

the methylene peak. Thermal reversion was observed by heating a degassed sample, originally containing 91% quadricyclene and 9% norbornadiene at 140° for 14 hours. At the end of that period the sample contained 56% quadricyclene and 44% diene. Vapor chromatography indicated the presence of no other products.

Acknowledgment.—This work was supported in part by a grant from the U. S. Atomic Energy Commission.

(6) National Science Foundation Predoctoral Fellow.

CONTRIBUTION NO. 2744 FROM THE
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RECEIVED SEPTEMBER 1, 1961

SODIUM ZEOLITE ZK-4, A NEW SYNTHETIC CRYSTALLINE ALUMINOSILICATE

Sir:

One of the most interesting and useful of the purely synthetic zeolites is zeolite A.¹ This is one of the few zeolites whose lattice composition has thus far been found to be essentially constant with an SiO₂/AlO₂ molar ratio of 0.96 ± 0.05.^{1,2} This apparent constancy of composition has been a matter of curiosity to some structural chemists interested in zeolites.

We recently synthesized a zeolite whose crystal structure is similar to, but whose chemical composition differs significantly from, zeolite A. Like zeolite A, the new compound (designated zeolite ZK-4) contains 24 tetrahedra in a cubic unit cell. The unit cell formula of sodium zeolite ZK-4 is Na₉[(AlO₂)₉(SiO₂)₁₅]·27H₂O compared with Na₁₂[(AlO₂)₁₂(SiO₂)₁₂]·27H₂O for sodium zeolite A. Because of the high SiO₂/AlO₂ ratio of zeolite ZK-4, a contraction of the unit cell compared with sodium zeolite A (*a*₀ = 12.32 Å.) is expected since the Si-O bond distance is shorter than the Al-O bond distance. X-Ray diffraction analysis disclosed *a*₀ = 12.16 ± 0.02 Å. for sodium zeolite ZK-4. By the method of Smith,³ the unit cell of the new zeolite subsequently was calculated to be 1.33% smaller than that of sodium zeolite A or *a*₀ = 12.15 Å. A summary of pertinent X-ray diffraction data for sodium zeolite ZK-4 is presented in Table I.

Some of the molecular sieve properties of sodium zeolite ZK-4 are markedly different from those of sodium zeolite A as shown in Table II.

Of particular significance is the ability of sodium zeolite ZK-4 to adsorb appreciable quantities of *n*-paraffins compared with sodium zeolite A. This property of the new zeolite probably is related to the smaller number of sodium ions per unit cell compared with sodium zeolite A. When 30 to 40% of the sodium ions in zeolite A are replaced by calcium ions, the resulting zeolite is capable of adsorbing straight chain hydrocarbons. At this level of exchange the unit cell of zeolite A contains an

(1) (a) D. W. Breck, W. G. Eversole and R. M. Milton, *J. Am. Chem. Soc.*, **78**, 2338 (1956); (b) D. W. Breck, W. G. Eversole, R. M. Milton, T. B. Reed and T. L. Thomas, *ibid.*, **78**, 5963 (1956); (c) R. M. Milton, U. S. Patent 2,882,243 (1959).

(2) R. M. Barrer and W. M. Meier, *Trans. Faraday Soc.*, **54**, 1074 (1958).

(3) J. V. Smith, *Acta Cryst.*, **7**, 479 (1954).

TABLE I

X-RAY DIFFRACTION DATA—SODIUM ZEOLITE ZK-4					
(<i>h, k, l</i>)	<i>d</i> , Å.	<i>I</i> / <i>I</i> _{max}	(<i>h, k, l</i>)	<i>d</i> , Å.	<i>I</i> / <i>I</i> _{max}
100	12.07	100	600	2.033	4
110	8.57	71	621	1.904	2
111	7.025	50	541	1.881	1
210	5.422	23	622	1.835	1
220	4.275	11	630	1.813	1
300	4.062	48	444	1.751	1
311	3.662	59	632	1.737	1
320	3.390	33	710	1.718	4
321	3.244	64	641	1.669	4
410	2.950	60	721	1.653	1
411	2.862	14	722	1.611	1
420	2.727	8	730	1.595	1
421	2.661	4	650	1.558	1
332	2.593	13	652	1.510	1
422	2.481	2	811	1.501	1
430	2.435	1	821	1.465	1
511	2.341	2	653	1.450	1
521	2.225	2	831	1.415	1
440	2.162	2	751	1.405	1
441	2.120	1	654	1.385	1
530	2.080	1	744	1.349	1
531	2.061	1	910	1.345	1

TABLE II

ADSORPTIVE CAPACITIES OF ZEOLITES ZK-4 AND A AT ROOM
TEMPERATURE

	G. sorbed/100g. activated zeolite ^a			Water
	<i>n</i> -Hexane	<i>n</i> -Octane	3-Methyl-pentane	
NaA	0.4(20)	0.5(13) ^{1c}	0.3(20)	28.9(24) ^{1b}
CaA	12.6(20)	15.4(11) ^{1c}	.2(20)	30.5(24) ^{1b}
KA	0.2(20)	0 (11) ^{1c}	.2(20)	22.2(19) ^{1c}
NaZK-4	12.5(20)	12.6(11)	.2(20)	24.8(12)
KZK-4	0.4(20)	0.3(11)	.2(20)	19.5(12)

^a Vapor pressure, mm., of adsorbate in equilibrium with adsorbent given in parentheses.

average of 9.6 to 10.2 cations. These data suggest that perhaps the nine sodium ions in zeolite ZK-4 occupy sites in the lattice similar to those occupied by the cations in calcium exchanged sodium zeolite A. Studies are currently underway in an attempt to establish the location of monovalent cations in the new zeolite. As shown in Table II, the new sodium zeolite can separate straight-chain from branched-chain hydrocarbons and potassium zeolite ZK-4 can separate water from both straight-chain and branched-chain hydrocarbons.

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RECEIVED AUGUST 28, 1961

REACTIONS OF THE *t*-NITROBUTYL ANION RADICAL Sir:

Although the e.s.r. spectra of anion radicals of aromatic nitro and dinitro compounds have been studied,^{1,2,3,4} no similar information is available for aliphatic nitro compounds. In contrast to the stable anion radicals derived from either sub-

(1) R. L. Ward, *J. Chem. Phys.*, **30**, 852 (1959).

(2) D. H. Geske and A. H. Maki, *J. Am. Chem. Soc.*, **82**, 2671 (1960).

(3) R. L. Ward, *ibid.*, **83**, 1296 (1961).

(4) A. H. Maki and D. H. Geske, *J. Chem. Phys.*, **33**, 825 (1960).