MORAL DIFFERENTIAL ENTROPY OF ADSORPTION ORTA- XYLENE IN ZEOLITE Ag ZSM-5

Tolibjon Abdulkhaev[1],
Shakhnoza Kuldasheva[2],
Ma'rufjon Asfandiyorov[3]
[1]Namangan Institute of Engineering and Technology Namangan, Uzbekistan Email: abdulxayev1987@gmail.com
[2]Institute of General and Inorganic Chemistry of Academy Sciences of the Republic of Uzbekistan, Tashkent, Uzbekistan
[3]Tashkent University of Information Technologies named after Muhammad al-Khwarizmi

Annotation

This paper presents the adsorption of o-xylene in zeolite AgZSM-5 at a temperature of 303 K. To measure the isotherms and differential heats of adsorption, we used a system consisting of a universal high-vacuum adsorption unit and a differential modified microcalorimeter of the Tiana-Calve DAK-1-1A type connected to it. The adsorption entropy of o-xylene was calculated from isotherms and differential heats of adsorption using the Gibbs-Helmholtz equation. It has been determined that, in general, the molar differential entropy of o-xylene adsorption is lower than the entropy of liquid o-xylene, which indicates a sharp limitation of the mobility of o-xylene molecules in the zeolite.

Keywords: adsorption, heat of adsorption, thermodynamics, entropy, adsorption isotherm, entropy, calorimeter, o-xylene.

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 (pore size and architecture), chemical properties (Si/Al ratio) and nature of non-lattice cations, which affect the adsorption and catalytic properties of crystalline materials controlled by the structure, number and nature of the materials they contain. active centers. However, the questions of the specific structure of zeolites are still unclear, in particular, those related to the problem of the settlement of active centers, the mechanism of adsorption of polar and nonpolar molecules, the nature and participation of defects in adsorption.

Today, the processes of adsorption of steam and gases are the main chemical processes in the world. Therefore, a certain (clear) chemical composition and structure of zeolites makes it possible to obtain them and their theoretical and practical application. In the adsorption of aromatic hydrocarbons, the influence of the size of the molecules is more important than their nature, and the adsorption of all aromatic hydrocarbons, large toluene, causes a decrease in the zeolite lattice constants **a** and **c** and an increase in the constant **b**. No less important is another adsorbate, which differs from benzene and toluene by two methyl groups in the p-position -p-xylene.

In [1], the parameters of a ZSM-5 zeolite crystal upon adsorption of p-xylene and the localization sites of adsorption molecules were determined by X-ray diffraction analysis [1]. One of the independent molecules is located at the intersection of the channels, its axis is parallel to the axis of the main channel, the other in the sinusoidal channel is tightly compressed by lattice atoms, which leads to a change in the lattice. It is shown that during adsorption in sinusoidal channels, the lattice symmetry of the zeolite framework changes from monoclinic to orthorhombic.

In recent years, there has been increased interest in a commercially attractive process for the separation of xylene isomers by membranes using ZSM -5 zeolite. However, the limited number of data available in the literature does not allow one to judge the complex interaction between nanopores of the ZSM -5 structure (host) and xylenes molecules (guest) [2]. The most studied is p -xylene, the kinetic diameter of which is 0.6 nm. However, the adsorption of o-xylene on synthetic zeolites, which have almost the same kinetic diameter as p-xylene and differ in the arrangement of the methyl group, has not been practically studied. This paper presents the molar differential entropy of o - xylene adsorption on AgZSM-5 zeolite at a temperature of 303 K. The unit cell of the investigated zeolite Ag ZSM -5 contains 1.72 cations (304 μmol/g). Differential molar adsorption-calorimetric studies of the adsorption of o-xylene in AgZSM-5 zeolite were carried out on an adsorption-calorimetric installation. The molar differential adsorption entropy (ΔS_d) of o-xylene in AgZSM-5 was calculated from the isotherm and differential heats of adsorption according to the Gibbs–Helmholtz equation (the entropy of liquid o-xylene was taken as zero) [3, 4]:

$$\Delta S_a = \frac{\Delta H - \Delta G}{T} = \frac{-(Q_a - \lambda) + A}{T}$$

where, λ is the heat of condensation, ΔH and ΔG are the change in enthalpy and free energy during adsorption from the standard state to the adsorbed state.

