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# ADSORPTION THERMODYNAMICS OF CARBON DIOXIDE AND n-HEPTANES IN HZSM-5 ZEOLITE

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## Abstract

Differential heats and isotherms of carbon dioxide and n-heptane adsorption in a zeolite $H_{3.25}$ZSM-5 have been measured by Tian-Calvet-type microcalorimeter and volumetric system at 303 K. Based on the data obtained, the mechanism of n-heptane adsorption and (CO2)n/$H^+$ complexes formation in the zeolitic matrix of $H_{3.25}$ZSM-5 is revealed. The adsorption isotherms are quantitatively reproduced by VOM theory equations.

**Keywords:** zeolite ZSM-5, isotherm of adsorption, carbon dioxide, n-heptane, differential heats of adsorption.

## Introduction

Most of industrial processes are accompanied by the release of carbon dioxide. Being a product of combustion and greenhouse gas, it has set a global society issue of a need to its capture and reuse. One way of its regeneration is the use of the adsorption process. Potential material for the selective adsorption and separation of carbon dioxide is a well-organized system of microporous zeolites. In addition, a well-defined structure of zeolites is the cause of ever-increasing use of them as a model to study the interaction of adsorbed molecules with a solid surface. Their adsorptive properties can be modified by ion exchange and Si / Al ratio change.

Earlier studies were performed mainly with zeolites containing alkaline cations [1-4]. However, zeolite $H_{3.25}$ZSM-5 is much more effective catalyst of a number of practically important processes of oil refining and petrochemical industry than in compare with its predecessors.

There are data on the adsorption of carbon dioxide in the zeolites of ZSM-5 type, which have been prepared by various physical and chemical methods [5-7]. However, hitherto there is no data reliably reflecting energy and the mechanism of adsorption of carbon dioxide in the zeolite ZSM-5 in its hydrogen form.

Less attention is paid to energetics of non-specific adsorption of interacting molecules such as hydrocarbons. Adsorptive N-alkanes are those agents that do adsorb with high energy and fill the entire sorption space of zeolites ZSM-5 in contrast, for example, with benzene, which fills only ~ 70% of the pore space of ZSM-5 [8]. Consequently, n-alkanes can be used to characterize the zeolite's channels for assessment of the sorption volume, which ultimately is the quality indicator of the adsorbent.

## Objective

To study isotherms and main thermodynamic characteristics of adsorption and the mechanism of adsorption of carbon dioxide and n-heptane in zeolite of ZSM-5 type with exchangeable $H^+$ cations.

## Subjects and Methods

Adsorption studies were carried out with zeolite $H_{3.25}$ZSM-5. As adsorptives the quadrupole molecule of $CO_2$ and non-polar n-heptane molecule were selected. Adsorption-calorimetric method used in this paper provides a high-precision molar thermodynamic characteristics of adsorption systems and through them to reveal the mechanism of adsorption processes occurring in the adsorbent. As a calorimeter the microcalorimeter Tian-Calvet-type, with high accuracy and stability was used [8, 9].

## Results and discussion

The curve of the differential heats of adsorption ($Q_d$) of $CO_2$ in the zeolite $H_{3.25}$ZSM-5 at 303 K is shown in Figure 1. There is a heat wave-like fall with filling increase. In adsorption (a) of 0.56 mmol / g the curve of $CO_2$ condensation heat ($\Delta Hv$) reaches a level equal to 27 kJ / mol. Further else ~ 0.56 mmol / g of the adsorbate still adsorbs with a heat close to the heat of condensation. The length of the first section (0.56 mmol / g) exactly corresponds to the number of protons contained in the unit of the zeolite cell. This region corresponds to the ion-quadrupole interaction of $CO_2$ with protons to form a monomeric complexes of $CO_2/H^+$ in the zeolite matrix. Considering the fact that the zeolite's matrix itself does not appreciably adsorbs carbon dioxide at a temperature of 303 K, a second section (following 0.56 mmol/g) can be attributed to the formation of the dimer complexes $(CO_2)_2/H^+$ in the zeolite ZSM-5 matrix.

Acidic centers in $H_{3.25}$ZSM-5 are heterogeneous and differ greatly in their adsorption energy. The first section can be divided into five sub-sections in accordance with the wavelike curve $Q_d$. The first 0.06 mmol/g of protons possess the most strong acidic properties, the heat in this region is reduced from 60 down to 42 kJ/mol.

