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Adsorption and adsorption-induced deformation of NaX zeolite under high pressures of carbon dioxide

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Isotherms of carbon dioxide adsorption and adsorption-induced deformation of pelletized crystalline NaX zeolite at pressures of 0.2—5.4 MPa and temperatures of 195—423 K are measured. The adsorption deformation is positive at low zeolite micropore filling ($a < 1$ mmol g^{-1}) at all temperatures, *i.e.*, the zeolite suffers expansion. Further, as the amount of the adsorbed substance increases, the adsorption deformation curves pass first through a maximum and then through a minimum. In the range of high fillings ($a > 7$ mmol g^{-1}) the NaX zeolite shows dramatic expansion.

Key words: adsorption, zeolite, adsorption-induced deformation, carbon dioxide, high pressures.

Adsorption of gases and vapors is usually studied assuming inertness of solid state.[1] However, the studies performed over wide ranges of temperatures and pressures show that the adsorption deformation of an adsorbent should be taken into account for the correct calculation of thermodynamic parameters of the system.[2] Non-inertness is a specific property of microporous adsorbents, for example, of crystalline zeolites, which are carriers of adsorption field and are deformed upon adsorption.

Adsorption deformation of zeolites A, X, and Y during adsorption of polar (H_2O, CO_2) and nonpolar adsorptives (Xe, Kr) has previously been studied.[3,4,5] When nonpolar gases (Xe, Kr) are adsorbed, the adsorbent first undergoes compression, which is transformed into expansion with further filling of the micropore volume.[4,5] In the case of an adsorptive with a high dipole or quadrupole moment (H_2O, CO_2), progressive adsorption leads first to expansion followed by compression and finally to a second expansion.[3]

Correct calculation of the thermodynamic parameters of the adsorption system requires data on adsorption deformation over the whole interval of temperature and pressures, especially at high pressures where deformation makes the greatest contribution to the thermodynamic parameters of the system. For the inert gas xenon—zeolite NaX system[6] under pressures below 12 MPa, the corrections to the differential molar isosteric heat of adsorption reaches 60%. For carbon dioxide adsorption, zeolite deformation changes not only the sizes and structure of pores in solids, but also modifies the adsorption field of the adsorbent because "specific" adsorption interaction with the CO_2 molecule results in the displacement of Na^+ cations.[7] Thus, it is necessary to find a correlation between the adsorption and deformation parameters of the adsorption system.

Experimental

Crystalline zeolite NaX $0.98Na_2O \cdot Al_2O_3 \cdot 2.36SiO_2 \cdot 0.02H_2O$ was used. According to X-ray structural data,[8] the unit cell parameter of this completely crystalline zeolite (r_0) is 2.496 nm, the density of the zeolite with micropores is 1.429 g cm^{-3}, and the micropore volume is 0.32 cm^3 g^{-1}.[8] The sample for measurements of deformation represented a cylinder 12 mm in diameter and 81 mm in length prepared by compacting the crystalline zeolite powder under pressure of 1.5 kbar.

Adsorption was measured on zeolite NaX granules. Gaseous carbon dioxide was purified by the rectification and adsorption methods so that the concentration of impurities did not exceed 0.012.

Adsorption at pressures below 100 kPa was studied using a vacuum gravimetric technique, and for measurements at higher pressures a volumetric-gravimetric high-pressure setup described previously was used.[9] The error of adsorption measurement was ±1%. The pressures within intervals of 0.2—1000 Pa and 0.1—100 kPa were determined with errors of ±0.04 and ±2 Pa, respectively. Pressures higher than atmospheric were measured on a manometers of 0.15 class. The 195—423 K temperature interval was specified using liquid and electric thermostats with an error not exceeding ±0.2 K. The $p—v—T$ data[10] were used for the calculation of the absolute adsorption, *viz.*, the complete content of the adsorptive in micropores.

Adsorption deformation of zeolite granules was experimentally measured in a high-pressure cell of an adsorption-dilatometric setup[11] by the displacement of a core of a differential converter, which was in contact with the sample. Zeolite samples were evacuated at a room temperature to a residual pressure of ~10 Pa and then at 620 K for 12 h to a residual pressure of 0.1 Pa. The first measurements showed that the adsorption deformation curves of the sample had a hysteresis. To achieve reproducibility, the zeolite was multiply saturated with carbon dioxide and evacuated. After 40—50 saturation cycles, the adsorption deformation curves became reproducible. The relative error of measurements of deformation was $\pm 1 \cdot 10^{-5}$.

