

## **DIFFERENTIAL HEATS OF TOLUENE ADSORPTION ON ZEOLITE Cu<sup>2+</sup>ZSM-5**

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### **Annotation**

This article presents the results of differential heats and entropy of adsorption of toluene 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<sup>2+</sup> 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. This work shows how calorimetric data can be used to complement crystal structure results and detect subtle adsorbent/adsorbate interactions at the molecular level.

**Key words:** zeolite, silicalite, adsorption, adsorption centers, heat, enthalpy, free energy, entropy, microcalorimeter, toluene.

Worldwide, adsorbents derived from natural raw materials and synthetic way are widely studied and used in industry, construction, agriculture and other fields [1-5].

The phenomenon of adsorption of gases and vapours underlies many chemical and biological processes and the interest of researchers has long been driven by the need to solve purely practical problems. The study of adsorption energy of gases and vapours is of paramount importance not only for understanding interesting phenomena and practically valuable processes occurring on various synthetic zeolites, but also for accumulation, systematization and standardization of the most important thermodynamic characteristics of heterogeneous systems, one of whose components is zeolite.

Natural and synthetic zeolites have found wide application as adsorbents. Synthetic zeolites are aluminosilicate, microporous adsorbents with not only high selective adsorption but also the ability to separate substances, with different size, shapes of adsorbate molecules. They are distinguished by their strictly crystalline structure and large specific surface area. The zeolite

pores are spherical cavities connected by channels. Nowadays industrial companies manufacture different grades of zeolites, which have different cations and sizes of pores. The most practical application is for zeolites, type A, X and ZSM-5.

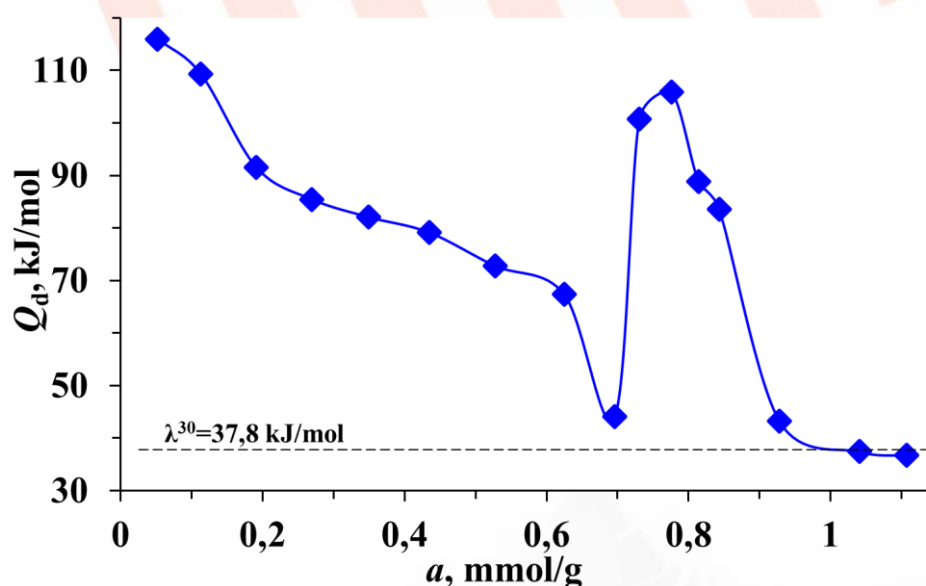
Toluene is the only aromatic hydrocarbon whose adsorption does not cause a change in zeolite lattice size. In the adsorption of aromatic hydrocarbons, the influence of molecular size is more important than their nature and the adsorption of all aromatic hydrocarbons, larger than toluene, causing a decrease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

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. The adsorption-calorimetric method applied in this work reveals the mechanism of adsorption processes occurring on adsorbents and catalysts [6-10].

Differential heat of adsorption together with other differential adsorption energetic characteristics (enthalpy, free energy and entropy) most fully characterise the physical, chemical, crystallochemical and geometrical nature of the adsorbent surface and allows the study of adsorption phenomena on a molecular structural level.

In this work, we studied the differential heats of toluene adsorption in  $\text{Cu}^{2+}$ ZSM-5 zeolite ( $\text{Si}/\text{Al}=27.5$ ) at a temperature of 303 K. Before starting the experiment, the adsorbent was evacuated at 723 K for 10 hours to high vacuum ( $10^{-5}$  torr).

The differential heat of adsorption of toluene in  $\text{Cu}^{2+}$ ZSM-5 zeolite is shown in Figure 1. The adsorption heats for toluene are rather complex. Figure 2 shows that the adsorption heats of toluene in  $\text{Cu}^{2+}$ ZSM-5 zeolite changes stepwise with increasing filling. The initial heat of adsorption (without taking into account adsorption on the impurity centre) is 116 kJ/mole. Depending on the adsorption filling, the enthalpy forms a step and decreases from 116 kJ/mole to ~84 kJ/mole with an adsorption of 0.3 mmole/g.



**Figure 1:** Differential heat of adsorption of toluene on  $\text{Cu}^{2+}$ ZSM-5 zeolite.

Horizontal dashed line condensation heat.

The content of copper cations, according to the chemical composition of EC, is 0.3 mmole/g, zeolite i.e. the heat drop from 116 kJ/mole to 84 kJ/mole for the adsorption of 0.3 mmole/g associated with the adsorption of one toluene molecule on one  $\text{Cu}^{2+}$  cation. The amount of high-energy adsorbed toluene corresponds to the scheme  $1\text{C}_6\text{H}_5\text{CH}_3:\text{Cu}^{2+}$ . With increasing adsorption there is the formation of  $\text{Cu}^{2+}$  cation complexes with two toluene molecules with a decrease in heat from 84 kJ/mol to 70 kJ/mole at 0.6 mmole/g adsorption, i.e. forms  $2\text{C}_6\text{H}_5\text{CH}_3:\text{Cu}^{2+}$ .

Further adsorption proceeds in zigzag channels (second stage) and in straight channels (third stage) of zeolite, i.e. the part where no  $\text{Cu}^{2+}$  cations, because they correspond to the heat of adsorption of toluene in these channels (numerous data on the heat of adsorption of benzene on different cationic forms of ZSM-5 zeolite and silicalite). Considering that the dispersion potential in zig-zag channels are higher, it can be assumed that adsorption first takes place in the zig-zag channels.

After zig-zagging toluene is adsorbed in straight channels. The reason for the inflated heat at high fills seems to be the lithium copper, with which toluene can interact due to the induction effect.

Calorimetric studies of toluene adsorption in  $\text{Cu}^{2+}$ ZSM-5 zeolite have been carried out. Differential heats in  $\text{Cu}^{2+}$ ZSM-5 zeolite have been obtained. A correlation between the adsorption-energy characteristics was found and the molecular mechanism of toluene adsorption in  $\text{Cu}^{2+}$ ZSM-5 zeolite was revealed in the entire filling area. Toluene adsorbed in the  $\text{Cu}^{2+}$ ZSM-5 zeolite is located in the first coordination sphere with the  $\text{Cu}^{2+}$  cation, forming dimeric complexes. The heat of adsorption correlates with the number of copper cations in the zeolite structures. No adsorption of toluene was observed in the second coordination sphere. It is shown that the adsorption properties of ZSM-5 zeolites depend on the type of cation, as well as on the structure of fragments of the ZSM-5 zeolite structure. It has been established that the charge density significantly affects the mechanism, energy of adsorption and the number of adsorbed molecules.

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