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DETERMINATION OF THE INHIBITORY EFFICIENCY OF THE INHIBITOR SYNTHESIZED BASED ON MALEIC ANHYDRIDE BY THE ELECTROCHEMICAL METHOD

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Abstract: In this manuscript, the isotherm of the adsorption of toluene molecules in the Cs^+ cationic form of the MFI-type synthetic zeolite 5-modification at a temperature of 303 K and the adsorption mechanism obtained in the experiment in the relative pressure coordinate are presented. The adsorption isotherm was measured using a universal high-vacuum device. Differential values of Gibbs free energy were calculated from thermodynamic equilibrium values. Based on the values of free energy, the adsorption isotherm was recharacterized by the three-state equation of micropore saturation theory. It was demonstrated that the values obtained in the experiment and the theoretically estimated values agree, and that the amount of cations in the zeolite is correlated with the coefficient of adsorption in the first term of the theory of volumetric filling of micropores equation. At a relative pressure value of P/P_s=0.06, it was determined that the saturation coefficient of MFI zeolite in the form of Cs^+ cation is equal to θ=66 %

Keywords: adsorption, isotherm, free energy, pressure, temperature, relative pressure, toluene, cation.

Introduction. Cations, which are the main active centers of zeolites, and their valence play an important role in the adsorption of polar, nonpolar, and quadrupolar

molecules of different physicochemical natures. The main thermodynamic characteristics of the adsorption of polar inorganic molecules (water, test molecules such as ammonia with binary inorganic chemical bonds, alcohols from organic substances, and aromatic hydrocarbon molecules were determined. Through this, the number of energetically main active centers (cations) in crystallographic positions of the same structure and the amount, nature, and strength of secondary active centers of zeolite are determined [1–3]. Alkali metals exhibit stoichiometric interaction not only with polar molecules, but also with non-polar and quadrupole molecules in modification 5 of cationic MFI type zeolites. Furthermore, the enthalpy of adsorption of water, ammonia, methanol, ethanol, benzene, para-, orta-, metaxylol molecules, isotherm, entropy change and thermal equilibrium time stepwise change are stoichiometric o shows the interaction. As a result of this stoichiometric interaction, there is a stepwise change in the main thermodynamic parameters in the formation of adsorbate/adsorbent ion-molecular complexes of different ratios depending on the physico-chemical nature, charge, and amount of cations in the zeolite [4–8].

The effect of different cationic forms of MFI-type zeolites 5-modification on the adsorption of aromatic hydrocarbons is studied by direct experimental measurement of isobars and adsorption isotherms. Adsorption of benzene and xylenes in the hydrogen cationic form of MFI-type zeolites showed stronger binding in their relatively monovalent alkali cation forms. In addition, the difference in the amount of benzene and xylene adsorption in the sodium and proton (hydrogen) cationic forms of this zeolite was evident [9].

Adsorption of water from polar and sufficiently small adsorbates was studied by the authors [10-13] using the method of molecular dynamics in the hydrophobic and non-cationic form of MFI zeolite, that is, the adsorption of water molecules in the nanopores of silicalite-1 (Si/Al→∞) and the adsorption of water in hydrophobic nanopores at the molecular level mechanism, conformation, stoichiometric interactions and spontaneous condensation of water are described.

It was shown by the authors [4, 14, 15] that in the sodium form of MFI zeolite, ammonia molecules form an $8NH_3{:}Na^+$ complex with sodium cations, and 24 hydrogen molecules wrap around the sodium cation in the center of the cross section of the straight and sinusoidal channels of the zeolite.

Using X-ray diffraction analysis, changes in zeolite crystal structure parameters during adsorption of various organic dyes on MFI zeolite were studied. It has been shown that the size variation of the zeolite lattice depends on both the nature of the adsorbed molecules and their size. Adsorption of paraffins (C_6, C_8, C_{14}) leads to an increase in all dimensions of the zeolite crystal lattice, the largest changes are observed for tetradecane. Of the aromatic hydrocarbons, only toluene does not change the dimensions of the zeolite lattice during adsorption.

From the analysis of the literature, it became clear that the adsorption of toluene in the Cs^+ cationic form of MFI type zeolites has not been sufficiently studied. In this article, the adsorption mechanism of toluene molecules in the form of nanostructured MFI

synthetic zeolite with cesium cation (Cs^+ZSM-5) is analyzed based on the experimentally obtained results of the adsorption isotherm and the values processed in the general equation of the volume saturation theory of micropores (VMOT). In order to describe the adsorption properties of cesium cation zeolite with respect to toluene, the isotherm of the dependence of the amount of adsorption on the equilibrium relative pressure was studied. This MeZSM-5 type zeolite has a ratio of silicon content to aluminum content of Si/Al=27.5 and the amount of Cs^+ cations is 0.54 mmol/g.

