

Adsorption Energetics In Zsm-5 Zeolites

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Abstract: This article highlights the study on the determination of differential heat, isotherm, thermokinetics and entropy of water, carbon dioxide, normal heptane, benzene, methanol, ethanol adsorption on ZSM-5 zeolites, using adsorption-calorimetric method at a temperature of 303 K. The type and number of formed ion-molecular complexes, as well, the mechanism of adsorption of the studied molecules were ascertained. In the zeolite structure, thermokinetics of adsorption and the discovery of the migration laws of exchange cations are considered the adsorption energy of gases and vapors in a flawless zeolite. From the beginning to the saturation, the adsorption isotherm was described by the two- and three-term mathematical equations of STMP.

Keywords: Isotherm, adsorption heat, entropy, thermokinetics, ion-molecular complexes, ZSM-5 zeolite, carbon dioxide, n.heptane, benzene, methanol, ethanol adsorption calorimeter

1. INTRODUCTION

Nowadays, several various scientific researches have been conducted in a number of developed countries on the production of zeolites used in the purification and drying of natural gas and petroleum products from additives. In particular, many scientific and practical innovations have been achieved on the basis of the results obtained by adsorption microcalorimetric device in determining the production of zeolites, their adsorption and active catalytic properties, the structure of pores, the number, strength and nature of active centers.

In the technology production 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 benzol; study of the chemical crystal structure of adsorbents using xylene molecules; conformation of ion-molecular complexes formed during adsorption and determination of adsorption thermodynamics are topical issues.

ZSM-5 zeolites are being used as a very effective catalyst in the production of high-octane fuel products from petroleum products. Moreover, the cationic form of ZSM-5 zeolites is selected as a catalyst in the production of high-octane benzene from non-petroleum products. Therefore, there is a growing interest in studying the adsorption and catalytic properties of this type of zeolites. There, as a result of the interconnection among small-sized organic molecules in the intersection of straight and zigzag channels of ZSM-5 zeolite, the amount of branched-chain hydrocarbons increases, resulting in a high octane number in benzene. In particular, the molecules adsorbed for the purpose of the probe assess to explain the reason for the manifestation of such properties as hydrophobic-hydrophilic bifunctionality in zeolites [1].

In 1965, Sokoni Mobile Oil (the first U.S.A company to carry out the synthesis) discovered a large family of silicon-containing zeolites with a unique structure of the ZSM-5 type ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 5\div 100$ and more) [2; p.74.]. Their structure is the same and has no natural analogues.

Zeolites are aluminosilicates with this carcass structure. One of the unique properties of aluminosilicates is the specific location of Al in their structure. In zeolites, as in other aluminosilicates, Al, like Si, is in a state of tetrahedral coordination over oxygen and isomorphically replaced by silicon in the common silicon oxygen carcass.

It is clear that the energy of an adsorption agent consists of the sum of the specific energies (electrostatic polarization, dipole and quadrupole interactions) and nonspecific (dispersed) interactions. In the state of water adsorption, specific interactions predominate in zeolites. Adsorption of water vapor is energetically beneficial only in the presence of hydrophilic groups (cations, OH-groups, Lewis centers) in zeolites. Hydrocarbons are adsorbed nonspecifically and therefore the presence of strong adsorption centers is not necessary for such adsorption.

The basic attention is directed towards the study of the adsorption of various substances in zeolites ZSM-5. Because of the fact that the distance between the adsorption centers is very large, zeolite is very suitable for model study of adsorption capacity. [2].

2. THE OBJECT AND METHODS OF RESEARCH

Considering abovementioned facts, we aimed to study the interaction of water, benzene, carbon dioxide, methanol 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 elementary cell is formed. The experiments were performed on an adsorption-microcalorimetric device with high vacuum and sensitivity. Before the initiation of the experiment, the sample is heated for 10 h, at 723K, under vacuum at 10^{-4} Pa in the pumped state. The experiment was performed using an adsorption-calorimetric device and method [3; p.39-55.]. Adsorption heat and isotherm values were calculated at 303 K.

3. RESULTS AND DISCUSSIONS OF THE RESEARCH

Differential heat and isothermal values of water adsorption on ZSM-5 zeolite at 303⁰K were calculated [4]. From these values the differential molar entropy of adsorption is derived. The isothermal value of adsorption was compared using the equation of microporosity saturation theory (STMP). They consist of 6 steps in total. At each stage, a stoichiometric compatibility 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. $(\text{NH}_4^+\text{AlO}_2)_{1,35}(\text{SiO}_2)_{94,65}$; $(\text{H}^+\text{AlO}_2)_{3,25}(\text{SiO}_2)_{92,75}$; $(\text{Li}^+\text{AlO}_2)_{4,36}(\text{SiO}_2)_{91,64}$ 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, with an average of 18.2 adsorbents per cation, and $(\text{H}_2\text{O})_n/(\text{NH}_4^+)$ $n=18,2$ complex clusters are formed. This is mainly explained by the validity of the ammonium cation.

