Reports of the Academy of Sciences of the USSR

Academician M. M. DUBININ

1964

SovietRxiv

Fig. 1. Adsorption isobars of various gases on zeolite NaA at $p = 700$ mm Hg.

Figure 1: Fig. 1. Adsorption isobars of various gases on zeolite NaA at $p = 700$ mm Hg.

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1964. Volume 159, No. 1

PHYSICAL CHEMISTRY

Academician M. M. DUBININ

MOLECULAR-SIEVE PROPERTIES OF SYNTHETIC ZEOLITES OF TYPES A, X, AND Y IN VARIOUS ION-EXCHANGE FORMS

The molecular-sieve properties of zeolites are usually characterized by the critical diameters of molecules ([1]) that are capable of passing, at a measurable rate, through the narrower openings or windows connecting the large cavities of zeolite crystals. The maximum critical diameters of the penetrating molecules are taken as the diameters of the windows.

The penetration of molecules through zeolite windows has the characteristic features of a process associated with the presence of an activation energy. Figure 1 shows ([2]) adsorption isobars for argon, nitrogen, and carbon monoxide for the sodium form of zeolite A, or NaA. The shape of the isobars is typical for an activated adsorption process. The greater the activation energy E of the process of molecular penetration, the more sharply the rate of molecular penetration, or the adsorption rate, decreases with decreasing temperature. Equilibrium states in adsorption are realized only for the portions of the isobars beyond the maxima of the curves, where adsorption is characterized by a negative temperature coefficient. For lower temperatures, the adsorption amounts reached within the time adopted for the experiments differ from the equilibrium adsorption amounts by the more, the lower the temperature. Therefore, the nonequilibrium adsorption amounts for the regions of the isobars to the left of the maxima in Fig. 1 decrease sharply with decreasing temperature, and at temperatures below -196° adsorption in the cavities of zeolites becomes immeasurably small.

Fig. 1. Adsorption isobars of various gases on zeolite NaA at $p = 700$ mm Hg.

In light of the facts set forth above, it is most rational to characterize the molecular-sieve properties of zeolites by the activation energies of the processes

of molecular penetration through the windows into the cavities of zeolite crystals for a series of molecules with different properties, in particular sizes. Unfortunately, such data are absent from the literature. The concept of the diameters of zeolite windows, which in essence has a kinetic character, is, although illustrative, a cruder and more conditional description of the molecular-sieve properties of zeolites. First of all, this characteristic is not a constant quantity but depends on temperature, as is directly indicated by the isobars in Fig. 1. Therefore it should be regarded as a certain conditional quantity having an effective character, and called the effective window diameter (d_e). Qualitatively, the effective window diameters vary inversely with the activation energies E of the process of molecular penetration through the windows into the zeolite cavities.

The effective diameters of the windows connecting the large cavities of zeolites of types A, X, and Y depend on the X-ray structural diameters of the windows and on the nature of the ion-exchange cations present in a delocalized state in the large cavities of the zeolites. The X-ray structural diameters of the free apertures of the oxygen windows are practically constant quantities for each type of zeolite. However, the penetration of molecules through the windows is associated with displacement of cations located in the large cavities near the window apertures. We shall conventionally call this effect blocking of the windows by cations—

According to experimental data, for NaA $d_e \approx 4$ Å, and for KA $d_e \approx 3$ Å. It is evident that, when the windows are blocked by K^+, whose dimensions are larger than those of Na^+, the activation energy of the process by which molecules penetrate through the windows into the zeolite cavities increases and, correspondingly, the effective diameter of the windows decreases.

For various ion-exchange forms of zeolites of types A and X, the effective diameters of the windows d_e connecting the large cavities, according to experimental estimates, are as follows: for NaA $d_e \approx 4$ Å, CaA $d_e \approx 5$ Å, NaX $d_e \approx 9$ Å, and CaX $d_e \approx 8$ Å. The difference in the values of d_e between the zeolite types is determined mainly by the X-ray structural diameters of the openings of the eight-membered oxygen windows in zeolite A and, correspondingly, of the twelve-membered oxygen windows in zeolites X. The opposite character of the change in d_e on going from the Na to the Ca forms of zeolites A and X has not yet had a reasonable explanation. It should be sought in the structural features of zeolites A and synthetic faujasites, i.e., zeolites X and Y, in the properties and number of ion-exchange cations entering into the composition of the aluminosilicate frameworks of the zeolites.

