STUDY OF WATER SORBATION OF CAA (M-34) ZEOLITIC IN ADSORBTSION MICROCALORIMETRIC DEVICE

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ABSTRACT

The differential heat, isotherm, differential entropy, and thermokinetics of carbon dioxide adsorption on CaA (M-34) zeolite were measured at 303 K. Based on the results obtained; the mechanism of water adsorption in CaA (M-34) zeolite from initial filling to saturation is described in detail. The adsorption isotherm was described using the VOM equation.

Keywords: Isotherm, adsorption heat, entropy, thermokinetics, ion-molecular complexes, CaA (M-34) zeolite, H_2O, adsorption calorimeter.

INTRODUCTION

Natural zeolites are a large group close to the composition and properties of crystalline aluminosilicates. One of the important properties of zeolites is their ability to exchange ions, in addition they are able to selectively separate and reabsorb various substances.Synthetic analogues of natural zeolites of faujazite and mordenite, which are structurally and topologically close to natural materials, are produced on an industrial scale and are widely used in practice.Such zeolites are more suitable for

research, very suitable for industrial requirements due to the large number of pores and the stability of their structure. [1-2].

The secondary structure of zeolites is defined as a cubic octahedron cut by the elements. Cuboctahedrons form LTA (A) type zeolites through four-member prisms, and FAU (X and Y) type zeolites through six-member prisms. The cations in the active centers of the zeolites are located in the center of the prism. Cupoctahedrons combine to form the zeolite type, forming large α-voids. In LTA zeolite, eight-membered rings, and in FAU-type zeolites, twelve rings combine to form voids. The main element for zeolites of the MFI (ZSM-5) type is a piece of five- and six-membered rings. Such fragments are connected in chains, which in turn form layers [3].

The industrial use of zeolites and their derivatives is growing year by year. The development of a scientific basis for the preparation and use of zeolites has become an independent field of fundamental research [4]. In practice, the most common adsorbents are CaA, NaA, and KA zeolites used to dry liquids and gases. The latter is also used to dry bioethanol [5]. Interestingly, the more hydrophobic the adsorption, the deeper the purification. At a temperature of 20 °C and a humidity of compressed air of 10%, the equilibrium adsorption of water in zeolites reaches a level of 10 mmol/zeolite for NaA and NaX [6].

RESEARCH METHODS AND AREAS

Synthetic CaA (M-34) type zeolite (Si/Al=1) was used for calorimetric study. The composition of the elemental cells of zeolite obtained for the study is CaA (M-34) - $Na_3Ca_9[(AlO_2)_{12}(SiO_2)_{12}]$ $27H_2O$. Absolute water was selected for adsorption. The determination of CaA (M-34) zeolite water adsorption was carried out in a high-vacuum adsorption microcalorimetric device [7-8].

The adsorbates were first frozen and then cleaned in a vacuum pump. The microcalorimeter allows you to measure the heat energy released over a long period of time. In the determination of adsorption measurements was carried out in a high-vacuum adsorption device and calculated by the capillary method, low absorption of adsorbates increases the accuracy of adsorption measurements.

RESULTS AND DISCUSSIONS

The amount of adsorption (N) per unit cell (e.ya) is expressed in H_2O units. Figure 1 shows the adsorption isotherm (ln) of water adsorption on CaA (M-34) zeolite at a temperature of 303 K at a relative pressure of ~ 10-6 p/p^0 (p^0 - water vapor pressure, $p^0(303K) = 4,42$ kRa). The adsorption isotherm was studied in several fragments.In the first fragment, the water adsorption isotherm of CaA (M-34) zeolite is initially ln ($p/p°$) = -16,96, r-0,000001375 millimeters of mercury, the adsorption amount starts from N=0,493 H_2O/e.ya.

