

ГРАНУЛИРОВАННЫЕ НИЗКОМОДУЛЬНЫЕ ЦЕОЛИТЫ ДЛЯ ИЗВЛЕЧЕНИЯ КАТИОНОВ Со

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В работе дана характеристика гранул цеолитов LTA и SOD, которые были синтезированы с использованием предварительной ультразвуковой обработки. Методами рентгеновской дифракции и ИК-спектроскопии установлено, что исследуемые образцы содержат около 100% фазы LTA или SOD. Показано, что частицы цеолита LTA имеют размер области когерентного рассеяния 780 нм и величину среднеквадратичных микродеформаций 0,05%, в то время как у частиц цеолита SOD этот параметр составляет 462 нм, а дефектность кристаллической решетки 0,15%. Определены значения площади удельной поверхности гранул цеолитов, значения которых составляют 148,8 и 115,6 м²/г для LTA и SOD, соответственно. Отмечено, что гранулы цеолита SOD практически не имеют микрорпор. Получены равновесные кривые насыщения гранул цеолитов катионами кобальта в зависимости от концентрации Со²⁺ в водном растворе хлорида кобальта. Показано, что во всем исследованном диапазоне концентраций Со²⁺ емкость цеолита LTA на 30% больше, чем у цеолита SOD, что может быть объяснено двумя основными причинами. Во-первых, это более высокое значение площади удельной поверхности у цеолита LTA. Во-вторых, это особенности строения каркасов цеолитов. А именно, цеолит LTA имеет α -полости, которые имеют большую доступность для Со²⁺. Также установлено, что при увеличении температуры емкость цеолитов по катионам кобальта возрастает. Обнаружено, что на ИК спектрах обоих цеолитов после насыщения появляется новая полоса поглощения с волновым числом при 1390 см⁻¹. Кроме того, в насыщенных кобальтом цеолитах отмечено увеличение размера элементарной ячейки и рост дефектности частиц. В совокупности эти факты указывают на протекание катионного обмена. Показано, что 1 г цеолита LTA обеспечивает практически полную очистку 50 мл раствора от катионов ⁵⁷Со в динамическом режиме.

Ключевые слова: цеолит LTA; цеолит SOD; катионы кобальта; катионный обмен

GRANULATED LOW-MODULUS ZEOLITES FOR EXTRACTION OF Co CATIONS

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The paper gives a characteristic of LTA and SOD zeolite pellets, which were synthesized using preliminary ultrasonic processing. By X-ray diffraction and IR spectroscopy methods, it was established that the investigated samples contained about 100% of the LTA or SOD phase. It was shown that zeolite LTA particles have a dimension of coherent scattering region of 780 nm and root mean square microdeformations of 0.05%, while SOD zeolite particles have this parameter about 460 nm and the defectiveness of crystal lattice is 0.15%. The values of the specific surface area of zeolite pellets were determined, the values of which are 148.8 and 115.6 m²/g for LTA and SOD, respectively. It was noted that the SOD zeolite pellets have virtually no micropores. Equilibrium curves were obtained for the saturation of zeolite pellets with cobalt cations depending on the concentration of Co²⁺ in an aqueous solution of cobalt chloride. It was shown that in the entire investigated range of Co²⁺ concentrations, the LTA zeolite capacity is 30% higher than that of the SOD zeolite which can be explained by two main reasons. Firstly, this is a higher specific surface area of the LTA zeolite. Secondly, these are structural features of the zeolite frameworks, namely, LTA zeolite has α -cavities which are more accessible for Co²⁺. It is also shown that with increasing temperature, the zeolites capacity on cobalt cations grows. It was discovered that a new absorption band with a wave number at 1390 cm⁻¹ appears on the IR spectra of both zeolites after saturation. In addition, an increase in the size of the unit cell and a growth in the defectiveness of particles were noted in cobalt-saturated zeolites. Taken together, these facts point to the cation exchange. It was shown that 1 g of LTA zeolite provides almost complete purification of 50 ml of the solution from ⁵⁷Co cations in a dynamic mode.