Next 0.10 mmol/g of protons are adsorbed with energy increasing up to 43 kJ/mol, and then falling down to 35 kJ/mol. The third subsection (0.13 mmol/g) $Q_d$ increases up to 36 kJ/mol, and falls down to 30.7 kJ/mol. In a fourth subsection (0.14 mmol/g), the heat of adsorption increases up to 33.9 kJ/mol, and falls down to 27.9 kJ/mol, and finally, a fifth subsection (0.15 mmol / g) $Q_d$ increases up to 30.7 kJ/mol, and falls down to the heat of condensation of $CO_2$ equal to 27 kJ/mol. Considering the propensity of carbon dioxide to the association, the wavelike nature of the heat of adsorption change can be attributed to the imposition of the heat of adsorption of the adsorbate - adsorbate interactions on the general background of the adsorbate – adsorbent interaction.

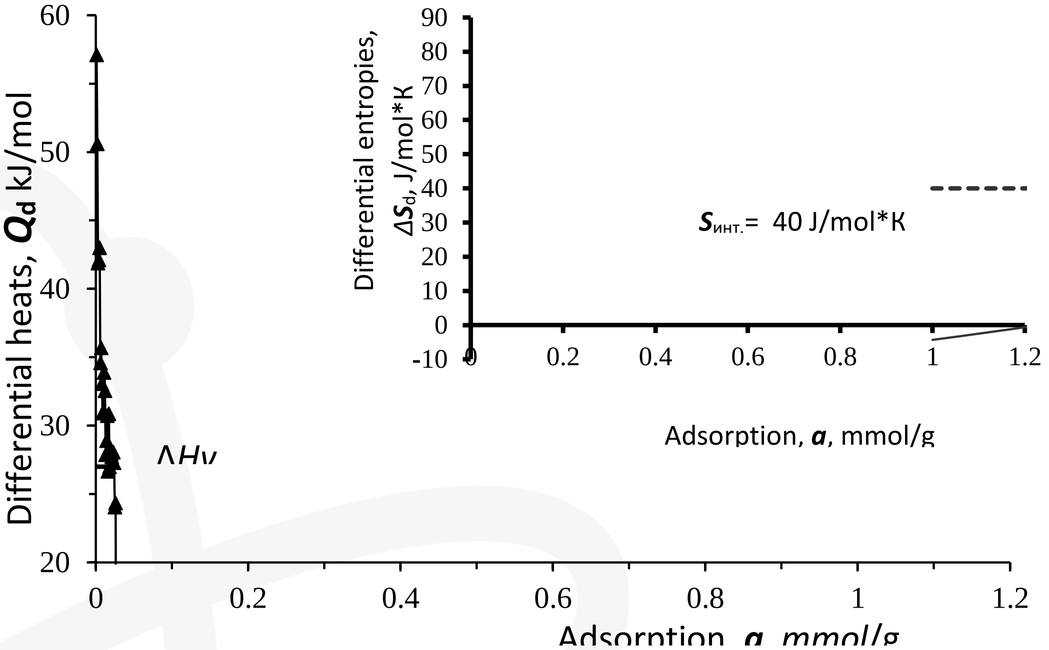

Figure 1. Differential heats of adsorption, $Q_d$, of carbon dioxide molecules, (*a*), in $H_{3,25}ZSM$-5 zeolite at 303 K. The horizontal dashed line is the heat of condensation of bulk carbon dioxide. Top: corresponding differential molar entropy of adsorption. The entropy of liquid carbon dioxide is taken as zero. Dashed line is integral mean molar entropy.

