

SYNTHETIC PHILLIPSITE

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ABSTRACT

Zeolite ZK-19 synthesized by phosphate complexing, with molar $\text{SiO}_2/\text{Al}_2\text{O}_3=4$ to 16 and $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})=0.3$ to 0.85 has X-ray diffraction patterns nearly identical to natural phillipsites. The structure is destroyed by heating at 350°C.

INTRODUCTION

The influence of phosphate on the crystallization of zeolites has been reported previously (Kühl, 1968). In that publication the preparation of zeolite ZK-19 (phillipsite structure) of a wide range of silica to alumina ratios by the phosphate-complexing technique was mentioned briefly. This note supplements the information given previously and describes the properties of zeolite ZK-19.

EXPERIMENTAL

The general technique of zeolite preparation by the phosphate-complexing method has been reported (Kühl, 1968). Zeolite ZK-19 is most conveniently prepared with metasilicate or waterglass as the silica source. When metasilicate is used, a product of a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio in the range of 3 to 4.5 can be obtained. For higher silica contents waterglass is preferred. Pure zeolite ZK-19 crystallizes from mixtures having silica to alumina molar ratios in the range of 4 to 16 and $\text{Na}_2\text{O}/(\text{Na}_2\text{O}+\text{K}_2\text{O})$ molar ratios in the range of about 0.3 to about 0.85.

Using a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of 8 or 10 in the reaction mixture, zeolite ZK-19 with a silica to alumina molar ratio of about 4.8 can be obtained by employing tripotassium phosphate together with sodium aluminate and waterglass. If part of the tripotassium phosphate is substituted by trisodium phosphate, silica to alumina molar ratios of 4.1 to 4.8 are obtained. If either the tripotassium phosphate or the trisodium phosphate is substituted by the corresponding secondary phosphate, the resulting zeolite, ZK-19, has a silica to alumina molar ratio of about 5. Zeolite ZK-19 of a $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio of about 6 to 6.3 crystallizes from a reaction mixture prepared with secondary phosphates only.

PROPERTIES OF ZEOLITE ZK-19

Crystal structure. Zeolite ZK-19 crystallizes in rods that are nearly always twinned (Figure 1). They are similar in appearance to some of the crystals found by Sheppard and Gude (1968) in tuffs of Lake Tecopa.

The X-ray diffraction pattern of zeolite ZK-19 (Table 1) agrees with that of a sodium potassium phillipsite from the pelagic sediments of the Pacific Ocean as reported by Steinfink (1962), who found the material to be of orthorhombic symmetry with $a=9.96_5$, $b=14.25_2$, $c=14.25_2$ Å. There are also certain similarities to the X-ray diffraction pattern of the

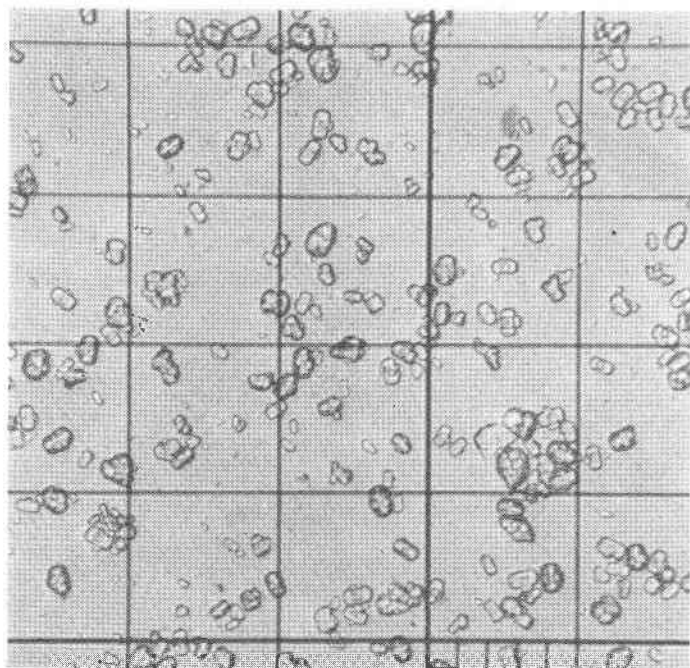


FIG. 1. Crystals of synthetic zeolite ZK-19. Size of grid 20 μm .

phillipsite used by Hoss and Roy (1960). There are some significant differences, however. A number of lines reported as strong by Hoss and Roy (1960) are only weak to medium in the X-ray diffraction pattern of zeolite ZK-19, and the lines with $d = 5.03, 4.13, 3.26, 3.23,$ and 3.15 occur as shoulders. On the other hand, different procedures in measuring the intensities of these lines may account for some of the discrepancies. Major similarities are noticed also between zeolite ZK-19 and a phillipsite found in saline lakes and reported by Hay (1964), although a very strong line of the China Lake phillipsite ($d = 3.10$) does not appear in zeolite ZK-19. No agreement with zeolite ZK-19 can be found in the larger d -values of a phillipsite mentioned by Barrer and Baynham (1956).

