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GIBBS FREE ENERGY OF AMMONIA ADSORPTION IN LTA ZEOLITES

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ABSTRACT. This paper presents experimentally obtained values of the adsorption isotherm of ammonia molecules in LTA zeolites at a temperature of 303 K. The Gibbs free energy was calculated from the equation describing the work performed during the change in gas volume at constant temperature. A regular relationship between the amount of ammonia adsorbed and the Gibbs free energy in LTA zeolites was established. Under experimental conditions, it was determined that the change in the Gibbs free energy of ammonia adsorption for these zeolites varies, particularly depending on the quantity of cations present in the zeolite structure. It is shown that the Gibbs free energy is dependent on the cation content of LTA zeolite.

Keywords: adsorption, free energy, isotherm, pressure, relative pressure, microcalorimeter, ammonia.

Introduction. Among LTA-type zeolites, 3A, 4A, and 5A zeolites represent the most widely used class in practice, differing in their cation composition. Although all these zeolites possess the same LTA crystal framework, the effective pore aperture size and the electrostatic properties of active sites vary significantly depending on the type of exchangeable cations [1].

Zeolite 3A (KA) is obtained from NaA zeolite through ion exchange of sodium cations with potassium cations. Due to the relatively larger ionic radius of potassium, the effective diameter of the 8-membered ring pore openings in zeolite 3A is approximately 3.0 Å. This enables selective adsorption of small polar molecules, particularly water molecules, while restricting the of larger organic molecules such as methanol and ethanol into the pores [2]. Therefore, zeolite 3A is mainly used for drying alcohols and removing moisture from natural gas and air [3].

Zeolite 4A (NaA) is the most widely распространённая form among LTA zeolites, with an effective pore opening diameter of approximately 4.1 Å. This allows the adsorption of water, ammonia, methanol, ethanol, as well as certain small gas molecules [4]. Zeolite 4A possesses a high ion-exchange capacity and is widely used as an adsorbent in water softening processes, where it эффективно captures calcium and magnesium ions [5].

Zeolite 5A (CaNaA) is obtained from zeolite 4A by partial exchange of sodium cations with Ca^{2+} cations. Due to the higher charge density of calcium cations, the effective pore opening diameter in zeolite 5A is approximately 5.0 Å. This enables the selective adsorption of molecules such as normal paraffins, CO_2, N_2, and O_2 [6].

According to the literature, zeolite 5A exhibits higher selectivity toward normal paraffins compared to isoparaffins and aromatic hydrocarbons. This property enables its effective use as an adsorbent in petrochemical processes, particularly for hydrocarbon fractionation and gas separation [7]. In addition, it has been shown that the presence of Ca^{2+} cations leads to the formation of a strong electrostatic field, which enhances ion–molecule interactions in zeolite 5A [8].

In general, although zeolites 3A, 4A, and 5A possess the same crystal framework, their pore sizes, selectivity, and the types of adsorbates they can accommodate differ significantly depending on their cation composition. This allows LTA zeolites to be purposefully selected for specific technological applications [9-10].

Materials and Methods. In this study, an adsorption-calorimetric method was employed, in which the adsorption isotherm was first measured, followed by the theoretical calculation of the Gibbs free energy. The adsorption isotherm was determined with high accuracy and stability using a system based on a Tian-Calvet type DAK-1-1A differential automated microcalorimeter connected to a high-vacuum apparatus.

In the adsorption study, the change in Gibbs free energy during ammonia adsorption on Ca_4Na_4A zeolite at 303 K was analyzed and compared with the corresponding changes observed for $Ca_3Na_{1.2}A$ and Ca_9Na_3A zeolites. The general chemical composition of the zeolite unit cell can be expressed as $Ca_nNa_m[(AlO_2)_{12}(SiO_2)_{12}]$, where *n* and *m* denote the amounts of calcium and sodium cations, respectively.

Based on the chemical composition of Ca_4Na_4A zeolite, the total amount of calcium and sodium cations in 1 g of the zeolite is 2.38 mmol/g. However, the active sites of the zeolite framework are associated with S_I, S_{II}, and S_{III} positions, and adsorbate molecules can be sorbed only at the S_{II} and S_{III} sites. Therefore, not all calcium and sodium cations present in the zeolite structure fully participate in the adsorption process.

