

Thermodynamics of hydrogen sulfide adsorption in Zeolite LiX

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Abstract. Sulfur compounds adversely affect the technological process of oil and gas refining, as well as the release of sulfur-containing compounds into the atmosphere, polluting the environment. Oil and gas processing is carried out using microporous adsorbents with high sorption capacity in the purification of gases containing sulfur. This is one of the most efficient methods in oil refining and gas processing. In research work, the adsorption of gases containing sulfur in their composition is carried out in various ways. When determining the formation complex, the main centers of Li-ionic molecules, it was possible to obtain a more accurate idea of the adsorption mechanism at the stages of absorption of hydrogen sulfide molecules into Li-zeolites using a highly sensitive adsorption calorimeter. In our study, in the process of adsorption of hydrogen sulfide on the LiX zeolite, the results of differential adsorption heat, isotherm, entropy, and thermal equilibrium time (thermokinetics) based on obtained in a high vacuum adsorption device are accurately revealed. Based on exact formulas, it was proved how many hydrogen sulfide molecules are adsorbed in the zeolite that died under vacuum conditions.

1 Introduction

The growing interest in zeolites is associated with their wide involvement in industrial technologies as catalysts, and therefore, researchers are making efforts in an attempt to synthesize new types of zeolite materials [1-3]. Synthetic materials such as aluminophosphate microporous [4-5] and siliceous [6-7] structures have been developed to optimize catalytic processes. The active sites in them include acid sites, which are associated with the presence of extra lattice metal cations (alkaline, alkaline earth, and transition cations). The activity of centers in them often depends on the structure of zeolites and is studied by the spectroscopic method, attachments for molecular samples [1]. In particular, acidic properties are analyzed at the molecular level using weakly interacting molecular probes by IR spectroscopy. However, works devoted to the study of the acidic

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properties of zeolites using the calorimetric method, which provides reliable and quantitative information, are not enough. In this report, we have focused mainly on LiX zeolite, which has a wide range of applications.

Zeolites - porous crystals, are adsorbents since the charges on their surface are concentrated in cations of small sizes, and negative charges are dispersed over many oxygen atoms of aluminum and silicon-oxygen tetrahedra. It is of interest to study on this surface the adsorption of substances containing atoms specifically interacting with cations.

The structure of X zeolites consists of supercages with almost spherical symmetry, with a diameter of ~ 0.125 nm and a window size of ~ 0.74 nm. Each cavity is connected to four other cavities arranged tetrahedrally. The structure also contains sodalite cavities connected by double six-membered rings. Univalent extra lattice cations predominantly occupy different crystallographic positions I, I', II and III'.

Adsorption processes can be studied in various ways. Rarely there are studies carried out by the calorimetric method on a high-vacuum adsorption device when calculating the number of adsorbed molecules. Using this method, research work was carried out with synthetic zeolites, clay minerals, and other substances with sorption properties. [8-16, 23-35].

2 Methods and materials

The composition of the studied zeolite is $\text{Li}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}$. To dry and purify hydrogen sulfide, it was passed through a column with zeolite. Differential molar adsorption-calorimetric studies of the adsorption of hydrogen sulfide in the LiX molecular sieve were carried out using the device described in [17, 18]. Dissolved gases were removed by freezing the adsorbent followed by evacuation. The use of the method of compensation of heat fluxes by the Peltier effect made it possible to increase the accuracy of measuring the heats of adsorption by an order of magnitude. The calorimeter allows you to measure the heat released for an unlimited time. Adsorption measurements were carried out on a universal high-vacuum volumetric setup, which made it possible to carry out adsorption measurements and dosage of the adsorbate with great accuracy.

3 Results and discussion

If we take into account that the size of the super cavity of type X zeolite is greater than 7 Å, and the size of the hydrogen sulfide molecule is less than 4 Å, then the adsorbate (H_2S) molecules will be adsorbed.

