Reports of the Academy of Sciences of the USSR

PHYSICAL CHEMISTRY

1964

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1964. Volume 156, No. 2

PHYSICAL CHEMISTRY

Academician M. M. DUBININ, E. G. ZHUKOVSKAYA

FEATURES OF THE ADSORPTION OF VAPORS BY MICROPOROUS ADSORBENTS

Synthetic zeolites of types A and X are examples of microporous adsorbents for whose dehydrated crystals we have information, from independent X-ray structural data, on the shape, dimensions, and volumes of the micropores (^{1,2}). Therefore, investigation of the equilibrium adsorption of vapors of various substances on zeolites with different parameters of the microporous structure makes it possible to draw conclusions about the nature of the filling of the adsorption space and about certain properties of substances in the adsorbed state. These conclusions can be tested on experimental material for microporous adsorbents of another nature.

The features of adsorption on zeolites as on heteropolar adsorbents, caused by electrostatic interactions, appear the more strongly the greater the electrical asymmetry of the adsorbed molecules. They are manifested predominantly at low and medium fillings of the adsorption space and are weakly expressed at relatively high fillings, corresponding usually to the broad range of equilibrium relative pressures investigated.

As microporous adsorbents for the investigation, crystalline zeolites CaA and NaX, synthesized by S. P. Zhdanov under laboratory conditions, and two samples of active carbons AU-1 and AU-2 with limiting parameters of their microporous structure were used. The volume of the large cavities of zeolite CaA, calculated from X-ray structural data, was $v_{\text{BA}} = 0.278$ cm^3/g (^{1}), and their formal geometrical specific surface was $s_{\text{BA}} = 1640$ m^2/g (^{3}). Correspondingly, for zeolite NaX, $v_{\text{BX}} = 0.322$ cm^3/g (^{2}) and $s_{\text{BX}} = 1400$ m^2/g (^{3}). For AU-1, the constant B of the adsorption equation of the theory of volume filling of microporous adsorbents (^{4}) was $B = 0.407 \cdot 10^{-6}$, and correspondingly for AU-2, $B = 1.00 \cdot 10^{-6}$ (standard vapor: benzene). As a comparison served an adsorbent with an "open surface" –a relatively finely porous silica gel SM ($v_s = 0.61$ cm^3/g, $r_m = 21$ Å).

To determine the isotherms of equilibrium adsorption of vapors of nitrogen, argon, oxygen, and carbon monoxide at 77.3°K, and of other vapors at 293°K, a gravimetric adsorption apparatus was used (^{5}). The conditions for preparation of the adsorbents and for the measurements are described in (^{1,2}). From the equilibrium adsorption values for a range of relative pressures averaging $1 \cdot 10^{-4}$–$2 \cdot 10^{-1}$, the limiting adsorption values a_0 in mmol/g were calculated from the adsorption equation (^{6}).

The ratios of the limiting adsorption values of various vapors a_0 for zeolites CaA and NaX, given in Table 1, average $a_0^{\mathrm{CaA}}/a_0^{\mathrm{NaX}} = 0.861 \pm 0.028$, i.e., to an accuracy of up to 3% they are constant. The mean value agrees well with the ratio of the calculated volumes of the large cavities of the zeolites, $v_{\mathrm{BA}}/v_{\mathrm{BX}} = 0.863$, and differs significantly from the ratio of their formal geometrical surfaces, $s_{\mathrm{BA}}/s_{\mathrm{BX}} = 1.17$. Thus, for zeolites, the limiting adsorption values correspond to volume filling of their micropores.

Mean molar volumes of the ultimately adsorbed vapors v^* are quotients of the calculated volumes of the large cavities of zeolites v_{B} by the limiting adsorption values a_0. In Table 1, the obtained values of v^* are compared with the molar volumes of normal liquids v at the corresponding temperatures. v for Ar at 77.3°K corresponds to a supercooled liquid.

