L. N. KVITKOVSKII, Academician of the Academy of Sciences of the Turkmen SSR S. R. SERGIENKO

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

L. N. KVITKOVSKII, Academician of the Academy of Sciences of the Turkmen SSR S. R. SERGIENKO

SORPTION BY TYPE A MOLECULAR SIEVES

Synthetic zeolites are crystalline aluminosilicates of sodium or calcium, in which Na or Ca atoms play the role of an ion-exchange cation. The crystal lattice of zeolites is characterized by rather large interionic distances in certain directions (4-12 Å); this leads to the formation of channels. Zeolites are synthesized from aqueous solutions, and therefore the channels formed in the crystal lattice are filled with water, which is removed upon heating (1). The cavities thus formed can be filled by molecules of other substances whose dimensions are commensurate with certain distances in the crystal lattice. The crystal lattice of zeolites has been studied quite well (2-5).

According to X-ray structural analysis, the unit cell of a synthetic type A zeolite crystal consists of 24 ions Al + Si and 48 oxygen ions (6). The negative charge of the crystal lattice is compensated by ion-exchange cations. One unit cell of type A zeolite (with Na as the cation) contains one large cavity of practically spherical shape, 11.4 Å in diameter, with 6 octagonal windows formed by oxygen ions, 4.2 ± 0.2 Å in diameter, and one small cavity, also approximately spherical in shape, 6.6 Å in diameter, with 8 windows, 2.0-2.5 Å in diameter (2). Of special interest is the large cavity and, above all, its through windows. In the large cavity the windows do not have a strictly cylindrical shape, and their diameter varies within certain limits (4.11-4.47 Å), which is somewhat lower than the experimentally found value of the apparent diameter, equal to 4.2-4.75 Å (2). As was shown by M. M. Dubinin and co-workers (8), at low temperatures the rate of sorption by NaA zeolite of molecules whose dimensions are close to the dimensions of the windows becomes negligibly small because of their high activation energy. Thus, for example, nitrogen at $-195°$ C is practically not sorbed by NaA zeolite, whereas CaA zeolite sorbs nitrogen at this temperature at a high rate.

Fig. 1. Critical dimensions of some gas molecules

When considering the question of sorption by synthetic zeolites of particular molecules, it is customary to estimate the dimensions of the latter according to the principle of additivity of covalent radii for diatomic and polyatomic nonpolar molecules, or according to the additivity of ionic dimensions calculated on the basis of data for the crystal lattice of polar molecules, taking into account their

Figure 3

Figure 1: Figure 3

Figure 4

Figure 2: Figure 4

spatial arrangement (see Fig. 1, ([1], [7])). However, as noted above,

Fig. 2. Forces of interaction between molecules as a function of their mutual distance (+q –attraction, −q –repulsion, *l* –distance between the centers of the molecules)

the magnitude of the window diameter fluctuates, and the windows inside are screened by the electric field; therefore, in order for a sorbate molecule, whose critical size is close to the size of the window, to pass through it into a large cavity, a certain additional amount of energy must be expended. Consequently, sorption will proceed with a considerable activation energy, depending on the dimensions of the sorbate molecule; to some extent it is analogous to the dependence of intermolecular forces on the distance between interacting molecules (see Fig. 2).

Fig. 3. Dependence of the kinetic diameters of molecules on temperature.

To overcome the energy barrier of the window of a synthetic zeolite, a molecule being sorbed with a critical size close to the size of the window must possess a certain reserve of kinetic energy, direction of motion, spatial orientation, and capacity for deformation for diatomic and polyatomic gas molecules. The kinetic energy of a molecule, which depends on temperature, and its critical diameter are the principal factors governing the process of sorption by molecular sieves. These two properties of the sorbate molecule are conveniently expressed in the form of the kinetic diameter, which is determined experimentally from the viscosity of the gas, assuming that the molecule has a spherical shape (see Fig. 3, (9, 10)).

Fig. 4. Sorption isobars. *a* –argon, *b* –nitrogen, *v* –methane, *g* –krypton.

In our study, to determine the sorption isobars, we used a sample of synthetic zeolite NaA No. 20, synthesized in the laboratory of I. E. Neimark. A 4 g sample of zeolite was placed in a glass ampoule and, for 2 hours, evacuated at a residual pressure of $1 \cdot 10^{-2}$ mm Hg and a temperature of 400°. The ampoule was then cooled to a temperature 1-2° above the boiling point of the gas being sorbed (but not below −195°C) and connected to a measuring burette, with a reading accuracy of 0.1 cm^3, filled with the gas under investigation. Thereafter the temperature of the ampoule with the sorbent was gradually raised (heating rate 1° in 3 min). Throughout the entire experiment, atmospheric pressure was maintained in the burette, and the amount of sorbed gas was measured. At the beginning of the temperature increase, the quantithe amount of gas in the burette increased, since desorption from the secondary porous structure of the molecular sieve was taking place. At a certain temperature, characteristic for each gas, uptake was observed; the onset of this could be recorded at a sorption value equal to 0.01–0.02% of saturation (see Fig. 4). In Fig. 4 the dashed portions of the curves were obtained by extrapolation, while the data for the main part of the curve (solid line) were obtained under equilibrium with respect to sorption and desorption. As can be seen from the figure, in certain temperature intervals the sorption rate becomes negligibly small, and gas uptake practically ceases.

We give the dimensions of the kinetic diameters of gas molecules, calculated at the temperatures of the onset of sorption:

Gas	Argon	Krypton	Nitrogen	Methane
Temperature of onset of sorption, °C	−165	−94	−155	−139
Kinetic diameter, Å	4.55	4.55	4.43	4.91

As can be seen from the data presented, at the initial sorption temperature the spherical atoms of the inert gases have identical values of the kinetic diameter; for the nitrogen molecule it is somewhat lower (−2.6%), and for methane it is higher (8%). These discrepancies are apparently connected with the deviation of the shapes of nitrogen and methane molecules from a sphere.

Received
19 IX 1962

REFERENCES

1. V. Ya. Nikolina, I. E. Neimark, M. A. Piontkovskaya, *Usp. khim.*, **29**, 9, 1089 (1960).
2. M. M. Dubinin, *Izv. AN SSSR, OKhN*, 1961, No. 7, 1183.
3. T. V. Beed, D. W. Brack, *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. Schoemaker, *J. Am. Chem.*, **82**, 1041 (1960).
6. M. M. Dubinin, *DAN*, **138**, No. 4, 866 (1961).
7. R. M. Barrer, *Brennstof Chem.*, **35**, 325 (1954).
8. M. M. Dubinin, M. M. Vyshegorodtseva et al., *Izv. AN SSSR, OKhN*, 1961, No. 3, 369.

9. *Brief Handbook of Physicochemical Quantities*, L., 1957, p. 99.
10. Landolt-Börnstein, *Anfl.* 6, 1, T. 1, 1950, S. 325.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.