SiO_2, 63.5. Portion 2: Na_2O, 19.5; Al_2O_3, 19.2; SiO_2, 61.3. Portion 3: Na_2O, 18.4; Al_2O_3, 19.7; SiO_2, 63.0. These results show that the uncalcined sample did not undergo exchange with sodium ions, whereas the calcined sample did. The latter reaction probably involved exchange of hydrogen (or hydronium ion) by sodium ion.

Bases are preferred to salts for ion exchange of calcined zeolite ZK-4. For example, potassium zeolite ZK-4 was readily obtained by treating calcined zeolite ZK-4 with potassium hydroxide solution. Treatment with potassium chloride solution, on the other hand, led to massive destruction of the zeolite crystal lattice.

Discussion

A discussion of the probable locations of the sodium ions in the lattice of dehydrated sodium zeolite ZK-4 has been published.[8] The adsorptive properties of the sodium, potassium, and calcium forms of zeolite ZK-4 were reported earlier, as were the X-ray diffraction data of the sodium form.[2]

Barrer and Denny reported their nitrogenous analog of zeolite A, species N–Q, as having a unit-cell parameter a_0 = 12.13 A.[4] The corresponding values for sodium zeolite ZK-4 and sodium zeolite A are 12.16 and 12.32 A.[2,3] Using Smith's method, the value of a_0 for ZK-4 is calculated to be 12.15 A for a Si:Al ratio of 1.67, in excellent agreement with the measured value.[9] Similar calculations indicate that the Si:Al ratio of species N–Q should be about 1.8 to have a_0 = 12.13 A. Thus, it is almost certain that species N–Q is indeed a silica-rich analog of zeolite A, as Barrer and Denny surmised. In the work reported here, about 20% of the zeolite cations are tetramethylammonium ions; the remainder are sodium. Species N–Q contained only nitrogenous cations. Perhaps hydrogen ion was also present, as suggested by the authors. The nitrogenous cations appeared to be a mixture of dimethyl- and trimethylammonium ions, although the initial reaction mixture contained only tetramethylammonium ion. These workers implied that the rate of formation of species N–Q is determined by the rate of hydrolysis of the quaternary ammonium ion to the simpler methylammonium ions. The present work shows that a silica-rich analog of zeolite A need not involve nitrogenous cations other than tetramethylammonium ion.

Quantitative yields of zeolite ZK-4 were obtained, whereas species N–Q was obtained in "low yield." The presence of sodium ion in ZK-4 preparative mixtures probably accounts, in some unknown way, for the excellent yields of the zeolite. The silica enrichment observed in zeolite ZK-4 is in line with the notions of Barrer and Denny. They suggested that a limitation on the number of tetrahedral aluminum ions in the lattice is imposed by filling the void volume of the zeolite with large cations such as methylammonium ions. Work in these laboratories has shown that zeolite A analogs with Si:Al ratios of 2.7–3.0 have about 60% of the cation sites occupied by nitrogenous cations and that the remaining 40% of the cations are sodium.[10]

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[8] G. T. Kerr, *J. Phys. Chem.*, **66**, 2271 (1962).

[9] J. V. Smith, *Acta Cryst.*, **7**, 479 (1954).

[10] R. L. Wadlinger and E. J. Rosinski, unpublished work.

CONTRIBUTION FROM THE MOBIL OIL CORPORATION, RESEARCH DEPARTMENT,
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Chemistry of Crystalline Aluminosilicates.
III. The Synthesis and Properties of Zeolite ZK-5[1]

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A doubly charged cation, 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane, is used in conjunction with sodium ion to synthesize a crystalline aluminosilicate of novel structure. About one-half of the cation sites in the new substance, designated zeolite ZK-5, are occupied by sodium ions, and the remainder by nitrogenous cations whose composition and structure are unknown. Zeolite ZK-5 has adsorptive properties similar to those of zeolites A and ZK-4 since the unit cell of each contains a large central cage, a truncated cuboctahedron whose six faces consist of planar eight-membered rings.

