Investigation of *ortho*-xylene adsorption in H$_{3.25}$ZSM-5
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Изучение адсорбции *орто*-ксилола в цеолите H$_{3.25}$ZSM-5
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Abstract: *in present investigation the full thermodynamic functions of ortho-xylene adsorption in H$_{3.25}$ZSM-5 zeolite have been studied in details. The correlation between adsorption-energetic characteristics and crystal chemical structure of H$_{3.25}$ZSM-5 has been found. The mechanism of ortho-xylene adsorption in H$_{3.25}$ZSM-5 from zero to saturation was discovered.*

Аннотация: *в работе детально изучены полные термодинамические характеристики адсорбции орто-ксилола в цеолите H$_{3.25}$ZSM-5. Найдена корреляция между адсорбционно-энергетическими характеристиками и кристаллохимическим строением H$_{3.25}$ZSM-5 и выявлен молекулярный механизм адсорбции орто-ксилола во всей области заполнений.*

Keywords: *isotherm, differential heat and entropy, H$_{3.25}$ZSM-5, ortho-xylene, adsorption calorimetry.*
Ключевые слова: *изотерма, дифференциальные теплота и энтропия, H$_{3.25}$ZSM-5, орто-ксилол, адсорбционная калориметрия.*

Localization adsorbed molecule in the porous system of zeolites is the most important for conception of sorbate-sorbate and sorbates- adsorbent interaction, which effect on catalytic, adsorptive properties of the system in the final. Heightened interest has been observed for commercial attractive process of xylene isomers division by membrane from ZSM-5 in recent years [1, 2]. However, limited numbers data existing in the publication does not allow to predetermine on compound interaction between the nanopores of the structure ZSM-5 and xylene molecule [3].

Para-xylene is the studied, kinetic diameter is equal to 0.6 nm [4]. H$_{3.25}$ZSM-5 adsorbs para-xylene in quantity about 8 molecules on unit cell (mole/unit cell), filling all free spaces of the H$_{3.25}$ZSM-5.

It was presented that interest to investigate the adsorption of (a) ortho-xylene, kinetic diameter which is equal to 0.68 nm. Zigzag channel of H$_{3.25}$ZSM-5 zeolite is elliptical with dimensions of 6.2 and 4.6 Å. Therefore, the adsorption is possible only in case of strong deformation of the H$_{3.25}$ZSM-5 structure.

Unit cell of the investigated HZSM-5 zeolite contains 3.25 protons. Differential molar adsorption-calorimetric studies of ortho-xylene adsorption in the H$_{3.25}$ZSM-5 zeolite were conducted on the instrument described in [5, 6]. Using the method of compensation of heat flows by Pelter effect allowed more than one order to increase the accuracy of measuring the heat of adsorption. Adsorptive measurements were carried out on universal high-vacuum volume machinery, allowing to carry out adsorptive measurement and adsorbate dose with high precision.

Before the steam inlet of water, sample was heated and subjected to high vacuum pumping at 450º C for 10 hours. Before measuring water carefully cleaned and degassed.

Figure 1 shows the differential heat of ortho-xylene adsorption (Q$_d$) in H$_{3.25}$ZSM-5 zeolite. The curve has a complicated stepped form, which is interrupted by wavy views. In the future, these waves on the curve for simplicity we will call conditional steps, their appearance is also connected with structural changes in the zeolite matrix in the interaction of the adsorbate - adsorbent. In general there is a good correlation between the steps and the regularities of ortho-xylene adsorption with zeolite. The high-energy area extends to 0.53 mmol/g, which corresponds exactly to the number of protons in the H$_{3.25}$ZSM-5 unit cell.

In this area, the heat is reduced from 130 to 50 kJ/mol. Second is relative low-energy area extending from 0.52 to 1.04 mmole/g, i.e. it is also equal to the number of adsorbed molecules in the first section of ortho-xylene molecule per unit cell. It is characterized by a slightly lower heat of adsorption from 50 to 43 kJ/mol. It is evident that there is bond between the two areas. Qd stepped curve in the high-energy area indicates heterogeneity of adsorption centers with which the ortho-xylene forms π-complexes.

