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Differential Heat of Ammonia Absorption in Pentasil Type Zeolites

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ABSTRACT: The differential heat, of NH_3 adsorption in zeolite $Li^+_{4,36}$; $Na^+_{4,36}$; $K^+_{3,6}$and $H^+_{3,25}$-ZSM-5 were measured at 303K. Based on the data obtained, a detailed mechanism for the adsorption of NH_3 in zeolite $Li^+_{4,36}$; $Na^+_{4,36}$; $K^+_{3,6}$and $H^+_{3,25}$-ZSM-5from zero filling to saturation is disclosed.

KEYWORDS: adsorption heats, ion-molecular complexes, zeolite $Li^+_{4,36}$; $Na^+_{4,36}$; $K^+_{3,6}$and $H^+_{3,25}$-ZSM-5, NH_3, adsorption calorimetry

I. INTRODUCTION

Adsorption processes of vapors and gases are the main physicochemical processes that allow a certain chemical structure and composition of zeolites, their production and theoretical and practical use. The structure of the zeolite surface is very important for understanding the chemical reactions in phase fission. In order to describe the reactions that occur on the surface, it is necessary to have accurate information about the nature, number, strength and distribution of the surface centers involved in the adsorption and catalytic processes. These data are very important for modeling chemical processes on the surface and to determine the mechanism of reactions and stoichiometry on the surface. The relatively complete description of the adsorbent surface by its physical, chemical and crystallochemical nature is determined by the differential heat of adsorption (*Qd*) and other differential adsorption-energy characteristics (entropy, free energy and heat capacity) [1,2,3].

II. SIGNIFICANCE OF THE SYSTEM

To study the basic thermodynamic characteristics of adsorption, an adsorption-calorimetric method was used, which provides sufficient information about the surface area, crystal chemistry, kinetics, and the mechanism of formation of ion-molecular clusters. Adsorption-calorimetric method has a special place among the clearly systemically sensitive methods for studying the guest-host interaction.The study of literature survey is presented in section III, methodology is explained in section IV, section V covers the experimental results of the study, and section VI discusses the future study and conclusion.

III. METHODOLOGY

The adsorption-calorimetric method used in this work allows to obtain high-precision molar thermodynamic characteristics and to reveal a detailed mechanism of adsorption processes in adsorbents and catalysts. Adsorption measurements and adsorption doses are carried out using a common adsorption unit, in the working part of which only symbolic valves are used, which are replaced by lubrication of the valves [4,5]. The unit provides the dose of adsorbate by gas-volume and volume-liquid methods. The experiment is performed on a DAK 1-1 calorimeter device with high accuracy and reliability.

IV. EXPERIMENTAL RESULTS

In this study, $Li^+_{4,36}$;$Na^+_{4,36}$;Differential temperatures of ammonia adsorption in ZSM-5 zeolites with cation $K^+_{3,6}$ and $N^+_{3,25}$ were studied.

In this section, we study the differential heats of adsorption of ammonia in zeolite $Li_{4,36}$ZSM-5. The investigated zeolite contains 1,5 H^+ and 2,9 Li^+ and a minimum amount of structural defects. Earlier [9], studies of the adsorption of ammonia in LiZSM-5 zeolite with a lower charge density of 3,4 Li/eu were carried out. The curve of

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differential heats of adsorption (*Qd*) of ammonia in zeolite $Li_{4,36}$ZSM-5 has a stepwise character (Fig. 1). The curve starts from 110 kJ/mol and gradually decreases to 25,84 kJ/ mol. Each step reflects the stoichiometric interaction of protons and Li^+cations with a base molecule -NH_3. From the composition of the studied zeolite, it was found that the concentration of H^+ protons is 0,23mmol/g, and Li^+cations – 0,47 mmol/g.

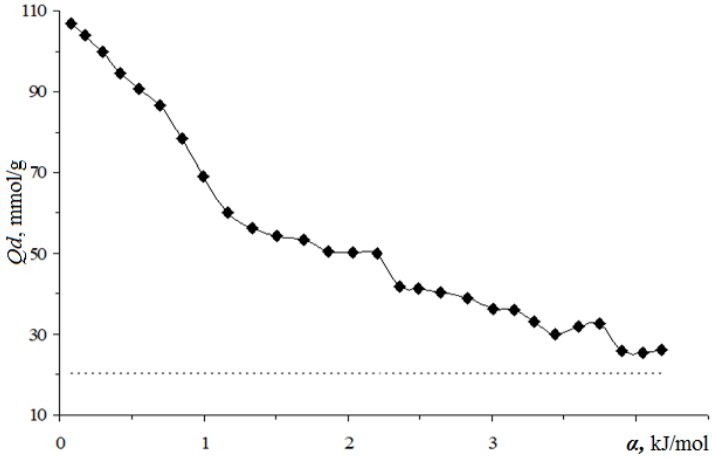

Fig. 1.Differential heats of adsorption of ammonia in zeolite $Li_{4,36}$ZSM-5.Horizontal dashed line - heat of condensation

