ENTHALPY AND THE MECHANISM OF WATER ADSORPTION IN ZEOLITE Ag ZSM-5

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Annotation
This paper presents the differential heat of water adsorption on the AgZSM-5 zeolite at a temperature of 303 K. A correlation between the adsorption-energy characteristics is found and the molecular mechanism of water adsorption in the AgZSM-5 zeolite is revealed in the entire filling region. The stepwise nature of the heat of water adsorption is revealed. It has been determined that water molecules with silver cations in zeolite form a high-energy nano-ion-molecular complex in the first coordination sphere. It was also found that water molecules are adsorbed only in the first and second coordination spheres corresponding to saturation.

Keywords: adsorption, enthalpy, differential heat of adsorption, thermodynamics, calorimeter, water.

In the world, adsorbents obtained from natural raw materials and synthetically obtained zeolites are widely used in various fields of industry, construction and agriculture. Adsorbents of selective action and a wide range of applications - zeolites - are widely used. The most common area of their application is the oil and gas industry. The extraction of sulfur compounds, carbon dioxide and aromatic hydrocarbons, as well as the removal of water from natural and associated petroleum gas, is important for it due to the fact that they cause corrosion of pipe steel grades. Natural gas purification from water and drying are also important for gas processing enterprises. The solution of these problems is achieved through the use of adsorption technology and the creation of new adsorbents and catalysts

studied by colloid chemistry, the development of theoretical positions on the nature of active centers of dispersed substances [1-6].

Currently, one of the most popular materials for selective adsorption and separation in the world are nano porous molecular sieves - zeolites. They are of interest because of the ability to control their texture, chemical properties and nature outside the lattice cations, which affect the adsorption and catalytic properties of crystalline materials, regulated by the structure, number and nature of the active centers they contain. However, the specifics of the structure of zeolites are still unclear, in particular, those related to the problem of the settlement of acid sites, the mechanism of adsorption of polar and nonpolar molecules, the nature and participation of defects in adsorption.

Therefore, a comprehensive study of the physicochemical and especially energy characteristics of zeolites is of great theoretical and practical importance. Today, the processes of adsorption of steam and gases are the main chemical processes in the world. In this regard, the accumulation and systematization of the most important thermodynamic characteristics of adsorption systems, one of the components of which is zeolite, acquires great importance. In addition, the adsorption-calorimetric method used in this work makes it possible to reveal the mechanism of adsorption processes occurring on adsorbents and catalysts.

The adsorption-calorimetric method used in this work makes it possible to obtain high-precision molar thermodynamic characteristics, as well as to reveal the detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Energetically homogeneous centers (cations) in the same type of crystallographic positions are determined by measuring the differential heats of adsorption of such test molecules as water, methanol and ammonia. Pure silica zeolites, such as silicalite, show hydrophobicity, that is adsorption of water on these zeolites is very low.

To characterize the adsorption properties of the zeolite, differential heats (enthalpies) and isotherms of water adsorption were measured, and the entropy and free energy of water adsorption in Ag ZSM-5 zeolite were calculated. This paper presents the differential heat of water adsorption.

The heats of adsorption of polar molecules on the Ag ZSM-5 zeolite are characterized by a stepwise decrease, indicating the stoichiometric interaction of these molecules with Ag^+ cations compensating the negative lattice charge. The differential heats of water vapor adsorption on CsZSM-5 zeolite are shown in Fig.1. The differential heats of water adsorption on the Ag ZSM-5 zeolite have a rather complex form (Figure 1). The initial heat of adsorption (excluding

adsorption on the impurity center) is 122 kJ/mol. Depending on the filling of water adsorption, the enthalpy decreases from 122 kJ/mol to ~80 kJ/mol at an adsorption of 0.3 mmol/g.

