Physical Chemistry

S. P. Zhdanov, N. N. Buntar' -Samulevich, M. E. Ovsepyan

1965

SovietRxiv

Fig. 1. Model of the structure of chabazite, constructed from double six-membered rings of Si, Al—O tetrahedra

Figure 1: Fig. 1. Model of the structure of chabazite, constructed from double six-membered rings of Si, Al—O tetrahedra

Abstract

Full Text

Physical Chemistry

S. P. Zhdanov, N. N. Buntar' -Samulevich, M. E. Ovsepyan

Synthetic Chabazites and Their Adsorption Properties

(Presented by Academician M. M. Dubinin on 27 VIII 1964)

After the discovery of the molecular-sieve effect in adsorption on natural chabazite (⁀1), adsorption on this zeolite was the subject of a number of special studies ($^{2-}$6). However, the molecular-sieve features of chabazite could not for a long time be reconciled with the existing conceptions of its structure, and only structural studies carried out in recent years ($^{7-}$9) made it possible to bring the molecular-sieve properties of this zeolite into agreement with the structure of its crystal lattice. The Si, Al—O framework of chabazite is formed by mutually connected double six-membered rings of alumino- and silicoxygen tetrahedra. Figure 1 shows an idealized model of the rhombohedral cell of chabazite ($a = 9.37$ Å, $\alpha = 92°01'$ (^{8})). The double six-membered rings lie at the corners of the unit cell. Such an arrangement of the six-membered blocks leads to the formation in the unit cell of one ellipsoidal cavity, connected with adjacent cavities by four-membered, six-membered, and eight-membered windows.

Fig. 1. Model of the structure of chabazite, constructed from double six-membered rings of Si, Al—O tetrahedra

In the real structure of chabazite, the double six-membered rings of tetrahedra are deformed to different degrees depending on the degree of hydration of the chabazite (⁀8, ⁀9), which also leads to deformation of the large eight-membered windows. In dehydrated Ca-chabazite the eight-membered windows prove to be approximately rectangular, with dimensions of 3.1 and 4.4 Å; in hydrated chabazite they have a round shape (⁀8), as in the model in Fig. 1. The unit cell of chabazite includes one large (ellipsoidal) cavity and one small one, formed at the center of the double six-membered rings. The accessibility of the large cavity for adsorption of molecules of different sizes is limited by the dimensions of the eight-membered windows. The diameter of the six-membered windows leading into the small cavities must be about 2.3 Å (^6). The composition of the unit cell of chabazite, without taking exchange cations into account, corresponds to the composition of the double six-membered ring of tetrahedra $(\mathrm{Al}+\mathrm{Si})_{12}\mathrm{O}_{24}$. The content of exchange cations in the unit cell depends on the ratio $\mathrm{Si}:\mathrm{Al}=x$. In natural chabazites, according to data from various authors (^9, ^10, ^11, ^6, ^12), the values of x vary from 1.0 to 3.0.

Synthetic chabazites were first obtained and studied by R. M. Barrer (13, 6). However, the data published in (13, 6) concern only potassium zeolites and their ion-exchange derivatives. Data on sodium synthetic chabazites are still more scanty. In the literature (14), the chemical composition is given for only one sample of synthetic sodium chabazite.

We have investigated the crystallization conditions of various zeolites from sodium, potassium, and sodium-potassium silica-alumogels over the entire range of compositions in which gels can form, and it has been established that these zeolites, under the appropriate conditions, can readily be obtained even at temperatures not exceeding 100° (15–17).

Table 1

Natural chabazite according to (18), d, Å	Natural chabazite according to (18), I	Synthetic chabazites: sodium Na-192, d, Å	Synthetic chabazites: sodium Na-192, I	Synthetic chabazites: potassium K-57, d, Å	Synthetic chabazites: potassium K-57, I	Synthetic chabazites: sodium-potassium Na, K-104*, d, Å	Synthetic chabazites: sodium-potassium Na, K-104*, I	Natural chabazite according to (18), d, Å	Natural chabazite according to (18), I	Synthetic chabazites: sodium Na-192, d, Å	Synthetic chabazites: sodium Na-192, I	Synthetic chabazites: potassium K-57, d, Å	Synthetic chabazites: potassium K-57, I	Synthetic chabazites: sodium–potassium Na, K-104*, d, Å	Synthetic chabazites: sodium–potassium Na, K-104*, I
9.3	10	9.26	med.	9.34	weak	9.34	strong	2.52	5	–	–	2.54	weak	–	–
6.9	4	6.85	v. strong	6.90	med.	6.85	med.	2.31	4	2.29	v. weak	2.29	med.	2.29	med.
5.6	6	5.40	v. weak	5.50	v. weak	5.57	weak	2.09	4	2.08	med.	2.09	weak	2.08	med.
5.0	6	5.00	v. strong	5.14	med.	5.07	strong	1.93	2	1.90	v. weak	1.90	weak	1.92	v. weak
4.8	4	–	–	–	–	–	–	1.88	4	–	–	–	–	1.86	v. weak
4.35	8	4.26	strong	4.29	med.	4.29	strong	1.81	8	1.80	med.	1.82	med.	1.80	med.
3.90	6	3.93	v. weak	3.96	v. weak	3.96	v. weak	1.74	5	1.71	med.	1.72	med.	1.72	med.
3.62	6	3.58	v. weak	3.56	v. weak	3.57	v. weak	1.65	4	1.67	v. weak	1.64	v. weak	1.66	v. weak

