

DIFFERENTIAL HEAT OF ADSORPTION OF AMMONIA ON LTA ZEOLITE

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Abstract

This paper presents the results of differential heat of adsorption of ammonia in Ca₅Na₃A zeolite (MSS-624) at a constant temperature of 303 K. A system consisting of a universal high-vacuum adsorption unit coupled to a Tian-Calvet type differential microcalorimeter, DAK-1-1A, was used to measure the differential heat of adsorption. A correlation between adsorption-energy characteristics was found, and the molecular mechanism of ammonia adsorption in Ca₅Na₃A zeolite (MSS-624) in the whole filling region was also revealed. A stepwise change in the differential heat of adsorption depending on the amount of Na⁺ and Ca²⁺ cations in the zeolite has been established. Ammonia molecules initially form tetrameric ion-molecular complexes 4NH₃:Na⁺ in the first coordination sphere with sodium cations and monomeric ion-molecular complexes 2NH₃:Ca²⁺ with calcium cations

Keywords: adsorption, heat, enthalpy, thermodynamics, microcalorimeter, ammonia, adsorption mechanism, cation, sodium, calcium.

A unique class of compounds, zeolites, is widely used in various industries, namely petrochemical, gas processing, chemical, food, construction, agriculture, energy, medicine, and many others due to their properties. Natural zeolites with good separating properties are rare, so the production of synthetic zeolites is carried out on an industrial scale. The most widespread in relation to adsorption processes are the so-called low modulus zeolites, LTA (international classification, Linde Type A). However, the main directions of zeolite synthesis have a number of disadvantages: high sensitivity to the concentration of reagents and process temperature, significant duration of the process and formation of a large amount of waste water.

Therefore, the search for new approaches to the directed synthesis of low-modulus zeolites is currently an urgent problem.

Natural and synthetic zeolites have found wide application as adsorbents. Zeolites are most widely used in gas and petrochemistry, adsorption, separation of vapours and gases and removal of impurities from gases and solutions. Zeolites A, X and other synthetic zeolites have the greatest practical application.

Globally, in the production of environmentally friendly fuel materials from natural gas and oil, harmful compounds contained in their composition have a negative impact on technological processes and product quality. In the processes of natural gas drying, in order to obtain fuels that meet the standards, it is important to purify from nitrogen and Sulphur-containing compounds. This process is carried out with the help of microporous synthetic zeolites. Therefore, the synthesis of microporous adsorbents with high sorption capacity and the achievement of new scientific and practical results is important

Studies of adsorption processes of polar, nonpolar, quadrupole and aromatic molecules are carried out in the world to determine the mechanism and thermodynamic functions, including the following priority directions: synthesis of microporous adsorbents; improvement of their composition; synthesis of synthetic zeolites and determination of their adsorption properties; enhancement of selectivity of their absorption properties due to the exchange of cations in the composition of zeolites of A, X, Y and LSX types. The research carried out in the world is mainly aimed at studying the structure of zeolites and the arrangement of cations in them.

The aluminosilicate skeleton of type A zeolites consists of cubo-octahedral structural units. Each cubo-octahedron is built of 24 elementary structural units - AlO_4 and SiO_4 tetrahedrons, and the adjacent tetrahedrons have common oxygen ions. Each cubo-octahedron contains 24 ions (Al+Si) bound by 36 oxygen ions. Each cubo-octahedron has six four-membered and eight six-membered windows [1-7]

There are few data on the study of the mechanism and thermodynamic functions of the adsorption process of NH_3 molecules

There are a large number of data on adsorption in LTA-type zeolites, which have been obtained by various physicochemical methods of investigation. However, the data obtained by adsorption-calorimetric method are few, which puts on the agenda the task of further detailed study of adsorption properties of zeolites of Ca_5Na_3A (MSS-624) type and obtaining the main thermodynamic characteristics of these systems

The adsorption-calorimetric method used in this work makes it possible to obtain highly accurate molar thermodynamic characteristics, as well as to reveal detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. A modified DAK- 1-1A thermally conductive microcalorimeter with high accuracy and stability was used as a calorimeter. We used a BARATRON B627 membrane manometer to measure equilibrium pressures. Despite

its external insulating shells, it is not adiabatic because the heat released in it is introduced from the calorimetric chamber as it is released and dissipated in a large metal block. Although the temperature of the calorimetric chamber changes only slightly, the apparatus cannot be called strictly isothermal; it exhibits small changes in temperature, which are unavoidable, and serve as the basis of measurement.

