Adsorption deformation of zeolite NaX at high pressures of xenon

*A. A. Fomkin and A. L. Pulin**

Institute of Physical Chemistry, Russian Academy of Sciences,
31 Leninsky prosp., 117915 Moscow, Russian Federation.
Fax: +7 (095) 952 5308

The deformation of pellets of crystalline zeolite NaX upon adsorption of Xe at pressures from 0.001 to 7 MPa and temperatures from 252.5 to 333 K was studied. In the temperature range studied, the relative linear deformation of zeolite crystals is negative in the initial adsorption region. When the adsorption of Xe increases, its value passes through a minimum and then increases sharply taking positive values at high adsorption volume filling of micropores.

Key words: adsorption; zeolite, crystal deformation; high pressure.

The authors of the majority of studies of adsorption of gases and vapor believe that the adsorption deformation of a solid adsorbent is negligible.[1] This assumption is valid for adsorbents with a relatively low specific surface and is quite inappropriate for microporous adsorbents, almost all of whose atoms participate in adsorption interaction as one of the components of the "solid solution." [2] Therefore, the majority of studies of adsorption deformation are performed with microporous carbon adsorbents and zeolites.[3] It is especially important to take into account the adsorption deformation in studies of adsorption in wide temperature and pressure ranges, because the energy parameters of the adsorption process depend substantially on the change in the properties of the adsorbent.[4] The purpose of this work is to study the deformation of crystalline zeolite NaX upon adsorption of xenon.

Experimental

An inductive type dilatometer designed and customized for measurement of small deformations of solids upon adsorption in the pressure range from 0.1 to 20 MPa and the temperature range from 77 to 473 K was used. The scheme of the dilatometer is presented in Fig. 1: the core (*1*) of the inductive converter (*2*) of linear movement is attached to the rod (*3*) that rests on the quartz plate (*4*) located on the sample (*5*). The sample is placed inside the tube (*6*) of fused quartz, which is placed into the metallic tube (*7*) attached to the body of the dilatometer. The change in the length of the sample results in movement of the core, which is recorded by a V7-38 digital voltmeter using a differential transformer. The dilatometer is connected with a high-pressure adsorption setup with pipe (*8*). The adsorption setup has been described previously.[5]

The sample is a cylinder 91 mm in length consisting of granules of pellets of zeolite NaX 12 mm in diameter and

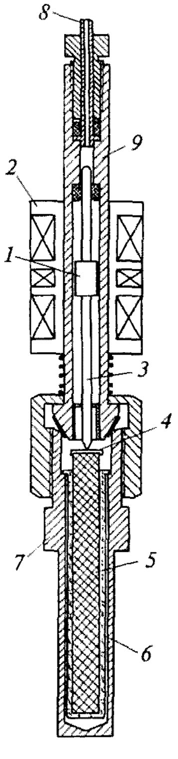

Fig. 1. Scheme of the dilatometer for measurement of adsorption deformation of solid states: *1*, core; *2*, inductive converter; *3*, rod; *4*, quartz plate; *5*, sample; *6*, quartz tube; *7*, metallic tube; *8*, connecting pipe; *9*, body of the dilatometer.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 336—338, February, 1996.

15—25 mm in length. It is placed into a flat-bottomed quartz tube with the inner diameter of 12.2 mm.

Zeolite granules were obtained by molding at ~1.5 kbar. The sample was at first activated in air for 12 h at 620 K, then placed into the dilatometer, and evacuated for 8 h at 570 K to the residual pressure of 0.1 Pa.

During the experiments, the temperature of the section of the dilatometer, which contained the sample, was maintained constant by a liquid-type ultrathermostat with an accuracy of 0.1 K. The remaining volume of the dilatometer, along with the inductive converter and the high-pressure setup, were thermostated in an air thermostat at 303 K. The pressure was measured by a vacuum gage (model 1227, accuracy class 0.25) and by MP-60 and MP-600 load-piston manometers (accuracy class 0.05).

The inductive converter of movement of the dilatometer was calibrated at 303 K using a set of standard plates 0.01—1 mm in width. The dilatometer was calibrated by temperature and pressure changes on a "model" of fused quartz, whose form and size were the same as those of the analogous zeolite sample.

