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ISOTHERM OF BENZENE ADSORPTION AND DIFFERENTIAL HEAT OF ADSORPTION ON AgZSM-5 ZEOLITE

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Abstract: Benzene, toluene, and para-xylene (kinetic diameters ~0.58 nm) are easily adsorbed onto ZSM-5 zeolites. The molecules of aromatic hydrocarbons repeatedly attach to the OH groups, migrate along the external surface of the zeolite before entering the micropores or desorbing. Molecules that can enter the micropores, such as benzene, toluene, and xylene, are adsorbed more rapidly onto the SiOHA1 groups compared to the SiOH groups. For o-xylene molecules, which find it difficult to enter the pores, the adsorption rate on the remaining SiOH groups significantly increases. As the adsorption volume reaches saturation, the cation-free part of the zeolite, i.e., the silicalite portion, continues the adsorption process, resulting in two maxima and two minima. At an adsorption value of 1.53 mmol/g, the differential heat decreases to 54 kJ/mol. If we assume the density of benzene at experimental temperature to be the same as that in normal liquid form and calculate the volume occupied by the benzene molecules at saturation, we find that the AgZSM-5 zeolite occupies about ~0.16 cm^3/g of the sorption volume, which constitutes approximately 94.7%. Thus, based on the experimental data, the following conclusion can be drawn: In the adsorption of benzene on AgZSM-5 zeolite, the benzene molecules localize around the active centers, forming a sandwich-like structure around the silver sites

Keywords: AgZSM-5 zeolite, benzene, microcalorimetry, adsorption, differential heat, isotherm.

Introduction. Natural gas is a mixture composed of methane and its homologs, as well as inorganic substances such as hydrogen, nitrogen, hydrogen sulfide, carbon dioxide, helium, and inert gases. Since methane is the main component of natural gas (up to 94%), it is being used as an additional source for the synthesis of organic compounds. Aromatization of methane is a promising method for converting hydrocarbon gases, enabling the production of benzene, toluene, xylenes, and heavier molecular aromatic hydrocarbons such as naphthalene and alpha-methylnaphthalene. This process is considered a hydrocarbon gas shifting reaction that takes place in the presence of catalysts. Among the catalysts used in the stepwise transition process to aromatization, ZSM-5 zeolites show significant effectiveness due to their structure, which ensures the stability of metal ions during the transition process, particularly when cations migrate within the zeolite channels and voids. To achieve high efficiency in the synthesis of aromatic hydrocarbons from methane, it is necessary to have active cationic zeolite catalysts that possess the most optimal combination of physical and chemical properties.

The presence of molecular pores and voids in ZSM-5 zeolite causes the sorption and desorption of substances with appropriate sizes, including aromatic hydrocarbons that are slightly larger than the size of the zeolite channels, such as those with an average diameter of 6 Å [1]. ZSM-5 zeolites with different Si/Al ratios and various cation types have been used as catalysts in the aromatization of methane. Specifically, H-, Ga-, Zn-, and Pt-Cr/ZSM-5 synthetic zeolite catalysts have been applied for the synthesis of aromatic hydrocarbons from methane [2-3]. High selectivity towards benzene was observed in catalysts with a zeolite pore structure where the pore diameter was close to the kinetic diameter of the benzene molecule [4].

In ZSM-5 zeolites, benzene, toluene, and para-xylene (with kinetic diameters of ~0.58 nm) are easily adsorbed. The molecules of aromatic hydrocarbons repeatedly attach to OH groups, migrate along the external surface of the zeolite, or enter the micro-pores before desorption. Molecules that can enter the micro-pores, such as benzene, toluene, and xylenes, are adsorbed more rapidly to the SiOHA1 groups compared to SiOH groups. For ortho-xylene molecules, which have difficulty entering the pores, the adsorption rate to the remaining SiOH groups significantly increases.

The authors [5] identified that aromatic hydrocarbons are adsorbed only in the straight and intersecting channels of ZSM-5 zeolite. However, the molecular mechanism by which benzene molecules interact in different cationic forms of pentasil-type zeolites has not been fully elucidated. They explained these complex transformations by the various directions and redistribution of the adsorbate within the silicalite channels, but the specific mechanisms of these transformations were not discussed.

Research methods and materials. The strength of the adsorbate-adsorbent interaction, and consequently the "acidity strength," can be assessed through temperature-programmed desorption of the adsorbate. However, a more direct and precise approach to determining acidity, its center distribution, and thermal equilibrium time is the adsorption-calorimetric method, which provides data during the adsorption process. The adsorption-calorimetric technique employed in this study enables the acquisition of high-precision molar thermodynamic data and facilitates the identification of the detailed mechanisms underlying adsorption processes in adsorbents and catalysts. Adsorption measurements and quantification of the adsorbate were conducted using a universal high-vacuum adsorption apparatus, which allows for the precise dosing of the adsorbate through both gas-volumetric and liquid-volume methods. A modified Tiana-Calve microcalorimeter (DAK-1-1A) was used as the calorimetric device, offering high accuracy and stability.

