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WATER VAPOR ADSORPTION ISOTHERM ON ZEOLITE AgZSM-5

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Abstract:

Objective. This paper presents the isotherm of water molecule adsorption on AgZSM-5 zeolite at a temperature of 303 K. The adsorption isotherm was measured using an improved microcalorimeter connected to a universal high vacuum apparatus. Differential values of free energy were calculated from thermodynamic equilibrium values. The relationship between the adsorption amount and energy properties of water molecules in AgZSM-5 zeolite, as well as the sorption mechanism from the initial zone to the saturation zone, and it was found that water molecules fill 56.3% of the volume of zeolite. It was proved that 85% of the total adsorption amount is at a relative pressure of P/Ps=0.3. The adsorption isotherm was recharacterized by the three-state equation of the micropore saturation theory, and it was shown that the theoretically calculated values were in full agreement with the experimentally obtained values.

Research method. The adsorption isotherm was measured with high accuracy and stability using a system consisting of a Tiana-Calve differential automated microcalorimeter (DAK-1-1A) connected to a universal high-vacuum apparatus. The adsorption-calorimetric method used in this research makes it possible to obtain high-precision molar thermodynamic descriptions, as well as to reveal detailed mechanisms of adsorption processes occurring in adsorbents. Adsorption measurements and adsorbate dosing were performed using a high-vacuum adsorption device. The device allows dosing of adsorbate by gas-volume and liquid-volume methods. Baratron B627 diaphragm pressure gauge was used to measure equilibrium pressure down to 0.8 mmHg. The adsorption-calorimetric method allows the research of nanostructured adsorbents, the detailed discovery of the main thermodynamic properties and mechanisms of adsorption processes occurring in adsorbents and catalysts.

Results. It was found that water adsorption on AgZSM-5 zeolite at a temperature of 303 K is the main thermodynamic characteristics from the initial area to the saturation pressure, there is a regular relationship between the adsorption amount and energy characteristics, the adsorption mechanism, the sorption volume and energy values of this zeolite are higher than monovalent cation zeolites. In the process of adsorption, the formation of an ion/molecular complex at the intersection of straight and sinusoidal channels between water molecules and Ag cations was proved.

Conclusion. The results of the carried out adsorption-calorimetric research allow to obtain the main thermodynamic functions of the studied systems, which are necessary for the development of theoretical concepts of physical adsorption, as well as for the calculation of processes and devices of sorption technology.

Keywords: adsorption, heat of adsorption, free energy, adsorption isotherm, pressure, relative pressure, entropy, kinetics, calorimeter, water.

Introduction. Cations, considered the main active center of zeolites, play an important role in the adsorption of polar, non-polar and quadrupole molecules. By determining the main thermodynamic characteristics of the adsorption of test molecules such as water, methanol and ammonia, the number of energetically active centers (cations) in the same type of crystallographic positions is determined [1-5].

A stepwise decrease in the heat of adsorption of polar molecules in zeolites of the ZSM-5 type with alkali metal cations indicates the stoichiometric interaction of these molecules with cations that compensate for the negative charge of the lattice. For example, water and alcohols Cu(H2O)10+2, Cs(H2O)6+, Li(H2O)4+ Na(H2O)4+, Na(CH3OH)4+, Na(C2H5OH)4+, K(H2O)4+, H(H2O)4+, NH4(H2O)4+ ion-molecular complexes have a step-like change [6-12].

The effect of different cationic forms of ZSM-5 zeolites on water adsorption is studied by direct experimental measurement of isobars and adsorption isotherms. It has been shown that water molecules are more strongly bound in monovalent alkaline cation forms compared to adsorption in zeolite in N+ cationic form. In addition, the difference in the amount of water adsorption in NaZSM-5 and NZSM-5 zeolites was evident [13]. Using the method of molecular dynamics, the authors [14-17] studied the adsorption of water molecules in the pores of hydrophobic ZSM-5 zeolite, that is, silicalite-1. As a result of the study, the adsorption properties of water in hydrophobic nanopores at the molecular level were determined and the spontaneous condensation of water was described.

In the adsorption of ammonia, the authors showed the formation of Na(NH3)8 complex. 24 hydrogen molecules form a wrap around the Na cation in the center of the intersection of straight and zigzag channels of zeolite [6, 18, 19].

In this work, the properties of adsorption interaction of water molecules with AgZSM-5 nanostructured synthetic zeolite are considered. To characterize the adsorption properties of zeolites, the dependence of the adsorption amount of water molecules on the equilibrium pressure, that is, the isotherm and kinetics, were determined. The amount of Ag+ cations in this ZSM-5 (Si/Al=27.5) zeolite is 0.304 mmol/g.