The spacings of Steinfink's phillipsite have been calculated from the lattice parameters (Steinfink, 1962). Although some theoretical lines have not been detected in the X-ray diffraction pattern of zeolite ZK-19 (they are presumably very weak), it is evident that Steinfink's phillipsite agrees more closely with zeolite ZK-19 than with any natural zeolite mentioned in Table 1.

No synthetic zeolite reported in the literature fits Steinfink's phillipsite

TABLE 1. COMPARISON OF THE X-RAY DIFFRACTION PATTERN OF ZEOLITE ZK-19 WITH THOSE OF PHILLIPSITES

Barrer (1956)		ZK-19		Steinfink (1962)		Roy (1960)		Hay (1964)				K-M Barrer (1959)	
<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>hkl</i>	<i>d</i> Å	<i>I</i>	Waucoba Lake		China Lake		<i>d</i> Å	<i>I</i>
								<i>d</i> Å	<i>I</i>	<i>d</i> Å	<i>I</i>		
—	—	8.17	19	8.167	101	8.04	vw	8.12	30	8.15	20	8.26	ms
7.64	vs	—	—	—	—	—	—	—	—	—	—	—	—
—	—	7.13	88	7.126	002	7.14	vs	7.08	80	7.08	100	7.15	s
—	—	—	—	—	—	6.37	w	—	—	—	—	—	—
—	—	5.37	19	5.369	121	5.37	w	5.34	50	5.34	30	5.37	m
5.24	m	—	—	—	—	—	—	—	—	—	—	—	—
—	—	5.03	sh 11	5.039	022	5.04	m	5.01	50	4.99	40	5.05	ms
4.98	m	4.98	34	4.982	200	4.96	m	—	—	—	—	—	—
4.25	ms	4.29	12	4.288	103	4.27	vw	4.26	60	4.28	10	4.32	m
—	—	4.13	sh 7	4.106	113	4.11	s	—	—	—	—	—	—
—	—	4.08	26	4.083	220	4.08	m	4.08	40	4.08	25	—	—
—	—	—	—	3.953	032	3.95	w	—	—	—	—	—	—
—	—	3.68	3	3.674	123	—	—	—	—	3.65	10	—	—
—	—	—	—	3.563	004	3.58	vw	—	—	—	—	—	—
—	—	—	—	3.457	014	3.45	m	—	—	—	—	—	—
—	—	3.26	sh 15	3.266	141	3.28	m	3.24	70	3.24	50	3.25	vs
—	—	3.23	sh 13	3.235	301	3.23	s	3.23	—	—	—	—	—
3.18	s	3.18	100	{ 3.187 024 }		3.19	vs	3.17	100	—	—	3.18	vs
—	—	—	—	{ 3.183 133 }		—	—	—	—	—	—	—	—
—	—	3.15	sh 16	3.155	311	3.13	s	—	—	—	—	—	—
—	—	—	—	3.097	232	3.09	vw	—	—	3.10	100	—	—
2.94	m	2.94	30	2.946	321	2.92	s	2.93	40	2.93	25	2.97	ms
—	—	2.89	5	2.898	240	2.89	vw	—	—	—	—	—	—
—	—	—	—	—	—	2.87	vw	—	—	—	—	—	—
—	—	—	—	—	—	2.80	vw	—	—	—	—	—	—
2.71	ms	2.74	23	2.740	{ 105 }	2.74	s	2.72	30	2.73	25	2.73	s
—	—	—	—	—	{ 143 }	—	—	—	—	—	—	—	—
—	—	2.685	31	2.685	224	2.69	s	2.67	30	—	—	—	—
2.52	m	2.56	6	2.558	125	—	—	—	—	—	—	—	—
—	—	2.54	4	2.543	323	—	—	—	—	2.54	10	2.54	m
—	—	2.51	6	2.519	044	—	—	—	—	—	—	—	—
2.40	m	2.39	5	2.395	341	—	—	—	—	—	—	2.42	m
—	—	2.34	7	{ 2.343 016 }		—	—	—	—	—	—	—	—
—	—	—	—	{ 2.337 252 }		—	—	—	—	—	—	—	—
—	—	2.24	5	{ 2.248 244 }		—	—	—	—	—	—	—	—
—	—	—	—	{ 2.233 422 }		—	—	—	—	—	—	—	—
—	—	2.05	6	2.053	226	—	—	—	—	—	—	—	—

sh = shoulder.

