International Journal of Future Generation Communication and Networking
Vol. 13, No. 4, (2020), pp. 246–252

Energetic Characteristics Of The Process Of Adsorption Of Benzene In Zeolites Nax And Nay

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Annotation.

A comparative adsorption-calorimetric study of the adsorption processes occurring in type X and Y zeolites used in the petrochemical industry for the drying and purification of hydrocarbons was carried out, and complete precision thermodynamic parameters were obtained for the adsorption of benzene, selected as a probe molecule, by NaX and NaY zeolites. A correlation was found between the adsorption-energy characteristics and the crystal-chemical structure of adsorbents, and the molecular mechanism of adsorption, localization, conformation, and state of ion-molecular clusters in the matrix of zeolites NaX and NaY were established

Key words: Zeolites, composition, purification, hydrocarbons, adsorption, crystallographic positions, calorimetric data, catalytic activity, volumetric-liquid methods

Introduction

Zeolites are carcass-shaped aluminosilicate crystals composed of alkaline and alkaline earth metals, heated to constant temperature, aluminum and silicon oxides are not exposed to water and slowly evaporate, during which time carcasses are formed for the entry of small molecules consisting of regular channels and cavities [1]. Because synthetic zeolites have the same composition and structure, they are used for more industrial purposes than natural zeolite analogues [1].

Zeolites have a number of unique properties that are widely used in gas purification and separation, as well as in catalysis. These properties are related to the fact that the interaction of molecules with cations occurs in a sterically limited volume of a tetrahedral lattice. The presence of

ISSN: 2233-7857 IJFGCN

water has a huge influence on the distribution of cations, therefore the host is the guest interaction [2,3]. A small polar water molecule enters into a specific interaction with the host.

This interaction changes as the host cavities are filled with adsorbate. Zeolites are currently the most important catalysts for the processing of various hydrocarbons in the refinery industry. However, it is not clear to date whether their catalytic activity is related to the existence of specific active centres or porous structures. Systematic fundamental research into the theoretical bases of adsorption processes is necessary for the scientific justification of the causes of catalytic activity of zeolites, in order to organize the production of highly efficient products meeting modern quality requirements, occurring at the Zeolites at the molecular-structural level.

The aim of the work is to establish a stoichiometric relationship between the precision calorimetric data of differential heat adsorption of the test molecule of benzene on energetically homogeneous (cations) Centres located at the same crystallographic positions of the NaX and NaY zeolites and the number of adsorbed benzene molecules at those centres. Studies have been carried out on a universal high-vacuum volumetric unit allowing the dosing of adsorbate by both gas-volume and volumetric-liquid methods with an accuracy of 0.1%.

All faujasite-type zeolites exhibit high adsorption activity in hydrocarbon drying and purification processes, as well as catalytic activity in petrochemical and petroleum refining processes [4]. Benzene was selected as a probe molecule for the study of adsorption centres and porous structure of zeolites of X and Y. The study yielded molar differential thermodynamic characteristics and also studied the thermockinetics of benzene adsorption in the zeolites NaX and NaY.

Materials and methods

The adsorption calorimetry measured the molar differential heat of adsorption of benzene in the zeolites NaX and NaY having the same crystalline structure, but the differences in the Si/Al ratio (the Si/Al ratios for the NaX and NaY zeolites are respectively 2.49 and 2.43). Composition of the elemental cell of the studied zeolite NaX: $H_6Na_{80}(AlO_2)_{86}(SiO_2)_{106}$, and zeolite NaY: $HNa_{55}(AlO_2)_{86}(SiO_2)_{106}$. Absolute benzene was selected for adsorption. In the determination of NaX end NaY zeolite benzene adsorption was carried out in a high-vacuum adsorption microcalorimetric device. [5,6].

The adsorbates were first frozen and then cleaned in a vacuum pump. Palte effect The use of heat flux compensation method increases the accuracy of adsorption heat measurement. A differential calorimeter allows you to measure the amount of heat released over a long period. In the determination of adsorption, measurements were carried out in a high-volume volumetric adsorption device, low absorption of adsorbates increases the accuracy of adsorption measurements.

