

# DIFFERENTIAL HEAT ADSORPTION AND MECHANISM OF TOLUENE VAPOR ON ZSM-5 TYPE ZEOLITES

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**Abstract.** *This article presents the results obtained by the adsorption-calorimetric method of differential heat and the mechanism of adsorption of toluene on ZSM-5 type zeolites with copper and cesium cations. To measure isotherms and differential heat of adsorption, a system was used consisting of a universal high-vacuum adsorption unit and a differential modified microcalorimeter of the Tiana-Calvé type, DAK-1-1A, connected to it, which directly gives quantitative and qualitative characteristics of the nature and forces of adsorption interaction. A correlation was found between the adsorption-energy characteristics and the molecular mechanism of toluene adsorption in Cs<sub>3.17</sub>ZSM-5 and Cu<sub>1.7</sub>ZSM-5 zeolites was revealed throughout the entire filling region. Toluene, adsorbed in the Cs<sub>3.17</sub>ZSM-5 zeolite, is located in the first coordination sphere with the Cs<sup>+</sup> cation, forming dimer-toluene complexes; in the Cu<sub>1.7</sub>ZSM-5 zeolite, it is located in the first coordination sphere with the Cu<sup>2+</sup> cation, forming dimer-toluene complexes. 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:** *adsorption, heat of adsorption, temperature, free energy, entropy, microcalorimeter, toluene, ammonia.*

## 1 Introduction

One of the main tasks of physical-chemical and colloidal chemistry is the study of the number, strength and nature of active centers of dispersed substances, which allows solving numerous theoretical issues of adsorption and catalysis.

Around the world, adsorbents obtained from natural raw materials or synthetically are widely studied and used in industry, construction, agriculture and other fields [1–6]. However, before using these adsorbents in production, it is necessary to study their adsorption, energy and catalytic characteristics in laboratory conditions.

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

Adsorbents of selective action are widely used, and nanoporous molecular sieves - zeolites - belong to a wide range of applications. The most common area of their application is the oil and gas industry. It is important to extract sulfur compounds, carbon dioxide and aromatic hydrocarbons, as well as remove water from natural and associated petroleum gas due to the fact

that they cause corrosion of pipe steel grades. Purification of natural gas from water and drying are also important for gas processing enterprises. The solution to these problems is achieved through the use of adsorption technology and the creation of new adsorbents and catalysts studied by colloidal chemistry and the development of theoretical principles about the nature of the active centers of dispersed substances.

Proposed new applications of zeolites described in the literature include: molecular electronics, quantum dots/circuits, zeolite electrodes, batteries, nonlinear optical materials, and chemical sensors. Recently, research has emerged on the use of zeolites as low dielectric constant materials for microprocessors [7-8]. It is indicated that zeolites have a great future in electrical engineering, membrane technology, and also as indicators (sensors).

Natural and synthetic zeolites have found wide application as adsorbents [3-5]. Synthetic zeolites are aluminosilicate, microporous adsorbents that have not only high selective adsorption, but also the ability to separate substances with different sizes and shapes of adsorbate molecules. They are distinguished by their strictly crystalline structure and large specific surface area. Currently, industrial enterprises produce different brands of zeolites, differing in cations and pore sizes. The most widely used zeolites are types A, X and ZSM-5.

Knowledge of the nature of active sites and estimation of their concentration is a prerequisite for any attempt to classify adsorbents. The adsorption and catalytic properties of zeolites largely depend on the structure of their porous structure, the number, strength and nature of the active centers they contain. Therefore, a comprehensive study of the physicochemical and especially energy characteristics of ZSM-5 type zeolites is of great theoretical and practical importance. In this regard, the accumulation and systematization of the most important thermodynamic characteristics of adsorption systems, one of the components of which is zeolite, becomes of 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.

Highly efficient catalysts for various processes in the petrochemical and oil refining industries are catalysts of the ZSM-5 type. Therefore, a comprehensive study of the adsorption properties of ZSM-5 type zeolites provides useful information about the structural characteristics and possibilities of practical application. Adsorption on these zeolites is highly dependent on the cations present in the structure. Due to the large space between adsorption sites, zeolite is ideal for model studies of adsorption behavior.