During the first experiments we have established that the deformation of zeolite granules is irreversible. Therefore, the sample was "trained" by multiple cycles of an increase in the xenon pressure to 10 MPa followed by a decrease in the pressure to 0.01 kPa. The deformation curve becomes reproducible after approximately 50 cycles.

Crystalline zeolite NaX of the composition $0.98\ \mathrm{Na_2O}\times\mathrm{Al_2O_3}\times2.36\ \mathrm{SiO_2}\times0.02\ \mathrm{H_2O}$ was used. Its unit cell parameter is 2.496 nm according to X-ray diffraction data. Xenon (spectral purity grade) was used as the adsorbate.

Results and Discussion

It is likely that adsorption deformation of zeolite pellets is caused by the deformation of zeolite crystals upon adsorption.

This is confirmed, in particular, by the reversibility of the curves of adsorption deformation, which comes after the multicycle adsorption-desorption "training" of the zeolite.

The curves of the relative adsorption deformation $\eta = \Delta l/l_0$ (l_0 is the initial length of the sample, Δl is a change in the length of the sample) of zeolite NaX crystals dependent on the Xe pressure at 252.5, 271.7, 303, and 333 K are presented in Fig. 2. It follows from Fig. 2 that the relative adsorption deformation of zeolite NaX crystals is negative in the range of the initial coverages, *i.e.*, crystallites are compressed. When the adsorption increases, the deformation values continue to decrease and reach minima, then the extension comes, and the sign of the relative adsorption deformation changes from negative to positive. Absolute values of the positive relative deformation (extension) exceed by almost an order of magnitude the maximum negative deformation (compression).

The temperature effect on the adsorption deformation of zeolite NaX crystals is most pronounced at xenon pressures higher than 1 atm ($\ln(p) = 11.5$).

The dependences of the relative adsorption deformation of zeolite NaX on the value of Xe adsorption under isothermal conditions are presented in Fig. 3. The data obtained previously[6] for this system in the temperature range of 150—370 K and the pressure range of 0.1—13 MPa were used to recalculate the pressure per adsorption value under the conditions of dilatometric measurements. The effect of an increase in the adsorption is the same as the effect of an increase in the pressure (see Fig. 2). The compression is observed at the initial coverages, it becomes maximum at the minimum point, and the deformation increases sharply at the high volume filling of zeolite micropores, going to the region of positive deformations.

It follows from Fig. 3 that for all temperatures studied the region of compression of zeolite crystals shifts

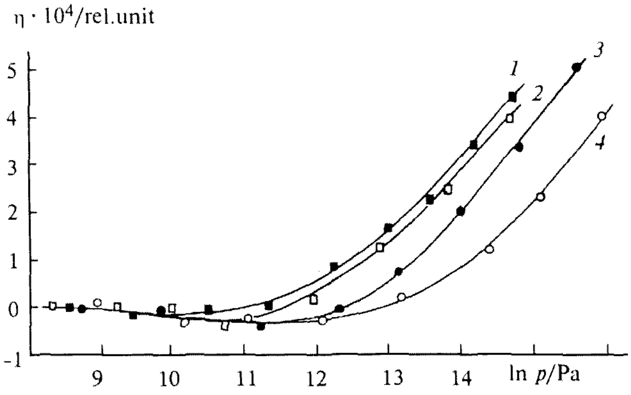

Fig. 2. Pressure dependences of the relative linear deformation of zeolite NaX at T/K: 252.5 (*1*); 271.7 (*2*); 303.0 (*3*); 333.0 (*4*).

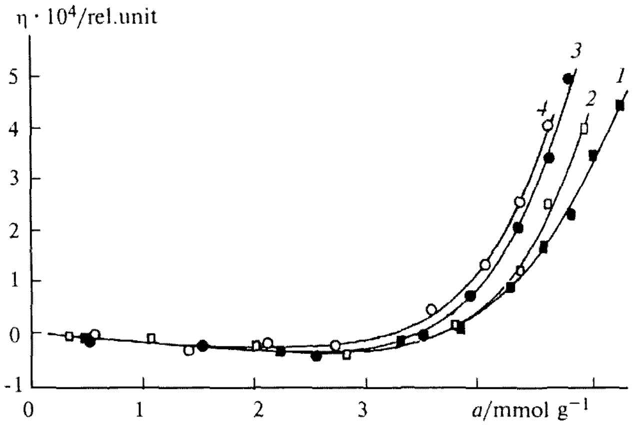

Fig. 3. Dependences of the relative linear deformation of zeolite NaX on the adsorption value at T/K: 252.5 (*1*); 271.7 (*2*); 303.0 (*3*); 333.0 (*4*).

