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Ethanol Adsorption Energy in Pentacyl Type Zeolite

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ABSTRACT: The isotherm, differential heat, isotherm, entropy differential, and thermokinetics of ethanol adsorption in zeolite (NH4) 1,35ZSM-5 were measured at 303K. Based on the data obtained, a detailed mechanism for the adsorption of ethanol in zeolite (NH4) 1,35ZSM-5 from zero filling to saturation is disclosed. Adsorption isotherm processed by the TOZM equation

KEYWORDS: Isotherm, adsorption heats, entropy, thermokinetics, ion-molecular complexes, zeolite (NH4) 1.35ZSM-5, ethanol, adsorption calorimetry

I. INTRODUCTION

At present, nanoporous molecular sieves, zeolites, are one of the most demanded materials for selective adsorption and separation in the world. They are of interest because of the ability to control their texture (pore size and architecture), chemical properties (Si / Al ratio) and the nature of extra-lattice cations, which affect the adsorption and catalytic properties of crystalline materials, controlled by the structure, number and nature of the active centers. However, the structural specifics of zeolites are still unclear, in particular, those related to the problem of the dispersal of active centers, the mechanism of adsorption of polar and nonpolar molecules, the nature and participation of defects in adsorption. [1]

II. SIGNIFICANCE OF THE SYSTEM

In this articles isotherm, differential heat, isotherm, entropy differential, and thermokinetics of ethanol adsorption in zeoliteThe 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

The gas chromatographic method and temperature-programmed desorption investigated the adsorption and desorption of ethanol, water, n-hexane and n-octane on silicalite. According to these data, the sorption volume of silicalite for ethanol adsorption is ~ 0,136 cm3 / g, not negativized, which is close to the Vs value obtained from methanol adsorption. The initial activation energy of desorption (Ed) of ethanol is ~ 65 kJ / mol at a = 0,26 mmol / g. Do not negate the behavior of the Ed curves of ethanol on silicalite; The amount of ethanol adsorbed on silicalite, respectively, at 298 K was 13,8 molecules / e. (or a ~ 2.39 mmol / g), at 333 K, 11,3 molecules / e. (a ~ 2.0 mmol / g), at room temperature, 14,0 molecules / e. (a ~ 2.43 mmol / g), and on the HZSM-5 zeolite (Si / Al = 12) at room temperature ~ 16,5 molecules / e. (a ~ 2,84 mmol / g). [2]

IV. EXPERIMENTAL RESULTS

Zeolite ZSM-5 crystallizes in the rhombic system (monoclinic P21 / n) with the crystal lattice parameters, a = 2.01, b = 1.99 and c = 1.33 nm. The crystal lattice parameters of the zeolite (orthorhombic system Pnma) a = 2.006, b = 1.980 and c = 1.33 nm. The composition of the unit cell of the primary crystals of silicalite can be expressed as / 4TPAON96SiO2 /. As a result of calcination of the product at 773 K, the organic part is removed and a homogeneous

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microporous adsorbent of the composition 4OH96SiO2 is obtained. Zeolites ZSM-5 and ZSM-11 in Na-form have a unit cell composition, which is expressed by the formula

$$K_nAl_nSiO_{96-n}O_{192}{\sim}16H_2O$$

where n <27 for ZSM-5 and n <16 for ZSM-11. The crystal lattice density of ZSM-5 zeolites is 17,9 per 1 nm-3 (T = Si + Al). [3]

After the direct synthesis of high-silica zeolites using quaternary ammonium bases (ZSM zeolite series), the synthesis of the pure silica analogue of ZSM - silicalite, the catalytic conversion of lower alcohols to high-octane gasoline on zeolite ZSM-5, interest in studying their adsorption and catalytic properties has sharply increased. It is of interest, in particular, to elucidate the cause of the manifestation of hydrophobicity of high-silicon zeolites.

We set a goal - to probe the structure of the adsorbing cavities of almost defect-free silicalite synthesized in a fluoride medium (group of Prof. Pataran J., Milleus, France) using bifunctionally (hydrophobic-hydrophilic) interacting methanol and ethanol molecules.

The differential heats of ethanol adsorption on zeolite NH4ZSM-5 are shown in Fig. 1. Q_d of ethanol, as well as in the case of methanol, in the initial filling region (up to 0,52 mmol / g) is significantly overestimated (reaching 150 kJ/mol).

