Adsorption Thermodynamics in Zeolites of ZSM-5 Type

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ABSTRACT. Differential heat, isotherm, thermokinetics and entropy of water, carbon dioxide, n.heptane adsorption on ZSM-5 zeolites were studied using adsorption-calorimetric method at 303 K. The mechanism of adsorption of the studied molecules and the type and number of formed ion-molecular complexes were determined. Thermokinetics of adsorption in the zeolite structure and the discovery of the migration laws of exchange cations, the adsorption energy of gases and vapors in a flawless zeolite. The adsorption isotherm is described by the two- and three-term mathematical equations of VOM from the beginning to the saturation.

KEYWORDS: Isotherm, adsorption heat, entropy, thermokinetics, ion-molecular complexes, ZSM-5 zeolite, carbon dioxide, heptane, adsorption calorimeter

I. INTRODUCTION

Today, in a number of developed countries, a lot of research has been done on the extraction of zeolites used in the purification and drying of natural gas, petroleum products from additives. In particular, many scientific and practical innovations are being achieved in the production of zeolites, their adsorption and active catalytic properties, the structure of the pores, the number, strength and nature of the active centers based on the results obtained by adsorption microcalorimetric device.

In the development of technology for obtaining adsorbents with high adsorption properties, it is necessary to substantiate appropriate scientific solutions in a number of areas, including the identification of nanostructures of adsorbents and analysis of adsorption processes between them; study of the chemical crystal structure of adsorbents using non-polar n-heptane, quadrapol carbon IV oxide and aromatic benzene, xylene molecules; Determination of the conformation and adsorption thermodynamics of ion-molecular complexes formed during adsorption is a topical issue. ZSM-5 type zeolites are used as a very effective catalyst in the production of high-octane fuel products from petroleum products. In addition, the cationic form of ZSM-5 zeolites is selected as a catalyst in the production of high-octane gasoline from non-petroleum products. Therefore, there is a growing interest in studying the adsorption and catalytic properties of this type of zeolites. At the same time, small-sized organic molecules ZSM-5 zeolite increase the amount of branched-chain hydrocarbons due to the interconnection at the intersections of straight and zigzag channels, resulting in a high octane number in gasoline. In particular, the molecules adsorbed for the purpose of the probe help to explain the reason for the manifestation of such properties as hydrophobic-hydrophilic bifunctionality in zeolites [1; P.5-6.].

The main focus is on the study of the adsorption of various substances in zeolites of the type ZSM-5. It can be seen that the dependence on cations present in the adsorption structure in zeolites is large. Since the distance between the adsorption centers is very large, zeolite is very suitable for model study of adsorption capabilities. [2; P. 10-33.].

II. SIGNIFICANCE OF THE SYSTEM

In article differential heat, isotherm, thermokinetics and entropy of water, carbon dioxide, heptane adsorption on ZSM-5 zeolites were studied using adsorption-calorimetric method at 303 K. 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

In view of the above, we aimed to study the interaction of water, carbon dioxide, n-heptane molecules with the active centers and channels of ZSM-5 zeolite, which is synthesized almost flawlessly. ZSM-5 zeolite is synthesized as a result of processing of high-silicon minerals in fluorine medium. As a result of processing the active centers of the synthesized zeolite analogues by means of ammonium salts, a catalytic adsorbent with a high adsorption activity corresponding to each elemental cell is formed. The experiments were performed on an adsorption-microcalorimetric device with high vacuum and sensitivity. Before the start of the experiment, the sample is heated for 10 h, at 723K, under a vacuum of 10–4 Pa in the pumped state. The experiment was carried out using an adsorption-calorimetric device and method [3; P.39-55.]. Adsorption heat and isotherm values were calculated at 303 K.