Methods and materials. One of the methods for determining the acidity strength, distribution of active centers, differential enthalpy and heat equilibrium time of natural adsorbents or synthetic zeolites is the adsorption-calorimetric measurement method. This method makes it possible to obtain high-precision molar thermodynamic descriptions, to reveal sorption mechanisms in adsorbents. The adsorption experiment was carried out using a high vacuum adsorption device. It enables the measurement of the adsorbate content in a capillary with an inner diameter of 0.1 mm as well as in gas volume.

The adsorption device is a glass-vacuum device consisting of capillary microburettes and mercury valves. The device is an adsorbent ampoule inside a microcalorimeter, for measuring low pressures (from 10^{-5} torr to 0.8 torr) from B627 baratron, 0.8 torr it consists of a measuring part with a mercury U manometer for measuring pressures and above, a capillary for gas storage and preparation, adsorbates in the liquid phase, and a vacuum pump system for creating a high vacuum.

Adsorption study The sorption of toluene on CsZSM-5 zeolite was studied at a temperature of 303 K. The unit cell composition of zeolite is CsZSM-5 - $Cs_{3,17}[(SiO_2)_{95,23}(AlO_2)_{3,17}]$, according to its chemical composition, 1 gram of CsZSM-5 zeolite contains 0.54 mmol/g of cesium cations. The amount of cesium cations in the elementary cell is equal to 3.17, and one elementary cell consists of 4 straight and intersecting sinusoidal channels, so 80% of 1 elementary cell contains cesium cations.

Results. The isotherm of toluene adsorption on CsZSM-5 zeolite in the equilibrium relative pressure coordinate P/P_s is presented in Fig. 1. At low saturations, the equilibrium pressure is equal to $P/P_s=4{,}1\cdot10^{-4}$ (P=0.015 torr) and this indicates strong adsorption of toluene in the initial area. In general, the adsorption isotherm is flexible at low pressures, indicating the presence of strongly interacting adsorption sites.

In Fig. 1, the initial ($P/P_s=4{,}1\cdot10^{-4}$, P=0,015 torr) area of toluene adsorption $P/P_s=0.64$ (P=23.5 torr) up to, Figure 2 shows the adsorption isotherm at low equilibrium pressures and the isotherm from the initial area to the relative pressure $P/P_s=0.01$ (P=0.34 torr) for a clear view of the mechanism.

The steep rise of the adsorption isotherm at low pressures represents the adsorption of toluene molecules on the homogenous, basic and initially active center of the zeolite.