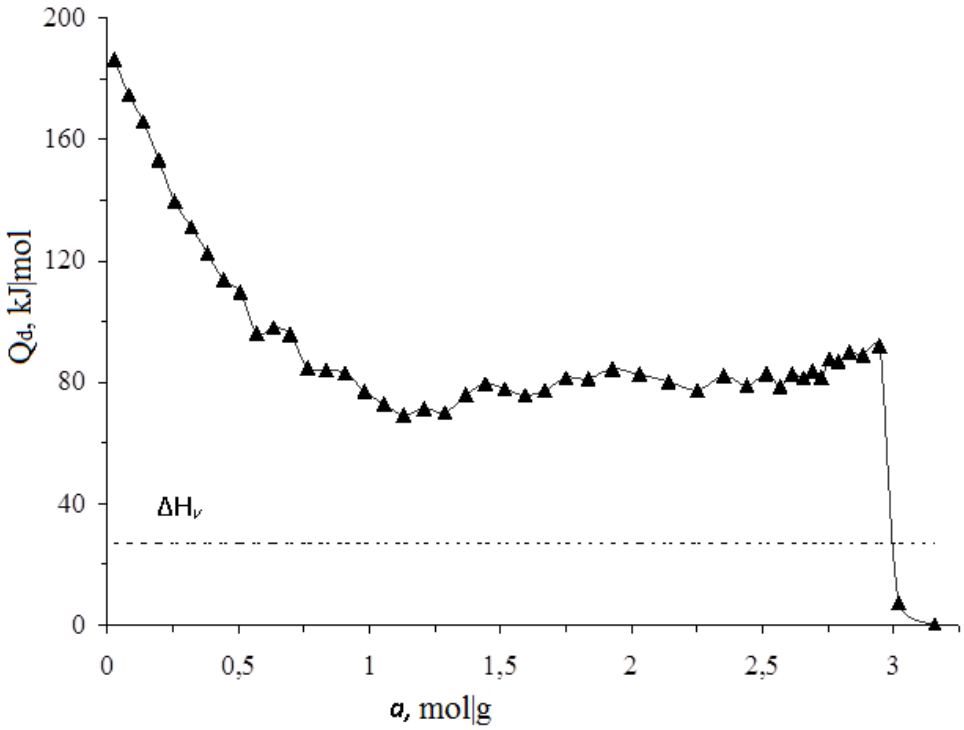

Fig. 1. Differential heat of adsorptionand ethanol in zeolite NH4ZSM-5 at 303 K.

The Q_d curve of ethanol on NH4ZSM-5 zeolite has four sections: the first is in the filling region from 0 to 0,57 mmol / g, ethanol molecules are adsorbed with increased heat, and Q_d drops from 186,4 to 96,25 kJ / mole; the second is in the region from a = 0,52 to ~ 1.13 mmol / g, where ethanol molecules are adsorbed with constant heat of ~ 96-69 kJ / mol; the third - in

ranges from a = 1,13 to 1,59 mmol / g, the Qd curve forms two plateaus (-69,15 kJ / mol and ~ 79,5 kJ / mol) and falls from 80 to ~ 75 kJ / mol at a = 1,59 mmol / g; and finally, the fourth - in the region from a = 1,6 to 2,25 mmol / g, where the heats are constant and equal to ~ 76 kJ / mol. Next, the Q_d curve passes through a small maximum (~ 92,16 kJ / mol) at ~ 2,95 mmol / g, and then drops to the heat of condensation at a ~ 3 mmol / g. The presence of a maximum on the Q_d curve of ethanol is due to the intermolecular interaction of the adsorbed molecules with each other. As in the case of methanol, the Q_d curve has

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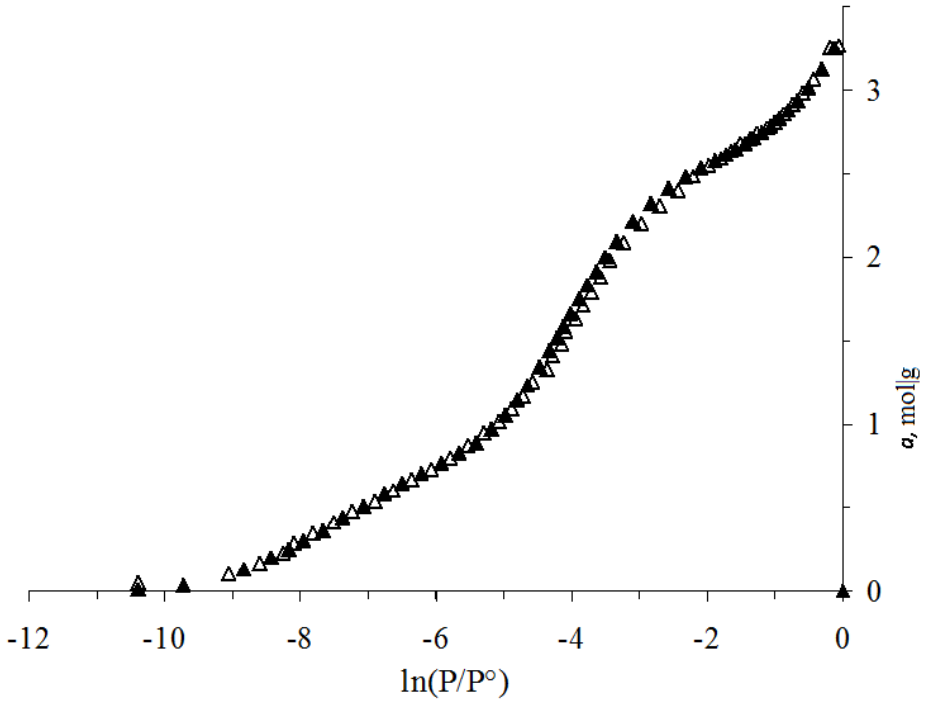

Fig. 2. Ethanol adsorption isotherm in zeolite NH4ZSM-5 at 303K. ▲ experimental data and Δ calculated using the theory of micropore volumetric filling (POSM)

Stepped view, although the 4th step is smoothed. Adsorption of 2.25 mmol / g of ethanol corresponds to the specific interaction of ethanol with ammonium cations. Further, adsorption proceeds in the remaining volume of zeolite channels. From the considered differential heats of adsorption of polar molecules of water, methanol and ethanol, it is seen that the change in heats is stepwise, which indicates a discrete homogeneity of the NH4ZSM-5 zeolite cavities.