Table 1. Characteristic points of the deformation isotherms upon xenon adsorption on zeolite NaX

T/K	$\eta_{max}\cdot 10^4$ /rel. unit	a_{max} /mmol g^{-1}	$\eta_{min}\cdot 10^4$ /rel. unit	a_0 ($\eta = 0$) /mmol g^{-1}
252.5	5.05	5.39	−0.3	3.78
271.7	4.96	5.10	−0.4	3.68
303.0	5.38	4.92	−0.3	3.45
333.0	4.75	4.76	−0.3	3.19

toward the lower filling as the temperature increases, and the maximum compression reaches the values of η_{min} = (0.3—0.4) $\cdot 10^{-4}$ (Table 1). The further growth of the adsorption results in the extension of zeolite, and the deformation isotherms pass through the points, in which the parameters of zeolite correspond to their initial sizes ($a = a_0$, $\eta = 0$).

The maximum values of adsorption measured and of relative adsorption deformation are presented in Table 1. It follows from Table 1 that an increase in temperature results in a shift of the point of zero deformation (a_0) to lower fillings. The intersection on the curve to the right of this point corresponds to considerable extension of zeolite crystals, at which the derivative $(\partial\eta/\partial a)_T$ increases sharply. The maximum relative extension of zeolite (η_{max}) is greater by more than an order of magnitude than the maximum relative compression (η_{min}). A specific feature of the deformation curves is the finiteness of the negative derivative $(\partial\eta/\partial a)_T$ at $a \to 0$, which contradicts the result obtained previously,[7] according to which $(\partial\eta/\partial a)_T \to (-\infty)$ at $a \to 0$.

As follows from Table 1, the maximum linear deformations of zeolite NaX crystals amount to hundredths of a percent. Therefore, they can be neglected in calculations of the adsorption of xenon in the pressure range studied. Nevertheless, the behavior of the deformation curves, *i.e.*, the derivatives $(\partial\eta/\partial a)_T$ and $(\partial\eta/\partial T)_a$, can contribute substantially to calculations of thermodynamic functions of adsorption systems.[8] In particular, the estimations show that the corrections to isosteric adsorption heats for the xenon—zeolite NaX system introduced, taking into account the noninert character of an adsorbent, can reach 40 %.

References

1. *Eksperimental'nye metody v adsorbtsii i khromatografii* [*Experimental Methods in Adsorption and Chromatography*], Ed. A. V. Kisilev, Izd-vo MGU, Moscow, 1973 (in Russian).
2. B. P. Bering, A. L. Maiers, and V. V. Serpinskii, *Dokl. Akad. Nauk SSSR*, 1970, **193**, 1, 119 [*Dokl. Chem.*, 1970, **193** (Engl. Transl.)].
3. O. K. Krasil'nikova, Ph. D. (Chem.) Thesis, Institute of Physical Chemistry, Acad. Sci. USSR, Moscow, 1977 (in Russian).
4. A. A. Fomkin, in *Trudy VI Vsesoyuzn. konf. po teor. voprosam adsorbtsii* [*Proc. VI All-Union Conf. on Theoretical Problems of Adsorption*], Nauka, Moscow, 1987, 11 (in Russian).
5. E. V. Chkhaidze, A. A. Fomkin, V. V. Serpinskii, and G. V. Tsitsishvili, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1985, 974 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1985, **34**, 886 (Engl. Transl.)].
6. A. A. Fomkin, V. V. Serpinskii, and B. P. Bering, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, 1244 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1975, **24**, No. 6 (Engl. Transl.)].
7. V. V. Serpinskii and T. S. Yakubov, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1981, 75 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1981, **30**, No. 1 (Engl. Transl.)].
8. A. A. Fomkin, D. Sci. (Phys.-Math.) Thesis, Institute of Physical Chemistry, RAS, Moscow, 1993 (in Russian).

Received June 29, 1995