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Crystalline Zeolites. I. The Properties of a New Synthetic Zeolite, Type A

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The properties of a new zeolite, a hydrated crystalline sodium aluminosilicate, are described and the syntheses of 14 new zeolite species and 6 of the 35 known zeolites are announced. The new zeolite, designated type A, is represented by the formula: $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]\cdot 27H_2O$. The structure is cubic, a_0 = 12.32 Å., space group O_h^1-Pm3m, and is characterized by a 3-dimensional network consisting of cavities 11.4 Å. in diameter separated by circular openings 4.2 .Å in diameter. Removal of the crystal water leaves a stable crystalline solid containing mutually connected intracrystalline voids amounting to 45 vol. % of the zeolite. A high capacity adsorbent is produced which readily occludes molecules of a certain size and shape but excludes others. Sodium ions, accessible to the intracrystalline voids or pores, undergo cation exchange readily in aqueous solution. Replacement of sodium ions by calcium ions effectively enlarges the pore openings so straight chain hydrocarbons are readily adsorbed but branched chain hydrocarbons are excluded.

Introduction

Although similar in chemical composition, the crystalline zeolites are completely different in structure from the gel-type aluminosilicates commonly referred to as zeolites. As members of an unusual group of minerals, the zeolites have been known for many years.[1] Structurally, the zeolites of importance as adsorbents consist of a 3-dimensional network of SiO_4 and AlO_4 tetrahedra with each oxygen shared with another tetrahedron so the ratio $O/(Al + Si) = 2$. Electrical neutrality is achieved by the inclusion of alkali or alkaline earth ions such as Na^+, K^+, Ca^{++}, Sr^{++} or Ba^{++} and interstitial voids contain water molecules which may be removed reversibly or replaced by other species. Depending on the size of these interstitial voids, other molecular species may be readily adsorbed, slowly adsorbed, or completely excluded.[2]

Molecules which enter zeolite channels are tenaciously adsorbed so that desorption temperatures are generally higher than for other adsorbents.

The synthesis of two new lithium zeolites and a rubidium zeolite has been reported by Barrer and White[3] and Barrer and McCallum.[4]

Crystalline zeolites prepared in this Laboratory include mordenite, chabazite, erionite, faujasite and gismondite, in addition to 14 species which have no natural occurrence. The novel properties of one of these species, designated as zeolite type A, which has not been found in nature, are reported here. Future publications will report the properties of other synthetic zeolites prepared here and the properties of some of the natural zeolites which, due to their rarity, have not been studied previously.

Experimental

A. Synthesis.—The synthetic type A zeolite was prepared as the sodium form by the crystallization of sodium aluminosilicate gels. Details of this synthesis will be published elsewhere.

B. Analysis.—After solution in dilute hydrochloric acid, SiO_2 and Al_2O_3 were determined by standard methods.[5] Alkali metals were determined by a Beckman flame spectrophotometer; magnesium, calcium and thallium by titration with the disodium salt of ethylenediaminetetraacetic acid; barium by precipitation as barium sulfate; copper, cadmium, zinc, cobalt and nickel by polarographic methods; and silver and mercury by thiocyanate titration. The water content of the type A zeolite was determined by equilibrating the zeolites over water at its vapor pressure at room tempera-

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[1] E. S. Dana, "System of Mineralogy," 6th Ed., John Wiley and Sons, New York, N. Y., 1942, pp. 570-610.

[2] R. M. Barrer, *Ann. Reports Progr. Chem., Chem. Soc. London*, **41**, 31 (1944); *Quart. Rev. (London)*, **3**, No. 4, 293 (1949); W. Eitel, "The Physical Chemistry of the Silicates," University of Chicago Press, Chicago, Ill., 1954, pp. 994-1021.

[3] R. M. Barrer and E. A. D. White, *J. Chem. Soc.*, 1561 (1952); 1267 (1951); R. M. Barrer, *ibid.*, 127 (1948).

[4] R. M. Barrer and N. McCallum, *ibid.*, 4029 (1953).

[5] W. F. Hillebrand, G. E. F. Lundell, J. I. Hoffman and H. A. Bright, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953.

ture and measuring the loss in weight on heating at 800°. In some instances, water was determined by measuring the amount of water adsorbed by the zeolite after activating at 350° in an ultimate vacuum of 10^{-5} mm.

C. X-Ray Diffraction.—X-Ray powder diffraction patterns were obtained on a Geiger counter spectrometer with pen recorder using filtered copper K_α radiation. Powder patterns were obtained of activated specimens by first removing the crystal water from the powder contained in the specimen holder by heating *in vacuo* at 350°, transferring the specimen to the spectrometer and then shielding with dry helium during the recording of the pattern.

Laue, rotation and oscillation photographs of a hydrated single zeolite Type A crystal were obtained on an oscillation camera with helium shielding.

D. Determination of Physical Properties.—Indices of refraction were determined by the Beckè line oil-immersion method. Densities of fully hydrated zeolite crystals were determined by the method of Midgely.[6]

Electron micrographs and electron diffraction patterns were obtained on a RCA EMU-2E microscope. Infrared spectra were obtained on powder specimens employing the method of Launer,[7] on a Perkin-Elmer Model 21 recording infrared spectrophotometer.

E. Adsorption Studies.—Adsorption isotherms were measured in a system containing several balances of the McBain-Bakr type, employing quartz helical springs with a sensitivity of 20 cm./g.[8]

Zeolite specimens were activated by removing the water of hydration at 350° in an ultimate vacuum of 10^{-5} mm. Silica gel specimens were activated similarly at 175° and alumina specimens at 350°. Isotherms for the adsorption of nitrogen and argon at −78 and 0° were measured by a standard volumetric method. A circulating apparatus was employed for determining rates of gas adsorption.[9]

F. Materials.—For purposes of comparison, other adsorbents studied were: 1, natural chabazite, Colorado variety obtained from Ward's Natural Science Establishment, Rochester, New York. *Anal.* 9.2% CaO, 1.5% Na_2O, 0.4% K_2O, 17.9% Al_2O_3, 50.0% SiO_2, 21.0% H_2O, ($0.93\ CaO \cdot 0.14\ Na_2O \cdot Al_2O_3 \cdot 4.75\ SiO_2 \cdot 6.65\ H_2O$); 2, silica gel, Davison silica gel, commercial grade 40, 6-12 mesh, 3, activated alumina, Alcoa F-1 activated alumina.

Adsorbates employed in adsorption measurements were generally of 99% purity or better.

Results

A. Chemical Composition.—The average oxide ratios of 30 different type A zeolite preparations were found by chemical analysis to be: 0.96 ± 0.04 Na_2O, 1.00 Al_2O_3, 1.92 ± 0.09 SiO_2. The water content of fully hydrated type A was found to be 22.2 wt. %. When the hydrochloric acid gelatinization test of Murata[10] was applied, the A zeolite dissolved completely to yield a clear solution which set to a firm silicic acid gel.

B. Physical Properties.—The crystal density of hydrated type A zeolite was found to be 1.990 ± 0.004 g./cc. Densities of various cation-exchanged type A zeolites are given in Table I. Type A crystals are isotropic with a refractive index of 1.463 for the hydrated crystals diminishing to 1.385 when the adsorbed water is removed. As generally prepared the type A zeolite crystals are cubic with edges averaging 1–5 μ in length. Larger single crystals up to 25 μ on edge were grown on occasion, but further growth produced penetration twins and polycrystalline masses.