1. The secondary and overall structural unit of the zeolites under consideration is the cubooctahedral structural unit, or cubooctahedron (CO), consisting of 24 silicon- and aluminum-oxygen tetrahedra. Taken in isolation, a CO is a polyhedron with a small cavity inside. Into this cavity lead 8 six-membered and 6 four-membered oxygen windows. The X-ray structural diameters of their openings are ~ 2 Å and fractions of an Å, respectively. These windows are inaccessible for the penetration of adsorbed molecules

into the small cavities of the zeolites under consideration. In the structure of zeolite A, adjacent cubooctahedra are connected by four-membered oxygen bridges, and the centers of the COs are located at the nodes of a primitive cubic lattice. This means that, for adjacent COs, the oxygen atoms of the four-membered oxygen windows are shared, i.e., all 6 four-membered oxygen windows of each CO are used for bonding. The spaces between the COs are large cavities of the zeolite crystal. Each large cavity is connected with adjacent large cavities by means of 6 eight-membered oxygen windows. From the large cavity, 8 six-membered windows lead into the small cavities. The elementary crystal cell of zeolite A contains one large cavity [2–5].

In the structure of faujasite, the centers of the COs are located at the nodes of a diamond-type crystal lattice (face-centered cubic lattice). Each CO is connected with adjacent COs by means of 4 six-membered oxygen bridges, i.e., 4 six-membered oxygen windows of each CO are used for the bonds between COs. The oxygen atoms of these windows become common to adjacent COs. The spaces between COs form the large cavities of the zeolite. Each large cavity is connected with neighboring cavities by four twelve-membered oxygen windows. From the large cavity only 4 six-membered oxygen windows lead into the small cavities. The cubic elementary cell of faujasite contains 8 large cavities and, correspondingly, 8 COs. Its parameter is approximately twice as large as the parameter of the elementary cell of zeolite A [5,6].

The aluminosilicate framework of the elementary cell of zeolite A, containing one large cavity, includes 24 $(\mathrm{Si},\ \mathrm{Al}) - \mathrm{O}$ tetrahedra [4]. Correspondingly, the aluminosilicate framework of the elementary cell of faujasite consists of 192 $(\mathrm{Si},\ \mathrm{Al}) - \mathrm{O}$ tetrahedra [6] with 8 large cavities, or of $192 : 8 = 24$ tetrahedra calculated per large cavity. Therefore, the compositions of the aluminosilicate frameworks referred to one large cavity are identical for zeolites A and faujasites and are expressed by the formula:

$$\left[\frac{2n}{i}\,\mathrm{M}\cdot 2n\,\mathrm{Al}\cdot nx\,\mathrm{Si}\cdot 48(\mathrm{O})\right], \tag{1}$$

where

$$x = \mathrm{SiO_2}/\mathrm{Al_2O_3} \tag{2}$$

molar ratio of silicon dioxide to aluminum oxide, and M is a cation with charge i. The cations compensate the excess negative charge of the aluminosilicate framework of the zeolite. The coefficient n is determined from the condition:

$$2n + nx = 24, \tag{3}$$

whence

$$n = \frac{24}{2 + x}. \tag{4}$$

In accordance with (1), the number of cations $[M^{i+}]$, calculated per one large cavity, is expressed as:

$$[M^{i+}] = 2n/i. \tag{5}$$

2. Let us consider the characteristics of the molecular-sieve properties of the Na and Ca forms of zeolites under complete ion exchange. For zeolite NaA, according to (5), there are 12 Na^+ per one large cavity ($x = 2$, $i = 1$, $n = 6$). According to X-ray structural Fourier-analysis data, 8 of the 12 Na^+ are localized in the openings of the six-membered windows leading into the small cavities, while the remaining 4 Na^+ are in the large cavity in a nonlocalized state. Since the eight-membered windows connecting the large cavities are shared by adjacent large cavities, one large cavity has 3 "calculated" windows. Thus, in each large cavity there are 4 Na^+ for 3 calculated windows, and the aperture of each of them can be blocked, in the sense mentioned above, by Na^+. Therefore, for NaA, $d \approx 4$ Å is determined by an eight-membered oxygen window blocked by Na^+. On going to CaA, in the large cavity there will be 2 nonlocalized Ca^{2+} for 3 calculated windows. As a result, 1 calculated window, or in all 2 eight-membered windows out of the 6 windows connecting the large cavities, remain unblocked by cations. Therefore, for CaA, $d \approx 5$ Å is determined by eight-membered oxygen windows not blocked by cations.

For the Na forms of synthetic faujasites, i.e., zeolites X ($x = 2.2$-3.3) and Y ($x = 3.3$-5), according to formulas (4) and (5), $[Na^+]$ varies from 11.4 to 6.86. For industrial NaX samples, $x \approx 2.7$ and $[Na^+] = 10.2$. Of these, 4 Na^+ block the six-membered windows leading into the small cavities, and 6.2 Na^+ are nonlocalized in each large cavity for 2 calculated twelve-membered oxygen windows. Consequently, each such window can be blocked by Na^+, and therefore $d \approx 9$ Å for NaX is determined by twelve-membered windows blocked by Na^+. On going to CaX, in each large cavity there will be 3.1 nonlocalized Ca^{2+} for two calculated windows. Therefore, $d \approx 8$ Å for CaX is determined by twelve-membered oxygen windows blocked by Ca^{2+}. The decrease in d in this case is due to the increase in the charge and partly in the size of the ion blocking the window when passing from the Na to the Ca form of the zeolite.