The adsorption study was carried out on Cu2+ZSM-5 zeolite at a temperature of 303 K. The unit cell composition of zeolite is Ag1.72 [(SiO2)96.63(AlO2)1.72].

Results. The differential heat of adsorption of benzene on AgZSM-5 zeolite is shown in Figure 1. The adsorption differential heat can be divided into three stages with an increase in the degree of saturation.

In the initial stage of adsorption, the differential heat of benzene adsorption on AgZSM-5 zeolite decreases from approximately 200 kJ/mol at 0.1 mmol/g adsorption to

120 kJ/mol. At 0.3 mmol/g adsorption, the heat further decreases to 80 kJ/mol, and the initial monodentate $1C_6H_6^+$ ion-molecular mechanism is formed within the first coordination sphere. During the formation of the dimer $2C_6H_6^+$ and trimer $3C_6H_6^+$ complexes, at 0.9 mmol/g adsorption, the heat decreases almost linearly to 61 kJ/mol, and the adsorption process terminates within the first coordination sphere.

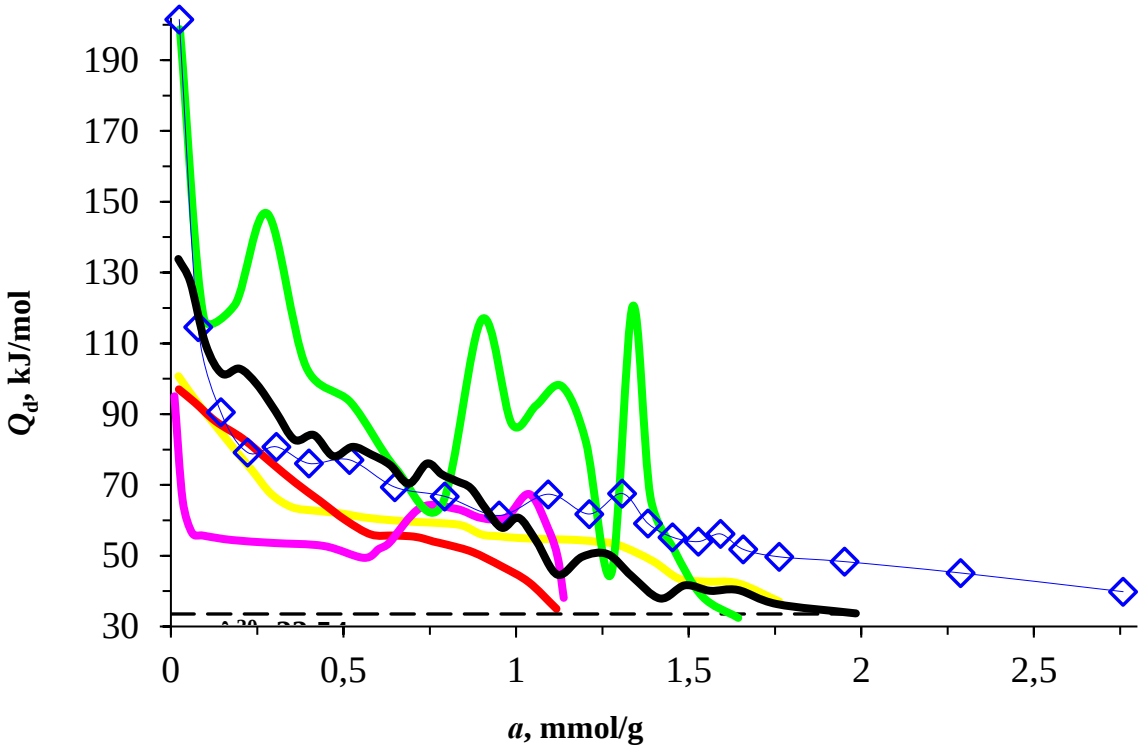

Fig. 1. Differential heat of adsorption (Qd) of benzene on ZSM-5 zeolites and silicalite with Ag^+ Cu^{2+}, NH_4^+, Cs^+, Li^+ cations at 303 K. The bar graph shows the condensation value of benzene at 303 K.

With the saturation of the sorption volume, the cation-free part of the zeolite, i.e., the silicalite component, continues the adsorption process, producing two maxima and two minima, with the differential heat of adsorption decreasing to 54 kJ/mol at an adsorption value of 1.53 mmol/g. Then, at an adsorption value of 2.76 mmol/g, the differential heat decreases linearly from 54 kJ/mol to 40 kJ/mol, and the process concludes.

