Thermodynamic values of the adsorption of methanol and ethanol molecules in zeolite NH4ZSM-5

Tolibjon Abdulkhaev¹, Shakhnoza Kuldasheva², Gulnara Razimova², Mukarram Aripova³ and Sherzod Toshev⁴

¹Namangan Engineering Technological Institute, Namangan, Uzbekistan
²Institute of General and Inorganic Chemistry of Academy Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan
³Tashkent State Technical University, Tashkent, Uzbekistan
⁴Bukhara Engineering Technological Institute, Bukhara, Uzbekistan

E-mail: master64511@gmail.com

Abstract. Differential heats, isotherm, entropies and thyromimetics of methanol and ethanol adsorption in the NH₄ZSM-5 zeolite were measured at 303K. The isotherm of adsorption was quantitatively reproduced on the basis of TVOM theory. The detailed mechanism of methanol and ethanol adsorption in (NH₄)₁₃ZSM-5 zeolite from zero filling to saturation was discovered.

1. Introduction
Today, in a number of developed countries, zeolites of the ZSM-5 type are used as a very effective catalyst in the production of environmentally friendly petroleum products, that is, high-octane fuel products. In addition, the ammonium form of ZSM-5 zeolites was chosen as a catalyst in the production of non-petroleum products, that is, high-octane gasoline from methyl alcohol. Therefore, there is growing interest in studying the adsorption and catalytic properties of this type of zeolite. At the same time, small ZSM-5 methanol molecules increase the amount of branched chain hydrocarbons due to interconnection at the intersection of straight and zigzag channels, resulting in a high octane number in gasoline. The results of the analysis of the adsorption of ethanol on zeolite ZSM-5 show that the value of the differential heat of adsorption in the direct and zigzag channels is parallel to the adsorption of methyl alcohol. In particular, alcohol molecules adsorbed to the probe help to explain the reason for the manifestation of hydrophilic bifunctional properties in zeolites. Before the start of the experiment, the samples were heated for 10 h at 723 K in a vacuum of 10⁻⁴ Pa in a pumped state. The experiment was carried out using an adsorption-calorimetric device and technique [1]. Adsorption temperatures and isothermal values are calculated at 303 K.

2. Methods
Analysis of thermodynamic functions of isotherm, differential heat, differential entropy and thermokinetics of adsorption of methanol and ethanol vapors in defect-free zeolite NH₃03ZSM-5 at 303K. The adsorption isotherm was processed by the equation of a three-stage TOMF (theory of volumetric filling of microgravity). Based on the data obtained, the mechanism of complete adsorption of methanol and ethanol vapors in a defective zeolite from the initial pressure to the saturated vapor pressure is revealed.
3. Results and discussion

When synthesizing zeolites ZSM-5 from basic salts, crystals analogs of NH$_4$ZSM-5 and ZSM-5 with various metals in their active centers, especially in the form of hydroxyl groups on the zeolite surface, have defects [2]. Adsorbates such as methyl and ethyl alcohol are also very effective in determining the degree of defectiveness of these zeolites. The reason for the large difference in the heat of adsorption from the initial stages of adsorption can be explained by the strong bond of ethanol molecules with NH$_4^+$ cations located in the center of the zeolite. The differential heat of methyl alcohol is 150-80 kJ/mol, which is explained by the unhindered interaction of methyl molecules with ammonium cations on active sites located at the intersections of zeolite channels. In this case, due to the presence of strong hydrogen bonds in the alcohol molecule, the interaction of strongly negatively charged methoxyl and ethoxyl groups with the network of oxygen atoms depends on the heat release range of NH$_4^+$ cations 187 - 75 kJ/mol. Adsorbed methyl and ethyl alcohols NH$_4$ZSM-5 were confirmed by studies using a high-vacuum adsorption device.

![Figure 1. Differential heat of adsorption of methyl and ethyl alcohols at 303 K in zeolite NH$_4$ZSM-5.](image)

From the temperature difference during the adsorption of polar ethanol and methanol molecules, it can be seen that the temperature change occurs gradually, which indicates that the voids of the NH$_4$ZSM-5 zeolite are relatively homogeneous. The differential heat of adsorption of ethanol is, on average, ~ 10 - ~ 12 kJ/mol higher than that of methanol $Q_d$ in NH$_4$ZSM-5, which corresponds to an increase in heat in the CH$_2$ group.

The isotherm of ethanol adsorption in zeolite NH$_4$ZSM-5 is practically saturated at $a = 3.1$ mmol/g. The adsorption isotherm is visible at the initial stage of saturation, as well as in the presence of strong centers of ethanol adsorption. The isotherm has flexibility at $a \sim 2.25$ mmol / g. If we equate the density of ethanol in the zeolite to the normal liquid level at the test temperature and calculate the volume occupied by ethanol molecules during saturation, it becomes clear that the ethanol channels NH$_4$ZSM-5 are filled by ~ 96%.
The isotherm of ethanol adsorption in zeolite NH4ZSM-5 is described by the three-dimensional equation of TOMF (theory of volumetric filling of microgravity).

\[
a = 0.992 \exp\left(-\frac{A}{19,30}\right) + 1.442 \exp\left(-\frac{A}{10,70}\right) + 0.916 \exp\left(-\frac{A}{2.79}\right)
\]

(1)

In methanol, a slight decrease in the initial isothermal point leads to a sharp increase in pressure to -8.28 due to the interaction of the active centers of the zeolite with hydroxyl groups in the molecules of methanol and ammonium cations due to the interference of secondary adsorbates. This indicates the presence of strong centers of influence, as is observed in the case of a zeolite with a large number of cations in the initial region due to the presence of strong centers of the zeolite.