Key words: LTA zeolite; SOD zeolite; cobalt cations; cation exchange

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INTRODUCTION

Zeolites are aluminosilicates that have regular cavities in the crystal lattice. The zeolite framework is formed by TO₄ tetrahedra (where T = Si⁴⁺, Al³⁺, etc.). The excess charge (in the case of T = Al³⁺) is compensated by the mobile metal cations (Na⁺, K⁺, etc.) [1, 2]. Therefore, zeolites with a Si:Al ratio close to 1 have the maximum number of exchange cations. For this reason, one of the applications of low-modulus zeolites is the extraction of metal cations (including radioactive isotopes) from solutions [3-5]. In particular, LTA and SOD zeolites have Si:Al = 1, which makes them very attractive as cation exchange material.

The empirical formula of LTA zeolite is [Na₁₂][Al₁₂Si₁₂O₄₈], and of SOD zeolite is [Na₆][Al₆Si₆O₂₄]. β -cages are the basic building units of the framework of both zeolites and consist of 24 T-atoms [1]. In the SOD zeolite framework, β -cages are linked through simple T4-rings (S4Rs); in LTA zeolite, β -cages are combined through double T4-rings (D4Rs) and form α -cages in the zeolite framework, which are confined to simple T8-rings (S8Rs) [6].

The traditional method of zeolite synthesis is hydrothermal zeolitization of metakaolin in a solution of alkali and sodium aluminate [7, 8]. This method is

characterized by a long process time and sensitivity to synthesis conditions [9-11]. Another drawback of these methods is the preparation of zeolites in powder form which for industrial applications requires the use of a binder (eg clay) [12]. In Refs [13, 14], methods for the preparation of granulated binder-free zeolite have been described, which are also characterized by a significant synthesis time. To intensify the zeolites synthesis, ultrasonic processing seems to be very promising [15, 16]. The use of ultrasound allows not only to reduce the synthesis time, but also to optimize the porous structure of zeolites [17-20], which, of course, will positively affect the cation exchange processes [2, 4, 5, 12].

Thus, the aim of this work is to study the cation exchange properties of LTA and SOD zeolites in the process of extracting the Co cation from aqueous solutions.

EXPERIMENTAL PART

For research, granulated binder-free LTA and SOD zeolites with size of pellets 3 mm have been synthesized from metakaolin and sodium hydroxide using ultrasonic (22 kHz) pre-treatment. The procedure for preparing pellets of these zeolites has been described in detail in Refs [21, 22].

The powder X-ray diffraction (XRD) patterns were recorded on DRON-3M X-ray diffractometer (CuK α radiation, Ni-filter, scan rate was 1 min⁻¹). Since LTA and SOD zeolites have a cubic lattice [1], the unit cell size was calculated according to the corresponding equation using data on interplanar distances obtained from XRD and Miller's indexes. The dimension of the coherent scattering region and the value of root mean square microdeformations were determined from broadening the reflection profile using the Selyakov–Scherrer equation [23].

The Fourier transformed infrared (IR) spectra were measured by Shimadzu IRPrestige-21 spectrometer. The absorption bands were identified using data Ref [24].

N₂ adsorption-desorption isotherms were measured at 77 K on the Micromeritics ASAP-2400 analyzer. Samples were outgassed at 573 K before the adsorption measurements. The specific surface area of zeolites and pore volume were calculated using the BET equation.

Since zeolites are supposed to be used for cleaning solutions with a low concentration of metal cations, only the starting sections of the sorption curves were studied. To research the cation exchange properties of zeolites, aqueous CoCl₂ solutions with a concentration of 0.1 to 1.0 mg Co/ml were used. The zeolite pellets were placed in a solution and kept for 7 days in order to achieve equilibrium. The concentration of the Co²⁺ cation was measured by the photocalorimetric method.

To study the dynamic capacity of zeolite, a model solution of cobalt chloride with a concentration of 0.01 mg/ml was prepared. The activity of 1 ml of ⁵⁷Co solution was 2920 Bq. The installation for ⁵⁷Co extraction under dynamic modes was a glass column with a diameter of 7.5 mm; zeolite mass was 3 g; the

flow rate of the solution was 1 ml/s. The content of ⁵⁷Co after the column was monitored by the activity of the solution, which was measured using an OSGI Eu-152 gamma spectrometer.