Results. Figure 1 illustrates the variation of Gibbs free energy during ammonia adsorption in LTA zeolites.

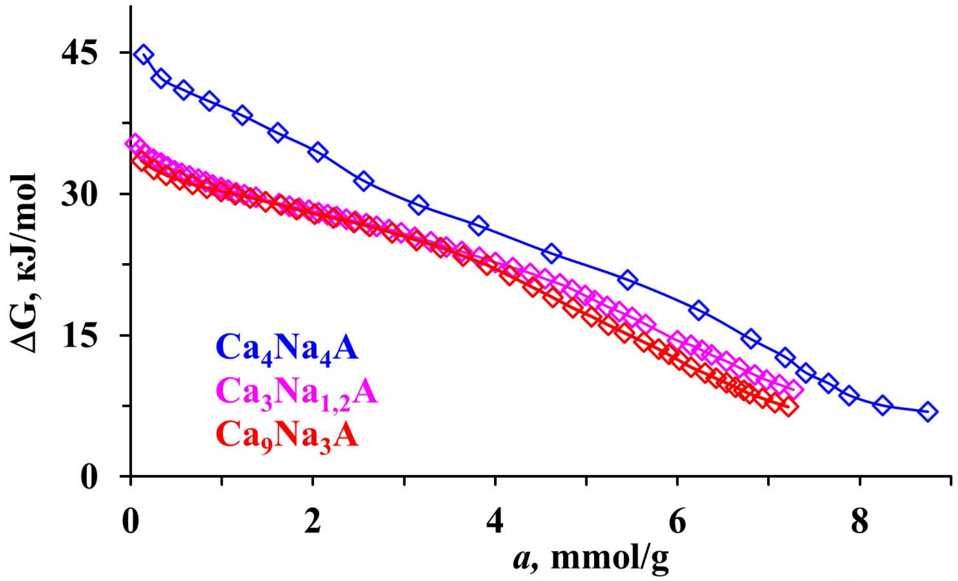

Figure 1. Variation of Gibbs free energy during ammonia adsorption in LTA zeolites. ◇ - Ca_4Na_4A, ◇ -$Ca_3Na_{1,2}A$, ◇ -Ca_4Na_4A.

The Gibbs free energy can also be expressed using the following equation:

$$\Delta G=\Delta H-T\Delta S$$

where ΔH is the enthalpy of adsorption, which is typically exothermic (i.e., has a negative value), and ΔS is the change in entropy, which is generally negative due to the restriction of the translational freedom of gas molecules upon adsorption. Therefore, for the adsorption process to be spontaneous, the condition $\Delta G < 0$ must be satisfied.

In the graph, the ΔG values are presented as positive quantities. Therefore, for a correct interpretation in terms of sorption, the following convention is adopted: the larger the value, the more thermodynamically favorable the transition of ammonia from a free state to a confined (adsorbed) state in the zeolite, i.e., the equilibrium constant is higher. This relationship is expressed as:

$$\Delta G=-RT\ln(P/P_s)=-RT\ln K$$

A larger value corresponds to a more negative ΔG. If the graph is interpreted as representing -ΔG, then an increase in ΔG indicates an enhancement of adsorption.

From the general trend of the graph, it can be observed that as the amount of adsorption increases, the value of Gibbs free energy decreases. This behavior can be explained by the following mechanistic and thermodynamic factors governing the sorption process:

1. **Energetic heterogeneity (active sites with different strengths).** In zeolites, ammonia molecules initially occupy the strongest adsorption sites, i.e., regions near cations with high electrostatic potential. At this stage, the equilibrium constant is high, and ΔG (or its magnitude/opposite-sign representation) exhibits relatively large values. As these high-energy sites become saturated, subsequent molecules are adsorbed onto weaker sites, leading to a decrease in the equilibrium constant and, consequently, a reduction in the value of ΔG.
2. **Pore filling and steric constraints.** As the adsorption amount increases, the number of molecules within the pores also rises. When NH_3 molecules become closely packed, their orientation and diffusion are restricted, and access to certain adsorption sites becomes hindered. This reduces the thermodynamic favorability of additional adsorption.
3. **Adsorbate-adsorbate interactions.** At high surface coverage, NH_3-NH_3 interactions (such as dipole–dipole interactions and clustering via hydrogen bonding) become significant. Although these interactions may, in some cases, slightly stabilize adsorption, they are generally secondary compared to the interaction between the adsorbate and the active adsorption centers. Overall, this leads to a continued decrease in the Gibbs free energy. The downward trend of the curves observed in the graph reflects a gradual transition within the sorption environment of the zeolite from high-energy adsorption sites to lower-energy sites as adsorption progresses.