As can be seen in Figure 2, the values of the theoretical calculated data overlap with the experimental data, and for a complete description of the isotherm, it is sufficient to divide this equation into isotherms of three parts.

The isotherm of adsorption of methanol on NH4ZSM-5 is similar to the isotherm of adsorption of ethanol, but differs from each other in the insignificant value of adsorption at saturation. Although the
The essential difference between methanol and ethanol is that NH₄ZSM-5 lacks hydrophilic centers, with prolonged adsorption, the alcohol molecule saturates almost the entire channel and various parts of the NH₄ZSM-5 zeolite.

![Figure 3](image)

**Figure 3.** Differential entropy of adsorption of methyl and ethyl alcohols at 303 K on NH₄ZSM-5 zeolite.

The molar differential entropy (ΔSd) of alcohol adsorption is the isotherm and differential heat of adsorption according to the Gibbs-Helmholtz equation:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-\Delta G - \lambda + A}{T}$$  \hspace{1cm} (3)$$

Where λ is the heat of condensation, ΔN and ΔG are the change in enthalpy and free energy during adsorption during the transition from the standard state to the adsorbed one.

The entropy diagram is shown in figure 3. The molar differential entropy of ethanol adsorption has a wavy shape. Starting from -420.5 J/mol K, the differential entropy at low saturation changes from ~2.9 mmol/g to ~3 mmol/g, which is formed as a result of the adsorbate-adsorbate interaction. The lowest minimum value on the ethanol differential entropy curve indicates the firm arrangement of ethanol molecules in the zeolite channels and their intersections. The molar differential entropy of adsorption of methanol increases from -250 to -100 J/mol K, that is, from a very small minimum to a sharply higher value. This is due to the fact that the primary methanol molecules adsorbed in the zeolite channels form an ion-molecular complex with ammonium active centers, as a result of which the entropy curve is below the entropy of liquid methyl alcohol. As the degree of saturation increases, the entropy value sharply increases from the entropy of the liquid to the entropy of the vapor. The average integral values of entropy are correspondingly lower than the liquid value at ~84.34 J/mol K. Thus, the differential and integral entropy indicate the state of motion of each adsorbed alcohol molecule in the zeolite.

It can be seen from the graph that ethyl alcohol binds more strongly to the active site than methyl alcohol. In zeolite NH₄ZSM-5, the equilibrium time of adsorption of ethyl alcohol molecules at the intersection of zigzag channels and straight channels initially starts from 9.38 hours, where the
adsorption value is 0.059 mmol/g. Adsorption takes about 7 hours with an equilibrium time in the range of 0.26-0.35 mmol/g. In this case, the equilibrium time is 4.38 hours, and the adsorption is 0.94 mmol/g.

Figure 4. Equilibrium time of adsorption of methyl and ethyl alcohols at 303 K on NH₄ZSM-5 zeolite.

When the adsorption reaches 2.5 mmol/g, the equilibrium time gradually decreases and reaches equilibrium after 3 hours. After passing 2.5 mmol/g, the equilibrium time sharply decreases to 1.42 hours. The equilibrium of the methyl alcohol molecules (up to 0.58 mmol/g) occurs very slowly, and then sharply accelerates. In this case, the equilibrium time is reduced from 8.4 hours to 1.6 hours. During the initial adsorption, it takes a long time for the strong binding of alcohol molecules to active sites. At later stages, the binding of the adsorbate to the adsorbate takes less time (1-2 hours). The decrease in the time of adsorption equilibrium by 30 minutes at the final stage is explained by the fact that as a result of the interaction of completely adsorbed molecules with non-adsorbed molecules in this adsorption volume, they remain in a vapor state.

4. Conclusion
The differential heat of adsorption of ethanol in zeolite NH₄ZSM-5 has the shape of a wavy step. Initially, the differential heat of adsorption is 186.40 kJ/mol. A decrease in the differential heat of adsorption is observed until the adsorption reaches 0.57 mmol/g. A total of 3 mmol/g ethanol is adsorbed on this zeolite. The adsorption isotherm was described by the TOZM equation. It can be seen from the entropy lines that ethanol is very strongly adsorbed into the zeolite channels. In the zeolite matrix, ethanol forms an unexcited state, that is, the entropy of a solid. The average integral entropy is -167.89 J/mol·K. The adsorption equilibrium time is initially long; gradually the adsorption equilibrium time decreases, decreasing to several hours at the end of the process.

References
[1] Abdulkhaev T D, Kuldasheva Sh A and Rakhmatkarieva F G 2019 Differential heat and adsorption isotherm of carbon monoxide in zeolites of the NH₄ZSM-5 type Journal of Chemistry and Biology 11(65) 77-9
[2] Abdulkhaev T D, Kuldasheva Sh A and Yakubov Yu Yu 2019 Interaction of methanol molecules
with active centers and channels of zeolite (NH₄)₁₃₅ZSM-5 Journal of Chemistry and biology 8(62) 52-6

[3] Abdulkhaev T D, Kuldasheva Sh A and Yakubov Yu Yu 2019 Ethanol adsorption energy in pentacyl type zeolite International Journal of Advanced Research in Science, Engineering and Technology 6(11) 11747-50

[4] Abdulkhayev T D, Kuldasheva Sh A and Yakubov Yu Yu 2019 Differential entropies of water adsorption in zeolite NH₄ZSM-5 LXIV International correspondence scientific and practical conference “International scientific review of the problems and prospects of modern science and education” (Boston: USA) 7-8

[5] Abdulkhayev T D 2019 Differential entropies of water adsorption in zeolite NH₄ZSM-5 XV international scientific specialized conference international scientific review of the problems of natural sciences and medicine (Boston: USA) 13-7