Adsorsation of Metanol $H_{3,25}$ZSM-5in Cheoliti

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ABSTRACT . In this articleseveral studies conducted around the world have mainly covered the structure of the zeolites and their position on the cations. However, the mechanism, thermodynamic properties of the adsorption processes of aromatic, quadrupole, polar and non-polar molecules are not well studied, and information about them is scarce. Apart from these, the adsorption process is mainly done on X-ray and spectroscopy methods, and there is a lack of data on scientific research in calorimetry.

KEYWORDS:NZSM-5 xeolite, methanol, ion-molecular complex, adsorption isotherm, differential heat, entropy and thermokinetics.

I. INTRODUCTION

Complete thermodynamic characteristics (ΔH, ΔF andΔS) and isotherms of adsorption of the alcohol molecule in the NZSM-5 zeolite were obtained and proved on the basis of two- and three-dimensional mathematical equations of the microwave volume saturation theory (MHTN);

The adsorption of methanol vapor adsorption, differential heat, differential methanolentropy, and thermokinetics in NZSM-5 zeolite at 303K were determined. The adsorption isotherm was processed by three-dimensional MHTN (microwave theory of saturation). Based on the data obtained, the complete adsorption mechanism of methanol vapor adsorption from primary to saturated vapor pressure in dehydrated zeolite was identified.

Currently, ZSM-5 zeolites are used in a number of developed countries as a catalyst for obtaining octane fuel from petroleum products. In addition, the hydrogen form of ZSM-5 zeolites is also used as a catalyst for the production of non-oil products, such as octane gas above methyl alcohol. Therefore, there is a growing interest in studying the adsorption and catalytic properties of zeolites of this type. At the same time, small methyl alcohol molecules increase the amount of branched chain hydrocarbons due to the overlap of the ZSM-5 zeolite at the intersection of straight and zigzag ducts, resulting in higher octane content in gasoline [2]. In particular, the molecules of alcohol, which are adsorbed for probe, help to reveal the bifunctional properties of hydrophobic-hydrophilic properties in zeolites. In view of the foregoing, we refer to the biophysicist Patran J. We aimed to study the interaction of methanol molecules with active centers and channels of the NZSM-5 zeolite synthesized with almost perfect defect from (Million, France) [3]. The processing of high silicon minerals in fluoric environments results in the synthesis of ZSM-5 zeolite. By processing ammonium salts active centers of the zeolite anologues directly synthesized, catalytic adsorbents with high adsorption activity of +3.25 ion per each elemental cell (N) are formed.

Prior to the experiment, the sample was heated for 10 h at 723K under vacuum 10-4 Pa. The experiment was conducted using an adsorption-calorimetric device and method [1]. Adsorption heat and isothermal values were calculated at a temperature of 303 K.

II. SIGNIFICANCE OF THE SYSTEM

In this articleseveral studies conducted around the world have mainly covered the structure of the zeolites and their position on the cations.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

Investigation of the interaction of adsorbed alcohol molecules on the NZSM-5 zeolite using the adsorption-stheiometric method based on the results obtained in the laboratory using a high-vacuum adsorption device enables the use of completely new approaches in the calculation of adsorption chemical technology processes.

IV. EXPERIMENTAL RESULTS

When ZSM-5 zeolites are synthesized by base salts, there are defects in the form of hydroxyl groups of NZSM-5 and ZSM-5 analog crystals, which contain different metals at the active centers [2]. The adsorption of methyl alcohol is also very effective in determining the degree of defectability in these zeolites.

The adsorption from the early stages of adsorption is due to the high adsorption rate of 128-80 kJ/moldue to the unimpeded interaction of methyl molecules with ammonium cations at the active centers at the intersection of the zeolite channels. The interaction of methoxyl groups with high negative charge and oxygen atom grid due to the presence of strong hydrogen bonds in the alcohol molecule depends on the thermal generation of H^+cations 100 - 75 kJ/mol. The state of the adsorbed methyl alcohol NZSM-5 is confirmed by a study using a high-vacuum adsorption device.

