ENTROPY AND THERMOKINETICS OF TOLUENE ADSORPTION ON Cu^{2+}ZSM-5 ZEOLITE

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Annotation

This paper presents the results of the main (ΔH, ΔF and ΔS) thermodynamic characteristics and the time of establishment of adsorption equilibrium depending on the amount of adsorption of toluene in Cu^{2+}ZSM-5 zeolite. The isotherms and differential heat of adsorption were measured using 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, which directly gives quantitative and qualitative characteristics of the nature and forces of adsorption interaction. A correlation between the adsorption-energy characteristics was found and the molecular mechanism of toluene adsorption in Cu^{2+}ZSM-5 zeolite was revealed in the entire filling area. It has been determined that the average molar entropy of toluene adsorption in CuZSM-5 zeolite indicates that the mobility of toluene molecules in the zeolite is lower than the liquid phase and is close to the mobility of the solid phase, which indicates a strong inhibition of the mobility of toluene molecules on cations.

This paper presents the results of basic (ΔH, ΔF and ΔS) thermodynamic characteristics of toluene adsorption in CuZSM-5 zeolite. For measurements of isotherms and differential heat of adsorption, a system consisting of a universal high-vacuum adsorption unit and an attached differential modified Tian-Calve microcalorimeter DAC-1-1A was used to provide direct quantitative and qualitative characteristics of the nature and forces of adsorption interaction. The correlation between the adsorption-energy characteristics was found and the molecular mechanism of toluene adsorption in CuZSM-5 zeolite in the whole filling region was revealed. Toluene adsorbed in CuZSM-5 zeolite is located in the first coordination sphere with Cu^{2+} cation, forming two-dimensional complexes. It was found that the charge density significantly affects the mechanism, the energy of adsorption and the number of adsorbed molecules. It was determined that the average molar entropy of toluene adsorption in CuZSM-5 zeolite indicates that the mobility of toluene molecules in zeolite is below the liquid phase and close to that of the solid phase, indicating that the mobility of toluene molecules

on cations is strongly inhibited. This work shows how calorimetric data can be used to complement crystal structure results and detect subtle adsorbent/adsorbate interactions at the molecular level.

Keywords: zeolite, adsorption, adsorption isotherm, heat of adsorption, free energy, entropy, kinetics, microcalorimeter, toluene.

Nanoporous molecular sieves - zeolites - are currently one of the most sought-after materials for selective adsorption and separation in the world. They are of great interest due to the possibility to adjust their texture (pore size and architecture), chemical properties (Si/Al ratio) and the nature of off- lattice cations, which influence the adsorption and catalytic properties of crystalline materials regulated by the structure, number and nature of the active centres they contain. Today, vapour and gas adsorption processes are major chemical processes in the world. Therefore, a certain (clear) chemical composition and structure of zeolites enables their production and theoretical and practical application.

A comprehensive study of physical-chemical and especially energetic characteristics of zeolites of ZSM-5 type is of great theoretical and practical importance. Energy characteristics, due to strict definiteness of chemical composition and crystal structure of zeolites, should be well reproduced and can be applied in practical calculations or theoretical discussions. However, a number of questions on the specificity of zeolite structure, especially those related to the problem of spreading of active centres, mechanism of adsorption of polar and non-polar molecules, nature and participation of defects in adsorption, are still unclear. The solution of these questions is decisive for the successful application of adsorbents and the directional regulation of their properties, and also makes it possible to study and establish general regularities of adsorption and catalysis.

Among aromatic hydrocarbons, benzene, toluene and p-xylene are the easiest to adsorb on zeolites of ZSM-5 type (all of them have kinetic diameter of 0.58 nm). The adsorption of benzene, toluene and p-xylene on a silicate has been studied in [1-6]. The differential heats of adsorption of benzene and toluene on silica have a complex dependence on the degree of filling [2-5]. The adsorption heat curves for benzene and toluene showed minima and maxima. The authors attributed them to redistribution and reorientation of the adsorbed molecules at fills above 0.5.

