ADSORPTION CHARACTERISTICS OF ZSM-5 ZEOLITE ANALOGUE BASED ON NATURAL MINERAL RAW MATERIALS

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Abstract. *Differential heats, isotherm, differential entropies and thyromimetics of trietilamin adsorption in the ZSM-5 zeolite were measured at 303K. The isotherm of adsorption was quantitatively reproduced on the basis of VOM theory. The detailed mechanism of trietilamin adsorption in ZSM-5 zeolite from zero filling to saturation was discovered.*
Keywords: *differential heats, isotherm, differential entropies, and thyromimetics, ionmolecular complexes, ZSM-5 zeolite, trietilamin, adsorption calorimetry.*

Introduction. The study of the adsorption properties of zeolites provides useful information about their structural characteristics and practical applications. Also, with the help of adsorption measurements, it is possible to obtain information about various factors related to the structure of a particular zeolite (for example, the size of channels, the size of pores, the amount of cations, etc.). The main focus is on the research of adsorption of various substances on ZSM-5 type zeolites. It can be seen that it is strongly dependent on the cations present in the adsorption structure in zeolites. Because the distance between the adsorption centers is very large, zeolite is very suitable for model research of adsorption capacity [1, 2]

Obtained results and their interpretation. On the basis of scientific research, we tested new sorbents based on mineral raw materials for cleaning oil industry products from waste. The tests were carried out in several stages, which are listed below.

The purpose of synthesizing adsorbents is to obtain new types of import-substituting and cost-effective adsorbents with highly effective adsorbent properties based on local raw materials. When obtaining adsorbents, samples of Angren kaolin enriched from local raw materials were treated with high temperature, cleaned with low-percentage, i.e. 1-10% NSl acid solutions, and various samples were taken. The obtained sample solutions were repeatedly filtered and the physico-chemical properties and thermodynamic properties of the obtained samples were studied. A sample of the new sorbent with its external appearance is a fine, polyfractional powder of light yellow color. Test samples were prepared from adsorbents for the necessary production facilities.

In the qualitative processing of petroleum products, their physico-chemical properties were determined and ZSM-5 type zeolite analogs synthesized from local raw materials (table-1) and adsorbates, aromatic substances, sulfur substances and nitrogenous compounds were selected as adsorbents. In order to determine the mechanism of adsorption of these studied molecules and the resulting ion-molecular complex, experimental tests were carried out in the production and technical laboratory of Chinaz Oil Refinery.

Table 1

Comparison of the chemical composition of imported, domestic and recycled ZSM-5 zeolite analogues

Sample	composition, mass. %					
	SiO_2	$A1_2O_3$	H^+	NH_4^+	Na^+	Other substances
ZSM-5 (import)	96,6	3,33	0,01	0,02	0,015	-
ZSM-5-1 analog-1 (local)	94,3	5,1	0,014	-	-	0,586
ZSM-5-2 analog-2 (local)	94,9	4,7	-	0,05	-	0,65
ZSM-5-3 analog-3 (local)	94,2	4,9	-	-	0,04	0,86
ZSM-5 type zeolite analogue was treated with 1-10% HCl acid	94,2	3,8	0,56	0,085	0,01	0,06

The test results of purification of automobile gasoline, diesel fuel, base oils and wastewater from harmful substances of Chinaz Oil Refinery to determine the adsorption properties of various compounds on new ZSM-5 zeolites are shown in the following table (table-2,3,4).

Table 2

The results obtained in the purification of diesel fuel at "Chinoz NQZ" with the help of ZSM-5 zeolite analogues in the purification of sulfur and nitrogen substances

№	Substance name	F.I, mg/l	Before cleaning (mg/l)	After cleaning (mg/l)
1	Sulfuric substances	0,10	0,5	0,10
2	Nitrogen compounds	0,3	0,8	0,05

Table 3

The results of the removal of sulfur substances and benzene using ZSM-5 zeolite analogs in the purification of automobile gasoline at "Chinaz NQZ" (maximum permissible concentration (F.I))

№	Substance name	F.I, mg/l	Before cleaning (mg/l)	After cleaning (mg/l)
1	Sulfuric substances	0,05	0,5	0,05
2	Benzene	5,0	11	5,0

Table 4

The results obtained from the treatment of base oils and waste water using ZSM-5 zeolite analogs at "Chinoz NQZ"

№	Substance name	F.I, mg/l	Before cleaning (mg/l)	After cleaning (mg/l)
1	ammonia	0,39	2,8	0,5
2	benzene	0,1	1,2	0,1
3	para-ksilol	0,15	3,5	0,1
4	n-penten	0,5	2,4	0,35

Based on the obtained results, it is possible to evaluate the new adsorbent positively, taking into account that it shows indicators even lower than the F.I values.

