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DIFFERENTIAL ENTROPY OF ETHANE ADSORPTION ON LTA-TYPE ZEOLITE

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Abstract: It was established that at the initial stage of adsorption (a<0.5 mmol/g), the differential enthalpy values reach 65-70 kJ/mol, which is associated with the strong interaction between ethane molecules and the Ca^{2+} and Na^{+} cationic centers. With further surface coverage, a gradual decrease in enthalpy to 25-30 kJ/mol is observed, indicating a transition to less energetically favorable micropores and predominantly physisorption interactions. The change in entropy increases with the degree of adsorption, reflecting a decrease in the structural order of the adsorbed layer. The results provide deeper insight into the energetic heterogeneity of the zeolite surface and the adsorption mechanism of hydrocarbons in microporous aluminosilicate frameworks.

Key words: zeolite, adsorbent, adsorption, enthalpy, entropy, mechanism, microcalorimeter, ethane.

Introduction:

The adsorption–calorimetric method, based on direct measurement of thermal effects during adsorption, provides precise determination of adsorption heats. The Tian–Calvet microcalorimeter of type DAK-1-1A enables accurate detection of heat effects down to 10^{-6} J, allowing detailed analysis of the thermokinetics and thermodynamics of gas adsorption on microporous materials [1].

In addition to adsorption, LTA-type zeolites are widely used as solid acid and ion-exchange catalysts. Their catalytic activity is attributed to the presence of strong Brønsted and Lewis acid sites, which arise due to partial cation substitution in the framework [2]. In particular, Ca- and Na-containing zeolites show high activity in dehydration, isomerization, and cracking of light hydrocarbons.

The regular microporous structure provides a molecular-sieve effect - the ability to selectively pass and adsorb molecules of specific sizes - which defines the selectivity of the catalyst. Moreover, zeolites are resistant to high temperatures and chemical agents, allowing multiple regeneration cycles without loss of activity [3, 4].

In the oil and gas industry, LTA-type zeolites are used for drying natural gas, removing CO_2 and H_2S, and separating hydrocarbon fractions. Due to their high stability and adsorption capacity, they are employed in pressure swing adsorption (PSA) and temperature swing adsorption (TSA) units for purification and concentration of light hydrocarbons. Furthermore, Ca-Na zeolites are applied in isomerization and dehydrogenation reactions of ethane and propane, which are essential steps in olefin production [5, 6].

Therefore, the LTA zeolite is a multifunctional material combining high sorption capacity, thermal stability, and catalytic activity. The investigation of differential enthalpy and entropy of ethane adsorption on this zeolite is of both fundamental importance - for understanding the nature of adsorption interactions - and practical significance for the design of efficient adsorbents and catalysts in the petrochemical and chemical industries.

The results obtained are expected to refine the physico-chemical understanding of the interaction of small hydrocarbons with the cationic centers of LTA-type zeolites and may contribute to the development of advanced adsorbent materials for environmental and technological applications.

Research methods:

The ethane gas flow from the cylinder was passed through a purification system consisting of a zeolite 5A filter and a liquid nitrogen trap to eliminate traces of moisture and impurities. The system pressure was measured using a precision manometer (accuracy ±0.01 kPa), and the quantity of introduced gas was controlled by dosing microvalves. Each ethane portion (≈0.01 mmol) was introduced into the cell containing the degassed zeolite, and after reaching thermal equilibrium (within 15-20 min), the corresponding heat effect was recorded. After a series of gas injections, the dependences of the differential enthalpy Q(a) and entropy ΔS(a) on the amount of adsorbed substance (*a*, mmol/g) were determined.

The uncertainty in the determination of the amount of adsorbed ethane did not exceed ±3%, while the error in measuring the heat effect was within ±2%. Each experimental series was repeated at least three times; discrepancies in enthalpy values did not exceed 0.5 kJ/mol, confirming the high reproducibility of the results. The temperature stability of the setup and precise pressure control ensured the accuracy of low heat-effect measurements, which is particularly important when studying physisorption interactions with low binding energies.

Results and discussion:

The energetic heterogeneity of the LTA zeolite surface is manifested in the exponential dependence of Q on adsorption, which is well consistent with the Polanyi adsorption potential theory. This indicates the presence of a narrow range of high-energy sites (associated with Ca^{2+} cations) and a broader distribution of weakly bound regions (associated with Na^{+} cations).

This behavior is consistent with the concept of **thermodynamic compensation**, where a decrease in enthalpy is accompanied by an increase in entropy, maintaining an approximately constant Gibbs free energy (ΔG≈-10 to -15 kJ/mol). Such a relationship is typical for adsorption processes in which the energetic differences between active sites are small and the entropic contribution becomes dominant at higher surface coverages [7]. Taken together, the thermodynamic parameters (ΔH, ΔS, and ΔG) show that ethane adsorption on Ca_5Na_3-LTA is **exothermic, reversible, and physicochemical** in nature, proceeding with negligible structural changes in the zeolite framework.

