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METHODOLOGICAL JOURNAL<http://mentaljournal-jspu.uz/index.php/mesmj/index>ENTHALPY AND ENTROPY CHANGE OF METHANETHIOL
ADSORPTION IN ZEOLITE CaA (M-22)**Mirzokhid Kokhkarov**

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ABOUT ARTICLE

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Abstract: The article presents experimentally obtained values of the differential enthalpy of methanethiol adsorption on zeolite CaA (M-22) of the LTA type at 303 K. The enthalpy values were measured using a Tian-Calve DAC-1-1A microcalorimeter connected to a universal high-vacuum device. Differential values of free energy (Gibbs energy) were calculated from the equilibrium values of pressure. Based on the experimentally measured values of differential heat and Gibbs energy, the change in adsorption entropy and its average value were theoretically calculated using the Gibbs-Helmholtz formula. A regular relationship is shown between the amount of methanethiol adsorption on zeolite CaA (M-22), the values of differential enthalpy and the changes in entropy. The mechanism of adsorption from the initial adsorption zone to the reduction zone by the heat of methanethiol condensation and the law of filling the zeolite volume with methanethiol molecules were also determined. Based on the regular change in the values of differential enthalpy depending on the amount of Na⁺ and Ca²⁺ cations in the zeolite, it was established that methanethiol molecules first form mono- and dimer complexes 2CH₃SH:Na⁺ with sodium cations, then monomer 1CH₃SH:Ca²⁺ ion-molecular complexes with calcium cations.

INTRODUCTION

In order to obtain clean gas from primary natural gases, various environmental problems arise from year to year as a result of insufficient cleaning of additional chemicals contained in them, as well as the release of harmful gases from the burning of secondary gas in industry and production into the atmosphere. As a result of burning natural gas, the sulfur contained in it releases various sulfur compounds that are dangerous for humans, and a large amount of carbon (IV) oxide is released into the atmosphere, which has an increasing negative impact on human health. Therefore, the demand to prevent environmental problems is increasing year by year. Adsorbents are widely used to avoid these problems, that is, to dry and clean gases. In particular, the role of synthetic zeolites in the oil and gas industry is incomparable for their adsorption and catalytic properties. Therefore, it is important to synthesize zeolites with high adsorption and catalytic properties, to apply the results of research studies on increasing the level of their selectivity [1-8].

In order to obtain environmentally friendly gas from natural gases, the demand for drying them from water vapor, removing gases such as hydrogen sulfide, and preventing environmental problems caused by the release of greenhouse gases, including carbon (IV) oxide into the atmosphere, is increasing year by year. For this purpose, synthetically produced zeolites are widely used to avoid the above-mentioned problems. It is important to achieve scientific and practical innovations based on the results of research conducted on the synthesis of zeolites with high adsorption and catalytic properties, increasing the level of their selectivity [9-11].

At present, for the synthesis of zeolites with nanoporous molecular beads for adsorption processes all over the world, the selection of raw materials with suitable adsorption properties to obtain zeolites with the ability to selectively absorb substances of different physicochemical nature, the determination of the complete thermodynamic properties of the synthesized zeolites, the formation of ion-molecular complexes in the zeolite matrix, it is necessary to justify scientific solutions such as determining the state of localization, thermokinetics of adsorption and cation exchange in the zeolite structure, studying the law of migration of cations in the zeolite matrix, and determining the complete molecular mechanisms of adsorption processes in zeolite.

Zeolites are characterized by the names of MFI, MOR, FAU, LTA based on the composition and structure of the crystal lattice, as well as their sorption and catalytic properties [12], and their main thermodynamic properties of catalysis and adsorption of molecules of different physicochemical nature are fundamentally different from each other [13-17].

The difference in the aluminosilicate structure of A and X zeolites consists in the location of cubic tetrahedral structural units in the phase, that is, in the voids [12; 14; 17]. In type A zeolite, the cuboctahedrons form a regular cubic lattice. Each cuboctahedron is joined by six adjacent four-membered oxygen bonds. The spaces between the eight cuboctahedrons form large pores [13]. According to the Si/Al ratio of the zeolite, the amount of negative charges of the crystal lattice changes, and different amounts of cations are introduced for full or partial compensation. These cations can be alkali metals or alkaline earth metals. Adsorption and catalytic properties of zeolites change depending on the type of cation. Before using it in various fields of manufacturing industries, it is necessary to study its adsorption properties.