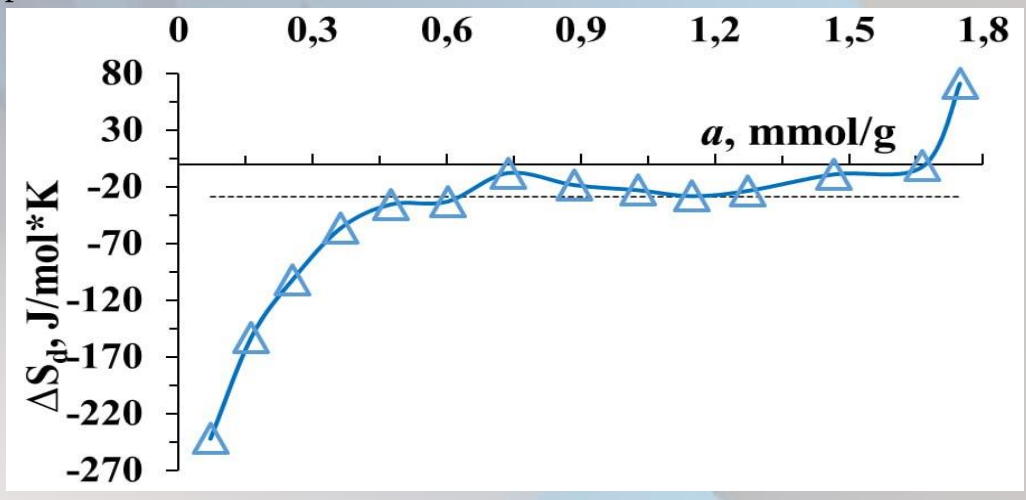

Figure 1. Differential molar entropy of o-xylene adsorption in AgZSM-5 zeolite at 303 K . The dashed line is the average molar integral entropy. The entropy of liquid o-xylene was taken as zero.

The dependence of the molar differential entropy of o-xylene adsorption (ΔS_d) on zeolite Ag ZSM-5 on filling is shown in Fig. 1 (the entropy of liquid o-xylene is taken as zero). It differs sharply from the entropy of o-xylene adsorption on KZSM-5, HZSM-5, and NH_4ZSM-5 zeolites, which indicates the different character of o-xylene adsorption in these zeolites [5]. In general, it is located below the entropy of liquid o-xylene, and than from the entropy above in zeolites, which indicates a sharp limitation of the mobility of o-xylene molecules in the zeolite. At low fillings, ΔS rises from the minimum value (-250 J/K·mol) to -70 J/K·mol at an adsorption of 0.3 mmol/g. The content of Ag^+ cations, according to the chemical composition of EA, is ~0.3 mmol/g, the first maximum corresponds to the completion of the formation of the monomeric complex, that is amount of adsorbed o-xylene corresponds to the scheme $1C_8H_{10}$:Ag^+. It confirms the strong interaction of o-xylene with the Ag^+ cation in a ratio of 1:1. Further ΔS_d gradually rises to -33 J/K·mol with adsorption of 0.6 mmol/g, forming $2C_8H_{10}$:Ag^+ ion-molecular complex. Thus, the formation of a two-dimensional molecule/cation complex is completed. Further, the entropy does not change until adsorption is 1.3 mmol/g. Then the entropy increases to the entropy of liquid o-xylene at adsorption of 1.7 mmol/g. This entire section of the entropy curve corresponds to the adsorption of o-xylene without any noticeable participation of Ag^+ cations, that is in channels and crosshairs that do not contain the Ag^+ cation. In general, the entire curve is located in the negative region. Naturally, the region of strong adsorption is characterized by low entropy values, which indicates a strong localization of the adsorbate in the zeolite matrix. But, in general, the characteristic of the state of the adsorbate in the zeolite is the average molar integral entropy of adsorption, which is equal to -28 J/K·mol, which indicates a sufficient in a strongly hindered state of o - xylene in the AgZSM-5 matrix, that is the mobility of o-xylene in zeolite AgZSM-5 is lower than the mobility of o-xylene in the liquid phase and is close to its mobility in the solid phase.

The work studied in detail the molar differential entropy of o-xylene adsorption in zeolite AgZSM-5 at a temperature of 303 K. A correlation between the adsorption-energy characteristics and the crystal-chemical structure of AgZSM-5 was found, and the molecular mechanism of o-xylene adsorption in AgZSM -5 was revealed.

Literature

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