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ENERGETICS OF THE HOST-GUEST INTERACTIONS IN NALTA MOLECULAR SIEVES. THE STEPWISE NATURE OF THE HEAT CURVE OF ADSORPTION.

[1]Raxmatkarieva Firuza Gayratovna
Doctor of chemical sciences, professor.
Tashkent Institute of Inorganic Chemistry,
[2]Davlatova Odina Zakirjonovna
Namangan Institute of Engineering and Technology is a doctoral candidate.
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ABSTRACT

The paper analyzes the isotherm and differential heats of adsorption of carbon dioxide in NaLTA and establishes the molecular host-guest mechanism of interactions in the molecular sieve matrix.

Carbon dioxide is a strategic gas in many industrial processes. Excessive emission of carbon dioxide into the atmosphere leads to a global greenhouse effect [1]. Solving this problem with the help of adsorption techniques is economically advantageous. The most suitable for this purpose are molecular sieves [2,3,4]. The adsorption properties of molecular sieves can be regulated by varying the size and shape of the pores, the Si/Al ratio and the nature of the extraframework cations [5,6]. It has been found that nanoporous molecular seaves NaA [7] and CaA [8] zeolites are good absorbers of carbon dioxide, since the Na^+ and Ca^{2+} cations [9] provide strong electrostatic interaction with carbon dioxide [10].

The regularities of adsorption of water in NaY molecular sieve were considered in [11] research work. It was found out that an appreciable amount of water is adsorbed in β-cavities. The carbon dioxide molecule is somewhat larger than the water molecule and therefore at room temperature it is unable to penetrate into the β-cage through six-member oxygen windows with a diameter of 2.6 Å and to form host-guest clusters with sodium cations there. However, cations themselves can migrate from β- to α-cage under the influence of adsorbed molecules [12].

The aim of the study was to establish a stoichiometric relationship between the heats of adsorption of the test carbon dioxide molecule (guest) on homogeneous adsorption sites in NaLTA (host) and number of adsorbed on these sites molecules.

The study was carried out on a universal high-vacuum volumetric set, which allows the dosage of adsorbate to be carried out both with gas-volume and bulk-liquid methods with an accuracy of 0.1% [13, 14]. Differential heats of adsorption were measured using a heat-conducting

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microcalorimeter of the Tiana-Calvet type. The use of the method of heat-flux compensation by the Peltier effect made it possible to increase the accuracy of the detected heat by 10-15 times [14].

Prior to the introduction of carbon dioxide, the sample was heated and subjected to high vacuum evacuation at 723 K for 10 hours. Figure (curve a) shows the differential heats of adsorption (Q_d) of CO_2 in NaA at 303 K. The intermittent line is the heat of condensation of carbon dioxide at 303 K (ΔH_v = 27 kJ / mol). For NaA Q_d begins at ~ 82 kJ / mol and decreases to 57.4 kJ/mol at 0.4 CO_2 per pseudo-elementary cell (u.c.) (the real unit cell is 8 times larger) Further Q_d forms a step, decreasing from 57.4 to 52.91 kJ/mol at 1 CO_2/u.c. Further adsorption is accompanied by the formation of one more step (wave) with a length of 1.0 CO_2/u.c. in the range of adsorption (N) from 1.0 to 2.0 CO_2/u.c. with Q_d varying from 52.91 to 52.78 kJ/mol. Next is an extended step extending from 2.0 to 5.0 CO_2/u.c followed by another step with a length of 1.0 CO_2/u.c. (from 5.0 to 6.0 CO_2/u.c). The process is completed by passing the curve through 2 maxima with a length of 1.0 CO_2/u.c. In total, NaA zeolite contains 7 CO_2 /u.c.