Table 1

			CaA	CaA	CaA	NaX	NaX	NaX	
Substance	T, °K	v, cm^3/mol	a_0, mmol/g	v^*, cm^3/mol	v^*/v	a_0, mmol/g	v^*, cm^3/mol	v^*/v	$a_0^{\mathrm{CaA}}/a_0^{\mathrm{NaX}}$
H_2O	293.2	18.0	15.50	17.9	0.99	17.95	17.9	0.99	0.863
N_2	77.3	34.7	8.27	33.6	0.97	9.55	33.7	0.97	0.866
CO	77.3	34.5	8.61	32.3	0.94	9.71	32.2	0.93	0.886
n-C_5H_{12}	293.2	115.0	2.26	123.0	1.07	2.56	126.0	1.09	0.883
O_2	77.3	26.2	9.02	30.8	1.17	10.86	29.7	1.13	0.831
Ar	77.3	27.3	8.58	32.4	1.19	10.27	31.4	1.15	0.835

According to the data of Table 1, the molar volumes of the ultimately adsorbed substances v^* are identical, to within 3%, for the zeolites CaA and NaX. The molar volumes of adsorbed water, nitrogen, and carbon monoxide differ little from the corresponding values for bulk liquid phases. The largest deviations of the mean molar volumes of the ultimately adsorbed substances are observed for oxygen and argon.

Since for nitrogen and carbon monoxide (small deviations), oxygen, and argon (substantial deviations) the average numbers of ultimately adsorbed molecules, calculated per one large cavity of the zeolite, differ little (13.6–14.9 for CaA and 16.0–17.8 for NaX), the noted deviations are due to differences in the packing of the adsorbed molecules in the micropores of the zeolites.

Table 2

Fig. 1. Nitrogen adsorption isotherms at 77.3°K on NaX zeolite containing preadsorbed water, in mmol/g: 1 –0; 2 –1.43; 3 –3.2; 4 –4.41; 5 –5.81; 6 –6.98

Figure 1: Fig. 1. Nitrogen adsorption isotherms at 77.3°K on NaX zeolite containing preadsorbed water, in mmol/g: 1 –0; 2 –1.43; 3 –3.2; 4 –4.41; 5 –5.81; 6 –6.98

Adsorbent	Substance	T, °K	a_0, mmol/g	W_0, cm^3/g	W^{Ar}, cm^3/g at $v_0 =$ 27.3 cm^3/mol
CaA	N_2	77.3	8.27	0.29	–
CaA	Ar	77.3	8.58	0.27	0.23
NaX	N_2	77.3	9.55	0.32	–
NaX	Ar	77.3	10.27	0.33	0.28
AY-1	N_2	77.3	16.37	0.57	–
AY-1	Ar	77.3	16.79	0.54	0.46
AY-2	N_2	77.3	9.54	0.33	–
AY-2	C_6H_6	293.2	3.72	0.33	–
AY-2	Ar	77.3	10.59	0.34	0.29
CM	N_2	77.3	17.7	0.61	–
CM	H_2O	293.2	33.7	0.61	–
CM	C_6H_6	293.2	6.91	0.61	–
CM	C_6H_{12}	293.2	5.60	0.61	–
CM	Ar	77.3	21.6	0.69	0.59

The anomalous values of the molar volumes of ultimately adsorbed oxygen and argon on CaA and NaX zeolites may be characteristic only of the zeolites studied, or they may have general significance for microporous adsorbents of another nature. To clarify this fundamentally important question, adsorption isotherms of argon and some other substances were studied on the active carbons AY-1 and AY-2 with different microporous structures and, for comparison, sorption isotherms for silica gel CM. Since, for silica gel, the principal process of pore-volume filling is capillary condensation of vapors, the limiting sorption values a_s were determined at relative pressures equal to unity. From the limiting adsorption values a_0 (sorption a_s for silica gel), the following were calculated

limiting adsorption volumes W_0 (sorption volumes v_s), with the molar volumes of normal liquids v being used for all substances, and, for argon, the mean value $v^* = 31.9 \pm 0.5$ cm^3/mol for the zeolites studied. The experimental results are given in Table 2, whose last column contains the values W_0 and v_s for argon, calculated using the molar volume $v = 27.3$ cm^3/mol for a normal liquid supercooled to 77.3°K.

Fig. 1. Nitrogen adsorption isotherms at 77.3°K on NaX zeolite containing

Fig. 2. Dependence of the limiting adsorption values a2 at 77.3°K on the amounts of preadsorbed water a1 on NaX zeolite for: argon (1) and nitrogen (2)

Figure 2: Fig. 2. Dependence of the limiting adsorption values a2 at 77.3°K on the amounts of preadsorbed water a1 on NaX zeolite for: argon (1) and nitrogen (2)

preadsorbed water, in mmol/g:
1 –0; 2 –1.43; 3 –3.2; 4 –4.41; 5 –5.81; 6 –6.98

Fig. 2. Dependence of the limiting adsorption values a_2 at 77.3°K on the amounts of preadsorbed water a_1 on NaX zeolite for: argon (1) and nitrogen (2)

From the data of Table 2 it follows that, for all the microporous adsorbents studied, the molar volumes of limitingly adsorbed argon are practically identical and differ substantially from the molar volume of a normal supercooled liquid. In capillary condensation of vapors in silica gel SM, in all cases, including argon, the molar volumes of the limitingly adsorbed substances practically do not differ from the molar volumes of the corresponding bulk liquids.

