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TEM contrast enhancement by adsorption of erbium ions on the inner surface of micro-mesoporous silica particles

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Abstract. A simple and facile method is proposed for treatment of the inner surface of micro-mesoporous spherical particles of amorphous silica with the solutions of heavy element salts, which allows direct visualization of the particles' porous structure by the transmission electron microscopy (TEM) technique. The method is based on the adsorption of ions of heavy elements (on the example of Er³⁺ ions) by the surface of the pores, which makes it possible to enhance the contrast in the TEM image. The particles before and after erbium ions adsorption are characterized by means of TEM, nitrogen porosimetry and energy dispersive X-ray spectroscopy. It is demonstrated that the developed method for the particles' surface functionalization allows implementing erbium adsorption without affecting the morphology and inner structure of particles. It is shown that erbium content after the adsorption procedure does not exceed 0.1 at.% and the pore structure of silica particles remains the same – the specific surface area, volume and pore size do not change.

Keywords: porous silica, adsorption, transmission electron microscopy, erbium ions, microporosity

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Материалы конференции

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Увеличение контраста ПЭМ изображений микро-мезопористого кремнезема за счет адсорбции ионов эрбия внутренней поверхностью частиц

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Аннотация. Предложен простой и технологичный метод обработки внутренней поверхности микро-мезопористых сферических частиц аморфного кремнезема, позволяющий визуализировать их пористую структуру методом просвечивающей электронной микроскопии (ПЭМ). Метод основан на адсорбции ионов тяжелых элементов (на примере ионов эрбия) поверхностью пор частиц, что позволяет увеличить контраст на ПЭМ изображениях. Показано, что адсорбция ионов эрбия не влияет на внутреннюю структуру частиц кремнезема – удельная поверхность, объем и размер пор не меняются.

Ключевые слова: пористый кремнезем, адсорбция, просвечивающая электронная микроскопия, ионы эрбия, микропористость

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Introduction

Porous silica particles are of great interest due to their inertness, biocompatibility and high adsorption capacity and are used in a wide variety of applications [1]. The porosity is one of the main characteristics of the particles in practical use. It determines the significance of the detailed study of the porous structure in order to fabricate materials with the required properties such as specific surface area, size, morphology and volume of pores. A number of methods are used to study the porous structure, in particular, adsorption porosimetry, small-angle X-ray scattering, transmission and scanning electron microscopy (TEM and SEM) [2–4]. Direct visualization of nanosize pores within the submicron particles by microscopic methods is quite intricate due to the low contrast (because of a low atomic numbers of silicon and oxygen). In ordered channel-like materials (e.g. SBA-15) mesopores can be observed due to their regular spatial arrangement and orientation of the channels along a certain axis, while micropores in the channel walls are not visible. The introduction of a contrast agent (NaCl) into the reaction mixture during synthesis made it possible to visualize micropores in SBA-15 by SEM [4]. When studying the micro-mesoporous particles of amorphous silica synthesized earlier by us [5], the study of the porous structure by the TEM method becomes even more complicated due to the fact that the pores inside the particles are disordered. In this case, the interpretation of TEM images, which are, in some approximation, the projection of the density of a complex three-dimensional structure, is significantly difficult. To enhance the TEM contrast, we developed a method for the adsorption of heavy metal ions by the surface of pores, which made it possible to directly visualize their porous structure.

Materials and Methods

Materials. Cetyltrimethylammonium bromide (CTAB), $C_{16}H_{33}N(CH_3)_3Br$, 99+% (Acros); aqueous ammonia (NH_3), 24% wt., $\geq 99.99\%$; ethanol (C_2H_5OH), 95% wt.; deionized water (H_2O) 10 M Ω ; tetraethoxysilane (TEOS), $Si(OC_2H_5)_4$, 99+% (Acros); [3-(methacryloyloxy)propyl] trimethoxysilane (MPTMOS), $H_2C=C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$, 98% (Aldrich); hydrochloric acid (HCl), 37% wt., ACS reagent grade; erbium sulfate octahydrate ($Er_2(SO_4)_3 \cdot 8H_2O$), 99.9%, (Acros); nitric acid (HNO_3), 60% (Aldrich).

Methods. In the present study we used spherical micro-mesoporous silica particles (MMSP) with a diameter of 405 ± 25 nm. MMSP were synthesized according to the method developed by us via basic hydrolysis of (80% mol. TEOS + 20% mol. MPTMOS) in $NH_3-H_2O-C_2H_5OH$ -surfactant mixture [5]. The molar ratio of the reagents (TEOS+MPTMOS): $NH_3:H_2O:C_2H_5OH$:CTAB was 1:60:370:230:0.2. The temperature of the reaction mixture was 65 °C, the synthesis duration – 1 h. To remove organics, the particles were washed with an alcoholic solution of HCl (0.01 M) and then were annealed in a flow of O_2 at a temperature of 400 °C for 5 h.