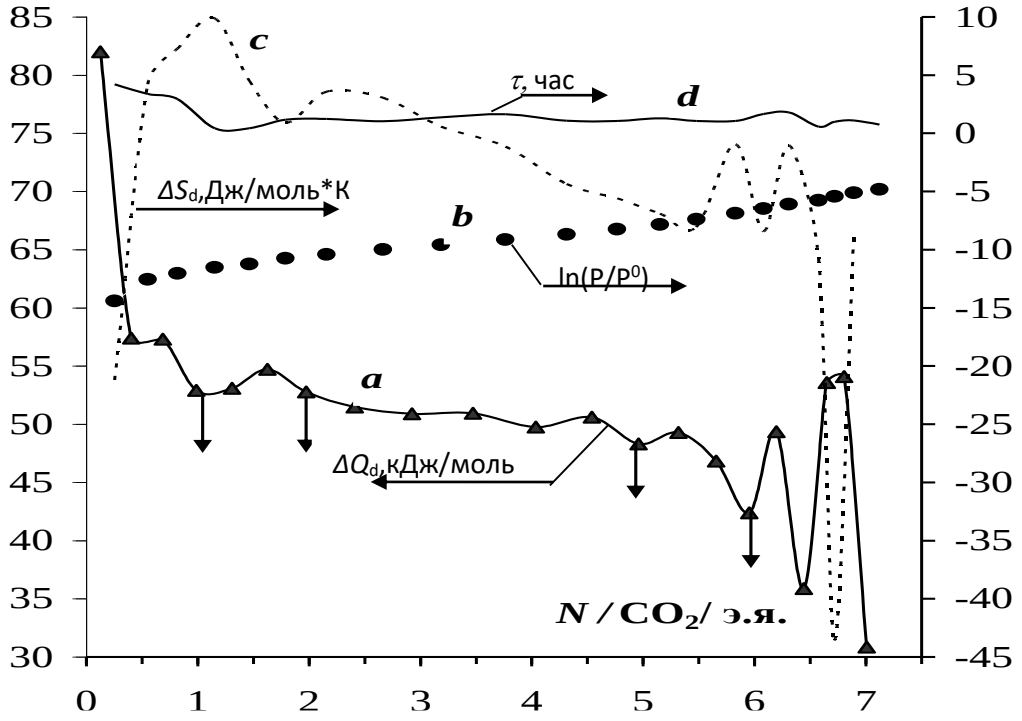

Fig. Adsorption of carbon dioxide in NaA at 303 K: a – is the differential heats; b - isotherm; c - entropy; d - thermokinetics.

In molecular sieve type A, not all cations occupy the same position in the lattice. There are 3 main types of cation localization sites. Places SI - in the center of six-membered oxygen rings, where NaI cations are located in the center of six-membered oxygen rings, occupying all the places. The SII centers, where the NaII cations are located in the plane of the eight-membered oxygen rings slightly shifted from the center. Finally, SIII sites, where NaIII cations are localized opposite the four-membered rings and are located inside the α-cavities by about 1.7 Å from

the ring plane in the amount of one Na^+ per α-cavity.

The stepwise nature of the heat curve of adsorption is considered in connection with the stoichiometric interaction of CO_2 molecules with coordinatively unsaturated Na^+ cations in various energetically homogeneous centers of the cages of NaA molecular sieve. For a quantitative description of the process, the calorimetric data were contingently divided into five sections in accordance with the steps on the Q_d curve: the first from 0 to 1 CO_2/u.c. (1 CO_2/u.c.), the 2nd - from 1 to 2 CO_2/u.c. (1 CO_2/u.c), and the third - from 2 to 5 CO_2/u.c (3 CO_2/u.c.), the 4th - from 5 to 6 CO_2/u.c. (1H_2O/u.c.) and finally the 5th - from 6 to 7 CO_2/u.c. (1H_2O /u.c).

Interpretation of results is a model of the molecular picture. In the initial adsorption region, we observe two sections with a length of 1 CO_2/u.c each. Obviously, for the quadrupole CO_2 molecule, the SIII and SII centers due to ion-dipole interaction with Na^+ cations are more favorable than SI, because the degree of coordination unsaturation (c.u.) of H^+ and Na+ cations in SIII and Na^+ in SII significantly exceeds c.u. degree of the cations in SI, in which they are surrounded by six strongly shielding cations of oxygen atoms. In addition, the energy of adsorption of CO_2 with sodium cations in the NaX and NaY molecular sieves in the analogous position is 36 kJ/ mol [15], while the curve Q_d (fig. a) is much higher in the main filling region. Besides this, in this position, sodium is slightly advanced toward the β-cage, as studies have shown for adsorption of water in NaA. Therefore, SI cations should be excluded as the main centers of adsorption. But we can not exclude them as additional centers of adsorption.