D = doublet.

structure as closely as does zeolite ZK-19. The crystal structure of Barrer's species K, Na-*M* (Barrer, Baynham, Bultitude, and Meier, 1959) was not published. The X-ray diffraction pattern of species K-*M* (Barrer and Baynham, 1956), which is presumably identical in structure with K, Na-*M*, differs to some extent from that of phillipsite, as re-

ported by Steinfink. Also, the silica to alumina molar ratio is only about 3.

Thus, in summary, since the crystal system, lattice parameters and the twinning described above (Fig. 1) for ZK-19 are all identical to those reported by Steinfink, we conclude that zeolite ZK-19 is the best synthetic analog of the phillipsite crystal structure. It crystallizes, however, in a form richer in potassium than natural phillipsite.

Ion exchange, thermal stability and sorption properties. Zeolite ZK-19 has been crystallized with Na/(Na+K) ionic ratios of 0.1 to 0.6 (Table 2). Complete conversion to the potassium form can readily be achieved by ion-exchange with four batches of 1 N-potassium chloride solution (Table 3). By the same procedure with 1 N-sodium chloride solution only 80 to 90 percent exchange was obtained (Table 4). This indicates a certain selectivity for potassium. The calcium exchange was even less complete (Table 5); in batch treatments only between 70 and 80 percent exchange was obtained.

Zeolite ZK-19 has been synthesized with SiO₂/Al₂O₃ molar ratios in the range of about 3.0 to about 6.25. The potassium form of zeolite

TABLE 2. SORPTION CAPACITIES OF ZEOLITE ZK-19

SiO ₂ /Al ₂ O ₃	Na	Sorption, g/100g ^a	
	Na+K	n-C ₆ H ₁₄	H ₂ O
3.26	0.32	0.94	3.2
3.35	0.39	0.31	1.0
3.90	0.27	0.25	1.5
4.19	0.43	0.51	5.7
4.26	0.35	0.59	11.1
4.30	0.51	0.62	7.0
4.33	0.24	0.66	13.0
4.74	0.46	0.69	5.6
4.79	0.14	0.49	12.3
4.90	0.38	0.25	9.6
5.08	0.37	0.20	11.9
5.10	0.26	0.34	13.7
5.16	0.28	0.10	12.6
5.39	0.16	0.34	13.4
6.00	0.26	0.10	12.9
6.22	0.18	0.11	12.8

^a The sorption capacities were measured at 25°C and 20 mm Hg (n-C₆H₁₄) or 12 mm Hg (H₂O), respectively.

TABLE 3. POTASSIUM EXCHANGE OF ZEOLITE ZK-19

SiO ₂ /Al ₂ O ₃	Na	Sorption, g/100g of zeolite ^a	
	Na+K	n-C ₆ H ₁₄	H ₂ O
3.26	0.002	0.31	11.9
3.35	0.006	1.58(?)	11.8
3.90	0.002	0.21	12.2
4.74	0.009	0.74	12.0

^a n-C₆H₁₄ at 25°C and 20 mm Hg; H₂O at 25°C and 12 mm Hg.

ZK-19 of all SiO₂/Al₂O₃ ratios is thermally stable and sorbs about 12g of water per 100g of dry zeolite (at 25°C and 12mm Hg); the n-hexane sorption, on the other hand, is low. The crystal structure of zeolite ZK-19 is destroyed when the sodium or calcium forms are calcined at 350°C. However, the higher the silica to alumina ratio, the more potassium can

TABLE 4. SODIUM EXCHANGE OF ZEOLITE ZK-19

SiO ₂ /Al ₂ O ₃	Na	Sorption, g/100g of zeolite ^a	
	Na+K	n-C ₆ H ₁₄	H ₂ O
4.79	0.87	0.35	1.42
5.16	0.92	0.29	0.24
6.00	0.82	0.30	0.43

^a n-C₆H₁₄ at 25°C and 20 mm Hg; H₂O at 25°C and 12 mm Hg.

TABLE 5. CALCIUM EXCHANGE OF ZEOLITE ZK-19

SiO ₂ /Al ₂ O ₃	2Ca	K	Sorption, g/100g of zeolite ^a	
	Na+K+2Ca	Na+K+2Ca	n-C ₆ H ₁₄	H ₂ O
4.19	0.78	0.22	0.33	0.82
4.34	0.66	0.26	0.58	0.45
4.79	0.49	0.49	0.45	6.6
5.08	0.58	0.38	0.51	2.48
5.16	0.71	0.28	0.26	1.70
5.39	0.46	0.50	0.43	4.80
6.22	0.57	0.40	0.14	8.65

^a n-C₆H₁₄ at 25°C and 20mm Hg; H₂O at 25°C and 12 mm Hg.

be substituted by sodium without loss of thermal stability. All zeolite ZK-19 samples with a potassium level of less than 60% of the cations were found to be thermally unstable.

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