As mentioned above, 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 (Figure 1). As the activity of the cations in the active center increases, the adsorption rate in them also increases. For example, ZSM-5 zeolite with Li^+ at the active center involves 32 H_2O / e.core in average respectively, in NaZSM-5 zeolite, this amount is equal to 34 H_2O / e.core., in CsZSM-5 zeolite, 45 H_2O / e.core are absorbed. In addition, the degree of adsorption is also related to the hydrophilic property of zeolite. MFI-type zeolites have a higher hydrophilicity level than most synthetic zeolites, i.e., 1.4–2.4. In ZSM-5 zeolite, a slight slowing of the isothermal point in the initial part causes a sudden increase in pressure due to the interference of the secondary adsorbate on the primary adsorbate, as a result of the interaction of the active centers of the zeolite with hydroxyl groups in water molecules, cations such as ammonium, hydrogen, lithium and sodium, which have different sizes and structures.

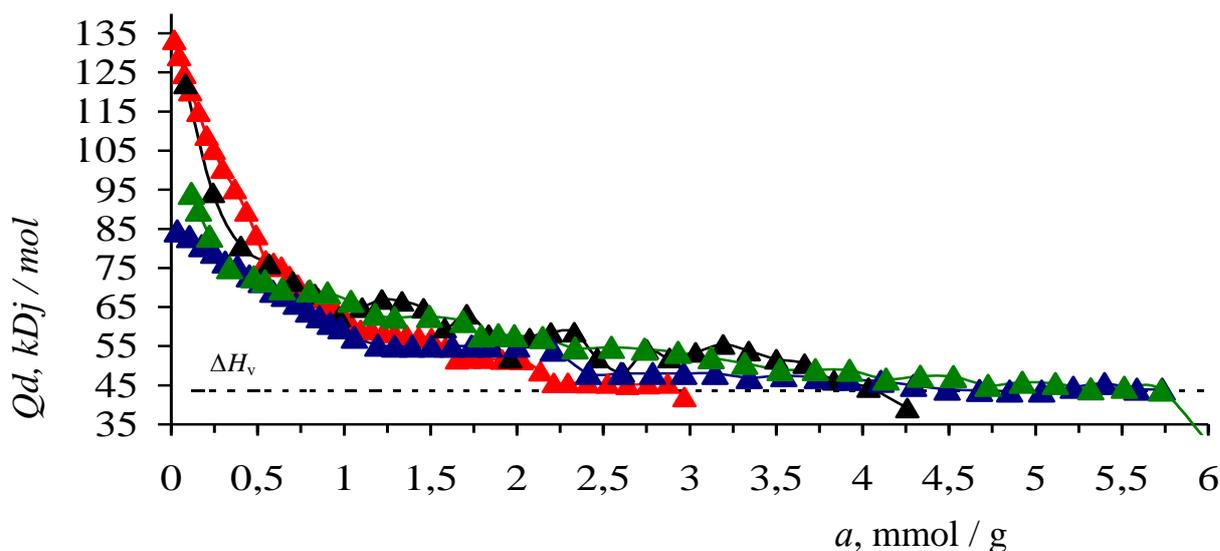


Figure 1. The differential heat values Q_d of water vapor adsorption on ZSM-5 zeolites with cation \blacktriangle - H^+ , \blacktriangle - NH_4^+ , \triangle - Li^+ , \triangle - Na^+ at 303 K.

Barcodes are the condensation value of water vapor at 303 K.

This has a large number of cations in the initial adsorption due to the presence of strong centers of zeolite at the intersection of the straight and reverse channels. It indicates the tendency of the centers to form aquacomplexes as a result of zeolite adsorption. 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 volumetric saturation theory of volumetric saturation (STMP) [5].

The basic equation of STMP for the adsorption processes under study is calculated with the following formule:

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

where, a - the adsorption amount in mmol/g;

a_0 - is the detected adsorption in mmol / g,

$A = PT \ln (P/P^0)$ - the amount of work done by 1 mole of gas (kJ / mol),

E - the characteristic energy of the adsorbent (kJ / mol);

n - parameter related to the structure of the porous area of the adsorbent.