IV. EXPERIMENTAL RESULTS

Differential heat of adsorption and isothermal values of water adsorption on ZSM-5 zeolite at 3030K were calculated [4; P.423-430.]. From these values the differential molar entropy of adsorption is derived. The isothermal value of adsorption was compared using the equation of the theory of micro-pores saturation (VOM). They consist of 6 steps in total. At each stage, a stoichiometric match between the active centers of zeolite and water vapor can be seen. As a result of chemical analysis, it was determined that the cation in the zeolite corresponds to each elemental cell, i.e. $(NH^+4AlO_2)_{1,35}(SiO_2)_{94,65}$; $(H^+AlO_2)_{3,25}(SiO_2)_{92,75}$; $(Li^+AlO_2)_{4,36}(SiO_2)_{91,64}$; $(K^+AlO_2)_{3,6}(SiO_2)_{92,4}$; $(Na^+AlO_2)_{3,4}(SiO_2)_{92,6}$ is the general formula for each elementary cell. This figure indicates that the water adsorption on the ammonium cation is greater if it is comparable within the cations. This means that a total of 24.6 water molecules are adsorbed into the elemental cell, corresponding to an average of 18,2 adsorbents per cation, and $(H_2O)n/(NH^+_4)$ n=18,2 complex clusters are formed. This is mainly explained by the validity of the ammonium cation.

As mentioned above, in Figure 1, there are a total of 6 steps in the adsorption heat graph, in the first step, water molecules with an active center are 100% adsorbed to form tetraaquacomplexes. As the activity of the cations in the active center increases, the adsorption rate in them also increases. For example, ZSM-5 zeolite with an active center of Li$^+$ averaged 32H$_2$O/e.ya. 34H$_2$O/e.ya. in NaZSM-5 zeolite, 17,33H$_2$O/e.ya. in HZSM-5 zeolite, 36H$_2$O/e.ya. H$_2$O/e.ya. adsorbed. The degree of adsorption is also related to the hydrophilic property of the zeolite. MFI-type zeolites have a higher hydrophilicity level than most synthetic zeolites, i.e., 1,4–2,4.
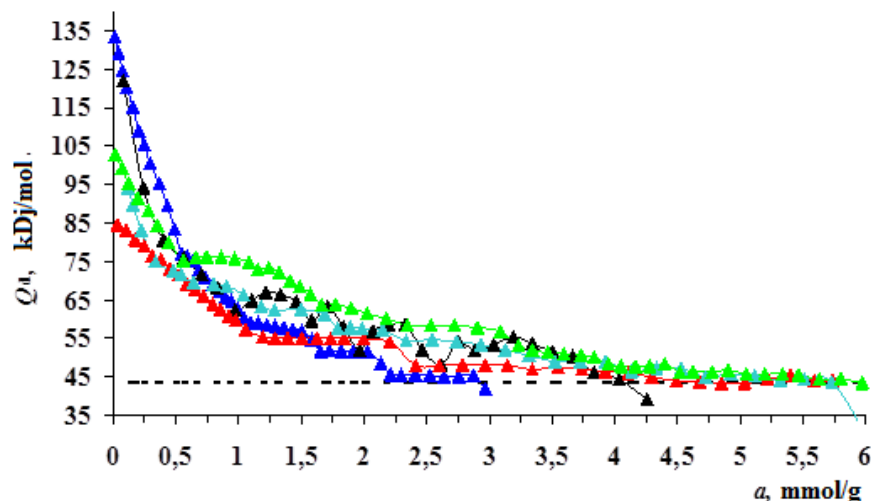
Figure 1 shows the differential heat values Qd of water adsorption in ZSM-5 zeolites with cation 30 ▲-Na$^+$, ▲-Li$^+$, ▲-NH$_4$$^+$, ▲-H$^+$, ▲-K$^+$ at 303 K. Barcodes Condensation value of water at 303 K.

In ZSM-5 zeolite, a slight slowing of the isothermal point in the initial part interferes with the pressure of the secondary adsorbate to the secondary adsorbate due to the interaction of the active centers of the zeolite with hydroxyl groups in water molecules of different sizes and structures, such as ammonium, hydrogen, lithium, sodium and potassium. . This indicates the tendency of the centers to form an aquacomplex as a result of the adsorption of zeolite

with a large number of cations in the initial adsorption due to the presence of strong centers of zeolite at the intersection of the forward and reverse channels. In addition, a sharp rise in the isotherm, i.e., these curves, is reflected in the formation of adsorbate-adsorbate systems in the zeolite-containing nanopores and their interaction.

