Energy of adsorption of polar molecules on NaLSX zeolite

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Abstract. The article presents precision data of isotherms and total thermodynamic characteristics, i.e. ΔH, ΔF and ΔS of H_2O adsorption on NaLSX zeolite. The stepwise nature of the change in the heat of adsorption on the studied systems with surface filling is revealed, and the molecular mechanism of water adsorption on NaLSX zeolite in the entire filling area is revealed. It was found that the polar water molecule is adsorbed in the NaLSX zeolite in an amount of 31.8 H_2O/1/8 e.u., of which 25.3 are in super cavities, and 6.5 are in β-cavities.

1 Introduction

One of the main tasks of colloid chemistry is the study of the number, strength and nature of active centers of dispersed substances, which makes it possible to solve numerous theoretical problems of adsorption and catalysis. Due to the high adsorption and catalytic activity of zeolites, they are widely used in many areas of industry and technology. Among them, first of all, it should be noted deep drying and purification of oil products and natural gas, environmental protection and catalysis.

The unrelenting interest in structural studies of zeolites is stimulated by the fact that they are widely used in chemical technology. The regular structure of zeolites can be easily modified, making it possible to obtain a wide range of adsorbents and catalysts suitable for various reactions. The nature of acidic and basic sites and the distribution of lithium and sodium cations in the zeolite matrix are among the most important problems in surface chemistry.

The authors of [1] synthesized zeolite LSX (Low Silica Type X) by microwave heating. LSX zeolite is synthesized using conventional and microwave heating methods. In both cases, the zeolite is characterized by high crystallinity and purity, a low Si/Al molar ratio, and a potassium concentration per unit cell (~ 7 wt.%). It is noted that microwave heating reduces the duration of the synthesis, which is due to the uniformity of heating. Microwave heating also reduces the nucleation and crystallization times. The catalytic properties of the zeolite were tested on the example of the alkylation of toluene with methanol, and no difference was noted in the catalytic properties of both zeolites.

In [2], the adsorption separation of N_2 and A_2 was carried out by some zeolites in Li - ion-exchange form with a high degree of exchange. Lithium zeolite types 4A, 13X, and LSX with a high degree of exchange were obtained by the multiple IR method in aqueous solution. IA and output dynamic curves of N_2 and Ar were measured on these zeolites at 25°C. It was shown that zeolite LiNaA, LiNaX and LiLSX. The study of the adsorption dynamics shows that when using zeolite in an almost completely Li-cation-exchange form, the separation of N_2 and Ar can be carried out in a convenient pressure range. The study of the adsorption dynamics shows that when using zeolite in an almost completely Li-cation-exchange form, the separation of N_2 and Ar can be carried out in a convenient pressure range.

For the studied pressure range, the best separation was obtained at a pressure of 0.6 MPa, while out of the three studied zeolites, zeolite LiLSX possesses the best separation properties. A study of nitrogen and oxygen adsorption on LSX zeolites has been undertaken [3]. The adsorption of nitrogen and oxygen on zeolites of the LiLSX type in CaLSX at temperatures (-50°C), 20°C, 70°C in the pressure range 0.01-1.2, 1.5 atm was studied. Nitrogen adsorption on LiLSX zeolite at all temperatures is about 5-6 times higher than oxygen adsorption. This indicator for the CaLSX zeolite reaches 3. The differential heat of adsorption of nitrogen is approximately 10-12 kJ/mol compared to oxygen for CaLSX and decreases for nitrogen in the range 0.01-1 mmol / g from ~ 30 to ~ 20 kJ/mol. mole. For zeolite LiLSX, the heat of nitrogen adsorption falls in the range 0.03-0.6 mmol / g from ~ 38 to ~ 25 kJ / mol. For nitrogen, the heat of adsorption is 15-17 kJ/mol higher than for oxygen. The activation energies for diffusion of nitrogen and oxygen on LiLSX zeolite are 2-3 times higher than on CaLSX, and are, respectively, 9-10 kJ/mol and 2-4 kJ/mol [3].

The equilibrium sorption properties of nitrous oxide on type X zeolite with a low silicon content were established in [4]. The thermodynamic functions of N_2O sorption on NaLSX and CaLSX zeolites in the form of

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spherical granules bound by clay are described. Thermodynamic functions were determined from adsorption isosteres and compared with the previously published thermodynamic functions of CO_2 adsorption on NaLSX zeolite. Additional information was obtained by simulating adsorption by the Monte Carlo method.