The adsorption of methanol in the NZSM-5 zeolite is 3,54mmol/g (Figure 1). The limited amount of adsorption (V_o) for methanol is 0,138 cm^3/g (theoretical $V_o = 0,184$ cm^3/g. A reduction of 23% of the requested volume of zeolite for methanol can be interpreted as the result of methanol exhibiting its hydrophobicity in OH groups and the "chain" in the CH_3 group. As a result, CH_3OH molecules are not strongly adsorbed to the entire micropore volume: adsorption occurs directly at the zigzag channels and their intersections.
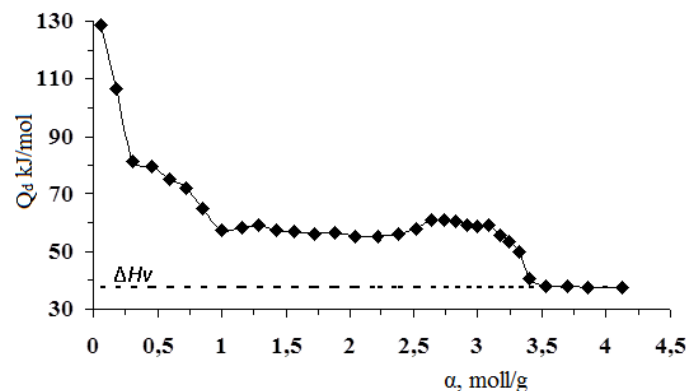
**Fig- 1. Differential adsorption heat of methyl alcohol in zeolite H$_{3,25}$ZSM-5 at 303 K.
Horizontal dashed line - heat condensation at 303 K.**

Only non-properly aligned chain molecules of n-alkanes can strongly complement the adsorption volume and their liquid aggregate volume is 0,184 cm^3, close to the crystallographic value of the zeolite channels and pores. The dimensionless form of our sample shows the theoretical absorption of CH_3OH for n-alkane, which differentiates it from the previously studied ZSM-5 [3], indicating a 15% lower value associated with the presence of amorphous phase.

The slight increase in the isothermal point in the initial part indicates a sharp increase in pressure due to the secondary adsorption interference due to the interaction of ammonium cations with hydroxyl groups in the methanol molecules of the active centers in the zeolite. This indicates the presence of strong centers of zeolite, as observed in the case of a defective zeolite with a large number of cations in the initial region due to the presence of strong centers. In addition, the sharp increase in the isotherm, that is, these curves are caused by the manifestation of the adsorbate-adsorbate systems in the nanoparticles of the zeolite that are characterized. The adsorption isotherm of methanol (Fig.2) is well described by the equation for microwave volume saturation theory (MHTN)[4,5]. The basic MHTN equation for the adsorption processes studied is as follows:

$$a = a_0 \cdot \exp\{-[A/E]^n\} \quad (1)$$The formula is calculated as follows

where α is the amount of adsorption of mmol/g; a_0 - The measured adsorption at mmol/g, A = PTln (По / П) mole of gas (kJ/mol), the characteristic energy of the adsorbent (kJ/mol); n is a parameter related to the pore space of the adsorbent. The adsorption isomer of methanol in the NZSM-5 adsorbent is characterized by the three-axis MHTN equation. The parameters of the first-time equation for the methanol- NZSM-5 adsorbent are $A_{01}= 1,176$ mmol/g, $E_1 = 22,34$ kJ/mol, and $N_1 = 4$; for the second period, $A_{02} = 1,743$ mmol / g, $E_2 = 8.48$ kJ / mol and $N_2 = 5$; for the third period, $A_{03} = 1,453$ mmol/g, $E_3 = 1.75$ kJ/mol and $N_3 = 1$.

$$a = 1,176\exp[-(A/22,34)^4] + 1,743\exp[-(A/8,48)^5] + 1,451\exp[-(A/1,75)^1] \quad (2)$$

As shown in Figure 2, it is sufficient to divide this equation into three parts isotherms for the overlapping of theoretical computational data with experimental data and for a complete description of the isotherm. The isothermal adsorption of methanol adsorption to NZSM-5 is similar to that of ethanol adsorption isotherm, with saturation constraint being insufficient. Although the significant difference between methanol and ethanol between Vo is due to the lack of sufficient hydrophilic centers in NZSM-5, the alcohol molecule absorbs almost all channels and various parts of the NZSM-5 zeolite over long periods of adsorption.
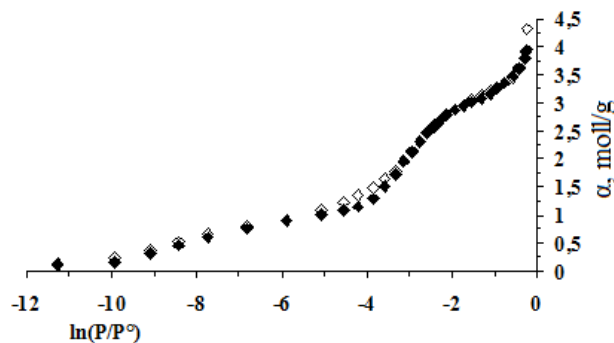

Figure 2 - Isoterm of methyl alcohol adsorption in zeolite $H_{3,25}ZSM-5$ at 303 K.
◊ - Experimental data.♦ - the Points calculated by means of TOZM equations.

