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Basic Thermodynamic Characteristics and Mechanism of n-Hexane Adsorption in Zeolite AgZSM-5

**Tolibjon Abdulkhaev, Shakhnoza Kuldasheva, Khayot Bakhronov,
Ilmira Absalyamova**

Doctoral student, Namangan institute of engineering and technology, Namangan, Uzbekistan

Professor, Institute of General and Inorganic Chemistry, Tashkent, Uzbekistan,

Associate professor, Tashkent University of Information Technologies named after Muhammad al-Khwarizmi,
Tashkent, Uzbekistan

Associate, Tashkent University of Information Technologies named after Muhammad al-Khwarizmi, Tashkent,
Uzbekistan

ABSTRACT. This article presents isotherms and main thermodynamic characteristics of n-hexane adsorption in AgZSM-5 zeolite obtained by the calorimetric method. The adsorption isotherm is described by the three-term equation of the theory of volume filling of micropores (VMOT). A correlation between the adsorption-energy characteristics was found and the molecular mechanism of n-hexane adsorption in AgZSM-5 zeolite was revealed in the entire filling area. n-Hexane adsorbed in AgZSM-5 zeolite is located in the first coordination sphere with Ag^+ cations, forming tetrameric complexes. It has been found that the charge density significantly affects the adsorption mechanism, adsorption energy, and the number of adsorbed molecules. This paper shows how calorimetric data can be used to complement crystal structure results and reveal subtle adsorbent/adsorbate interactions at the molecular level.

KEYWORDS: Zeolite, silicalite, adsorption centers, adsorption, filling, heat, isotherm, temperature, volume, pressure, condensation, n-hexane, microcalorimeter.

I. INTRODUCTION

Zeolite catalysts indicate high activity for a wide range of chemical reactions, which compares their activity with the activity of enzymes. However, in view of their diversity and the multiplicity of their active sites, the mechanism of action of these catalysts is still a matter of debate. In [1], the change in the unit cell parameters of the ZSM-5 zeolite during the adsorption of various organic dyes was studied by X-ray diffraction analysis. It is shown that the change in the size of the zeolite lattice depends both on the nature of the adsorbed molecules and on their sizes. Adsorption of paraffins (C_6 , C_8 , C_{14}) leads to an increase in all sizes of the zeolite unit cell, with the greatest changes being observed for tetradecane.

Optical microscopy and X-ray diffraction analysis have shown that silicalite-1 crystals expand upon adsorption of C_4 – C_8 alkanes and isobutane at room temperature [2]. The linear expansion of crystals with a size of 200 μm in the direction of the c axis is 0,20 – 0,45%. During the adsorption of n-pentane, n-hexane, and n-heptane, the maximum linear expansion in the b direction is $\approx 0,54\%$. During the adsorption of hexane and n-heptane, the maximum volume expansion is 1.2%. At the same time, during the adsorption of benzene, the volume of the unit cell of the zeolite almost does not change. The expansion in the a direction for all molecules, except for isobutane, is the smallest. In the adsorption of n-hexane, the expansion at 180 K is greater than at room temperature. It was noted that the expansion of ZSM-5 zeolite crystals during the adsorption of n-alkanes reduces the size of defects in a polycrystalline zeolite membrane and changes the n-octane flux through defects. The adsorption-induced expansion of zeolite crystals is reversible. In the work of Tamm H. and Shtah H. [3], on the basis of calorimetric studies and data [4], it was proposed to divide 1/4 of the unit cell of the zeolite into three adsorption sites with approximately the same volume: 1st - pores between adjacent intersections in straight pores; 2nd - pores between adjacent intersections in zigzag pores; 3rd - crossroads. According to [5], the unit cell of silicalite consists of two straight and four zigzag channels. The length of straight and zigzag channels was also determined, which is 2.006 and 0.67 nm, respectively. Close values were obtained by the authors of [6] - 1.98 and 0.67 nm. There is a large number of data on the adsorption of hydrocarbons in



zeolites of the pentasil type, which were obtained by various physicochemical methods of research. 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.