The adsorption isotherm of water is well described by the equation of the theory of volume saturation of micropores (VOM) [5; pp. 15.].

The basic equation of VOM for the adsorption processes under study is written as follows:

$$a = a_0 \cdot \exp\{-[A/E]^n\} \qquad (1)$$

by this formula is calculated as follows:

where a is the adsorption amount in mol/g; a_0 is the detected adsorption in mol/g, $A = PTln(P/P^o)$ is the amount of work done by 1 mole of gas (kJ/mol), E is the characteristic energy of the adsorbent (kJ/mol); is a parameter related to the structure of the porous area of the n-adsorbent. The adsorption isotherm of water in the adsorbent NH_4 ZSM-5 is characterized by the three-dimensional equation of VOM.

$$a = 9{,}82 \exp[-(A/16{,}94)^4] + 2{,}165 \exp[-(A/4{,}36)^2] + 1{,}772 \exp[-(A/1{,}74)^1]$$

The adsorption isotherm of water in the adsorbent $H_{3,25}ZSM$-5 is characterized by the three-dimensional equation of VOM.

$$a = 1{,}48 \cdot e^{-\left(\frac{A}{14{,}18}\right)^2} + 0{,}74 \cdot e^{-\left(\frac{A}{5{,}26}\right)^2} + 0{,}78 \cdot e^{-\left(\frac{A}{0{,}99}\right)^1}$$

$Li_{4,36}ZSM$-5 the adsorption isotherm of water in the adsorbent is characterized by the three-dimensional equation of VOM.

$$a = a_{01} \exp[-(A/E_{01})^{n_1}] + a_{02} \exp[-(A/E_{02})^{n_2}] + a_{03} \exp[-(A/E_{03})^{n_3}]$$

These values are: $a_{01} = 0{,}851$ mol/g, $E_{01} = 18.22$ kDj/mol i $n_1 = 2$; for the second member $a_{02} = 1{,}63$ mol/g, $E_{02} = 6{,}3$ kDj/mol and n2 = 2; the third member values are $a_{03} = 1{,}748$ mol/g, $E_{02} = 2{,}094$ kDj/mol, and n3=2.

The molar differential entropy of water adsorption increases from -220 J/mol·K_0 J/mol • K, i.e. from a very small minimum to a sharply higher value. As mentioned above, the primary water molecules adsorbed into zeolite channels are ionically-molecularly strongly bound to the active centers of cations. The molar differential entropy of water adsorption isotherms and the adsorption differential heat according to the Gibbs-Helmholtz equation are calculated on the basis of the following equation:

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

where l is the heat of condensation, ΔH and ΔG are the enthalpies and changes in free energy during adsorption in the standard state.

The mean integral values of entropy are correspondingly much smaller than the liquid value of 0-(-50) J/mol • K, respectively. Thus, the differential and integral entropy indicates the state of motion of each adsorbed water vapor in the zeolite. Therefore, the entropy curve is below the liquid water entropy. This value indicates that the entropy value changes from liquid entropy to vapor entropy as the saturation rate increases.

In ZSM-5 zeolite, the equilibrium of adsorption at the intersection of zigzag channels and straight channels of water molecules is very slow, then accelerates. At the same time, the equilibrium time is reduced from almost 12-18 hours to 4-5 hours. In the initial adsorption, it takes a long time for the water molecules to bond firmly with the active sites. In the later stages, the time between cation (3-4 hours) and adsorbate-adsorbate bonds between water molecules is less (1-2 hours). The decrease in the adsorption equilibrium time to ~ 10 minutes in the final stage is explained by the fact that at this adsorption volume they remain in the vapor state as a result of the interaction of fully adsorbed molecules with non-adsorbed molecules.

The study of the adsorption energy of gases is crucial for understanding the interesting data and practically complex processes that occur in the adsorption of adsorbents on various adsorbents, as well as for studying, systematizing and standardizing the most important thermodynamic properties of heterogeneous systems.

