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**LSX ZEOLITE BASED MICROPOROUS ADSORBENTS
FOR INDUSTRIAL PROCESSES OF ADSORPTIVE GAS SEPARATION**

**МИКРОПОРИСТЫЕ АДСОРБЕНТЫ НА ОСНОВЕ ЦЕОЛИТА LSX
ДЛЯ ПРОМЫШЛЕННЫХ ПРОЦЕССОВ
АДСОРБЦИОННОГО РАЗДЕЛЕНИЯ ГАЗОВ**

A.I. Akmalov, G.F. Garieva, I.N. Pavlova, O.S.Travkina,
FSBEI NPE “Ufa State Petroleum Technological University”, Ufa,
the Russian Federation

Institute of Petrochemistry and Catalysis of the Russian Academy of Sciences
Ufa, the Russian Federation

Акмалов А.И., Гариева Г.Ф., Павлова И.Н., Травкина О.С.,
ФГБОУ ВПО «Уфимский государственный нефтяной технический
университет», г. Уфа, Российская Федерация

Институт нефтехимии и катализа Российской академии наук,
г. Уфа, Российская Федерация
e-mail: artur_akmalov@mail.ru

Abstract. Among the factors influencing the adsorption activity of zeolites should give the number of cations in the zeolite , their availability for the adsorbate molecules and cationic charge density and radius of the cation.

Synthesized samples of powdered zeolite LSX high phase purity and 100% crystallinity in NaK , Li, Na, K , Ca and Mg - forms. By X-ray analysis and the low-temperature nitrogen adsorption was studied the effect of the chemical nature of the cation exchange on the phase composition and characteristics of the porous structure of the zeolite LSX. The equilibrium adsorption capacity of the sample zeolite type LSX in NaK, Li, Na, K , Ca and Mg- forms of the water vapor .

It has been shown that zeolite type LSX high degree of crystallinity and phase purity in Li- Na- forms can be synthesized starting from NaK- form, and K, Ca and Mg- forms - only from its Na- form.

According to the low-temperature nitrogen adsorption determined that by replacing the cations NaK cations Li and Na, an increase, and when replacing the cations K , Ca and Mg - decreased availability of the crystal structure of the microporous zeolite LSX.

Found that replacing cations can affect the limiting adsorptive capacity for water vapor ion-exchanged forms of zeolite LSX in the range of 0.27-0.34 cm³/g. Maximum values of the equilibrium water adsorption capacity are characteristic of zeolite LSX in Li- form.

Аннотация. Среди факторов, влияющих на адсорбционную активность цеолитов, следует назвать количество катионов в цеолите, их доступность для молекул адсорбата, а также плотность заряда катиона и радиус катиона.

Синтезированы образцы порошкообразного цеолита LSX высокой фазовой чистоты и близкой к 100% степени кристалличности в NaK, Li, Na, K, Ca и Mg - формах. Методами рентгенофазового анализа и низкотемпературной адсорбции азота было исследовано влияние химической природы обменного катиона на фазовый состав и характеристики пористой структуры цеолита LSX. Определены равновесные адсорбционные емкости образцов цеолита LSX в NaK, Li, Na, K, Ca и Mg- формах по парам воды.

Показано, что цеолит типа LSX высокой степени кристалличности и фазовой чистоты в Li- и Na-формах можно синтезировать из исходной NaK-формы, а в K, Ca и Mg-формах - только из его Na- формы.

По данным низкотемпературной адсорбции азота определено, что в результате замены катионов NaK на катионы Na и Li наблюдается увеличение, а при замене на катионы K, Ca и Mg - уменьшение доступности микропористой структуры кристаллов цеолита LSX.

Установлено, что заменой катионов можно влиять на предельные адсорбционные емкости по парам воды ионообменных форм цеолита LSX в интервале значений 0,27-0,34 см³/г. И максимальные значения равновесных адсорбционных емкостей по воде, характерны для цеолита LSX в Li-форме.

Key words: adsorbents, LSX zeolite, synthesis, ion-exchange forms, adsorptive gas separation.

Ключевые слова: адсорбенты, цеолит LSX, синтез, ионообменные формы, адсорбционное разделение газов.

Introduction

Industrial processes of adsorptive separation of gas mixtures, including air separation, are based on use of microporous adsorbents. At present time air separation for nitrogen and oxygen preparation is 20% realized with use of adsorptive technologies [1-6]. It's known that the most perspective adsorbents in these processes at present time are A, X and LSX zeolites in different ion-exchange forms.