Since Ca^{2+} and Na^+ cations in LTA type CaA (M-22) zeolite are considered the main active centers, as well as the amount of cations is in different proportions, the sorption amount of adsorbate molecules changes accordingly. By determining the main thermodynamic characteristics of the adsorption of test molecules such as polar water and ammonia, the amount, nature and strength of energetically active centers in the same type of crystallographic positions are determined [18-21].

From the analysis of the literature, it became clear that the basic thermodynamic properties and adsorption mechanisms of gas and vapor molecules with different physical and chemical properties in SaA forms of LTA type zeolite have not been thoroughly studied. In addition, adsorption recommendations have been studied by X-ray and spectroscopy methods, but there is not enough information about the scientific research studies in which the adsorption mechanism has been fully studied. The study of LTA zeolites will help in the targeted synthesis of zeolites and their use as adsorbents in various technological processes.

MATERIALS AND METHODS

Microcalorimetric and isosteric methods are used to determine the heat of adsorption in sorption processes. The isosteric method is a theoretical calculation method requiring the measurement of isotherms at different temperatures. However, sufficient errors can occur in the phase transition regions of the isosteres. Another method of measuring the heat of difference, which is convenient in every respect and based on direct experience, is the calorimetric study. There are adiabatic, isothermal and heat conduction methods of calorimetric measurement. A calorimetric method with high accuracy and stability is a heat transfer method, and almost 99% of the heat released in the sorption process is dissipated as heat energy. The improved DAC-1-1A heat transfer microcalorimeter was used in this research. Its full description can be found in the authors' works [14-21].

The In this work, the isotherm and entropy of ammonia adsorption in zeolite CaA (M-22) at 303 K have been studied. The unit cell composition of this zeolite is represented by $\text{Ca}_{2,975}\text{Na}_{1,194}(\text{SiO}_2)_{12}(\text{AlO}_2)_{12}$ and consists of positions S_I , S_{II} and S_{III} . According to the chemical composition, the amount of calcium cations per 1 g of zeolite is 1.89 mmol/g and the amount of sodium cations is 0.76 mmol/g.

RESULT AND DISCUSSION

First of all, it should be noted that due to the high pressure of saturated hydrogen sulfide vapor ($P_s=1515$ torr) at an experimental temperature of 303 K, we were unable to obtain a complete adsorption isotherm of hydrogen sulfide in zeolite CaA (M-22). The differential enthalpy of adsorption of methanethiol molecules on SaA (M-22) zeolite at 303 K from the subsaturation region to the heat of condensation of methanethiol was experimentally measured. The mechanism of the sorption process, as well as the enthalpy values in the initial area of methanethiol adsorption in this zeolite, were found to be almost 30-40 kJ/mol less than the adsorption enthalpy of polar and non-polar molecules of different natures, for example, ammonia [17-20]. During the adsorption process, it was shown that methanethiol molecules form ion-molecular complexes of different proportions with Na^+ and Ca^{2+} cations in S_{II} and S_{III} positions of zeolite.

The authors [10-20] found that the differential enthalpy of adsorption of molecules of different physicochemical nature, including molecules of different sizes, in zeolites such as MFI, MOR, FAU, LTA has a stepped form. Figure 1 shows the graph of the differential enthalpy of adsorption of CH_3SH molecules on CaA (M-22) zeolite. In general, differential heat is wave-like and step-like, and can be divided into 3 areas. The differential heat changes by a factor of ~ 0.8 mmol/g in the first 2 areas, and by a factor of ~ 1.9 mmol/g in the next 1 area. The differential heat of adsorption in the initial region with an adsorption amount of 0.01 mmol/g is ~ 95 kJ/mol. As the amount of adsorption increases, the differential enthalpy at 0.45 mmol/g linearly decreases to 65 kJ/mol, forming an initial minimum.

