ADSORPTION OF METHANE ON NaX ZEOLITE IN THE SUBCRITICAL AND SUPERCRITICAL REGIONS

É. V. Chkhaidze, A. A. Fomkin,
V. V. Serpinskii, and G. V. Tsitsishvili

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Most studies of the adsorption of methane on zeolites are limited by comparatively narrow ranges of the change in the adsorption equilibrium parameters. Applied to the CH_4–NaX zeolite system, the limitation of the range of measured pressures [1-3] or temperatures [4-5] does not permit obtaining the overall characteristics of the adsorption process in the subcritical and supercritical regions of methane. The fruitfulness of studies of adsorption in such broad ranges of changes in the adsorption equilibrium parameters was noted in the study of adsorption of Xe, Kr, and Ar on NaX zeolite [6]. It was found for these adsorption systems that the adsorption isosteres in pressure ranges from 0.1 Pa to 20 MPa and temperature ranges from 100 to 600°K are satisfactorily approximated by straight lines. The adsorption isosteres which are interrupted on the saturated vapor pressure line subsequently continue linearly in the supercritical region. Passage of the isosteres through the usual critical temperature of the adsorbed gas does not result in any change in their slopes.

In developing this research, we studied the adsorption of CH_4 on NaX zeolite in the conditions reported above, including the critical parameters of methane.

EXPERIMENTAL

Adsorption was measured by the volumetric method on the setup described in [7] with small changes in the method of measurement of high pressures (Fig. 1). The adsorbent was in ampul 1, connected to high-vacuum valve 2, which permitted delivering the gas studied from the storage part of the setup to the high-pressure measurement section. The pressure of the gas studied was created by evaporation of the substance from the condensed phase by a small volume. Ampul 1 was connected with bellows-inductive pressure converter 3. The inside of pressure converter 3 was filled with oil and communicated with type MP-60 or MP-600 dead-weight pressure gauge tester 8 through a tube. The pressure of the gas above the adsorbent acted on bellows 4 and moved core 5 of differential transformer 6. The unbalance of the electrical circuit was converted into the electric signal of null-indicator 7. The readings of null-indicator 7 were set to zero by decreasing or increasing the pressure of the oil with the dead-weight pressure gauge tester, and the equilibrium pressure of the gas over the adsorbent was measured in this way. Since the sensitivity of the bellow-inductive converter with the null-indicator was ∿10 Pa, the error of measurement of the pressure was determined by the error of the dead-weight pressure gauge testers, which have a precision class of 0.05.

The adsorption of CH_4 on NaX zeolite in the range of pressures from ~0.1 Pa to ~20 MPa and temperatures from 120 to 600°K was measured on this setup. NaX zeolite with a composition of $0.98\ Na_2O \cdot Al_2O_3 \cdot 2.36\ SiO_2 \cdot 0.02\ H_2O$ [8] and CH_4 with a purity of 99.92% were used in the experiments. Before the experiments began, the zeolite was evacuated for 20 h at 700°K to a residual pressure of <0.01 Pa.

The adsorption was calculated with the difference in the amount of substance delivered and the amount of substance found outside of the micropores of the adsorbent [9]. The volume of adsorbent together with the micropores was calculated with x-ray structural data [8]. Corrections were made for temperature transpiration using $\varphi_g = 6$ in the Liang equation [10] in the region of the lowest equilibrium pressures and low temperatures. In the region of low pressures where the gas can be considered ideal, the amount of substance in the gas phase was determined by the Clapeyron–Mendeleev law. The tabular data in [11] were used with high pressures where the gas is not ideal.