In the initial high-energy stage, benzene forms a π-complex with the Ag^+ cation, and this complex is localized at the intersections of the straight and sinusoidal channels. Subsequent adsorption of benzene molecules occurs in the sinusoidal (second stage) and straight (third stage) channels of the zeolite, as the levels of adsorption heat correspond to the benzene adsorption heats in these channels (consistent with the adsorption heat of benzene in various cationic forms of ZSM-5 zeolite and silicalite).

The isotherm of benzene adsorption on AgZSM-5 zeolite in semi-logarithmic coordinates is presented in Figure 2. The isotherm corresponds to the change in

differential adsorption heat and confirms the formation of the tetramer $3C_6H_6$:Ag^+ ion-molecular complex. From the initial region up to an adsorption amount of 0.9 mmol/g, the isotherm changes almost linearly (the isotherm obtained based on the BET method consists of a straight line up to an adsorption of 0.9 mmol/g). At low saturation levels, the equilibrium pressures reach $P/P_s = 9.2 \times 10^{-5}$ (P = 0.011 mmHg), indicating that benzene molecules are strongly bound in the adsorption process on AgZSM-5 zeolite. The isotherm reaches approximately 3 mmol/g at an equilibrium pressure of $P/P_s = 0.74$ (or 88 mmHg). Assuming the density of benzene is similar to that of normal liquid at the experimental temperature, and calculating the volume occupied by the benzene molecules at saturation, it can be observed that AgZSM-5 zeolite occupies approximately ~0.16 cm^3/g of its sorption volume, which corresponds to ~94.7% of the total sorption capacity [6].

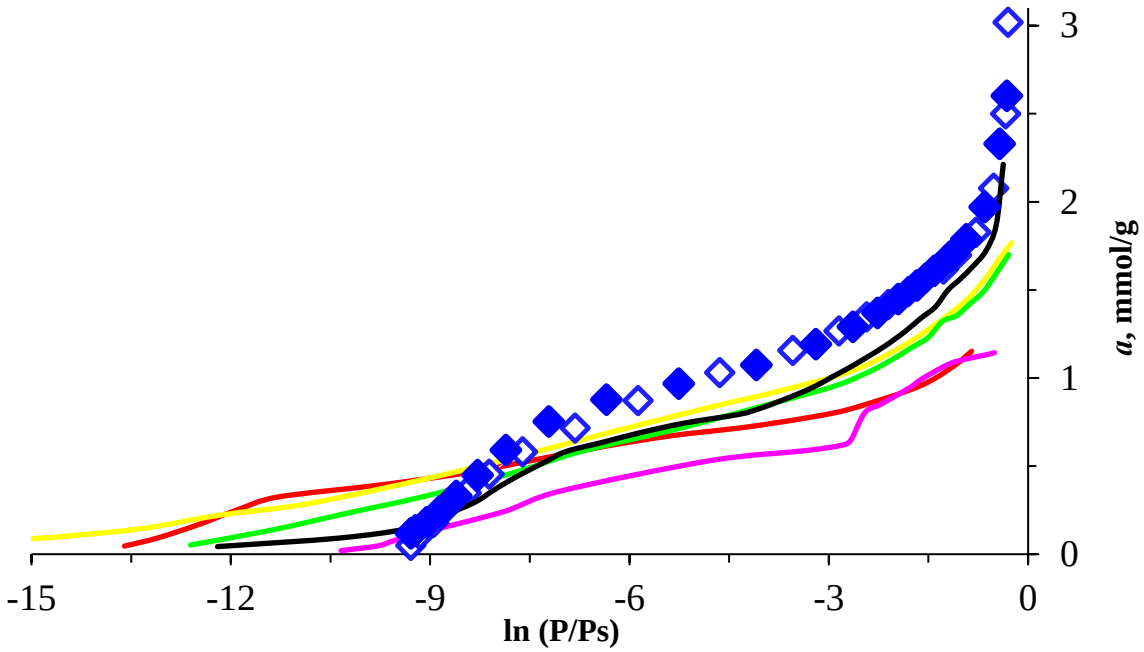

Figure 2a. Isotherm of benzene adsorption in logarithmic coordinates on Ag^+ Cu^{2+}, NH_4^+, Cs^+, Li^+ cationic ZSM-5 zeolites and silicalite-ZSM-5 zeolites at 303 K. ◊ represents the experimental values, and ♦ represents the values calculated using the volumetric saturation theory for micropores (BET method).

The isotherm of benzene adsorption on AgZSM-5 zeolite was redefined using the three-term equation of the BET method [6]:

$$a=0{,}812\exp[-(A/14{,}28)^{10}]+1{,}428\exp[-(A/6{,}06)^{1}]+1{,}043\exp[-(A/0{,}99)^{2}]$$

where a is the adsorption (mol/g), and $A=RT\ln(P_s/P)$ is the work required to transfer 1 mole of gas from the gas phase to the saturated surface phase at equilibrium pressure. The theoretical data calculated from this equation match the experimental data shown in Figure 2a.