When the initial adsorption isotherm of hydrogen sulfide molecules is equal to 0.145 mmHg, $\ln$ -exponent will be equal to -11.78. The growth of the isotherm diagram goes with a slight change until the value of the adsorption isotherm reaches $\ln = -8.9$. Then there is an increase in adsorption in the vertical position. The saturation pressure of hydrogen sulfide is 17936 mmHg. The adsorption isotherm of hydrogen sulfide on zeolite LiX was studied at pressures up to 760 mm Hg.

A good correlation is observed between the heats of adsorption and the isotherm. The isotherm (Figure 1), as well as the heats of adsorption, have three segments. During adsorption on Li^+ cations in the position S_{III} , it rises sharply, then inclines towards the adsorption axis and grows up to 0.5 mmol/g (S_{I}). After the inflection, the isotherm with a slight slope to the adsorption axis grows linearly until saturation (S_{II}).

The adsorption isotherm of hydrogen sulfide on the LiX molecular sieve is satisfactorily described by the three-term equation of the theory of volume filling of micropores [19, 20]

$$a = 47.22\exp[-(A/45.40)^{30}] + 46.91\exp[-(A/27.83)^3] + 10650\exp[-(A/15.36)^3],$$

where: a - adsorption in micropores in mmol/g, $A=RT \ln(P^0/P)$ – adsorption energy in kJ/mol.

On fig. 2 shows a plot of differential heat (Q_d) versus number (a) of hydrogen sulfide adsorption molecules in LiX zeolite. Thermal condensation (ΔH_v) of hydrogen sulfide adsorption is indicated by dotted lines. Relatively constant differential heat of adsorption of hydrogen sulfide occurs in the range from 0.25 mmol/g to 3.67 mmol/g and this value is ~ 2.31 times higher than the value of thermal condensation of the adsorbate. Each change in the differential heat of adsorption of hydrogen sulfide molecules has its own specific sorption properties.

The differential heat, starting from 55.63 kJ/mol, decreases to 49.38 kJ/mol, where adsorption is between 0.02-0.25 mmol/g. At this stage, due to the fact that hydrogen sulfide molecules have a small volume, they are adsorbed in the part of the LiX zeolite close to the 12-ring entrance windows, that is, in the S_I cavity. This is due to the interaction of hydrogen sulfide with oxygen atoms that bind aluminum and silicon, forming an α -super cavity, causing a high level of differential heat of adsorption. Hydrogen sulfide interacts with the Li^+ cation in the S_I cavity, which is located between six rings that form zeolite structures consisting of oxygen atoms that bind aluminum and silicon.

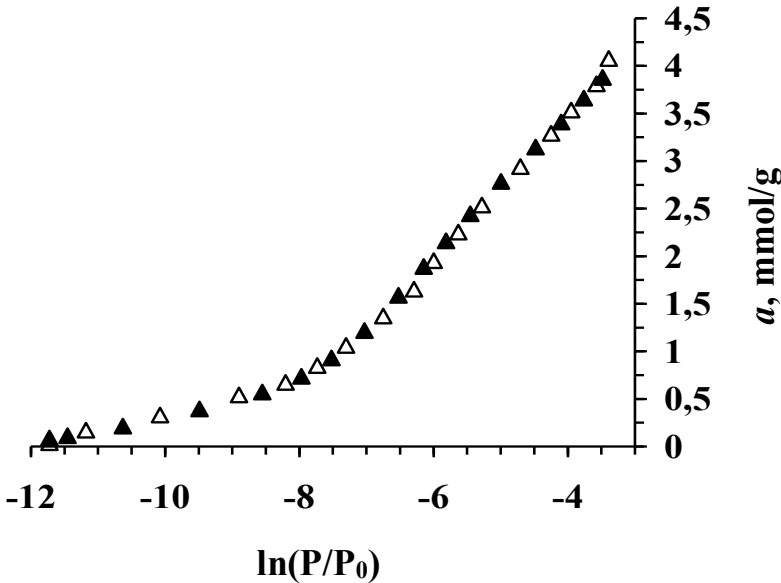


Fig. 1. Hydrogen sulfide adsorption isotherm in LiX zeolite at 303 K. Δ -experimental value; $\blacktriangle$ -value of the point, calculated on the basis of the equations of the theory of volumetric filling of micropores