RESULTS AND DISCUSSION

According to XRD data (Table 1), zeolites are pellets in which the basic crystalline phases are LTA and SOD. The sizes of the zeolite unit cells are close to published data [1]. The dimension of the coherent scattering region of LTA zeolite particles is more than 1.5 times larger than that of SOD. At the same time, the defectiveness of the LTA crystal lattice is 3 times less than the defectiveness of the SOD, as evidenced by the values of root mean square microdeformations.

The IR spectra of the samples confirm the XRD data. So, the IR spectrum of zeolite LTA (Fig. 1, I) contains absorption bands at 470 and 420 cm⁻¹, which are attributed to external deformation vibrations of T–O bonds in the β -cell of zeolite [24]. The absorption band at 560 cm⁻¹ corresponds to internal deformation vibrations in D4Rs through which β -cells in the LTA zeolite framework are connected. The wide and intense band in the wavenumbers range of 1240–820 cm⁻¹ is a set of absorption bands that correspond to symmetric and asymmetric stretching vibrations of the Si–O and Al–O bonds as well as to deformation vibrations of the Si–O–Al bonds. The IR spectrum of zeolite SOD contains characteristic bands at 710 and 665 cm⁻¹, which correspond to internal and external symmetric stretching vibrations in S4Rs (Fig. 2, I). In the spectra of both zeolites, a wide absorption band in the range 1800–1560 cm⁻¹ is observed. This band corresponds to bending and stretching vibrations of water molecules [25].

Table 1

Characterization of crystalline structure of granular zeolites

Таблица 1. Характеристика кристаллической структуры гранулированных цеолитов

Zeolite type		Percentage of the crystalline phase of zeolite, I, %	Unit cell size, a, Å	Dimension of the coherent scattering region, D _{CSR} , nm	Value of root mean square microdeformations, ϵ , %
LTA	starting	98	24.76	780	0.05
	after saturation	96	24.79	772	0.11
SOD	starting	99	8.88	462	0.15
	after saturation	96	8.92	456	0.19

Measurements of the parameters of the porous structure of zeolites show that the specific surface area and total pore volume of the LTA zeolite are approximately 30% greater than that of the SOD zeolite (Table 2). It should also be noted that the SOD zeolite pellets have virtually no micropores.

Investigations of the static capacity of granulated zeolites showed that the cation exchange capacity of LTA zeolite is approximately 30% higher than

Table 2

Characterization of porous (by BET) structure of granular zeolites

Таблица 2. Характеристика пористой (по БЭТ) структуры гранулированных цеолитов

Zeolite type	Specific surface area, S, m ² /g	Total pore volume, V _t , cm ³ /g	Micropore volume, V _{mp} , mm ³ /g
LTA	148.8	0.041	0.007
SOD	115.6	0.033	0.001

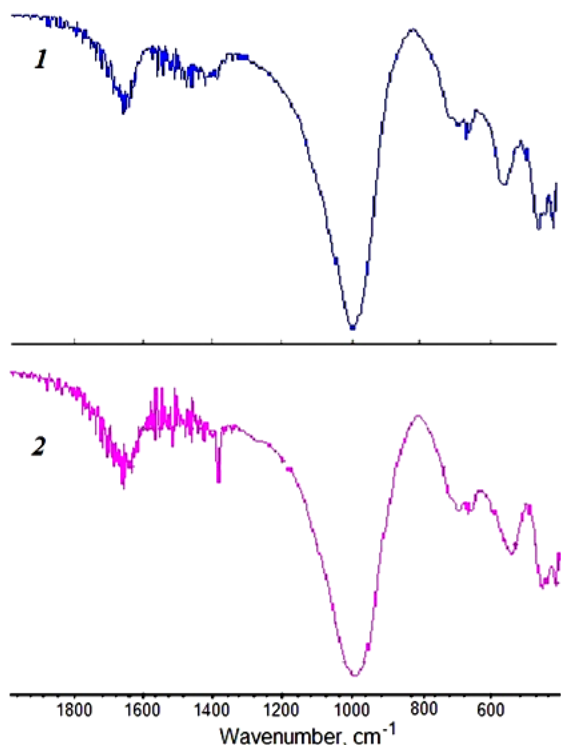


Fig. 1. IR spectra of LTA zeolite. 1 – initial; 2 – after saturation with cobalt cations

