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NEW SYNTHETIC SODIUM ZEOLITES AND THEIR ADSORPTION PROPERTIES

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The now widely known synthetic sodium zeolites NaA and NaX (Linde molecular sieves 4A and 13X) are obtained by direct crystallization from alkaline silica-alumina gels under conditions of low-temperature synthesis. Both zeolites crystallize in one and the same temperature range (70–150°), but from gels differing in composition, each in its own crystallization field ([1–3]). Zeolite NaA crystallizes from gels in which the ratio $SiO_2 : Al_2O_3 \leq 2$; zeolite NaX is formed from gels in which this ratio can vary from 2 to 15. At the same time, variation in the composition of silica-alumina gels has almost no effect on the composition of zeolite A, in different samples of which the ratio $Na_2O : Al_2O_3 : SiO_2 = 1 : 1 : 2$, or is close to this. In contrast to zeolite A, in the case of zeolite X only the ratio $Na_2O : Al_2O_3$ is constant (it, as in all other zeolites, is equal or close to 1), whereas the ratio $SiO_2 : Al_2O_3$ may vary, depending on the composition of the initial gels, from 2.2 to 3.5.

Consequently, there are possibilities for obtaining NaX zeolites that differ substantially in composition. But since a change in the relative content of Al in the aluminosilicate framework of the zeolite lattice must inevitably lead to a change in the content of Na^+ cations, which compensate the excess negative charge of the aluminosilicate tetrahedra and are located in the channels and cavities of the framework, differences may be expected in the adsorption properties of zeolites of type X that differ in composition. Attention should also be drawn to the fact that the adsorption properties of various samples of zeolite A, obtained under different conditions, may also change substantially despite very small differences in the composition of these samples. The reasons for these differences cannot yet always be explained.

Other synthetic zeolites, known as Linde molecular sieves 5A and 10X, are Ca forms of zeolites A and X, and Linde zeolite 3A is the potassium form of zeolite A. All these zeolites are therefore derivatives of zeolites A and X, obtained from them by ion exchange, and not by direct crystallization of the corresponding silica-alumina gels. However, in the system Na_2O—Al_2O_3—SiO_2—H_2O, other sodium zeolites can also be obtained by direct hydrothermal synthesis. Thus, Barrer obtained sodium mordenite ([4]) in this system at temperatures above 250°, and, under conditions of low-temperature synthesis (60–200°), two new zeolites,

named zeolites P and S ([1]). The first of these (P), in its crystal structure, is close to the natural zeolites of the phillipsite group, and the latter (S) to chabazite.

In studying the conditions of zeolite formation in the system Na_2O—Al_2O_3—SiO_2—H_2O at temperatures of 70-200° over a wide range of composition variation, we succeeded in obtaining, in addition to zeolites NaA and NaX, three new zeolites, named zeolites B, E, and Zh. X-ray studies showed that zeolites B and E, obtained by us, are close to Barrer' s zeolites P and S in chemical composition, structure, and refractive indices of the crystals, but not

are quite identical to them. Differences are observed not only in the size and shape of the crystals, but certain discrepancies are also found in the position and intensity of the lines of the X-ray patterns and in the interplanar spacings ([3]). Zeolite Zh proved to be a new sodium zeolite, having no analogues either

Table 1

Zeolite type	Chemical composition of anhydrous zeolites, expressed as the molar ratio of oxides	Refractive indices of crystals*
NaA	$Na_2O \cdot Al_2O_3 \cdot 2SiO_2$	1.470–1.472
NaX	$Na_2O \cdot Al_2O_3 \cdot (2.2–3.5)SiO_2$	1.450–1.457
E	$Na_2O \cdot Al_2O_3 \cdot (4.1–4.3)SiO_2$	1.466–1.470
S (Barrer)	$Na_2O \cdot Al_2O_3 \cdot 5SiO_2$	1.458
B	$Na_2O \cdot Al_2O_3 \cdot (3.2–3.5)SiO_2$	1.474–1.480
P (Barrer)	$Na_2O \cdot Al_2O_3 \cdot (3.3–5.3)SiO_2$	1.455–1.493
Zh	$Na_2O \cdot Al_2O_3 \cdot 2.1SiO_2$	1.489–1.492

* These data refer to hydrated zeolites.

among natural zeolites or among previously described synthetic zeolites. In chemical composition, zeolite Zh is close to zeolite NaA, but differs from it in the conditions of formation, structure, adsorption properties, and refractive indices of the crystals.

Table 1 gives data on the chemical composition and refractive indices of synthetic sodium zeolites of various types obtained under conditions of low-temperature hydrothermal synthesis.

Differences in the structure of zeolites NaA and Zh are clearly revealed by comparing the position and intensity of the peaks of ionization X-ray patterns and the interplanar spacings calculated from these X-ray patterns (Fig. 1). A more

Fig. 1. Comparison of the interplanar spacings of zeolites NaA and Zh

Figure 1: Fig. 1. Comparison of the interplanar spacings of zeolites NaA and Zh

complete characterization of the structure of zeolite Zh can be obtained from the Debyegram. Data from the calculation of the Debyegram obtained on zeolite Zh powder are given in Table 2.