The content of silver cations, according to the chemical composition of the EA, is 0.304 mmol/g, that is the drop in heat from 122 kJ/mol to 80 kJ/mol upon adsorption of 0.3 mmol/g is associated with the adsorption of one water molecule to one cation a Ag^+. The amount of high-energy adsorbed water corresponds to the scheme $1H_2O:Ag^+$. Further, with an increase in adsorption, there is a successive formation of complexes of the Ag^+ cation with two, three, and four water molecules with a decrease in heat from 80 kJ/mol to 47 kJ /mol. The minimum on the curve corresponds exactly to the tetrahedral Ag^+ complex with four water molecules. Further, the enthalpy changes in waves up to 45 kJ/mol during the adsorption of $9H_2O:Ag^+$. This completes adsorption in the first coordination sphere. Ag^+ complexes with nine water molecules due to their size can fit only in the crosshairs of straight and zigzag zeolite channels.

After the formation of the $9H_2O:Ag^+$ ion-molecular complex, adsorption proceeds in the so-called silicalite part of the ZSM-5 zeolite, i.e. parts where there are no Ag^+ cations, with heat close to the heat of condensation. Total adsorption is 18 water molecules per cation. In general, the heat of water adsorption on the Ag^+ cation is much higher than on Cs^+, Li^+, Na^+ and silicalite (Figure 1).

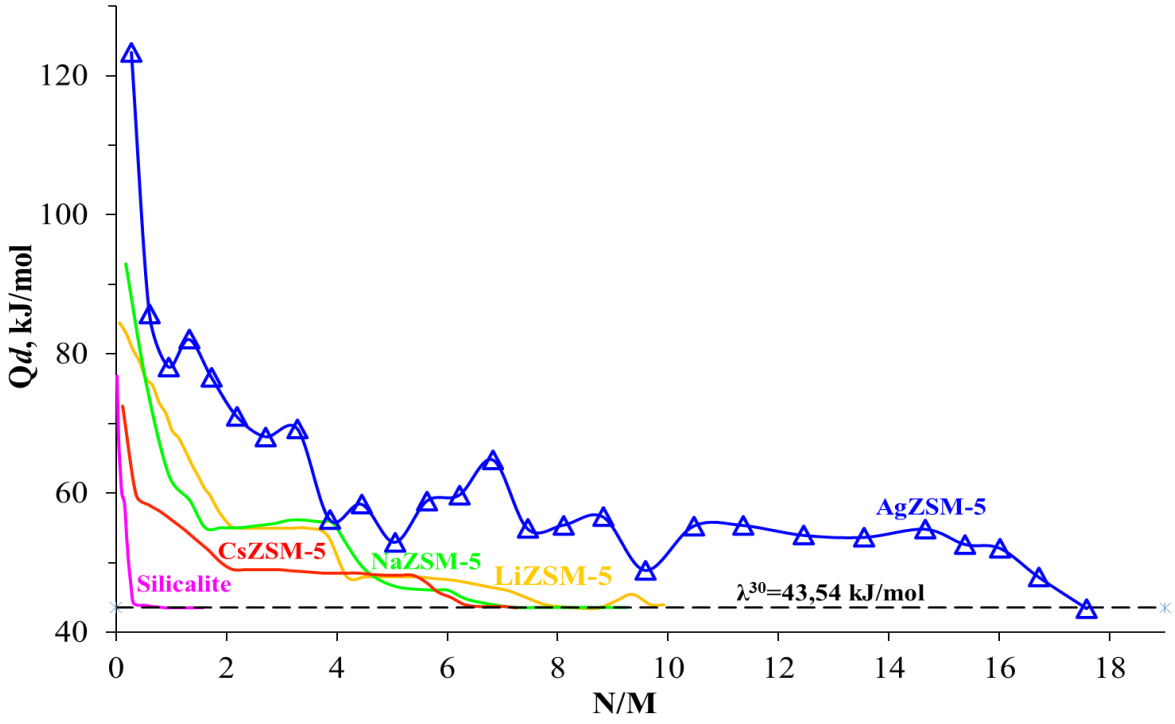

Figure 1. Differential heats of water adsorption on ZSM -5 zeolites. The horizontal dashed line is the heat of condensation.

This paper presents the correlation between the adsorption-energy characteristics and reveals the molecular mechanism of water adsorption in AgZSM -5 zeolite in the entire filling area. It was determined that small polar water molecules with silver cations in zeolite form high-energy nano ion-molecular complex in the first coordination sphere. It was also found that water molecules are adsorbed only in the first and second coordination spheres corresponding to saturation. Adsorption of water molecules in the third coordination sphere was not observed.

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