In [5], the vibrational motion frequencies and diffusion coefficients of N_2 and O_2 adsorbed in LiLSX were determined by the neutron scattering method. Measurements were carried out for the same component at 260K with different fillings. The experimental value of the longitudinal frequency N_2 in the interaction with Li cations is compared with the results of quantum chemical calculations. According to the data of quasi-elastic neutron scattering, O_2 diffusion occurs faster than N_2. The Darken approximation turns out to be inaccurate, with the corrected values of the diffusion coefficients N_2 and O_2 decreasing with increasing filling.

The crystal structures of faujasite types of dehydrated LSX zeolites with two different degrees of Li exchange 85% and 100% were studied at room temperature by neutron powder diffraction [6]. Both structures were purified in the space group Fd^3 and were alternating (Si) silicon and - (Al) aluminum lattice tetrahedra. All extralattice cations have been detected.

Partially mixed zeolite LSX (Low silica X) with the composition $Li_{82}Na_{14}Si_{96}Al_{96}O_{384}$, a = 24.6845 (1) Å, has the following location: center I` = 32 Li, center II = 32 Li, center III = 18 Na. A fully substituted LSX zeolite with the composition $Li_{95}NaSi_{96}Al_{96}O_{384}$, a = 24.6845 (1) Å, has the following location: center I` = 32 Li, II = 32 Li, III = 15 Li and III` = 16 Li.

The study of the authors of [7] is devoted to the comparison of the 17O NMR spectra of zeolites of the LTA and LSX types. A comparative study of ^{17}O NMR of various cation-exchange zeolites of the LTA and LSX types was carried out. LSX samples containing divalent cations contain resonances with close chemical shifts relative to the spectra previously assigned to "bare" framework oxygen atoms in the Ca-LTA and Sr-LTA systems. The data are consistent with trends in the spectra of LTA and LSX type zeolites with monovalent cations, which show an increase in the average chemical shift with increasing cation radius. The spectrum of Li-LSX, like Na-LSX, can be attributed to the T-O-T bond angles. The study of gas sorption on Li-LSX facilitates the identification of framework oxygen atoms forming β-cavities and demonstrates the sensitivity of ^{17}O shifts to gas adsorption.

The authors of [8] studied the adsorption of nitrogen and oxygen on industrial zeolites NaX, CaE and LiLSX. At a temperature of 773 K and pressures up to 100 kPa, nitrogen adsorption isotherms were measured, and on the basis of the theory of volumetric filling of micropores using the condition of linearity of isosteres, the calculations of nitrogen and oxygen adsorption at a temperature of 293 K and pressures up to 10 MPa are given. The obtained isotherms satisfactorily describe the data obtained experimentally.

Zeolites of the LSX type are interesting objects for scientific research: they are porous bodies characterized by a specific skeletal structure and regular geometry of pores (intracrystalline cavities and channels). An important feature of zeolites is the ability to vary the chemical composition of crystals and the geometric parameters (shape and size) of intracrystalline pores, i.e. the possibility of their structural and chemical modification, which can be carried out either by varying the conditions for direct synthesis of zeolites, or by changing the chemical composition of zeolite crystals of the same structural type. This fact makes zeolites very convenient objects for studying adsorption equilibria, the nature of adsorption interactions, the mechanism and kinetics of catalytic reactions, molecular sieve effects, and diffusion of molecules in fine pores of controlled sizes [9].

For 20 years, zeolites have been used in industry for air purification using PSA (pressure swing adsorption) [10]. The nitrogen adsorption capacity of LSX correlates with the amount of positively charged Li cations. Zeolites LiX and LiY are widely used as catalysts for isomerization of olefins [11]. In [12], the dispersal of Li cations in a zeolite matrix was determined. For this, classical diffraction methods are used, especially for single crystals. However, obtaining a single crystal of zeolite is difficult and therefore, mainly, the method of X-ray diffraction of powders is used.

Refinement of the results obtained on the basis of these methods is time-consuming. There is another problem - the presence of mobile cations and molecules in zeolites. Since Li cations contain only two effective electrons, the neutron diffraction technique should be used to study it instead of X-ray analysis.

It is also advisable to use the solid state NMR technique. For example, recently, using 23Na MAS and DOR NMR spectroscopy [13], the location of six components related to different crystallographic positions of Na cations was studied. Forano and colleagues [14] published the first results on the characterization of Li cations in anhydrous LiX zeolite (Si / Al = 1.25). It was found that the cations are located in three positions in the β - and super cavities.