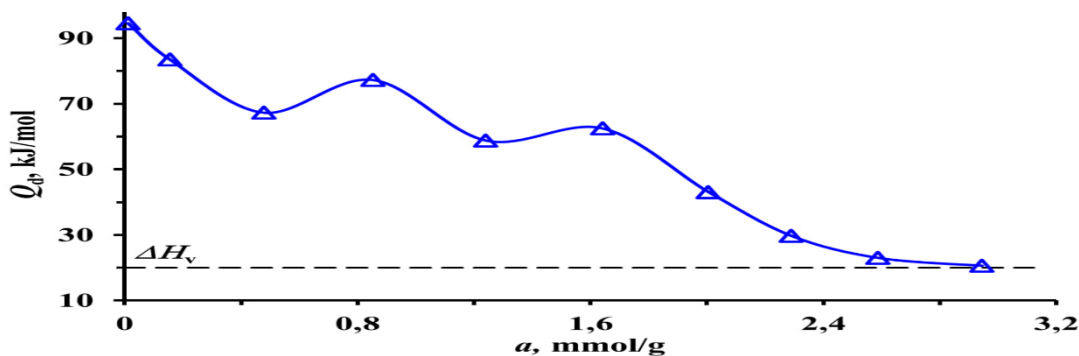


Figure 1. Differential heat (Q_d) of methanethiol adsorption on CaA (M-34) zeolite at 303 K. The dashed line is the heat of condensation of methanethiol at 303 K at 303 K.

As the sorption volume becomes saturated, the differential enthalpy increases to 77 kJ/mol at ~0.8 mmol/g adsorption. This amount of adsorption is equal to the amount of sodium cations in the zeolite (0.76 mmol/g). Therefore, the initial CH₃SH molecules are adsorbed on the sodium cations contained in the zeolite. Therefore, in the minimum-maximum change in the amount of adsorption in the range of 0.45-0.8 mmol/g of differential heat, CH₃SH molecules form an adsorbate/adsorbent monomer 1CH₃SH:Na⁺ ion-molecular complex with sodium cations in a ratio of 1:1. ~0.8 mmol/g adsorption amount increases the differential enthalpy by 10 kJ/mol, first, the initially adsorbed methanethiol molecules are completely localized in the zeolite, and secondly, as a result of the mutual Vaan-der-Waals interaction force (induction effect) between the initially adsorbed and next adsorbed methanethiol molecules (induction effect) energy is released.

As the sorption volume of zeolite becomes saturated, the differential enthalpy decreases to 59 kJ/mol at the adsorption amount of 1.24 mmol/g, and the differential enthalpy increases to ~63 kJ/mol at the adsorption amount of ~1.6 mmol/g. The amount of this adsorption is twice that of sodium cations contained in zeolite, that is, it is 2 times larger. So, CH₃SH molecules with Na⁺ cations form dimer 2CH₃SH:Na⁺ ion-molecular complex at the second maximum. As the differential enthalpy increases as a result of the Q_d induction effect in the mono complex, the differential enthalpy increases by 3 kJ/mol due to the Vaan-der-Waals interaction of methanethiol molecules.

The dependence of the amount of adsorption on the differential enthalpy of zeolite content by ~0.8 mmol/g was observed in the subsequent sorption process. Therefore, the sorption process of methanethiol molecules in the 1st coordination sphere with the sodium cation in the zeolite is completed.

The differential enthalpy decreases from 63 kJ/mol to the enthalpy change of liquid methanethiol at the experimental temperature, and the sorption process in this zeolite ends with the formation of an ion-molecular complex of methanethiol molecules 1CH₃SH:Ca²⁺ with calcium cations in the zeolite.

The dependence of the change in molar differential entropy (ΔS_a) of adsorption of CH₃SH molecules on CaA (M-34) nanostructured zeolite on adsorption saturation is presented in Fig. 2 (the entropy of liquid methanethiol is taken as zero). The adsorption entropy was calculated by the following Gibbs-Helmhols formula:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + RT \ln P_s / P}{T} \quad (1)$$

where, λ is the heat of condensation, ΔH and ΔG are the changes in the adsorption enthalpy and free energy from the standard state to the adsorbed state.