For the theory of adsorption of vapors by microporous adsorbents, investigation of the molar volumes of substances in the adsorbed state at various degrees of filling of the volume of the adsorption space is of considerable importance. One possible way of solving this problem consists in changing the micropore volume of a zeolite by preadsorption, at a significantly higher temperature, of different amounts of a strongly adsorbed vapor, followed by study of the isotherms of low-temperature vapor adsorption on the modified adsorbents thus obtained. NaX zeolite was chosen as the adsorbent; water was chosen as the preadsorbed vapor; and nitrogen and argon were chosen as the substances for adsorption studies at 77.3°K on the modified zeolite. The experimental procedure is described in ([7],[8]).

As an example, Fig. 1 shows nitrogen adsorption isotherms at 77.3°K, in the coordinates of the linear form of the adsorption equation of the theory of volume filling of microporous adsorbents ([4]), for NaX zeolite containing different amounts of preadsorbed water. Similar results were obtained in experiments with argon. From the intercepts cut off by the straight lines on the ordinate axis, the limiting adsorption values of nitrogen (argon) a_2 were calculated for NaX zeolite samples containing amounts of preadsorbed water a_1. Figure 2 shows the dependence of a_2 on a_1, which, to a sufficiently satisfactory approximation, is linear in the range of water fillings of the zeolite adsorption space from 0 to 0.4:

$$a_2 = A - \alpha a_1, \tag{1}$$

where for nitrogen $\alpha = 0.553$ and for argon $\alpha = 0.598$, while the quantities A are equal to the values a_0 for the vapors under consideration, given in Table 1.

Equation (1) follows directly from the concept of the volumetric filling of the adsorption space $v_{\text{B.X}}$ of NaX zeolite by the preadsorbed and adsorbed substances, with constancy of their molar volumes v_1^* and v_2^* in the adsorbed state:

$$v_{\text{B.X}} = a_1 v_1^* + a_2 v_2^* \tag{2}$$

From equations (1) and (2) it follows that:

$$v_1^* = \alpha v_2^*. \tag{3}$$

Using the values of v_2^* for nitrogen and argon given in Table 2, we calculated from (3) the molar volumes of preadsorbed water v_1^* from experiments with nitrogen (18.6 cm^3/mol) and experiments with argon (18.8 cm^3/mol). Their practical constancy indicates the constancy of the molar volumes v_2^* of adsorbed nitrogen and argon within the range of variation of the adsorption-space volume of NaX zeolite from 0.322 to 0.193 cm^3/g, corresponding to fillings in adsorption experiments over a wide interval of equilibrium relative pressures. The results obtained, taking into account the data of work ([9]), are in agreement with the basic principles of the theory of volumetric filling of microporous adsorbents. In addition, it should be noted that microporous adsorbents form a special variety of porous adsorbents with a different character of filling of the adsorption space and with specific features of adsorption interactions as compared with porous adsorbents having an open surface.

The authors express their gratitude to S. P. Zhdanov for providing zeolite samples, and to K. O. Murdmaa and E. F. Polstyanov for studies of the adsorption isotherms of water and n-pentane on zeolites.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Received
29 I 1964

CITED LITERATURE

1. M. M. Dubinin, S. P. Zhdanov et al., *Izv. AN SSSR, ser. khim.* (in press).
2. M. M. Dubinin, S. P. Zhdanov et al., *Izv. AN SSSR, ser. khim.* (in press).
3. M. M. Dubinin, *Izv. AN SSSR, ser. khim.*, 1964, No. 2.
4. K. M. Nikolaev, M. M. Dubinin, *Izv. AN SSSR, OKhN*, 1958, 1165.

5. B. P. Bering, M. M. Dubinin et al., *ZhFKh*, 31, 712 (1957).
6. M. M. Dubinin, E. G. Zhukovskaya et al., *Izv. AN SSSR, OKhN*, 1962, 2113.
7. B. P. Bering, M. M. Dubinin et al., *DAN*, 130, 793 (1960).
8. E. G. Zhukovskaya, Dissertation, Moscow, 1963.
9. B. P. Bering, V. V. Serpinskii, *DAN*, 148, 1331 (1963).

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

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