The adsorption isotherm of water in NH_4ZSM-5 adsorbent is characterized by the three-dimensional equation of STMP.

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

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

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

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

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

These values consists of the following: $a_{01}=0,851$ mmol/g, $E_{01}=18,22$ kDj/mol and $n_1=2$; for the second member $a_{02}=1,63$ mmol / g, $E_{02}=6,3$ kDj / mol and $n_2=2$; the third member values are $a_{03}=1,748$ mmol / g, $E_{02}=2,094$ kDj / mol, and $n_3=2$.

The molar differential entropy of water adsorption increases from -220 J/mol•K to 0J/mol•K, i.e. from a very small minimum to a sharply higher value. As mentioned above, the primary water molecules adsorbed into the zeolite channels form an ion-molecular di- and tetra-aquacomplex that is firmly bound to the active centers of the cations without any barriers, isotherms and adsorption differential heat are calculated according to ΔS_d Gibbs-Helmholtz equation of molar differential entropy of water adsorption, based on the following equation:

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

Where, where λ -the heat of condensation,

ΔH and ΔG - the changes in enthalpy and free energy during adsorption in the standard state.

The mean integral values of entropy are correspondingly lower than the liquid value - 43.54 J / mol · K. 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, a large time is required for the strong bonding of the water molecules 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 ~ 30 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 important 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 has a Si/Al = 23 <x ratio. The adsorption isotherm was measured by the volumetric method. The amount of CO₂ adsorption on ZSM-5 zeolite was expressed in mmol / g, and the isotherm index was

expressed in $\ln(P/P^0)$. From the adsorption isotherm lines of CO₂ molecules to ZSM-5 zeolites, it can be seen that initially a gradual increase to 0.75 mmol / g is observed, followed by a straight line increase to ~ 1.5 mmol / 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 mmol / g can be explained by the penetration of carbon monoxide molecules into the zeolite zigzag channels, followed by a straight line saturation of the zeolite into the straight channels. When the adsorption amount is a-1.41 mmol/g, the pressure is P=609 mm.merc. The theory of volumetric saturation of CO₂ adsorption isotherm to NH₄ZSM-5 was described using the two-term equation [6]:

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

Carbon monoxide adsorption on ZSM-5 zeolite Q_d differential heat has a curvilinear phase character. Figure 2 shows the differential heat Q_d of CO₂ adsorption on ZSM-5 at 303 K.

The heat of condensation of carbon (IV) -oxide at 303 K ($\Delta H_v=27$ kJ / mol) is given in the pulister straight lines. The interaction of CO₂ with cations is mainly accompanied by the formation of binary complexes during adsorption. CO₂ adsorption does not start with high heat at the beginning of adsorption 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.

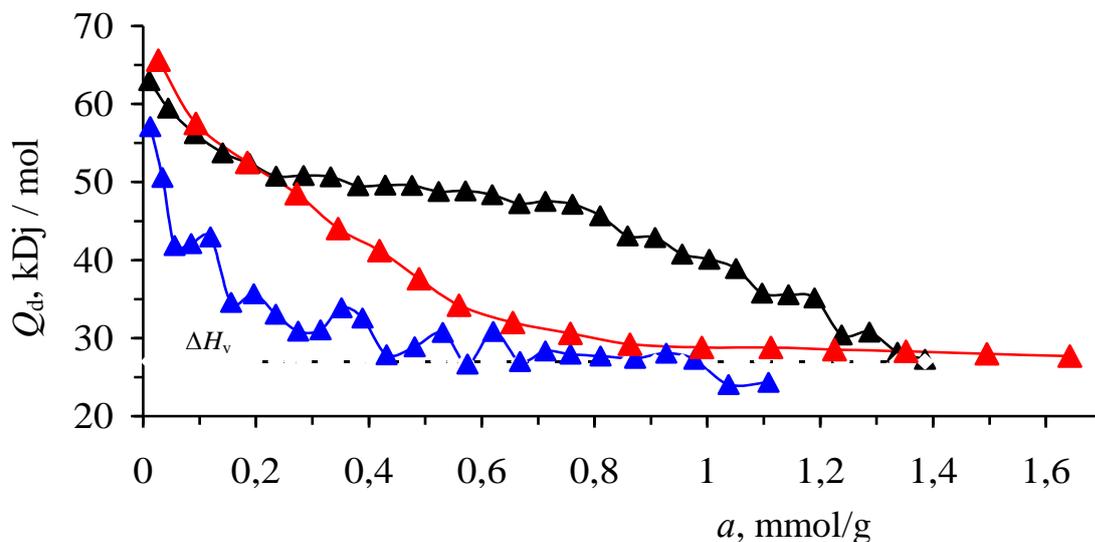


Figure 2. The differential heat values Q_d of CO₂ adsorption on ZSM-5 zeolites with ▲ -Li⁺, ▲ -NH₄⁺, ▲ -H⁺ cations at 303 K.