Equilibrium pressure for small fillings at the adsorption isotherm reaches $P/P^o=4\cdot10^{-5}$. Before adsorption equal to ~ 0.56 mmol / g, corresponding to the total number of protons, isotherm looks like concave, with further increase in adsorption it is almost rectilinear. $CO_2$ adsorption isotherm for zeolite $H_{3.25}ZSM$-5 is described by two-term equation of the theory of volumetric micropore occupancy (VMOT):

$$a = 1.808 \exp[-(A / 12.07)^2] + 0.863 \exp[-(A / 13.07)^5],$$

where a – is adsorption, mmol/g, A = RTln (P°/P) – is a transfer work of 1 mmol of gas from the surface (pressure P°) into the equilibrium gas phase (pressure P).
Differential molar entropy of adsorption of n-heptane in the zeolite $H_{3,25}ZSM\text{-}5$ is calculated for the Gibbs-Helmholtz equation and is presented in Fig.1, top. Entropy as a whole is located above the entropy of liquid carbon dioxide. In accordance with the curve of differential heats of adsorption the curve of $\Delta S_d$ wavelike rises to fill ~ 0.56 mmol / g, then it is constant, and closer to saturation it continues to grow. Reacting of carbon dioxide with protons in a ratio 1:1 passes at lower entropy. Integral average mole entropy ($S_{int}$) at 40 J/mol*K is above the entropy of liquid carbon dioxide, which indicates a significantly higher mobility of carbon dioxide molecules in the zeolitic matrix.
$CO_2$ adsorption time of establishment of equilibrium in the low carbon dioxide sorption filling space (up to 0.16 mmol/g) is slowed and reaches 1 hour, while the remaining space is filled within 12-18 minutes, sometimes rising up to 1 hour at a = 0.73 mmol / g and 36 min for a = 1 mmol/g.
Adsorption heats of n-heptane in $H_{3,25}ZSM\text{-}5$ zeolite at low fillings (up to 0.09 mmol/g) are reduced from 100 kJ/mol down to 90 kJ/mol (Figure 2). The cause of excessive heats at low fillings are protons, with which n-heptane reacts by means of induction effect. The total number of protons is much greater (0.52 mmol/g, according to n-heptane adsorption, which a little bit less than in case of $CO_2$ adsorption), however a significant contribution to the total energy of absorption is made with the protons possessing the greatest acidity.

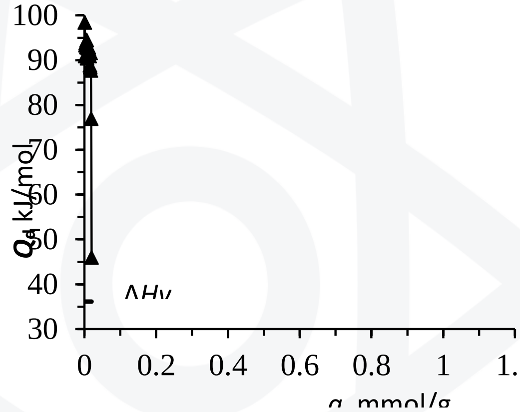

Figure 2 – Differential heats of adsorption of n-heptane in zeolite $H_{3,25}ZSM\text{-}5$ at 303 K. The horizontal dashed line – the heat of condensation.

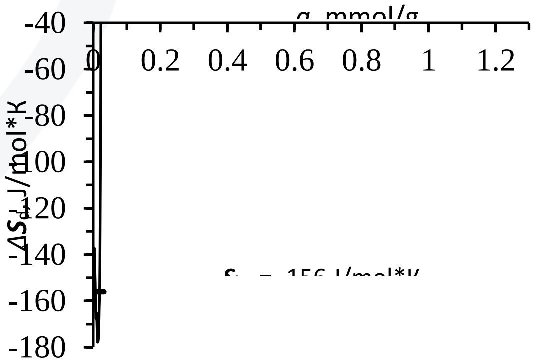

Figure 3 – Differential molar entropy of adsorption of n-heptane in zeolite $H_{3,25}ZSM\text{-}5$ at 303 K. The entropy of liquid n-heptane is chosen for zero. The horizontal dashed line – is integral mean molar entropy.

The heat of adsorption of n-heptane in silicalite being a pure silica analogue of ZSM-5 at the zero filling is ~ 80 kJ/mol, which is ~ 10kJ/mol is lower than a heat of adsorption in $H_{3,25}$ZSM-5, if one takes the overall level of the curve $Q_d$. Contribution to the total energy of absorption gives the dispersion component of interaction energy with the protons. In the adsorption of relatively small molecules of n-hydrocarbons it is observed an increase in the heat of adsorption due to the collective interaction between the adsorbed hydrocarbon molecules (adsorbate-adsorbate). In the case of n-heptane, as a whole, we are seeing the constancy of heat almost at the entire area of fillings (changes occur within 2-3 kJ/mol). Apparently, n-heptane molecules from the beginning of the filling are tightly packed into the zeolite channels in energetically favorable positions without remarkable interaction adsorbate-adsorbate. At the end of the process the adsorption heat abruptly drops to the heat of condensation of n-heptane.