Natural chabazite according to ([18]), d, Å	Natural chabazite according to ([18]), I	Synthetic chabazites: sodium Na-192, d, Å	Synthetic chabazites: sodium Na-192, I	Synthetic chabazites: potassium K-57, d, Å	Synthetic chabazites: potassium K-57, I	Synthetic chabazites: sodium-potassium Na,K-104*, d, Å	Synthetic chabazites: sodium-potassium Na,K-104*, I	Natural chabazite according to ([18]), d, Å	Natural chabazite according to ([18]), I	Synthetic chabazites: sodium Na-192, d, Å	Synthetic chabazites: sodium Na-192, I	Synthetic chabazites: potassium K-57, d, Å	Synthetic chabazites: potassium K-57, I	Synthetic chabazites: sodium-potassium Na,K-104*, d, Å	Synthetic chabazites: sodium-potassium Na,K-104*, I
3.42	4	3.42	strong	3.42	v. weak	3.42	strong	1.57	4	–	–	1.58	v. weak	1.55	v. weak
3.24	6	3.16	weak	3.25	strong	3.22	v. weak	1.53	4	1.52	v. weak	1.54	v. weak	1.52	v. weak
2.93	10	2.91	v. strong	2.93	v. strong	2.92	v. strong	1.42	4	1.40	weak	1.43	weak	1.40	weak
2.62	4	2.59	med.	2.62	weak	2.59	strong	1.34	4	1.32	weak	1.32	weak	1.32	weak

* This zeolite was obtained in our laboratory by B. G. Novikov.

Table 1 compares the interplanar spacings and intensities of the principal lines of natural chabazite and of synthetic Na- and K-chabazites. From the data in Table 1 it is evident that the Na-, K-, and K,Na-chabazites obtained by direct synthesis from alkaline silica-alumogels are, in their structure, close both to one another and to natural chabazite.

Table 2 gives data from chemical analyses of sodium, potassium, and sodium-potassium synthetic chabazites.*

Asterisks in the table mark the cationic forms of the corresponding chabazites obtained by ion exchange.

The crystal lattice of natural chabazite is destroyed at 640° ([20]). The thermal stability of different samples of synthetic chabazites varies substantially. Alongside samples whose structure begins to break down already at temperatures of 200–250°, there are samples with a lattice just as stable as that of natural chabazites. The thermostability of the chabazite lattice increases with an increase in the Si : Al ratio in it ([18]).

Adsorption of N_2 and Ar at −196° and of H_2O at 18° was investigated on various synthesized chabazites. As is evident from the adsorption isotherms shown in Figs. 2 and 3, the various samples differ very strongly in their adsorption properties. Potassium chabazites obtained by direct synthesis adsorb almost no N_2 or Ar. Complete replacement of Na^+ in sodium chabazites by K^+ by ion exchange considerably decreases

* The analyses were kindly carried out in the laboratory of E. N. Egorova, to

whom the authors are very grateful.

capacity for adsorption of N_2 and Ar. Replacement of K^+ by Na^+ and Ca^{2+} in potassium chabazites leads to a certain increase in the adsorption of N_2 and Ar, as well as of water. Sodium chabazites obtained by direct synthesis adsorb both nitrogen and argon in considerably larger amounts. Some samples approach natural chabazite in the magnitude of adsorption of these gases. As in the case of natural chabazite (^{6}), replacement of $2Na^+$ by Ca^{++} leads to a significant increase in the adsorption of N_2 and Ar.

