

# Determination of water adsorption mechanisms in NH<sub>4</sub>ZSM-5 and HZSM-5 zeolites

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**Abstract.** This article covers the results of a study on the determination of the differential heat, isotherm and entropy of water vapor in ZSM-5 zeolites at a temperature of 303 K using the adsorption-calorimetric method. The type and number of ion-molecular formed complexes, as well as the mechanism of adsorption of the studied molecules, were determined. By studying their energetic properties, it is possible to determine the chemical composition and crystal structures of the zeolites. The adsorption isotherm was described by two- and three- had mathematical equations of the TVSM (the theory of volumetric saturation of microgroups) from the beginning to saturation. An analysis of the obtained results proved that NH<sub>4</sub>ZSM-5 and NZSM-5, which are used as catalysts, can be used as zeolites.

## 1 Introduction

Every year, the demand for environmentally friendly fuel produced from petroleum products that meets Euro-5 quality standard is growing in the world. In order to successfully and effectively implement this task, zeolites used for cleaning natural gas, oil and petroleum products from harmful impurities, as well as for drying them, are becoming increasingly important. Important scientific and practical results in this case can be obtained by using an adsorption microcalorimetric installation, with the help of which experimental studies can be carried out to study their adsorption and active catalytic properties, the structure of micropores, determining the number, strength and nature of active centers.

In the world, research in the field of synthesis and study of the structure of zeolites, their use in the process of purification of natural gas and wastewater for the development of scientific foundations to substantiate the chemical structure of adsorbent crystals by studying the adsorption processes of nonpolar n-heptane molecules, polar water molecules, methyl and ethyl alcohol, quadrupole carbon monoxide molecules (IV) and aromatic benzene, determination of conformation, localization and mechanism of molecular adsorption, and also to establish the laws of thermokinetics of adsorption in the structure of zeolites.

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The role of Science in the rational way of solving the problematic issues arising in the development of natural resources on this day is incomparable. Therefore, an important place is occupied by the use of such issues through the use of sorbents that are environmentally friendly, in the processes of separation of natural gas, wastewater from additives [1-2].

Zeolite-crystal materials of the MFI series (silicalite, ZSM-5 and their modified samples) are considered one of the relatively well-studied micro-porous synthetic materials. To study the physico-chemical properties of adsorption in zeolites, the complete thermodynamic properties of adsorption are studied with high accuracy through the calorimetric method in a high vacuum adsorption microcalorimetric device [3]. The porous (porous) system of these types of zeolites is composed of medium-sized pores, consisting of straight and zigzag channels, as well as channel intersections. To compensate the negative charge distributed by the limited number of oxygen structural atoms located next to the Si/Al Exchange Center, the zeolite contains positively charged cations. In our object are the cations  $\text{NH}_4^+$  and  $\text{H}^+$ . The ability to separate impurities at a higher rate is a good indicator of the quality of the mebrana, since adsorption coatings are considered lower and less likely to be blocked by one molecule by another.

## 2 Object and methods of research

Before starting adsorption – calorimeter studies, the zeolite samples are pressed into tablets, then crushed to a size of 1 mm, and then filled by placing them in an ampoule. The ampoule with the sample is connected to the vacuum line and placed in the oven until  $10^{-5}$  Pa vacuum, air is removed using a vacuum pump at 723 K for 7 hours. After that, the weight of the adsorbent in the vacuum is determined and connected to the adsorption device, an ampoule with zeolite is connected to the cell with a calorimeter, which falls unhindered [4].

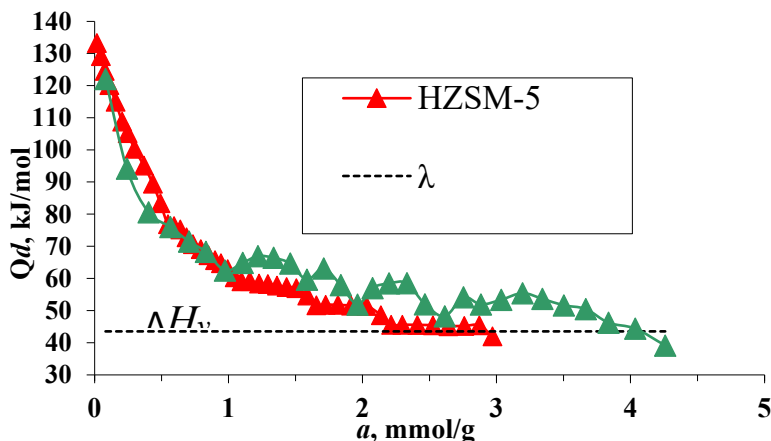
## 3 Discussion of research results

The measured differential heat of adsorption ( $Q_d$ ) consists of approximately 30 experimental points (Figure 1), each of which corresponds to an isothermal (30°C) balance in saturation with this pressure and sorbate. In the study of the sorbate/sorbent adsorption system, the extraction of balanced points in such quantities is not considered by using other structure-sensitive methods, for example, in diffraction methods [5].