The functionalization of the inner surface with Er^{3+} ions was carried out by the method of capillary impregnation of particles with an erbium sulfate solution. The process technology was based on the technique developed by us previously for the adsorption of Ni^{2+} ions by mesoporous silica particles [6]. In this case, a weighed portion (0.5 g) of particles was added to 5 ml of



0.01M $\text{Er}_2(\text{SO}_4)_3$ solution and subjected to ultrasonic treatment for 2 h, after which the resulting suspension was left for a day. During the impregnation, erbium ions were adsorbed by active silanol groups on the inner surface of cylindrical silica nanochannels within MMSP [5, 6]. To remove excess $\text{Er}_2(\text{SO}_4)_3$, the particles were sedimented by centrifugation, and the supernatant was separated. After that, the particles were dried in air at 60 °C and then subjected to heat treatment at 200 °C for 30 min. To remove bulk erbium compounds from the outer surface of the MMSP and nanocrystallites from their pores, the particles were immersed with a 5M HNO_3 and kept for 2 h, after which the particles were centrifuged and the supernatant was poured off. The procedure was repeated twice. The resulting particles were then washed twice with deionized water.

Transmission electron microscopic measurements were performed using a Jeol JEM-2100F microscope (accelerating voltage 200 kV, point-to-point resolution 0.19 nm) equipped with Bruker XFlash 6T-30 energy dispersive X-ray (EDX) spectrometer. 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).

Results and Discussion

Fig. 1 shows TEM images with different magnifications of MMSP before (Fig. 1, *a*) and after (Fig. 1, *b*) adsorption of Er^{3+} ions. It can be seen that adsorption of erbium does not affect the size and the shape of the particles which remain the same. At the same time the porous structure of the particles becomes much more clearly visible due to the presence of an element with high *Z* number on the pore surface. One can see features with the sizes of 2.5 nanometers on the high-resolution TEM images of the particles' surface region (Fig. 1, *b*), which are indistinguishable in the case of untreated particles (Fig. 1, *a*). This value corresponds to the inner diameter of the nanochannels calculated from the results of nitrogen porosimetry (see below). Thus, the proposed technique for treatment of micro-mesoporous silica particles with Er^{3+} ions made it possible to visualize pores on high-resolution TEM images.

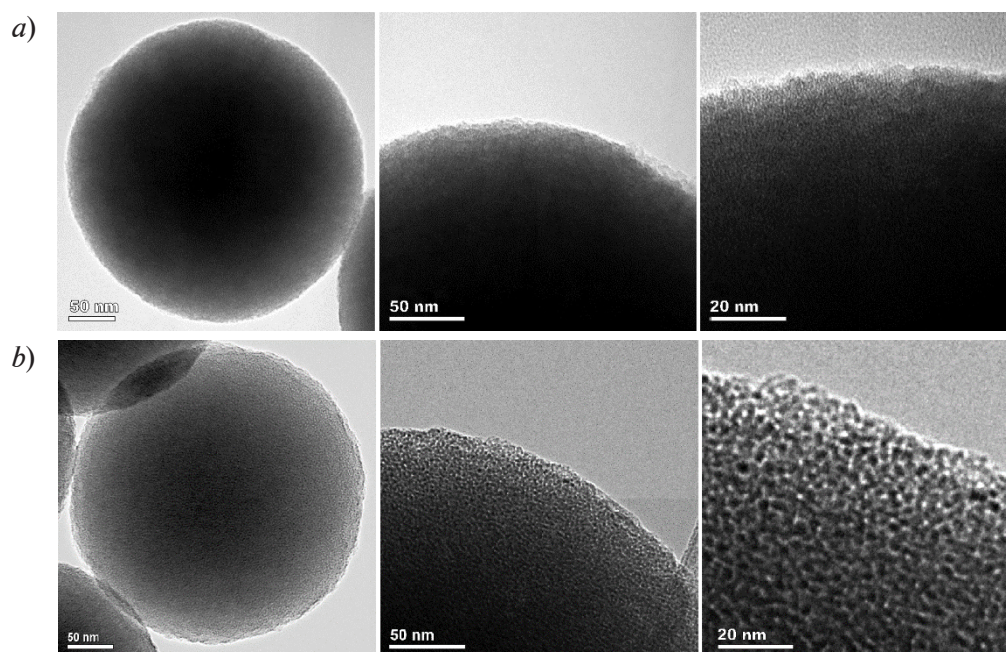


Fig.1. TEM images of micro-mesoporous silica particles before (*a*) and after (*b*) functionalization with erbium ions