II. SIGNIFICANCE OF THE SYSTEM

Zeolites are currently the most important catalysts for the processing of various hydrocarbon feedstocks. Synthetic zeolites ZSM-5 with various cations 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

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 μ W thermal power). It can be used confidently 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 adsorption mechanism. Despite its outer insulating shells, it is not adiabatic, as the heat released in it is introduced from the calorimeter chamber as 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 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

IV. EXPERIMENTAL RESULTS

The adsorption isotherm of n-hexane on zeolite $Ag_{1.72}ZSM-5$ in semilogarithmic coordinates is shown in Figure 1. The isotherm, concave at low relative $P/P_s=0,000245$ interacting adsorption centers. The content of silver cations, according to the chemical composition of the EC (elementary cell), is 0,302 mmol/g, i.e. the amount of adsorbed n-hexane corresponds to the $1C_6H_{14}:Ag^+$ scheme. Starting from $P/P_s=0,000376$ (0,0704 torr) with adsorption of 0,3 mmol/g, a monoion-molecular complex $1C_6H_{14}:Ag^+$ is formed and the isotherm rises steeply up to relative pressures $P/P_s=0,000494$ (0,093 torr) at adsorption of 1,23 mmol/g and forms a step. This step of the adsorption isotherm fully corresponds to the ionic-molecular mechanism of the $4C_6H_{14}:Ag^+$ tetra complex. Further, the relative pressures rapidly increase to $P/P_s=0,615$ at an adsorption of 2,27 mmol/g. This means that the following n-hexane molecules are adsorbed in the non-cationic parts of the zeolite, i.e. in straight and sinusoidal channels, known as the silicalite part.

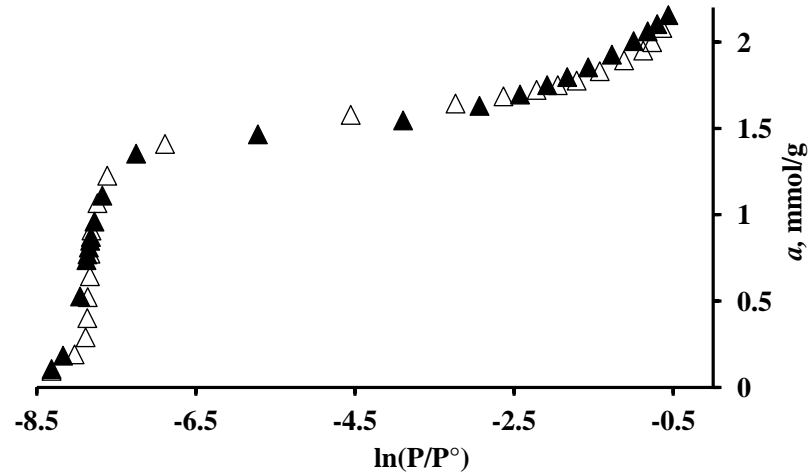


Figure 1. Adsorption isotherms of n-hexane on AgZSM-5 zeolite. Δ -experimental points, \blacktriangle -points calculated using VMOT

The n-hexane adsorption isotherm on AgZSM-5 zeolite is described by the two-term VMOT equation [7, 8]:

$$a = 0.679 \exp[-(A/20.23)^{20}] + 0.738 \exp[-(A/19.96)^{60}] + 0.992 \exp[-(A/19.96)^1] \quad (1)$$

Figure 2 shows that the calculated data are in good agreement with the experimental data.

The differential heat of adsorption of n-hexane on AgZSM-5 zeolite is shown in Figure 2. The differential heat of adsorption changes in a wave-like manner. At low fillings, it decreases from 93 kJ/mol to 86 kJ/mol, forming the first step with the ion-molecular mechanism $1C_6H_{14}:Ag^+$ at adsorption of 0,3 mmol/g. Further, the heat changes in waves up to 85 kJ/mol at 0,6 mmol/g, forming the second step with the $2C_6H_{14}:Ag^+$ mechanism. The next two molecules of n-hexane with constant heat form the $4C_6H_{14}:Ag^+$ complex at an adsorption of 1,23 mmol/g. As mentioned above, the content of silver cations, according to the chemical composition of EC (elementary cell), is 0.302 mmol/g, i.e. the number of cations in the zeolite corresponds to the stages of each emerging ion-molecular mechanism.

Subsequent n-hexane molecules are adsorbed without the participation of cations, and the heat of adsorption coincides, as in the case of silicalite, i.e. without the cationic part in the structure. The differential heat curve of n-hexane adsorption on AgZSM-5 zeolite corresponds to the adsorption isotherm.