Barcodes are condensation value of CO₂ at 303 K.

During the initial CO₂ adsorption, entropy is observed to be in the liquid state motion. In general, at the beginning of adsorption and until the end of adsorption, carbon (IV) oxide molecules assumed liquid state entropy values. The initial 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 CO₂ molecules in the zeolite matrix.

Based on the data obtained, the adsorption of the CO₂ molecule in ZSM-5 zeolites of different cations takes place in two sections. In the first section, CO₂ 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 equilibrium time is initially higher at NH₄ZSM-5, i.e., the equilibrium is reached in 5.8 hours. In other ZSM-5 zeolites, this figure is 1-1.5 hours. In this case, the amount of adsorption is 0.01 mmol/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 [7]. In particular, they are most effective in the processes of isomerization, deparaffinization, cracking and aromatization in the oil refining industry, mainly in the liquid period. 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 are indicators 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 (Q_d) was measured using a high-precision adsorption calorimetric device described above [6]. The adsorption isotherm of n-heptane at 303 K in ZSM-5 zeolite was studied. The equilibrium relative pressure at the initial saturation of n-heptane adsorption on this zeolite is $P/P^0=2,26 \cdot 10^{-4}$. The adsorption isotherm grows linearly at a certain angle to $a=1$ mmol / g, indicating sorption of cations in the elementary cell, then bends toward the adsorption axis and increases linearly again to 1.5–2 mmol/g and then approaches the ordinate axis.

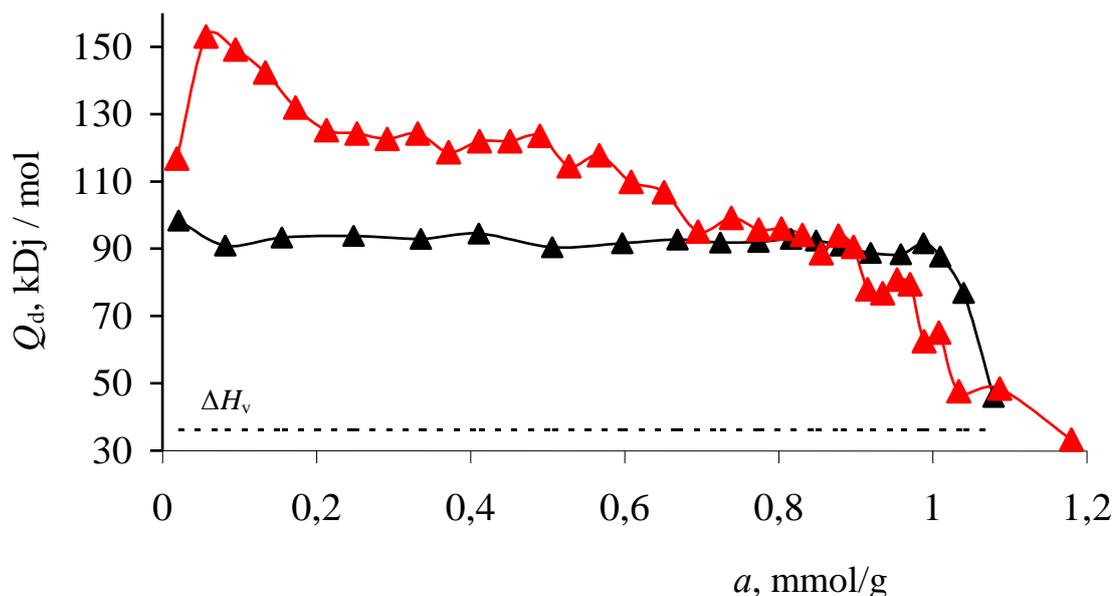


Figure 3. The differential heat values Q_d of heptane adsorption on ZSM-5 zeolites with \blacktriangle - NH_4^+ , \blacktriangle - H^+ cations at 303 K. Barcodes are condensation value of heptane at 303 K.