Depending on the acidity of these centers, which is combined with the coordination unsaturated protons, the adsorption energy is changed. As it is possible to count the number of centers with certain acidity. The growth of the heat of adsorption is usually connected with the imposition on the heat of adsorption of the adsorbate-adsorbent heat of adsorption adsorbate-adsorbate. However, between the molecules of ortho-xylene, located in

the crosshairs of channels, there is a sufficiently large distance to reveal the effect of the interaction of the adsorbate-adsorbate. The observed increase in the heat of adsorption after a = 0.2 mmol/g, apparently, due to the structural changes occurring in the zeolite. The sharp reduction of the heat of adsorption in comparison with the heat of adsorption of para-xylene in the ZSM-5 to a = 0.2 mmol/g depended the loss of energy due to very close contact of the ortho-xylene with zeolite walls.
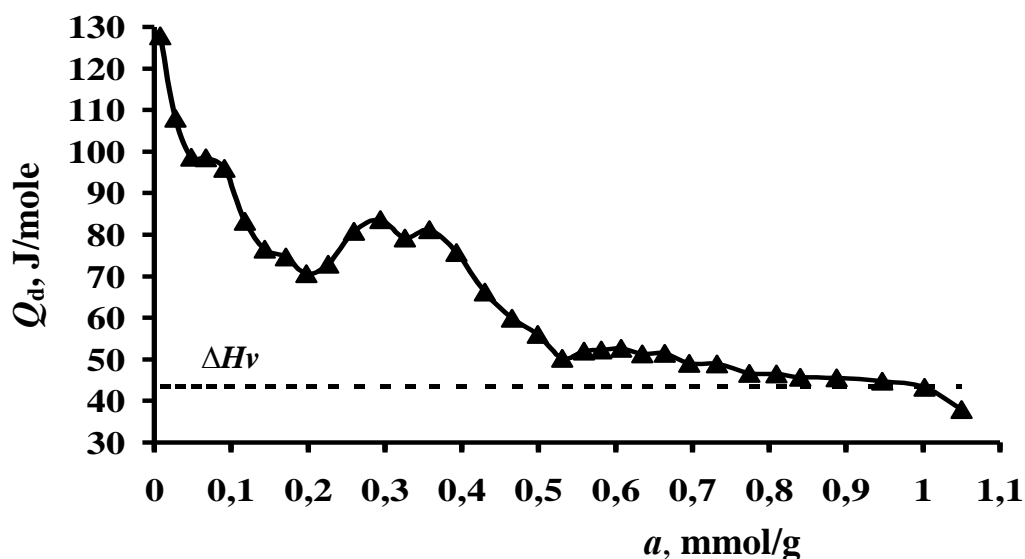

Fig. 1. The differential heat of adsorption of ortho-xylene in the $H_{3.25}ZSM-5$ zeolite at 303K. Dashed line is the heat of condensation of ortho-xylene at 303 K

It is known that ZSM-5 zeolite structure readily subjected to deformation during adsorption. It is possible that adsorption of adsorbate molecules partially expanded channels, leading to increase of heat due to more full value manifestation of the dispersion interaction of the adsorbate-adsorbent. Adsorption occurs in the second area with 34 kJ/mol heat lower than for adsorption of para-xylene in $H_{3.25}ZSM-5$ close to the heat of condensation of ortho-xylene 43.46 kJ/mol).
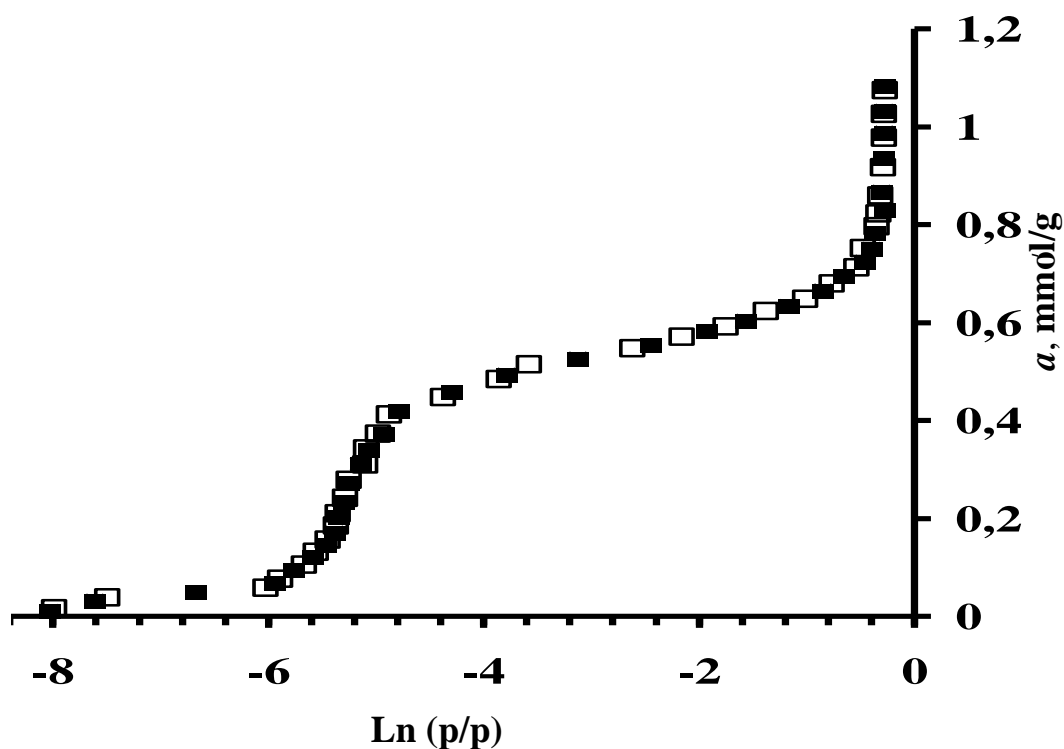

