organic groups are almost absent in the spectra of MSP-w (Fig. 3,*a*, curve 3) and MSP-a (Fig. 3,*a*, curve 5). At the same time, a set of weak absorption bands in the regions $1300\text{--}1500 \text{ cm}^{-1}$ and $2750\text{--}3025 \text{ cm}^{-1}$ is observed in the spectrum of MSP-vac (Fig. 3,*a*, curve 4). These bands are more pronounced in the spectra of CTAB and as-synthesized MSP-CTAB (Fig. 3,*a*, curves 1, 2) and attributed to the different vibrational modes of CH, CH₂, CH₃ and N-CH₃ groups characteristic of CTAB. The band in the range $1540\text{--}1570 \text{ cm}^{-1}$ (Fig. 3,*a*, curves 2, 4) results from simultaneous N–H and C–N vibrations. The N–H vibrations are caused by the CTAB decomposition products containing amino groups present in the sample. The presence of these groups causes a slight decrease in the porosity of MSP-vac particles compared to MSP-w and MSP-a (Fig. 3,*b*).

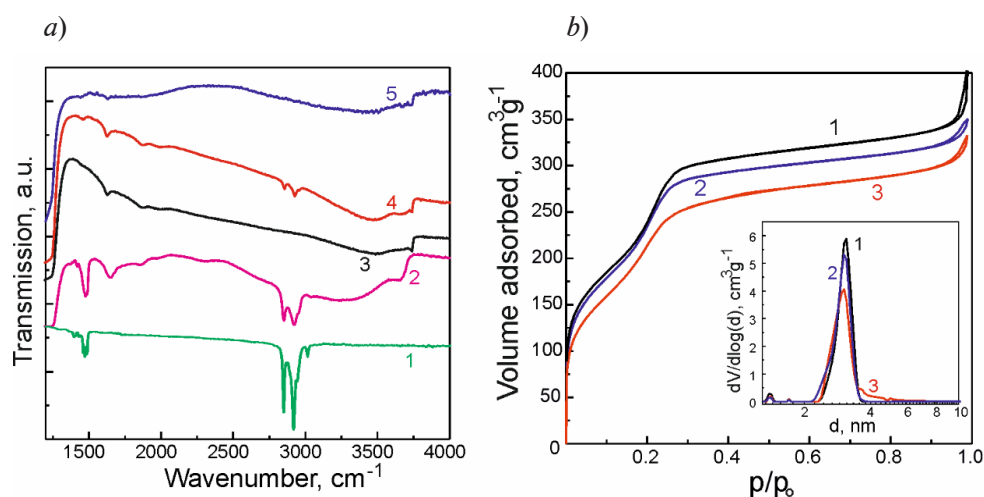


Fig. 3. FTIR spectra: (1) bulk CTAB, (2) MSP-CTAB as-synthesized, (3) MSP-w, (4) MSP-vac, (5) MSP-a (a). N₂ adsorption and desorption isotherms at 77 K and NLDFT pore size distribution (inset) for synthesized particles: MSP-w (1), MSP-a (2), MSP-vac (3) (b)

The nitrogen adsorption and desorption isotherms of the MSP after removing of CTAB by different methods are shown in Fig. 3,*b*. For all the samples the adsorption isotherms have a step-like shape, which is typical of mesoporous materials [10]. The BET specific surface area and pore volume values were found to be: $838 \text{ m}^2\text{g}^{-1}$, $0.64 \text{ cm}^3\text{g}^{-1}$ for MSP-w; $822 \text{ m}^2\text{g}^{-1}$, $0.54 \text{ cm}^3\text{g}^{-1}$ for MSP-a; $770 \text{ m}^2\text{g}^{-1}$, $0.52 \text{ cm}^3\text{g}^{-1}$ for MSP-vac. Pore size distribution calculated by NLDFT for all the samples has a well pronounced peak at 3.1 nm (Fig. 3,*b*, inset). It can be seen that the porosity characteristics of all types of particles are comparable.



Conclusion

A method of low temperature vacuum annealing is developed for CTAB removal from as-synthesized MCM-41-like mesoporous silica particles, which does not affect their size and porous structure. The measured value of the zeta potential of the particles annealed in vacuum was found to be -34 mV, which determines their aggregative stability in an aqueous suspension. The obtained values of specific surface area and pore volume were found to be $\sim 800 \text{ m}^2\text{g}^{-1}$ and $\sim 0.5 \text{ cm}^3\text{g}^{-1}$, respectively, which is comparable with the values for MCM-41 type materials obtained by traditional annealing in air. The proposed approach for the pore-forming template removal from MCM-41-like materials in vacuum is fast, facile and alternative to the thermal calcination and chemical treatment methods.

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