Assuming that the density of n-heptane adsorbed on the zeolite is a normal liquid and the volume occupied by the n-heptane molecule at saturation temperature (303 K) for the experiment, the share of the induction component in the total energy is ~ 0.182 kJ/mol. In $\text{NH}_4\text{ZSM-5}$, the adsorption isotherm of n-heptane is represented by the complete STMP 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. [8]

The adsorption isotherm of n-heptane in ZSM-5 zeolite is represented by the two- and three-dimensional STMP equations [9].

The adsorption heat of N-heptane in silica was ~ 80 kJ/mol at the initial saturation of pure silica analog ZSM-5, which was found to be ~ 26 kJ/mol smaller than the adsorption heat of $\text{NH}_4\text{ZSM-5}$ relative to the total Q_d curve. 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 uniform flow of heat can be explained by the orderly course 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 in the adsorption of relatively small molecules of h-hydrocarbons. Thus, from the beginning of the adsorption process, n-heptane molecules follow the mechanism of "adsorbate-adsorbate" action, 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 of the 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 NH₄ZSM-5 zeolite. The basis of this equation is differential heat and isotherm. Saturation of zeolite channels with n-heptane occurs in the form of a differential entropy curve in all parts.

Entropy lasts up to 1 mmol/g at -140 - 150 J/mol·K, and entropy up to 1.3 mmol/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 occurs when the entropy of n-heptane is immobile. 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 cross-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 a straight channel and an intersection area is 0.99 nm, and a zigzag channel and an intersection area are 1.21 nm. Hence, the most optimal localization point 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 8-6 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.

The mechanisms of benzene adsorption isotherms from ZSM-5 to zeolites from initial saturation to saturation were studied. The isothermal graphic coordinate axes are characterized by logarithmic ($\ln(P/P_s)$) and adsorption amount (a, mmol/g) signs. Adsorption isotherms initially start at 0.01-0.02 mmol / g, with an isotherm value of -11-13 $\ln(P/P_s)$. With small changes, the isothermal lines gradually rise. These changes in isothermal lines are explained by the adsorption of zeolite on cations in zigzag channels.

The benzene adsorption isotherm to NH₄ZSM-5 zeolite was described using the equation of the saturation theory of three-dimensional micropores (STMP) [10; P.50-70].

The differential heat of benzene adsorption on ZSM-5 zeolites is shown in Figure 4. The fact that the adsorption heat decreases along the curve during the transition from high to low energy indicates that one molecule of benzene is adsorbed on two cations. The adsorption heat in the zigzag channels is high in both sections. The high rate of adsorption differential heat indicates the formation of π -complexes ($C_6H_6/(cat^+)$) in cations containing ZSM-5 zeolite. In the second section, the formation of $C_6H_6/(cat)$ complexes through the adsorption π -bond proceeds along zigzag channels. Once the benzene is adsorbed in the zigzag channels, the zeolite is adsorbed into the straight channels. Benzene adsorption in straight channels is accompanied by a gradual decrease in differential heat.

