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Abstract

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On the Structure and Adsorption Properties of Zeolite Zh

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In our previously published work ([1]), devoted to the properties of synthetic sodium zeolites, some preliminary data were given on the structure and adsorption properties of a new sodium zeolite, originally called product Zh. From the Debyegram obtained for one of the samples, the interplanar spacings, the indices of the corresponding planes, and the lattice constant of the cubic lattice of this zeolite were calculated in ([1])*. X-ray studies of other samples of zeolite Zh, obtained under different conditions, showed that the sample studied in ([1]) apparently contained small amounts of some crystalline impurities, which gave three very weak lines on the Debyegram; these were attributed in ([1]) to zeolite Zh, but did not appear on the Debyegrams of other samples. Excluding these three lines from the calculations substantially changes the plane indices and the constant of the cubic lattice of zeolite Zh given in ([1]).

The refined X-ray structural data obtained from the Debyegram of a zeolite Zh sample that did not contain the above-mentioned lines are given in Table 1.

Table 1

hkl	*d*, Å	Line-intensity characteristic	*hkl*	*d*, Å	Line-intensity characteristic
110	6.28	Strong	240	1.98	Weak
–	5.12	Very weak	233	1.89	Medium
200	4.44	Weak	224	1.81	Medium
–	3.97	Very weak	134	1.74	Strong
112	3.63	Very strong	125	1.62	Weak
220	3.14	Medium	440	1.57	Very strong
130	2.81	Very strong	334	1.52	Strong

Fig. 1. Junctions of cubooctahedral units in the structure of zeolite Zh

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hkl	*d*, Å	Line-intensity characteristic	*hkl*	*d*, Å	Line-intensity characteristic
222	2.56	Very strong	244	1.48	Medium
123	2.37	Medium	235	1.44	Medium
400	2.22	Very weak	620	1.40	Very weak
411	2.09	Strong	541	1.37	Medium

The constant a_0 of the cubic lattice of zeolite Zh, obtained from the data in Table 1, proved to be 8.88 ± 0.04 Å. This value corresponds to the values of a_0 for sodalite and basic sodalite ([2], [3]). Comparison of the interplanar spacings and intensities of the corresponding lines of zeolite Zh and natural sodalite from the Lovozero massif ([4]) also indicates the similarity of the structure of zeolite Zh to the structure of sodalite.

However, despite the far-reaching structural similarity to sodalite or basic sodalite, zeolite Zh differs very substantially from them in chemical composition and adsorption properties. The composition of the unit cell of sodalite, as is known, corresponds to the formula $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$, while the composition of basic sodalite (hydrosodalite) is $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaOH \cdot nH_2O$ ([2], [5]). In natural hydrosodalite, hydroxyls are present along with

* High-quality Debyegrams were taken by Yu. G. Sokolov using a tube with a cobalt cathode. The authors are grateful to him for this and for consultations during the calculations.

with Cl^- ions (4). Barrer and Falconer (6) express the composition of basic sodalite by the formula: $Na_2O \cdot Al_2O_3 \cdot 2.05SiO_2 \cdot 0.34NaOH \cdot 1.51H_2O$. In contrast to sodalite and basic sodalite, the lattice of zeolite Zh contains no excess Na^+ ions whose charge is compensated by Cl^- or OH^- ions; according to chemical analyses of several samples, its composition corresponds to the formula $Na_2O \cdot Al_2O_3 \cdot 2.1SiO_2 \cdot pH_2O$.