SI Vratislav and colleagues [15] studied the structure of NaLSX. The reaction of methyl iodide with Na cations was used to obtain anchor methyl groups in the zeolite structure, which was monitored by 13C MAS NMR spectroscopy. Samples of neutron diffraction were obtained at 298 and 723 K on a KSN - 2 diffract meter, which was placed in a research reactor LVR - 15. All structural parameters of the samples were given in [1–2, 16]. The following authors [17-21] have dealt with the issues of energy, electrical mechanisms and the energy of adsorption of the adsorbent.

Purpose of the work: Investigation of the energy and mechanism of adsorption of polar molecules on NaLSX zeolite.

2 Research methods

We carried out adsorption studies on NaLSX zeolite. The unit cell composition of the NaLSX zeolite is $Na_{96}Si_{96}Al_{96}O_{384}$. Before the start of the experiment, the adsorbent was pumped out at 723 K for 10 hours to a

high vacuum (10^{-3} Pa). The adsorption-calorimetric method used in this work allows one to obtain high-precision molar thermodynamic characteristics, as well as to reveal the detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and dosage of adsorbate were carried out using a universal high-vacuum adsorption unit, in the working section of which exclusively mercury gates were used, replacing lubricated taps. The installation allows for dosage of the adsorbate both by gas-volumetric and volumetric-liquid methods. A modified DAK 1-1 calorimeter with high accuracy and stability was used as a calorimeter. To study the adsorption properties of zeolites, water was chosen as the adsorptive.

The adsorption of water in microporous zeolites is of great scientific and technical interest due to the widespread use of zeolites as catalysts, adsorbents for drying, purification, and separation of gases and liquids [22].

The behavior of water in the structure of zeolites was studied by various methods [16, 23]. In dehydrated zeolites, exchangeable cations that compensate for the negative charge of alumino-oxygen tetrahedra are localized in certain energetically favorable positions of the adsorbent structure. One of the main methods for diagnosing the structure of crystalline adsorbents is X-ray diffraction.

Using this method, one can obtain information on the localization of cations in the structure of the adsorbent. However, it is not suitable for studying the host/guest interaction in the H_2O/NaLSX adsorption system, since Na differs little from H_2O in the number of electrons, and therefore it is difficult to distinguish them. The only alternative to this method is the adsorption calorimetry method, which provides detailed information on the formation of ion / molecular complexes in the zeolite matrix in a wide range of fillings, ranging from zero values to saturation. Zeolite NaLSX is a new faujasite type zeolite with Si/Al = 1. Until recently, the studied zeolites had Si/Al>1.09. According to [6], the distribution of cations in the zeolite structure is as follows: 4 cations per 1/8 of the unit cell (1/8 e.u.) are located in the S_I position (in the six-membered rings connecting cuboctahedra and hexagonal prisms), 4 cations per 1/8 e.i. are located in the S_{II} position (in six-membered rings connecting cuboctahedrons and large cavities) and the remaining 4 cations at 1/8 e.u. are located in position S_{III}(at the four-membered rings of the large cavity). In total, there are 12 cations per 1/8 e.u., or the super cavity, or 96 cations per unit cell. As seen from the composition, zeolites have a very high charge density. Figure 1 shows the adsorption isotherm (a) of water in NaLSX zeolite. The isotherm does not change smoothly with increasing pressure, but has kinks, each of which reflects the transition from the adsorption of one type of centers to another.

It is known [24] that adsorption on microporous zeolites proceeds according to the bulk filling mechanism. Using the provisions of the theory of Polyany and generalizing a large experimental material, Dubinin M.M. with colleagues came to the conclusion

about the possibility of using the Weibul distribution function as the distribution function of the adsorption volume over the value of the potential for describing adsorption on microporous adsorbents.

With regard to the distribution of the degree of filling over the adsorption potential, the Weibull distribution function is represented by the ratio:

$$\Theta = \exp\left[-\left(A / E\right) n\right] \qquad (1)$$

Where, E and n are parameters independent of temperature.

The value of E is called the characteristic adsorption energy. The exponent n is expressed in integers from 1 to 6, depending on the structure of the adsorbent. A is the work of adsorption, i.e. the work of transferring 1 mol of gas from the surface of a liquid adsorbate (pressure P °) into an equilibrium gas phase (pressure P):

$$A = RT\ln\left(P / P °\right) \qquad (2)$$

The degree of adsorbent filling can be represented as the ratio of the adsorption value a to the maximum adsorption a0. Then from equation (1) we get:

$$a = a0\exp\left[-\left(A / E0\right)\right] n \qquad (3)$$

In [24], the possibility of a complete description of the isotherm was shown using the polynomial equation of TOZM (up to 3^x).