The differential heat of carbon (IV) oxide adsorption on ZSM-5 zeolite was measured using a high-precision vacuum adsorption calorimetric device. The ZSM-5 zeolite sample mainly has a Si/Al=23 <x ratio. The adsorption isotherm was measured in a volumetric manner. The amount of SO_2 adsorption on ZSM-5 zeolite was expressed in mol/g, and the isotherm index was expressed in ln (P/P^0). From the adsorption isotherm lines of SO_2 molecules to

ZSM-5 zeolites, it can be seen that initially a gradual increase to 0,75 mol/g is observed, followed by a straight line increase to ~1,4 mol/g. At small saturations we can see that the adsorption isotherm index is -16,20 ln (P/P^0). The gradual increase in adsorption isotherms to 0,75 mol/g can be explained by the penetration of carbon (IV) oxide molecules into the zeolite zigzag channels and the subsequent increase along the straight line by the saturation of the zeolite into the straight channels. When the adsorption amount is a-1,41 mol/g, the pressure is R = 609 mm.sim.ust. The theory of volumetric saturation of SO2 adsorption isotherm to NH₄ZSM-5 was described using the two-term equation.

$$a=10,12\exp[(A/22,09)^2]+11,92\exp[(A/12,19)^5]$$

Adsorption of carbon monoxide on ZSM-5 zeolite Qd differential heat has a curvilinear phase character. Figure 2 shows the differential heat Qd of CO_2 adsorption on ZSM-5 at 303 K.

The heat of condensation of carbon (IV) -oxide at 303 K (ΔHv=27 kJ/mol) in the pulister straight lines is given. The interaction of CO_2 with cations is mainly accompanied by the formation of binary complexes during adsorption. In CO_2 adsorption, the adsorption does not start at high heat at the beginning, i.e. ~ 60 - 70 kJ/mol.

The differential molar entropy of carbon (IV) oxide adsorption on ZSM-5 zeolite at 303 K was calculated according to the Gibbs-Helmholtz equation using isotherms and differential adsorption temperatures.
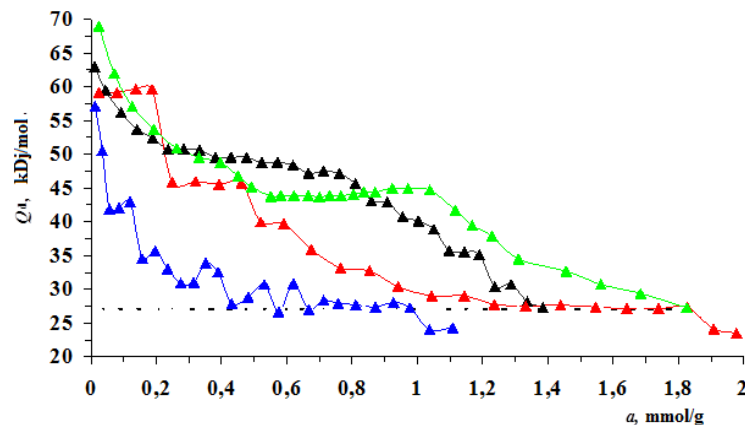
Figure 2 shows the values of the differential heat of adsorption of SO_2 Qd in ZSM-5 zeolites with cation ▲-Li⁺, ▲-NH₄⁺, ▲-H⁺, ▲-K⁺ at 303 K. Barcode Condensation value of SO_2 at 303 K.

During the initial SO_2 adsorption, entropy is observed to be in the liquid state motion. In general, carbon (IV) oxide molecules assumed liquid state entropy values at the beginning of adsorption and until the end of adsorption. The minimum value of the initial adsorption entropy reaches -54.78 J/mol • K in ammonium cation zeolites. The average molar integral entropy of adsorption is 15,24 J/mol • K and much lower than that of liquid carbon (IV) oxide, indicating the localization of CO_2 molecules in the zeolite matrix.

Based on the data obtained, the adsorption of the CO_2 molecule in ZSM-5 zeolites of different cations takes place in two sections. In the first section, CO_2 molecules form monocomplexes coordinated around cations. In the second section, it can be concluded that it is adsorbed with the formation of dicomplexes.