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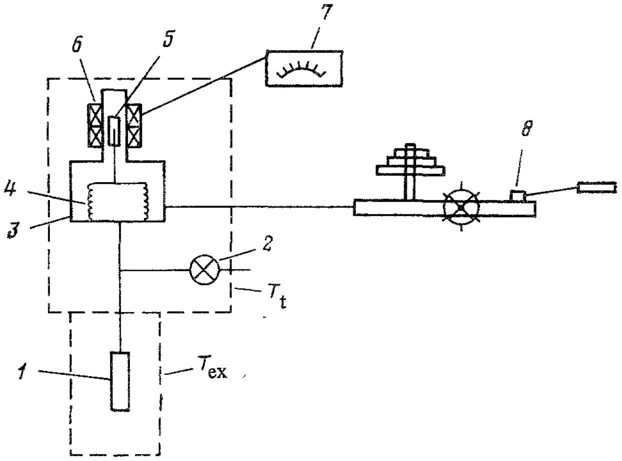

Fig. 1. High-pressure measurement circuit: T_{ex}: experimental temperature; T_t = 303°K: temperature of the air thermostat.

DISCUSSION OF RESULTS

The adsorption isotherms for CH_4 on NaX zeolite (Fig. 2) have a relatively extensive region ($a \leq 0.3$ mmole/g) in the initial segment in which adsorption increases proportionally to the pressure. The dependence $\log K_H = f(1/T)$, where $K_H = (\partial a/\partial p)_T$ is the Henry constant, can be approximated by a straight line (Fig. 3). The temperature dependence of the Henry constant obtained with molecular-statistical calculations in the atom-atom approximation, are shown in Fig. 3 [12]. Despite the major difference, the Henry constants calculated from excessive [12] and absolute adsorption quantitatively differ little. The calculated K_H and their temperature dependences are close to the experimental findings. It would be difficult to expect any better agreement, since at least two causes of the differences are possible. First, there is the difference in the chemical composition of the zeolites studied (in [12, the NaX zeolite had the chemical composition of $Na_{0.97}(AlO_2)(SiO_2)_{1.48}$). The second cause is the approximate nature of the molecular-statistical calculations. The initial isosteric heat of adsorption Q can be calculated with the slope of the experimental curve (see Fig. 3)

$$\ln K_H = \frac{Q}{RT} + C_0 , \tag{1}$$

where C_0 is the integration constant. The heat was equal to ~18.4 kJ/mole, which is in good agreement with the value of the initial heats of adsorption of 17.6-18.8 kJ/mole reported in [1, 13, 14]. As for inert gases, the isosteres of adsorption of CH_4 on NaX zeolite are well approximated by straight lines in the entire range of pressures and temperatures studied (Fig. 4). In addition, as in adsorption of Xe on NaX zeolite, the CH_4 adsorption isosteres, which are interrupted at the saturated vapor pressure line, subsequently continue linearly in the supercritical region. The linearity of the adsorption isosteres is thus realized in significantly broader ranges of the change in the adsorption equilibrium parameters then previously believed [15]. As observed in [6], this property opens up new possibilities for adsorption equilibrium calculations at high pressures based on the existing vast experimental material obtained in the usual vacuum apparatus.

The calculations of the charge pattern of the adsorption field of the large cavity of NaX zeolite in adsorption of CH_4 performed in [16] permitted representing the initial stages of the adsorption process in more detail. A fragment of the charge map is shown in Fig. 5: point E corresponds to the cation in position SIII, point D corresponds to the cation at SII; point B is the center of the large window; line FG is the boundary of the large window. Region BED represents 1/24 of the surface of the large cavity. The values of the potential energy are indicated by the numbers on the curves. The point of the deepest minimum is located near the boundary of the large window. The depth of the potential well at relatively low temperatures significantly exceeds the energy of the kinetic motion of the molecules ($\Delta E \gg kT$). The first adsorbed molecules thus fill these adsorption sites. Consideration of the steric relations thus suggests that there are 5-6 such adsorption sites in each cavity

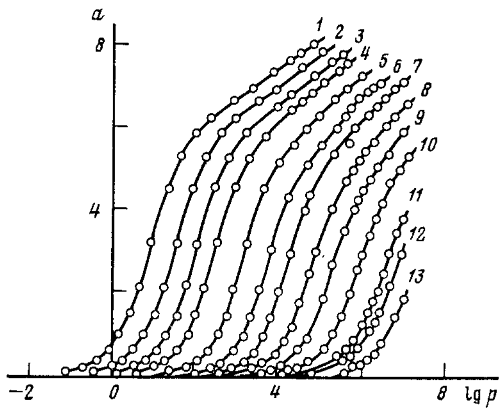

Fig. 2. Isotherms of adsorption of CH_4 on NaX zeolite (*a*, mmole/g) at T, °K: 1) 120; 2) 130; 3) 140; 4) 150; 5) 170; 6) 190; 7) 210; 8) 240; 9) 273; 10) 330; 11) 410; 12) 450; 13) 550 (P, Pa).