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Such a treatment of the compacted sample of NaX zeolite results, most likely, in the disruption of weak mechanical contacts between crystalline splices. At the same time, the strongest mechanical contacts formed in pressed samples continue to retain the polycrystalline aggregates in the sample due to which its sizes and shape remain unchanged.

The measurement of each adsorption isotherm and dilatometric curve was preceded by the evacuation of the adsorbent at 620 K for 12 h to a residual pressure of 0.1 Pa with the purpose of decomposing of carbonates, which can be formed by the modification of zeolite with carbon dioxide.[12]

Control measurements of CO_2 adsorption on zeolite NaX showed that this preparation of the zeolite sample did not change its adsorption properties as compared to those of the synthesized zeolites and secured reproducibility of the dilatometric curves.

Results and Discussion

The adsorption isotherms of CO_2 on zeolite NaX are reversible over the whole temperature interval between 195 and 423 K . At low temperatures and pressures ($p < 100$ Pa), the diffusion of the CO_2 molecules was drastically retarded in micropores, due to which the time needed to establish adsorption equilibria reached 4—5 h. The results of measurements are presented as isotherms in Fig. 1. The data obtained agree satisfactorily with the previously published results for similar systems.[13,14,15] The most striking difference between our data and the previous results is observed in the region of high pressures and large pore fillings. However, the calculations of the total adsorption of CO_2 in zeolite NaX along the line of saturated vapor pressure of carbon dioxide performed by the Dubinin—Nikolaev method[16] are closer to our measurements.

If the amount of adsorbed CO_2 is plotted as a function of pressure, the isotherms are convex over the pressure range studied and contain no Henry region. For the plot a *vs.* ln$p$, all isotherms contain an inflection point at $a \simeq 4.0$ mmol g^{-1} and they are shifted toward higher pressures with temperature. The coefficient of total adsorption $\alpha = -(\partial \ln a_0/\partial T)_{p=ps}$ calculated from the experimental adsorption isotherms at $T < T_{cr}$ is equal to $0.8 \cdot 10^{-3}$ K^{-1}, which is close to the theoretical value of $1.5 \cdot 10^{-3}$ K^{-1} obtained by the Dubinin—Nikolaev method.

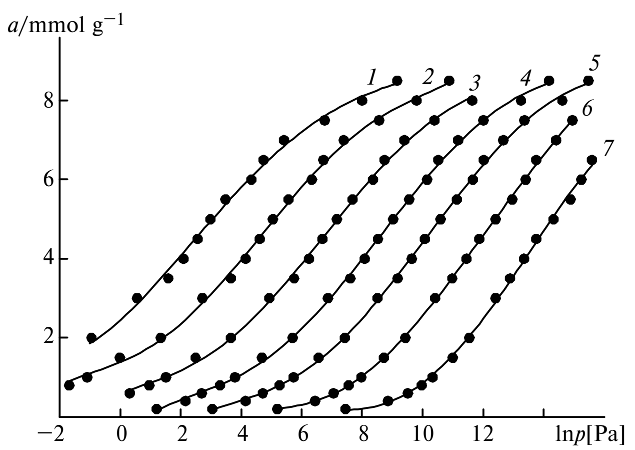

Fig. 1. Adsorption isotherms of CO_2 on zeolite NaX at different temperatures (K): *1*, 195; *2*, 216; *3*, 243; *4*, 273; *5*, 305; *6*, 353; and *7*, 423.

The relative linear adsorption deformation $\Delta L/L$ as a function of the carbon dioxide pressure for zeolite NaX was studied along with measuring adsorption isotherms at the same temperatures. The results are presented in Fig. 2 in the coordinates $\Delta L/L$—(ln$p$) at 195—423 K. As follows from Fig. 2, these functions have a complicated character. An initial expansion of the sample with pressure, which is especially significant for 353 and 423 K, is observed at all temperatures. As the CO_2 pressure increases, expansion changes to compression, which is most pronounced at 195 K. In all cases, the further increase in the equilibrium CO_2 pressure results in a sharp expansion of zeolite NaX, exceeding compression by 5—10 times. A trend for adsorbent compression was traced at 305 and 353 K in the region of highest pressures (>30 bar).