The adsorption isotherm tends towards the adsorption axis in the range ln (p/p°)= -16,96 to ln (p/p°)= -13,91, where the amount of adsorption is N=3,024 H_2O/e. Here the adsorption pressure is in the range from r-0,00001375 mm.sim.ust to r-0,000029 mm. In the second fragment, the adsorption isotherm rises in the form of a steep slope until ln (p/p°)= -11,12, and the adsorption reaches N=11,37 H_2O/e.ya. In the third fragment, the isotherm again partially bends towards the adsorption axis in the range ln (p/p°)= -11,12 to ln (p/p°) = -5,43, where the amount of adsorption is N=16,13 H_2O/e.ya. is equal to.
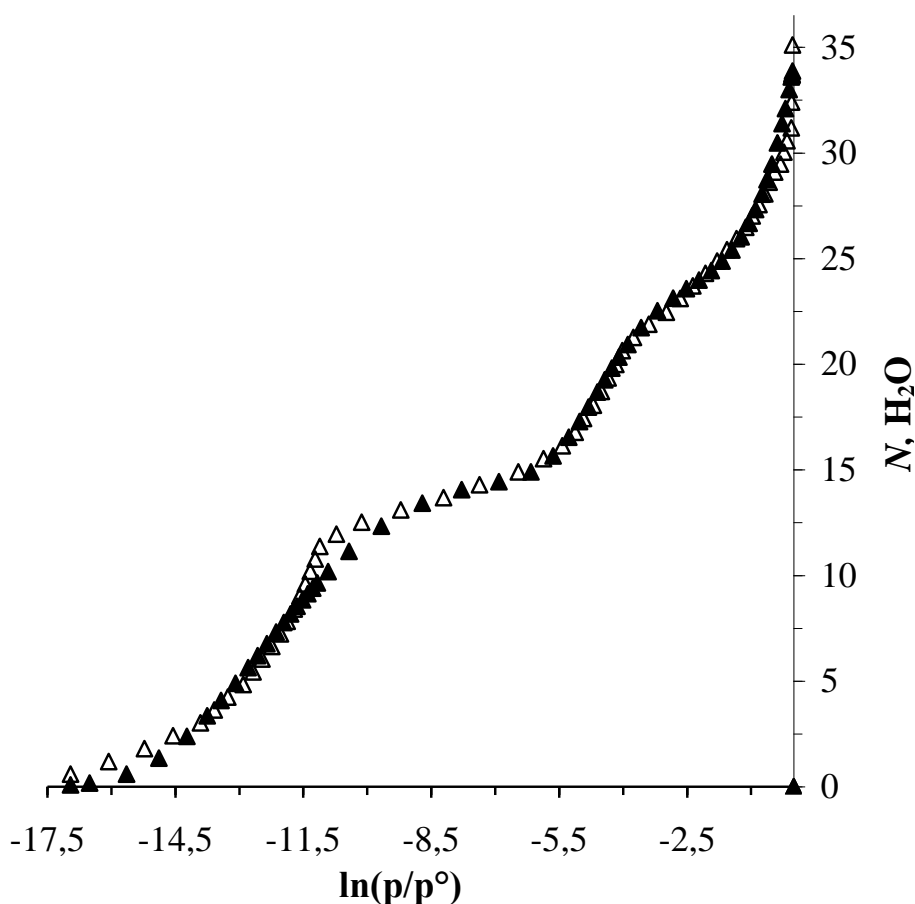

FIGURE 1. Ads-experimental value of water adsorption isotherm in CaA (M-34) zeolite at 303 K;
▲ points calculated using the equation of -*VOM*

Atmospheric pressure in these ranges is r-0,00047 mm.sim.ust. from r-0,14 mm.sim.ust.ida.

Then in the fourth fragment the isotherm marks rise from ln (p/p°) = - 5,43 to ln (p/p°) = -3,76 in a partially vertical form, and the adsorption is N=16,12 H_2O/e.ya and N=21,26 H_2O/e.ya. in the fifth fragment, the adsorption (ordinate) approaches the axis sharply, continuing in a vertical line until saturation.