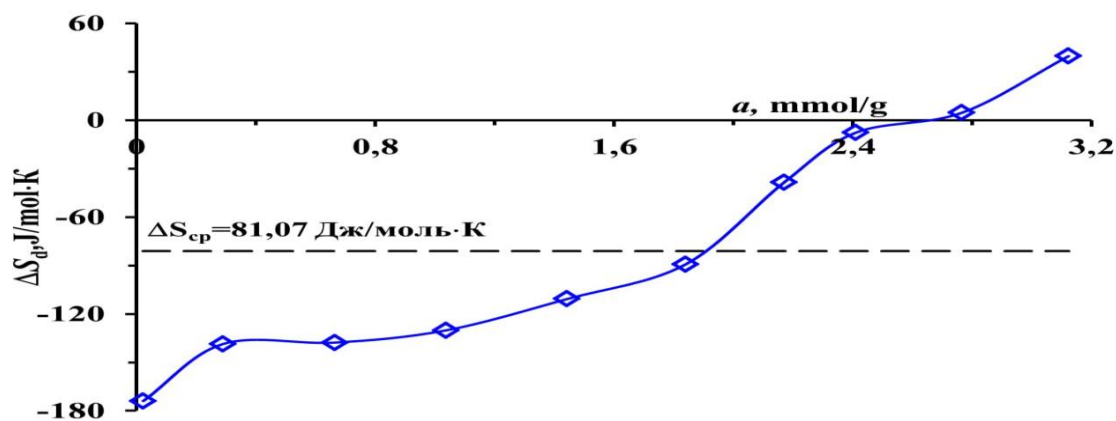


Figure 2. Molal differential entropy change (Qd) of CH₃SH adsorption on CaA (M-22) zeolite at 303 K. The dashed line is the mean entropy change.

In general, the adsorption entropy changes undulatingly according to each generated ion-molecular mechanism, and it is sufficiently lower than the entropy value of liquid CH₃SH, which indicates that the mobility of CH₃SH molecules in zeolite is limited. The change in entropy and formation of each ion-molecular complex corresponds to the differential heat. Entropy is -174 J/mol·K at an adsorption amount of 0.22 mmol/g in the initial region. With the saturation of the sorption volume, at an adsorption amount of 0.29 mmol/g, the entropy forms a step from -174 J/mol·K to -139 J/mol·K and does not change up to ~0.8 mmol/g adsorption. This value is equal to the amount of Na⁺ cation in zeolite (0.76 mmol/g), that is, CH₃SH molecules are adsorbed on Na⁺ cations in zeolite. CH₃SH molecules form an adsorbate/adsorbent monomer 1NH₃:Na⁺ ion-molecular complex with Na⁺ cations as explained in the enthalpy change.

The entropy increases to -100 J/mol·K at ~1.6 mmol/g adsorption, forming a dimer 2CH₃SH:Na⁺ complex in the ratio of adsorbate/adsorbent 2:1. A small bend in this enthalpy change corresponds to a step in the formation of a dimer ion-molecule complex in the differential enthalpy. The wave-like change of entropy is the result of the release of additional energy as a result of the Vann-der-Waal (induction effect) interaction between the initially adsorbed ammonia molecules and subsequent molecules.

With the saturation of the sorption volume, the entropy of 2.4 mmol/g adsorption increases to -8 J/mol·K, forming the trimer 3CH₃SH:Na⁺ ion-molecular complex, and the sorption process ends with Na⁺ cations in the zeolite. The entropy in the subsequent adsorption of CH₃SH molecules increases from the entropy of liquid CH₃SH at the experimental temperature and is equal to 40 J/mol·K at 3.2 mmol/g adsorption.

CONCLUSION. The adsorption differential enthalpy change of CH_3SH on CaA (M-22) nanostructured zeolite was determined in an adsorption-calorimetric study. The entropy change of CH_3SH molecules and its average value were calculated based on the values of the Gibbs free energy calculated from the values of the differential heat of adsorption and the pressure in thermodynamic equilibrium. It was found that the change of adsorption differential enthalpy and molar differential entropy is proportional to the amount of Na^+ cations in the zeolite. It was found that trimeric $3\text{CH}_3\text{SH}:\text{Na}^+$ ion-molecular complexes form in the 1st coordination sphere with Na^+ in S_{II} and S_{III} positions of zeolite. The values of the entropy change of the adsorption of ammonia molecules are sufficiently lower than the entropy value of the liquid state at the experimental temperature, and its average value is $-71 \text{ J/mol}\cdot\text{K}$. This indicates that the mobility of ammonia molecules in the zeolite matrix is close to the mobility of ammonia in the solid state.

The results of the adsorption-calorimetric research obtained on the basis of the experiment allow to obtain the main thermodynamic functions of the studied systems, which are necessary for the development of theoretical concepts of chemical and physical adsorption in synthetic zeolites of the LTA type, including CaA, as well as in the calculation of sorption technology processes and devices in practice.

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