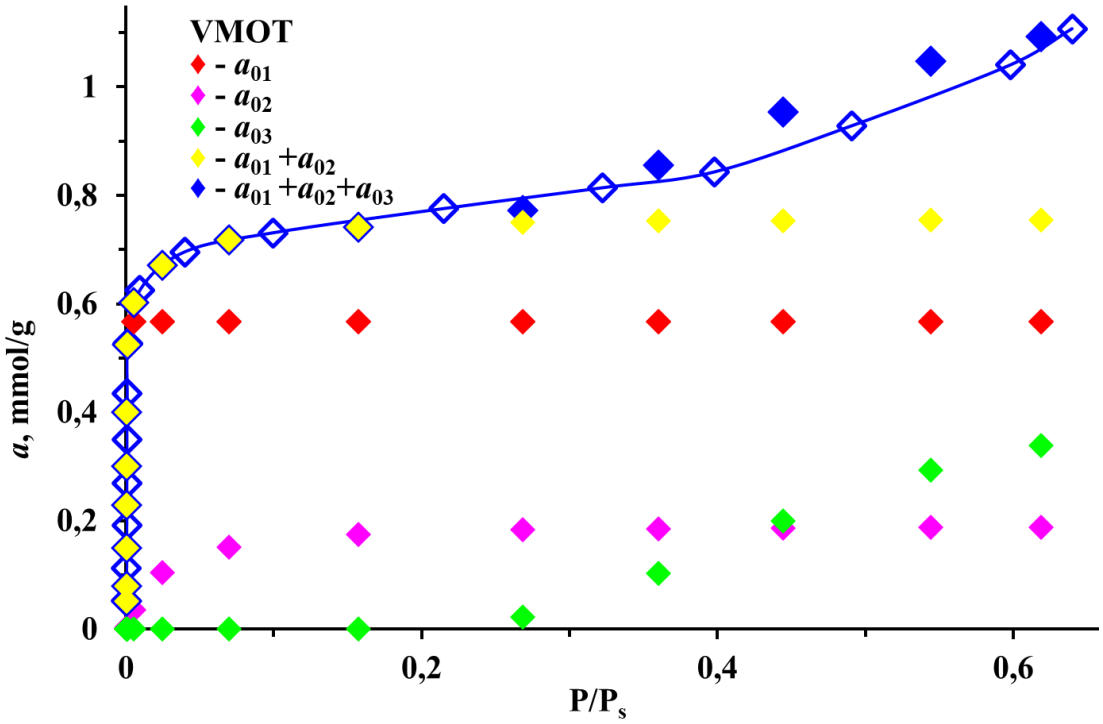

Figure 1. Isotherm of toluene adsorption on CsZSM-5 zeolite in P/P$_s$ coordinate. ◊- values obtained in the experiment, ♦, ♦, ♦, ♦, ♦ - values calculated in the general equation of the theory of volume saturation of micropores (VMOT).

The adsorption isotherm rises steeply up to P/P$_s$=13,5·10^{-4} (P=0.05 torr) (Figures 1-2). The amount of cesium cations is 0.54 mmol/g according to the chemical composition of zeolite CsZSM-5 - $Cs_{3,17}[(SiO_2)_{95,23}(AlO_2)_{3,17}]$, which is 0.53 mmol/g of adsorption at equilibrium pressure. Hence, toluene molecules form an adsorbate/adsorbent first coordination sphere with cesium cations in a 1:1 ratio, that is, an adsorbate/cation mono $1C_7H_8{:}Cs^+$ ion-molecular complex. From this complex, the equilibrium pressure begins to increase. P/P$_s$=0,4 relative (P=14.6 torr) pressure and 0.84 mmol/g, and P/P$_s$=0.64 relative (P=23.5 torr) pressure and changes linearly up to 1.11 mmol/g adsorption. Both linear changes are equal to 0.3 mmol/g, which is half of the cesium cations in the zeolite. Therefore, 2 cesium cations in the toluene/cation monomer complex are formed by the next one toluene molecule with the mutual π complex. Further toluene molecules are sorbed in the adsorbate/adsorbate third coordination sphere as a result of Vaan-der-Waals interaction with initially adsorbed toluene molecules. The authors explained this by the decrease of the differential enthalpy to the condensation heat of toluene after 0.9 mmol/g adsorption [16]. A general ion-molecular complex corresponds to the following scheme:

$$1C_7H_8{:}Cs^+{:}C_7H_8{:}Cs^+{:}1C_7H_8$$

Figure 1 shows the adsorption isotherm of toluene molecules on SsZSM-5 zeolite in the relative pressure coordinate, isotherm calculated by the general equation of the theory for the volume filling of micropores (VMOT). The adsorption isotherm from the initial region to the saturation state is described using the three-term of VMOT equation[17]:

$$a=0.567\exp[-(A/18.97)^{25}]+0.188\exp[-(A/11.12)^{3}]+0.388\exp[-(A/2.34)^{3}] \quad (1)$$

where, α is the adsorption value (mmol/g), $A=RT\ln P_s/P$ is the work (kJ/mol) in transferring 1 mmol of toluene vapor (pressure P_s) to the equilibrium gas phase (pressure P).