As shown by our studies of water adsorption on nosean, sodalite, and basic sodalite, nosean and sodalite practically do not adsorb water, while basic sodalite absorbs only very small amounts of it after heating in vacuum. In contrast, zeolite Zh, having

Fig. 1. Junctions of cubooctahedral units in the structure of zeolite Zh

a structure similar to that of sodalite, can adsorb up to 18% water by weight of the previously dehydrated sample. The sodalite lattice, as is known (5), is built of the same cubooctahedral units as the lattices of zeolites of types A and X, with the only difference that in the sodalite lattice the neighboring cubooctahedra have in common four-membered rings of silicoalumino-oxygen tetrahedra, whereas in zeolite A only the vertices of these tetrahedra, or four-membered oxygen rings, are common, and in zeolite X the neighboring cubooctahedra are linked by common six-membered oxygen rings. Consequently, in zeolite Zh, which has a structure similar to sodalite, the cubooctahedra must be packed considerably more densely than in zeolite A and especially X. With sodalite packing of cubooctahedra, no large cavities or channels are formed between them. The cavity located at the center of the cube formed by eight cubooctahedra in their sodalite packing in the lattice of zeolite Zh corresponds exactly in its geometry to the cavity inside each cubooctahedron (Fig. 1). Therefore, in the unit cell of zeolite Zh there are altogether $1 + 8 \cdot \frac{1}{8} = 2$ cubooctahedral cavities, equivalent to the small cavities of zeolites A and X. The entrances to these cavities are the six-membered oxygen rings of the cubooctahedra, whose free diameters are about 2.2 Å (7). There should be no other pathways for the penetration of molecules into crystals of zeolite Zh.

Zeolite Zh can, evidently, adsorb only molecules of the smallest dimensions. Indeed, as was shown earlier (1), zeolite Zh adsorbs only water well, whereas the adsorption of other substances (N_2, Ar, C_4H_9OH) on it is extremely small.

The question of the accessibility of small cavities in crystals of synthetic zeolites of types A and X for the adsorption of water molecules has not yet received a definite answer. Studies of adsorption on zeolite Zh show that the cavities inside the cubooctahedra of sodalite cages ([5]) are at least accessible for the adsorption of water molecules, and to a considerable extent also for ethanol molecules.

Since the limiting adsorption volume for water molecules during adsorption on zeolite Zh is restricted by the volume of the cubooctahedral cavities, it is of interest to compare the experimentally measured values of water adsorption on zeolite Zh with the total volume of these cavities in the crystal lattice of the zeolite. Figure 2 gives the isotherms of adsorption of water on various samples of zeolite Zh obtained under different conditions. As is seen from these isotherms, at $P/P_s = 0.5$, when capillary condensation in the voids between zeolite crystallites should still be excluded, water adsorption amounts, for different samples, to 0.133–0.175 g/g. The hysteresis of the isotherm for sample Zh_{442} and the clearly nonequilibrium character of the adsorption points for this sample, as well as for sample Zh_{554}, indicate that the equilibrium adsorption values for these samples must exceed the measured ones. The adsorption isotherm obtained on sample Zh_{352} is reversible over the entire range of P/P_s, from the smallest values up to 0.8. The first point of the isotherm for this sample was obtained after holding for 2 days. Therefore there is every reason to believe that the isotherm obtained for sample Zh_{352} describes equilibrium adsorption and that this isotherm may be used for calculations. One gram of zeolite Zh_{352} at $P/P_s = 0.5$ absorbs

Figure 2

Figure 2: Figure 2

0.175 g H_2O. In order to determine what part of the volume of the cubooctahedral cavities in the lattice of zeolite Zh is filled with water under these conditions, or how many water molecules penetrate into each such cavity at $P/P_s = 0.5$, it is necessary to adopt some value for the volume of the cubooctahedral cavity and to proceed from the structural analogy between sodalite and zeolite Zh. In doing so, however, it is necessary to take into account the substantial differences in the chemical composition of zeolite Zh and sodalite. The mass of the unit cell of zeolite Zh can be calculated from the composition of the unit cell of sodalite, corresponding to the formula $3Na_2O \cdot 3Al_2O_3 \cdot 6SiO_2 \cdot 2NaCl$, with exclusion of the 2 molecules of NaCl located inside the cubooctahedra in the sodalite structure and absent in the structure of zeolite Zh. The unit cell of zeolite Zh thus has the composition $6Na + 6Al + 6Si + 24O$. Its mass in oxygen units will be

$$M_{\text{cell}} = (23 \cdot 6) + (27 \cdot 6) + (28.06 \cdot 6) + (16 \cdot 24) = 852,$$

and in grams

$$M_{\text{cell}} = 852 \cdot 1.665 \cdot 10^{-24} = 1.41 \cdot 10^{-21} \text{ g}.$$