Figure 1 presents water vapor adsorption differential heat  $Q_d$  in the  $\text{NH}_4\text{ZSM-5}$  zeolite. They consist of 6 tiers in total: (from 0 to 0.97; from 0.97 to 1.58; from 1.58 to 1.96; from 1.96 to 2.61; from 2.61 to 3.5; from 3.5 to 4.26). In each step, a stoichiometric match can be seen between the active centers of the zeolite and the water vapor. As a result of chemical analysis, it was determined that 1.35 ammonium cations ( $\text{NH}_4^+$ ) in the zeolite content correspond to each elemental cell, i.e.  $(\text{NH}_4^+\text{AlO}_2)_{1.35}(\text{SiO}_2)_{94.65}$  is the general formula for each elemental cell. This means that a total of 24.6 water molecules are adsorbed to the elementary cell, with an average of 18.2 adsorbates per cation, and  $(\text{H}_2\text{O})_n/(\text{NH}_4^+)$   $n=18.2$  complex clusters are formed. For example, an average 32  $\text{H}_2\text{O}/\text{el.c}$  to ZSM-5 zeolite with  $\text{Li}^+$  in the active center, respectively, 34  $\text{H}_2\text{O}/\text{el.c}$ . to NaZSM-5 tseolit, 45  $\text{H}_2\text{O}/\text{enthalpy}$  to CsZSM-5 tseolit adsorbed. In addition, the degree of adsorption is also related to the hydrophilic property of the zeolite.

Differential heat of water vapor adsorption is also supplied to the HZSM-5 zeolite. The initial heat of adsorption is around 133 kJ/mol, corresponding to the strongly adsorbed water quantity of  $\text{H}_2\text{O}:\text{H}^+$  scheme [6-7]. The staggered drop in differential heat indicates that outside the main channels, protons in a state shielded by water are ejected. The adsorption of the second, third and fourth molecules passes in the range heat at a value of 75.3-45.61

kJ/mol, and after completion it drops sharply to 41.67 kJ/mol. These two molecules of water ends with the formation of a tetrahedric ion – dipole complex. This complex is located at the intersection of straight and zigzag channels. Another 1 molecule is adsorbed with heat greater than the condensation heat value. Considering also the adsorption in cation, a total of 5 water molecules are adsorbed in this zeolite.



**Fig. 1.** Illustrates water adsorption differential heat values ( $Q_d$ ) in ZSM-5 tseolites with a cation of  $\blacktriangle$  -  $H^+$ ,  $\blacktriangle$  -  $NH_4^+$  at 303 K. The condensation value of water in the bar lines 303 K.

Based on the variable heat from 134 kJ/mol of  $Q_d$  to condensation heat, it can be divided into 6 sectors. Each stage reflects the process of serial formation of multi-dimensional  $(H_2O)_n/H^+$  complexes, and in this case changes from  $n - 1$  to 4. The effect of structural deflections of the crystal lattice in the form of an on group attached to Si/Al atoms is observed. Usually silanol deflections have initial heat values of 100 kJ/mol and higher. In the first sector (0 - 0.55 mmol/g), the adsorption of water is carried out with a sharp drop in heat (134 - 77 kJ/mol). This condition is caused by special interaction with the first sorbed molecules of water and all 0.55 mmol/g  $H^+$  cations in a 1:1 ratio. In the second sector (0.55 – 1.1 mmol/G), the heat varies from 77 to 59.15 kJ/mol, and in this the formation of  $((H_2O)_2/H)$  clusters takes place. In the third (1.1 – 1.65 mmol/G) and fourth sectors (1.65 – 2.21 mmol/G), the heat varies from 59.15 to 51.67 kJ/mol and from 51.67 to 43.54 kJ/mol. In this, tri - and tetraacvacomplexes are formed, which are located at the intersections of straight and zigzag channels. The appearance of three more sections occurs as a result of the combination of the next 1 water molecule with a tetraacvacomplex at relatively low thermal values. This situation can most likely take place in the second coordinate sphere.