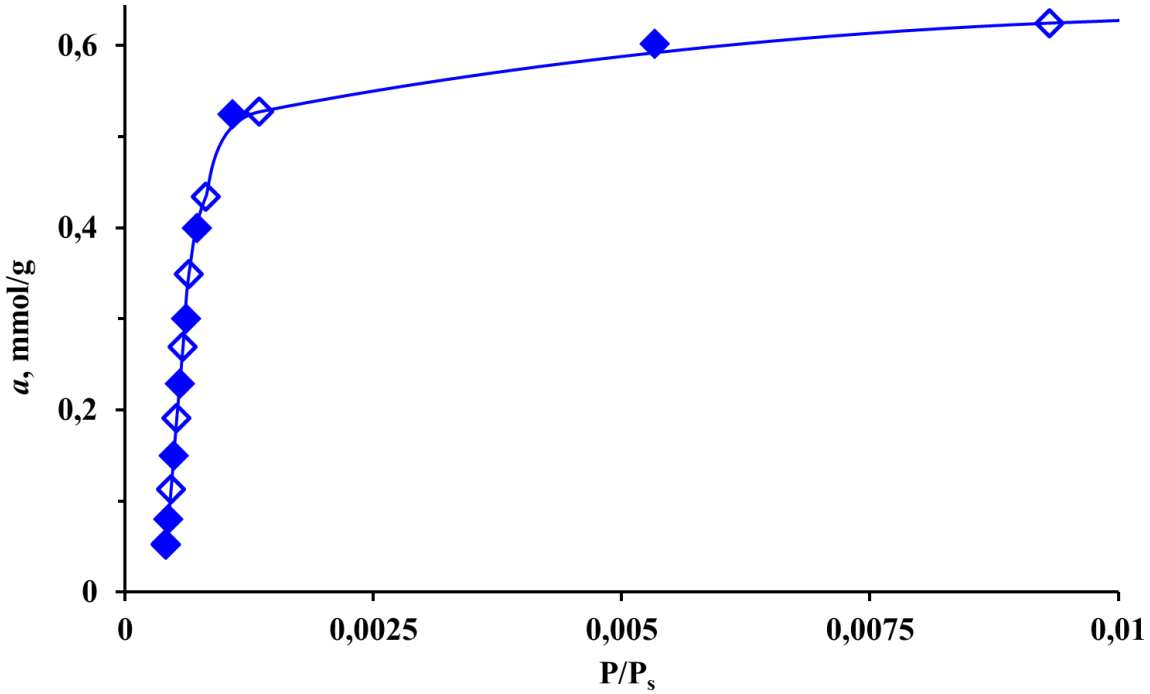

Figure 2. Isotherm of toluene adsorption on CsZSM-5 zeolite at relative pressure $P/P_s<0,01$. ◊-values obtained in the experiment, ♦-values calculated in the equation of the volume saturation theory of micropores (VMOT).

The amount of adsorption $a_{01}=0.567$ mmol/g in equation (1) is equal to the amount of cesium cations in the zeolite (0.54 mmol/g). Therefore, the VMOT theory confirms that toluene molecules form an adsorbate/adsorbent mono $1C_7H_8:Cs^+$ ion-molecular complex with cesium cations in a ratio of 1:1. The isotherm calculated on the basis of equation (1) rises steeply up to the adsorption amount of 0.54 mmol/g and the relative pressure $P/P_s=0.005$ due to the coefficient $a_{01}=0.567$ mmol/g, confirming the sorption in the primary active center of the zeolite (Fig. 1). The second and third terms of the equation do not affect the isotherm change at all. At relative pressures $P/P_s>0,005$, the adsorption value of the 1st term of equation (1) does not change, that is, the sorption process does not depend on pressure. This represents the completion of the sorption process in the initial active center. From a relative pressure of $P/P_s>0,005$, the second term of equation (1) starts to become active.

This is due to the sorption of toluene in the next active center of the zeolite and continues up to the relative pressure $P/P_s=0,16$, and the second isotherm also changes parallel to the ordinate axis. The sum isotherm of terms 1 and 2 of the equation fully

corresponds to the isotherm obtained in the experiment up to the relative pressure P/P_s=0,16.

At relative pressures P/P_s>0,16, the 3rd term of equation (1) is activated. The adsorption quantities a_{02}=0,188 mmol/g and a_{03}=0.388 mmol/g in the equation mean adsorption on non-homogeneous parts of zeolite. Additionally, their sum $a_{02}+a_{03}$=0.576 mmol/g is equal to the amount of cesium cations in zeolite. This confirms the adsorption mechanism described based on the experimental isotherm.

Conclusion. In CsZSM-5 nanostructured synthetic zeolite, toluene molecules are adsorbed at high energy values up to relative pressure P/Ps =0.16. The total adsorption amount is ~1,1 mmol/g, and in the first coordination sphere, an ion-molecular complex with the ratio $1C_7H_8$:Cs^+:C_7H_8:Cs^+:$1C_7H_8$ is formed, and this complex is located at the intersection of the straight and zigzag channels of zeolite. 0.3 mmol/g toluene molecules form a π complex with two cesium cations. Adsorption of toluene molecules was not observed in the second coordination sphere, the cation-free silicalite portion of the zeolite. In the third coordination sphere, adsorbate/adsorbate 0.3 mmol/g of toluene are connected under the influence of the Waan-der-Waals force. 55% of the total adsorption amount corresponds to the relative pressure P/Ps=0.16. Toluene molecules fill 65% of the micropores of zeolite. This is 35% more than the volume occupied by toluene in the cation-free form of zeolite. At a relative pressure value of P/P_s=0.06, the saturation coefficient of MFI zeolite in the form of Cs^+ cation is equal to θ=66%.

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