Research methods and materials. The strength of the adsorbate-adsorbent interaction and, consequently, the "acidity strength" can be analyzed by conducting temperature-programmed desorption of adsorption. A more direct and accurate way to determine the acidity, the distribution of its centers, and the thermal equilibrium time is the adsorption-calorimetric measurement method obtained during the adsorption process.

The adsorption-calorimetric method used in this work allows obtaining high-precision molar thermodynamic descriptions and revealing the detailed mechanisms of adsorption processes taking place in adsorbents and catalysts. Adsorption measurements and quantification of adsorbate were performed using a universal high vacuum adsorption device. The device allows to provide the measured amount of adsorbate both by gas-volumetric and volumetric-liquid methods. A modified Tiana-Calve microcalorimeter DAK-1-1A was used as a calorimeter with high accuracy and stability.

The adsorption device is a glass-vacuum device consisting of capillary microburettes and mercury valves. The device consists of an adsorbent ampoule inside a microcalorimeter, a B627 baratron for measuring low pressures (from 10-5 mmHg to 1 mmHg), 1 mmHg. 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.

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 corresponding isotherm of water adsorption on AgZSM-5 zeolite in logarithmic coordinates is presented in Figure 1 and it confirms the energetic data [20]. At small saturations, the equilibrium pressure is 0.0046 mmHg. ($P/P_s=1,45\cdot10^{-4}$) reaches. This indicates strong adsorption of water to forms of hydrogen, ammonium, cesium and silicalite [21-23]. The adsorption isotherm was brought up to 5.35 mmol/g (or 17.6 molecules/cation) at a relative pressure of P/Ps=0.67 (or R=21.16 mmHg). If the density of water in AgZSM-5 zeolite is taken as a normal liquid at the experimental temperature and compared with the volume occupied by a water molecule at saturation, then water occupies ~0.0963 cm3/g of the sorption volume of AgZSM-5 zeolite and makes up ~56.3%. This value is ~53% in Cu2+ZSM-5 form of ZSM-5 zeolite, ~51% in CsZSM-5 zeolite, and ~54% in LiZSM-5 zeolite.

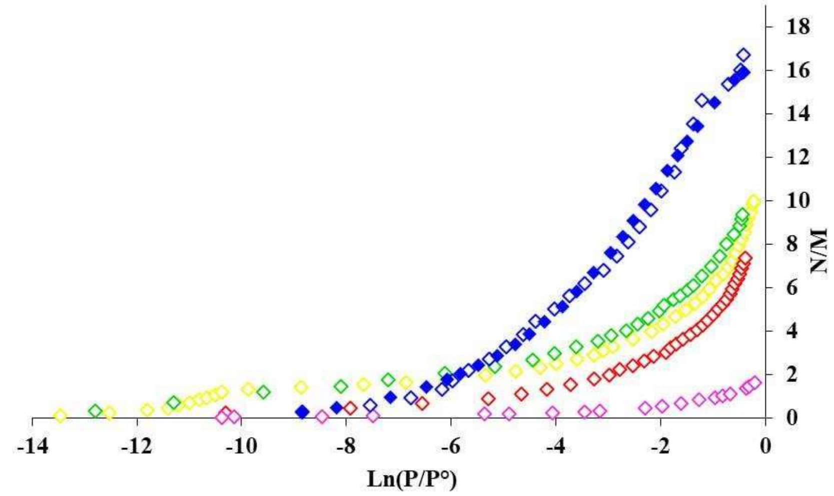

Figure 1. Adsorption isotherm of water molecules in ZSM-5 zeolites with ◊-Ag^+, ◊-Cs^+, ◊-Li^+, ◊-Na^+ cations and ◊-silicalite at a temperature of 303 K. ♦-values of the general equation of micropore volume saturation theory

The adsorption isotherm shows that silver cations are in a strong ion-molecular complex bond with water molecules in the initial region. The isotherm initially moves linearly towards the abscissa axis at the adsorption amount of 0.3 mmol/g up to P/Ps=0.00115 (R=0.0367 mmHg). The formation of a step in the amount of this adsorption means the formation of a monomeric 1N2O:Ag ion-molecular complex, as in differential heating. After the 1N2O:Ag complex, P/Ps=0.009 (R=3 mmHg) increases linearly and steeply upwards with an adsorption amount of 2.74 mmol/g. process is completed. Next, water molecules are adsorbed in the right sinusoidal channels of the zeolite, that is, in the cation-free parts. After 15N2O:AgZSM-5 adsorption, the equilibrium pressure begins to increase sharply. Therefore, six water molecules are sufficiently strongly bound even in the non-cationic part of the zeolite. The next three water molecules form an isotherm step on adsorption. In general, the adsorption isotherm is above lithium, cesium, sodium, ammonium, and protonated forms of ZSM-5 zeolite.

