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SOME SYNTHETIC POTASSIUM ZEOLITES AND THEIR PROPERTIES

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The conditions for the direct synthesis of potassium zeolites and the properties of crystals of synthetic potassium zeolites have as yet been little studied. Some information on the hydrothermal synthesis of potassium zeolites and their adsorption properties is reported in works ([1],[2]). According to ([1]), under conditions of hydrothermal synthesis from alkaline potassium silica-alumina gels, three potassium zeolites were obtained: potassium chabazite, potassium phillipsite, and a zeolite called K-F, which has no analogues among known natural zeolites. The optimum crystallization temperatures for all these zeolites, according to ([1]), lie in the range 120-250°, i.e., under conditions of autoclave synthesis. However, in that work only a very narrow range of gel compositions was investigated, and therefore more detailed studies of the crystallization conditions of potassium zeolites, covering a broader range of compositions of the initial gels and especially the region of temperatures below 100°, are of scientific and practical interest.

We investigated the entire range of possible formation of alkaline silica-alumina gels in the system $K_2O—Al_2O_3—SiO_2—H_2O$ with an H_2O content in the gels from 70 to 95%. Crystallization was carried out at 90°. It turned out that, for the synthesis of potassium zeolites, autoclave conditions are not necessary—potassium zeolites can readily be obtained also at a temperature of 90°. Under these conditions it was possible to obtain four types of potassium zeolites: chabazites and phillipsites differing in composition, a zeolite of type K-F, and a new type of potassium zeolite, not previously described in the literature, which we have named K-I. The chemical composition and refractive indices of the synthesized crystals of potassium zeolites are given in Table 1.

Table 1

Types of zeolites	Chemical composition	Refractive indices
Potassium chabazites	$K_2O \cdot Al_2O_3 \cdot (2.0–4.2)SiO_2 \cdot (3.8–6.2)H_2O$	1.464—1.491
Potassium phillipsites	$K_2O \cdot Al_2O_3 \cdot (3.5–4.4)SiO_2 \cdot (3.8–4.4)H_2O$	1.486—1.489

Types of zeolites	Chemical composition	Refractive indices
K-F	$K_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3.4H_2O$	1.470
K-I	$K_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 3.8H_2O$	1.475

Zeolites of each type crystallize within the limits of their own crystallization field from gels whose compositions are bounded by definite limits of variation in the content of their components. Attention should be drawn to the fact that, from potassium silica–alumina gels, it was not possible to obtain analogues of the widely known sodium synthetic zeolites of types A and X, although we studied in detail those regions of gel compositions from which, under these same conditions, sodium zeolites A and X can be obtained without any difficulty.

The assignment of the synthesized zeolites to one type or another was established on the basis of a comparison of ionization X-ray patterns and of the interplanar spacings calculated from them. For the new zeolite K-I, powder Debyegrams were taken and electron-microscopic studies were carried out*.

Fig. 1 gives an electron-microscopic photograph of crystals of zeolite K-I, in which it is clearly seen that the crystals of this zeolite have the form of well-faceted thin hexagonal plates. The individual poorly formed crystals visible in the photograph probably belong to impurities of zeolite K-F. Fig. 2 gives a microdiffraction pattern obtained from a single crystal of zeolite K-I. From this photograph it is evident that the crystal lattice of zeolite K-I belongs to the hexagonal type.

Table 2

Line intensity estimate	*hkl*	*d* exp., Å	*d* calc., Å	Line intensity estimate	*hkl*	*d* exp., Å	*d* calc., Å
v s	001	13.26	13.2	s	222	2.99	2.99
v s	100	11.60	11.60	s	400	2.91	2.90
sl	110	6.72	6.70	med	320	2.66	2.66
sl	111	6.00	5.98	sl	410	2.53	2.53
sl	200	5.80	5.80	sl	500	2.31	2.32
v sl	210	4.43	4.38	sl	501	2.28	2.28
sl	211	4.16	4.16	sl	331	2.21	2.23
sl	300	3.90	3.86		420	–	2.19
med	301	3.70	3.71	sl	510	2.07	2.08
sl	220	3.36	3.35	v sl	520	1.84	1.83
sl	310	3.23	3.21	sl	523	1.72	1.71

Line intensity estimate	*hkl*	*d* exp., Å	*d* calc., Å	Line intensity estimate	*hkl*	*d* exp., Å	*d* calc., Å
med	311	3.12	3.13	v sl	530	1.66	1.66

Calculations of the lattice constants of this zeolite were made from the powder Debyegram. The interplanar spacings were indexed for a hexagonal lattice. The corresponding data for the experimental and calculated d and hkl are given in Table 2.

The constant a of the hexagonal lattice was calculated from the dependence $a = f(d)$ from the values of d for planes with $l = 0$. In this way $a = 13.41 \pm 0.02$ Å was obtained. The lattice period along the c axis was calculated from the quantities $3a^2l^2/4c^2$ for planes with $l \neq 0$, which could be done only with an accuracy of ± 0.2 Å; $c = 13.2 \pm 0.2$ Å was found.