Toluene is the only aromatic hydrocarbon whose adsorption does not cause a change in zeolite lattice size. In the adsorption of aromatic hydrocarbons, the influence of molecular size is more important than their nature and the adsorption of all aromatic hydrocarbons, larger than toluene, causing a decrease of lattice constants a and c and an increase of constant b [6].

A large number of data on the adsorption of organic substances in pentasil-type zeolites are available, which have been obtained by various physico-chemical methods of investigation [7-16]. The adsorption-calorimetric method applied in this work reveals the mechanism of adsorption processes occurring on adsorbents and catalysts.

The studied zeolite ZSM-5 contains polyvalent cation Cu^{2+} (0.3 mmole/g), which is much smaller in size than Na^{+}. The unit cell composition Cu^{2+}ZSM-5-$Cu_{1,72}[(SiO_2)_{96,63}(AlO_2)_{3,37}]$, the Cu^{2+} cation contentis on average ~1.72/e.c. In this work isotherms, differential heat, entropy and kinetics of toluene adsorption Cu^{2+}ZSM-5 (Si/Al=27,5) at 303 K were studied. Before starting the experiment, the adsorbent was evacuated at 723 K for 10 hours to high vacuum (10^{-5} torr).

The corresponding entropy diagram is shown in Figure 1. As can be seen, ΔS_d is significantly lower than the entropy of liquid toluene.

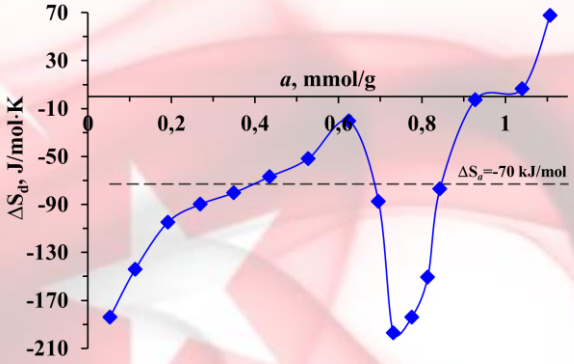

Figure 1. Entropy of toluene adsorption in Cu^{2+}ZSM-5 zeolite.

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Consequently, the adsorption thermodynamics definitely indicate a strongly localized nature of the adsorbed toluene on Cu^{2+}ZSM-5. ΔS_d gradually increases from -185 J/K·mole to a maximum value of -20 J/K·mole at 0.3 mmole/g adsorption.

The entropy also confirms the strong interaction of toluene with the Cu^{2+} cation up to filling 0.3 mmole/g, as well as in the heat and adsorption isotherm, i.e. strong interaction of toluene with Cu^{2+} cation in a 1:1 ratio. Further ΔSd changes in a wave-like manner and rises sharply to the entropy of liquid toluene at 1.11 mmole/g.

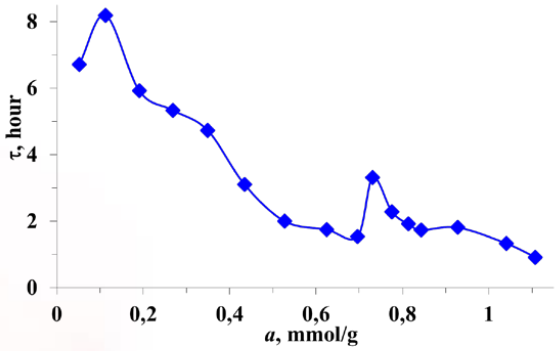

Figure 2. Adsorption equilibrium time as a function of toluene adsorption value in Cu^{2+}ZSM-5 zeolite.

The time of establishment of adsorption equilibrium of toluene on Cu^{2+} zeolite ZSM-5 (Figure 2) at small fillings up to 0.1 mmole/g varies from~ 6.7 hours to 8.2 hours and further decreases until filling 0.6 mmole/g (until complete molecules/cation complex formation in the ratio $C_6H_5CH_3$:Cu^{2+}-2:1)). Starting from 0.6 mmole/g filling the adsorption process slows down dramatically, reaching a maximum (~3.5 hours) at 0.72 mmole/g filling. Then the adsorption rate gradually increases and an equilibrium is reached at 1.11 in 1 hour.

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