The results demonstrate that Ca_5Na-LTA combines high energetic capacity and stability, making it a promising adsorbent for the separation of C_1-C_2 hydrocarbon mixtures. Its use is suitable for natural-gas purification and ethane recovery in PSA and TSA units.

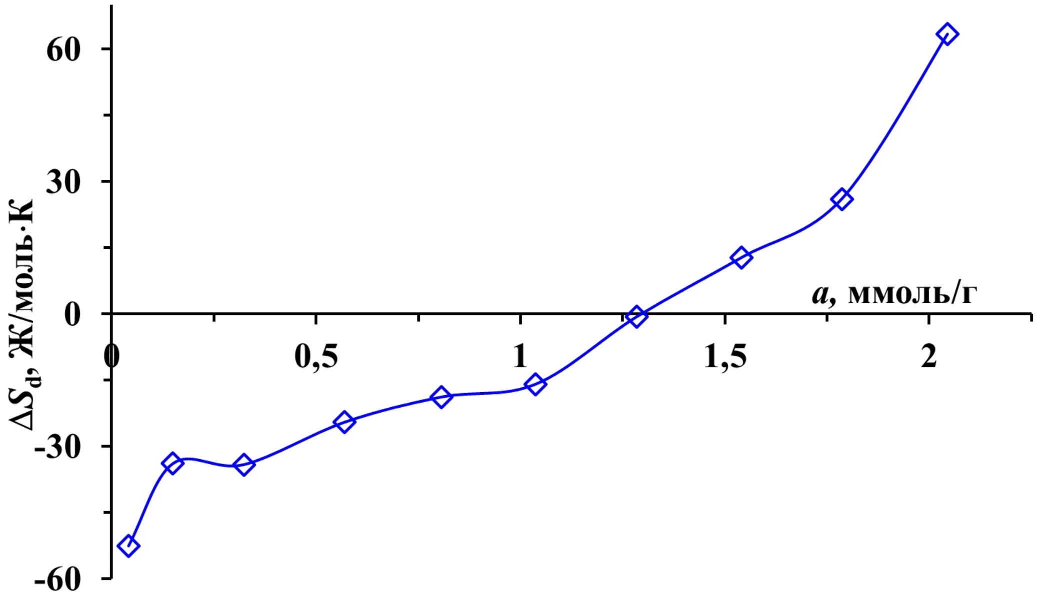

Fig. 1. Differential molar entropy of ethane adsorption on Ca_4Na_3-LTA zeolite.

Figure 1 shows the dependence of entropy change (ΔS) on the amount of adsorbed ethane. In the initial region, negative values of ΔS (–60 to –40 J/mol · K) are observed, indicating reduced molecular mobility upon fixation near the cationic centers. As the degree of micropore filling increases, the entropy rises and approaches zero at saturation, which is attributed to the weakening of orientational interactions and the transition toward less ordered adsorption states [6].

Comparison with other sorbents shows that in terms of enthalpy and selectivity, Ca_5Na_3-LTA surpasses NaX zeolites and activated carbons, approaching the performance of CaY zeolite, while exhibiting superior thermal stability and cyclic durability.

The **scientific novelty** of this study lies in obtaining, for the first time, direct calorimetric data on the thermodynamic parameters of ethane adsorption on Ca-Na LTA zeolite, allowing quantitative characterization of the energetic heterogeneity of the microporous surface. The **practical significance** of the results lies in their applicability for optimizing adsorption conditions and developing new sorbents and catalysts based on modified zeolites.

Thus, the study of the differential enthalpy and entropy of ethane adsorption on LTA-type zeolite has revealed the mechanism of interaction and the energetic structure of the surface, providing a fundamental basis for the design of new, efficient materials for use in the oil and gas industry.

Conclusion. Analysis of the energetic parameters revealed that the surface of the Ca_5Na_3-LTA zeolite is energetically heterogeneous, and the active sites differ in the strength of their electrostatic fields. A clear thermodynamic compensation effect was observed: the decrease in adsorption heat is accompanied by an increase in entropy, maintaining the Gibbs free energy at a nearly constant level of -10 to -15 kJ/mol. These findings confirm the physicochemical, exothermic, and reversible **nature of ethane adsorption.**

Comparison with other microporous materials (zeolites 5A, NaX, CaY, MOF-5, and activated carbons) showed that Ca_5Na_3-LTA exhibits higher initial enthalpy values and, consequently, greater selectivity toward ethane. Its high thermal stability and structural robustness make this material promising for gas purification and separation processes in the oil and gas industry-particularly for separating methane–ethane and ethane–ethylene mixtures, as well as for use in PSA and TSA sorption systems.

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