Various physicochemical properties of ZSM-5 were investigated using various characterization techniques including BET surface area, scanning electron microscopy, Fourier transform infrared, X-ray diffraction, etc. [9-12]

Among the aromatic hydrocarbons on ZSM-5 type zeolites, benzene, toluene and p-xylene are most easily adsorbed (all of them have a kinetic diameter of 0.58 nm) [13-26]. Using pressure modulation methods and time-resolved fast IR spectroscopy, the elementary stages of adsorption and transfer of benzene, toluene, and o- and n-xylene molecules from the gas phase to hydroxyl groups on the surface of zeolite H/ZSM-5 (SiOH groups) and inside the zeolite pores (SiOHA1 group) [15]. Adsorption on these acidic sites of zeolites proceeds by the usual mechanism of physical adsorption. It was noted that aromatic hydrocarbon molecules move freely along the outer surface of the zeolite before they reversibly attach to OH groups, enter micropores, or are desorbed. Molecules that can enter micropores (benzene, toluene, n-xylene) are adsorbed faster on SiOHA1

groups than on SiOH groups. For o-xylene molecules, whose entry into the pores is stereochemically hindered, the rate of adsorption on the remaining SiOH groups increases significantly.

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 larger than toluene causes a change in the parameters of the lattice constants. Using X-ray diffraction analysis in [26], the parameters of the ZSM-5 zeolite crystal during the adsorption of n-xylene and the localization sites for the adsorption of molecules were determined. 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 has been shown that during adsorption in sinusoidal channels, the symmetry of the zeolite framework lattice changes from monoclinic to orthorhombic. It was shown in [17] that at 303 K benzene fills a significantly smaller part of the micropore volume of ZSM-5 zeolite than p-xylene, although both molecules have the same cross-section. In this case, p-xylene is adsorbed in approximately the same amount as n-hexane, i.e., almost completely fills the micropore volume of ZSM-5 zeolite. The authors associate such differences in the adsorption of benzene and p-xylene with additional interaction forces between the hydrogen atoms of the methyl group and more convenient packing of p-xylene molecules. The repacking of p-xylene molecules is especially clearly visible in the adsorption isotherm at 343 K.

There is a large amount of data on the adsorption of various substances in ZSM-5 type zeolites with copper and sodium cations, which were obtained by various physicochemical research methods. However, there is little data obtained by the adsorption-calorimetric method, which puts on the agenda the task of further detailed study of the adsorption properties of ZSM-5 type zeolites with copper and sodium cations in relation to toluene molecules, as well as obtaining the basic thermodynamic characteristics of these systems. 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.

## **2 Testing methods**

When determining differential heats of adsorption, two main methods are used: calorimetric and isosteric. To find isosteres, it is necessary to measure the adsorption isotherm at different temperatures. In the regions of phase transitions of adsorption isosteres, large errors arise [31].

Another method for measuring differential heats of adsorption is a calorimetric study, in which it should be noted that direct calorimetric measurements of the dependence of the heat of adsorption on the amount of adsorbed substance (or on the degree of filling) are very important. In studies of differential heats of adsorption, mainly three types of calorimeters were used. These are adiabatic, isothermal and thermally conductive calorimeters. Among the various types of calorimeters, the most suitable for slowly occurring processes is the heat-conducting calorimeter [32]

For measurements of isotherms and differential adsorption heats a system consisting of a universal high-vacuum adsorption unit and a Tian-Calvet-type, DAK-1-1A thermally conductive differential microcalorimeter connected to it was used, which has high accuracy and stability. The instrument's calorimeter sensitivity is extremely high and its reliability is high (it can measure about 0.2  $\mu$ W thermal power). It can be used with confidence to measure the heat of processes of

almost unlimited duration. The calorimeter makes it possible to obtain the thermokinetics of the process of adsorption systems under study, which is very important for elucidating the mechanism of adsorption [33].

Despite its outer insulating shells, it is not adiabatic, as the heat released in it is introduced from the calorimeter chamber as it is released and dissipated into the large metal block. Although the temperature of the calorimeter chamber changes only slightly, the instrument cannot be called strictly isothermal; it detects small temperature changes, which are unavoidable and form the basis of measurements.

Most of the heat (about 99%) released into the calorimeter chamber is dissipated into the calorimeter block immediately after release. Only about 1% of the heat released remains in the calorimeter chamber, raising its temperature very slightly. The measurement is mainly concerned with the heat flux that passes through the surface of the calorimeter chamber and the calorimeter block.

The adsorption-calorimetric method used in this work provides highly accurate molar thermodynamic characteristics and reveals detailed mechanisms of adsorption processes occurring on adsorbents and catalysts. Adsorption measurements and adsorbate dosing were carried out using a universal high-vacuum adsorption unit. The unit allows adsorbate dosing by both gas-volume and volume-liquid methods. We used a BARATRON B 627 membrane pressure gauge to measure the equilibrium pressures [31-33].