Therefore, the formation of high-energy complexes should be associated with cations in positions SIII and SII. Since the cations in position SIII are 1.7 Å away from the adsorbent wall and are the most accessible to adsorbing molecules, then, apparently, they should be energetically preferable in comparison with SII cations in eight-membered oxygen windows. And, indeed, the first two sections correlate with the number of cations in position SIII, therefore, their appearance is associated with the adsorption of CO_2 on them and the formation of high-energy complexes. As in the case of water, we attribute the high energetic heats at the lowest fillings to the adsorption of CO_2 on protons (H^+), then adsorption proceeds on Na^+ cations. But unlike water, carbon dioxide is a quadrupole molecule with weak charges at the ends compared to water. In addition, the distance between the cations in SIII and SI, as well as between SII and SI, roughly corresponds to the size of the carbon dioxide molecule. And if we take into account that cations in positions SIII and SII have high mobility, then the most likely configuration is the configuration when carbon dioxide forms a bidentate complex at the ends of which the proton or sodium in positions SIII and sodium in position SI. (H^+ or Na) IIIO=C=ONaI).

In the second section, the number of CO_2 molecules adsorbed on SIII cations is doubled $(CO_2)_2/H^+$ and $(CO_2)_2/Na^+$. The third section corresponds exactly to the number of cations in the SII position. Carbon dioxide forms three $(CO_2)/Na^+$ complexes with SII cations in the α-cage, each of which also closes on the cation SI (NaIIO=C=ONaI) at the opposite end. The fourth section is a single molecule (CO_2)/u.c. corresponds to the addition of a

third carbon dioxide molecule to the double complex with the formation of $(CO_2)_3/H^+$ and $(CO_2)_3/Na^+$ complexes oriented opposite to Na^+ in SI. Finally, the fifth section is one molecule per u.c. is characterized by the passage of the curve through two high maxima. The appearance of the maxima is explained by the reorientation of the CO_2 molecules to complete the formation of the four-dimensional cluster.

The addition of the fourth CO_2 molecule to the sodium cation in SIII is impossible due to steric considerations. Therefore, The appearance of the maxima is explained by the reorientation of the CO_2 molecules to complete the formation of the four-dimensional (multidentate) cluster , at the center of which the cation H^+ (first maximum) and Na^+ (second maximum) from at position SIII, tetrahedrally are surrounded by four carbon dioxide molecules, each of which adjoins the opposite end to sodium in position SI. Considering that the distance between the opposite cations in the SI α-cage position and the cluster size, as well as the energy gain from the bidentate interaction, it can be argued that such a cluster can be located only in the center of the α-cage of NaA.

The presence of protons in NaA is shown by numerous experiments. Our atomic-absorption determination of sodium also showed a deficiency of Na^+ in NaA sample [16]. And a very important conclusion that follows from the heats of adsorption of carbon dioxide is that we managed to localize the initial position of protons in the structure of NaA. The protons are located at position SIII and their concentration is $0.4H^+$ per unit cell or 40% of cations SIII, or 3.3% of all cations localized in NaA.

Thus, when NaA molecular sieve is saturated with carbon dioxide from 12 cations of sodium per u.c. 11 are involved in the adsorption interaction, only one cation in the SI position does not participate in the adsorption process. This is due to the absence of a partner cation, and for a monodentate interaction there is no possibility, since a relatively large carbon dioxide molecule cannot come close to a cation shielded by oxygen atoms to form a sufficiently strong bond, although the space around this center is sufficient to accommodate this complex.

Conclusion. Thus, when saturated, NaA zeolite contains 7 molecules of carbon dioxide per u.c. All of them are located in α-cages. β-cages do not participate in the adsorption process. Of the seven adsorbed molecules, four form a cluster at the center of which the H^+ or Na^+ cation is located (initially located at position SIII), surrounded by four molecules of carbon dioxide, whose opposite ends are closed on Na^+ cations at position SI. The three remaining carbon dioxide molecules form three bidentate complexes with cations in positions SII and SI. To form the eighth complex in NaA, there is enough space, but for a monodentate complex, the last cation in the SI position, which is not involved in adsorption, does not have enough strength to retain the carbon dioxide molecule.

The mobility of CO_2 molecules adsorbed in the NaA matrix is much higher than that of the carbon dioxide molecules in the liquid. The rate of adsorption in the formation of a monomeric adsorption complex is slowed down and reaches 4-5 hours. At higher fillings, the process is accelerated and the establishment time of adsorption equilibrium is stabilized in the interval from 1 to 1 hour 40 minutes.

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