The differential heats of ethanol adsorption are on average ~ 10 - ~ 12 kDc / mol higher than the Qd of methanol on NH4ZSM-5, which corresponds to the increment of heat on the CH2 group.

The ethanol adsorption isotherm on the NH4ZSM-5 Neolithic and the triggers developed along the relative pressure axis of its part are shown in Fig. 27. The isotherm is brought to almost saturation (a = 3.1 mmol / g at P / Ps = 0.75) o. About the same amount of ethanol is adsorbed on HZSM-5 zeolite (Si / Al = 12) at room temperature.

In the initial filling region, the adsorption isotherm is convex, as well as in the case of methanol (Fig. 2), indicating the existence of strongly interacting adsorption centers. Further, the isotherm has an inflection at a ~ 2.25 mmol / g. The isotherm of ethanol adsorption on zeolite NH4ZSM-5 corresponds to type 1 according to Brunauer's classification 1.

If we take the density of ethanol in zeolite the same as that of a normal liquid at the test temperature and calculate the volume occupied by ethanol molecules at saturation, it turns out that ethanol fills the channels of NH4ZSM-5 by ~ 96%. Thus, the sorption volume of zeolite calculated from the adsorption of ethanol and methanol is the same and equal to 0.177 cm3 / g. The adsorption isotherm of ethanol on zeolite NH4ZSM-5 is described by the two-term equation of TOZM from small fillings to ~ 3 mmol / g:

a = 0.992exp [- (A / 19,30) 5] + 1,442exp [- (A / 10,70) 5] + 0,916exp [- (A / 2.79) 1] (1)

Figure 2 shows the isotherm of ethanol adsorption on NH4ZSM-5 in semi-logarithmic coordinates. As can be seen from the figure, the experimental data are in good agreement with the calculated ones.

The molar differential entropy of ethanol adsorption on zeolite NH4ZSM-5, deposited from the entropy of liquid ethanol, has a wavy appearance.

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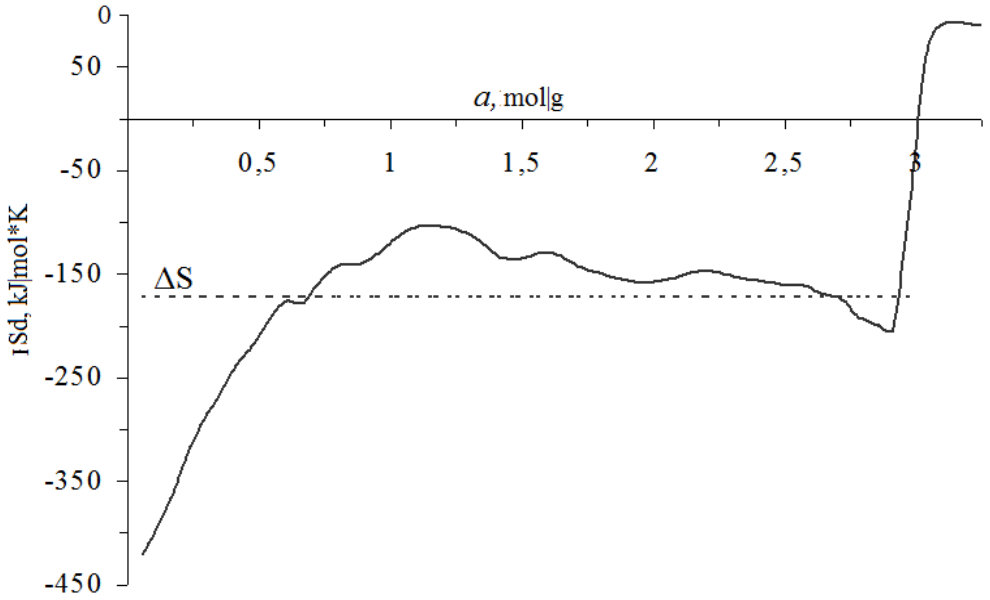

Fig. 4. The time to establish adsorption equilibrium depending on the amount of ethanol adsorption in zeolite NH4ZSM-5 at 303K.

V. CONCLUSION AND FUTURE WORK

The dependence of the time for the establishment of adsorption equilibrium on filling is shown in Fig. 1. It can be seen that up to an adsorption value of 0,352 mmol/g, the process proceeds slowly (on average, τ = 8 h). It's connected with.

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