Adsorption properties of the synthesized sorbent were determined by microcolorimetric and Mag-Ben-Bakra devices, as well as the surface of porous channels on its surface, and positive results were obtained. Triethylamine was selected as the adsorbate to determine the outer surface. Taking into account the structure of the molecule, we can interpret it as follows: at the first stage, it is adsorbed on the external surface of the ZSM-5 analogue as a "plug", that is, one ethyl group sinks into the channel as an anchor; in the second step, the remaining two come to the surface and do not allow the molecule to enter the channel. If we take into account that the potential inside the channel is much higher than the potential outside, then this external structure of the adsorbate is very favorable from the energetic point of view. Because the trimethylamine ZSM-5 channels, partially entering the silicalite channel, are affected by the voltage fields that close the opposite walls [3].

Therefore, the heat of adsorption of the first point on the curve of the differential heat of adsorption of triethylamine in ZSM-5 analogue (Fig. 1) is 121.6 kJ/mol. The rest of the points show the adsorption in the entrance channels of the external surface with a sharp decrease. If we look at the surface of the outer surface, we can see its unevenness, which prevents the large molecule of triethylamine from fully interacting with all the outer atoms of the crystal, resulting in low temperatures. Adsorption is polymolecular, and the presence of a maximum in the curve indicates the transition from one adsorption layer to another.

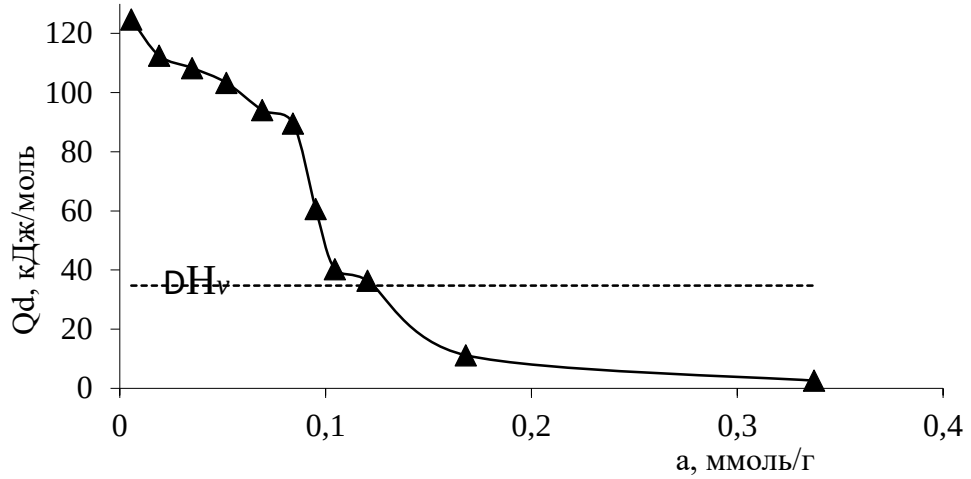

Figure 1. The values of the differential heat of adsorption (Qd) of triethylamine on the ZSM-5 zeolite analog at 303 K are presented. The dashed lines are the condensation value of triethylamine at 303 K.

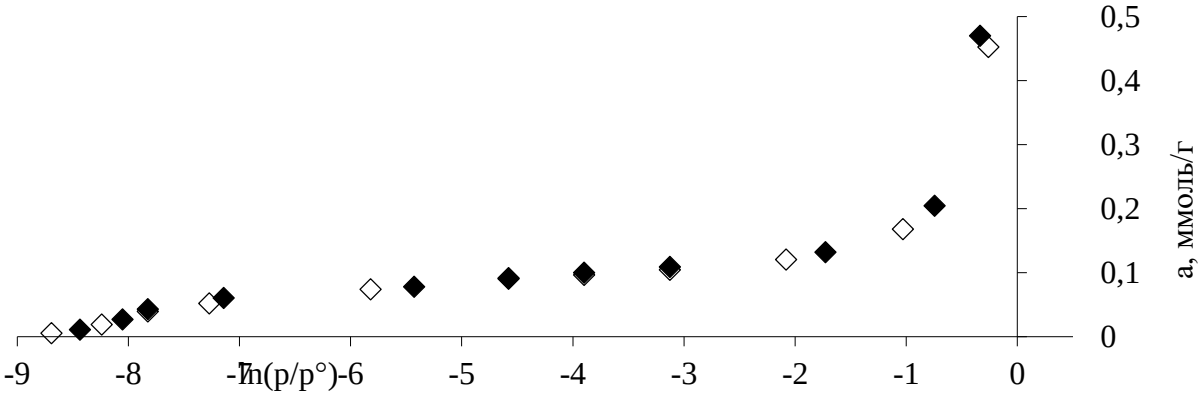

Figure 2. Adsorption isotherm of triethylamine on ZSM-5 zeolite analog at 303 K. ◊- values of the general equation of the theory of volume saturation of micropores (MHTN).