A total of 4,42mmol/g was adsorbed. On average, there is 6 NH_3 for each ion. Thus, the first high-energy step from 110 to 86,7 kJ/mol with a length of 0,69 mmol/g demonstrates the adsorption of ammonia on H^+ protons and Li^+cations in a 1:1 ratio. The second step from 86,7 to 59,9 kJ/mol with a length of 0,47 mmol/g indicates the adsorption of ammonia exclusively on Li^+cations. A detailed analysis of the steps showed that 6 ammonia molecules are adsorbed on saturation on protons and cations.

The adsorbent was synthesized in Miluse (France) in a fluoride medium, the composition of the studied zeolite $Na_{4,36}$ZSM-5 (Si/Al = 22) is distinguished by a high concentration of Na^+cations and a minimum content of defects. Differential heats of adsorption of ammonia in zeolite $Na_{4,36}$ZSM-5 are shown in Fig. 2.The figure shows that the heat of adsorption changes stepwise

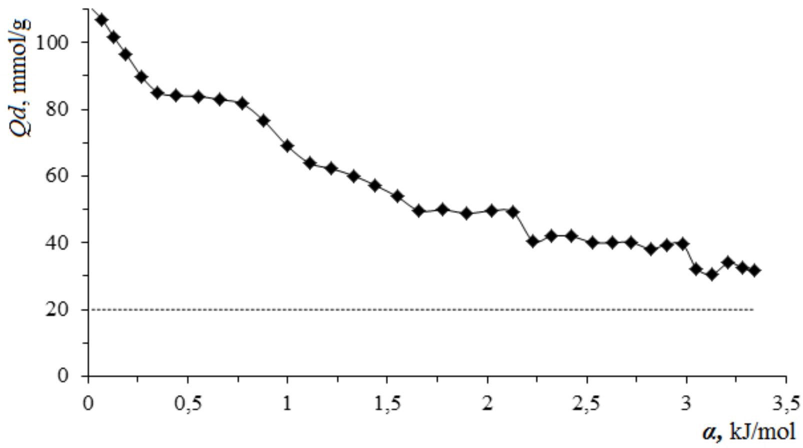

Fig. 2.Differential heats of adsorption of ammonia in zeolite $Na_{4,36}$ZSM-5 at 303K.The horizontal dashed line is the heat of condensation.

The initial heat of adsorption decreases linearly from 110 kJ/mol to 85 kJ/mol with adsorption equal to 0,37mmol/g, then to a=0,75 mmol/g, ammonia is adsorbed with a heat that changes little with filling ~84 kJ/mole. Adsorption from 0,75 to 1,67 mmol/g is again accompanied by a sharp decrease in heat to 50 kJ/mol. In this region, two sections can be distinguished with heat varying from ~84 to 63 kJ/mol in the adsorption range 0,75-1,1 mmol/g and with heat varying from 63 to 50 kJ/mol in the range 1,1-1,67 mmol/g. Further, a stepwise decrease in heat continues

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and on the curve we observe 2 more gentle steps: ~50 kJ/mol (from 1,67 to 2,25 mmol/g) and ~40 kJ/mol (from 2,25 to 3 mol/g) ... The first three steps correlate with the adsorption of ammonia on cations Na^+ located in different crystallographic positions. These cations are conventionally called Na^+ I and Na^+ II. Ammonia is adsorbed on Na^+ I in a 2:1 ratio, and on Na^+ II - 1:1. Further, this ratio is retained and at saturation $6NH_3$ is adsorbed on Na^+ I, and 3 NH_3 on Na_+ II. Earlier [7,8,9], the adsorption of ammonia in the NaZSM-5 zeolite with a lower charge density of 2,9 Na/eu was investigated and it was shown that there are 8 ammonia molecules for each sodium cation and that these complexes are located at the crosshairs of the channels.