TABLE I

EFFECT OF CATION EXCHANGE ON THE DENSITY AND LATTICE CONSTANT OF ZEOLITE TYPE A

Cation content per unit cell	Density 25°/4, g./cc.	a_0, Å.
12 Na	1.99	12.32
12 K	2.08	12.31
7.8 Li, 4.2 Na	1.91	12.04
4.3 Rb, 7.7 Na		12.31
3.8 Cs, 8.2 Na	2.26	12.30
9.6 Tl, 2.4 Na	3.36	12.33
4 Mg, 4 Na	2.04	12.29
6 Ca	2.05	12.26
5.5 Sr, 1 Na		12.32

C. X-Ray Crystallography.—X-Ray powder diffraction patterns of the hydrated type A zeolite and the calcium-exchanged type A zeolite are given in Table II. By direct comparison with the diffraction patterns of known natural zeolites and with data tabulated in the ASTM Index of X-Ray Diffraction Data, the type A zeolite was identified as a new crystalline species. Chemical composition and other physical properties establish it beyond any doubt as a new zeolite. Zeolite type A is cubic with a unit cell dimension of 12.32 Å. Although cation exchange produced small changes in the lattice constant as shown in Table I, the simple cubic structure was retained. Structure analysis, which will be discussed in another publication, has shown that the probable space group is O_h^1-Pm3m with a unit cell composition expressed by the type of structure formula described by McConnell[11] as $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}] \cdot 27H_2O$. The structure of the type A zeolite is a 3-dimensional network of alternating AlO_4 and SiO_4 tetrahedra, 12 of each per unit cell. Interstices are occupied by 12 sodium ions (or 6 divalent ions by exchange) and 27 molecules of water.

The aluminosilicate framework of the type A zeolite is based on units which contain 4 AlO_4 and 4 SiO_4 tetrahedra in a rigid compact group. These units link together to form a ring of 8 oxygen atoms in the center of each face of the unit cell and an irregular ring of 6 oxygen atoms at each corner on the 3-fold axis. In the center of the unit cell is a large cavity, 11.4 Å. in diameter, which is connected to 6 like cavities by the 8-membered rings which form restricted openings 4.2 Å. in diameter. In addition, the large cavity is connected to 8 small cavities 6.6 Å. in diameter by the 6-membered rings which produce openings 2.0 Å. in diameter. There are 2 interconnecting pore systems, one consisting of 11.4 Å. cavities separated by 4.2 Å. restrictions and the other 11.4 Å. cavities alternating with 6.6 Å. cavities separated by 2.0 Å. restrictions.

A model of the type A structure is shown in Fig. 1. Only the oxygen framework appears since silicon and aluminum ions occupy tetrahedral holes. Central cages of the unit cell are connected by the 4.2 Å. holes and through smaller 6.6 Å. cavities by 2.0 Å. holes on the 3-fold axis. In the dehydrated zeolite crystal, sodium ions occupy positions in the center of the 6-membered rings. On rehydration these ions may shift to permit passage of water

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(6) M. G. Midgely, *Acta Cryst.*, **4**, 565 (1951).

(7) P. J. Launer, *Am. Mineralogist*, **37**, 764 (1952).

(8) Obtained fron Houston Technical Laboratory, 2218 Branard Street, Houston, Texas.

(9) W. K. Lewis, E. R. Gilliland, B. Chertow and W. P. Cadogan, *Ind. Eng. Chem.*, **42**, 1319 (1950).

(10) K. J. Murata, *Am. Mineralogist*, **28**, 545 (1943); *U. S. Geol. Survey Bull.*, **950**, 25 (1946).

(11) D. McConnell, *Am. Mineralogist*, **37**, 609 (1952).

TABLE II

X-RAY DIFFRACTION DATA—TYPE A ZEOLITES

(h,k,l,)	Sodium A d, Å.	 $I/I_{max.}$	Calcium A d, Å.	 I/I_m
100	12.294	100	12.243	100
110	8.706	69	8.664	39
111	7.109	35	7.075	32
200	....	..	6.121	12
210	5.508	25	5.478	20
211	5.031	2	5.002	4
220	4.357	6	....	..
221, 300	4.107	36	4.084	35
310	....	..	3.875	2
311	3.714	53	3.696	34
222	....	..	3.539	4
320	3.417	16	3.398	18
321	3.293	47	3.276	38
400	....	..	....	..
410, 322	2.987	55	2.972	32
411, 330	2.904	9	2.888	9
331	....	..	....	..
420	2.754	12	2.741	7
421	2.688	4	2.676	3
332	2.626	22	2.614	24
422	2.515	5	2.502	7
430, 500	2.464	4	2.451	7
431, 510	....	..	....	..
511, 333	2.371	3	2.359	3
520, 432	2.289	1	....	..
521	2.249	3	2.238	3
440	2.177	7	2.166	8
441, 522	2.144	10	2.141	8
530, 433	2.113	3	2.103	5
531	2.083	4	2.074	2
600, 442	2.053	9	2.042	4
610	....	..	....	..
611 532	....	..	....	..
620	....	..	....	..
621, 540, 443	1.924	7	1.914	4
541	1.910	4	1.891	3
533	...	..	....	..
622	1.858	2	....	..
630, 542	1.837	3	....	..
631	....	..	....	..
444	....	..	....	..
700, 632	1.759	2	....	..
710, 550, 543	1.743	13	1.733	11
711, 551	....	..	....	..
640	....	..	....	..
720, 641	1.692	6	1.683	4
721, 633, 552	1.676	2	1.667	2
642	1.667	2	....	..
722, 544	1.632	4	1.623	2
730	....	..	1.608	5
731, 553	1.604	6	....	..
650, 643	1.577	4	1.569	4
732, 651	....	..	....	..
800	....	..	....	..

molecules through the 2.0 Å. holes. Four remaining sodium ions in the unit cell occupy positions in or adjacent to the 4.2 Å. holes.

Structural stability on removing adsorbed water from the type A zeolite is shown by the data in Table III which compares X-ray line intensities of the hydrated and dehydrated zeolite. Generally, removal of adsorbed water increases the intensities of the stronger reflections.

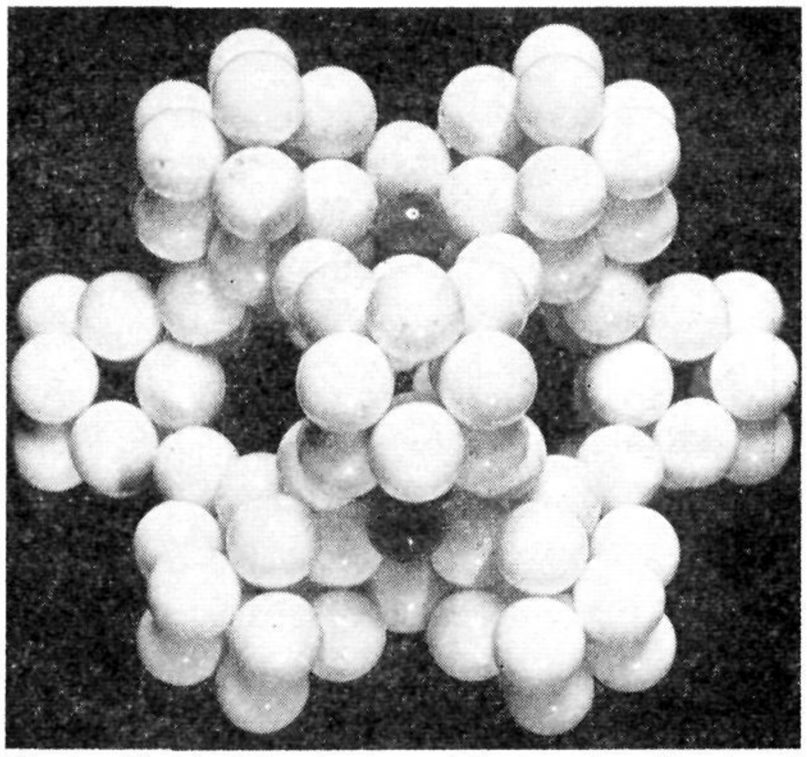

Fig. 1.—Model of the structure of the type A zeolite viewed perpendicular to the (110) plane.

