

ANALYSIS OF AMMONIA ADSORPTION ISOTHERM ON ZEOLITE CaA (M-22) IN THE THEORY OF VOLUME SATURATION OF MICROPORES

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Abstract

The article presents experimentally obtained values of the adsorption isotherm of ammonia molecules in synthetic zeolite SaA (M-22) at a temperature of 303 K and calculated values based on the theory of volume saturation of micropores. The isotherm of ammonia molecules in CaA (M-22) nanostructured zeolite was studied and the free energy values were calculated. Tetramer $4\text{NH}_3:\text{Na}^+$ in the first coordination sphere with sodium cations in the S_I and S_{II} positions of zeolite, dimer $2\text{NH}_3:\text{Ca}^{2+}$ ion-molecular complexes with calcium cations in the first coordination sphere, then two ammonia molecules with the initially adsorbed ammonia molecules in the second coordination sphere $\text{Ca}^{2+}:2\text{NH}_3:2\text{NH}_3$ - was found to form molecular complexes. It was proved that the mechanism based on the coefficients of the adsorption amount obtained on the basis of the volume theory of micropores fully corresponds to the mechanism based on the values obtained in the experiment. It was found that 65% of the total adsorption amount up to 50 torr corresponds to the adsorption of sodium and calcium cations, the main active centers of zeolite.

Keywords: adsorption, free energy, isotherm, pressure, ammonia, VMOT.

The results of adsorption-calorimetric research obtained on the basis of experience 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.

Today, in the world, the following scientific solutions for the synthesis of nanoporous molecular bubble zeolites for adsorption processes are justified, including: the selection of raw materials with suitable adsorption properties to obtain zeolites with selective absorption properties; determination of complete thermodynamic properties of synthesized zeolites; formation of ion-molecular complexes in the zeolite matrix, determining the state of localization; studying thermokinetics of adsorption and cation exchange in the zeolite structure,

migration of cations; the complete molecular mechanism of zeolite adsorption should be determined.

Aluminum and silicon atoms in aluminosilicate zeolites can be replaced by 3-5 valence elements such as gallium, germanium, phosphorus, which are close to them in nature, and their sorption and catalytic properties can be changed [1]. Another characteristic of these zeolites is the presence of water molecules in the internal structure of the crystal, when heated to a temperature of 450^oC, water molecules evaporate without breaking the structure of the crystal lattice, and the possibility of ion exchange due to the mobility of alkaline, alkaline earth cations and water molecules in the zeolite [2-4].

Based on the structure and composition of the crystal lattice of zeolites, zeolites are characterized by the names of MFI, MOR, FAU, LTA, regardless of their highest symmetry, which can choose sorption properties and catalysis characteristics [5] and their main thermodynamic properties of catalysis and adsorption of polar, non-polar and quadrupole molecules of different nature are fundamentally different from each other [6-11].

MFI, MOR, FAU, LTA and other types of zeolites form adsorbate/adsorbent ion-molecular complexes of different ratios depending on the amount of cations, which are the main adsorptive active centers. For example, in MFI zeolite modification 5 form of sodium cation, the formation of 8NH₃:Na⁺ ion-molecular complex is formed by ammonia adsorption, and 24 hydrogen molecules form a wrap around sodium cation in the intersection of zeolite channels [12-14].

The adsorption-calorimetric method used in this article allows obtaining the basic thermodynamic characteristics with high accuracy and revealing the detailed mechanisms of sorption processes in zeolite. The experiment was carried out using a universal high-vacuum adsorption device. The device is adapted to measure the amount of adsorbate by both gas-volumetric and liquid-volumetric methods. A modified Tian-Calve type DAK-1-1A microcalorimeter was used as a microcalorimeter with high accuracy and stability.

In the adsorption study, the adsorption of ammonia on CaA (M-22) zeolite at 303 K was studied and the adsorption isotherm was fully analyzed. The unit cell composition of this zeolite is Ca_{2,975}Na_{1,194}(SiO₂)₁₂(AlO₂)₁₂. Based on its chemical composition, the amount of calcium cations in 1 g of zeolite is 1.89 mmol/g and the amount of sodium cations is 0.76 mmol/g.