The purpose of our research was to develop a practically perspective way of synthesis of powder (from 1,0 to 10 μm) LSX-type zeolite of high phase purity and close to 100 % crystallinity degree in NaK, Li, Na, K, Ca and Mg - forms, as well as to define characteristics of porous structure and adsorption properties of synthesized adsorbents.

Experimental

LSX-type zeolite is usually synthesized in NaK- form. We synthesized powder NaKLSX zeolite according to the methods provided in [7].

Li, Na, K, Ca and Mg- forms were obtained from NaK-LSX, by ion-exchange in solutions of applicable chlorides. The ion-exchange experiments were conducted in isothermal batch reactor at 70 °C, with initial salt concentra-

tion in the solution being 70 g/l (excess of the second exchange cation against sodium).

The chemical composition of liquid and solid phases was analyzed by gravimetric method and also by methods of complexometric titration and flame photometry [8].

The phase composition of zeolites was determined by X-ray phase analysis on the automatic diffractometer PHILIPS PW 1800. For determination the technique of Debye-Scherrer (powder diffraction technique) was used. Conditions: $\theta/2\theta$ -scanning; retainer rotation – 1 rpm.sec⁻¹; anode material – cuprum; range – 5-55°/2 θ ; step – 0,05°; step exposition – 2 seconds; anode voltage and current – 40 kW and 30 mA correspondingly. X-ray patterns were identified according to the reported diffraction data [9]. Relative crystallinity of zeolites was measured as ratio of obtained samples' reflection intensities to intensities of standard sample's reflection.

For measuring the specific surface (S_N , m²/g) and pore volume (V_p , cm³/g) of synthesized samples the method of low-temperature (77,4K) nitrogen adsorption on "Sorptomatic-1900" ("Fisons") apparatus was used [10-11]. Degassing of samples was carried out at 400°C to the remaining vacuum of 10⁻⁶mm Hg. S_N value was measured basing on the surface area of nitrogen molecule of 0,162nm², the nitrogen density in normal liquid state of 0,808g/cm³. S_N measuring precision made $\pm 5\%$.

For determining the equilibrium adsorption capacities (cm³/g) by H₂O - A(H₂O) of the obtained adsorbents the desiccator way, which is widely accepted in industrial practice, was used [12].

Results and Discussion

Among factors affecting adsorptive activity of zeolites it's necessary to mention, in the first place, the quantity of cations in a zeolite, their availability to adsorbate molecules, as well as cation charge density and cation radius. Availability

of cations for adsorption depends on features of crystalline structure of the given type zeolite, and also on the total number of cations: the bigger it is the more cations will be arranged accessively. The number of zeolite cations is strongly dependent on Si/Al ratio. Thus, a great achievement of adsorbent synthesis for the last ten years is the synthesis of low-silicate X (LSX) zeolite, with its Si/Al being equal to 1, as opposed to the ordinary X zeolite, with its Si/Al being equal to 1,25-1,50[13]. In LSX zeolite, unlike A and X zeolites, the negative charge of crystal lattice is compensated by Na and K cations.

Table 1 provides the research results of the influence of nature of exchange cation and number of ion-exchange treatments on the degree of Na and K cations exchange for Li, Na, K, Ca and Mg cations in NaKLSX zeolite.

Table 1. Influence of the number of treatments on the degree of exchange in NaKLSX zeolite

Number of treatments	Exchange degrees of Na and K cations in NaKLSX zeolite for the cations				
	Li	K	Na	Ca	Mg
1	0,67	0,50	0,66	0,68	0,41
2	0,75	0,67	0,78	0,79	0,50
3	0,90	0,77	0,97	0,81	0,59
4	0,93	0,79	0,98	0,85	0,64

The provided results show that LSX zeolite requires three exchange treatments to achieve the maximum exchange degree. Further increase of their number shows no significant influence on exchange degrees. The obtained results are in good agreement with the reference data [14, 15].

With ion-exchange of Na and K cations for Li, Na, K, Ca and Mg cations in the specified conditions, the exchange degrees have been found to make 0,93, 0,98, 0,79, 0,85 and 0,64 respectively.

Maximum values of exchange degrees of Na and K cations do not coincide with those studied in the given work and are due to the difference of cations' own sizes and energy of their hydration.