TABLE III

COMPARISON OF INTENSITIES OF HYDRATED AND DEHYDRATED ZEOLITE TYPE A

Reflection (h,k,l)	Intensity, arbitrary scale Hydrated	 Dehydrated
100	86	173
110	59	100
111	30	28
210	21	55
211	2	5
220	5	5
300, 221	31	29
311	46	39
320	14	4
321	40	17
410, 322	47	26
420	10	5
332	19	18
421	4	4
422	4	2.5
500, 430	4	7
333, 511	3	3
520, 432	1	2.6

D. Electron Diffraction.—Interplanar spacings from the electron-diffraction pattern of zeolite type A were essentially the same as those obtained by X-ray diffraction.

E. Infrared Absorption Spectra.—The infrared absorption spectra characteristic of zeolite type A and two ion-exchanged forms are given in Table IV.

F. Thermal Stability and Decomposition Products.—As shown by X-ray diffraction patterns, the basic type A structure remained intact after heating in air at 350° and one atmosphere for 475 hr., *in vacuo* at 350° for 350 hr., in carbon dioxide at 350° and one atmosphere for 336 hr., and in ethylene at one atmosphere and 350° for 456 hr. Although unaffected by heating in air at one atmosphere and 700° for 6 hr., zeolite type A recrystallized at 800° in air in less than 2 hr. to a β-cristobalite-like structure.

Table IV

Infrared Spectra of Some Type A Zeolites

Type A		Calcium-exchanged type A		Zinc-exchanged Type A	
Wave length, μ	Intensity	Wave length, μ	Intensity	Wave length, μ	Intensity
3.1	M	2.75	S	2.7	M
6.1	W	3.75	S	6.15	M
9.9	VS	6.15	M	8.75	S
15.0	VW	8.89	M	9.3	S
..	..	9.99	VS	9.9	VS
..	..	10.84	VS	11.25	VS

Table V

Adsorptive Capacities of Type A and Calcium-Exchanged Type A Zeolites

Adsorbate	Critical dimension, Å.	Temp., °C.	Pressure, mm.	G./g. activated zeolite		Cc. liq./cc. act. zeolite	
				Sodium A	Calcium A	Sodium A	Calcium A
H_2O	3.15	Room	24	0.289	0.305	0.446	0.48
		100	24	.193	.205		
CO_2	2.8	Room	700	.188	.244		
CO	2.8	−196	61	.008	...		
		− 78	700	.114	.153		
		0	750	.055	.070		
		Room	700	.041	...		
O_2	2.8	−196	132	.254	.307		
		−183	750	.242	.276	.327	.422
		− 78	740	.060	.096		
A	3.84	−196	150	.001	.358		.401
		− 78	700	.048	.084		
N_2	3.0	−196	700	.006	.239		.465
		− 78	700	.088	.115		
NH_3	3.8	Room	700	.147	.195		
SO_2		Room	700	.365	.366		
H_2S		Room	400	.239	.299		
BF_3		Room	550	.009	.012		
CH_3OH		Room	90	.189	.232	.369	.460
C_2H_5OH		Room	51	.132	...	.259	
n-C_3H_7OH		Room	19	.037	.190		
Ethylene oxide	4.2	Room	700	.218	...	.382	
Ethane	4.2	Room	700	.074	.087		
Ethylene	4.25	Room	700	.084	.091		
Acetylene	2.4	Room	700	.114	...		
Propane	4.89	Room	600	.017	.130		
Propylene	5.00	Room	700	.116	.136		
Butene-1	5.1	Room	400	.029	.154		
n-Butane	4.89	Room	700	.002	.131		.342
n-Pentane	4.89	Room	205	.002	...		
Cyclopropane	4.75	Room	700	.00	.125		
Isobutane	5.58	Room	400	.006	.005		
Benzene	6.8	Room	90	.003	.002		
CCl_3F	6.9	Room	700	.003	.007		
CCl_2F_2	4.93	Room	700	.003	.084		
$C_2Cl_2F_4$		Room	700	.006	.012		

Similarly, calcium-exchanged type A zeolite was thermally stable at 700° but at 800° converted to a material amorphous to X-rays. When heated for 2 days in pure water or 5% sodium hydroxide solution, the type A zeolite was unaffected structurally or in its adsorptive properties. In solutions containing 10% or more sodium hydroxide, the zeolite was converted irreversibly to a synthetic sodalite of the composition $3(Na_2O{\cdot}Al_2O_3{\cdot}2\ SiO_2){\cdot}NaOH{\cdot}8H_2O$.

G. Adsorption Properties of the Type A Zeolites.—The capacities of the type A zeolites for a series of adsorbates as determined from adsorption isotherms are given in Table V. Also listed are the calculated critical dimensions of certain of the adsorbate molecules. The critical dimension is defined as the diameter of the circumscribed circle of the cross section of minimum area. These were calculated from available bond lengths, bond angles and van der Waals radii.[12]

Isotherms in Fig. 2 compare the low temperature adsorption of oxygen and nitrogen on type A zeolite and natural chabazite and the adsorption of straight chain and branched chain hydrocarbons on calcium-exchanged type A zeolite and chabazite. Figures 3 and 4 show isobaric adsorption on the type A zeolite as a function of the extent of potassium or calcium exchange. Curves showing the rate of adsorption of various adsorbates on type A zeolite are given in Fig. 5. Increasing the degree of dehydration was found to increase the adsorptive capacity of the type A zeolite and increasing the temperature of dehydration up to 350° produced maximum adsorptive capacity. Similarly, the

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(12) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca, N. Y., 1948, p. 189; M. L. Huggins, This Journal, **75**, 4126 (1953).