Results and discussions

Differential molar adsorption calorimeter studies of the adsorption of benzene in the molecular sieves NaX and NaY have been performed on the instrument described in [5,6]. The dissolved gases were removed by freezing the adsorption and then pumping it out. The adsorption measurements were carried out on a universal high-vacuum volumetric installation, allowing for adsorption measurements and dosing of adsorbate with high accuracy. In our previous research, benzene adsorption on X and Y type zeolites consisting of Na^+ and Li^+ cations was studied [7-10].

Differential heat adsorption of benzene in zeolites NaX and NaY at 303 K are shown in figure 1. Q_d curves have a complex wave-like form. Each fragment on the curves reflects the stoichiometric relationship between the number of homogeneous adsorption centers and the number of adsorbed molecules.

During benzene adsorption, 9 fragments were isolated by zeolite NaX: 0 – 0.31 (I fragment), 0.31 – 0.91 (II), 0.91 – 1.54 (III), 1.54 – 2.2 (IV), 2.2 - 2.8 (V), 2.8 - 3.64 (VI), 3.64 - 4.17 (VII) и 4.17 – 4.53 (VIII) 4.53 - 4.88 (IX) $C_6H_6/(1/8)$.

In total, each supercavity (1/8c.e) adsorbs 4.88 $C_6H_6/(1/8)$ c.e The location of the cations in the supercavities (1/8 c.e) of the original NaX is the following: 4 cations Na+ in the position of SI' (in the sodalite cavity),4 cations in the position of SII, the remaining 2.75 cations Na in the position of SIII', both positions in the supercavity [11]. The first and second high-energy fragments on the Q_d curve with heat varying from 98 kJ / mol to 80 kJ / mol (I) and from 81.3 to 83 kJ / mol (II) are assigned to benzene adsorption on Na cations in position SIII'. Then the adsorption of 4 molecules of benzene (III, IV, V, VI, VII, VIII stage, a from 0.85 to 4.85 $C_6H_6/(1/8)$ c.e) flows on the cations of Na^+ at SII

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position, the number of which is also four per supercavity. Section VIII completes the adsorption of benzene on SIII ' and brings it to 1 benzene molecule per supercavity. The adsorption of a further 0.35 C_6H_6/(1/8) c.e (IX section) occurs in a vacant twelve-window NaX. At most in this and previous series, we believe that the curve is caused by the reorientation of benzene in zeolite cavities to create more densely packaged molecules.

