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# **Isotherm and Differential Heats of Meta-Xylene Adsorption on Zeolite CuZSM-5**

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**ABSTRACT:** This article presents the results of the thermodynamic characteristics of adsorption of metaxylene in  $\text{Cu}^{2+}$ ZSM-5 zeolite 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 Tian-Calve type DAK- 1-1A. A correlation between the adsorption-energy characteristics was found and the molecular mechanism of metaxylene adsorption in  $\text{Cu}^{2+}$ ZSM-5 zeolite was revealed in the entire filling area. A stepwise nature of the heat of adsorption of meta-xylene was revealed. It has been established that cations in  $\text{Cu}^{2+}$  zeolite are located in screened positions of the ZSM-5 zeolite crystal lattice. The adsorption of a metaxylene molecule leads to the migration of  $\text{Cu}^{2+}$  cations from the zeolite lattice to the crosshairs formed by the intersection of straight and zigzag channels and the formation of ion/molecular complexes of various multiplicity in them.

**KEYWORDS:** Adsorption, heat of adsorption, thermodynamics, enthalpy, adsorption isotherm, entropy, thermokinetics, calorimeter, metaxylene.

## **I.INTRODUCTION**

Zeolites are currently the most important catalysts for the processing of various hydrocarbon feedstocks. Synthetic zeolites ZSM-5 are highly efficient catalysts for these processes. The study of the adsorption properties of zeolites provides useful information about the structural characteristics and possibilities of practical application. Using adsorption measurements, one can obtain data on various factors, for example, channel sizes, pore volume, cation localization, etc., associated with the structure of a particular zeolite. Of particular interest is the study of the adsorption of various substances in zeolites of the ZSM-5 type. Adsorption on these zeolites strongly depends on the cations present in the structure and on the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio. Because of the large space between adsorption sites, zeolite is ideal for model studies of adsorption behavior.

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 contained in them. Therefore, a comprehensive study of the physicochemical and especially energy characteristics of zeolites of the ZSM-5 type 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, 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.

Various physicochemical properties of ZSM-5 have been investigated using various characterization methods, including X-ray diffraction, BET surface area (Brunauer-Emmett-Teller), infrared Fourier transform, scanning electron microscopy and calorimetric methods [1-18].



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The elementary stages of adsorption and transfer of benzene, toluene, and o- and n-xylenes molecules from the gas phase to hydroxyl groups on the surface of H/ZSM-5 zeolite (SiOH groups) and inside zeolite pores (SiOHA1 groups) [19].

Among the aromatic hydrocarbons, benzene, toluene and p-xylene are the most easily adsorbed on ZSM-5 type zeolites (all of them have a kinetic diameter of 0,58 nm). Studies of the adsorption of benzene, toluene, and paraxylene in silicalite are the subject of works [20–23]. Adsorption on the acid sites of zeolites proceeds according to the usual mechanism of physical adsorption. It was noted that aromatic hydrocarbon molecules move freely over the outer surface of the zeolite before they reversibly attach to OH groups, enter micropores, or desorb. Molecules capable of entering micropores (benzene, toluene, n-xylene) adsorb faster on SiOHA1 groups than on SiOH groups. For o-xylene molecules, whose entry into the pores is sterically hindered, the rate of adsorption on the remaining SiOH groups increases significantly.

The adsorption and catalytic properties of hydrocarbons depend not only on the shape and size of the zeolite pores, but, as mentioned above, on the  $\text{SiO}_2/\text{Al}_2\text{O}_3$  ratio, as well as on the type of cation. From the point of view of the nature of the sorbent, ZSM-5 and silicalite behave in the same way; the pore size and adsorption capacity of both zeolites are the same.

There are a large number of data on the adsorption of hydrocarbons in zeolites of the pentasil type, which were obtained by various physicochemical methods of investigation. However, there are few 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 respect to hydrocarbon molecules, as well as polar molecules, and obtaining the main thermodynamic characteristics of these systems.