In this work, the heats of ammonia adsorption in zeolite Ca₅Na₃A (MSS-624) at 303 K have been studied. The unit cell composition of this zeolite is represented by Ca₅Na₃[(AlO₂)₁₂(SiO₂)₁₂] and consists of SI, SII and SIII positions. According to the chemical composition, the amount of Ca²⁺ cations per 1 g of zeolite is 2.95 mmol/g, the amount of Na⁺ cations is 1.77 mmol/g. First of all, it should be noted that due to the high saturation pressure of ammonia (P_s = 8750 torr) at the experiment temperature of 303 K, we were not able to obtain the full isotherm of ammonia adsorption on zeolite Ca₅Na₃A (MSS-624).

Differential heats of adsorption of ammonia vapour on zeolite Ca₅Na₃A (MSS-624) are presented in Fig.1. In general, the heat of adsorption varies in a wavelike manner. The curve of differential heat of adsorption of ammonia on zeolite Ca₅Na₃A (MSS-624) can be divided into 6 sections corresponding to the region of high heat of adsorption. These are the adsorption of an average of 4 ammonia molecules on Na⁺ cations, when the heat varies from 136 kJ/mol to 43 kJ/mol; and a region of relatively low (from 43 kJ/mol to a condensation heat of 20 kJ/mol) - another 1 ammonia molecule on Ca²⁺ cations. The initial heat of adsorption is 136 kJ/mol. At higher fillings, the heat decreases to 86 kJ/mol and they undergo a minimum at adsorption of 1.77 mmol/g, forming a mono 1NH₃:Na⁺ ion-molecular complex.

Further, ammonia molecules with Na⁺ cations successively form a dimer 2NH₃:Na⁺ complex at 3.54 mmol/g adsorption, a trimer 3NH₃:Na⁺ complex at 5.3 mmol/g adsorption and a tetramer 4NH₃:Na⁺ ion-molecular complex at 7 mmol/g adsorption.

Adsorption of the following ammonia molecules proceeds with a wavy heat change, then decreases again to the heat of condensation, i.e. one ammonia molecule adsorbed on Ca²⁺ cations. The total adsorption of ammonia on the zeolite Ca₅Na₃A (MSS-624) is 6 molecules (~10 mmol/g) of ammonia.

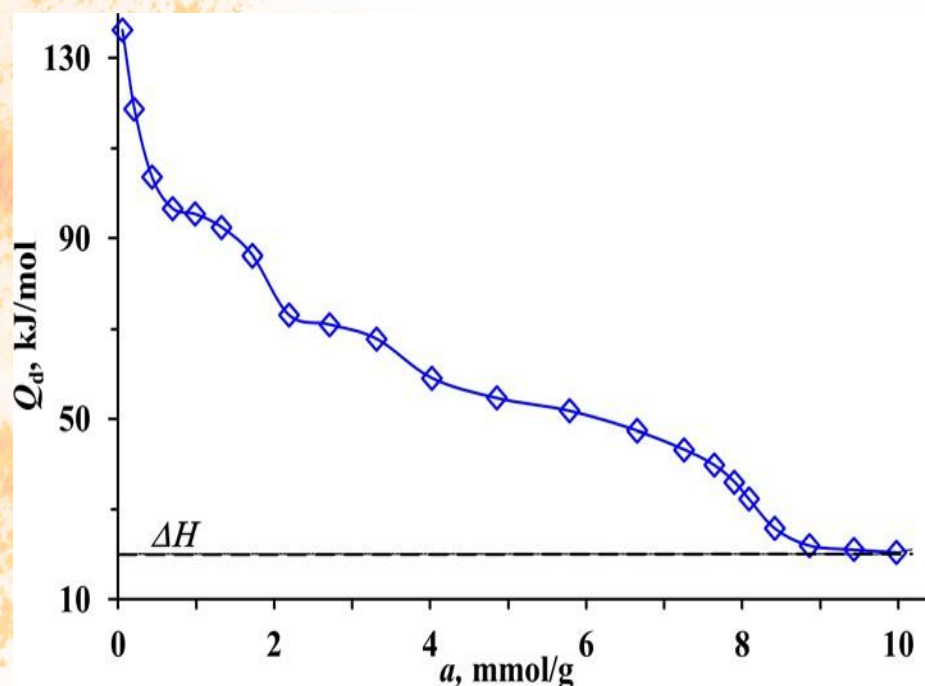


Figure 1. Differential heats of adsorption of ammonia on zeolite Ca₅Na₃A (MSS- 624) at 303 K. The horizontal dashed line is the heat of condensation.

In general, the heat of ammonia adsorption (Fig.1) on zeolite Ca₅Na₃A (MSS-624) is significantly lower than on Ca₅Na₃A (MSS-624) [8-10]. The increased heat of ammonia adsorption on the zeolite Ca₅Na₃A (MSS-624) is characterized by the high surface charge density of Na⁺ and Ca⁺² cations.

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