ISOTHERM AND SORPTION MECHANISM OF AMMONIA ADSORPTION ON CAA ZEOLITE (M-34)

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Abstract: *This paper presents the values of ammonia adsorption isotherms on synthetic zeolite CaA (M-34), obtained experimentally at a temperature of 303 K. The adsorption isotherm was measured with high accuracy and stability using a system consisting of a differential automatic microcalorimeter of the Tiana-Calve DAK-1-1A type, connected to a universal high-vacuum installation. Differential values of free energy, that is Gibbs energy, were calculated from the equilibrium values of pressure. Based on the general equation of the volume theory of micropores (VMOT), the coefficients of the mathematical apparatus of the isotherm were determined from the values of the Gibbs energy. On zeolite CaA (M-34), a regular relationship was established between the adsorption value and the energy properties of the sorption of ammonia molecules, the sorption mechanisms and the regularity of filling the zeolite volume with ammonia molecules.*

Key words: *adsorption, adsorbent, pressure, isotherm, free energy, microcalorimeter, ammonia.*

The key role of zeolite catalysts in the processes of oil refining industry, gas and petrochemistry, as well as organic synthesis has significantly stimulated the creation of new highly effective catalytic systems based on them. However, further progress in this area is significantly hampered by the lack of detailed information on the mechanism of synthesis of these materials, and on the influence of the mechanism of zeolite synthesis on their physicochemical, catalytic and adsorption properties, as well as due to the lack of methods for targeted regulation of these properties during synthesis. All this fully determines the relevance of this work, aimed at studying the mechanism of synthesis of zeolite of the LTA structural type and searching for ways of targeted regulation of its physicochemical and catalytic properties.

Today, for catalysis and sorption processes, synthesis of zeolites with selective absorption properties in accordance with the kinetic sizes of adsorbate molecules in zeolites with nanoporous molecular structures such as LTA, MOR, MFI, FAU [1], as well as to determine the main thermodynamic properties of adsorption of adsorbates of different physicochemical nature in these zeolites , the formation of ion-molecular complexes in the zeolite matrix, determination of the localization and stereochemistry of molecules, the thermokinetics of adsorption in the micropores of zeolite, the implementation of cation exchange in order to increase the sorption and catalysis properties, it is necessary to study the laws of migration of cations, and to determine the molecular mechanisms of sorption in zeolite [2-8].

The adsorption and catalytic properties of hydrocarbons depend not only on the shape and size of the zeolite pores, but also on the SiO2/Al2O3 ratio, as well as on the ratio and types of cations. There is a large amount of data on the adsorption of gases and vapors in LTA-type zeolites, which were obtained by various physicochemical methods of study. However, there is little data obtained by the adsorption-calorimetric method, which puts on the agenda the task of further detailed study of the adsorption properties of LTA-type zeolites in relation to gas and vapor molecules, as well as polar and non-polar molecules, and obtaining the main thermodynamic characteristics of these systems.

Analysis of the literature showed that the main thermodynamic properties and adsorption mechanisms of polar, nonpolar and quadrupole molecules in LTA zeolite CaA(M-34) have not been thoroughly studied. The study of zeolites of the LTA type will help in the targeted synthesis of zeolites and their use as adsorbents of various technological processes. This article presents the results of adsorption differential heat and entropy change, as well as the mechanism of adsorption, obtained by the method of adsorption-calorimetric experiment on synthetic zeolite of ammonia CaA (M-34).

For measurements of isotherms and differential adsorption heats a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAK-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the mechanism of adsorption [9-13].

In this adsorption-microcalorimetric study, the adsorption isotherm of ammonia in CaA (M-34) zeolite at the temperature of 303 K was studied, the regular change of the adsorption amount to the equilibrium pressure and the adsorption mechanism were analyzed. The unit cell composition of this zeolite is represented by Ca9Na3(SiO2)12(AlO2)12)27H2O. Based on its chemical composition, the amount of Ca2+ cations in 1 g of zeolite is 1.91 mmol/g and the amount of Na+ cations is 0.96 mmol/g.