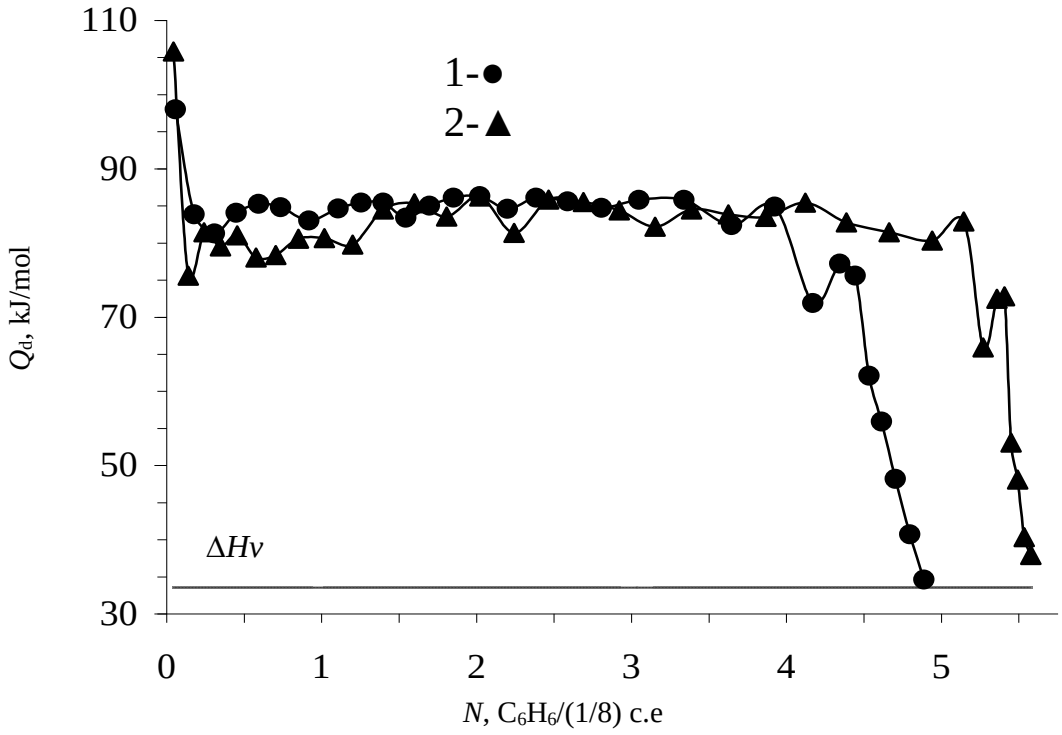

Figure 1. The differential heat of adsorption of benzene in zeolites NaX (1) and NaY (2) at 303 K. The horizontal dotted line is the heat of condensation of benzene at 303 K.

In the case of NaY, 5 fragments are isolated: 0 - 0.14 (I fragment), 0.14 - 1.20 (II), 1.20 - 2.24 (III), 2.24 - 3.15 (I'), 3.15 - 3.87 (IV), 3.87 - 4.94 (V), 4.94 - 5.27 (IV') and 5.27 - 5.58 (V) C_6H_6/(1/8) cell element. The cation settlement in NaY is the following: 1 cation Na in position S_I (in the center of the hexagonal prism), 2 cation Na in position $S_{I'}$ (in the sodalite cavity) and 4 cation in position S_{II} (in the supercavity). The first high-energy fragment on the Q_d curve with heat varying from 106 kJ/mol to 75.6 kJ/mol is attributed to the adsorption of benzene on cation Na at the SIII position.

There are five main adsorption centers in NaY: 4 at SII and 1 at $S_{III'}$ '[11]. Each section corresponds to the adsorption of a molecule with a center in a ratio of 1: 1. In two cases, the section consists of two subsections - I + I '(0.14 + 0.91 = 1.05 C_6H_6/(1/8) c.e.) and IV + IV' (0.72 + 0.33 = 1.05 C_6H_6/(1/8) c.e.)

Sections II, III, IV+IV' and V demonstrate the adsorption of benzene on cations localized at S_{II} position. These tetrahedral complexes are located in the supercavity. Section 5 is responsible for the adsorption of benzene on cations SIII' in the immediate vicinity of the 12-member oxygen zeolite windows.

The extrapolation of the Q_d curve to the zero filling is cut off on the axis of the heat of adsorption of benzene in micropores, honeycombed from the adsorption on cations Na^+ and the dispersion interaction of benzene with the walls of the cavities. To release the energy of the ion-quadrupole interaction from the total energy of the adsorption, subtract the energy of the adsorption of benzene on the cation-less zeolite US-Y equal to 38 kJ/mol. For ceolite NaX, the ion-quadrupole

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energy contribution on cation at SIII position is 62 kJ/mol, and on cation SII 36 kJ/mol; for Nay this contribution is 39 kJ/mol.

The temperature drops sharply after In the final stage, the temperature rises slightly and falls sharply at 303 K depending on the temperature of the benzene condensation. Modeling of the benzene / zeolite system shows that the fifth benzene molecule is located in a 12-ring oxygen window that separates the superpowers from each other (position W). For zeolites with Na^+ cations in X and Y zeolites, this position has been discussed several times [13,14].

Figure 2 shows the adsorption isotherms of benzene by NaX and NaY zeolites. At 4 C_6H_6/(1/8)c.e, the adsorption insulation of benzene in the zeolite NaX (Figure 2 a) is convex and extends to very low relative pressures P/P^0.

This area corresponds to strong adsorption of benzene on cations at SIII' and SII positions. The final phase of adsorption is characterized by rapid growth of pressure and saturation of zeolite NaX with benzene. The insulation of the adsorption of benzene in the zeolite NaY (Figure.2 b) is slightly concave at low filling, then almost linearly upwards (in a narrow equilibrium pressure interval) after 5 C_6H_6/(1/8) c.e. is bent towards the axis of adsorption and grows until the adsorption axis intersects.