Figures 1 and 2 show X-ray patterns of NaKLSX zeolite, and also its ion-exchange forms LiLSX, KLSX, NaLSX, CaLSX and MgLSX with limit values of exchange degree.

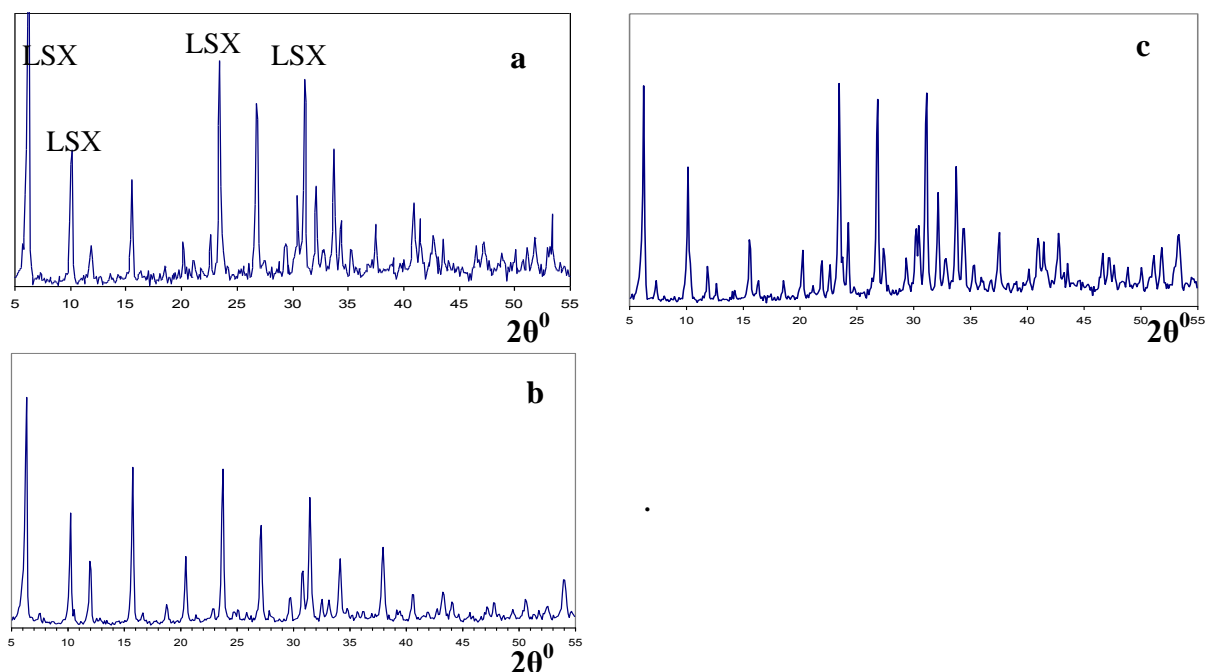


Figure 1. Diffractograms of NaKLSX(a), LiLSX(b) and NaLSX(c) samples after heat treatment at 450 C, 3h

According to the X-ray diffraction analysis provided in Figure1, the crystallinity degree of NaKLSX(1a), LiLSX(1b) and NaLSX(1c) zeolite samples is close to 100%.

Other results are observed in preparation of K, Ca and Mg-forms of LSX zeolite. The X-ray patterns given in Figure 2 prove that KLSX(2a), CaLSX(2b) and MgLSX(2c) samples show partial amorphization of their crystal structure which makes 19, 32 and 30% respectively. The X-ray patterns also show diffraction peaks which are characteristic of A-type zeolite.

In order to solve this problem in [16] it is suggested to obtain a more stable LSX zeolite in Na-form with the exchange degree being at least 0,98, and to use it for obtaining other ion-exchange forms of LSX zeolite.