Рис. 1. ИК спектры цеолита LTA. 1 – исходный; 2 – после насыщения катионами кобальта

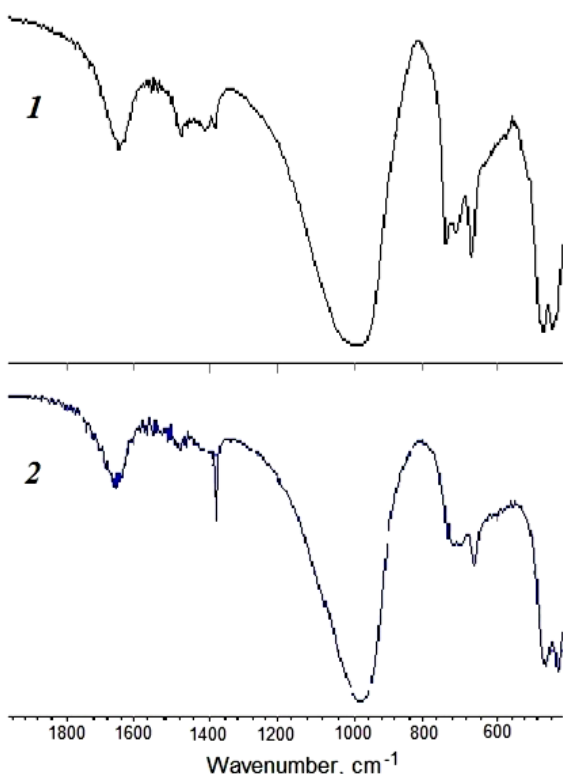


Fig. 2. IR spectra of SOD zeolite. 1 – initial; 2 – after saturation with cobalt cations

Рис. 2. ИК спектры цеолита SOD. 1 – исходный; 2 – после насыщения катионами кобальта

that of SOD (Figs. 3 and 4). Since these zeolites are supposed to be used for the purification of highly dilute solutions, it is especially important that the LTA capacity for cobalt cations is higher at low (up to 0.03 mg/ml) Co^{2+} concentrations. Since these zeolites are supposed to be used for the purification of highly dilute solutions, it is especially important that the LTA capacity for cobalt cations is higher at low (up to 0.03 mg/ml) Co^{2+} concentrations. The higher capacity of LTA zeolite compared to SOD with an equal ratio of Na:(Al + Si) is due to two reasons. Firstly, LTA zeolite has a larger specific surface area. Secondly, LTA zeolite, unlike SOD, has α -cavities in its crystal structure which increases the availability of Co^{2+} to the sites of mobile sodium cations in the zeolite framework.

Another regularity of the dependences of the capacity of zeolites from the solution concentration is an increase in the absorption capacity of samples with

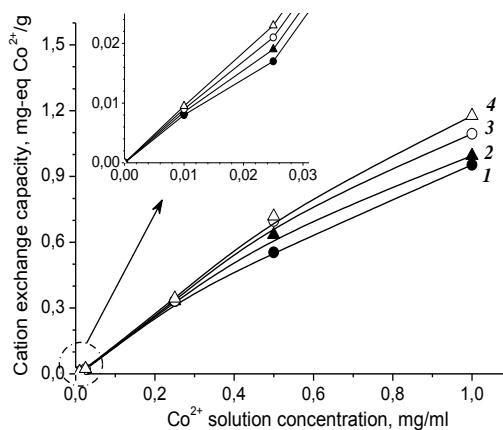


Fig. 3. Static capacity of the LTA zeolite depending on the concentration of cobalt cations. Temperature, °C: 1 – 25; 2 – 40; 3 – 50; 4 – 60
Рис. 3. Статическая емкость цеолита LTA в зависимости от концентрации катионов кобальта. Температура, °C: 1 – 25; 2 – 40; 3 – 50; 4 – 60

