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Abstract

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Adsorption of Vapors on Crystalline Adsorbents —Molecular Sieves

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Recently, considerable interest has been shown in the study and use of crystalline adsorbents that have been called molecular sieves ([1−8]). These adsorbents have pores with a cross section of several angstroms and therefore are capable of absorbing appreciable amounts only of those substances whose molecules have a transverse size smaller than the diameter of the adsorbent pores. The phenomenon of adsorption of various substances by natural crystalline adsorbents having pores of molecular dimensions (persorption) was studied earlier by a number of investigators ([9]). However, natural molecular sieves (mainly chabazite and, to a lesser extent, other zeolites) occur in nature, as a rule, in disseminated form, without forming large deposits. The use of synthetic molecular sieves, which can be obtained in large quantities and in their properties surpass natural ones, opens new possibilities in the field of separation of gases and liquids. In this connection, the preparation and study of the adsorption properties of synthetic molecular sieves is of great interest.

In the present communication, data are presented on the adsorption of vapors of polar and nonpolar substances, the molecules of which have different configurations and sizes, on two samples of molecular sieves, which are artificial minerals prepared by the author at the Grozny Petroleum Scientific-Research Institute. In the crystalline structure of the prepared molecular sieves there are very small interstices, owing to which they possess the ability for selective adsorption of a number of substances. In their crystalline structure both of the above-mentioned molecular sieves are identical. We give the X-ray diffraction data obtained in their investigation by the powder method using Cu radiation:

d, Å	9.40	7.22	5.68	4.31	3.78	3.38	3.03	2.68	2.17	2.08	1.95	1.76	1.61	1.52	1.44	1.37	1.30
I	med.	med.	med. strong	med. strong	strong	strong	v. strong	strong	weak	med.	weak	med.	med.	strong	weak	weak med.	strong med.

In Fig. 1, *I* are shown the adsorption isotherms of vapors of water, methyl alcohol, normal hexane, isooctane (2,2,4-trimethylpentane), and benzene by molecular sieve 102, and in Fig. 1, *II*—of the same substances by molecular sieve 202.

Fig. 1. Adsorption isotherms of vapors of water, methyl alcohol, n-hexane, iso-octane, and benzene on molecular sieves

Figure 1: Fig. 1. Adsorption isotherms of vapors of water, methyl alcohol, n-hexane, iso-octane, and benzene on molecular sieves

Both molecular sieves possess a clearly expressed effect of selective adsorption of molecules of different configuration and size. Molecular sieve 102 adsorbs 0.32 cm^3 per 1 g of water, 0.26 cm^3 per 1 g of methyl alcohol, while adsorption of the larger molecules of normal hexane, isooctane, and benzene occurs to an insignificant extent. Molecular sieve 202 adsorbs 0.32 cm^3 per 1 g of water, 0.28 cm^3 per 1 g of methyl alcohol and, in addition, 0.22 cm^3 per 1 g of normal hexane, while isooctane and benzene are not adsorbed to any appreciable extent by this molecular sieve either.

The adsorption isotherms of vapors of those substances that are adsorbed by molecular sieves correspond in their form to Langmuir isotherms.

type. A characteristic feature of the adsorption isotherms of these substances on the molecular sieves studied is the attainment of high adsorption values at low relative pressure (up to 0.1). Increasing the relative pressure above 0.1 does not lead to a noticeable increase in adsorption; the slight rise of the isotherm observed in some cases in the region of relative pressures 0.9–1.0 is apparently associated with capillary condensation occurring in the spaces between individual small crystals of the molecular sieves.

Adsorption on molecular sieves is reversible: the desorption branches of all isotherms coincide with their adsorption branches. The specific surface area

Fig. 1. Adsorption isotherms of vapors of water, methyl alcohol, *n*-hexane, *iso*-octane, and benzene on molecular sieves

	H_2O	CH_3OH	*n*-C_6H_{14}	*iso*-C_8H_{18}	C_6H_6
Adsorption	a	b	v	g	d
Desorption	a_1	b_1	v_1	g_1	d_1

I —molecular sieve 102, *II* —molecular sieve 202

of the molecular sieves studied is enormous. Calculation of its value from the Langmuir isotherm equation, using data on the adsorption of methyl alcohol vapors, gives a value of about 1000 m^2 per 1 g.

Comparing the data on vapor adsorption on the molecular sieves described and on the Linde molecular sieves known in foreign practice[6], it may be noted that molecular sieve 102 is, in its adsorption properties, analogous to the Linde 4 Å molecular sieve, while 202 is analogous to the 5 Å molecular sieve. At the same time, the molecular sieves described differ from the Linde products in their crystal structure. This follows from comparison of the X-ray diffraction data given above with the published[6] results of an X-ray diffraction study of the crystal structure of Linde molecular sieves.

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CITED LITERATURE

1. R. M. Barrer, *J. Chem. Soc.*, **1948**, 127.
2. R. M. Barrer, E. A. White, *J. Chem. Soc.*, **1952**, 1561.
3. R. M. Barrer, J. Hinds, E. A. White, *J. Chem. Soc.*, **1953**, 1466.
4. R. M. Barrer, J. W. Baynham, *J. Chem. Soc.*, **1956**, 2882, 2892.
5. A. Guyer, W. Ineichen, P. Guyer, *Helv. Chim. Acta*, **40**, 6, 1603 (1957).
6. D. W. Breck, W. G. Eversole et al., *J. Am. Chem. Soc.*, **78**, 23, 5963 (1956).
7. E. B. Brien, *Petrol. Eng.*, **27**, 3, 35 (1955).
8. W. C. Ziegehain, *Petrol. Eng.*, **29**, 9, 6 (1957).
9. S. Brunauer, *Adsorption of Gases and Vapors*, IL, 1948.

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