ISOTHERM ADSORPTION OF TOLUENE AND ZEOLITE Cu^{2+}ZSM-5

Esonkulova Nazirahon[1],
Ahkmadov Majidjon[2],
Bakhronov Khayot[2]
[1]Namangan Institute of Engineering and Technology,
[2]Tashkent University of Information Technologies named after Muhammad al-Khwarazmi

Abstract
This paper presents the results of toluene adsorption isotherm in Cu^{2+}ZSM-5 zeolite. To measure the adsorption isotherm, we used a system consisting of a universal high-vacuum adsorption unit and a differential modified microcalorimeter of the Tiana-Calve type DAK-1-1A 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 was determined that at low fillings, the isotherm rapidly rises, which indicates strong adsorption of two toluene molecules on Cu^{2+} cations. At the experimental temperature, it was determined that the volume occupied by a saturated toluene molecule is 0.102 cm^3/g. This is 62% of the sorption volume of Cu^{2+}ZSM-5 zeolite. It has been established that copper cations simultaneously interact with π-electrons of benzene rings and with oxygen atoms of the lattice, hydrogen atoms of toluene molecules - with oxygen atoms of zigzag channels.

Keywords: zeolite, adsorption, adsorption isotherm, heat of adsorption, free energy, ion-molecular complex, microcalorimeter, toluene.

Volatile Organic Compounds (VOC's) visibly pollute the atmosphere and harm human health. These compounds destroy the ozone layer (1 molecule of chlorine compound destroys 100,000 molecules of ozone). The products of human industrial activity include aromatic hydrocarbons, chloralkenes, alcohols, carbon dioxide, which are strategic gases in many industrial processes. Large quantities of carbon dioxide are emitted into the atmosphere, causing global environmental problems. One way of recovering carbon dioxide is by using an adsorption process. Recently, the adsorption method has been increasingly used to reduce and control emissions as the most efficient and economical. The potential material for selective adsorption and separation of carbon dioxide into toxic chemicals is adsorbents. Therefore, a comprehensive study of the physico-chemical and especially the energy characteristics of adsorbents is of great theoretical and practical importance.
Worldwide, adsorbents derived from natural raw materials and synthetic way are widely

studied and used in industry, construction, agriculture and other fields [1-10]. Zeolites are most widely used in gas and petrochemicals, ion exchange (water purification and softening), adsorption and separation of vapours and gases and removal of impurities (particularly environmentally and biologically harmful) from gases and solutions. In addition, zeolites are increasingly being used in ecology, agriculture, animal husbandry, paper industry and construction [11].

Anticipated new applications of zeolites described in the literature include: molecular electronics, quantum dots/chains, zeolite electrodes, batteries, non-linear optical materials and chemical sensors. Recently, research has been reported on the use of zeolites as low dielectric constant materials for microprocessors.

One of the highly effective catalysts for various processes in the petrochemical and refining industry is ZSM-5 type catalysts. Particularly in the refining industry, in catalytic processes of isomerisation, deparaffinisation, cracking and aromatisation, especially in liquid phases, they have proven to be most effective. Nowadays conversion of methanol to hydrocarbons containing zeolite catalysts in acid medium is considered to be an important and feasible non-petroleum way of obtaining valuable chemicals.

Organic substances whose molecular size in cross-section does not exceed $5.5A^0$, are well adsorbed on all pentasils, but in different amounts (volumes). For example, while n-paraffins entirely fill the entire sorption volume of a silicate or ZSM-5, densely arranged in all channels by the end-to-end mechanism, benzene adsorbs in smaller amounts (60%) and appears to fill straight and zigzag channels. Aromatic hydrocarbons are adsorbed only in straight channels and cross-hairs of ZSM-5 zeolite. However, what is the molecular mechanism of the adsorption of benzene and toluene on pentasils is not yet clear. For example, the adsorption of benzene on silicalite is accompanied by complex changes, both in the shape of the isotherm and, especially, in the shape of the curve of the dependence of differential heats on adsorption values. These complex changes were attributed by the authors to various reorientations and redistributions of the adsorbate in the silicate channels, but the specific mechanisms of these changes were not considered.