In this work, the isotherm and differential heats of meta-xylene adsorption in  $\text{Cu}^{2+}$ ZSM-5 zeolite at a temperature of 303 K are studied. The ZSM-5 zeolite studied by us ( $\text{Si}/\text{Al}=27.5$ ) contains the polyvalent cation  $\text{Cu}^{2+}$  (0.3 mmol/g). The unit cell composition is  $\text{Cu}^{2+}\text{ZSM-5-Cu}_{1.69}[(\text{SiO}_2)_{96.63}(\text{AlO}_2)_{3.37}]$ .

## II. SIGNIFICANCE OF THE SYSTEM

Zeolites are currently the most important catalysts for the processing of various hydrocarbon feedstocks. Synthetic zeolites ZSM-5 are highly efficient catalysts for these processes. The study of methodology is explained in section III, section IV covers the experimental results of the study, and section V discusses the future study and conclusion.

## III. METHODOLOGY

When determining the differential heats of adsorption, two methods are basic: calorimetric and isosteric. To find isosteres, it is necessary to measure the adsorption isotherm at different temperatures. Large errors arise in the regions of phase transitions of adsorption isosteres.

Another method for measuring the 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. Three types of calorimeters were mainly used in studies of differential heats of adsorption. These are adiabatic, isothermal and heat-conducting calorimeters. Among various types of calorimeters, the most suitable for slow processes is a heat-conducting calorimeter. A modified heat-conducting microcalorimeter of the Tiania-Calve DAK-1-1A type, which has high accuracy and stability, was used as a calorimeter.

Adsorption measurements and dosage of the adsorbate were carried out using a universal high-vacuum adsorption unit. The installation allows the dosage of the adsorbate both by gas-volume and volume-liquid methods. Meta-xylene was dosed from a pre-calibrated microcapillary with a cross section of  $0,095 \text{ mm}^2$ . To measure equilibrium pressures, we used a BARATRON B 627 diaphragm pressure gauge.

We set the task of studying the adsorption of meta-xylene on  $\text{Cu}^{2+}$ ZSM-5 zeolite using the adsorption-calorimetric method. These data could provide information on the state of the  $\text{Cu}^{2+}$  cation, adsorption mechanism, conformation, and localization of the adsorbate/cation complex. In turn, this information can facilitate understanding of the mechanism of catalytic processes.

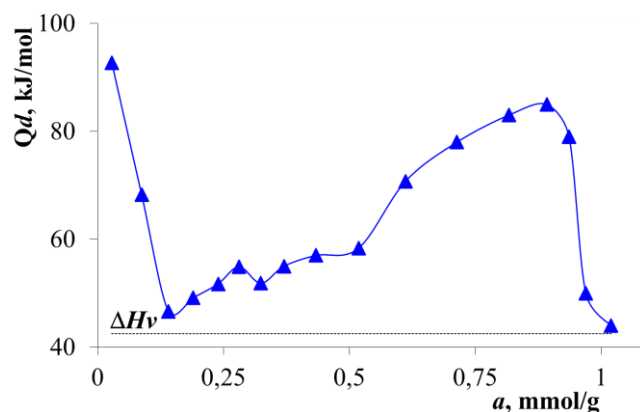
## IV. EXPERIMENTAL RESULTS

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. To characterize the adsorption properties of the zeolite, the differential heats and isotherms of meta-xylene adsorption were measured, and the entropy and free energy of meta-xylene adsorption were calculated.

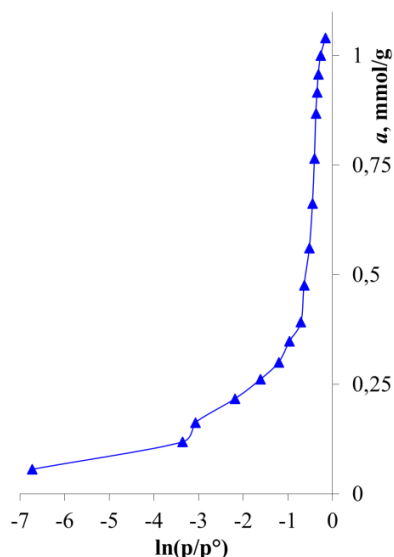
The differential heats of meta-xylene adsorption on  $\text{Cu}^{2+}$ ZSM-5 zeolite are shown in Fig.1. The heat of adsorption of meta-xylene on  $\text{Cu}^{2+}$ ZSM-5 zeolite differs from the heat of adsorption of meta-xylene, para-xylene, and benzene on zeolites NaZSM-5, LiZSM-5, KZSM-5, HZSM-5, and silicalite [8–10, 25–27], which indicates the different nature of the adsorption of aromatic hydrocarbons in these zeolites.