In the initial period of filling of the micropore volume, the interaction of CO_2 having a large quadrupole moment ($-4.1 \cdot 10^{26}$ e.s.u.)[17] with the Na^+ cations in the zeolite cavities makes a great contribution to the adsorption energy.[7,14] In addition, the important role of donor-acceptor interactions involving lone electron pairs of the oxygen atoms and vacant orbitals of the cations was stressed.[18,19] In the region of high pressures and, hence, high fillings of the micropore volume, a substantial effect is exerted by the dispersion forces of attraction and repulsion in the adsorbate and the forces of interaction of the adsorbed molecules with the opposite walls of micropores.[20]

Using adsorption isotherms (see Fig. 1), we calculated the adsorption deformation of the zeolite NaX sample at different adsorption values (Fig. 3). As can be seen in Fig. 3, at all temperatures the initial filling

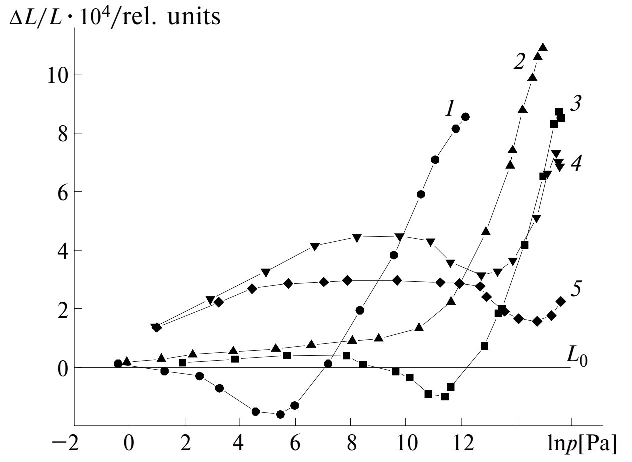

Fig. 2. Relative linear adsorption deformation of zeolite NaX as a function of the CO_2 pressure at different temperatures (K): *1*, 195; *2*, 273; *3*, 305; *4*, 353; and *5*, 423. L_0 is the line of zero deformation of the sample.

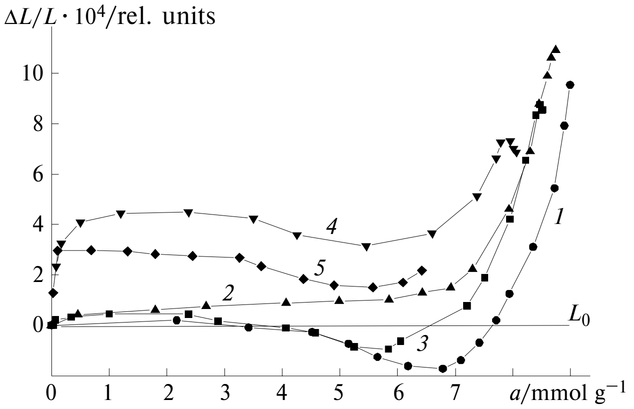

Fig. 3. Relative linear adsorption deformation of zeolite NaX as a function of the CO_2 adsorption at different temperatures (K): *1*, 195; *2*, 273; *3*, 305; *4*, 353; and *5*, 423.

of micropores with the sorbed CO_2 molecules at $a < 1.0$ mmol g^{-1} results in zeolite expansion, which is especially strong at high temperatures.

Further micropore filling to 3—3.5 mmol g^{-1} does not substantially deform the zeolite NaX crystals. However, at $a > 3$—3.5 mmol g^{-1} at all temperatures, except 273 K, compression reaching maximum values at $a \approx 5.5$—6.5 mmol g^{-1} occurs. The minimum in the adsorption deformation curves indicates, most likely, that the adsorption system exists in the energetically favorable state, which appears when rather stable CO_2 complexes (associates) are formed in micropores of the solid.[21] The further sharp expansion of the crystalline lattice of zeolite NaX at $a > 6$—7 mmol g^{-1} is due, most likely, to the rearrangement of the associates in the cavities and a decrease in the average distance between the adsorbed molecules related to a sharp growth in the inner pressure of the adsorbate in micropores. However, as follows from Fig. 3, expansion is replaced by compression in the region of highest pressures of the gas phase at 305 and 353 K. This change in the deformation sign[22] can be a result of the compression of the zeolite NaX crystals under the external pressure of carbon dioxide.

Our studies showed that during adsorption the adsorbent, *viz.*, zeolite NaX, undergoes a complex deformation of expansion and compression stipulated, to a high extent, by the specific interaction of carbon dioxide with the zeolite cations.

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