Introduction

The use of quaternary ammonium ions in the synthesis of crystalline aluminosilicates (zeolites) has been reported.[1,2] The organic cations used in those studies were monobasic, or singly charged. In the work reported here, 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane, a dibasic or doubly charged cation, is used in conjunction with sodium ion. During crystallization of the zeolite, the organic cation undergoes marked reaction to give a resinous substance; nevertheless, crystallization proceeds smoothly to yield a zeolite with a unique crystal structure. This new crystalline aluminosilicate has been called zeolite ZK-5.[3]

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[1] Part II: G. T. Kerr, *Inorg. Chem.*, **5**, 1537 (1966).

[2] R. M. Barrer and P. J. Denny, *J. Chem. Soc.*, 971 (1961).

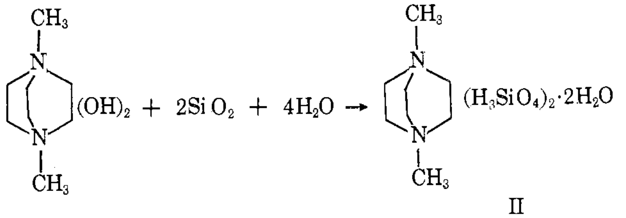
[3] G. T. Kerr, *Science*, **140**, 1412 (1963).

The organic impurity is removed from the otherwise pure zeolite by oxidative degradation.

Experimental Section

Apparatus and Reagents.—The apparatus used in this study has been described.[1] Reagent grade sodium aluminate, consisting of 36–37 wt % Na_2O and 41–42 wt % Al_2O_3, was the source of alumina in the synthesis of zeolite ZK-5. Davison silica gel was the silica source. Triethylenediamine, more systematically called 1,4-diazabicyclo[2.2.2]octane (trademark DABCO), was from the Houdry Process Corp. Eastman Kodak White Label methyl iodide was used for methylation of the diamine. Other reagents were analytical grade.

Synthesis of 1,4-Dimethyl-1,4-diazoniabicyclo[2.2.2]octane Bis(trihydrogen silicate) Dihydrate.—I was prepared using the method of Hromatka and Skopalik.[4] Solutions containing equimolar quantities of I and II were used in the synthesis of zeolite ZK-5. Silica gel, 9.2 g (0.153 mole of SiO_2), was dissolved with gentle heating in 102 ml of a 2.88 *N* solution (0.153 mole) of I. The silica readily dissolved, and the resulting solution was filtered to remove traces of insoluble residue.



I II

Left standing unstoppered at room temperature for several weeks, this silicate solution deposited large, transparent, hexagonal crystals of II. After they were removed from the mother liquor and air dried, these crystals were white and opaque. *Anal.* Calcd for $C_8H_{18}N_2 \cdot 2H_3SiO_4 \cdot 2H_2O$: C, 26.1; H, 7.60; N, 7.60; Si, 15.2; O, 43.4. Found: C, 25.78; H, 7.57; N, 7.26; Si, 15.1; O, 44.29 (by difference).

This crystalline silicate was synthesized for the first time during the course of these studies. Merrill and Spencer[5] have synthesized a number of monobasic quaternary ammonium silicates, but dibasic quaternary ammonium silicates have not yet been reported in the literature. The more pertinent X-ray diffraction data on this substance, derived from powder diffraction patterns using a Geiger counter spectrometer with pen recorder and filtered copper Kα radiation, are in Table I.

TABLE I

X-RAY DIFFRACTION DATA FOR 1,4-DIMETHYL-1,4-DIAZONIABICYCLO[2.2.2]OCTANE BIS(TRIHYDROGEN SILCATE) DIHYDRATE

d, A	I/I_{max}	*d*, A	I/I_{max}
11.0	1.00	2.82	0.30
8.7	0.60	2.70	0.30
6.1	0.30	2.57	0.10
5.4	0.20	2.35	0.10
4.2	0.30	2.20	0.05
4.0	0.30	2.14	0.10
3.7	1.00	2.08	0.05
3.45	0.30	2.01	0.10
3.35	0.05	1.97	0.05
3.13	0.40	1.92	0.10
2.91	0.20		

Synthesis of Zeolite ZK-5.—For the synthesis of zeolite ZK-5, the following ranges of mole ratios were used: $SiO_2:Al_2O_3$, 4–11; $Na_2O:Al_2O_3$ + $C_8H_{18}N_2O:Al_2O_3$, 6–19; $Na_2O:Al_2O_3$, 1.5–2.3; $H_2O:Al_2O_3$, 200–700. Usually a sodium aluminate solution was the only source of sodium although at times excess sodium hydroxide solution was also used. When the aluminate solution was mixed with the quaternary ammonium silicate solution, an amorphous gel was formed, as observed in other zeolite syntheses. The gel and mother liquor were then heated to approximately 100°, usually without stirring, for 3–9 days. Addition of zeolite ZK-5 seed to the reaction mixture reduced the crystallization time to 1–2 days.