The adsorption isotherm of toluene in Cu^{2+}ZSM-5 zeolite in semi-logarithmic coordinates is shown in Figure 1. Equilibrium pressures at low fillings reach $P/P_s=5.177\cdot10^{-5}$, indicating strong adsorption of toluene in zeolite Cu^{2+}ZSM-5. The adsorption isotherm is brought to 1.12 mmol/g at relative pressures of $P/P_s=0.64$ (or up to 24 torr). If the density of toluene in zeolite is assumed to be the same as that of a normal liquid at temperature of experiment and the volume occupied by toluene molecule at saturation is calculated, it turns out that toluene occupies ~0.102 cm^3/g sorption volume of zeolite Cu^{2+}ZSM-5, which is ~62 %.

Figure 1 shows that the adsorption isotherm of toluene on Cu^{2+}ZSM-5 is S-shaped with an almost vertical section in the middle. At small P/P_s~$5,2\cdot10^{-5}$ fills it rises rapidly upwards, indicating strong sorption of toluene. At medium fillings (~0,6 mmole/g and P/P_s~0,07) the isotherm forms a step. The content of Cu^{2+} cations, according to the chemical composition of EC (elementary cell), is 0.3 mmole/g, i.e. each cation interacts with two toluene molecules.

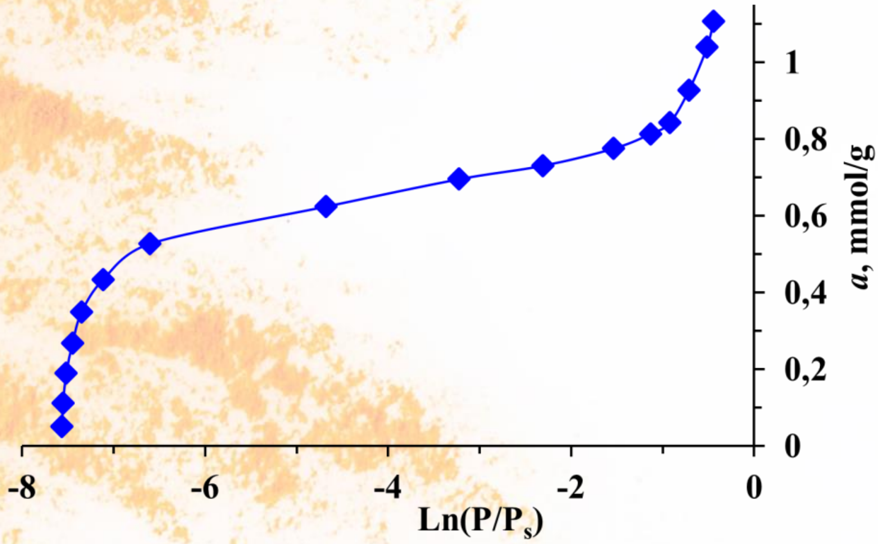

Figure 1: Adsorption isotherm toluene on Cu^{2+}ZSM-5 zeolite.

Apparently, a sandwich-like π-complex is formed with Cu^{2+} cation in the middle. The only question is where this complex is located - either completely in the channel intersections or in the straight channels with the toluene molecules strongly protruding into the channel intersections (less likely model). Apparently, the benzene rings form a dihedral angle equal to the angle between the zigzag. The ring planes are oriented perpendicular to the axes of the zig-zag channels.

With this conformation of the adsorption complex copper cations can simultaneously interact with π-electrons of benzene rings and with oxygen atoms of the lattice, and hydrogen atoms of toluene molecules - with oxygen atoms of zigzag channels.

At P/P_s=0.4 the fill degree of θ~0.76 (0.843 mmole/g) is achieved. Thus, the isotherm fits almost entirely within the narrow range P/P_s from $5.2 \cdot 10^{-5}$ to 0.4. Such a shape of the isotherm is characteristic of phase transformations of adsorbed substance and is one of the main phenomenological features of homogeneity of the sorption system as a whole. Comparing with the adsorption isotherm of benzene on silicate one could expect even more complicated character of isotherm changes with Cu^{2+}ZSM-5 filling (due to additional appearance of Al and Cu ions in silicate structure) but it didn't happen.

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