Fig. 3 gives the water adsorption isotherms on all four types of synthesized potassium zeolites. It is clear from the figure that synthetic potassium zeolites, like sodium zeolites, are very effective desiccants, since at the smallest relative pressures they

Table 3

Adsorption (cm^3/g)

Types and specimens of zeolites	H_2O, $p/p_s = 0.1$	H_2O, $p/p_s = 0.5$	C_2O_5OH, $p/p_s = 0.1$	C_2O_5OH, $p/p_s = 0.5$	C_4H_9OH, $p/p_s = 0.1$	C_4H_9OH, $p/p_s = 0.5$	N_2, $p/p_s = 0.1$
Chabazite 13	0.168	0.185	0.067	0.088	0.088	0.088	0.01
Chabazite 245	0.193	0.205	0.158	0.190	0.053	0.055	–
Phillipsite 242	0.145	0.164	0.060	0.080	0.020	0.030	–
K-F 253	0.200	0.220	–	–	–	–	0.010
K-I 105	0.175	0.182	–	–	–	–	0.006

absorb from 12 to 20% of water relative to their own weight. The rise of the

Electron-microscopic photograph of K-I zeolite crystals

Figure 1: Electron-microscopic photograph of K-I zeolite crystals

Microdiffraction pattern obtained from a single crystal of K-I zeolite

Figure 2: Microdiffraction pattern obtained from a single crystal of K-I zeolite

isotherms in the region $p/p_s = 0.8$-1.0 is probably due to capillary condensation in the secondary porous structure formed by contacting zeolite crystallites (^{4}).

The selectivity of adsorption on potassium zeolites is already apparent when comparing the magnitudes of adsorption of water, lower alcohols, and nitrogen (Table 3).

* Electron-microscopic studies of crystals of this zeolite were carried out at our request by L. S. Zhdanov. The authors express their gratitude to him for providing the photographs obtained.

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Fig. 1. Electron-microscopic photograph of K-I zeolite crystals

Fig. 2. Microdiffraction pattern obtained from a single crystal of K-I zeolite

From the data in Table 3 it is evident that all potassium zeolites are very fine-pored adsorbents.

The sodium analogs of potassium chabazites and phillipsites also display sharply pronounced selectivity, revealed when comparing the adsorption values of water, alcohols, and nitrogen (^{3}). However, the sizes of the channels in the lattice of potassium zeolites must still be smaller than in the corresponding sodium zeolites obtained by direct synthesis. Synthetic sodium chabazite, for example, adsorbs up to 0.15 cm^3/g of N_2 at $-196°$ (^{3}), whereas potassium chabazites practically do not adsorb nitrogen. This is apparently connected not only with the larger ionic radius of K^+ ($r = 1.33$ Å) in comparison with Na^+ ($r = 0.98$ Å), but also with the peculiarities of the arrangement of K^+ ions in the crystal lattice. A comparison of the adsorption capacity of synthetic sodium (^{3}) and potassium chabazites and phillipsites with respect to water vapor shows that the sorption values are always greater for sodium zeolites, and the difference substantially exceeds the difference in the total volumes of the K^+ and Na^+ cations calculated per 1 g of anhydrous zeolite.

Fig. 3. Water-vapor adsorption isotherms on various types of synthetic potassium zeolites. 1 –potassium chabazite, 2 –K-F, 3 –K-I, 4 –potassium phillipsite.

Replacement by ion exchange of K^+ with Na^+ in synthetic potassium chabazite also leads to an increase in the adsorption volume, but this increase is close to the difference in the total volumes of the K^+ and Na^+ ions. However, replacement of Na^+ by K^+ in sodium chabazite is accompanied by a significantly greater

Fig. 3. Water-vapor adsorption isotherms on various types of synthetic potassium zeolites. 1 –potassium chabazite, 2 –K-F, 3 –K-I, 4 –potassium phillipsite.

Figure 3: Fig. 3. Water-vapor adsorption isotherms on various types of synthetic potassium zeolites. 1 –potassium chabazite, 2 –K-F, 3 –K-I, 4 –potassium phillipsite.

decrease in adsorption than could be expected from the difference in cation volumes, and this must already be explained by complete blocking of some part of the cavity volume in the crystals of the initial Na-zeolite by the larger K^+ ions (Table 4).

Table 4

Zeolite	Total volume of cations, cm^3/g	Difference in total volumes, cm^3/g	Adsorption of H_2O at $p/p_s = 0.5$, cm^3/g	Difference in H_2O adsorption values, cm^3/g
Potassium chabazite	0.026	0.016	0.229	0.028
Its exchanged Na-form	0.010	0.016	0.257	0.028
Sodium chabazite	0.010	0.015	0.280	0.125
Its exchanged K-form	0.025	0.015	0.155	0.125

Studies were also carried out on the thermal stability of the zeolites obtained by us. It turned out that the thermal stability of the crystal lattice of different potassium synthetic zeolites is not the same. The lattice of zeolite K-I is destroyed already upon heating to 200°, whereas potassium chabazites can remain stable up to a temperature of 600°, i.e., they approach natural chabazite in thermal stability. However, some synthetic potassium chabazites become X-ray amorphous already after heating at 200°. All zeolite K-F samples, after heating at 400° for 15 h, completely retain their crystalline structure. The thermal stability of potassium phillipsites, as with chabazites, differs among different samples. This is apparently connected with the variable relative content of Si and Al in the crystal lattice of the different chabazite and phillipsite samples. According to our preliminary data, thermal stability increases with increasing SiO_2 content in the composition of the crystals.

The four types of potassium zeolites investigated in the present work do not exhaust all the potassium zeolites that can be obtained by their direct synthesis.

Other types of potassium zeolites may be obtained from gels with a lower water content; further investigations are needed both in the field of synthesis and in the study of the properties of these zeolites.

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