This process proceeds as follows: the amount of adsorption tends towards the isotherm adsorption axis in the range N=21,26 H_2O/e.ya from N=31,189 H_2O/e.ya, and then the adsorption at N=31,189 H_2O/e.ya isotherm ln (p/p°) = -3,76, rising to ln (p/p°)= -0.06 and approaching the adsorption axis, equaling N=35,10 H_2O/e.ya and reaching the end of the process. At the end of the process, the adsorption atmospheric pressure r-30,98 mm.sim.ust. and the water saturation approaches the vapor pressure.

The adsorption of water in the molecular sieves of CaA (M-34) was redefined using the three-dimensional equation of the theory of volumetric saturation of micropores [7,8].

N=14.765exp[A/32,42)^6]+8,434exp[A/12,18)^5]+11,048exp[A/2,28)^1],

Where: N-adsorption in micropores, (H_2O)/e.ya, A=RTln (P$^°$/P-1 H_2O/e.ya work done to transfer steam from the surface (P$^°$ pressure) to the equilibrium gas phase (R pressure) .

Figure 2 shows the differential heat (Q_d) of water adsorption on CaA (M-34) zeolite at a temperature of 303 K. Long lines are the heat of condensation of water below a temperature of 303 K (ΔHv = 43,5 kJ/mol).

In this zeolite, the adsorption heat is in the form of a wavy step. Water adsorption on CaA (M-34) zeolite (starting at N=0.29 H_2O/e.ya.) differential heat starts from ~ 89,35 kJ/mol, the differential heat drops sharply and Q_d-78,22 kJ/mol. goods. Due to the small size of the water molecules, they penetrate directly into the zeolite cavities and initially have a higher asdorption heat due to the contact of the silicon with the oxygen atoms that bind the aluminum. Here again, the same phenomenon is observed, until the water molecules are distributed to the cations in the zeolite micropores, they remain in a mobile state.

Then, when the adsorption reaches N=0,89 H_2O/e.ya, it gradually decreases to Q_d=78,22 kJ/mol. Then N=0,89 H_2O/e.ya N=3,328 H_2O/e.ya forms the first small step of high energy in the adsorption range (Q_d=78,22 to 76,72 kJ/mol).

Adsorption forms a second small step in the range N=3,238 to 5,74 H_2O/e.ya (Q_d=76,72 to 75,46 kJ/mol). These two step intervals are 2,438 H_2O/e.ya and 2,412 H_2O/e.ya. The adsorption heat of the steps decreases in a wavy manner from 75,46 kJ/mol to 74,26 kJ/mol. Two points are observed in the range of the third N=5,74 to 8,716 and the fourth from 8,716 to 12,238 H_2O/e.ya.
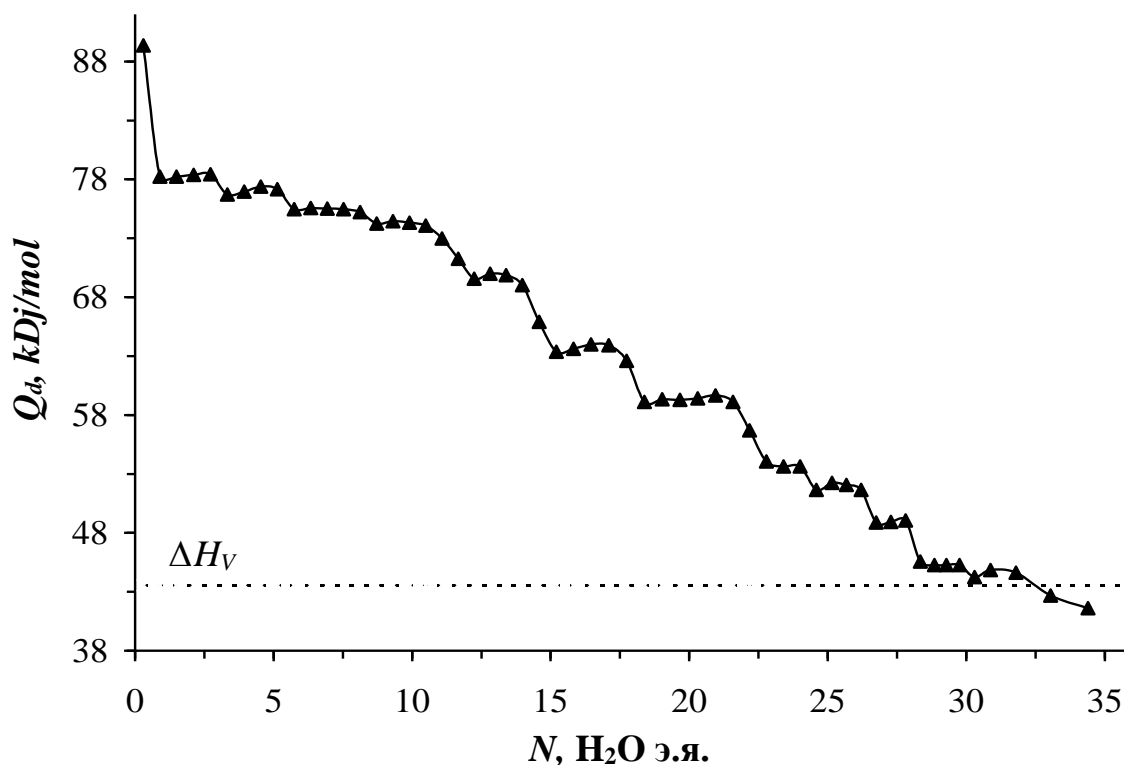
FIGURE 2. Differential heat of water adsorption on CaA (M-34) zeolite at 303K temperature.