For the limiting case of zeolite NaY at $x = 5$, $[Na^+] = 6.86$. According to the foregoing, in the large cavity there will on average be 2.86 nonlocalized Na^+ for two calculated windows. Therefore, for the sample of NaY under consideration one should expect $d \approx 9$ Å, i.e., a value typical for Na forms of faujasites. However, on going to CaY, under the condition of complete ion exchange, in each large cavity there will remain on average 1.43 nonlocalized Ca^{2+} for two calculated windows. This number of ions will be insufficient to block all the twelve-membered windows, and of the 4 windows connecting the large cavities,

Fig. 2. Dependence of adsorption (a_g, g/g) on zeolite type A on the degree of ion exchange of Na^+ for Ca^{2+}: 1 —nitrogen, −196°, 15 mm; 2 —*n*-heptane, 25°, 45 mm; 3 —propane, 25°, 250 mm

Figure 2: Fig. 2. Dependence of adsorption (a_g, g/g) on zeolite type A on the degree of ion exchange of Na^+ for Ca^{2+}: 1 —nitrogen, −196°, 15 mm; 2 —*n*-heptane, 25°, 45 mm; 3 —propane, 25°, 250 mm

one window will remain unblocked by Ca^{2+}. Therefore d for such a sample will be determined by unblocked twelve-membered windows and may increase to 10 Å or more. This conclusion can be verified experimentally.

3. The concepts set forth explain not only the opposite change in d on going from the Na to the Ca forms of zeolites A and X, but also make it possible to estimate the degrees of ion exchange α at which begin to pro—

the properties of Ca forms of zeolites may appear (8). Such an estimate is possible under the natural assumption that, during ion exchange, the first to be exchanged for Ca^{2+} are the Na^+ ions delocalized in the large cavities. If, of the total number $[Na^+]$ calculated per one large cavity, N Na^+ ions are in the delocalized state in the large cavity, then at the degree of ion exchange

$$\alpha = N/[Na^+] \tag{6}$$

the properties of the Ca forms of zeolites should appear. Thus, for NaA, $N = 4$ and $[Na^+] = 12$. According to formula (6), $\alpha = 0.33$, which is in good agreement with the experiments (2) shown in Fig. 2. For NaX samples with $x = 2.30$, studied in (7), $N = 7.2$ and $[Na^+] = 11.2$. According to formula (6), $\alpha = 0.64$. Below, from (7), we give the adsorption values of 1,3,5-triethylbenzene from solution in *n*-heptane; for its molecules the twelve-membered windows blocked by Na^+ are accessible, but the windows blocked by Ca^{2+} are inaccessible. The adsorption values of 1,3,5-triethylbenzene a are expressed in mmol/g. They correspond to shaped zeolites with 10% binder.

α	0	0.53	0.70	0.72	0.96	1.00
a, mmol/g	0.87	0.77	0.49	0.44	0	0

Fig. 2. Dependence of adsorption (a_g, g/g) on zeolite type A on the degree of ion exchange of Na^+ for Ca^{2+}: 1 —nitrogen, −196°, 15 mm; 2 —*n*-heptane, 25°, 45 mm; 3 —propane, 25°, 250 mm

From these data, the properties of CaX appear at α close to 0.7, in satisfactory agreement with the calculated estimate.

In an analogous manner it can be shown that, for Y zeolites, the increase in d_e noted above, instead of the typical decrease on going from the Na to the Ca form, may appear at a molar ratio $x > 4$.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
18 VII 1964

REFERENCES

1. R. M. Barrer, Brit. Chem. Eng., **4**, No. 5, 1 (1959).
2. D. W. Breck, W. G. Eversole et al., J. Am. Chem. Soc., **78**, 5963 (1956).
3. T. B. Read, D. W. Breck, J. Am. Chem. Soc., **78**, 5972 (1956).
4. R. M. Barrer, W. M. Meier, Trans. Farad. Soc., **54**, 1074 (1958).
5. L. Broussard, D. P. Shoemaker, J. Am. Chem. Soc., **82**, 1041 (1960).
6. R. M. Barrer et al., Trans. Farad. Soc., **53**, 1111 (1957).
7. L. I. Piguzova, A. S. Vitukhina, *Chemistry and Technology of Fuels and Oils*, No. 6, 17 (1963).
8. M. M. Dubinin, *Izv. Acad. Sci. USSR, Ser. Chem.*, 1964, No. 7.

Note: Figure translations are in progress. See original paper for figures.