The adsorption isotherm of n-heptane in the zeolite $H_{3,25}$ZSM-5 was investigated at a temperature of 303 K. At low coverage the equilibrium is established at a relative pressure $P/P^o=7*10^{-6}$, but the saturation the adsorption comes to 1.14 mmol/g at a relative pressure $P/P^o=0{,}58$ (44.46 mm Hg ). Isotherm increases linearly at a predetermined gradient to a = 0.52 mmol/g, which close to the number of protons in the unit cell, and then wave-like approaches toward the axis of adsorption. If we assume the density of n-heptane in the zeolite being the same as in normal liquid at the experimental temperature (303 K) and if we calculate the volume occupied by a molecule of n-heptane at saturation, we find that the n-heptane takes ~0.16 $cm^3/g$ of the sorption volume of $H_{3,25}$ZSM-5 zeolite that is ~11% less than the real volume (0.18 $cm^3/g$). This result indicates the presence of amorphous phase.

The adsorption isotherm of n-heptane in the zeolite $H_{3,25}$ZSM-5 is described by the three-term equation VMOT :

$$\mathbf{a} = 0.633\exp[-(A/26.72)^9]+0.337\exp[-(A/0.337)^5]+0.351\exp[-(A/2.44)],$$

where a – is adsorption mmol/g, $A = RT\ln(P^o/P)$ – is a transfer work for 1 mmol gas from the surface (pressure $P^o$) in the gas phase equilibrium (pressure P).

Differential molar entropy of adsorption of n-heptane in the zeolite $H_{3,25}$ZSM-5 is presented in Figure 3. Curve $\Delta S_d$ throughout the region of filling the zeolite channels by n-heptane is less than the entropy of the liquid n-heptane and has a very low negative values. Entropy being less than 0.52 mmol/g, which corresponds to the number of protons attributable to unit cell of $H_{3,25}$ZSM-5, does not change much with the filling and, on average, is at the level of ~ -132 J/mol*K. This confirms the thesis put forward earlier that from the process' beginning the molecule are tightly localized likely at the intersection of straight and zig zag channels, where the protons are located. However, the length of the intersection is 0.54 nm, and the length of n-heptane is 1.15 nm, therefore part of n-heptane should go to straight or zig zag channel sections. The length of the straight channel and the intersection is 0.99 nm, and a zig zag and intersection is 1.21nm. Given that the molecule of n-heptane in the zig zag channel is more tightly constricted by the framework atoms than the molecule in the straight channel, it can be assumed that the adsorption is initially take place in the intersections and zig zag channels , then in the intersections and the straight channels. Time of adsorption equilibrium of n-heptane in the zig zag channels and intersections zeolite $H_{3,25}$ZSM-5 (up to a = ~ 0.52 mmol/g) is too slow. It is reduced from more than 8 hours down to ~4 hours. At this stage the adsorption takes place in the zig zag channels and intersections. In the final stage of adsorption it is installed in less than 1 hour.

## Conclusion

The adsorption isotherms of carbon dioxide and n-pentane in $H_{3.25}$ZSM-5 satisfactorily is described by the equations VMOT. $CO_2$ and n-heptane's heat of adsorption in $H_{3.25}$ZSM-5 at zero filling are 60 and 91 kJ/mol, respectively. The differential heats of adsorption of $CO_2$ have two segments corresponding to the formation of two types of adsorption complexes with one and two molecules of carbon dioxide on average. The wavelike nature of the heat of adsorption is due to the imposition of heat of interaction of adsorbate-adsorbate on the general background of heat of adsorption of adsorbate-adsorbent. Condition of n-heptane in the zeolite matrix is solidlike but condition of carbon dioxide is closer to gaseous one. The heat of adsorption of n-heptane varies little with filling and is in average equal to ~ 91 kJ/mol. Induction component contribution to the total energy is about 12 kJ/mol. Adsorption of n-heptane in the channels is greatly slowed.
Adsorbent for ~ 11% consists of an amorphous phase.

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