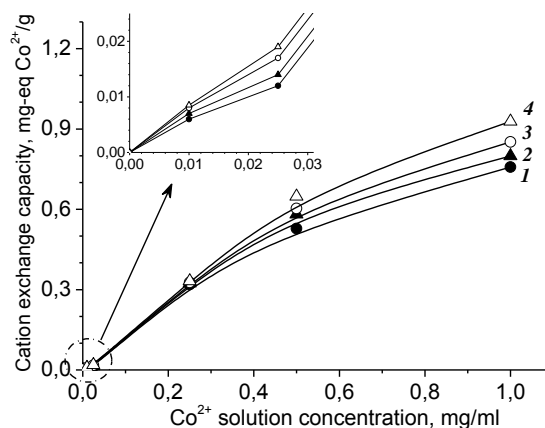
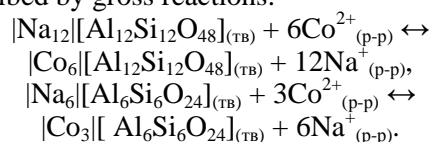


Fig. 4. Static capacity of the SOD zeolite depending on the concentration of cobalt cations. Temperature, °C: 1 – 25; 2 – 40; 3 – 50; 4 – 60
Рис. 4. Статическая емкость цеолита SOD в зависимости от концентрации катионов кобальта. Температура, °C: 1 – 25; 2 – 40; 3 – 50; 4 – 60

increasing temperature in the entire tested range of cobalt cation concentrations (Figs. 3 and 4). This is due to a decrease in the effective cation size which increases the absorption capacity of the zeolite [26]. Therefore, the extraction of cobalt cations from solutions by zeolites has a chemical nature, namely, cation exchange [2]. In the case of physical adsorption, we would observe the opposite regularities, namely, a decrease in sorption capacity with increasing temperature.

IR spectra of the samples confirm the occurrence of cation exchange. So, the spectra of the starting samples are fully consistent with the declared types of zeolites (Fig. 1 and 2, 1). On the IR spectra of the samples after saturation with Co^{2+} cations, an absorption band appears at 1390 cm^{-1} (Figs. 1 и 2, 2). This band may be associated with the appearance of new acid centers, most likely, Lewis acid centers, which form cobalt atoms [2, 24]. Thus, processes can be described by gross reactions:



Analysis of the crystal structure showed that after saturation with cobalt cations, the unit cell size and the root mean square microdeformations of both zeolites increase against the background of a decrease in the dimension of the coherent scattering region (Table 1). The combination of these facts can be explained as follows. The cobalt cation has a larger size than the sodium cation, therefore, when Na^+ is replaced by Co^{2+} , the zeolite frameworks are deformed which results in an increase in these parameters. The data of IR spectroscopy confirm the deformation of zeolite frameworks (Figs. 1 and 2, 2). In particular, the vibrational bands corresponding to the D4Rs groups in LTA zeolite and S4Rs in SOD zeolite are shifted to the long-wavelength region of the spectrum.

Dynamic capacity studies were carried out in a flow-through installation on LTA zeolite pellets. Tests have shown that 1 g of LTA zeolite can provide almost complete purification of 50 ml of the solution of ^{57}Co cations. Thus, the radioactivity of the solution decreases from 2920 to ~ 10 Bq (Fig. 5). Also, we can note that a satisfactory degree of purification in dynamic mode is achieved with a solution volume of about 60 ml per 1 g of LTA zeolite.

CONCLUSIONS

By X-ray diffraction and IR spectroscopy methods, it has been shown that zeolite granules contain almost 100% of the LTA or SOD phase. It has been found that the dimension of the coherent scattering region of LTA particles is 1.7 times larger, and the value of root mean square microdeformations is 3

times smaller than that of SOD zeolite. The specific surface areas of zeolite pellets have been determined, the values of which for LTA are 30% higher than for SOD. It has been noted that the SOD zeolite pellets have virtually no micropores.

Equilibrium curves have been obtained for the saturation of zeolite pellets with cobalt cations as a function of the concentration of Co^{2+} in an aqueous solution. It has been shown that in the entire studied range of concentrations, the capacity of LTA zeolite is 30% higher than that of SOD zeolite. It has been established that with increasing temperature, the zeolites capacity on cobalt cations increases which indicates the occurrence of cation exchange. These conclusions have been confirmed by the data of IR spectroscopy (the appearance of a new absorption band) and X-ray analysis (an increase in the size of the unit cell and the value of the root mean square microdeformations).

It has been shown that 1 g of LTA zeolite provides almost complete purification of 50 ml of the solution from ^{57}Co cations in a dynamic mode.

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