Thermodynamics of hydrogen sulfide adsorption in NaX zeolite

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Abstract. Sulfur-containing organic and inorganic compounds are the main harmful component of natural gas and oil, as well as products of their processing. Since sulfur compounds have acidic properties, their content leads to corrosion of technological parts in production processes. The content of hydrogen sulfide in the transported gas should not exceed 20 mg/m³. In Uzbekistan, motor vehicles run mainly on liquefied natural gas. Sulfur compounds in natural gas corrode gas cylinders, resulting in an explosion. If synthetic zeolites are used in manufacturing processes, as well as in small gas production, process degradation will be prevented. Synthetic zeolites are widely used in various industrial production processes due to their high sorption properties. This study makes it possible to study the localization and sorption structure of sulfur compounds in supercavities of zeolites of the faujasite type. The adsorption of hydrogen sulfide on NaX zeolite was carried out in a high vacuum adsorption unit. Based on the results obtained, the differential heat of adsorption, isotherm, entropy, and thermal equilibrium time (thermokinetics) were calculated.

1 Introduction

Zeolites of the X, Y type have a cubic face-centered lattice of the diamond type [1, 2]. The elementary cubic cell has an edge of 24.91 Å[2]. Each cuboctahedron is connected by four six-membered oxygen bridges. The unit cell of zeolites with the X structure contains eight cuboctahedrons and 16 corresponding six-membered oxygen bridges. Consequently, the unit cell contains 24 x 8 = 192 ions (Al + Si) and 36 x 8 = 288 oxygen ions, as well as 6 x 16 = 96 oxygen ions in six-membered bridges. The amount of cations required to compensate for the negative charge of the AlO₄ tetrahedra in zeolite X depends on the ratio to Al, which can vary from 1.1 to 1.5. Each large cavity communicates with four adjacent large cavities through twelve-membered oxygen windows, the diameter of which is 9-10 Å. Dubinin et al. [3] calculated the volumes of large cavities of NaX zeolites with different SiO₂/Al₂O₃ ratios based on X-ray diffraction data. As this ratio increases, the volumes of cavities decrease (due to the fact that the lengths of Si-O bonds are less than Al-O), but the number of unit cells per unit mass of dehydrated crystals increases, so the total volume of zeolites increases.

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According to [4], the volume of a large NaX zeolite cavity can vary within 900 – 950 \( \text{Å}^3 \). The number of large cavities per 1 g of NaX zeolite is \( 3.62 \times 10^{20} \) [5].

The structure of X zeolites consists of supercavities with almost spherical symmetry, with a diameter of \( \sim 0.125 \text{ nm} \) and a window size of \( \sim 0.74 \text{ nm} \). Each cavity is connected to four other cavities arranged tetrahedrally. The structure also contains sodalite cavities connected to each other by double six-membered rings. Univalent extralattice cations predominantly occupy different crystallographic positions I, I’, II and III’. In the case of hydrogen sulfide, the substitution of Ca\(^{2+}\) for Na\(^{+}\) leads to a sharp decrease in the shift of the absorption band of SH stretching vibrations compared to the spectrum of the gas phase [6]. No dependence of the vibrational frequency of SH [56] and the heat of adsorption [7] on filling up to 6±7 mol. / e-mail for zeolite CaNaA indicates that in this case, in contrast to H\(_2\)O, there should be no noticeable differences in the energies of interaction of H\(_2\)S with Na\(^{+}\) and Ca\(^{2+}\) cations.

From a practical point of view, water plays a key role in many practical processes such as ion exchange and separation. I did not find a complete explanation of the effect of pre-adsorbed water on the separation of hydrocarbons. At present, the ability to understand and explain the effect of water on the adsorption of hydrocarbons is a key problem [8]. From a theoretical point of view, water in zeolites is a model system for a wide range of experimental and theoretical studies to understand the effect on the structure [9], dynamics [10, 11], and thermodynamics [12, 13] of molecular fluids. Recently, a change in the localization of cations in a zeolite was predicted by molecular dynamics simulations [14, 15]. The authors of [16], using the Monte Carlo method, determined the distribution of cations under the influence of an adsorbed water molecule. Until recently, most theoretical studies have used a fixed position of cations [17, 18].

Adsorption processes can be studied in various ways. But studies based on the calculation of the number of adsorbed molecules by the calorimetric method on a high-vacuum adsorption unit are rarely carried out. Using this method, research work was carried out with synthetic zeolites, clay minerals and other substances with sorption properties [19-23].

2 Methods

The composition of the studied zeolite is \( \text{H}_6\text{Na}_{80}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106} \). 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 NaX molecular sieve were carried out using the device described in [24, 25]. Dissolved gases were removed by freezing the adsorbent followed by pumping out. 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.
There is a migration of protons from small to large space. Hydrogen sulfide with protons forms molecular monocomplexes due to weak bonds. The isotherm values are low (small) since the hydrogen sulfide molecules interacting with protons are firmly attached to the zeolite cavities.