The isotherm of water adsorption in  $NH_4ZSM-5$  differs from organic adsorbates in that there is less saturation restriction adsorption. Considering that  $NH_4ZSM-5$  does not have enough hydrophilic centers, over a long period of adsorption, water molecules saturate almost the entire channel and various parts of the  $NH_4ZSM-5$  zeolite.

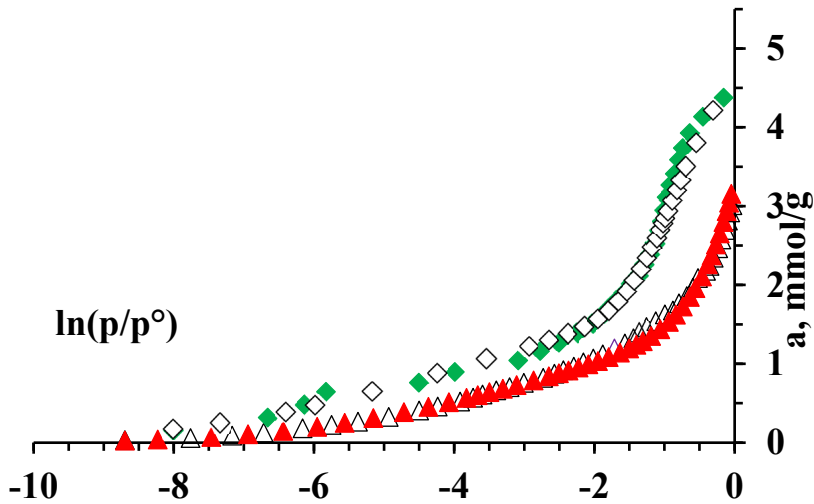
For water adsorption to the  $NH_4ZSM-5$  tseolite, the parameters of the first period equation are  $A_{01} = 9.82$  mmol / g,  $E_1 = 16.94$  kJ/mol and  $N_1 = 4$ ; for the second period,  $A_{02} = 2.165$  mmol / g,  $E_2 = 4.36$  kJ/mol and  $N_2 = 2$ ; for the third period,  $A_{03} = 1,772$  mmol / g,  $E_3 = 1.74$  kJ/mol and  $N_3 = 1$ .

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

In Figure 2, it can be seen that the values of theoretical computational data with experimental data overlap each other, and for a complete description of isotherms, it would be enough to divide this equation into three parts.

In accordance with the differential heat of adsorption, a solid adsorption area in the NZSM-5 seal is noted in a flat increase in the curve. When adsorption is continued, the isotherma decreases, and then the line increases flat until saturation. Complete adsorption forms a complex of  $5\text{H}_2\text{O}:\text{K}^+$  to each channel intersection. However, the formation of a high-energy one-dimensional complex also confirms the adsorption isotherm (Figure 2) [8-10]. In the hzsm-5 sealite, the water adsorption isotherm described by the TVSM (the theory of volumetric saturation of microgroups) equation is presented in semi-logarithmic coordinates (Figure 2). It is described using the three-hade TVSM equation from zero to saturation of the adsorbent:

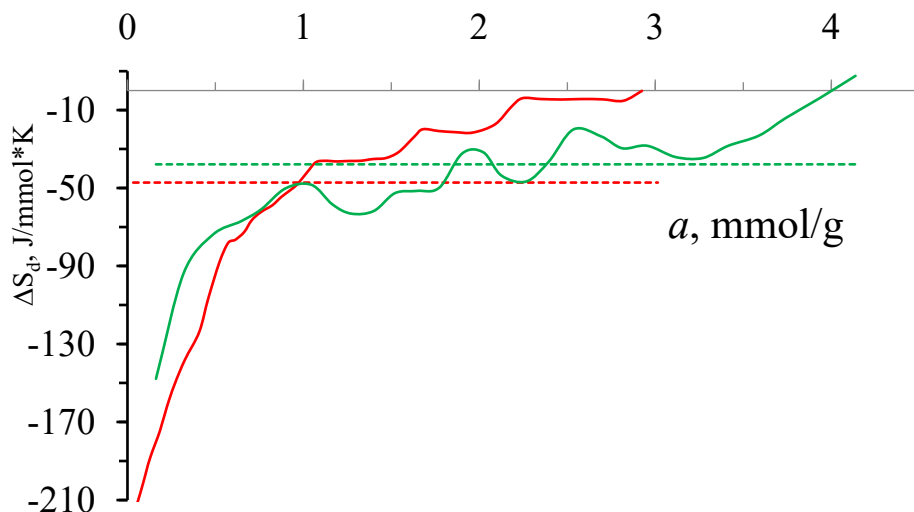
$$a = 1,48 \cdot e^{-\left(\frac{A}{14,18}\right)^2} + 0,74 \cdot e^{-\left(\frac{A}{5,26}\right)^2} + 0,78 \cdot e^{-\left(\frac{A}{0,99}\right)^1} \quad (2)$$