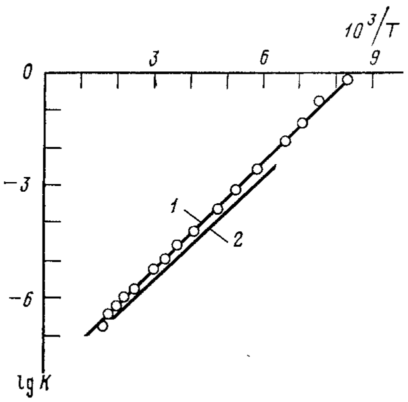

Fig. 3

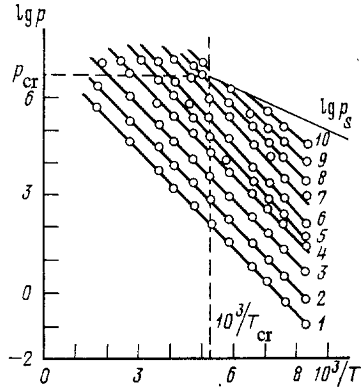

Fig. 4

Fig. 3. Temperature dependence of the Henry constant (K_H, mmole/g·Pa) in adsorption of CH_4 on NaX zeolite: 1) experimental; 2) calculation from [12]; T, °K.

Fig. 4. Isosteres of adsorption of CH_4 on NaX zeolite (*a*, mmole/g): 1) 0.1; 2) 0.4; 3) 2.0; 4) 4.0; 5) 5.0; 6) 6.0; 7) 6.5; 8) 7.0; 9) 7.4; 10) 7.8. Curve of log p_s: CH_4 saturated vapor pressure line.

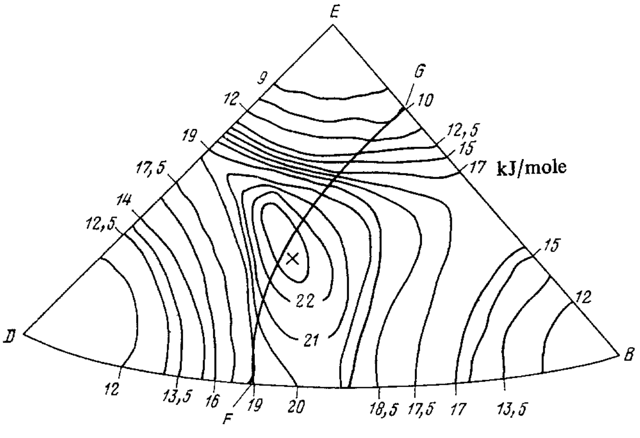

Fig. 5. Charge map of NaX zeolite in adsorption of CH_4 [12].

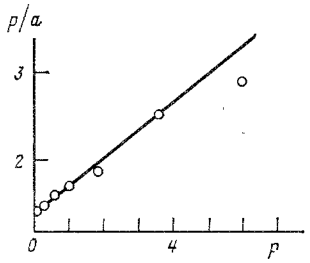

Fig. 6. Adsorption isotherm for CH_4 on NaX zeolite (a, mmole/g) at 120°K (p, Pa).

in the zeolite. The adsorbed molecules which occupy the most energetically advantageous positions in each cavity naturally realize the Langmuir adsorption model in space.

In the coordinates of the linear form of the Langmuir equation

$$\frac{p}{a}=\frac{1}{a_m K_L}+\frac{1}{a_m}p, \tag{2}$$

where a_m is the limit adsorption and K_L is the Langmuir constant, the experimental points of the initial portions of the adsorption isotherms are well appoximated by straight lines (Fig. 6). The value of a_m determined by the slope of the lines for the temperatures studied is approximately constant and is equal to ~3.5 mmoles/g, which corresponds to an average of 5.8 molecules per large cavity in the NaX zeolite.