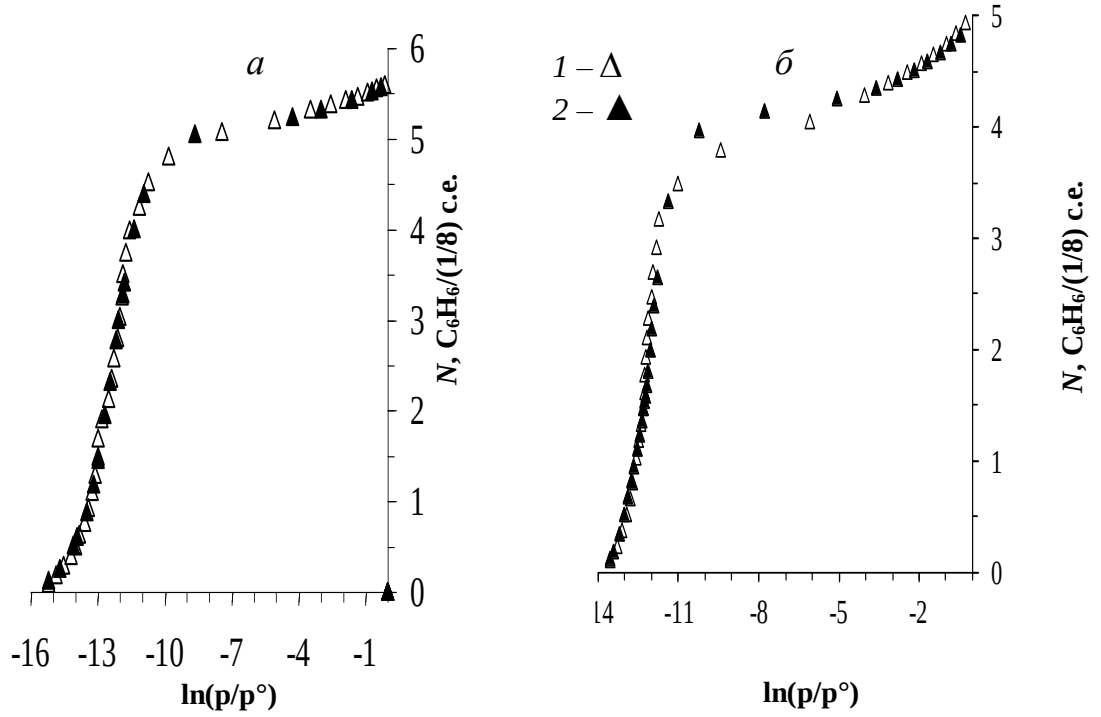

Fig 2. Benzene adsorption isotherms in zeolites NaX (a) and NaY (b) at 303K. 1 - experimental data; 2 - computed with the aid of the Theory of Volumetric Filling of Micro-Pores (TVFMP).

The benzene adsorption isotherms in the zeolites NaX (Fig. 2 a) and NaY (Fig. 2 b) are satisfactorily described by the three-dimensional equations of the volume micropore filling theory[12]:

$$N = 2{,}861\exp[-(A/31{,}54)^{15}] + 1{,}01\exp[-(A/31{,}07)^{39} + 1{,}1\exp[-(A/10{,}24)^{1}] \quad (1)$$

$$N = 1882\exp[-(A/34{,}36)^{10}] + 3103\exp[-(A/31{,}10)^{15}] + 633\exp[-(A/12{,}21)^{1}] \quad (2)$$

where N – adsorption in micropores in mmol/g,

$A = RT \ln(P^o/P)$ – adsorption energy in kJ/mol.

Using precision isotherm and differential adsorption heat, the differential molar entrances of adsorption (ΔS_d) by zeolites NaX and NaY by Gibbs-Helmholz equation, $\Delta S_d = -(Q_d - \Delta_v H)/T - R \ln(p/p^o)$ (Figure 3.4)where p^o is the vapour pressure of benzene at saturation, p^o (303K) = 4,24 kPa.