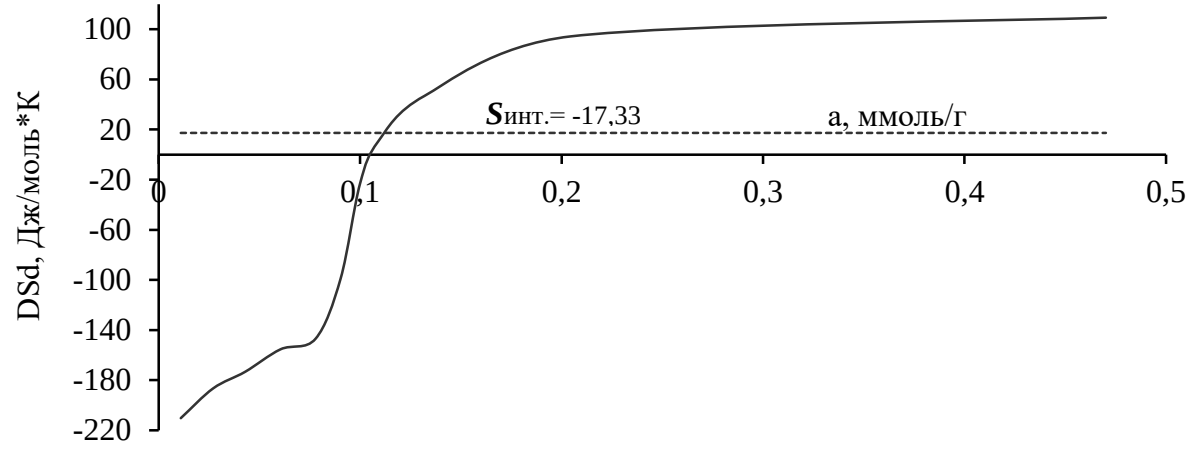

Figure 3. The differential entropy values (ΔSd) of triethylamine adsorption on the ZSM-5 zeolite analog at 303 K are presented. The entropy of liquid triethylamine is assumed to be zero.