The water adsorption isotherm on AgZSM-5 zeolite is also completely described using the equation of the three-member micropore volume saturation theory [25]:

$$a=0{,}837\exp[-(A/16{,}84)^3] + 4{,}153\exp[-(A/7.53)^2] + 0{,}650\exp[-(A/0{,}39)^1] \quad (1)$$

where, α - adsorption value (mmol/g), A=RTlnPs/P, the work done in transferring the gas from the surface (pressure P°) to the equilibrium gas phase (pressure R) (kJ/mol). It can be seen from Figure 1 that the values calculated in the theory of volume saturation of micropores agree with the values obtained in the experiment. Indices 1, 2 and 3 in the quantities of Equation 1 are descriptions of the interaction of adsorbates on cations. Quantities with an index of 1 describe the adsorption of a water molecule on cations with a strong interaction, an index of 2 - on relatively weak interactions on cations, and an index of 3 - weak interactions on cations. In the adsorption of water - AgZSM-5 system, based on the theory of volumetric saturation of micropores, the values of the terms of the equation (1) are equal to the following: for the first term a01=0.837 mol/g, E01=16.84 kJ/mol, n1=3; for the second term - a02=4.153 mmol/g, E02=7.53 kJ/mol and n2=2; for the third term - a03=0.65 mmol/g, E03=0.39 kJ/mol and n3=1.

Figure 2 shows an isotherm graph of relative pressure (P/Ps) as a function of the amount of adsorption. The isotherm corresponds to the Branauer 1 classification, that is, water is adsorbed in zeolite only in micropores. This zeolite does not have meso and macro pores.

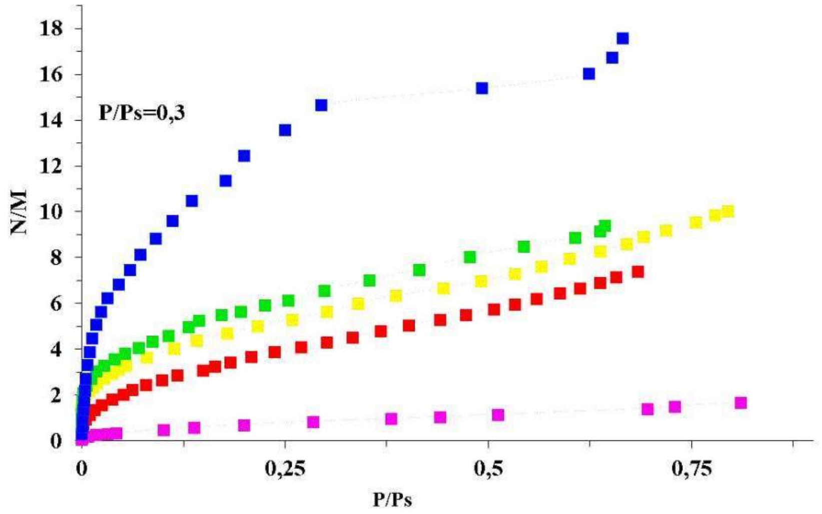

Figure 2. Isotherm of dependence of relative pressure (P/Ps) on the amount of water molecules adsorption in ZSM-5 zeolites with 🟦-Ag$^+$, 🟥-Cs$^+$, 🟨-Li$^+$, 🟩-Na$^+$ cations and 🟪-silicalite at a temperature of 303 K

From the isotherm, 15 water molecules are adsorbed at a relative pressure of P/Ps= 0.3, and a sharp increase in relative pressure is observed during the sorption of the next 3 water molecules. Therefore, the main mass of water (85%) is absorbed at low pressures. At this relative pressure, there is one water molecule in silicalite (53%), 4 water molecules in the cesium form of zeolite (60%), 6 water molecules in the lithium form (56%), 7 water molecules in the sodium form (70%), and 7 water molecules in the ammonium form (58 %) 10 water molecules are adsorbed [21-22, 25].

Conclusion. Water molecules are adsorbed at high energy values in AgZSM-5 nanostructured synthetic zeolite. The total amount of adsorption is 17.6 water molecules, and an ion-molecular complex with a ratio of 9N2O:Ag+ is formed in the first coordination sphere. Also, 8.6 more water molecules are adsorbed in the second coordination sphere, i.e. in the cation-free silicalite part of the zeolite. 85% of the total amount of adsorption corresponds to the relative pressure P/Ps=0.3. 56.3% of the volume of zeolite is filled with water molecules. This is 30% more than the volume occupied by water in the non-cationic form of zeolite. The isotherm of the water molecule in the silver cation form of ZSM-5 zeolite is above that of the monovalent alkali metal cation form. In the process of adsorption of water molecules, up to 0.3 mmol/g of adsorption, copper cations migrate from the hidden state to the intersection of the straight and zigzag channels of zeolite.

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