One gram of anhydrous zeolite contains

$$1 : 1.41 \cdot 10^{-21} = 0.706 \cdot 10^{21}$$

unit cells. Since each unit cell of zeolite Zh contains 2 cubooctahedral cavities, the number of such cavities per gram of zeolite will be

$$0.706 \cdot 10^{21} \cdot 2 = 1.412 \cdot 10^{21}.$$

Taking, according to ([8])

Fig. 2. Adsorption—desorption isotherms of water on zeolite Zh samples differing in preparation conditions: 1 —sample 352; 2 —sample 554; 3 —sample 442; black points—desorption.

the volume of a cubooctahedral cavity equal to 150 Å^3, we obtain for the total volume of such cavities in one gram of crystals of anhydrous zeolite Zh the value: $1.412 \cdot 10^{21} \cdot 150 = 0.212 \cdot 10^{24}$ Å^3, or 0.212 cm^3/g. Consequently, upon adsorption on zeolite Zh, water at $P/P_s = 0.5$ fills about 4/5 of the total volume of the cubooctahedral cavities in its framework, if the volume of adsorbed water is calculated from the density of liquid water under normal conditions. Since

1 g of zeolite Zh adsorbs 0.175 g of H_2O, or 9.7 mmole, on average about 4.1 molecules of H_2O are adsorbed in each cubooctahedral cavity.

The experimentally determined maximum value of water adsorption at $P/P_s = 0.5$ on zeolite Zh agrees well with the total volume of the cubooctahedral cavities in the sodalite framework of zeolite Zh, remaining somewhat smaller than this volume.

If, as studies of adsorption on zeolite Zh show, the cubooctahedral cavities with entrances into them about 2.2 Å in diameter prove accessible for adsorption of H_2O molecules (and, apparently, also for some other molecules, partially even for C_2H_5OH), then the observed differences in water adsorption on different samples of type-A zeolites ([9]) may be explained by the different accessibility of these cavities for adsorption in samples obtained under different conditions. The latter may be connected with different positions of the cations inside the cubooctahedral cavities. It is possible that the difference in the adsorption properties of different samples of zeolite Zh is also connected with this.

Thus, zeolite Zh, which has a framework of the sodalite type, differs from the latter in that the cubooctahedra of its framework do not contain additional Na^+ and Cl^- ions (or Na^+ and OH^-, as in ordinary sodalite), and precisely because of this circumstance zeolite Zh, unlike sodalite (nosean), is capable of adsorbing significant amounts of small molecules. The slow establishment of adsorption equilibrium during adsorption on zeolite Zh is connected with the difficulties of diffusion of molecules through the six-membered oxygen windows leading into the cubooctahedral cavities of the sodalite framework of this zeolite.

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CITED LITERATURE

[1] S. P. Zhdanov, N. N. Buntar' , DAN, **147**, No. 5, 1118 (1962).
[2] A. G. Betekhtin, *Course of Mineralogy*, Moscow, 1956.
[3] R. M. Barrer, J. W. Baynham et al., J. Chem. Soc., No. 1, 195 (1959).
[4] V. I. Gerasimovskii, A. I. Polyakov, L. P. Voronina, DAN, **131**, No. 2, 402 (1960).
[5] N. V. Belov, *Crystal Chemistry of Silicates with Large Cations*, Publishing House of the Academy of Sciences of the USSR, 1961.
[6] R. M. Barrer, J. D. Falconer, Proc. Roy. Soc., A **236**, 227 (1956).
[7] D. W. Breck, W. G. Eversole et al., J. Am. Chem. Soc., **78**, 5963 (1956).
[8] M. M. Dubinin, DAN, **138**, No. 4, 866 (1961).
[9] S. P. Zhdanov, N. N. Buntar' , in: *Synthetic Zeolites*, Publishing House of the Academy of Sciences of the USSR, 1962, p. 105.

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