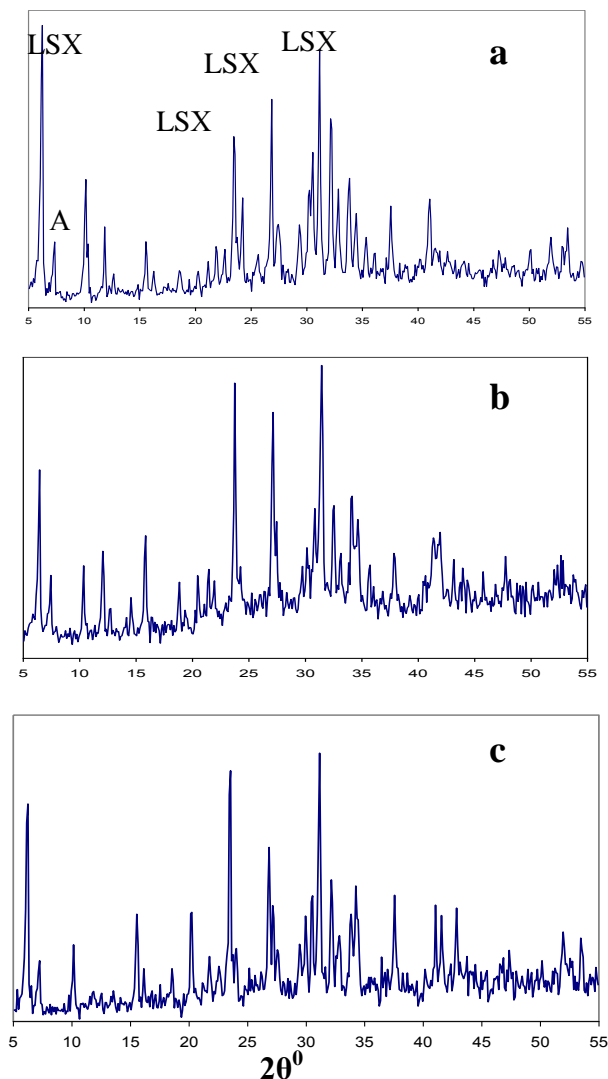


Figure 2. Diffractograms of KLSX(a), CaLSX(b) и MgLSX(c) samples after heat treatment at 450 °C, 3h

Table 2 provides the research results of the influence of nature of exchange cation and number of ion-exchange treatments on the degree of Na cations exchange for K, Ca and Mg cations in NaKLSX zeolite.

Table 2. Influence of the number of treatments on the degree of exchange in NaLSX zeolite

Number of treatments	Exchange degrees of Na cations in NaLSX zeolite for the cations		
	K	Ca	Mg
1	0,62	0,76	0,59
2	0,75	0,80	0,73
3	0,82	0,87	0,78

The provided results show that while obtaining K, Ca and Mg- forms of LSX zeolite from its Na-form, samples with bigger values of exchange degree were synthesized. According to the X-ray diffraction analysis, the crystallinity degree of the obtained ion-exchange forms of LSX zeolite makes 97-98%.

Table 3 provides the characteristics of porous structure of powder LSX-type zeolite in different ion-exchange forms with limit exchange degrees according to figures of low-temperature nitrogen adsorption.

Table 3. Specific surface* (S_N , m^2/g) and pore volume* (V_p , cm^3/g) of powder LSX-type zeolite in different ion-exchange forms

Name	NaKLSX	NaLSX	LiLSX	KLSX	CaLSX	MgLSX
S_N	687	716	722	606	456	401
V_p	0.260	0,278	0,321	0,263	0,305	0,259

* - according to figures of low-temperature nitrogen adsorption

It's known that microporous materials to which zeolite belong as well are characterized by volume filling of all the space available for adsorption [17, 18]. That's why the surface area value measured by method of low-temperature nitrogen (S_N) adsorption in which the calculations are based on monolayer surface coverage by nitrogen molecules is apparent. At the same time S_N value allows to measure the change of availability of microporous structure of zeolite's own crystals, since the temperature close to the temperature of liquid nitrogen which is used for S_N defining, makes nitrogen molecules diffuse zeolite cavities which have the diameter of pore entrance being at least 0.5nm [17].

The data given in table 3 prove that LSX zeolite, as a result of ion exchange for monovalent Na and Li cations, has S_N increased from $687m^2/g$ in parent LSX to 716 and $722m^2/g$ in NaLSX and LiLSX samples respectively. At the same time the ion exchange for monovalent K cation and bivalent Ca and Mg cations results in decrease of S_N value till 606, 456 and $401m^2/g$ respectively.

Thus, exchange of NaK cations for Na and Li results in increase, and exchange for K, Ca and Mg cations – in decrease of availability of microporous

structure of LSX zeolite crystals.

The research results of influence of the nature and composition of Li, K, Na, Ca and Mg cations in LSX zeolite on ultimate adsorptive capacities by water vapors $A(H_2O, \text{cm}^3/\text{g})$ are provided in table 4.