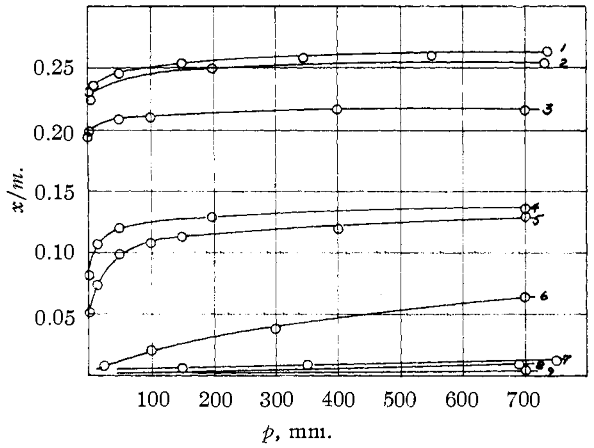

Fig. 2.—Adsorption isotherms for zeolite type A, chabazite and silica gel: 1, O_2 on type A, −183°; 2, N_2 on calcium-exchanged type A, −196°; 3, N_2 on chabazite, −196°; 4, propylene on calcium-exchanged type A, 25°; 5, propane on calcium-exchanged type A, 25°; 6, propane on silica gel, 25°; 7, propane on type A, 25°; 8, N_2 on type A, −196°; 9, isobutane on chabazite or calcium-exchanged type A at 25°. x/m = amount adsorbed in grams per gram of adsorbent.

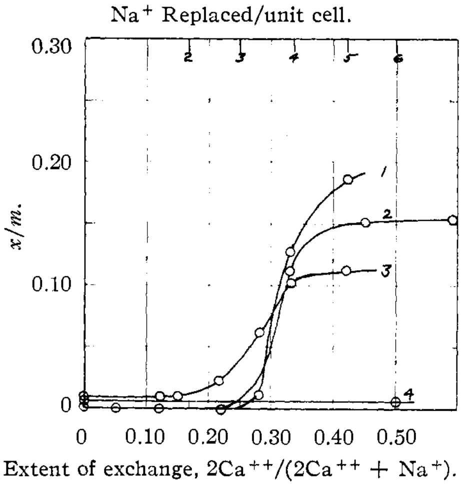

Fig. 3.—Effect of calcium exchange for sodium on the adsorptive properties of zeolite type A: 1, nitrogen, 15 mm., −196°; 2, *n*-heptane, 45 mm., 25°; 3, propane, 250 mm., 25°; 4, isobutane, 400 mm., 25°.

pre-adsorption of small amounts of polar molecules such as water, ammonia or methylamine greatly reduced the capacity for a second adsorbate as shown in Fig. 6.

The adsorption isotherms on the type A zeolite at −78° for the non-polar argon molecule, polar carbon monoxide, and nitrogen are compared in Fig. 7. Figure 8 shows the adsorption of water at 25 and 100° on type A zeolite, silica gel and alumina. Adsorption isobars of Fig. 9 compare the adsorption of argon, nitrogen and carbon monoxide on type A zeolite.

Table VI lists the surface areas of calcium-exchanged type A zeolite as determined by the BET method using adsorption of nitrogen at −196° and by the Langmuir equation using nitrogen at −196° and oxygen at −183°. The surface area of type A zeolite was determined by the Langmuir equation using oxygen adsorption at −183°.[13]

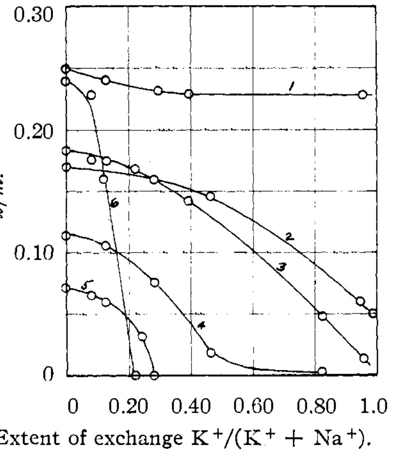

Fig. 4.—Effect of potassium exchange for sodium on the adsorptive properties of the type A zeolite: 1, H_2O at 4.5 mm., 25°; 2, CH_3OH at 4 mm., 25°; 3, CO_2 at 700 mm., 25°; 4, C_2H_2 at 700 mm., 25°; 5, C_2H_6 at 700 mm., 25°; 6, O_2 at 700 mm., −183°.

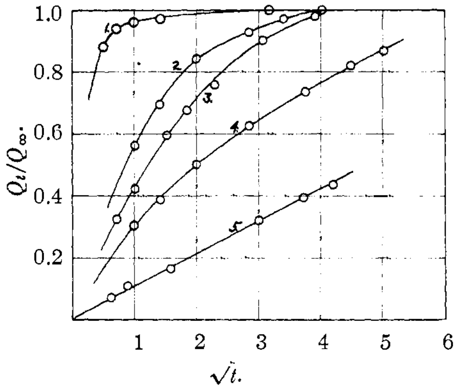

Fig. 5.—Adsorption kinetics on zeolite type A: Q_t = amount adsorbed after t minutes, g./g. adsorbent; Q_∞ = amount adsorbed at equilibrium, g./g. adsorbent: 1, CO_2 at 1 atm., 25°, Q_∞ = 0.188; 2, C_2H_4 at 1 atm., 25°, Q_∞ = 0.084; 3, C_2H_6 at 1 atm., 25°, Q_∞ = 0.074; 4, N_2 at 1 atm., −78°, Q_∞ = 0.088; 5, C_3H_8 at 1 atm., 25°, Q_∞ = 0.116.

TABLE VI

ZEOLITE TYPE A SURFACE AREAS (M.^{2}/G.)

Adsorbate	Method	Pressure, mm.	Sodium A	Calcium A
O_2, −183°	Langmuir	0.08-0.39	810	
		02-1.5		806
		50-400	785	
N, −196°	BET	0.1-0.5		745
	Langmuir	0.1-0.5		746
	BET	116-233		494
	Langmuir	116-233		802

Isosteric heats of adsorption of water, nitrogen and argon on type A and calcium-exchanged type A zeolites were calculated from adsorption isotherms for water at 25 and 100°, and nitrogen and argon at 0 and −78°. These are plotted as a function of x/m in Fig. 10.

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[13] R. M. Barrer and A. B. Robins, *Trans. Faraday Soc.*, **49**, 929 (1953).

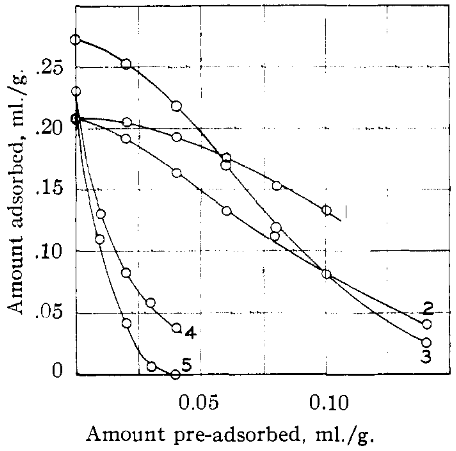

Fig. 6.—Effect of pre-adsorption on the adsorptive properties of zeolite type A: 1, *n*-Butane on calcium-exchanged type A with pre-adsorbed H_2O; 2, *n*-butane on calcium-exchanged type A with preadsorbed CH_3NH_2; 3, N_2 on calcium-exchanged Type A with preadsorbed CH_3NH_2; 4, O_2 on type A with pre-adsorbed H_2O; 5, O_2 on type A with pre-adsorbed NH_3. Amount pre-adsorbed is in units of cc. of liquid of normal density per gram activated adsorbent. Amount adsorbed is in cc. of liquid of normal density per gram of activated adsorbent.