**Fig. 2.** 303 K  $\blacklozenge$ -  $\text{NH}_4^+$ ,  $\blacktriangle$ - $\text{H}^+$  water adsorption isotherm in cation-ZSM-5 tseolites.  $\diamond$ ,  $\Delta$  - values of the general equation TVSM (the theory of volumetric saturation of microgroups).

In Figure 2 we can see the correspondence of experimental and calculated data. Water adsorption at cation active-center ZSM-5 the adsorbate pressure in the zeolites sharply increases in saturation when the isotherma curves are compared in the following sequence:  $\text{NH}_4\text{ZSM-5} > \text{HZSM-5}$ .

Figure 3 presents water adsorption differential entropy values ( $\Delta S_d$ ) in  $\text{NH}_4^+$ ,  $\text{N}^+$ , cation ZSM-5 tseolites at 303 K. Molar differential entropy of water adsorption from -150 to -50 J/mol·K i.e. dramatically higher value than a very small minimum, as described above, primary water molecules adsorbed to the zeolite channels formed a solid bonded ion - molecular tetra-aquacomplex with ammonium cation active centers without any obstacles molar differential entropy of water adsorption  $\Delta S_d$  according to the Gibbs-Helmhols equation isotherms and adsorption differential the heat is calculated based on the following equation. The average integral values of entropy are correspondingly smaller than the liquid value – 43.54 J/mol·K. Thus, differential and integral entropy indicate the state of motion of each adsorbed water vapor in the zeolite.



**Fig. 3.** Illustrates the water adsorption differential entropy values ( $\Delta S_d$ ) in ZSM - 5 zeolites with cation  $\bullet$ -  $\text{NH}_4^+$ ,  $\bullet$ - $\text{H}^+$ , at 303 K. The entropy of liquid water has been taken to be zero.

The total entropy value is below the liquid water entropy. In the initial area, the entropy of HZSM-5 zeolite water adsorption increases from -220 to 0 J/mol\*K. In adsorption of 1.65 mmol/g, entropy will have a value of -19 J/mol\*K. The above values also show that  $\text{NH}_4\text{ZSM-5}$  is more likely to attach water molecules to itself than HZSM-5. As the main reason for this, the cation  $\text{NH}_4^+$  is located correctly and at the intersection of zigzag channels. Therefore, we can see that the consistency in the bonds of the initial molecules with cations is lower than that of HZSM-5. The total number or mole value of adsorbed molecules is greater in  $\text{NH}_4\text{ZSM-5}$ , since the presence of migration patterns in HZSM-5, if we take all the thermodynamic characteristics of the studied system, then we can see a clear correlation between the obtained functions.

## 4 Conclusion

In the HZSM-5 zeolite, the water adsorption isotherm was delivered at a relative pressure of  $\sim 0.79$  to  $a = 2.97$  mmol/g. Under normal conditions of experimental temperature, 2.97 mmol/g of water occupies  $\sim 0.055$   $\text{cm}^3$  space, which is 30% of the volume of the zeolite sorption. In the case of the zeolite with  $\text{Si/Al} = 32$ , the water molecules fill 42% of the channels of the actual volume of the zeolite. This is  $\sim 12\%$  less than that of the zeolite, which has  $\text{Si/Al}=32$ . At the expense of ammonium cation in active centers, adsorption in  $\text{NH}_4\text{ZSM-5}$  in relation to the cation-free form went almost twice as much (silicate 9,8  $\text{H}_2\text{O}/\text{el.c.}$ ). Based on the results of the experiment, it is possible to know that both the heat of adsorption and the isotherm  $\text{NH}_4\text{ZSM-5}$  zeolite have an organophil property. Adsorption mechanisms based on adsorption isotherm and differential heat have been fully studied. The water molecules in the zeolite matrix are highly localized and are close to solid-state entropy in the zeolite channels. An analysis of the results obtained proved that  $\text{NH}_4\text{ZSM-5}$  and HZSM-5, which are used as catalysts, can be used as zeolites.

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