In the adsorption of carbon (IV) oxide molecules on the ZSM-5 zeolite, the initial equilibrium time is higher at NH4ZSM-5, i.e., the equilibrium is reached in 5,8 hours. In other ZSM-5 zeolites, this figure is 1-2 hours. In this case, the amount of adsorption is 0,01mol/g. In this case, the equilibrium time for the distribution of carbon (IV) oxide molecules into the zeolite channels lasts longer. It is then observed that the equilibrium time drops sharply from an hour to a few minutes.

There is a growing interest in studying the structure of zeolites using molecules adsorbed on their surface and interior parts. Their adsorption properties can be determined by ion exchange as well as changes in Si / Al ratios. For selective adsorption of zeolites, for example for their separation of hydrocarbon mixtures, their steric and energy properties are used. Catalytic properties are clearly demonstrated in ammonium forms of ZSM-5 zeolite. They are highly efficient catalysts for a number of processes in the petrochemical and oil refining industries [6; P.74]. In particular, they are most effective in the processes of isomerization, deparaffinization, cracking and aromatization in the oil refining industry, mainly in the liquid periods. Normal alkanes (n-alkanes) are adsorbents that are adsorbed with high energy and fill the entire sorption void of ZSM-5 zeolites, unlike benzene, for example, which fills only 70% of

the ZSM-5 porosity void. Therefore, n-alkanes can be used to characterize zeolite channels, to determine the sorption volume, which is an indicator of adsorbent quality.

In this study (Fig. 3), adsorption (a) adsorption of n-heptane on ZSM-5 zeolite at a temperature of 303 K was studied. The differential heat of adsorption (Qd) was measured using the high-precision adsorption calorimetric device described above. The adsorption isotherm of n-heptane at 303 K in ZSM-5 zeolite was studied. The equilibrium relative pressure at n-heptane adsorption initial saturation to this zeolite is $P/P_o = 2,26 \cdot 10^{-4}$. The adsorption isotherm grows linearly at a certain angle to $\alpha = 1$ mol/g, indicating sorption of cations in the elementary cell, then bends toward the adsorption axis and increases linearly again to 1,5–2 mol/g and then approaches the ordinate axis.
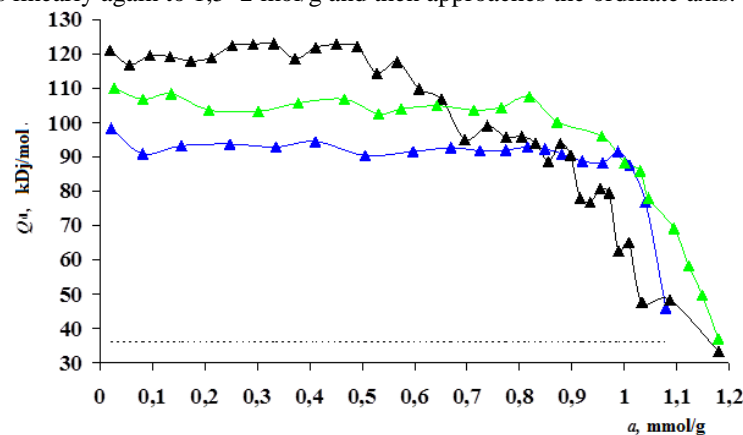

Figure 3 shows the differential heat values Qd of n-heptane adsorption on ▲-NH$_4^+$, ▲-H$^+$, ▲-K$^+$ + ZSM-5 zeolites at 303 K. Barcode Condensation value of n-heptane at 303 K.

Assuming that the density of n-heptane adsorbed on zeolite is a normal liquid and the volume occupied by the n-heptane molecule at saturation temperature (303 K) for the experiment, the contribution of the induction component to the total energy is ~ 0.182 kJ/mol. The adsorption isotherm of n-heptane in ZSM-5 is represented by the complete VOM equation. the state of n-heptane in the zeolite matrix is solid. This means that the adsorption in the intersecting areas and zigzag channels is very slow and the adsorbent consists of an amorphous phase. [7; P. 39-50]. The adsorption isotherm of n-heptane in ZSM-5 zeolite is represented by the two- and three-dimensional VOM equations.