Horizontal ring line condensing heat

At these stages, the adsorption temperatures decrease from 75,46 kJ/mol to 74,26 kJ/mol in the third stage and from 74,26 kJ/mol to 69,57 kJ/mol in the fourth stage. The third and fourth step intervals are 2,976 H_2O/e.ya and 3,522 H_2O/e.ya.

The adsorption amounts of the four small steps above make up the two large steps. In large stages, the adsorption heat decreased from 78,22 kJ/mol to 69,57 kJ/mol.

The difference between the four small steps above averages 8,65 kJ/mol. This means that water molecules are adsorbed on the unwanted mineral adsorbents in the zeolite. This indicates that the mineral adsorbents are mainly located in the S_{II} position in the zeolite superpore, which can be explained by the gradual gradual decrease in the adsorption heat.

When the adsorption reaches 12,238 H_2O/e.ya, a gradual sharp decrease in differential heat is observed, and the initial differential heat decreases from 69,57 kJ/mol to 63,37 kJ/mol. After that, the adsorption heat decreases from 63,37 kJ/mol to 59,10 kJ/mol in small steps.

The amount of adsorption decreases in the range of 59,3 kJ/mol to 54,05 kJ/mol in the range of 18,38 H_2O/e.ya to 22,78 H_2O/e.ya. The differential heat of adsorption

of water molecules on zeolite ranges from 69,57 kJ/mol to an average of 15 kJ/mol in the range of 54,05 kJ/mol.

This indicates adsorption on Na^+ cations located in the zeolite matrices, and the adsorption values range from 12,238 H_2O/e.ya to 22,78 H_2O/e.ya.

At this stage, 10,54 H_2O/e.ya water molecules are adsorbed on Na^+ cations. In this case $(H_2O)_nNa^+$ multidimensional complexes are formed. Adsorption from 54,05 kJ/mol to 45,58 kJ/mol In the form of the first four small steps, a differential heat drop across three steps is observed.

Here, too, the average adsorption differential heat goes with a difference of ~ 8,47 kJ/mol. In this three-step decrease, the adsorption and differential heat proceed as follows.The adsorb in the first small step is in the range of N=22,78 H_2O/e.ya to 24,59 H_2O/e.ya, the differential heat is from 54,05 kJ/mol to 51,65 kJ/mol, the second small step heat is 51,65 kJ./mol to 48,88 kJ/mol, N=24,59 H_2O/e.ya or 26,746 H_2O/e.ya.