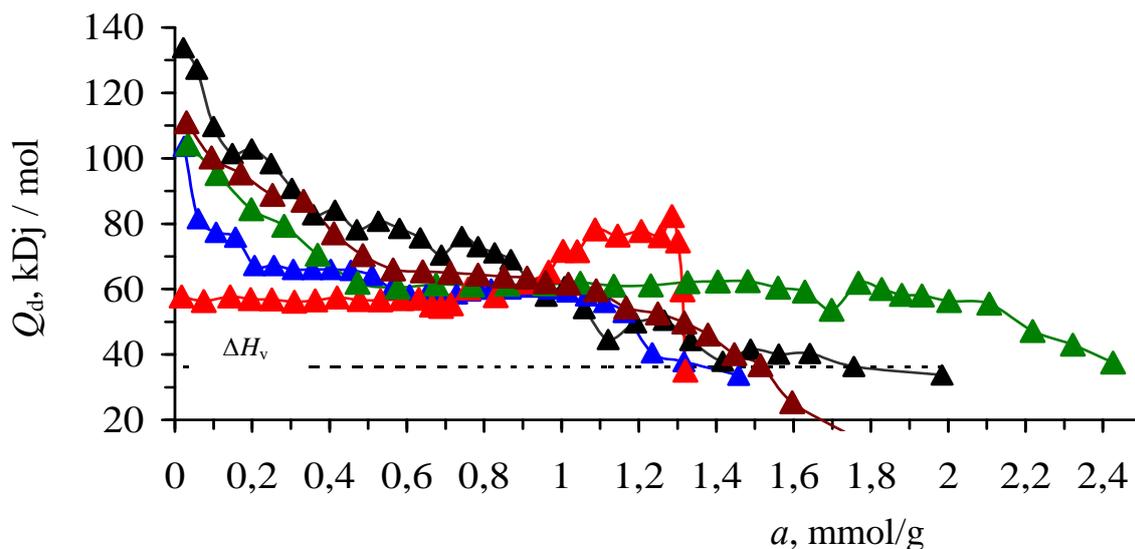


Figure 4. The differential heat values of Q_d of benzene adsorption in ZSM-5 zeolites with \blacktriangle -Na, \blacktriangle -Li, \blacktriangle - NH_4^+ , \blacktriangle - H^+ , \blacktriangle -silicalite cations at 303 K. Barcodes are condensation value of benzene at 303 K.

The adsorption differential entropy was calculated using the Gibbs-Helmholtz equation using the isotherm and differential heat value. In the initial saturation, the adsorption values range from 0.043 mmol/g to 0.25 mmol/g with entropy values ranging from -110-210 J/mol·K to -50-100 J/mol·K. Adsorption entropy indicates strong sorption of one benzene molecule into two stable cations at the intersection of zigzag and straight channels at initial saturation.

The initial saturation lasts from 5-6 hours to 3-4 hours. In this case, the adsorption rate is in the range of 0.04 mmol/g to 0.52 mmol/g. The high equilibrium time is explained by the formation of π -complexes that occur at high energies with cations at the active centers of the initially adsorbed benzene molecules. After 3-4 hours of adsorption equilibrium time, the zeolite continues in straight and zigzag channels.

Migration from the intersection of straight and zigzag channels to straight channels is observed in ZSM-5 zeolites with hydrogen and lithium cations, as well as the formation of ion-molecular complexes in the zeolite channels. Adsorption isotherms were described using the equation of volumetric saturation theory (STMP) of three-dimensional micropores. In zeolite channels, benzene is in solid state mobility. In this way, the adsorption mechanisms from initial saturation to saturation were fully studied.

Methanol adsorption was given in Figure 5, the differential heat value drops sharply, and the differential heat value is about 80 kJ/mol. The amount of differential heat then passes unchanged between 55 kJ/mol and 75 kJ/mol, then drops sharply until condensation of the respective alcohol molecules. The adsorption channels of ZSM-5 zeolite are a porous system in which molecular complexes appear in the form of "adsorbate-adsorbate" and "adsorbate-adsorbent" bonds. The adsorption of methanol at zero saturation is ~ 30.69 kJ/mol. The experimental values for ZSM-5 were more than 10 kJ/mol. The resulting structural defects of

the adsorbent have a significant effect on the adsorption heat as a whole, and the extrapolation method for zero saturation can lead to significant errors in determining the adsorption on the molecules. The heat content of CH₂-group increment is 10.0 kJ/mol. For example, the adsorption of water on NH₄ZSM-5 zeolite according to the thermal scheme is expressed as follows: Q_{H₂O}=Q_{CH₃OH}-Q_{CH₂}=30,69-10.0=20,69 kJ/mol. Direct calorimetric measurements confirmed this value, which is twice lower than the condensing heat at 303 K (43.5 kJ / mol). This result reveals the reason for the excellent hydrophilicity of NH₄ZSM-5 zeolite. The figure shows that the value of the adsorption energy in a zeolite with a cation active center of different sizes increases with the size of the cations in the active center.

