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

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Abstract: *The article presents the values of the isotherm of ammonia adsorption on synthetic zeolite CaA (M-34) obtained in the experiment at 303 K in relative pressure coordinates. The adsorption isotherm was measured with high accuracy and stability using a system consisting of a Tiana-Calve type DAK-1-1A differential automated microcalorimeter connected to a universal high-vacuum device. Under the experimental conditions (523 torr), the adsorption capacity of this zeolite with respect to* NH_3 *was expressed as 7.22 mmol/g per 1 g of zeolite. It was found that 49 % of the total adsorption was sorbed at an equilibrium pressure of 1 torr, 69 % at a pressure of 10 torr, 86 % at a pressure of 100 torr, and 100 % (7.22 mmol/g) at a pressure of 524 torr. It was proven that* NH_3 *molecules form tetrameric* $4NH_3$:Na *with sodium cations and dimeric* $2NH_3:Ca^{2+}$ *with calcium cations ion-molecular complexes in the first coordination sphere in positions* S_{II} *and* S_{III} *of the zeolite.*

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

In the production of high-octane gasoline and its components from petroleum and non-petroleum raw materials, such as methanol, in the purification and processing of petroleum and petroleum products, in order to obtain environmentally friendly gas from natural gases, their removal from various unnecessary chemical compounds, including degassing and dewatering, is currently used all over the world. The year by year increase in requirements to prevent the release of greenhouse gases into the atmosphere, which has become a major environmental problem, attracts the large-scale use and expansion of production of adsorbents. In order to avoid the problems mentioned above, synthetically produced zeolites are required to expand in size.

It is important to achieve scientific and practical innovations on the basis of the results of scientific and scientific-practical research conducted on the synthesis of high catalysis and sorption and special zeolites, increasing the level of their selectivity.

In addition to the fact that instead of aluminum and silicon in aluminosilicate zeolites, they can be replaced by germanium, gallium, phosphorus elements that are close to them in nature, they can change their sorption and catalytic properties [2], they are due to the presence of water molecules in the internal structure of the crystal, when heated at a temperature of 450^0 C, water molecules change the structure of the crystal lattice. It is the possibility of ion exchange due to the mobility of alkaline, alkaline earth cations and water molecules in the zeolite [3-5].

The adsorption of molecules of different physical and chemical nature in the forms of alkaline earth and alkaline earth metal cation LTA zeolites CaA(M-22), CaA(M-34), CaA(MISS-624) and CaA(Horst 50/50) was studied, their adsorption differential heat as a result of the stoichiometric effect was determined by the authors [6-8].

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 $Ca_9Na_3(SiO_2)_{12}(AlO_2)_{12})\cdot 27H_2O$. Based on its chemical composition, the amount of Ca^{2+} cations in 1 g of zeolite is 1.91 mmol/g and the amount of Na^+ cations is 0.96 mmol/g.

Figure 1 shows the values of the relative pressure dependence isotherm of molecular ammonia adsorption on CaA (M-34) zeolite obtained in the experiment in the P/Ps coordinate. The isotherm corresponds to the Brunauer type 1 classification, that is, ammonia molecules are adsorbed in the micropores of the zeolite.

The isotherm in the P/Ps coordinate confirms the sorption mechanism based on the isotherm in the logarithmic coordinates (Fig. 1). The isotherm was brought to the value of relative pressure P/Ps=0.06 (P=524 torr) and the amount of adsorption to 7.22 mmol/g. In the initial region, the value of equilibrium relative pressure P/Ps=0.0001143 (P=1 torr) and the amount of adsorption increases relatively slowly to 3.85 mmol/g. This is also due to the fact that the adsorbate-adsorbent interaction is strong. On the other hand, the amount of adsorption of 3.85 mmol/g is 4 times greater than the amount of sodium cations in zeolite

(0.96 mmol/g). As explained by the graph of the isotherm in logarithmic coordinates, ammonia molecules form a tetramer $4NH_3:Na^+$ ion-molecular complex with sodium cations contained in zeolite.