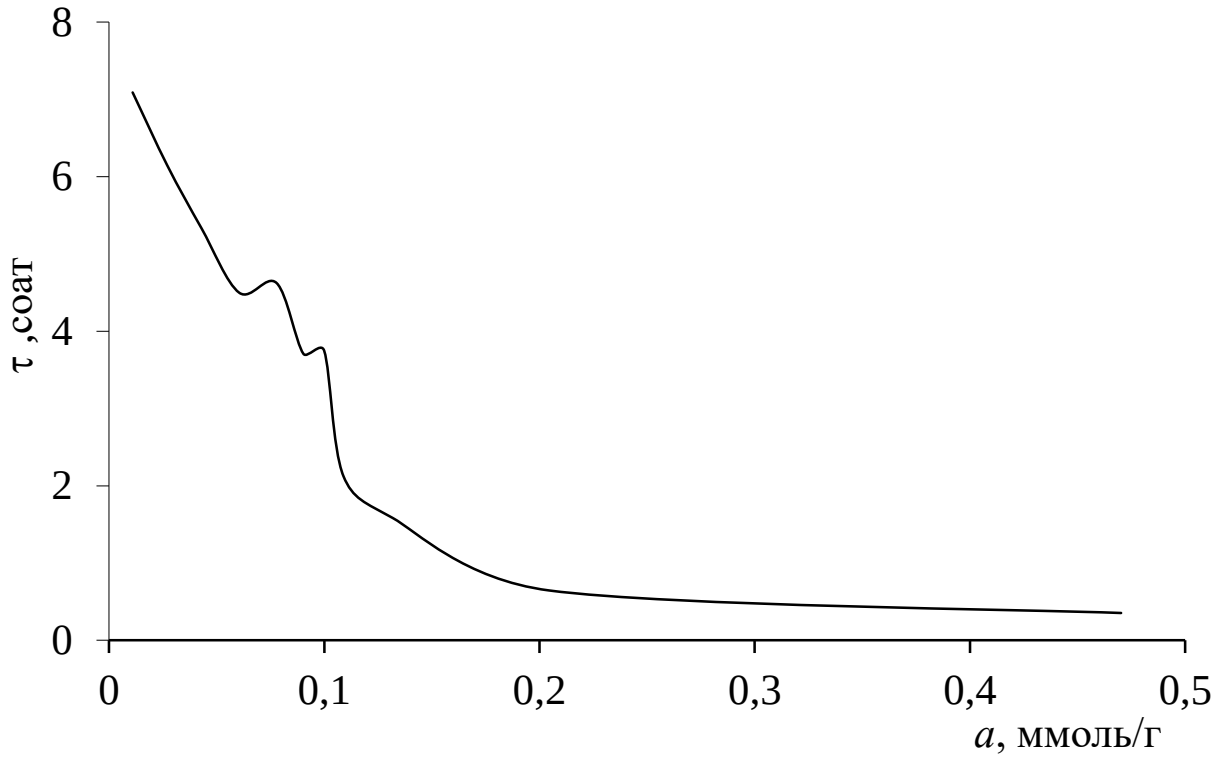

Figure 4. Dependence of thermal equilibrium establishment time on amount of triethylamine adsorption on ZSM-5 zeolite analog at 303 K

According to the triethylamine adsorption isotherm, the limiting sorption capacity of ZSM-5 is 0.12 mmol/g (Fig. 2).

In general, the isotherm is concave and belongs to the rare type III isotherms according to Branauer's classification. Up to α = 0.35 mmol/g, the adsorption varies little with pressure, then it increases sharply in a narrow range of pressure.

This appearance of the isotherm corresponds to the following cases, i.e., the cases of interaction of adsorbate molecules with the windows entering the channels on the outer surface of the adsorbent are rare cases. This is confirmed by the results of adsorption entropy (Figure 3). All this indicates the absence of strong defect centers on the outer surface of ZSM-5.

Along with adsorption, the adsorption thermokinetics for triethylamine slows down, that is, it reaches 7 hours (Fig. 4). At further saturations, the thermokinetics of triethylamine adsorption

accelerates from 6-7 hours to 30 minutes. The reason for this difference is that the large molecules of triethylamine hardly move in the external channels of ZSM-5 zeolite, while the adsorption of triethylamine on the external surface is carried out with small changes, and therefore the equilibrium time is quickly established and the thermokinetic curve decreases sharply. Physico-chemical indicators of ZSM-5 analog were found to be very close to defect-free silicalite: the external surface is equal to 1.74 m2/g, which is about 1/500 of the internal surface. The number of ZSM-5 entrance windows is 7.32*1018 in relation to 1 gram of adsorbent.

Summary. In K^+ and $NH4^+$ ZSM-5 zeolites, migration of cations from side channels to straight and zigzag channel junctions is not observed. Ion-molecular complexes are formed at the junctions of zeolite channels. That is, one cation has an average of 2.22 benzene molecules. Adsorption isotherms were described using the three-state micropore volumetric saturation theory (MHTN) equation. Benzene is in solid state mobility in zeolite channels. Adsorption mechanisms from initial saturations to final saturations were thoroughly investigated.

Adsorption of benzene on KZSM-5 zeolite begins with the formation of a p-complex bond between the cation and benzene molecules in the active centers at the intersection of the channels with an average heat of ~100-55 kJ/mol. Then localization of adsorbates continues in zigzag channels with heat of ~62 kJ/mol and adsorbed in straight channels with heat of x > ~ 58 kJ/mol. It turned out that the movement of benzene molecules in the channels was extremely slow.

K^+ and $NH4^+$ ZSM-5 zeolites are adsorbed by para-ksilol 100% (from 8 molecules per unit cell), ortho-ksilol - 75% (from 6 molecules per unit cell) and meta-ksilol - 37.6% (from 3 molecules per unit cell).

Since $NH4^+$ is larger in size and charge than K^+, the initial heat of adsorption is higher. It is observed that ortho-, meta-, para-ksilol are adsorbed with cations in the areas of connection of channels, forming a p-complex in the form of a reciprocal sandwich.

The isotherms and heat of triethylamine adsorption on the external surface of ZSM-5 zeolite analogs synthesized from local raw materials were studied. As a result, the presence of 2 different types of adsorption centers on the outer surface of zeolite was determined.

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