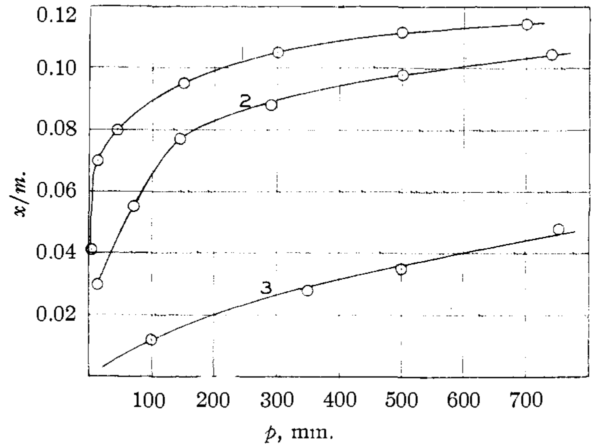

Fig. 7.—Adsorption of gases at −78° on zeolite type A: 1, CO; 2, N_2; 3, A.

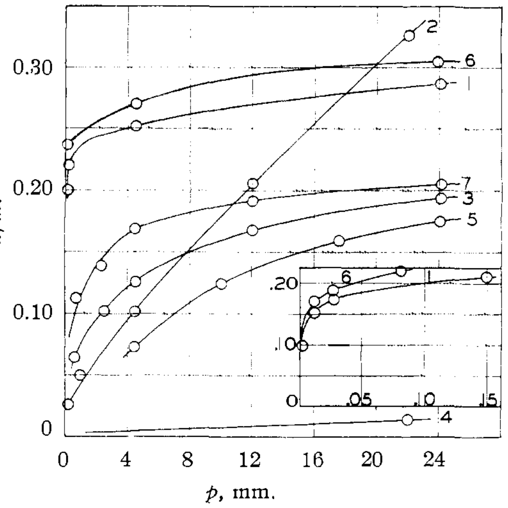

Fig. 8.—Adsorption of water on zeolite type A, silica gel and alumina: 1, type A, 25°; 2, silica gel, 25°; 3, type A, 100°; 4, silica gel, 100°; 5, alumina, 25°; 6, calcium-exchanged type A, 25°; 7, calcium-exchanged type A, 100°. Insert shows adsorption at low pressures.

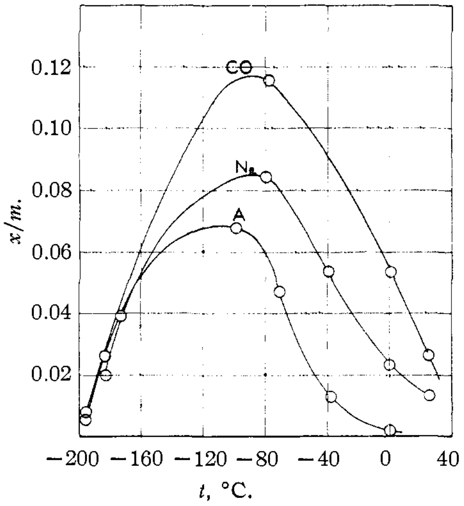

Fig. 9.—Isobaric adsorption of CO, N_2 and A at 700 mm. on zeolite type A.

H. Ion-exchange Reactions.—The first observed ion exchange reaction of zeolite type A was the apparent exchange of Na^+ for H^+. Thoroughly washed specimens of type A zeolite slurried in distilled water produced a *p*H of 10.0–10.5 which decreased slightly with increasing amounts of the zeolite. This hydrolytic equilibrium was reversed by adding small amounts of sodium chloride and the *p*H decreased to 6.0–6.5. The zeolites are unstable in acid solution but hydrogen exchange was achieved by first replacing the sodium by ammonium and subsequently heating the ammonium-exchanged type A zeolite at 350–400° to liberate free ammonia. After ammonium exchange to the extent of 35% or more of the original sodium, decomposition of the ammonium zeolite destroyed the crystal structure.

Cations that were exchanged for sodium in the type A zeolite included the following: Li^+, K^+, Rb^+, Cs^+, Tl^+, Ag^+, NH_4^+, Mg^{++}, Ca^{++}, Sr^{++}, Ba^{++}, Hg^{++}, Cd^{++}, Zn^{++}, Co^{++} and Ni^{++}. Ion-exchange equilibria and isotherms were determined in most cases. Typical exchange isotherms and equilibrium diagrams are shown in Figs. 11 and 12.

Differences in selectivities for various ions were apparent and for purposes of comparison an ar-

Table VII

Selectivity of Type A Zeolite for Various Ions in 0.2 *N* Solution at 25°

Ion	Selectivity[a] × (100)	Ion	Selectivity[a] × (100)
Ag^+	88	NH_4^+	39
Ca^{++}	72	Rb^+	36
Tl^+	~70	Li^+	33
K^+	46	Cs^+	31
Mg^{++}	43		

[a] Defined as the extent of cation exchange achieved by contacting the zeolite with a solution containing the exact equivalence of exchanging ion.

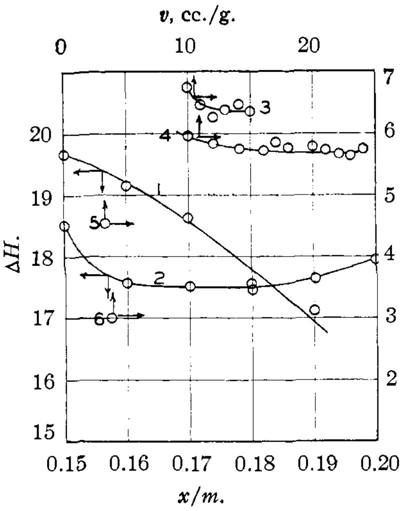

Fig. 10.—Isosteric heats of adsorption on type A zeolites: 1, H_2O on type A; 2, H_2O on calcium-exchanged type A; 3, N_2 on type A; 4, N_2 on calcium-exchanged type A; 5, A on calcium-exchanged type A; 6, A on type A. ΔH is in kcal./mole, v in cc. N.T.P.

bitrary index of selectivity was adopted which is defined as the extent of exchange achieved when the initial exchanging solution contained an amount of exchanging ion equivalent to the sodium present in the zeolite. Generally, solutions 0.2 N in exchanging ion were employed. Selectivities determined in this manner are listed in Table VII.

For dipositive ions the order of decreasing selectivity of the type A zeolite was determined to be

$$\mathrm{Zn} > \mathrm{Sr} > \mathrm{Ba} > \mathrm{Ca} > \mathrm{Co} > \mathrm{Ni} > \mathrm{Cd} > \mathrm{Hg} > \mathrm{Mg}$$

Although exchange with Ba^{++} proceeded readily, the type A crystal structure was completely destroyed. Likewise Cu^{++} and Fe^{+++} exchange were destructive. In the case of Rb^+ and Cs^+, a partial ion-sieve effect was observed. A 100% excess of Cs^+ in a 0.14 M solution at 90° produced only 31% exchange. Similarly, a 100% excess of Rb^+ as the chloride in 0.18 M solution produced 36% exchange at 90°. No exchange could be obtained with Ce^{+++}.