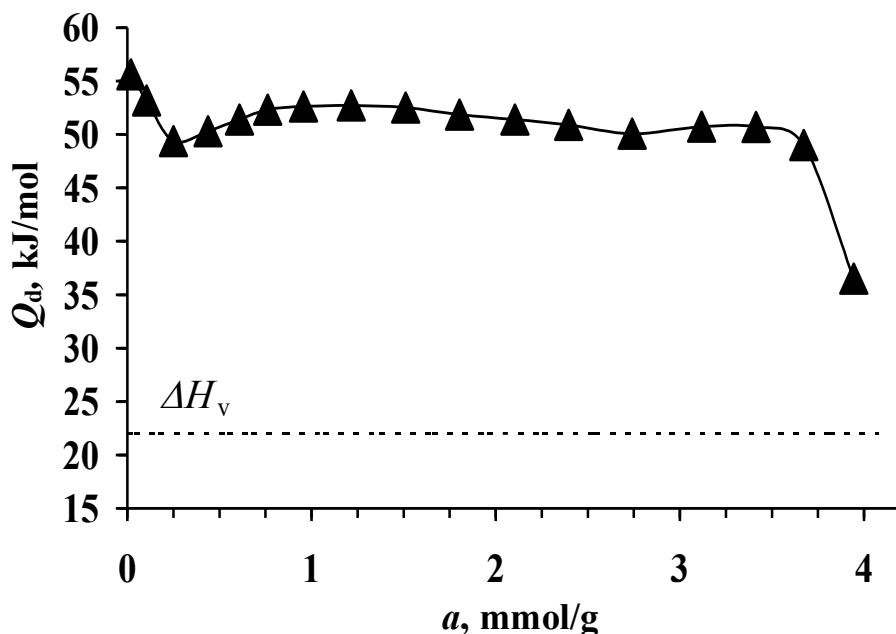


Fig. 2. Differential heat of adsorption of hydrogen sulfide molecules in LiX zeolite at a temperature of 303 K. Horizontal dotted lines – condensation of the heat of hydrogen sulfide adsorption at a temperature of 303 K.

The heat of adsorption increases from 49.38 kJ/mol to 52.33 kJ/mol, and the adsorption value ranges from 0.25 mmol/g to 0.75 mmol/g. When adsorbing the next 0.5 mmol/g of hydrogen sulfide molecules, the constant heat is ≈ 52 kJ/mol. A slight decrease in the heat of adsorption is observed during the sorption of hydrogen sulfide molecules after an adsorption amount of 0.76 mmol/g. The temperature drop continues to 2.76 mmol/g. The sorbing hydrogen sulfide then forms a second adsorption thermal constant. This constant value is ≈ 50 kJ/mol. This thermal stability is maintained up to 3.6 mmol/g. A sharp decrease in heat for subsequent sorbing molecules of hydrogen sulfide is observed an increase in the direction of thermal condensation. Thermal condensation of hydrogen sulfide is 22 kJ/mol.

The arrangement of four $\text{H}_2\text{S}/\text{Li}^+$ complexes has the shape of a tetrahedron, and such clusters fill almost all voids in active centers. At the final stage, the heat increases significantly and at 303 K drops sharply, depending on the heat of hydrogen sulfide condensation. Modeling of the hydrogen sulfide/zeolite system shows that the fifth hydrogen sulfide molecule is located in a 12-ring oxygen window separating the super cavities from each other (position W). For zeolites X and Y having Na^+ cations, this position has been repeatedly discussed [21,22].