### 3 Results and discussion

The adsorption-calorimetric method, used in this work, allows obtaining high-precision molecular thermodynamic characteristics, as well as revealing the detailed mechanism of adsorption processes, lubricants, adsorbents, and catalysts. For the characteristics of adsorption properties of zeolite by measuring the differential temperature of toluene and zeolites ZSM-5 with cations of medium and cesium, as well as calculation of free energy and entropy of adsorption of toluene.

In this work, the differential heats, entropy and adsorption mechanism of toluene in CsZSM-5 and Cu<sup>2+</sup>ZSM-5 zeolites at a temperature of 303 K were studied. The composition of the unit cell of CsZSM-5 is Cs<sub>3.17</sub>[(SiO<sub>2</sub>)<sub>95.23</sub>(AlO<sub>2</sub>)<sub>3.17</sub>], Cu<sup>2+</sup>ZSM-5 - Cu<sub>1.7</sub>[(SiO<sub>2</sub>)<sub>96.13</sub>(AlO<sub>2</sub>)<sub>3.87</sub>], the content of Cs<sup>+</sup> cations average □3.17/e.c. (elementary cell), the content of Cu<sup>2+</sup> cations average □1.7/e.c.

In the work of H.Tamm and H. Stach [27] on the basis of calorimetric studies and data of [28] it was proposed to divide 1/4 unit cell of zeolite into three adsorption sites of approximately equal volume: 1st - pores between adjacent junctions in straight pores; 2nd - pores between adjacent junctions in zigzag pores; 3rd - pore crossing. According to [29] the unit cell of ZSM-5 consists of two straight and four zigzag channels. The lengths of the straight and zigzag channels were also determined to be 2.006 and 0.67 nm, respectively. Similar values were obtained by the authors [30] - 1.98 and 0.67 nm.

For the adsorption heat of polar molecules on ZSM-5 zeolites a stepwise drop of adsorption heat is characteristic, indicating stoichiometric interaction of these molecules with Me<sup>+</sup> cations compensating the negative charge of the lattice [30-31]. Thus, for the adsorption of water and alcohols we have steps corresponding to the formation of Cu<sup>2+</sup>(H<sub>2</sub>O)<sub>10</sub>, Cs<sup>+</sup>(H<sub>2</sub>O)<sub>6</sub>, Li<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>, Na<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>, Na<sup>+</sup>(CH<sub>3</sub>OH)<sub>4</sub>, Na<sup>+</sup>(C<sub>2</sub>H<sub>5</sub>OH)<sub>4</sub>, K<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>, H<sup>+</sup>(H<sub>2</sub>O)<sub>4</sub>, NH<sub>4</sub><sup>+</sup>(H<sub>2</sub>O)<sub>4</sub> [32-37]. In the case of ammonia on the NaZSM-5 zeolite we unexpectedly found the formation of Na<sup>+</sup>(NH<sub>3</sub>)<sub>8</sub>

complexes. A ball is formed, in the centre of which there is  $\text{Na}^+$  cation, and on the outer shell 24 hydrogen atoms. This tangle is situated in the crossing of straight and zigzag channels of NaZSM-5 zeolite [38-39]. Ammonia molecules on the silicate are very little adsorbed. The heat of adsorption decreases linearly from 70 kJ/mole to 30 kJ/mole with 0.5 N/M adsorption [40-41].