Discussion

Although chemical analyses of a series of type A zeolite preparations indicated a SiO_2/Al_2O_3 ratio of 1.92, the correct ratio is believed to be 2 from symmetry requirements of the crystal structure. In addition, Loewenstein has shown that 2 aluminum ions cannot share the same oxygen and retain a coördination of 4, which means that the minimum SiO_2/Al_2O_3 ratio possible in a 3-dimensional network is 2 and rigorous alternation of SiO_4 and AlO_4 tetrahedra is required.[14] The space group O^1_h-Pm3m requires that the SiO_4 and AlO_4 tetrahedra centers be placed in 24 equivalent positions and a ratio of 1.92 cannot be accounted for. It is possible that a small amount of aluminum may be present as amorphous Al_2O_3 or occluded sodium aluminate in some of the preparations analyzed. Murata has shown that in 3-dimensional networks of minerals such as the zeolites, gelatinization will occur on decomposition by HCl if the Al/Si ratio is greater than 2:3.[10] The type A zeolite was found to follow this rule as expected since the Al/Si ratio is 2:2. Hence an ordered arrangement of the SiO_4 and AlO_4 tetrahedra is further confirmed.

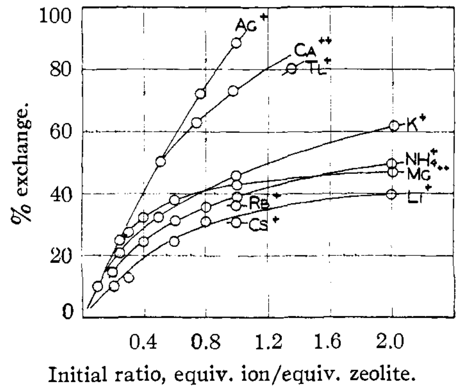

Fig. 11.—Ion-exchange isotherms for the type A zeolite in 0.2 N solution at 25°.

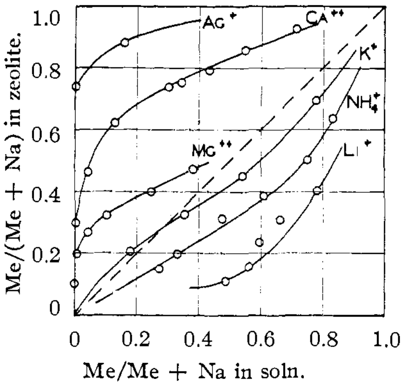

Fig. 12.—Ion exchange by type A zeolite in 0.2 N solution at 25°: Me/(Me + Na) is the ratio of equivalents of exchanging ion to the total equivalents of exchanging ion plus sodium.

The density and refractive index of type A zeolite are in accord with the properties of known zeolites. Because of the large internal void, zeolite type A has a lower density than most zeolites and the density increases with increasing atomic weight of the cation. The unit cell edge is noticeably smaller in the case of the lithium-exchanged type A zeolite but does not vary appreciably with other cations.

Certain trends concerning crystal growth were observed. Smaller crystals (1–5μ) show well developed (110) faces but as crystal growth proceeds, the (110) faces grow at a faster rate than the (100) faces and in the larger crystals no (110) faces are evident. Penetration twinning, common in natural zeolites such as chabazite, is in evidence. As growth proceeds, twinning becomes dominant, single crystals cease to grow above 25–30 μ in size, and larger polycrystalline aggregates prevail.

Retention of structure by the type A zeolite on loss of crystal water is clearly shown by the data of Table III. Increase in intensity on dehydration would be expected if the adsorbed water did not occupy definite lattice sites. Definite changes in the intensities of certain X-ray reflections such as the (100), (110) and (210), which increase and the

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[14] W. Loewenstein, *Am. Mineralogist*, **39**, 92 (1954).

(320), (321) and (332) which decrease indicate that some of the water occupies definite sites, or that some of the sodium ions shift their positions when coördinated water is removed. The readsorption of water returns the X-ray intensities to those of the normal hydrated type A zeolite.

Electron diffraction data indicated no surface structural differences peculiar to the crystal surface. Infrared spectra of Table IV illustrate the change produced in the Si–O absorption due to the cation present. The single strong band at 9.9 μ is separated into three when the sodium ion is replaced by divalent calcium and this separation increases when zinc replaces the sodium.

Exceptional stability was shown by the robust structure of the type A zeolite since it was found to be thermally stable at temperatures up to 700°. However, in basic solution, the type A structure is metastable with respect to sodalite, which is structurally similar, but is more compact and has less void space available to water molecules.

At 800°, the type A zeolite was found to recrystallize. An X-ray diffraction pattern of the recrystallized material was the same as that of β-cristobalite which indicates that it may be a stuffed derivative as discussed by Buerger.[15]

Adsorption isotherms of Fig. 2 are of the type obtained with zeolite adsorbents and compare the adsorption of natural chabazite with zeolite type A and calcium-exchanged type A. Calcium exchange for sodium in the type A zeolite increases the effective pore size, but not continuously as a function of the extent of exchange (Fig. 3). At a point corresponding to about 30% exchange or the substitution of 2 calcium ions for 4 sodium ions per unit cell of type A zeolite, molecules not normally adsorbed are readily occluded. The exchange of Mg^{++} for Na^+ produces identical results. Beyond this point cation exchange increases the pore volume slightly but does not further alter the pore size.

Replacement of the sodium ions by larger potassium ions effectively reduces the pore size, but this reduction occurs gradually with increasing extent of potassium exchange. Adsorption isobars in Fig. 4 illustrate this effect. Complete potassium exchange decreases x/m for water slightly and reduces methanol adsorption to about $^1/_3$; all other adsorbates tested were excluded. Based on the isobars of Fig. 4, the type A zeolite can be altered to exclude carbon dioxide and thus separate water vapor from carbon dioxide. Similarly, ethane and acetylene should be separated by a 30% potassium-exchanged type A zeolite. Other separations of molecules of critical dimensions less than 4 Å. should be possible by this method of ion exchange "tailoring."

In those cases where the adsorption measurements were made at $p/p_0 = 1$, adsorptive capacities were calculated as the volume of liquid adsorbed per unit volume of dehydrated zeolite. For these calculations, the density of the liquid adsorbate was taken as the normal density at the temperature concerned, and the density of the dehydrated zeolite was calculated from the hydrated density. It is evident that water molecules enter voids in the type A zeolite structure which are not accessible to larger molecules such as oxygen. These voids must correspond to the small cavities of the structure. Replacement of sodium ions by calcium ions increases the pore space available to oxygen by about 30%. The total void space in calcium-exchanged zeolite type A available to water comprises 48% of the zeolite by volume.

Based on the amount of water adsorbed by calcium-exchanged type A at 25° and $p/p_0 = 1$, the void space was calculated to be 883 Å.^{3} per unit cell. From the structure, each unit cell contains one essentially spherical cavity 11.4 Å. in diameter and one 6.6 Å. in diameter which together have a combined volume of 932 Å.^{3} The argon adsorptive capacity at −183° is equivalent to a volume of 755 Å.^{3} per unit cell which corresponds favorably with the calculated volume of the large cavity, 775 Å.^{3} Water must enter the small 6.6 Å. cavities while the argon molecule 3.8 Å. in diameter is too large to pass through the 2.0 Å. hole. The water adsorption capacity of the Type A zeolite is equivalent to a volume of 833 Å.^{3} per unit cell while the oxygen adsorption capacity accounts for a volume of 610 Å.^{3} per unit cell. In this case, water must enter the small cavities by displacing the sodium ion from its position in the center of the small 2.0 Å. hole.