In one active center of LiX zeolite, only 3.94 mmol/g of hydrogen sulfide molecules are adsorbed.

On fig. Figure 3 shows the differential entropy of hydrogen sulfide adsorption on LiX zeolite. When calculating the differential heat of adsorption of hydrogen sulfide on LiX zeolite, as well as the differential entropy, taking into account the value of the isotherm, the formula of the Gibbs-Helmholtz equation was used:

$$\Delta S_d = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_d - \lambda) + A}{T}$$

λ -thermal condensation, ΔH and ΔG - change of enthalpy and free energy, T – temperature, Q_d' - average differential heat capacity.

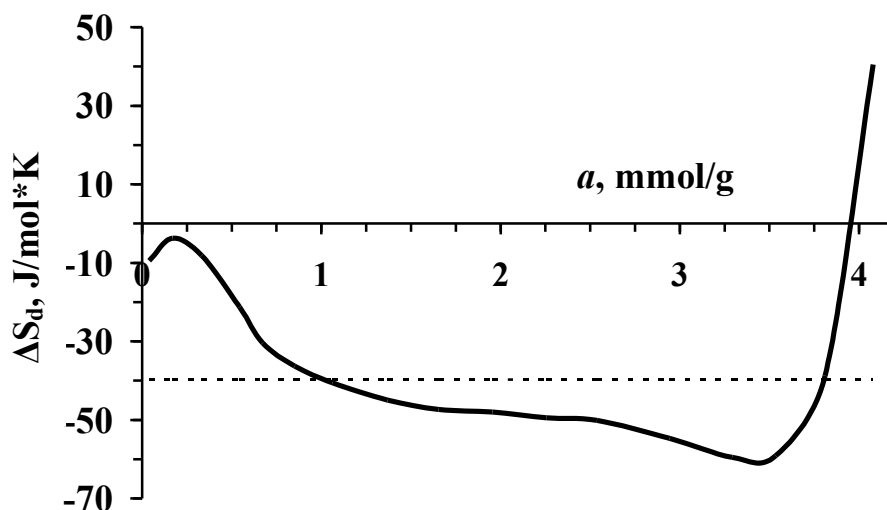


Fig. 3. The differential entropy of the hydrogen sulfide adsorption in the zeolite LiX at 303K. Entropy of liquid is taken as zero. The horizontal dashed line – mean molar integral entropy.

According to the results of the studies carried out in the study of the entropy of adsorption, the structure of the voids of the adsorbate, the surface area and the location of cations in the voids are considered. From the very beginning of the process, it is known that a high adsorption temperature indicates that hydrogen sulfide molecules at initial saturation are strongly adsorbed in the active centers of the zeolite, that is, the adsorbate molecules are in a stationary state.

The differential entropy of adsorption initially starts from -9.5 J/mol*K and the adsorption is $a = 0.04 \text{ H}_2\text{S/Li}^+$. And then there is a slight maximum increase in the adsorption entropy up to -3.7 J/mol*K. The adsorption of hydrogen sulfide molecules after 0.17 mmol/g is accompanied by a sharp decrease in entropy. When the adsorption rate reaches 3.54 mmol/g, the entropy reaches a minimum value of -59.04 J/mol*K. An increase in entropy is observed during the adsorption of adsorbate molecules after 3.54 mmol/g. The zeolite is adsorbed in cavity S_{II} in the range of adsorption from 0.5 mmol/g to 3.85 mmol/g in active sites. Since there are many empty pores in this part of the zeolite, the adsorption entropy values will be high, and the adsorbate molecules will be inactive, since the cations are not completely saturated with hydrogen sulfide molecules. The average integral entropy is -39.74 J/mol*K.