The data from table 4 proves that exchange of Na cations in NaLSX zeolite for Li cations smaller in size results in increase of $A(H_2O)$ values from $0,31 \text{cm}^3/\text{g}$ to $0,34 \text{cm}^3/\text{g}$ respectively. Exchange of Na cations for bigger K cations and bivalent Ca and Mg cations results in decrease of $A(H_2O)$ values from $0,31 \text{cm}^3/\text{g}$ in NaLSX sample to $0,28$, $0,27$ and $0,29 \text{cm}^3/\text{g}$ in KLSX, CaLSX and MgLSX samples respectively.

Table 4. $A(H_2O, \text{cm}^3/\text{g})$ of ion-exchange forms of NaKLSX zeolite

Zeolite's cationic form	$A(H_2O)$	Zeolite's cationic form	$A(H_2O)$
NaK-LSX	0,31	NaK-LSX	0,31
0,98Na-LSX	0,31	0,98Na-LSX	0,31
0,82K-LSX	0,28	0,87Ca-LSX	0,27
0,93Li-LSX	0,34	0,78Mg-LSX	0,29

Thus, cations exchange makes it possible to change ultimate adsorptive capacities by water vapors of ion-exchange forms of LSX zeolite within the value interval of $0,27-0,34 \text{cm}^3/\text{g}$.

The observed difference of $A(H_2O)$ values by 10-15% upward or downward during exchange of Na cations for Li, K, Ca and Mg cations may be due to decrease or increase of the limit volume for filling, as well as to possible distortion of zeolite's crystal structure.

However, increase or decrease of water vapor adsorption in ion-exchange forms of LSX zeolite shall not only be connected with sieving activity since sizes of "entrances" to big cavities after the exchange are still available for water molecules.

Other researchers' works [19] state that while filling the primary zeolite pores with water molecules and other polar molecules the latter ones are first of

all arranged near cations which compensate the charge of lattice; they are active centers of polar substances. Analyzing the obtained data it's easy to notice the correlation between hydration capacity of cations which compensate the charge of anion lattice and adsorbability of water vapors in the corresponding ion-exchange zeolite forms. Thus, the amount of adsorption of polar substances on zeolites is defined to a significant extent by interaction of molecule of the adsorbed substance with cations.

Conclusions

It was shown that LSX-type zeolite of high crystallinity and phase purity in Li- and Na-forms can be synthesized from the initial NaK-form, and in K, Ca and Mg-forms – only from its Na-form.

According to figures of low-temperature nitrogen adsorption it was determined that exchange of NaK cations for Na and Li cations resulted in increase, and exchange for K, Ca and Mg cations – in decrease of availability of microporous structure of LSX zeolite crystals.

It was found that exchange of cations might affect the ultimate adsorptive capacities by water vapors of ion-exchange forms of LSX zeolite within the value interval of 0,27-0,34 cm³/g. And maximum values of equilibrium adsorptive capacities for water are characteristic of LSX zeolite in Li-form.

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About the authors**Сведения об авторах**

A.I. Akmalov, Graduate Student, a Group MTP21-13-01, FSBEI NPE USPTU, Ufa, the Russian Federation

Акмалов А.И., магистр, группа МТП21-13-01, ФГБОУ ВПО УГНТУ, г.Уфа, Российская Федерация

e-mail: artur_akmalov@mail.ru

G.F. Garieva, Post Graduate Student, Institute of Petrochemistry and Catalysis of the Russian Academy of Science, Ufa, the Russian Federation

Гариева Г.Ф., аспирант, Институт нефтехимии и катализа Российской академии наук, г. Уфа, Российская Федерация

I.N. Pavlova, Candidate of Chemical Sciences, Institute of Petrochemistry and Catalysis of the Russian Academy of Science, Ufa, the Russian Federation

Павлова И.Н., канд. хим. наук, Институт нефтехимии и катализа Российской академии наук, г. Уфа, Российская Федерация

O.S. Travkina, Candidate of Chemical Sciences, Assistant Professor of the Chair «Technology of Oil and Gas », FSBEI NPE USPTU, Ufa, the Russian Federation

Травкина О.С., канд. хим. наук, доцент кафедры «Технология нефти и газа», ФГБОУ ВПО УГНТУ, г.Уфа, Российская Федерация