From the data of Table V, the Molecular Sieve character of the type A zeolite is evident. At −196°, the type A zeolite adsorbs oxygen but not nitrogen and at room temperature ethane and ethylene oxide but not propane or cyclopropane. The apparent pore size of the type A zeolite is therefore 4.2–4.75 Å. The adsorption of propylene (5.0 Å.) but not propane (4.9 Å.) shows that the zeolite is more selective for unsaturated hydrocarbons. The calcium-exchanged type A zeolite adsorbs larger molecules such as cyclopropane, *n*-butane and CCl_2F_2 but not benzene or isobutane. Calcium-exchanged type A has an apparent pore size of 5 to 5.6 Å.

From the X-ray data, the structural diameter of the larger pore in type A zeolites is 4.2 Å. and does not change with ion exchange but is fixed by the aluminosilicate framework. However, it is evident that the apparent pore size, as defined by critical dimensions of adsorbed molecules, can be either larger or smaller than the physical diameter and is altered by ion exchange. An interpretation of these effects has been correlated with the analysis made by Kington and Laing[16] of the adsorptive properties of natural chabazite based on the structure data of Wyart.[17]

The central cage of the chabazite unit cell is entered by 8 six-membered rings, 2 of which are regular, 3.1 Å. in diameter, and 6 of which are irregular and smaller, 2.2 Å. in diameter. The adsorptive properties of chabazite are those of a system of parallel, non-connecting channels as contrasted to the intersecting pore system of the type A zeolite.

Realizing that 6-membered oxygen rings in chabazite with a structural diameter of about 3.1

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(15) M. J. Buerger, *Am. Mineralogist*, **39**, 600 (1954).

(16) G. L. Kington and W. Laing, *Trans. Faraday Soc.*, **51**, 287 (1955).

(17) J. Wyart, *Bull. Soc. franç. Mineral.*, **56**, 81 (1933).

Å., must be considered as an energy barrier to be surmounted by entering molecules, Kington and Laing calculated that an argon molecule with an equilibrium diameter of 3.84 Å. will pass through the 3.1 Å. hole of chabazite with no repulsive energy while nitrogen (3.0 Å.) and methane (4.2 Å.) require activation energies of 7 to 14 kcal./mole and 3 to 9 kcal./mole, respectively. Propane (4.9 Å.) required an activation energy of 7 kcal./mole for adsorption on chabazite but is not adsorbed by type A at 25°. Calcium-exchanged type A, however, adsorbs linear hydrocarbons up to and including *n*-tetradecane at 25° while chabazite does not adsorb *n*-butane readily. We concluded, therefore, that sodium ions in or near the 8-membered rings in the type A zeolite reduce the effective size of the 4.4 Å. opening to less than 3.1 Å., whereas calcium ions in the calcium-exchanged type A zeolite are located so that the effective size of the 4.2 Å. holes is greater than 3.1 Å. Since it seems impossible for a 6-membered oxygen ring to present an effective pore diameter greater than 3.1 Å., the adsorption data are consistent with the structure analysis which showed that the larger openings were 8-membered oxygen rings.

As shown in Fig. 5, rates of adsorption were found to vary greatly depending on the adsorbate. In general, the rate of adsorption depends on the critical dimension of the adsorbate.[18] At 25°, carbon dioxide (2.8 Å.) is adsorbed rapidly while propylene (5.0 Å.) is adsorbed very slowly by the type A zeolite.

Small amounts of water or ammonia drastically reduces adsorption of oxygen. Although methylamine or water reduces the adsorption of *n*-butane or nitrogen on calcium-exchanged type A, the effect is not as great (Fig. 6). In the case of curve 1, the total volume of *n*-butane and water adsorbed increases with increasing pre-adsorption of water. A more efficient filling of the available pore volume is accomplished by water and *n*-butane together than by *n*-butane alone. In type A zeolite with smaller pores, preadsorption of polar molecules such as water or ammonia affect the adsorption of another material by clustering about the cations, blocking the channels and reducing the pore size. Although this occurs to some extent in the calcium-exchanged type A, the larger pores require partial filling by a small polar adsorbate such as water or methylamine in order to affect the adsorption of a second material such as *n*-butane. Preadsorption primarily reduces the available pore volume.

Due to the ionic nature of the zeolite surface, strong attraction and high heats of adsorption for polar adsorbate molecules is expected. Isotherms in Fig. 7 for the adsorption of CO, A and N_2 on type A zeolite at −78° confirm expectation. Isotherms in Fig. 8 for the adsorption of water on type A zeolite, silica gel and activated alumina clearly demonstrate the superior selectivity shown by the zeolite at low pressures. In addition, at 100° the type A zeolite absorbs water strongly while the silica gel has lost most of its capacity. The inset shows that the type A zeolite adsorbs 0.20 g. of water per gram at a pressure of 0.1 mm. and 0.10 g. per gram at 0.005 mm. Similarly, the type A zeolite was found to be more selective for unsaturated hydrocarbons over saturated hydrocarbons as illustrated in Fig. 2 which compares propane and propylene adsorption on calcium-exchanged type A zeolite.

Type A zeolite exhibits an inversion in isobars for the adsorption of carbon monoxide, nitrogen and argon at low temperatures shown in Fig. 9. At −196° these molecules do not possess sufficient activation energy to diffuse into the narrow zeolite pores. As the adsorption temperature increases, adsorption passes through a maximum and then decreases due to a decreasing p/p_0.

The surface areas in Table VI obtained by the Langmuir equation seem to be more constant over a wider pressure range than are those obtained by the BET method. From Langmuir plots which were linear over the range shown, the type A zeolite surface area appears to be 750–800 $m.^2/g$.

Isosteric heats of adsorption were calculated for the adsorption of water at room temperature and 100° and for nitrogen and argon adsorption at −78 and 0°. They are shown in Fig. 10 as a function of x/m. The adsorption heat for nitrogen is much higher than the heat of liquefaction (1360 cal./mole) even at saturation. Because of the pore size, adsorbed molecules are attracted by opposite walls and high heats are expected. These adsorption heats are higher than those observed by Dacey and Thomas[19] for a Saran charcoal.

The ion-exchange isotherms of Fig. 11 exhibit a wide range of selectivities. It can be seen, for example, that silver ion is removed quantitatively from solution until 60% exchange has been achieved.

Extensive exchange with Tl^+ and Ag^+, ionic radii 1.44 and 1.26 Å., respectively, was shown by type A zeolite but Rb^+ and Cs^+, radii 1.48 and 1.69 Å., respectively, are similar to Li^+ in that they exchange to only a limited extent. Thus, predictions on ion selectivities based on hydrated radii are not valid and unlike other ion exchange materials, the type A zeolite displays an ion-sieve effect. This was further confirmed by the observation that Ba^{++} of 1.35 Å. radius completely destroys the zeolite structure, while Ca^{++} (0.99 Å.) and Sr^{++} (1.13 Å.) can be exchanged readily. Apparently the cation sites in the structure will not readily accommodate a unipositive ion of the size of Cs^+ or a dipositive ion of the size of Ba^{++}. It is likely that the unipositive sites are not identical with the dipositive sites.

Hydrogen exchange beyond a certain point produced structural collapse probably because of the formation of OH groups and reaction with Al^{+++} ions in the structural framework. As shown in Fig. 12, the ion exchange of Type A zeolite with calcium or potassium is completely reversible with no hysteresis

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[18] R. M. Barrer and D. A. Ibbitson, *Trans. Faraday Soc.*, **40**, 206 (1944).