The differential heats of adsorption of meta-xylene on CuZSM-5 have a rather complex form (Figure 1). In the initial region, the heat of adsorption decreases linearly from 93 kJ/mol to 47 kJ/mol at an adsorption of 0.15 mmol/g. The linear decrease in the heat of adsorption is apparently associated with the adsorption of meta-xylene at the crossroads of channels with two  $\text{Cu}^{2+}$  cations; the amount of adsorbed meta-xylene corresponds to the  $\text{C}_8\text{H}_{10}:2\text{Cu}^{2+}$  scheme. The content of copper cations, according to the chemical composition of the EA, is 0,3 mmol/g. As the amount of adsorption increases, copper cations are redistributed, and the amount of adsorbed meta-xylene corresponds to the  $\text{C}_8\text{H}_{10}:\text{Cu}^{2+}$  scheme. This confirms that the adsorption of the meta-xylene molecule leads to the migration of  $\text{Cu}^{2+}$  cations from the zeolite lattice to the crosshairs formed by the intersection of straight and zigzag channels, as in the LiZSM-5 zeolite. Due to its small size,  $\text{Cu}^{2+}$ , like lithium cations, is located not in the main channels, but in side channels, where adsorbed molecules are unable to penetrate. The heat of adsorption increases linearly up to 55 kJ/mol at adsorption of 0,3 mmol/g and forms a step, then increases to 60 kJ/mol at adsorption of 0.6 mmol/g. The adsorbed meta-xylene corresponds to the scheme  $2\text{C}_8\text{H}_{10}:\text{Cu}^{2+}$ . Then, the heat of adsorption increases again and, forming a step (85 kJ/mol), decreases to the heat of condensation of 43 kJ/mol at an adsorption of 1.02 mmol/g.



**Figure 1. Differential heats of adsorption of meta-xylene in CuZSM-5.  
The horizontal dashed line is the heat of condensation**

The adsorption of the next two molecules of meta-xylene initially proceeds with an increase in heat to a level of 60 kJ/mol, with an adsorption of 0,6 mmol/g and the amount of adsorbed meta-xylene corresponds to the scheme  $2\text{C}_8\text{H}_{10}:\text{Cu}^{2+}$ , then again increases to 80 kJ/mol with adsorption of 0.9 mmol/g. The amount of adsorbed meta-xylene corresponds to the scheme  $3\text{C}_8\text{H}_{10}:\text{Cu}^{2+}$ . Due to its size, this complex can only fit in the intersections of straight and zigzag zeolite channels. Further, the heat of adsorption decreases to the heat of condensation and goes already in the "silicalite" part of the zeolite, i.e. in the part where there are no  $\text{Cu}^{2+}$  cations. The total adsorption of meta-xylene on CuZSM-5 zeolite is 1,02 mmol/g. This is 0,9 mmol/g more than in the adsorption of meta-xylene on silicalite. However, meta-xylene is adsorbed on silicalite at a rate of 0,12 mmol/g [8], i.e. this confirms the formation of a three-dimensional ion-molecular complex in the first coordination sphere and 0,12 mmol/g adsorption in the second coordination sphere.



**Figure 2. Meta-xylene adsorption isotherm in CuZSM-5.  
The horizontal dashed line is the heat of condensation**

Figure 2 shows the corresponding water adsorption isotherm on  $\text{Cu}^{2+}$ ZSM-5 zeolite in semilogarithmic coordinates. The adsorption isotherm of meta-xylene on  $\text{Cu}^{2+}$ ZSM-5 zeolite was adjusted to 1,02 mmol/g at relative pressures  $P/P_s=0,86$ . If we assume that the density of meta-xylene in the zeolite is the same as that of a normal liquid at the temperature of the experiment and calculate the volume occupied by a meta-xylene molecule upon saturation, then it turns out that meta-xylene occupies 0.15  $\text{cm}^3/\text{g}$  of the sorption volume of  $\text{Cu}^{2+}$  zeolite ZSM-5, which is 90%, i.e. completely occupies the space.