The adsorption heat of N-heptane in silica is ~ 80 kJ/mol at the initial saturation of pure silica analog ZSM-5, which is less than the adsorption heat of NZSM-5 zeolite NN4ZSM-5 zeolite by ~ 26 kJ/mol. detected. Given that the size of the ammonium ion is large, the contribution of the dispersion organizer is negligible. The contribution of induction constituents in cationic centers to the total adsorption energy is mainly ~ 20 kJ/mol. In this case, the constant flow of heat can be explained by the orderly flow of adsorption in the zeolite channels. This is due to the interaction of adsorbate-adsorbate molecules and the interaction between the absorbed molecules of hydrocarbons. an increase in the differential heat of adsorption is observed at the adsorption of relatively small molecules of n-hydrocarbons. Thus, from the beginning of the adsorption process, n-heptane molecules follow the mechanism of "adsorbate-adsorbate" effect, are densely packed in zeolite channels, at the end of adsorption the structure is partially changed, and the molecules are located in energetically favorable places and fill all pores. On the differential heat curve, in the final stage, extremums are observed, with a minimum adsorption heat of 98,60 kJ/mol and a maximum of 102,20 kJ/mol. At the end of the process, a sharp decrease in the adsorption differential heat n-heptane to the condensation heat line is observed.

The Gibbs-Helmholtz equation was used to calculate the differential entropy of n-heptane adsorption on NN4ZSM-5 zeolite. The basis of this equation is the differential heat and isotherm values. Saturation of zeolite channels with n-heptane occurs in the form of a differential entropy curve in all parts.

Entropy -140 - 150 J/mol • K lasts up to 1 mol/g and entropy up to 1,1 mol/g is below the mean integral entropy line. The differential entropy of adsorption has a very low negative value. This indicates that the n-heptane molecules in the zeolite channels are in an inert state and are very strongly adsorbed. This means that the entropy of n-heptane is in the liquid state. The theoretical ideas put forward above, that is, at the beginning of the process, the heptane molecules come together at the intersection of straight and zigzag channels where the cations are located. However, the length of the intersection channel is 0,54 nm and the length of the n-heptane molecule is 1,15 nm, which means that part of the n-heptane exits into a straight or zigzag channel. The length of the straight channel and the

intersection area is 0.99 nm, and the length of the zigzag channel and the intersection area is 1,21 nm. Hence, the most optimal concentration localization site of the adsorbate is the second pair of segments.

During the adsorption of the N-heptane molecule into zigzag channels and intersecting areas, the adsorption equilibrium is slow. In this case, the adsorption equilibrium time decreases from 8-12 hours to ~ 2-3 hours. The adsorption process is mainly manifested in zigzag channels and intersecting areas. The equilibrium time of adsorption in straight channels is completed in ~ 1-2 hours. In the final stages, the adsorption equilibrium time is reduced to a few minutes.

V. CONCLUSION AND FUTURE WORK

Data on the isotherms and thermodynamic properties (ΔH, ΔG and ΔS) of N_2O, CO_2, and n-heptanes in ZSM-5 zeolite are given in detail, the adsorption heat of the studied systems with low saturation is gradual, stepwise and adsorption properties are determined. Molecular mechanisms of adsorption of N_2O, CO_2, n-heptans on ZSM-5 zeolite, interrelationships between adsorption-energy characteristics were determined. Due to the ammonium cation in the active centers, the adsorption of water in the NH_4ZSM-5 zeolite was almost 2,5 times higher than in the cationless form (silicalite 9,8 H_2O/e.ya.). The differential heat of adsorption of ZSM-5 zeolite carbon monoxide was in the form of a curvilinear step, and in all experiments it was found that adsorption took place in 2 sections. N-heptane molecules are immobile in the zeolite channels, motionless, i.e., in the solid state entropy. Adsorption in intersecting areas and zigzag channels has been shown to proceed very slowly. In ZSM-5 zeolite it was found that the migration of slightly larger cations such as Na^+, K^+, NH_4^+ from the intersection of straight and zigzag channels to straight channels is not observed.

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