Adsorption of water on potassium synthetic chabazites is also usually lower than on sodium ones (Fig. 3), and complete replacement of sodium by potassium in sodium chabazites leads to a considerable decrease in the magnitude of water adsorption (isotherms 1 and 8 in Fig. 3). However, strictly speaking, comparison of adsorption values per 1 g of zeolites differing in chemical composition does not accurately reflect the adsorption capacity of different zeolites, since the adsorption values refer to unequal numbers of elementary

Table 2

Samples	Composition of zeolites in moles of oxides	Samples	Composition of zeolites in moles of oxides
Na-209	$0.83\ Na_2O \cdot Al_2O_3 \cdot 4.08\ SiO_2 \cdot 6.1\ H_2O$	K, Na-104	$0.70\ K_2O \cdot 0.30\ Na_2O \cdot Al_2O_3 \cdot 5.20\ SiO_2 \cdot 6.7\ H_2O$
Na-192 II	$0.87\ Na_2O \cdot Al_2O_3 \cdot 4.13\ SiO_2 \cdot 6.0\ H_2O$	K-13	$0.91\ K_2O \cdot Al_2O_3 \cdot 2.07\ SiO_2 \cdot 3.6H_2O$
Na-210	$0.89\ Na_2O \cdot Al_2O_3 \cdot 4.32\ SiO_2 \cdot 6.2\ H_2O$	K-245	$0.95\ K_2O \cdot Al_2O_3 \cdot 3.54\ SiO_2 \cdot 4.0H_2O$
Na-716	$0.86\ Na_2O \cdot Al_2O_3 \cdot 5.80\ SiO_2 \cdot 7.6\ H_2O$	K-57	$1.00\ K_2O \cdot Al_2O_3 \cdot 4.20\ SiO_2 \cdot 4.6H_2O$
Na*-57	$1.00\ Na_2O \cdot Al_2O_3 \cdot 4.20\ SiO_2 \cdot 4.6\ H_2O$	K*-192 II	$0.87\ K_2O \cdot Al_2O_3 \cdot 4.13\ SiO_2 \cdot 4.0H_2O$

unit cells and, consequently, to unequal numbers of cavities in which adsorption takes place. Table 3 gives the water contents in one unit cell of different chabazites, calculated from the composition of the crystals (Table 2) and the adsorption values at $P/P_s = 0.5$.

As can be seen from the data in Table 3, independent calculations of the number of mole-

Fig. 2 and Fig. 3 adsorption isotherms

Figure 2: Fig. 2 and Fig. 3 adsorption isotherms

Fig. 2. Isotherms of adsorption of nitrogen (a) and argon (b) on natural chabazite 1 (^{5}) (N_2 at −183.0° and Ar at −192°) and on synthetic samples (at −196°; 2 —Ca-192 III; 3 —Na-716; 4 —Ca*, Na, K —104 (0.79 CaO • 0.045* Na_2O *•* *0.165* K_2O*); 5 —Na, K 104; 6 —Na*, K-104 (0.78 Na_2O • 0.22 K_2O); 7 —Na-192 III; 8 —Na-192 II; 9 —Na-*57; 10 —Ca*-57 (0.60CaO • 0.40K_2O); 11 —K*-192 II; 12 —K-57; 13 —Na-192.

Fig. 3. Isotherms of adsorption of water at 18° on various synthetic chabazites: 1 —Na-192 II; 2 —Na-209; 3 —Na-210; 4 —Na, K-104; 5 —Na-*57; 6 —K-57; 7 —K-13; 8 —K*-192 II.

H_2O molecules contained in and adsorbed in the large and small cavities of the chabazite unit cell, for the same samples, turn out to be close. At the same time, for sodium zeolites these values are always greater than for potassium zeolites. The strong differences observed in the adsorption properties toward nitrogen and argon of sodium and potassium synthetic chabazites, of their different cationic forms, and also of different samples of purely sodium chabazites, despite the closeness of their X-ray structures, are difficult to explain solely in terms of differences in the sizes of the exchange cations and their content in the chabazite unit cell. Apparently, in order to explain these differences one must allow for the possibility of unequal deformation of the 8-membered windows leading into the large cavities in different cation-exchange forms and in different samples of chabazites obtained by direct synthesis. Since the dimensions of these windows in dehydrated chabazite