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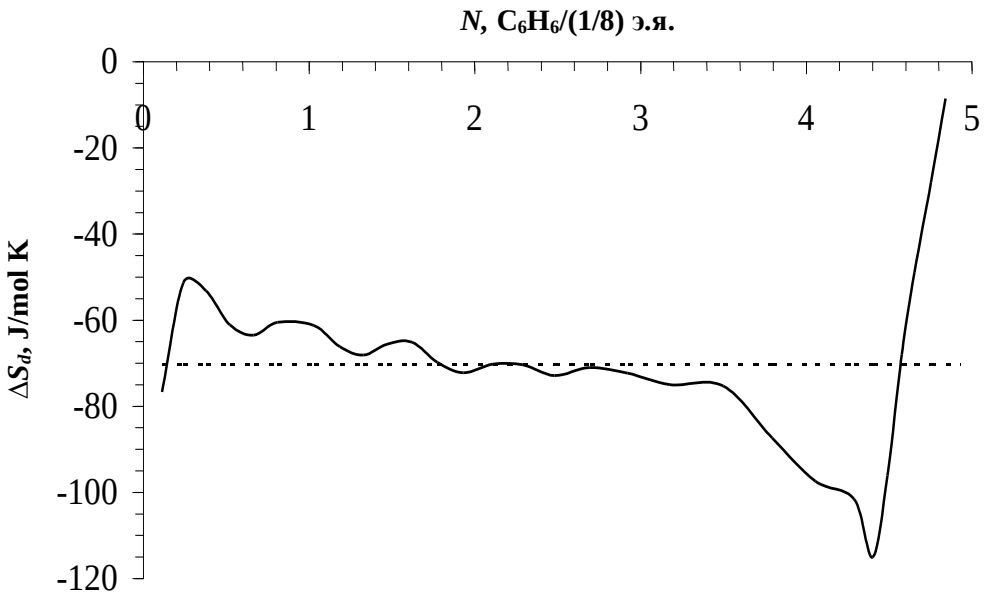

Figure 3. Differential entropy of the adsorption of benzene in the zeolite NaX at 303 K. The entropy of liquid benzene is assumed zero. The horizontal bar line is the middle mole integral entropy.

Both curves are located below the entropy of liquid benzene. When the benzene is adsorbed by zeolite NaX, the curve starts from low negative values (-76.68 J/mol*K) and increases to -53.23 J/mol*K at 0.31 C_6H_6/(1/8).c.e. Then there is a slow decline to -115 J/mol*K. When saturated, the curve rises sharply to the positive region. Integral entropy is markedly lower than the entropy of liquid benzene and is close to the entropy of crystalline benzene. This fact indicates that the status of benzene molecules in Zeolite NaX is close to solid-like ones. Entropy of adsorption in NaY, starting from -62.45 J/mol*K grows to -24.91 J/mol*K at 0.1 C_6H_6/c/e., then gradually and wavelengly declines to 110 J/mol*K at 5.39 C_6H_6/c.e. The deep minimum at the end of adsorption indicates strong localization of benzene molecules on the NaIII' and NaII. cations. The median molar integral entropy of benzene adsorption in zeolite NaY -62.45, indicating localization of benzene molecules in zeolite NaY.

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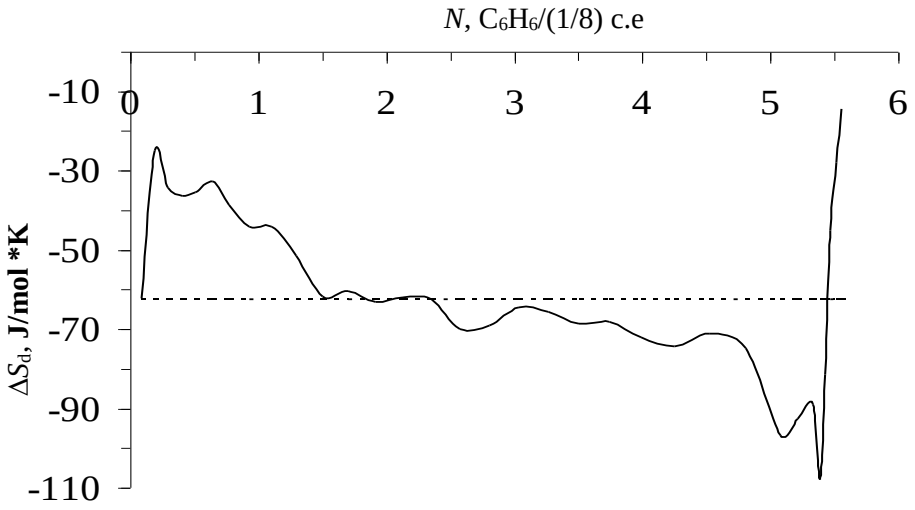