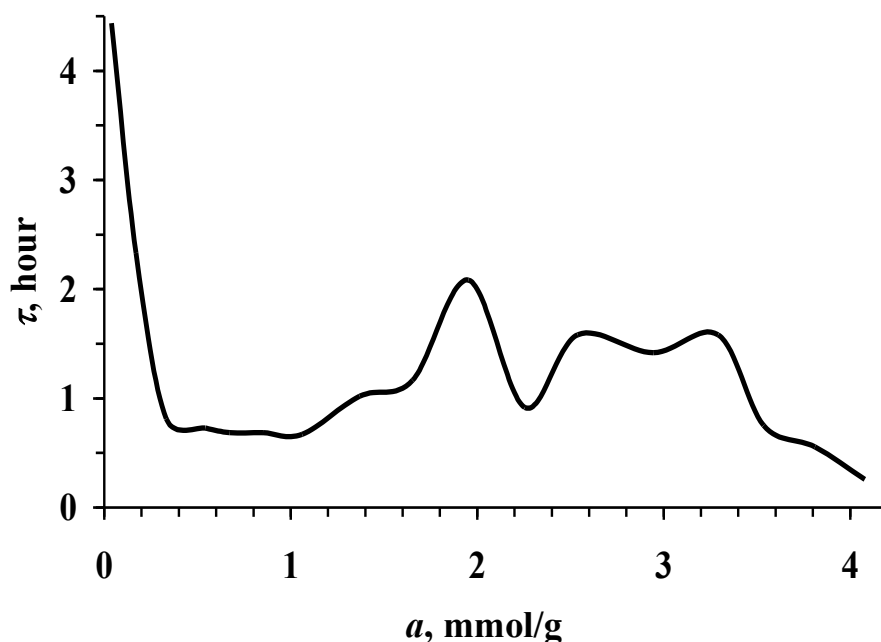


Fig. 4. The set-time of the adsorption equilibrium, depending on the size of the adsorption of benzene in the zeolite LiX at 303K

On fig. 4 shows the thermal equilibrium time (thermokinetics) of hydrogen sulfide adsorption on LiX zeolite. In this zeolite, the lines of temporary equilibrium first fall sharply from top to bottom, and then change in waves after 0.2 mmol/g. The equilibrium time of hydrogen sulfide adsorption on LiX zeolite is initially 4.98 hours, and upon reaching 0.2 mmol/g - 0.8 hours. At initial saturation, some time is required to establish the equilibrium of hydrogen sulfide adsorption due to the large number of unsorbed voids and the number of cations unaffected by the zeolite adsorbate in the supercavities. Then, when the adsorption amount reaches 2.02 mmol/g, the adsorption thermal equilibrium time is 2 hours. Subsequent hydrogen sulfide molecules are adsorbed in less than 2 hours. Hydrogen sulfide is not retained for long during equilibrium, as it interacts with cations in the cavities of the zeolite. At the end of the process, the equilibrium time is reduced to 10 minutes.

4 Conclusion

Thus, to saturate the cavities of the LiX zeolite with hydrogen sulfide, 0.25 mmol/g H_2S is adsorbed on the cations in the S_{III} cavity, 3.42 mmol/g in the S_{II} cavity, and -0.27 mmol/g H_2S is adsorbed on the cations of the S_{III} cavity. Of the 12 lithium cations that make up 1/8 of the zeolite matrix, only 5.925 are involved in the adsorption process. At the end of the process, the adsorbed hydrogen sulfide molecules are more densely adsorbed and 0.27 mmol/g of hydrogen sulfide molecules are redistributed again. The redistribution of hydrogen sulfide molecules begins mainly after the adsorption of 3.67 mmol/g. The average integral differential entropy is -39.74 J/mol*K, while hydrogen sulfide molecules are adsorbed in the zeolite matrix in a solid state. At initial saturation, adsorption takes a long time to reach thermal equilibrium time, i.e., lasts 4.9 hours. As saturation with hydrogen sulfide molecules, the thermokinetics of adsorption decreases by ten minutes.

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