Table 3

Samples	Average atomic composition of the unit cell	Number of unit cells in 1 g of zeolite $\times10^{-20}$	Adsorption H_2O, g/g at $P/P_s = 0.5$	Number of H_2O molecules per unit cell: from chemical composition	Number of H_2O molecules per unit cell: from adsorption values
Na-209	$H_{0\ 67}Na_{3\ 28}Al_{3\ 95}Si_{8\cdot 05}O_{24}$	7.58	0.277	12.0	12.2
Na-192 II	$H_{0\ 50}Na_{3\ 40}Al_{3\ 90}Si_{8\cdot 10}O_{24}$	7.55	0.280	11.8	12.4
Na-210	$H_{0\ 42}Na_{3\ 38}Al_{3\ 80}Si_{8\cdot 20}O_{24}$	7.56	0.281	11.8	12.4
Na-716	$H_{0\ 43}Na_{2\ 65}Al_{3\ 08}Si_{8\cdot 92}O_{24}$	7.71	–	11.8	–
K, Na-104	$K_{2\ 34}Na_{1\ 01}Al_{3\ 35}Si_{8\cdot 65}O_{24}$	7.25	0.270	11.7	12.2

Samples	Average atomic composition of the unit cell	Number of unit cells in 1 g of zeolite $\times 10^{-20}$	Adsorption H_2O, g/g at $P/P_s = 0.5$	Number of H_2O molecules per unit cell: from chemical composition	Number of H_2O molecules per unit cell: from adsorption values
K-13	$H_{0\ 53}Na_{3\ 37}Al_{5\ 00}Si_{6\ 10}O_{24}$	6.50	0.185	10.9	9.4
K-245	$H_{0\ 21}Na_{4\ 12}Al_{4\ 33}Si_{7\ 67}O_{24}$	6.85	0.205	9.3	10.0
K-57	$K_{3\ 85}Al_{3\ 85}Si_{8\ 15}O_{24}$	6.95	0.220	9.0	10.5
K *-192 II	$H_{0\ 50}K_{3\ 40}Al_{3\ 90}Si_{8\ 10}O_{24}$	7.10	0.155	6.8	7.4
Na *-57	$Na_{3\ 85}Al_{3\ 85}Si_{8\ 15}O_{24}$	7.46	0.257	10.4	11.4

are 3.1 and 1.4 Å (along two directions of the sides of the pseudorectangular window (8)), then for N_2 and Ar molecules with dimensions close to the dimensions of these windows (3.0—4.0 and 3.8 Å, respectively), the slightest deformation of the 8-membered windows can easily make the large cavities in the chabazite structure inaccessible to adsorption of these gases in some cases and accessible in others. Adsorption of the smaller water molecules proves less sensitive to such deformations.

The investigations carried out in our laboratory indicate that synthetic chabazites are not only interesting objects for the study of selective adsorption, but will undoubtedly find practical application as molecular sieves and highly effective adsorbents.

Institute of Chemistry of Silicates named after I. V. Grebenshchikov
Academy of Sciences of the USSR

Received
20 VII 1964

CITED LITERATURE

1. O. Weigel, E. Steinhof, *Zs. kristallogr.*, **61**, 125 (1925).
2. O. Schmidt, *Zs. phys. Chem.*, **133**, 263 (1928).
3. T. Baba, *Bull. Chem. Soc. Japan*, **5**, 190 (1930).
4. E. Rabinowitch, W. C. Wood, *Trans. Farad. Soc.*, **32**, 947 (1963); A. B. Lamb, J. C. Woodhouse, *J. Am. Chem. Soc.*, **58**, 2637 (1936).

5. R. M. Barrer, D. W. Riley, *J. Chem. Soc.*, 1948, 133.
6. R. M. Barrer, J. W. Baynham, *J. Chem. Soc.*, 1956, 2892.
7. L. S. Dent, J. V. Smith, *Nature*, **181**, 1794 (1958).
8. J. V. Smith, *Acta crystallogr.*, **15**, 835 (1962).
9. J. V. Smith, F. Rinaldi, *Acta crystallogr.*, **16**, 45 (1963).
10. A. N. Vinchell, G. Vinchell, *Optical Mineralogy*, IL, 1953.
11. A. G. Betekhtin, *Mineralogy*, Moscow, 1950.
12. V. I. Vernadskii, *Mineralogy*, vol. II, Moscow, 1912.
13. R. M. Barrer, J. W. Baynham, *J. Chem. Soc.*, 1956, 2882.
14. R. M. Barrer, J. W. Baynham et al., *J. Chem. Soc.*, 1959, 195.
15. S. P. Zhdanov, N. N. Buntar, *DAN*, **147**, 1118 (1962).
16. S. P. Zhdanov, N. N. Buntar, in: *Synthetic Zeolites*, Publ. House of the USSR Academy of Sciences, 1962, p. 105.
17. S. P. Zhdanov, M. E. Ovsepyan, *DAN*, **157**, 913 (1964).
18. V. I. Mikheev, *X-ray Determinative Manual of Minerals*, Moscow, 1957.
19. S. Brunauer, *Adsorption of Gases and Vapors*, IL, 1948.

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

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