In the third small step, it ranges from 48,88 kJ/mol to 45,58 kJ/mol. At the end of the process, the heat is divided into two fragments and the final section lasts from N=30,30 H_2O/e.ya to 34,39 H_2O/e.ya. In this case, the heat of adsorption decreases from 44,25 kJ/mol to 41,61 kJ/mol and is equal to the heat of condensation.

CaA (M-34) In the structure of zeolite there are 3 active centers, adsorption cavities, to which adsorbates are adsorbed. Active centers are based on alkaline and alkaline earth metals. In the first space, the Ca^{2+} cations are located at the center of the S_I six-membered oxygen rings that make up the sodality. In the second cavity, the Ca^{2+} and Na^+ cations are located slightly inside the plane of the S_{II} eight-membered oxygen rings, and finally in the third cavity, the Ca^{2+} cation S_{III} is located inside the α-cavity opposite the four-membered oxygen ring. It can be seen that the S_{III} and S_{II} cavities form the bulk of the adsorption as they are located within the supercosm. Because the cations in the S_I space are surrounded by cations of six strong protective oxygen atoms.
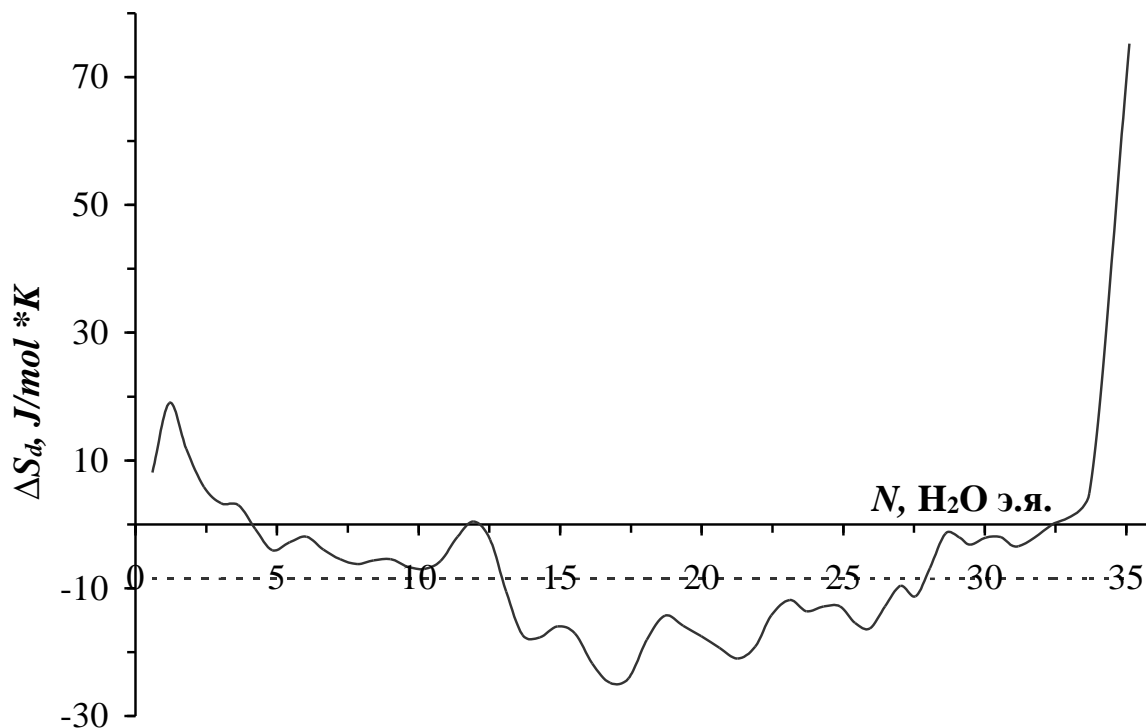
FIGURE 3. The differential entropy of water adsorption on CaA (M-34) zeolite is given.

CaA (M-34) in zeolite has a total of 34,39 H_2O e.ya. water molecules are adsorbed. of these, ~27,5 H_2O e.ya. in the S_{II} space, ~6 H_2O e.ya. in the S_{III} space. In the S_I space, it is 0,89 e.ya..