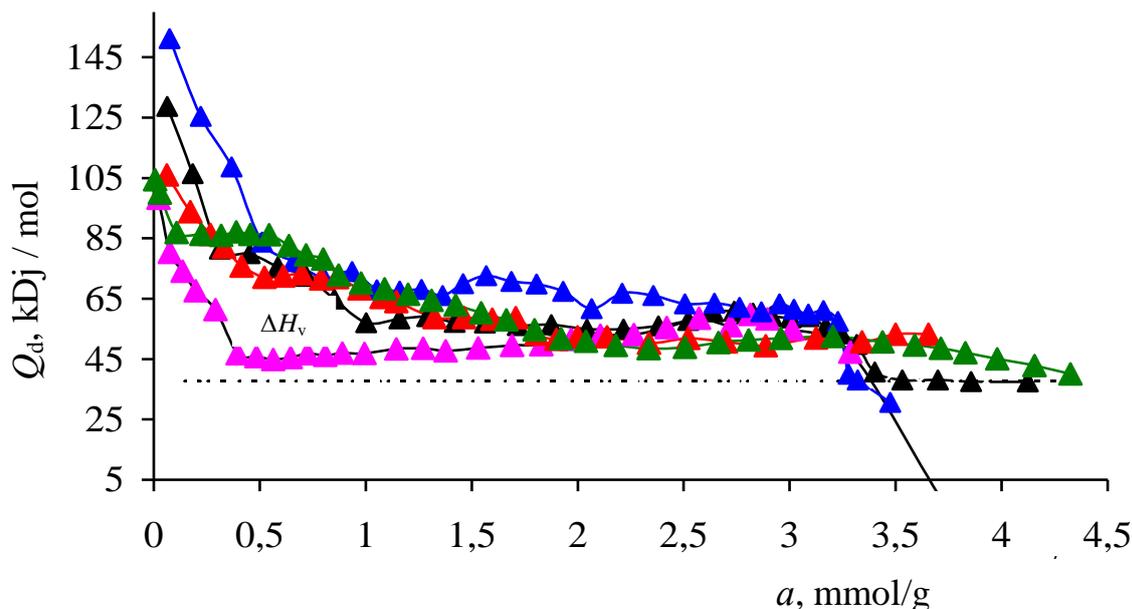


Figure 5. The differential heat values Q_d of methyl alcohol adsorption in ZSM-5 zeolites with \blacktriangle -Na, \blacktriangle -Li, \blacktriangle -NH₄⁺, \blacktriangle -H⁺, \blacktriangle -silicalite cations at 303 K. Barcodes are the condensation value of methyl

The molar differential entropy of alcohol adsorption ΔS_d isotherms and adsorption differential heat is calculated according to the Gibbs-Helmholtz equation:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T} \quad (2)$$

where, λ - the heat of condensation,

ΔH and ΔG - the enthalpy and free energy changes during the adsorption process from the standard state to the adsorbed state.

The increase in the molar differential entropy of methanol adsorption from -250 to -100 J/mol·K, ie from a very small minimum to a sharply higher value, is due to the fact that, as mentioned above, the primary methanol molecules adsorbed into zeolite channels form a molecular complex the line is below the entropy of liquid methyl alcohol, and as this saturation rate increases, the entropy value rises sharply from the liquid entropy to the vapor entropy. The mean integral values of entropy are correspondingly much smaller than the

liquid value. Thus, the differential and integral entropy indicates the state of motion of each adsorbed alcohol molecule in the zeolite.

In ZSM-5 zeolite, the equilibrium of adsorption of methyl alcohol molecules at the intersections of zigzag channels and straight channels is very slow and then accelerates sharply. At the same time, the equilibrium time is reduced from almost 9 hours to 1-1.6 hours. In the initial adsorption, a long time is required for the strong bonding of the alcohol molecules with the active sites. In the later stages, the adsorbate-adsorbate bonds take less time (1-2 hours). The decrease in the adsorption equilibrium time by 30 minutes in the final stage is explained by the fact that they remain in the vapor state as a result of the interaction of fully adsorbed molecules with adsorbed molecules in the adsorption volume.

In ethanol, as in methanol, the adsorption isotherm can be seen in the initial stage of saturation, as well as the presence of strong adsorption centers of ethanol. If we equate the ethanol density in the ZSM-5 zeolite to the normal liquid level at the test temperature and calculate the volume occupied by the ethanol molecules during saturation, it becomes clear what percentage of the ethanol ZSM-5 channels are filled. The adsorption isotherm of ethanol in ZSM-5 zeolite is characterized by the three-dimensional equation of STMP. The adsorption isotherm is shown in ZSM-5 in semi-logarithmic coordinates, and the values of the experimental results and the values calculated by the STMP equation correspond to each other [10-17].

The differential heat of ethanol adsorption on ZSM-5 zeolite is shown in Figure 6. The differential heat content of ethanol Q_d increases significantly at the initial saturation stage. The presence of a maximum value on the differential heat curve of ethanol occurs as a result of intermolecular interactions of adsorbed molecules with each other. In addition, the adsorption energy of ethanol corresponds to the interaction of the charge and size of ammonium cations with that of hydrogen. Subsequently, the adsorption energy values will be very small, especially in the initial adsorption, so that there are no cations in the cation-free ZSM-5 i.e. silicolite active centers.

It can be seen from the differential temperatures in the adsorption of the polar molecules of water, methanol and ethanol that the temperature change is gradual, indicating that the cavities of the ZSM-5 zeolites are discretely the same. The differential heat of ethanol adsorption is on average $\sim 10 - \sim 12$ kJ/mol higher than the Q_d value of methanol in ZSM-5, which corresponds to the increase in heat in the group CH_2 .