The adsorption isotherm of ammonia at a temperature of 303 K in CaA (M-34) zeolite was determined experimentally from the region of small saturations to the device range (600 torr), the main thermodynamic characteristics from the initial region to the saturation pressure and the regular relationship between the amount of adsorption and the mechanism of the sorption process were determined. During the adsorption process, it was shown that ammonia molecules form ion-molecular complexes of different proportions with Na+ and Ca2+ cations in SII and SIII positions of zeolite.

The logarithmic isotherm of the adsorption isotherm of ammonia in CaA (M-34) zeolite at 303 K is presented in Fig.1. At small saturations of the adsorption volume, the logarithmic value of the equilibrium relative pressure at the adsorption amount of 0.05 mmol/g is equal to Ln(P/Ps)=-13.3. Due to the high saturation pressure of ammonia (P=8750 torr), the experiment was conducted up to Ln(P/Ps)=-3. The amount of complete adsorption was equal to 7.22 mmol/g at this value of pressure.

Figure 1. Isotherm in logarithmic coordinates of ammonia adsorption on CaA (M-34) zeolite at 303 K temperature. △-experimentally obtained isotherm values, ▲-values calculated in the VMOT equation

The adsorption isotherm shows that ammonia molecules are strongly bound in CaA (M-34) zeolite in the initial region. In general, the isotherm has a convex appearance, which is due to the presence of strongly interacting adsorption centers in this adsorbent.

The isotherm is initially Ln(P/Ps)=-12.16 and a partial tilt towards the abscissa axis up to the adsorption amount of 0.84 mmol/g. As the sorption volume becomes saturated with ammonia molecules, at 2.87 mmol/g adsorption, the equilibrium relative pressure logarithm Ln(P/Ps)=-10.27 of the isotherm is 450 degrees relative to the ordinate and abscissa axes. changes linearly under the angle. The partial tilt at the initial region of 0.84 mmol/g and the linear change to the adsorption amount of 2.87 mmol/g are multiples of the amount of sodium cations in the zeolite (0.96 mmol/g). So, the initial ammonia molecules are adsorbed on the sodium cations contained in the CaA (M-34) zeolite, that is, NH_3 molecules at a small amount of adsorption form adsorbate/adsorbent monomer $1NH_3:Na^+$, trimer $3NH_3:Na^+$ ion-molecular complexes with Na^+ cations at an adsorption amount of 2.87 mmol/g does. The tetramer $4NH_3:Na^+$ forms an ion-molecular complex at the logarithmic value of adsorption of 3.91 mmol/g and relative pressure Ln(P/Ps)=-8.9 with the isotherm bending towards the abscissa axis. But the change of the isotherm in the subsequent adsorption of ammonia molecules does not depend on the adsorption of 0.96 mmol/g. This is due to the completion of the sorption process of ammonia molecules in the first coordination sphere with sodium cations in the zeolite.

After the tetrameric complex, the line of the isotherm changes towards the abscissa axis, which means that ammonia molecules are adsorbed on the second active center of the zeolite. The change of the isotherm depends on the amount of adsorption of 1.9 mmol/g. Therefore, subsequent ammonia molecules are adsorbed on calcium molecules in the zeolite. Ammonia molecules form dimer $2NH_3:Ca^{2+}$ ion-molecular mechanism with calcium cations. In general, ammonia forms an ion-molecular mechanism with metal cations in zeolite adsorbate/adsorbent in the ratio $6NH_3:Me$.

Figure 1 shows the isotherm of ammonia molecules adsorption on CaA (M-34) zeolite obtained experimentally and calculated based on the general equation of the volume saturation theory of micropores (VMOT). It can be seen from Figure 1 that the isotherm values calculated based on VMOT agree with the experimental values.

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