## V. CONCLUSION AND FUTURE WORK

Adsorption-calorimetric studies of the adsorption of a meta-xylene molecule on  $\text{Cu}^{2+}$ ZSM-5 zeolite have been carried out. It has been established that  $\text{Cu}^{2+}$  cations are located in screened positions of the ZSM-5 zeolite crystal lattice. The adsorption of a meta-xylene molecule leads to the migration of  $\text{Cu}^{2+}$  cations from the zeolite lattice into crosshairs formed by the intersection of straight and zigzag channels and the formation of ion/molecular complexes of various multiplicity in them. 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. Meta-xylene adsorbed on CuZSM-5 zeolite is located in the first coordination sphere with the  $\text{Cu}^+$  cation, forming three-dimensional meta-xylene complexes. These complexes are located at the crossroads of straight and zigzag canals.

## REFERENCES

- [1] M.Albahar, Ch.Li, V.Zholobenko, A.Garforth, The effect of ZSM-5 zeolite crystal size on p-xylene selectivity in toluene disproportionation Microporous and Mesoporous, Materials Volume 302, 1 August 2020, 110221.
- [2]. X.Niu, K.Wang, Y.Bai, Y.Du, Y.Chen, M.Dong and W.Fan, Selective Formation of Para-Xylene by Methanol Aromatization over Phosphorous Modified ZSM-5, Zeolites Catalysts 2020, 10, 484.
- [3]. D.Pan, X.Song, X.Yang, L.Gao, R.Wei, J.Zhang, G.Xiao, Efficient and selective conversion of methanol to para-xylene over stable H[Zn,Al]ZSM-5/SiO<sub>2</sub> composite catalyst, Appl. Catal., 2018, 557, 15–24. [CrossRef].
- [4]. Xomeritakis, G.; Nair, S.; Tsapatsis, M. Microporous Mesoporous Mater. The Location of o- and m-Xylene in Silicalite by Powder X-ray Diffraction// 2000. -Vol. 38. -P. 61-73.
- [5]. Nair S., Tsapatsis. The Location of o- and m-Xylene in Silicalite by Powder X-ray Diffraction // J. Phys. Chem. -B 2000. -Vol. 104. -P. 8982-8988.
- [6]. J.Li, K.Tong, Z.Xi, Y.Yuan, Z.Hu, Z.Zhu, High-efficient conversion of methanol to p-xylene over shape-selective Mg-Zn-Si-HZSM-5 catalyst with fine modification of pore-opening and acidic properties, Catal. Sci. Technol., 2016, 6, 4802–4813. [CrossRef]
- [7]. M.Rasouli, N.Yaghoobi, S.Chitsazan, M.Hossein, Sayyar Influence of monovalent cations ion-exchange on zeolite ZSM-5 in separation of para-xylene from xylene mixture Microporous and Mesoporous, Materials, Volume 150, 1 March 2012, pp.47-54.
- [8]. Г.Рахматқариев, А.Агзамходжаев, Ф.Рахматқариева. Дифференциальные теплоты адсорбции мета-ксилола в силикалите, Узбекский химический журнал, 2011, №2, pp.3-6.



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## International Journal of Advanced Research in Science, Engineering and Technology