The growth on the isotherm plot increased slowly until the adsorption rate reached 2 mmol/g. This is due to the localization of hydrogen sulfide molecules. Then, an increase in the isothermal adsorption curve in the vertical position was observed. The saturation pressure of hydrogen sulfide is equal to 17936 mm. atm. Isothermal adsorption of hydrogen sulfide on NaX zeolite was studied at pressures up to 1 atm, i.e. up to 760 mm. Hg.

An increase in the vertical position of the isotherm plot was observed in the range of 2 mmol/g - 5 mmol/g. This indicates the saturation of hydrogen sulfide molecules. It turned out that 4 - 5 molecules of hydrogen sulfide were in a highly excited state.

A good correlation is observed between the heats of adsorption and the isotherm. The isotherm (Fig. 1), as well as the heats of adsorption, have three segments. During adsorption on Na1+ cations in position SIII', it rises sharply, then inclines towards the adsorption axis and grows up to 0.5 mmol/g (SI'). After the inflection, the isotherm with a slight slope to the adsorption axis grows linearly until saturation (SII).

The adsorption isotherm of hydrogen sulfide on the NaX molecular sieve is satisfactorily described by the three-term equation of the theory of volume filling of micropores (TOFM) [26, 27]

\[ a = 2.42 \exp\left(-\frac{A}{20.06}\right) + 2.38 \exp\left(-\frac{A}{11.96}\right) + 1.98 \exp\left(-\frac{A}{8.14}\right), \]

Fig. 1. H2S adsorption isotherm in NaX zeolite at 303 K, \( \Delta \) experimental value; ▲ the value of the points calculated on the basis of the equations of the theory of volumetric filling of micropores (TOFM), where: \( a \) – adsorption in micropores in mmol/g, \( A=RT\ln(P_o/P) \) – adsorption energy in kJ/mol.

On Fig. 2 shows a graph of the change in differential heat (Qd, kJ/mol) depending on the amount of adsorbed hydrogen sulfide molecules (a, mol/g) on the NaX zeolite. The heat of condensation of hydrogen sulfide adsorption (\( \Delta H_v \)) is indicated by dashed lines. At initial saturation, the adsorption rate is 0.01 mmol/g, and the differential heat is 60.01 E3S Web of Conferences 402, 14037 (2023) TransSiberia 2023
In this case, the protons in the SI and SIII cavities migrate into superspace. Due to the migration of protons, the heat of adsorption is high. With the adsorption of 0.23 mmol/g of hydrogen sulfide molecules, the heat of adsorption is 50.91 kJ/mol. The relatively constant differential heat of adsorption of hydrogen sulfide molecules ranges from 0.24 mmol/g to 2.4 mmol/g, which is ~2.35 times higher than the thermal condensation of the adsorbate. The graph of the differential heat of adsorption of hydrogen sulfide molecules has a waveform, which indicates that each change occurs at certain sorption centers. In the range from 0.24 mmol/g to 0.99 mmol/g, 0.75 mmol/g of hydrogen sulfide is adsorbed. When the adsorption reaches 0.99 mmol/g, the value is 49.73 kJ/mol. The differential heat slightly increases from 49.73 kJ/mol to 50.37 kJ/mol, where 0.87 mmol/g of hydrogen sulfide is adsorbed. Hydrogen sulfide is adsorbed on a part of the NaX zeolite in the vicinity of the 12-ring entrance windows, that is, on metal cations in cavity SIII. This means that the molecules are sorbed into the a-space, since this center is close to a supercavity with respect to the SIII space.

At the next stage, adsorption proceeds in the range from 1.86 mmol/g to 2.80 mmol/g, while the heat of adsorption decreases from 50.37 kJ/mol to 46.02 kJ/mol. During the adsorption of hydrogen sulfide on the zeolite in the range from 2.80 mmol/g to 44 mmol/g, a change in the adsorption temperature to 48.35 kJ/mol is observed. When the next hydrogen sulfide molecule is adsorbed, the decrease in the heat of adsorption accelerates. At the end of the process, the heat of adsorption is 36.50 kJ/mol. This thermal stability is maintained up to 4.63 mmol/g. For subsequent hydrogen sulfide molecules, a sharp decrease in the heat of sorption is observed, that is, a tendency towards thermal condensation. The condensation temperature of hydrogen sulfide is 22 kJ/mol. The average differential heat during the adsorption of 3.76 mmol/g of hydrogen sulfide molecules is 49.63 kJ/mol. At this thermal value, hydrogen sulfide molecules interact with metal ions (H$_2$S) and form n/N$^+$ complexes. Initially, the monomer forms H$_2$S/H$^+$ complexes with protons. During adsorption in the range from 0.24 mmol/g to 4.0 mmol/g, the Na$^+$ cation forms polycomplexes with hydrogen sulfide molecules.