The formula of the Gibbs-Helmholtz equation was used to calculate the differential entropy using the differential heat and isothermal output of water adsorption on CaA (M-34) zeolite [9].

$$\Delta S_d = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_d - \lambda) + A}{T}$$

λ-thermal condensation, ΔH and ΔG-enthalpy and free energy change,

T-temperature, Q_d - average differential heat.

Figure 3 shows the differential entropy of water adsorption on CaA (M-34) zeolite.The differential entropy of adsorption initially starts at 8,09 J/mol *K. Then it rises to 19,04 J/mol *K. From 19,04 J/mol *K the entropy lines decrease sharply to -4,03 J/mol *K.

In this process, the water molecules are initially partially adsorbed on the metal cations in the six rings formed by the aluminum-silicon atoms that connect the sodalite cavities to form the zeolite, and then slowly pass into the α-cavity.

After falling to -4,03 J/mol *K, the adsorption entropy gradually decreases in a wavy form. The lowest value of entropy is -24,48 J/mol *K, and the adsorption is 16,76 H_2O/e.ya. After -24,48 J/mol *K, the entropy rises again in a wavy form, the adsorption is in the unexcited state of water molecules up to~ 7 H_2O/e.ya.

This is adsorbed into the S_{II} cavities of the zeolite matrix while forming small wavy line views. Due to the large number of cations in these cavities, the energy distribution in the migration and adsorption of cations is orderly and strongly adsorbed. The average integral entropy is -8,31 J/mol *K.

The equilibrium time of water adsorption on CaA (M-34) zeolite is initially 28.18 hours. The adsorption equilibrium time initially takes longer to distribute to the cations in the adsorbent (zeolite) due to the small number of adsorbate (water) molecules, i.e., until the adsorption equilibrium is decided. After that, the equilibrium time gradually decreases along the slow wavy line. The differential heat of water adsorption on CaA (M-34) zeolite goes in a stepwise manner. This condition can also be observed during equilibrium. We can explain the longer time it takes for the adsorption equilibrium to be determined by the adsorption process on the superpoints. This indicates that the adsorption takes place in the zeolite super void. Adsorption 27,54 H_2O/e.ya. after which the adsorption equilibrium time drops sharply.

CaA (M-34) the heat of adsorption of water in zeolites has a stepwise appearance, where all the steps form one- and multidimensional adsorption complexes $(H_2O)_n/Ca^+$ and $(H_2O)_n/Na^+$ in the matrix of CaA (M-34) zeolite. The adsorption isotherm is represented by the three-term VOM equation.
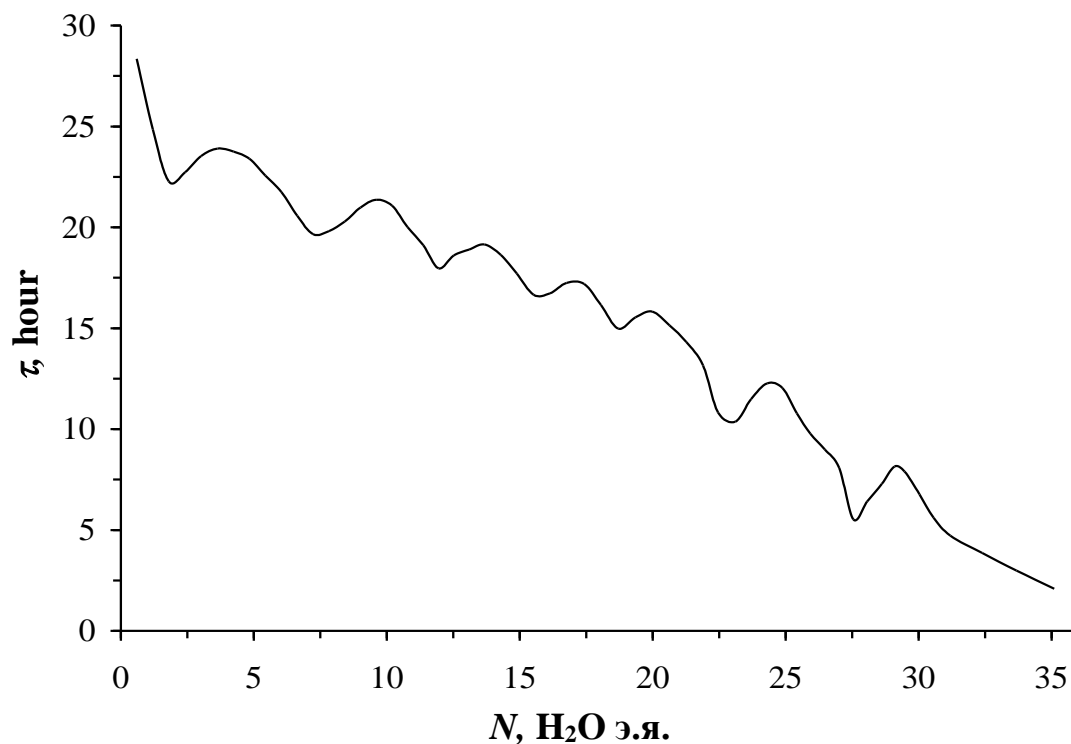
Figure 4. Water adsorption equilibrium time in CaA (M-34)