Next, ammonia molecules are adsorbed on calcium cations. When forming the ammonia/Ca^{2+} monomer $1NH_3:Ca^{2+}$ ion-molecular mechanism, the equilibrium relative pressure begins to increase relatively significantly. In the complete formation of the monomer $1NH_3:Ca^{2+}$ mechanism, the relative pressure at 5.85 mmol/g adsorption increases significantly up to P/Ps=0.0046 (P=40 torr).

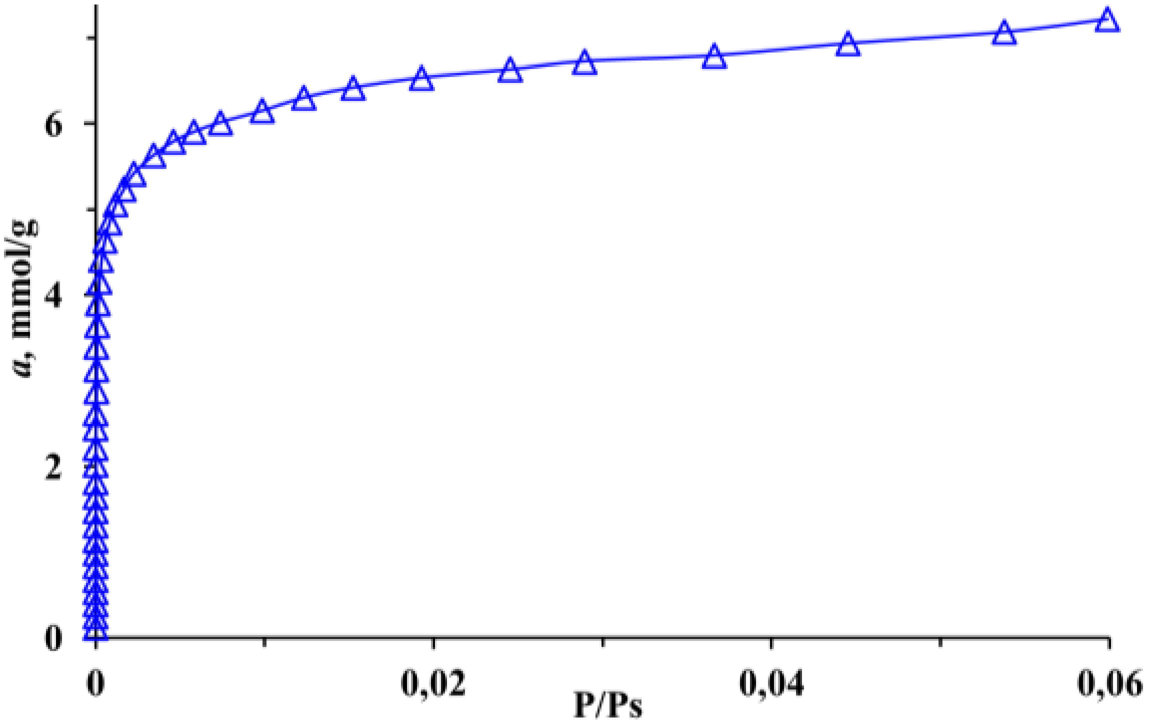

Figure 1. Isotherm of adsorption of ammonia molecules on CaA (M-34) zeolite at 303 K in P/Ps coordinate.

In the formation of the dimer $2NH_3:Ca^{2+}$ complex, the relative pressure increases sharply up to the experimental range of the device (P/Ps=0.06 or P=526 torr) and, in general, the formation of the $6NH_3:Me$ ion-molecular mechanism with the metal cations in the zeolite ammonia adsorption on CaA (M-34) zeolite ends with.

The results of the adsorption-calorimetric research obtained on the basis of the experiment make it possible 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 (M-34), as well as in the calculation of sorption technology processes and devices in practice.

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