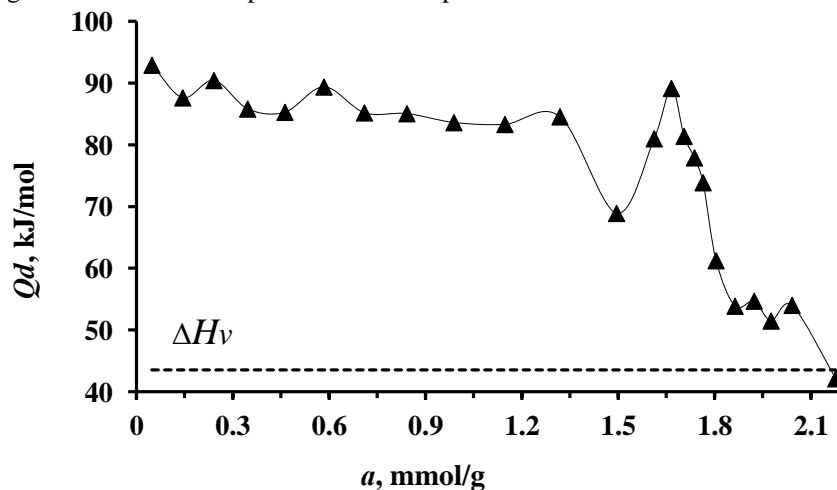


Figure 2. Differential heats of n-hexane adsorption on AgZSM-5 zeolite. The horizontal dashed line is the heat of condensation.

The cause of overestimated heats at low and high ($a > 1,5$) fillings, apparently, are silver cations, with which n-hexane can interact due to the inductive effect. Total adsorption is 7.5 molecules of n-hexane in terms of the cation



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V. CONCLUSION AND FUTURE WORK

Adsorption-calorimetric studies of the adsorption of the n-hexane molecule on Ag_{1.72}ZSM-5 zeolite have been carried out. Complete thermodynamic characteristics of n-hexane adsorption on Ag_{1.72}ZSM-5 zeolite have been obtained. Adsorption isotherms are described by the three-term equation of the theory of volume filling of micropores (VMOT). A stepwise nature of the heat of adsorption of n-hexane on Ag_{1.72}ZSM-5 zeolite was revealed. The length of the high heat region correlates with the number of silver cations in the zeolite structures. It has been determined that n-hexane adsorbed in Ag_{1.72}ZSM-5 zeolite is located in the first coordination sphere with Ag⁺ cations, forming tetrameric complexes.

REFERENCES

1. Pollack S.S., Gormley R.J., Wetzel E.L. Changes in the unit cell dimensions of ZSM-5 produced by the adsorption of organic liquids // *Adv. X Ray Anal.* Vol.29: Prog.34 thAnny.Conf., Snowmass, Colo, Aug. 5-9, 1985. New York; London, 1986. -pp.257-264.
2. Sorenson Stephanie G., Smyth Joseph R., Kocirik Milan, Zikanova Arlette, Noble Richard D., Falconer John L. Adsorbate-induced expansion of silicalite-1 crystals. // *Ind. And Eng. Chem. Res.* 2008. 47, no. 23, pp. 9611-9616.
3. Tamm H., Shtakh H. Calorimetric studies of the adsorption of cyclo-alkanes on silicalite // *Izv. USSR Academy of Sciences, Ser.Khim.* -1985. -№4. -pp.944-947.
4. Flanigen E.M., Bennet J.M., Grose R.W., Cohen J.P., Patton R.L., Kirdiner R.M. Silicalite a new hydrophobic crystalline silics molecular sieve // *Nature.* -1978. -v.271. -pp.512-516.
5. Wu P., Debebe A., Ma Y.N. Adsorption and diffusion of C₆ and C₈ hydrocarbons in silicalite // *Zeolites.* -1983. -v.3. -pp.95-97.
6. Suib S.L., Stuey G.D., Blattner R.I. Auger spectroscopy studies of natural and synthetic zeolites. 1.Surface and bulk compositions // *J.Catal.* -1980. -v.65. -pp.174-178.
7. Kh.N.Bakhronov, Ergashev O.K. Differential heats, isotherm and entropy of n-pentane adsorption in CsZSM-5 zeolite // *Universum: chemistry and biology.* Issue: 11(89), November 2021. Part 1. -pp.96-99
8. Izotova T.I., Dubinin M.M. Study of the microporous structure of activated carbons // *Journal of Physical Chemistry.* -1965. -v.39. -pp.2796-2803.
9. Rakhmatkariev G.U., Isirikyan A.A. Complete description of the adsorption isotherm by the equations of the theory of volumetric filling of micropores // *Izv.AN SSSR, Ser.khim.* -1988. -№11. -pp.2644-2645.
10. Yakubov Y.Yu., Rakhmatkarieva F.G. Differential heats and adsorption isotherm of n-hexane in HZSM-5 zeolite // *Universum: chemistry and biology.* Issue: 11(77) November 2020. Part 2. -pp.44-47
11. Bakhronov Kh.N., Ergashev O.K. Differential heats, isotherm and entropy of n-pentane adsorption in CsZSM-5 zeolite // *Universum: chemistry and biology.* 2021, No. 11(89), -pp.96-99.