[19] J. R. Dacey and D. G. Thomas, *ibid.*, **50**, 740 (1954).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE LINDE AIR PRODUCTS COMPANY, A DIVISION OF UNION CARBIDE AND CARBON CORPORATION]

Crystalline Zeolites. II. Crystal Structure of Synthetic Zeolite, Type A

BY T. B. REED AND D. W. BRECK

RECEIVED APRIL 23, 1956

The new synthetic zeolite, Type A, is cubic, a_0 = 12.32 Å., and X-ray data are consistent with space group O^1-Pm3m. The unit cell composition is $Me_{12/n}$ $[(AlO_2)_{12}(SiO_2)_{12}]\cdot NH_2O$ where Me is an exchangeable cation of charge n, and N varies from 20 to 30. The unit cell dimension varies slightly with the cation present. The aluminosilicate framework consists of 24(Si,Al)–O_4 tetrahedra which are joined to form 8-membered oxygen rings in the faces and distorted 6-membered rings on the 3-fold axes. A large cavity 11.4 Å. in diameter occupies the center of the cell and smaller 6.6 Å. cavities are located on the 3-fold axes. Probable positions of the cations in the lithium, sodium, thallium and calcium forms are indicated, and correlation of the structure with the adsorptive and ion-exchange properties of the Type A zeolite is discussed.

Introduction

A new synthetic crystalline zeolite, not known to exist in nature, has been reported recently and its properties described.[1] The novel adsorptive properties of certain zeolites after dehydration have been the subject of many investigations and are intimately related to their open crystal structure and pores of uniform dimensions.[2,3] In order to more completely understand the properties of the new zeolite, Type A, an X-ray structural analysis was undertaken and the results are reported here.

Only a few zeolite structures have been studied in detail. Analcite,[4,5] chabazite,[6,7] certain fibrous zeolites such as natrolite,[8] and the related felspathoids such as sodalite[9,10] have been the subject of structural investigations. Generally, these structures are based on the filling of space by Si(Al)O_4 tetrahedra as discussed by Wells.[11]

Experimental

The composition of the Type A zeolite is expressed by the structural formula $Me_{12}/_n[(AlO_2)_{12}(SiO_2)_{12}]\cdot NH_2O$ where Me represents exchangeable cations of charge n. The aluminosilicate framework, $[(AlO_2)_{12}(SiO_2)_{12}]$, will be designated by [A].

The largest crystals of the Type A zeolite that have been prepared are about 25 μ in diameter, so that most of the structural work was done from X-ray powder diffraction data obtained on a geiger-counter spectrometer as previously described.[1] Peak intensities (with no correction for Lorenz and polarization effects) for the fully hydrated and dehydrated Li^+, Na^+, Ca^{++}, Ag^+ and Tl^+ exchanged A zeolite are presented in Table I. Resolution of some of the ambiguous reflections of the sodium form was possible from single crystal photographs of a hydrated 25-μ crystal taken on an oscillation camera with helium shielding. Exposures of about 48 hr. produced easily visible darkening for the stronger reflections. Visual estimates of intensities from these oscillation photographs appear in Table I.

Chemical composition, unit cell dimensions, densities and adsorption volumes for water and oxygen are shown in Table II.

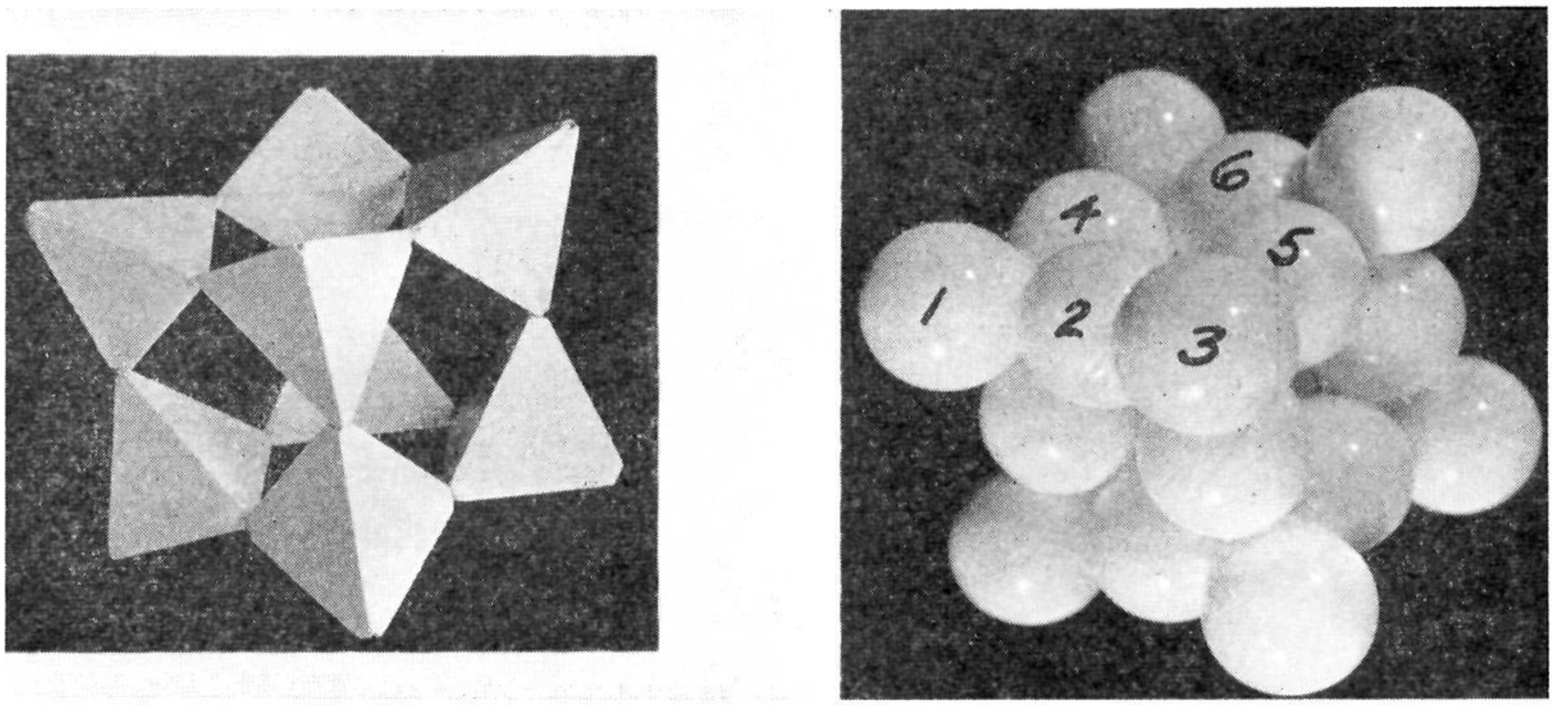

Fig. 1a, 1b.—Assembly of eight tetrahedra.

Structure Determination

No systematic extinctions are observed and the data are consistent with the space group O_h^1-Pm3m. An attempt to obtain phase information by heavy ion substitution failed. Although the silicate framework is unaltered by cation exchange, apparently the cations do not occupy the same sites. From reflections obtained with the lithium form, it was felt that the alumino-silicate framework could be

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(1) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, THIS JOURNAL, **78**, 5963 (1956).

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