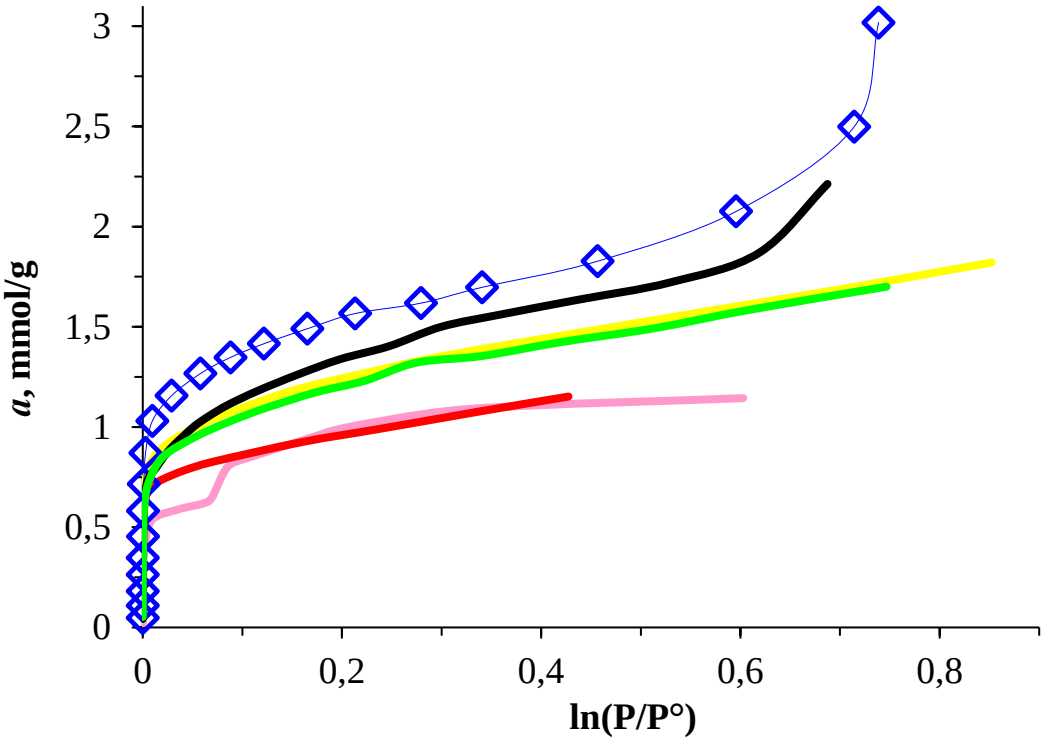

Fig.2b. Isotherm of benzene adsorption on Ag^{+} Cu^{2+}, NH_4^{+}, Cs^{+}, Li^{+} cationic ZSM-5 zeolites and silicalite-ZSM-5 303 K in the P/Ps coordinate.

The isotherm of benzene adsorption on AgZSM-5 zeolite in the P/P_s coordinates follows the Brunauer Type I classification for ethanol adsorption on zeolite (Figure 2b), meaning that the zeolite primarily consists of micropores. Thus, based on the experimental data, the following conclusion can be drawn: In the adsorption of benzene on AgZSM-5 zeolite, the benzene molecules localize around the active centers, forming a sandwich-like structure around the silver sites.

Conclusion. The main thermodynamic characteristics and isotherm of benzene adsorption on AgZSM-5 zeolite, from the initial region to saturation, were investigated, and the sorption mechanisms were identified. The adsorption heat equilibrium time for benzene molecules on AgZSM-5 zeolite was found to occur very slowly (over 10-12 hours) until a monomeric ion-molecular mechanism forms at the intersection of the straight and sinusoidal channels, involving silver cations. It was also demonstrated that benzene molecules at the channel intersections form ion-molecular complexes with silver cations in various ratios, such as benzene trimer complexes (3C6H6:Ag). On average, 5.2 benzene molecules were adsorbed per silver cation in each elementary cell of the AgZSM-5 zeolite. The adsorption isotherms were characterized using the three-phase micropore volume filling theory (VMFT) equation. In the case of benzene adsorption on AgZSM-5 zeolite, silver cations at the channel intersections form π-complex bonds with benzene molecules with an average differential heat of approximately ~100 kJ/mol. After an adsorption quantity of 0.9 mmol/g, the localization of the adsorbates in the sinusoidal

and straight channels was observed, with differential heats of ~60 kJ/mol in the sinusoidal channels and ~46 kJ/mol in the straight channels.

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