Fig. 1. Comparison of the interplanar spacings of zeolites NaA and Zh

Table 2

hkl	*d*, Å	Line-intensity char-acter-istic	*hkl*	*d*, Å	Line-intensity char-acter-istic	*hkl*	*d*, Å	Line-intensity char-acter-istic
111	7.25	very weak	233	2.68	weak	640	1.73	strong
200	6.28	strong	340	2.51	very strong	643	1.61	weak
112	5.12	very weak	234	2.33	medium	800	1.56	very strong
220	4.44	weak	144	2.18	very weak	820	1.52	strong
300	4.18	very weak	244	2.09	strong	822	1.47	medium
130	3.97	very weak	620	1.98	weak	832	1.43	medium
222	3.63	very strong	622	1.88	medium	840	1.40	very weak
400	3.14	medium	444	1.80	medium	842	1.36	medium
240	2.81	very strong						

Note. Lattice constant –12.55 Å.

Zeolite Zh crystallizes in the form of very finely dispersed (usually about 1 μ) crystals of irregular shape, not exhibiting birefringence. A practically important property of synthetic zeolites must be the high thermal stability of their crystalline lattice. Zeolites of the type

A and X are stable to heating up to temperatures of 700–750°. The sodium zeolites B and E obtained by us have low thermal stability; their crystal lattice is partially destroyed already upon heating in air at 300°. Among natural zeolites there are likewise varieties of low heat resistance (thomsonite, laumontite,

Fig. 2. Adsorption isotherms on synthetic zeolite Zh. 1 –H_2O, 2 –C_2H_5OH, 3 –C_4H_9OH at 18°, 4 –N_2, 5 –Ar at 195.6°

Figure 2: Fig. 2. Adsorption isotherms on synthetic zeolite Zh. 1 –H_2O, 2 –C_2H_5OH, 3 –C_4H_9OH at 18°, 4 –N_2, 5 –Ar at 195.6°

Fig. 3. Adsorption isotherms of water vapor on various synthetic sodium zeolites and some natural zeolites at 18°. 1 –NaX, 2 –E, 3 –NaA, 4 –B, 5 –desmine, 6 –Zh, 7 –natrolite

Figure 3: Fig. 3. Adsorption isotherms of water vapor on various synthetic sodium zeolites and some natural zeolites at 18°. 1 –NaX, 2 –E, 3 –NaA, 4 –B, 5 –desmine, 6 –Zh, 7 –natrolite

desmine, etc.). Zeolite Zh, like zeolites A and X, has high heat resistance; its crystal lattice is not destroyed even after calcination at 800°.

Studies of adsorption on zeolite Zh indicate the molecular-sieve properties of this zeolite, which appear already in the adsorption of substances whose molecules differ comparatively little in size (Fig. 2).

Fig. 2. Adsorption isotherms on synthetic zeolite Zh. 1 –H_2O, 2 –C_2H_5OH, 3 –C_4H_9OH at 18°, 4 –N_2, 5 –Ar at 195.6°

Fig. 3. Adsorption isotherms of water vapor on various synthetic sodium zeolites and some natural zeolites at 18°. 1 –NaX, 2 –E, 3 –NaA, 4 –B, 5 –desmine, 6 –Zh, 7 –natrolite

Even ethyl alcohol molecules penetrate with difficulty into the channels of the crystal lattice of zeolite Zh; even after prolonged exposure of the zeolite to alcohol vapors at a relative pressure $p/p_s = 0.5$, only about 1/3 of the pore volume of the zeolite is accessible to C_2H_5OH molecules. In the case of zeolite A, the pore volumes accessible to water and alcohol molecules are close. This indicates that the diameters of the channels in the lattice of zeolite Zh are smaller than the diameters of the "windows" (4.2 Å) leading into the large cavities of zeolite A. The channels in the lattice of zeolite Zh are already almost completely impermeable to argon molecules ($d \simeq 4$ Å), and adsorption of Ar at −195.6° on zeolite Zh is very small. The total pore volume of zeolite Zh accessible to water molecules is about 0.17 cm^3/g.

A comparative evaluation of the adsorption capacity of all the synthetic sodium zeolites obtained by us with respect to water vapor under static conditions is given in Fig. 3. The same figure also gives the adsorption isotherms of water on two natural zeolites studied in our laboratory. Data on the adsorption properties of zeolites P and S, synthesized by Barrer, have not been published.

As is evident from Fig. 3, appreciable adsorption of water molecules at the smallest p/p_s is characteristic of all synthetic sodium zeolites; at the same time, in magnitude of adsorption at the same relative pressures, different types of ze-

olites differ from one another in some cases very strongly. The latter is directly connected with differences in the packing density of silica- and alumina-oxygen tetrahedra in the crystal lattices of zeolites of different types and with the volumes of voids formed between them. A denser packing of the tetrahedral structural elements in

the crystal lattice of zeolite Zh, as compared with zeolite A, which is close to it in composition, is confirmed by differences in their refractive indices (see Table 1).

Thus, at present at least five types of sodium zeolites obtained synthetically under conditions of low-temperature hydrothermal synthesis are known; their properties have been studied to varying degrees, but even with respect to the most widely known zeolites A and X it cannot be said that they have been studied sufficiently fully. This applies all the more to the new zeolites, to investigations of the conditions of their formation, their properties, and the possibilities for their practical application.

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