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Figure 2 presents adsorption isotherm of ortho-xylene in $N_{3,25}ZSM$-5 zeolite. The figure shows that at low fillings equilibrium pressure is very low, which is indicative of the strength of the resulting π-complexes. In accordance with the heats of adsorption isotherm it is also consisted of two areas. The first is high-energy (up to ~ 0.53mmol/g) - sigmoid, which is characterized by a sharp rise in the middle of the area.

The adsorption isotherm of ortho-xylene in the $N_{3,25}ZSM$-5 zeolite is completely described by a three-term equation VOM [7]:

$$a = 0,493\exp[-(A/13,63)^{10}] + 0,314\exp[-(A/3,79)^1] + 11,499\exp[-(A/0,17)^1],$$

where a is adsorption in mmol/g, $A = R \cdot T \cdot \ln (P°/ P)$, work of transfer 1 mmol gas from the surface (pressure P) in the equilibrium gas phase (P pressure).

Fig. 3 shows the dependence of the differential mole entropy of ortho-xylene on the adsorption value in silicalite.

The molar differential entropy of adsorption (ΔS_d) ortho-xylene is calculated from the isotherms and differential heats of adsorption according to the Gibbs equation - Helmholtz (adopted as zero entropy of liquid ortho-xylene):

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

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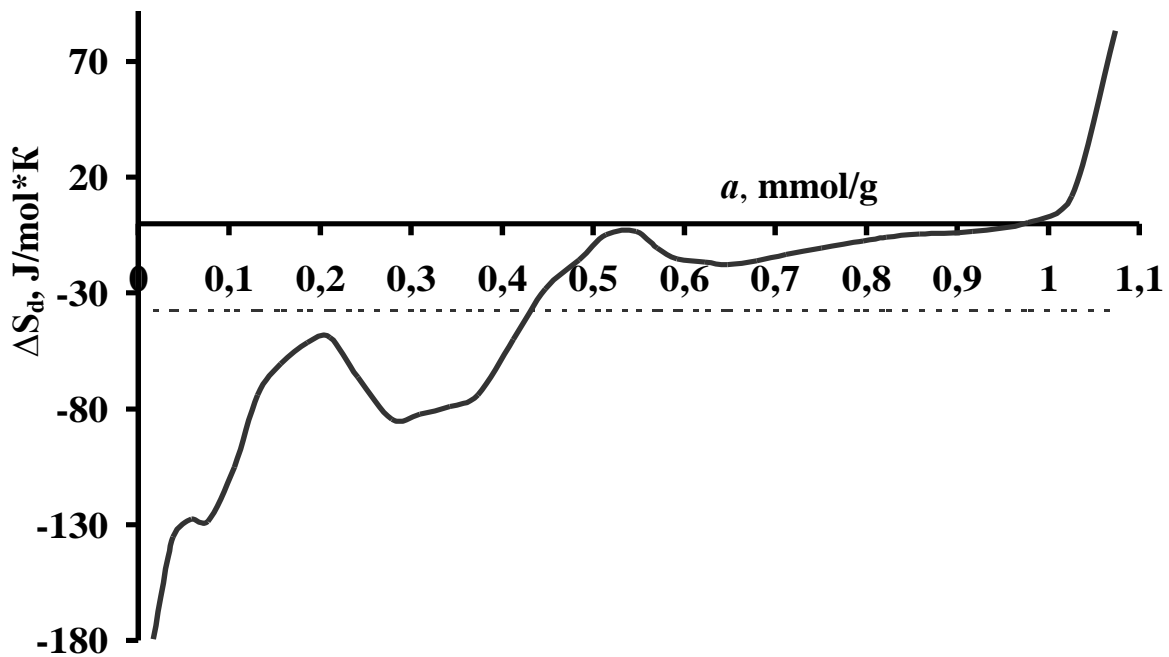

Fig. 3. The differential entropy of adsorption of ortho-xylene in N3,25ZSM-5 zeolite at 303K. Entropy of liquid ortho-xylene is taken as zero. The horizontal dashed line is the middle molar integral entropy.