Vol. 9, Issue 7, July 2022

- [9]. Kh.Bakhronov, O.Ergashev, Kh.Karimov, T.Abdulkhaev, Y.Yakubov, A.Karimov, Thermodynamic Characteristics of Paraxylene Adsorption in LiZSM-5 and CsZSM-5 Zeolites, AIP Conference Proceedings 2432, 050056 (2022); Published Online: 16 June 2022, <https://doi.org/10.1063/5.0090039>
- [10]. Г.Пименов, В.Скирда, В.Максименко, В.Морозов, О.Опанасюк, Изучение влияния природы адсорбированных молекул на фазовые переходы в силикалите типа ZSM-5 методами ЯМР и рентгеноструктурного анализа, Коллоидный журнал, 2004, №6, т.66, pp.802-806
- [11]. Xomeritakis, G.; Tsapatsis, M. Separation of Xylene Isomers by Membranes //Chem. Mater. -1999. -Vol. 11. -P 875-878.
- [12]. D.Olson, G.Kokotailo, S.Lawton, W.Meier, Crystal structure and structure - related properties of ZSM-5, J.Phys.Chem., 1981, v.35, pp.2238-2243.
- [13]. Х.Тамм, Х.Штах, Н.Регент, Калориметрические исследования адсорбции ароматических углеводородов на силикалите, Известия АН СССР, серия химическая, 1982, №12, pp.2820-2822.
- [14]. Y.Ma, Y.Lin, Adsorption of liquid hydrocarbons in silicalite, AIChE Symp.Ser., 1985, v.81. pp.39-44.
- [15]. C.Pope, Sorption of benzene, toluene and p-xylene on silicalite and HZSM-5, J.Phys.Chem., 1986, v.90, pp.835-837.
- [16]. H.Thamm, Calorimetric study on the state of aromatic molecules sorbed on silicalite, J.Phys.Chem., 1987, v.91, №1, pp.8-11.
- [17]. Ю.Тарасевич, В.Поляков, Х.Миначев, А.Пенчев, Исследование состояния воды и углеводородов в микропорах цеолитов ZSM-5 методом адсорбционной калориметрии, Коллоидный журнал, 1993, т.55, №1, pp.128-137.
- [18]. V.Roningsveld, F.Tuinstra, The location of P-xylene in a single crystal of HZSM-5 with a new, sorbate - induced, orthorhombic frame work symmetry, Acta crystallogr. B., 1989, v.45, №4, pp.423-431.
- [19]. Olson D.H., Kokotailo G.T., Lawton S.L., Meier W.M. Crystal structure and structure - related properties of ZSM-5 //J.Phys.Chem. -1981. -v.35. -P.2238-2243.
- [20]. Jentys A., Tanaka H., Lercher J. A. Surface processes during sorption of aromatic molecules on medium pore zeolites// J. Phys. Chem., 2005, BN6, -v.109, -P.2254-2261
- [21]. Ashtekar Sunil, Hastings Jeremy J., Gladden Lynn F. FT-Raman studies of single-component and binary adsorption in silicalite-1// J. Chem. Soc. Faraday Trans. 1998, N 8, -v.94, -P.1157-1161
- [22]. Пименов Г. Г., Скирда В. Д., Максименко В. Ю., Морозов В. П., Опанасюк О. А. Изучение влияния природы адсорбированных молекул на фазовые переходы в силикалите типа ZSM-5 методами ЯМР и рентгеноструктурного анализа.// Коллоид. ж. 2004, N 6, -т.66, С.802-806
- [23]. Song W., Justice R. E., Jones C. A., Grassian V. H., Larsen S. C. Synthesis, characterization, and adsorption properties of nanocrystalline ZSM-5 //Langmuir 2004, N 19, -v.20, -P.8301-8308
- [24]. Thamm H., Calorimetric study on the state of aromatic molecules sorbed on silicalite, J.Phys.Chem., 1987, v.91, №1, pp.8-11.
- [25]. Рахматкариев Г.У., Бахронов Х.Н., Белоковский В.М., Бодденберг Б., Исирикян А.А. Дифференциальные теплоты адсорбции паров бензола на пентасиловом цеолите NaZSM-5 //Узб.хим.журн. -1999. -№ 4. -С.34-37.
- [26]. Yakubov Yuldosh Yusupboevich, Rakhmatkarieva Furuza Gayratovna, Doliev G'olibjon Alisherovich, Khudaybergenov Mansur Saburovich Laws Of Adsorption Of Benzene, Methyl And Ethyl Alcohols In Pentasil-Type Zeolites//Solid State Technology Volume: 63 Issue: 6 Publication Year: 2020. PP. 9709-9716.
- [27]. Якубов Й.Ю., Рахматкариева Ф.Г. Изотерма, дифференциальные теплоты и энтропии адсорбции бензола в цеолите K3,6ZSM-5//Universum: химия и биология Выпуск: 12(78) . Декабрь 2020. Часть 2. С.25-29. (02.00.00, № 2)..