The highest ΔG values across nearly the entire range are observed for the Ca_4Na_4A zeolite. At the initial stage, the values are approximately 45 kJ/mol and decrease to about 7 kJ/mol with increasing sorption capacity. In the other two zeolites, the changes in Gibbs free energy are positioned at lower levels. The ΔG values are intermediate for $Ca_3Na_{1,2}A$ and, for the most part, lowest for Ca_9Na_3A. These differences can be explained by the nature of the cations and their spatial distribution within the

LTA structure. The cation–NH_3 complex formation and the associated electrostatic field arise from the coordination of NH_3 molecules to cations via the lone electron pair on nitrogen, acting as a Lewis base toward the cationic centers. The higher the charge density and field strength of the cation, the stronger its ability to retain NH_3 molecules. However, in practice, the strength of adsorption is not determined solely by the cation charge but also by its location within the pore or channel system, its accessibility to NH_3 molecules, and its effect on diffusion pathways. In addition, an optimal composition effect is observed, meaning that maximum affinity does not necessarily correspond to the highest Ca^{2+} content. Although increased Ca^{2+} content in $Ca_3Na_{1,2}A$ and Ca_9Na_3A да Ca^{2+} may theoretically increase the number of strong adsorption sites, Ca^{2+} ions located at specific positions may partially constrict pore openings or channel entrances, thereby limiting NH_3 diffusion and accessibility to active sites. As a result, the adsorption energy and the effective equilibrium constant may appear lower. Therefore, the lower Gibbs free energy values observed for Ca_9Na_3A in the graph indicate that, despite the presence of adsorption centers, a portion of them is sterically and diffusionally less accessible and thus less active.

In Ca_4Na_4A, the open and heterogeneous combination of adsorption centers arises from the mixed presence of Ca^{2+} and Na^+ cations. In such a system, the type and spatial distribution of active sites become more "mosaic-like," meaning that cations are not arranged uniformly but occupy different positions, forming energetically and structurally non-equivalent active centers. In certain regions, Ca^{2+} acts as a high-field adsorption center, whereas in others, Na^+ serves as a relatively weaker center. This configuration provides highly favorable high-energy sites for NH_3 at the initial stage of adsorption. As a result, ΔG starts from relatively high values and remains higher throughout the entire range, indicating that Ca_4Na_4A exhibits a greater thermodynamic affinity toward ammonia compared to the other zeolites.

The graph can be conventionally divided into three stages, providing a thermodynamic interpretation of the adsorption process. Stage I-Low (initial) coverage. High-energy adsorption sites are occupied, and ΔG (or -ΔG) exhibits large values. At this stage, NH_3 molecules are primarily coordinated to cationic centers, and strong adsorption, analogous to the formation of a first adsorption layer, dominates. Stage II- Intermediate coverage. Adsorption sites of moderate energy and favorable positions within the pore structure become occupied, leading to a gradual decrease in ΔG. In addition to cation-NH_3 interactions, adsorption within the framework becomes significant, and intermolecular interactions between adsorbed molecules begin to emerge. Stage III-High coverage (near saturation). The most energetically favorable sites are nearly fully occupied, and diffusion and steric constraints become increasingly significant. ΔG approaches its lowest values, and the curves continue to decrease, in some regions with a reduced gradient.

Conclusion. The thermodynamic behavior of ammonia adsorption demonstrates that as the adsorption capacity increases, the Gibbs free energy (ΔG) decreases. This trend is attributed to the energetic heterogeneity of the zeolite active sites, pore filling effects, and adsorbate–adsorbate interactions. The compositional effect shows that Ca_4Na_4A exhibits the highest thermodynamic affinity toward ammonia, $Ca_3Na_{1.2}A$ demonstrates intermediate behavior, and Ca_9Na_3A displays lower affinity across most of the range of Gibbs free energy values. These results indicate that, rather than the mere quantity of cations, their spatial distribution within the zeolite framework, accessibility, and diffusion pathways play a decisive role. An optimal cation distribution creates the most thermodynamically favorable sorption environment for NH_3.

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