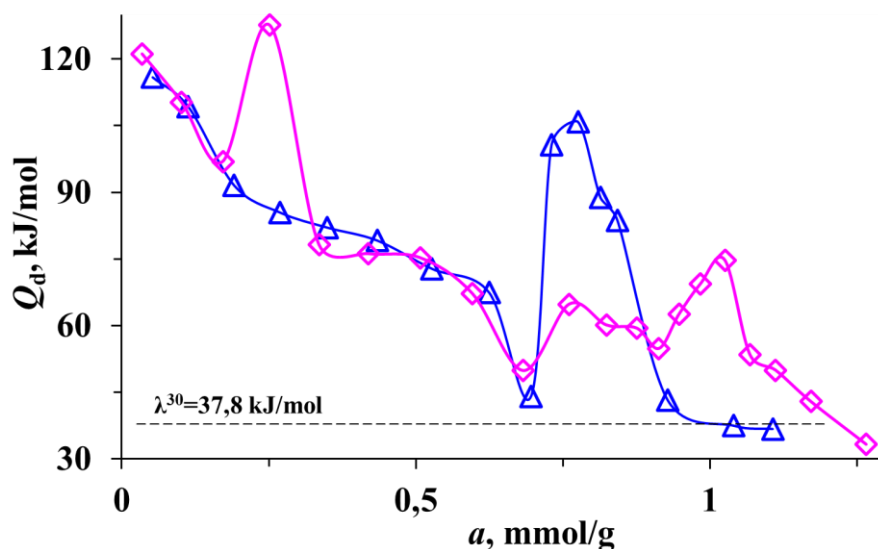
Organic substances, the molecular sizes of which do not exceed  $5.5\text{\AA}$  in diameter, are well adsorbed on all pentasils, but in different quantities (volumes). For example, if n-paraffins completely fill the entire sorption volume of silicalite or ZSM-5, densely located in all channels according to the "end to end" mechanism, then benzene is adsorbed in a smaller amount (60%) and, apparently, fills straight and zigzag channels [42]. The authors of [43-44] believe that aromatic hydrocarbons are adsorbed only in straight channels and in the crosshairs of ZSM-5 zeolite. However, what is the molecular mechanism of benzene adsorption on pentasils is not yet clear. For example, in [45] it was shown that the adsorption of benzene on silicalite is accompanied by complex changes in both the shape of the isotherm and, especially, the shape of the curve of the dependence of differential heats on adsorption values. They explained these complex changes by various reorientations and redistributions of the adsorbate in the silicalite channels, but the specific mechanisms of these changes were not considered.

The differential heats of adsorption of toluene in CsZSM-5 zeolite are presented in Figure 1. The heats of adsorption of toluene have a complex form. From Figure 1 it can be seen that the heat of adsorption of toluene in CsZSM-5 zeolite changes stepwise with increasing filling. The initial heat of adsorption is 118 kJ/mol. Depending on the occupancy of the adsorption, the enthalpy forms a step and decreases from 118 kJ/mol to  $\sim 73$  kJ/mol at an adsorption of 0.53 mmol/g.

The content of copper cations, according to the chemical composition of the e.c. (elementary cell), is 0.54 mmol/g, i.e. heat drop from 118 kJ/mol to 73 kJ/mol upon adsorption of 0.54 mmol/g associated with the adsorption of one toluene molecule on one  $\text{Cs}^+$  cation. The amount of high-energy adsorbed toluene corresponds to the scheme  $1\text{C}_6\text{H}_5\text{CH}_3:\text{Cs}^+$ . Forming a step in the formation of a mono  $1\text{C}_6\text{H}_6\text{CH}_3:\text{Cs}^+$  ion-molecular complex, the differential heat of adsorption increases to 106 kJ/mol, then decreases to the heat of condensation of toluene, forming a dimer  $2\text{C}_6\text{H}_6\text{CH}_3:\text{Cs}^+$  ion-molecular complex.

The reason for the increased heat at low fillings is apparently the  $\text{Cs}^+$  cations, with which toluene can interact due to the induction effect. Further, with increasing adsorption, the formation of a complex of the  $\text{Cs}^+$  cation with 2 toluene molecules occurs at adsorption  $\sim 1.1$  mmol/g, forming the second step, the heat of adsorption decreases to  $\sim 38$  kJ/mol. This  $2\text{C}_6\text{H}_6\text{CH}_3:\text{Cs}^+$  complex, given its size, can only be located in the crosshairs of straight and zigzag channels. In the second coordination sphere of ZSM-5 zeolite, that is, in the part of silicalite that does not contain cations and the third coordination sphere, the adsorption process of toluene was not observed.

The maximum sorption volume of zeolite for benzene, as can be seen from Fig. 1, is 1.1 mmol/g. The content of cesium cations, according to the chemical composition of the e.c. (elementary cell), is 0.54 mmol/g, i.e. each cesium cation interacts with two toluene molecules. Apparently, a sandwich-shaped  $\pi$ -complex with a cesium cation in the middle is formed. The only question is where this complex is located - either completely at the intersections of the channels (obvious for tetrahedral complexes, for example, with water and para-xylene [32-33]), or in straight channels with toluene molecules strongly protruding into the intersections of the channels (less likely model).



**Figure 1.** Differential heats of adsorption of toluene in  $\triangle$ -CsZSM-5 and  $\diamond$ -Cu<sup>2+</sup>ZSM-5 zeolites. The horizontal dashed line is the heat of condensation of toluene at a temperature of 303 K.