Figure 4. Differential entropy of the adsorption of benzene in the zeolite NaY at 303 K. Horizontal bark line is the mean mole integral entropy.

The time to establish the adsorption equilibrium of benzene in the zeolite NaX (Fig. 5, curve 1) with low filling is slowed (6-4 hours). When filled from 4.53 C_6H_6/(1/8) c.e. to 4.88 C_6H_6/(1/8)c.e. the curve passes through a maximum of (2-1 hour).

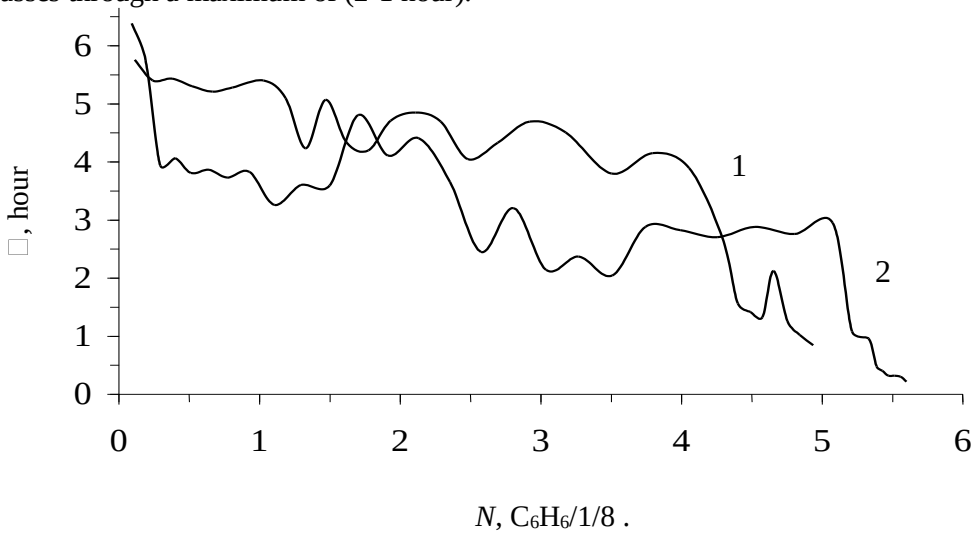

Figure 5. Adsorption equilibrium conversion time for benzene adsorption in zeolites NaX (1) and NaY (2) at 303K.

The deceleration at the end of the process appears to be due to the difficulty of moving large benzene molecules through the almost filled channels and the NaX [11] crossroads.

The adsorption equilibrium time curve (□) from the adsorption of the benzene in the zeolite NaY (Figure 5, curve 2), from 6 h, the waveform decreases to 3 h at N= 1.29 C_6H_6 c.e. to 1.71 C_6H_6 c.e., increases and drops again wave-like to 2.45 C_6H_6 c.e. The next constant remains from 2.45 C_6H_6 c.e.. to 5 C_6H_6 c.e. then falls to 1 hour.

Conclusion

A comparative study of the adsorption activity of synthetic fojazite zeolites has been conducted. With the aid of a high-vacuum adsorption calorimeter, thermodynamic parameters are

ISSN: 2233-7857 IJFGCN

determined - differential heat, isotherms and entropy of adsorption of benzene, selected as a probe molecule, The zeolites of NaX and NaY, as well as the time of the adsorption equilibrium of benzene in zeolites. A correlation between the adsorption-energy characteristics and the crystal-chemical structure of adsorbents has been found, a detailed molecular mechanism for adsorption of benzene in the zeolite matrix NaX and NaY has been identified, and the basic regularities of the adsorption have been established.

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ISSN: 2233-7857 IJFGCN