The isotherm of ammonia adsorption on CaA (M-22) zeolite in logarithmic coordinates is presented in Fig. 1.

Ammonia adsorption isotherm on CaA (M-22) zeolite is fully described using the three-state VMOT equation [15]:

$$a=4.77\exp[-(A/28.69)^7] + 2.015\exp[-(A/17.63)^4] + 5.6\exp[-(A/8.19)^3] \quad (1)$$

where, a is the adsorption value (mmol/g), $A=RT\ln P_s/P$ is the free energy and represents the work (kJ/mol) done in transferring the gas to the equilibrium gas phase. From Figure 1, it can

be seen that the calculated values in VMOT are in full agreement with the experimentally obtained adsorption amount up to 7 mmol/g. The first two terms of the equation represent the adsorption of ammonia molecules on the active centers of sodium and calcium cations of zeolite. The amount of adsorption in the formation of $4\text{NH}_3:\text{Na}^+$ and $1\text{NH}_3:\text{Ca}^{2+}$ is equal to 4.93 mmol/g, which corresponds to the value of $a_{01}=4.77$ mmol/g of equation 1. The amount of adsorption in the formation of $4\text{NH}_3:\text{Na}^+$ and $1\text{NH}_3:\text{Ca}^{2+}$ complexes is equal to 6.82 mmol/g, and the sum of the values of equation 1 $a_{01}=4.77$ mmol/g and $a_{02}=2.015$ mmol/g fully corresponds to 6.92 mmol/g.

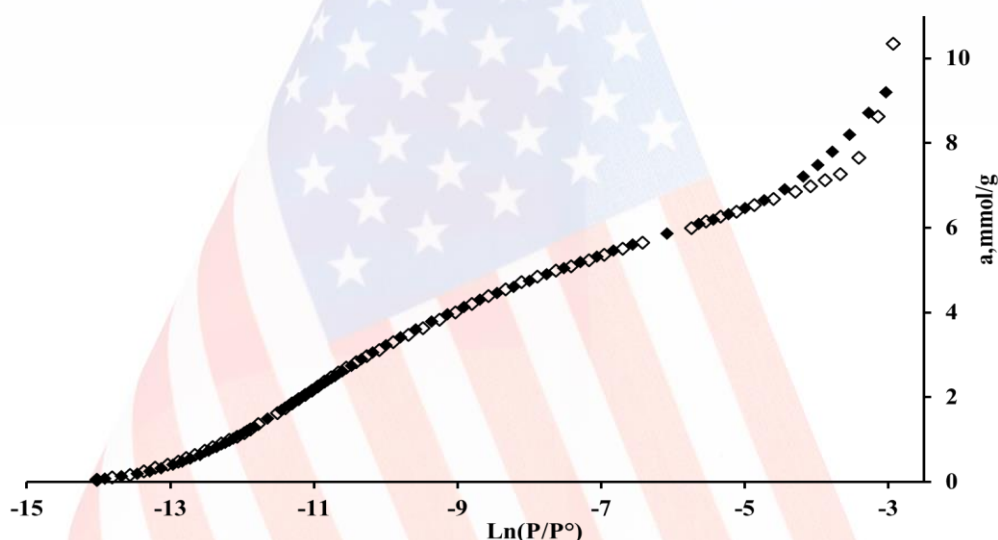


Figure 1. Adsorption isotherm of ammonia at 303 K on CaA (M-22) zeolite. In the ♦-experiment, ♦-values of the general equation of the theory of volumetric saturation of micropores (VMOT).

Since the adsorption process follows an exponential equation, the 3rd term of equation 1 has almost no effect from a small saturation pressure to a relative pressure of P/P_s ($R=120$ torr) and is weak. that is, it represents the sorption process resulting from the mutual Waa-der-Waals interaction of the adsorbate molecule in the second coordination sphere.

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