The subsequent increase in the pressure is related to filling of the remaining volume of the cavities inthe zeolite, resulting in a significant increase in adsorption. The maximum measured value of adsorption corresponds to ~13 molecules per large cavity in the zeolite.

CONCLUSIONS

1. The adsorption of methane on NaX zeolite in the subcritical and supercritical regions was studied, and it was found that the adsorption isoteres are linear in the range of pressures from ~0.1 Pa to ~20 MPa and in the range of temperatures from 120 to 600°K. The adsorption isosteres, interrupted at the methane saturated vapor pressure line, subsequently continue linearly in the supercritical region.

2. The first adsorbed molecules at relatively low temperatures are adsorbed in deep potential wells, which naturally realizes the Langmuir model of adsorption in zeolite.

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CATALYTIC PROPERTIES OF Fe^{3+} AND Cu^{2+} SILICATES WITH THE STRUCTURE OF ZEOLITES

L. A. Vostrikova, G. V. Echevskii, G. N. Nosyreva,
and K. G. Ione

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Crystalline aluminosilicates — zeolites — are widely used in catalytic processes in petrochemistry, petroleum refining, and the synthesis of artificial liquid fuels [1, 2].

The active sites in these catalysts are formed as a result of isomorphic substitution of the Si atoms in the silicate backbone by Al atoms [3]. It was shown in [4-6] that catalysts of the reaction of synthesis of hydrocarbons from methanol are obtained in hydrothermal crystallization of silica gel containing B(III), Fe(III), and Ga(III) compounds. A crystalline silicate with the structure of type ZSM zeolite, in which the Cu ions occupy positions with an octahedral oxygen environment and a different degree of deformation, while the Fe ions occupy sites with tetrahedral and octahedral symmetry [7], is formed as a result of the hydrothermal crystallization of silica sol containing Cu or Fe salts.

The selectivity of the reaction of synthesis of hydrocarbons from methanol in the presence of Fe and Cu silicates with the structure of zeolites, prepared in hydrothermal conditions, was studied as a function of the concentration of Fe_2O_3 and CuO in them.

EXPERIMENTAL

Silicates containing Al(III), Fe(III), and Cu(II) were prepared by hydrothermal crystallization of 25% silica sol in the presence of $(n\text{-}Bu)_4NBr$, NaOH, and the salts of the corresponding polycharged cations at 150°C in a steel autoclave with a Teflon bearing according to the method in [8]. All samples studied were decationized with a 0.1 N solution of $NH_4Cl + NH_4OH$ and were calcined at 480-520°C.

The degree of crystallinity of the samples was determined by x-ray analysis using the Cu Kα monochromatized radiation in the range of angles θ of 10-15°. A silicalite prepared according to [9] was used as the comparison reference. The specific surface was determined by thermal desorption of Ar adsorbed at the temperature of liquid nitrogen. Before the tests, a weighed portion of the sample was calcined to a constant weight at 550°C.

The catalytic activity was studied on a setup with a flow-circulation reactor with a circulation rate of 100-120. Liquid methanol was delivered by a liquid pump with a space velocity of 1-2 h^{-1}. Before delivery of the methanol, the catalyst was activated for 2 h in an air current at 530-550°C, and then cooled to the reaction temperature of 380° in an He current. The composition of the reaction products was analyzed chromatographically in columns packed with TRIS and SKVAlAN adsorbents.

DISCUSSION OF RESULTS

Crystalline silicates with x-ray diffraction patterns similar to the x-ray of type ZMS-5-11 zeolites and the silicalite described in [9] were obtained as a result of hydrothermal synthesis. Their reflections in the region of θ 4-15° coincide both with respect to the intensity and with respect to the interplanar distances [8]. The degree of crystallinity of the samples was no lower than 90% in comparison to the crystalline reference,

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