The molar differential entropy of ethanol adsorption in ZSM-5 zeolites differs in wave form from the entropy of liquid ethanol. At low saturation, the differential entropy is formed as a result of the adsorbate-adsorbate interaction. The last minimum value on the differential entropy curve of ethanol indicates the strong location of ethanol molecules in the zeolite channels and their intersections.

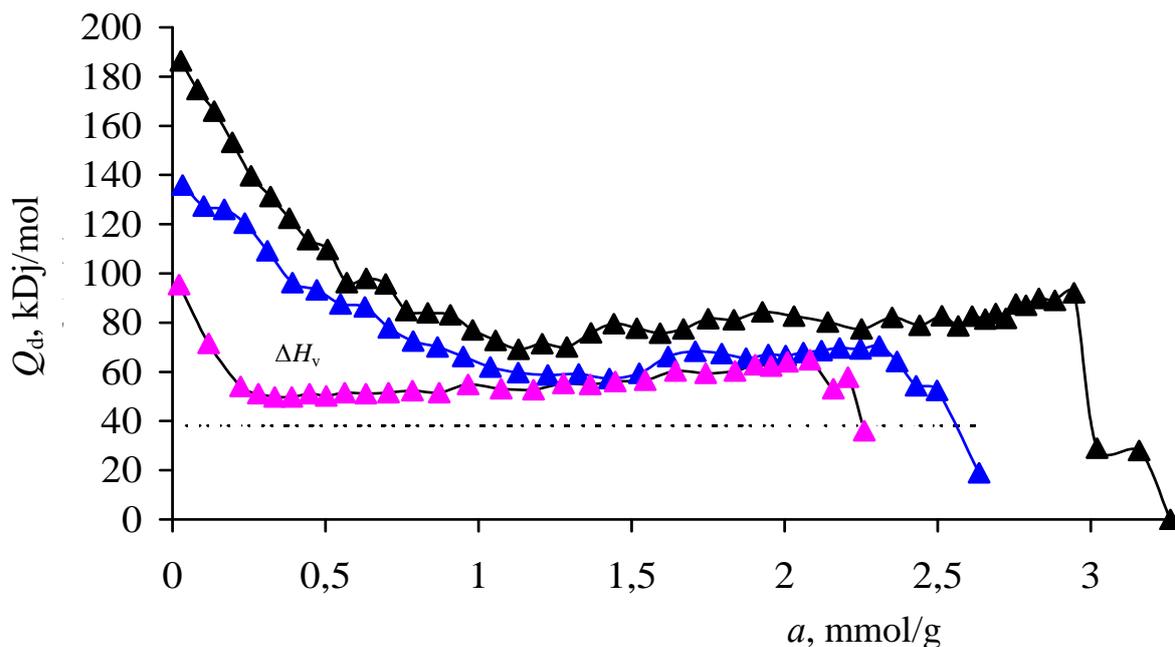


Figure 6. The differential heat values Q_d of ethyl alcohol adsorption in ZSM-5 zeolites with \blacktriangle - NH_4^+ , \triangle - H^+ , \blacktriangle --silicalite cations at 303 K.

Barcodes are the condensation value of ethyl alcohol at 303 K.

The timing for filling the adsorption equilibrium is in the form of a small wavy and stepped curve. The adsorption equilibrium time is initially high, gradually the adsorption equilibrium time decreases, falling to a few hours at the end of the process.

4. CONCLUSION

Detailed data on the isotherms and thermodynamic properties (ΔH , ΔG and ΔS) of H_2O , CO_2 , n-heptane, benzene and methyl, ethyl alcohols to ZSM-5 zeolite are given in detail. The adsorption heat of the studied systems with small filling is gradual, stepwise, and the adsorption properties are determined. Correlations between molecular mechanisms of adsorption of N_2O , CO_2 , n-heptane, benzene and methyl, ethyl alcohols on ZSM-5 zeolite, adsorption-energy characteristics were revealed. Due to the ammonium cation in the active centers, the adsorption of water in the $\text{NH}_4\text{ZSM-5}$ zeolite was almost twice as high as in the cationless form (silicalite 9.8 H_2O / e.core). 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. It has been shown that the adsorption of benzene molecules on cations containing ZSM-5 zeolite proceeds with the formation of π -complexes. 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^+ , Cs^+ , NH_4^+ from the intersection of straight and zigzag channels to

straight channels is not observed. Hydrophilicity levels and incrementality of zeolites were calculated from the adsorption of ethanol and methanol molecules.

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