3 Results and discussion

We were able to fully describe the isotherm of water adsorption on NaLSX zeolite with a three-term equation:

$$a = 9.59exp\left[-A / 30.11\right) 4\right]+ \\ +5.53exp\left[-A / 15.15\right) 6\right] +3.98exp\left[-A / 5.98\right) 2\right] \qquad (4)$$

where, a is the adsorption value in mmol/g, A = RTln (P/P°) is the adsorption work in kJ/mol. For the water - NaLSX system, the parameters of the equation for the first term are: a01 = 9.59 mmol/g, E01 = 30.11 kJ/mol and n1 = 4; for the second term a02 = 5.53 mmol / g, E02 = 15.15 kJ / mol and n2 = 6; and for the third term a03 = 3.98 mmol/g, E03 = 5.98 kJ/mol and n_3 = 2.

The most subtle information on ion-molecular interactions is provided by the differential heats of adsorption (Q_d) of water in the NaLSX zeolite (Fig. 2). The curve has a pronounced stepwise character, where each step stoichiometrically reflects the formation of multidimensional cation-water complexes with cations located in different crystallographic positions.

The following segments can be distinguished on the Q_d curve: the first, where a = 0 - 2.69 mmol/g, and the heat Q_d varies from 91 to 80, 3 kJ / mol; the second - a = 2.69 - 5.13 mmol/g, Q_d = 80.3 - 67 kJ/mol; third - a = 5.13 - 7.54 mmol/g, Q_d = ~ 68 kJ/mol; fourth - a = 7.54 - 9.87 mmol/g, Q_d = ~ 69 kJ/mol; fifth - a = 9.87 - 13.58 mmol/g, Q_d = ~ 70 kJ/mol; sixth - a = 13.58 - 17.32 mmol/g, Q_d = 67.5 - 55.5 kJ/mol; and, finally, the seventh - a = 17.32 - 18.69 mmol/g, Q_d = 55.5 - 46.6 kJ / mol.

The segments showed generally correlate well with the number of cations in different crystallographic positions. A difference was observed in the case of adsorption on cations in the $S_{III'}$ and $S_{I'}$ positions. Instead of 4 molecules $H_2O/1/8$ e.i. 4.6 water molecules are adsorbed on $S_{III'}$; therefore, the number of cations in the SI' position should be less. The number of cations in the S_{II} position exactly corresponds to the number indicated in [6].

Further, adsorption occurs on the same cations with the formation of multidimensional cation / water complexes. In total, 31.8 water molecules are adsorbed per 1/8 of the unit cell, of which 25.3 are in supercavities, 6.5 in β-cavities.

Using the precision values of differential heats of adsorption and adsorption isotherms, we calculated the differential molar entropy of adsorption (ΔS_d) of water on NaLSX (Fig. 3). The calculated data are plotted against the entropy of liquid water. In accordance with the stepped Q_d curve, the adsorption entropy curve has a polyextremal form. Each step has its own partial entropy of adsorption. The average molar integral entropy of water adsorption in the cavities of the NaLSX zeolite is - 20.28 J/mol*K.
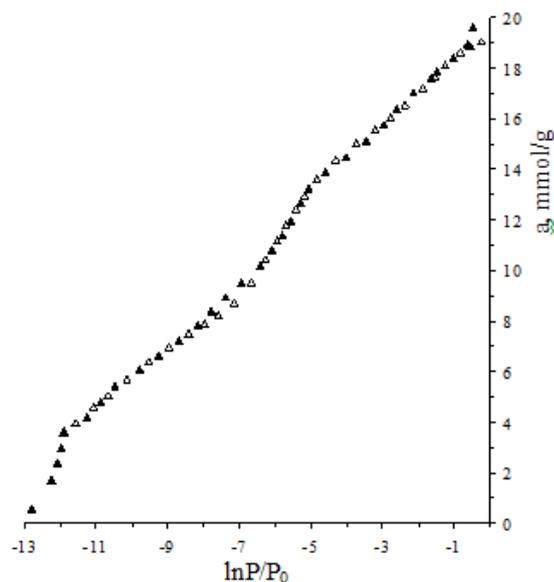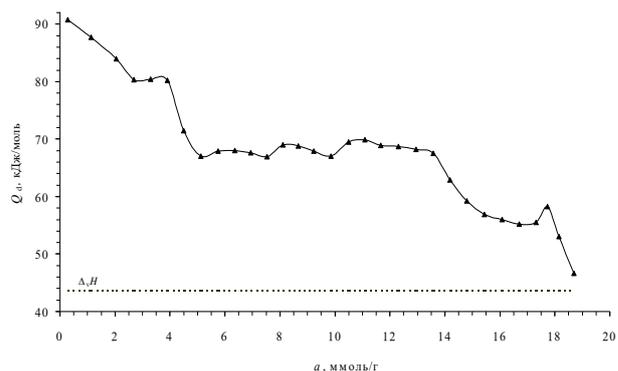

Fig. 2. Differential heats of adsorption of H_2O in NaLSX zeolite at 303 K. Horizontal dashed line - heat of condensation of H_2O at 303 K.