The nitrogen adsorption and desorption isotherms of the MMSP we synthesized are shown in Fig. 2, *a*. The isotherms have a step-like form characteristic of M41S silica materials and belong to type IV [7]. The specific surface area of the particles was calculated in the pressure range $0.05 \leq p/p_0 \leq 0.20$ by the BET method. According to the results of adsorption structural analysis, the specific surface area and pore volume of particles before and after treatment with erbium

sulfate solution also remained practically unchanged and were found to be $1630 \text{ m}^2\text{g}^{-1}$, $0.72 \text{ cm}^3\text{g}^{-1}$ and $1610 \text{ m}^2\text{g}^{-1}$, $0.71 \text{ cm}^3\text{g}^{-1}$, respectively (Fig. 2).

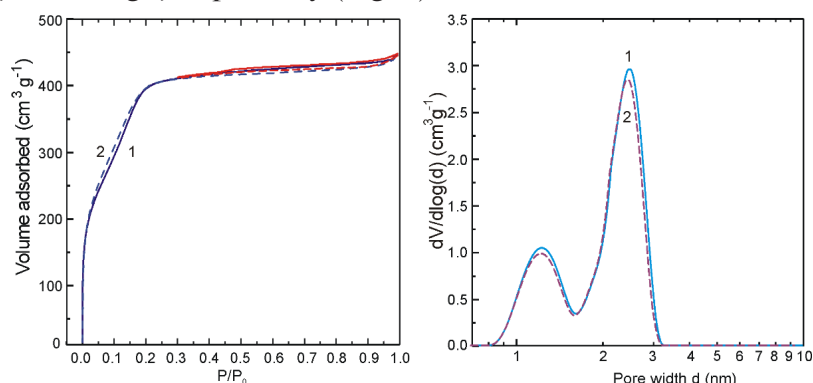


Fig. 2. N_2 adsorption and desorption isotherms at 77 K (a) and pore size distribution for particles before (1) and after (2) treatment with erbium sulfate solution (b)

The pore size distribution (Fig. 2, b curve 1) demonstrates that the synthesized MMSP contain pores ranging from 0.7 to 3.2 nm, which is in good agreement with the TEM data (Fig. 1, b). The adsorption of Er^{3+} ions does not change the diameter of the pores compared to the initial particles, which indirectly confirms a small content of erbium on the surface of pores. This also agrees with the EDX data (Fig. 3). There are no peaks corresponding to erbium observed on the spectrum, which indicates that its content does not exceed 0.1 % at. Peaks corresponding to Cu and C on the spectrum (Fig. 3) are due to the specimen support grid.

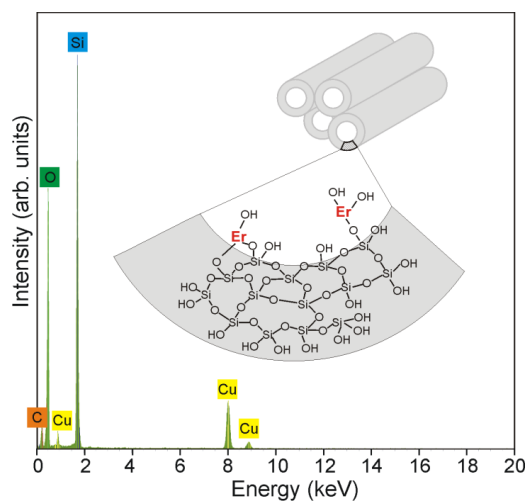


Fig. 3. EDX spectrum of MMSP after Er^{3+} adsorption. *Inset*: schematic representation of silica nanochannels with erbium ions adsorbed on the inner surface

Erbium was introduced into the pores of the MMSP so that erbium atoms were probably chemically bonded to the pore surface. The silanols on the inner surface of silica nanochannels demonstrate acidic behavior while erbium exhibits to a greater extent basic properties. Erbium oxy- and hydroxy silicates may form on the pore surface during the annealing. The similar compounds were observed in the MMSP/ Gd_2O_3 : Eu^{3+} composite [8]. After washing the MMSP/Er with concentrated HNO_3 only erbium atoms bonded to the surface silanols were present within the particles (Fig. 3, *inset*). The abundant erbium dissolved by acid was removed from the pores and the outer surface of the particles. Thus, as a result of treatment erbium-decorated inner surface of silica nanochannels were obtained.

Conclusion

A method is proposed for functionalization of the inner surface of silica with Er^{3+} ions in order to visualize pores inside micro-mesoporous particles by TEM. The proposed approach made



it possible to significantly enhance the contrast in TEM images of MMSP. It was shown that the adsorption of erbium ions does not affect the porous structure of particles. The developed technique is simple, easily reproducible, inexpensive, and can be applied to most porous materials in which it is required to study the internal structure.

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