The entropy of adsorption is also divided into two equal areas. To 0.53 mmol/g of entropy is wavy increased from - 180 J/mol * K to entropy of liquid ortho-xylene. In the second area entropy closes to the entropy liquid ortho-xylene. It is fact that area of strong adsorption is characterized by low values of entropy, which indicates on strong localization of the adsorbate in zeolite matrix and low - high values. However, in general, characteristic state of adsorbate in zeolite is integral middle molar integral adsorption entropy, which is equal to - 37.46 J/ mol *K, indicating that the locked state of ortho-xylene in the $H_{3,25}ZSM$-5 matrix.
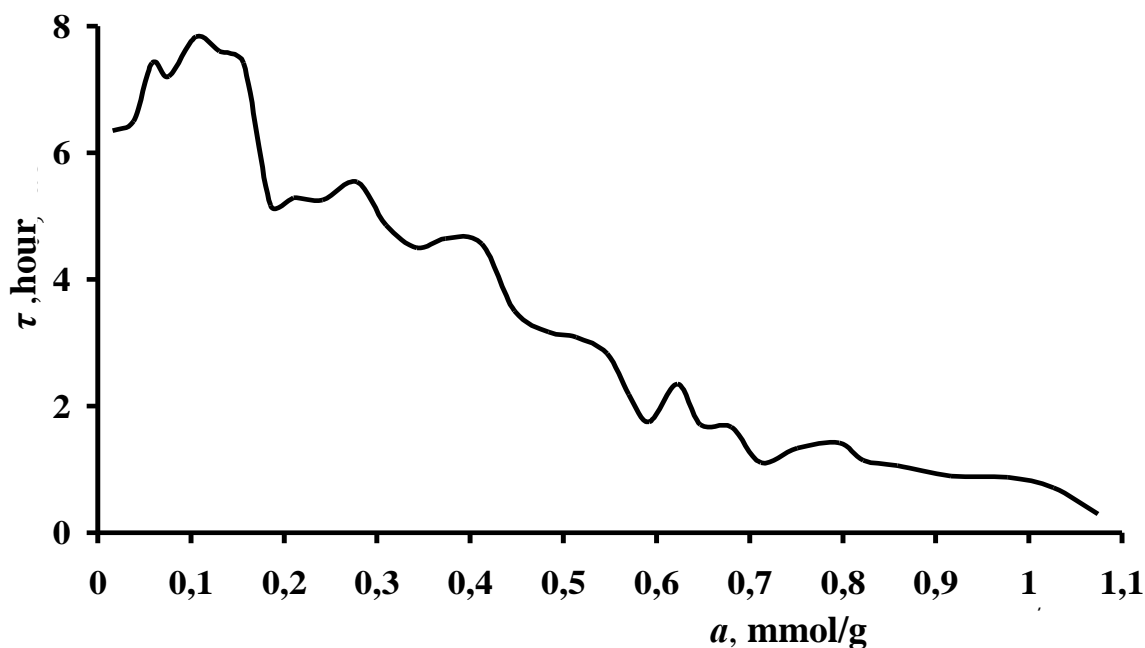
Fig. 4. Adsorption equilibrium time depending on the amount of adsorption of ortho-xylene in the $H_{3,25}ZSM$-5 zeolite at 303K

Dependence of adsorption interaction settling time on the adsorption wavy decreases from 6-8 hours to 15 minutes (Fig. 4). Delayed kinetics of adsorption in a first area connected with the difficulty of large molecules ortho-xylene advancement through channels having a markedly smaller cross section than the adsorbate.

Thus, the results obtained in this study confirmed the finding of earlier on the basis of study of differential heat of adsorption of ortho-xylene in silicalite (without cationic adsorbent) [8], that the adsorption of organic molecules, kinetic diameter exceeds the input into the zeolite window is possible in the case if the zeolite contains any organophilic center. Zeolite $H_{3,25}ZSM$- 5 adsorbs ortho-xylene in an amount equal to 2 molecules per proton, that is 75 % of the total sorption capacity.

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