This value indicates the hindered state of water molecules in the matrix zeolite is close to the mobility in crystalline water (in this diagram, the entropy of ice is - 26 J/mol*K). Figure 4. the dependence of the time of establishment of adsorption equilibrium (τ) on the filling of the zeolite with water is presented. At low fillings, equilibrium is established in more than 10 hours. With increasing pressure, the adsorption process is accelerated, and equilibrium is reached in ~ 2 hours. The slowdown in adsorption in the range from 2.69 to 5.13 mmol/g is due to the difficulty of penetrating water molecules into the β-cavity. The size of the 6-membered oxygen windows entering the β-cavity is 2.6-2.8 Å [22-25].
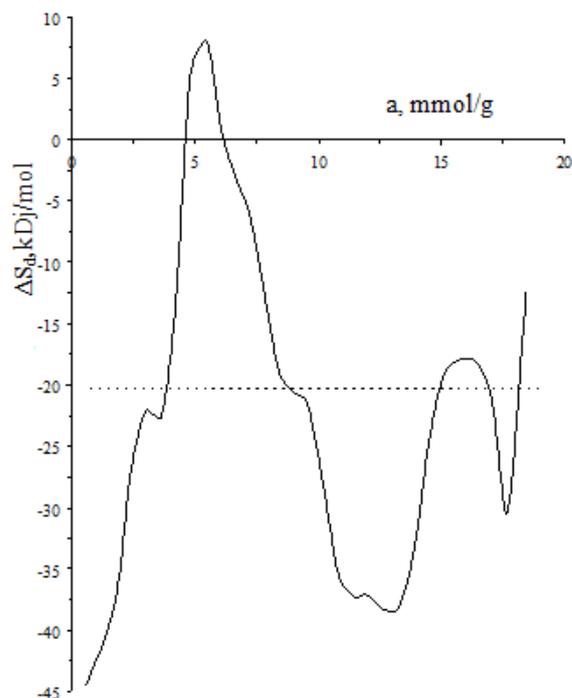

Fig. 1. Isotherm of H_2O adsorption on NaLSX zeolite at 303 K.

Fig. 3. Differential molar entropies of H_2O adsorption in NaLSX zeolite at 303 K. Horizontal dashed line - mean integral entropy. The entropy of liquid H_2O is taken to be zero.
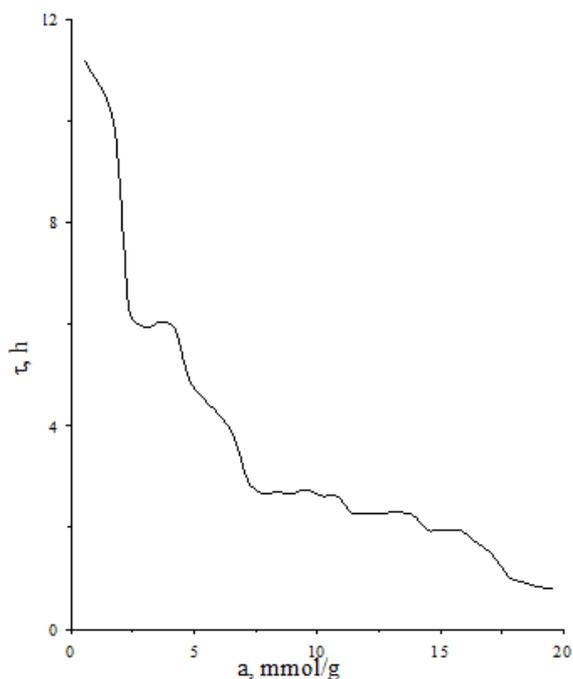
Fig. 4. The time to establish adsorption equilibrium depending on the amount of water adsorption in NaLSX zeolite at 303 K.

4 Conclusion

The stepwise nature of the change in the heat of adsorption on the studied systems with surface filling is revealed, and the molecular mechanism of water adsorption on NaLSX zeolite in the entire filling area is revealed. It was found that the polar water molecule is adsorbed in the NaLSX zeolite in an amount of 31.8 $H_2O/1/8$ e.u., of which 25.3 are in super cavities, and 6.5 are in β-cavities.

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