The differential adsorption heat (kJ) curve of ammonia in $N_{3,25}$ZSM-5 zeolite has a stepwise character (Fig. 3). The zeolite under study contains 3,25 N^+. The adsorption heat starts at 180 kJ/mol and gradually the condensation heat of liquid nitrogen decreases to 20 kJ/mol. The initial saturation reflects the stoichiometric interaction of protons with the step-based molecule - NH_3, in which the phenomenon of chemical adsorption is observed. A total of 3,22mmol/g of ammonia molecules are adsorbed on the studied HZSM-5 zeolite, which leads to the formation of adsorbent-adsorbent to 2,2 mmol/g of protons, 1 mmol/g of adsorbate-adsorbate. On average, 4 ammonia is adsorbed on each hydrogen ion. Thus, the first high-energy step varies from 180 to 64,87 kJ/mol, i.e., the adsorption of 0,55 mmol/g of ammonia on each proton is expressed in a 1:1 ratio. The adsorption of ammonia at 1,12mmol/g on secondary cations with a duration of 64,87 mmol/g to 41 kJ/mol indicates the formation of a $2NH_3$:H^+ ion-molecular complex. The adsorption heat of the next 2 ammonia molecules is almost constant, i.e. adsorbed with 30 kJ/mol of heat to form a $4NH_3$:H^+ ion-molecular complex, the adsorption differential heat drops to the condensing heat of liquid ammonia at 303K. A detailed analysis of adsorption showed that 4 ammonia molecules are adsorbed on cations during saturation. 1,1mmol/g ammonia molecules, ie the next 2 molecules adsorbate-adsorbate interact

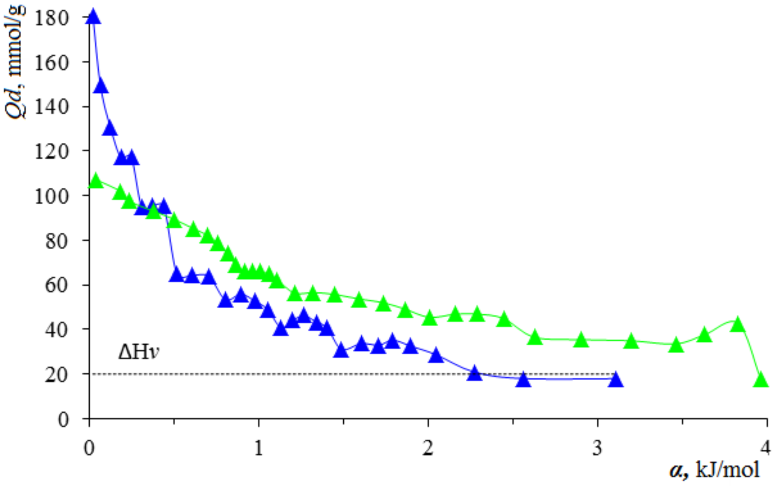

Figure 3 shows the differential heat values (Qd) of ammonia adsorption on ZSM-5 zeolites with ▲-K$^+$, ▲-H$^+$ cations at 303 K.Barcode Condensation value of ammonia at 303K.

In this study, the adsorption isotherms and basic thermodynamic characteristics of ammonia in zeolite, the stepwise nature of changes in adsorption temperature were determined. The complete adsorption mechanism of ammonia adsorption on K- and N-ZSM-5 zeolites is given. In zeolites, ammonia was initially found to be adsorbed on cations in a 1:1 ratio. In the final saturation, 4 ammonia molecules are adsorbed on the proton and 7 ammonia molecules on the potassium cations. The mobility of ammonia adsorbed in zeolite channels is limited. In this study [9], the formation of ammonia packaging complexes unexpectedly was found. An ion-molecular complex with Na^+cation in the center and 24 hydrogen atoms in the outer shell is formed. This Na^+: $8NH_3$ complex will be located in the cross-sections of the straight and zigzag channels of the ZSM-5 zeolite. The solvation of alkali metal cations with ammonia in solution and the gas phase are the subject of many theoretical and computational studies. The location of the cations on the surface and in the size of the pores, such as zeolites, is a more complex process, as the interaction of cations and adsorbate molecules with the anionic solid matrix must be taken into account, which may prevent complication in the cationmolecular system.

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V. CONCLUSION AND FUTURE WORK

Representatives of the pentacil family differ from each other in the range of aluminum-silicon-oxygen and almost identical exchange cations, which are completely identical. Their adsorption properties relative to the same substance can be expected to be essentially the same. However, in the study of the differential heat of adsorption of ammonia vapor at 303K, it was proved that these zeolites have similarities and significant differences in their adsorption properties. The adsorption heat of polar molecules in ZSM-5 zeolite is characterized by a gradual decrease in adsorption heat. This shows the stoichiometric interaction of the molecular lattice with the cations compensating for the negative charge. Thus, the steps of ammonia molecule adsorption correspond to the formation of complexes.

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