zeolite.

The final sorption volume of CaA (M-34) zeolite is ~34,4 H_2O/e.ya per elementary cell water molecule. The average integral entropy of the differential entropy of adsorption is -8,31 J/mol *K. Water molecules are strongly adsorbed in the solid state in zeolite superpower

REFERENCES:

1. A.A. Kubasov Zeolites - boiling stones / A.A. Kubasov // Soros Educational Journal. - 1988. - T. 7. - S. 70–76.

2. Breck D. Zeolite molecular sieves / D. Breck, trans. from English A.L. Klyachko, I. V. Mishin, V.I. Yakerson - Moscow: Peace. 1976 .-- 781 s.

3. Hölderich W.F. Zeolites and related materials in organic syntheses. Brönsted and Lewis Catalysis / W.F. Hölderich, H. van Bekkum // Studies in Surface Science and Catalysis. — 2001. — Vol. 137. — P. 821–910

4. Li X. One-step synthesis of H–b zeolite-enwrapped Co/Al2O3 Fischer–Tropsch catalyst with high spatial selectivity / X. Li, J. He, M. Meng, Y. Yoneyama, N. Tsubaki // Journal of Catalysis. — 2009. — Vol. 265. — P. 26–34. 197

5. Sircar S. Gas separation of zeolites. Handbook of zeolite science and technology. Chapter 22 / S. Sircar, A.L. Myers, ed. By S.M. Auerbach, K.A. Carrado, P.A. Dutta — New York: Dekker. 2003. — P. 1063–1104.

6. Rakhmukov B.Kh. Adsorption on a microporous adsorbent along the liquid - vapor equilibrium line (NaX zeolite - water) / B.Kh. Rakhmukov, I.I. Seliverstova, V.V. Serpinsky, A.A. Fomkin // News of the Academy of Sciences of the USSR. Chemical series. - 1979. - T. 28. - No. 11. - P. 2419–2422.

7. B.F. Mentzen, G.U. Rakhmatkariev. Host/Guest interactions in zeolitic nanostructure MFI type materials: Complementarily of X-ray Powder Diffraction, NMR spectroscopy, Adsorption calorimetry and Computer Simulations // Узб. хим. журнал. 2007, №6, С. 10-31.

8. U. Rakhmatkariev. Mechanism of Adsorption of Water Vapor by Muscovite: A Model Based on Adsorption Calorimetry // Clays and Clay Minerals, 2006 vol. 54. pp. 423-430.

9. Rakhmatkarieva F.G., Rakhmatkariev G.U. Ion-molecular complexes in nanostructured zeolites NaA and NaA (NaBO2) // Uzbek chemical journal, 2016, No. 4. - P.3-9.