The arrangement of four H$_2$S/Na$^+$ complexes has the shape of a tetrahedron, and such clusters fill almost all voids in the supercavity. At the final stage, the heat increases slightly.
and drops sharply at a temperature of 303 K, depending on the heat of hydrogen sulfide condensation. Modeling of the hydrogen sulfide/zeolite system shows that the fourth hydrogen sulfide molecule is located in the 12\(^{-}\) ring oxygen window and separates the supercavities from each other (position W). This position for zeolites X and Y with Na\(^{+}\) cations has been repeatedly discussed [28, 29].

NaX zeolite adsorbs only 4.63 mmol/g hydrogen sulfide molecules in one superpore. On Fig. 3 shows the differential entropy of hydrogen sulfide adsorption on NaX zeolite. The formula of the Gibbs-Helmholtz equation was used to calculate the differential entropy using differential heat and isothermal quantities of hydrogen sulfide adsorption on NaX zeolite.

\[ \Delta S_d = \frac{\Delta H - \Delta G}{T} = -\frac{Q_d}{T} - \lambda + A \]

\(\lambda\) thermal condensation, \(\Delta H\) and \(\Delta G\) enthalpy and change in free energy, \(T\) -

![Graph of differential entropy of hydrogen sulfide adsorption on NaX zeolite.](image)

\(a, \text{ m/mol/g}\)
Pores in this part are relatively larger than the other pores. Since the cations are not completely saturated with hydrogen sulfide molecules, the adsorption entropy values are high and the adsorbate molecules are in an inert state. The average integral entropy is -36.66 J/mol*K. The amount of adsorption after the value of 4.5 mmol/g of the hydrogen sulfide molecule gradually passes into the adsorbed state.

On Fig. 4 shows the thermal equilibrium time (thermokinetics) of hydrogen sulfide adsorption on NaX zeolite. During the experiment, adsorption was carried out on a microcalorimeter at two different voltages to accurately determine the adsorption process. Initially, hydrogen sulfide molecules were placed in the device as a reserve. Gradually, we directed the hydrogen sulfide molecules to the zeolite. The adsorption of a large number of hydrogen sulfide molecules was carried out at a voltage of 1171 mmV. And the adsorption of a small amount of hydrogen sulfide molecules was carried out at a free voltage. Studies carried out at free voltage provide additional energy. And this shows the Rakhmatkariev effect. In this zeolite, the thermal equilibrium time lines first fall sharply from top to bottom, and after 0.3 mmol/g become wavy. The equilibrium time of hydrogen sulfide adsorption on NaX zeolite is initially 4.79 hours. Equilibrium takes longer to establish due to the small number of hydrogen sulfide molecules and the large number of pores. At initial saturations, sometime is required for the stability of the equilibrium of hydrogen sulfide adsorption due to the large number of unsorbed voids and the amount of cations not affected by the adsorbate in micropores in the supercavities of the NaX zeolite. When the adsorption amount reaches 0.12 mmol/g, the adsorption thermal equilibrium time is 2.33 hours. Subsequent hydrogen sulfide molecules form small minimum and maximum values when adsorbed, and it takes 1.2 hours to reach equilibrium heat. The equilibrium time does not last long, since hydrogen sulfide interacts with cations in the cavities of the zeolite. At the end of the process, the equilibrium time is reduced to 10 minutes.

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

3 Conclusion
Thus, the hydrogen sulfide isotherm on synthetic NaX zeolites proceeds in three stages. At the first and second stages, the process proceeds with strong adsorption of the hydrogen sulfide molecule, and at the third stage, mainly between the adsorbent and the adsorbate. 4.0 mmol/g of H\textsubscript{2}S is adsorbed on cations in cavity SII, and 0.63 mmol/g of H\textsubscript{2}S is adsorbed on cations in cavity SIII. At the end of the process, the adsorbed molecules are adsorbed more densely, and 0.63 mmol/g of hydrogen sulfide molecules are redistributed. The redistribution of hydrogen sulfide molecules begins mainly after the adsorption of 4.53 mmol/g. 4.5 mmol/g of hydrogen sulfide is strongly localized in the supercavities of the zeolite. The average integral differential entropy is -36.66 J/mol*K, while hydrogen sulfide molecules are strongly adsorbed on the zeolite matrix in an unexcited state. In the initial stages of saturation, the adsorption of hydrogen sulfide molecules adsorbed on the zeolite takes somewhat longer to establish the thermal equilibrium time, i.e., 4.79 hours. As saturation with hydrogen sulfide molecules, the thermokinetics of adsorption decreases by several tens of minutes.

References
