DIFFERENTIAL ENTHALPY OF AMMONIA ADSORPTION ON ZEOLITE CAA (M-34)

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Abstract: *The article presents experimentally obtained values of the differential enthalpy of ammonia adsorption in synthetic zeolite CaA (M-34) at a temperature of 303 K. The differential enthalpy of adsorption was measured using a system consisting of a differential automatic microcalorimeter of the Tiana-Calve type DAK-1-1A type, connected to a universal high-vacuum device, has high accuracy and stabilityg). In zeolite CaA (M-34), a regular relationship was established between the adsorption value and the energy properties of ammonia molecules, as well as the sorption mechanism from the initial adsorption region to the region of ammonia condensation heat, and the patterns of filling the zeolite volume with ammonia molecules were determined. It has been proven that ammonia molecules form tetra 4NH3:Na+ in the first coordination sphere with sodium cations in positions SII and SIII of the zeolite and dimer 2NH3:Ca2+ in the first coordination sphere with calcium cations. It has been proven that the value of the differential enthalpy of ammonia adsorption depends on the type of cation in the zeolite.*

Keywords: *adsorption, adsorbate, differential heat, enthalpy, free energy, entropy, pressure, microcalorimeter, ammonia.*

Basic thermodynamic properties and adsorption mechanisms of polar, non-polar and quadrupole molecules in CaA-type zeolites have not been thoroughly studied. In addition, there is not enough information about scientific research studies in which adsorption characteristics were studied by X-ray and spectroscopy methods, and adsorption enthalpy was studied. The study of LTA zeolites will help in the targeted synthesis of zeolites and their use as adsorbents in 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).

In this adsorption study, the adsorption of ammonia in CaA (M-34) zeolite at a temperature of 303 K was studied, and the regular change of the differential enthalpy of adsorption according to the amount of adsorption and the amount of sodium and calcium cations in the zeolite composition was determined and fully analyzed. Based on the chemical composition of CaA (M-34) zeolite, the amount of calcium cations in 1 g of zeolite is 1.91 mmol/g and the amount of Na+ cations is 0.96 mmol/g.

The differential enthalpy of ammonia adsorption on CaA (M-34) zeolite was measured using a system consisting of a Tiana-Calve type DAK-1-1A differential automated microcalorimeter connected to a universal high vacuum device [1-6]. The adsorption-calorimetric method allows to study nano-, micro-, mesostructured adsorbents and their surface-active surfaces, to reveal in detail the main thermodynamic properties and mechanisms of adsorption processes in which adsorbents occur [7-12]. The differential

enthalpy values of NH3 adsorption on CaA (M-34) zeolite can be divided into 6 areas. The differential heat changes in the first 4 areas by a factor of 1 mmol/g, and in the last 2 areas by a factor of 1.9 mmol/g. The differential heat of adsorption in the primary region is 135 kJ/mol. As the amount of adsorption increases, at 0.96 mmol/g adsorption, the differential heat decreases to 81 mmol/g and forms an initial minimum, that is, initial NH3 molecules form an ion-molecular complex of adsorbate/adsorbent monomer 1NH3:Na+ with sodium cations.

NH3 molecules form a dimer 2NH3:Na+ ion-molecular complex with Na+ cations at an adsorption amount of 1.92 mmol/g and a differential heat of 73.6 kJ/mol, NH3 at an adsorption amount of 2.88 mmol/g and a differential heat of 65.9 kJ/mol trimeric 3NH3:Na+ ion-molecular complex with sodium molecules, at 3.88 mmol/g the heat decreases to 65 kJ/mol and forms tetramer 4NH3:Na+ ion-molecular complex. The dependence of the amount of adsorption on the differential enthalpy by a factor of 0.96 mmol/g is not observed in the subsequent sorption process. So, the adsorption of sodium cation in zeolite of ammonia molecules is completed. But the further change of differential enthalpy corresponds to the value of adsorption amount of 1.9 mmol/g. This value is equal to 1.91 mmol/g of calcium in zeolite. Hence, the subsequent ammonia molecules are adsorbed on calcium cations.

The differential heat of sorption is initially partially reduced to 53 kJ/mol during the transition from sodium cations to calcium cations, increases to 58 kJ/mol at the adsorption amount of 58 kJ/mol and forms the 4th maximum, at 34.5 kJ/mol adsorption 5.71 mmol/g in the amount of adsorption ammonia molecules with calcium in the 1st coordination sphere monomer 1NH3:Ca2+ ion-molecular mechanism, the differential heat initially increases by 7 kJ/mol, then the condensation heat of liquid ammonia decreases to 20 kJ/mol, dimer 2NH3:Ca2+ ion-molecular formation with the adsorption process of ammonia on CaA (M-34) zeolite ends.

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