Apparently, the benzene rings form a dihedral angle equal to the angle between the zigzag channels and the ring planes oriented perpendicular to the axes of the zigzag channels. With this conformation of the adsorption complex, the cesium cation can simultaneously interact with the  $\pi$ -electrons of the benzene rings and with the oxygen atoms of the lattice, and the hydrogen atoms of toluene molecules with the oxygen atoms of the zigzag channels.

The differential heats of adsorption of toluene in Cu<sup>2+</sup>ZSM-5 zeolite are presented in Figure 1. The heats of adsorption of toluene have a rather complex form than for CsZSM-5. When filling, the heat of adsorption of toluene in Cu<sup>2+</sup>ZSM-5 zeolite changes stepwise with increasing filling. The initial heat of adsorption (without taking into account adsorption on the impurity center) is 121 kJ/mol. Depending on the adsorption occupancy, the enthalpy increases from 121 kJ/mol to ~128 kJ/mol at an adsorption of 0.25 mmol/g. The reason for the increased heat on Cu<sup>2+</sup>ZSM-5 up to fillings of 0.25 mmol/g is apparently cesium cations, with which toluene can interact due to the induction effect and redistribution of toluene on cesium cations. Further, the heat of adsorption decreases to 78 kJ/mol with an adsorption of 0.33 mmol/g [48].

The content of copper cations, according to the chemical composition of the e.c. (elementary cell), is 0.3 mmol/g, i.e. heat drop from 128 kJ/mol to 78 kJ/mol upon adsorption of 0.33 mmol/g associated with the adsorption of one toluene molecule on one Cu<sup>2+</sup> cation. The amount of high-energy adsorbed toluene corresponds to the scheme 1C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>:Cu<sup>2+</sup>. As adsorption increases, complexes of Cu<sup>2+</sup> cations form with two toluene molecules with a decrease in heat from 78 kJ/mol to 67 kJ/mol with an adsorption of 0.6 mmol/g, i.e., forms 2C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>:Cu<sup>2+</sup>.

Next, adsorption occurs in zigzag and straight zeolite channels, i.e. parts where there are no Cu<sup>2+</sup> cations, since in terms of the level of heats of adsorption they correspond to the heats of adsorption of toluene in these channels (numerous data on the heats of adsorption of benzene on various cationic forms of ZSM-5 zeolite and silicalite). Total adsorption is 1.3 mmol/g in terms of cation.

Considering that the dispersion potential in zigzag channels is higher, it can be assumed that adsorption initially occurs in zigzag channels. After zigzag, toluene is adsorbed in straight

channels. The reason for the increased heat at high fillings is apparently copper cations, with which toluene can interact due to the induction effect.

The differential heat of adsorption in the cationic forms of copper and cesium zeolite is practically at the same level.

#### **4 Conclusion**

Adsorption-calorimetric studies of the adsorption of toluene with copper and cesium cations in ZSM-5 type zeolites were carried out. The differential heats of adsorption of toluene on CsZSM-5 and Cu<sup>2+</sup>ZSM-5 zeolites were obtained. A stepwise nature of the heat of adsorption of toluene was revealed. A correlation was found between the adsorption-energy characteristics and the molecular mechanism of toluene adsorption on CsZSM-5 and Cu<sup>2+</sup>ZSM-5 zeolites was revealed throughout the entire filling region. Toluene adsorbed in CsZSM-5 zeolite is located in the first coordination sphere with the Cs<sup>+</sup> cation, forming a dimer 2C<sub>6</sub>H<sub>6</sub>CH<sub>3</sub>:Cs<sup>+</sup> ion-molecular  $\pi$ -complex. In the second coordination sphere of CsZSM-5 zeolite, that is, in the part of silicalite that does not contain cations and the third coordination sphere, the adsorption process of toluene was not observed. Toluene adsorbed in Cu<sup>2+</sup>ZSM-5 zeolite is located in the first coordination sphere with the Cu<sup>2+</sup> cation and also forms a dimer 2C<sub>6</sub>H<sub>6</sub>CH<sub>3</sub>:Cu<sup>2+</sup> ion-molecular  $\pi$ -complex. In the second coordination sphere of Cu<sup>2+</sup>ZSM-5 zeolite, that is, in the part of silicalite that does not contain cations, 0.65 mmol/g of toluene is adsorbed, as well as in the third coordination sphere CsZSM-5, the adsorption process of toluene was not observed. The heat of adsorption correlates with the number of copper and cesium cation in zeolite structures. It has been shown that the adsorption properties of ZSM-5 zeolites depend on the type of cation, as well as on the structure of the fragments of the ZSM-5 type zeolite structure.

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