The differential thermal value of the methanol adsorption study drops sharply to 0,31mmol and the heat is 81,5 kJ. Heat volume with 0,31-1 mol/g goes unchanged between 81,5 and 57,4 kJ/mol and then drops sharply until the corresponding alcohol is condensed. The adsorption channels of the NZSM-5 zeolite are a nanowire system, where the collector is represented by ion-molecular complexes, "adsorbate-adsorbate" and "adsorbate-wall" bonds. Zero adsorption of methanol at ~37,69 kJ/mol, respectively. For NZSM-5, these values were more than 10 kJ/mol. Consequently, the systematic deficiencies of the adsorbent completely affect the adsorption heat and the extrapolation method for zero saturation can lead to significant errors in the adsorption of molecules. Thermal composition of the CH_2 group incubation is 10,0 kJ/mol. The adsorption of water in the NZSM-5 zeolite according to the heat scheme is as follows: $Q_{H2O}=Q_{CH3OH}-Q_{CH2}=37,69–10,0=27,69$ kJ / mol. Direct calorimetric measurements confirmed this value, which is almost twice lower than the condensation heat at 303 K (54,5kJ/mol). This result reveals the excellent hydrophobicity of the NZSM-5 cellolite.

Molyar differential entropy (ΔS_d) of alcohol adsorption is isotherms and adsorption differential heat according to the Gibbs-Helmholtz equation:

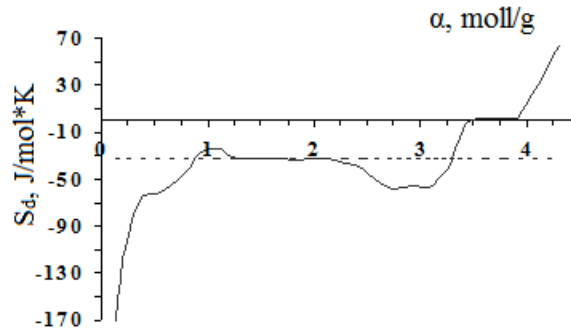$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T} \qquad (2)$$

Figure 3 - Differential mole entropy of methyl alcohol adsorption in zeolite $H_{3,25}ZSM-5$ at 303 K. The dashed line is the mean-size integral entropy. Entropy of liquid methyl alcohol is taken as zero.

The entropy diagram is shown in Figure 3. Molar Molecular Differential Entropy of Methanol Adsorption From -170 to -66,29 J/mol*K, which is sharply above the very small minimum, as mentioned above, the primary methanol molecules adsorbed to the zeolite channels form a strong ionic molecular complex with no barrier ammonium active centers. the entropy curve is below the liquid methyl alcohol entropy. And as this value increases with saturation, the entropy value increases sharply from the liquid entropy to the steam entropy. The mean integral values of entropy are much smaller than the fluid values -32,77J/mol*K, respectively. Thus, differential and integral entropy indicate the behavior of each adsorbed alcohol molecule in the zeolite.
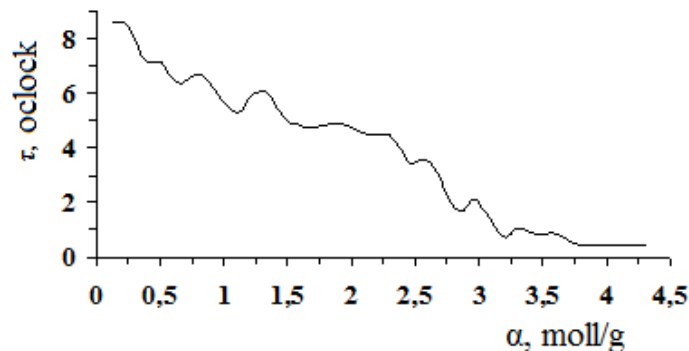

Figure 4 - Time to establish adsorption equilibrium depending on the amount of adsorption of methyl alcohol in the zeolite $H_{3,25}ZSM-5$ at 303 K.

In the NZSM-5 zeolite, the adsorption (up to 0,38mol/g) of the methyl alcohol molecules at the intersection of the zigzag-like channels and straight channels is slow and then accelerated sharply.

V. CONCLUSION AND FUTURE WORK

At the same time, the equilibrium time decreases from 6,71 to 0,74 hours. In the initial adsorption, it takes a long time to form a strong bond of alcohol molecules with active centers. In later stages, adsorbate-adsorbate bonds are less frequent (0,5-1 h). In the final step, the adsorption decrease in the equilibrium time by 30 min is explained by the fact that the adsorbed molecules retain their vapor state as a result of the interaction of molecules not fully adsorbed.

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