A typical reaction proceeded in the following manner. A solution of 3.45 g (0.0206 mole of Na_2O and 0.0138 mole of Al_2O_3) of sodium aluminate and 10 ml of water was placed in an erlenmeyer flask. Meanwhile, a solution of the quaternary ammonium silicate was prepared by dissolving 9.2 g (0.153 mole of SiO_2) of silica gel in 111 ml of a 2.74 *N* solution (0.156 mole) of 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane hydroxide solution, as previously described. This solution was poured into the flask with swirling. A gelatinous precipitate formed immediately. The flask was heated in a glycerol bath at 95–100°. Samples of the mixture were examined daily under a light microscope to estimate the degree of crystallization. After 5 days, the solid appeared to be entirely crystalline; the mixture was then heated for 3 additional days, and the solid product was collected on a filter. There was considerable alteration of the organic portion of the solution, resulting in the formation of much resinous solid intermixed with the zeolitic product. The solid product was washed with several hundred milliliters of water and calcined in air at 550°. All ion-exchange reactions and sorptive capacity measurements were carried out on the calcined zeolite.

Results

Composition.—The composition of a typical sample of ZK-5 is in weight per cent: Na_2O, 7.7; Al_2O_3, 24.5; SiO_2, 67.5; total, 99.7; in mole per cent: Na_2O, 8.3; Al_2O_3, 16.1; SiO_2; 75.6. The mole ratios were 4.7 for $SiO_2:Al_2O_3$ and 0.515 for $Na_2O:Al_2O_3$. Other samples had $SiO_2:Al_2O_3$ and $Na_2O:Al_2O_3$ mole ratios ranging from 3.5 to 5.1 and from 0.39 to 0.60, respectively. The mole ratio of $Na_2O:Al_2O_3$ was always less than 1.0. The difference was ascribed to nitrogenous cations. However, identification of these cations was precluded by the decomposition and/or rearrangement of the 1,4-dimethyl-1,4-diazoniabicyclo-[2.2.2]octane ion and resin formation that occurred during crystallization of the zeolite.

Crystal Structure.—That zeolite ZK-5 constitutes a new crystal structure is evident from its unique X-ray diffraction pattern. Meier and Kokotailo have determined the crystal structure of this zeolite and described in detail the relation between its structure and that of zeolite A.[6] The unit cells of both zeolites ZK-5 and A possess large central cages in the shape of truncated cuboctahedra; these cages are bounded by six planar eight-membered rings that lie on the faces of a cube. It is through these rings that straight-chain hydrocarbon molecules, for example, pass on adsorption into the zeolite crystal.

Ion-Exchange Properties.—The ion-exchange properties of zeolite ZK-5 are not well understood and are still being investigated. Table II gives a resumé of the results of attempts to prepare various cation forms of this zeolite using exchange techniques that are ordinarily effective for ion exchange of zeolites. Exchange solutions of 1–2 *M* concentration were used in excess, except for hydrochloric acid (0.5 *M*), which

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(4) O. Hromatka and C. Skopalik, *Monatsh.*, **83**, 38 (1952).

(5) R. C. Merrill and R. W. Spencer, *J. Phys. Chem.*, **59**, 187 (1955).

(6) W. W. Meier and G. T. Kokotailo, *Z. Krist.*, **121**, 112 (1965).

TABLE II

VARIOUS CATION FORMS OF ZEOLITE ZK-5

	Composition, mole %				Molar ratio		Sorption, g/100 g of sample		
Exchange solution	Na_2O	Other oxide	Al_2O_3	SiO_2	SiO_2/Al_2O_3	M_2O/Al_2O_3[a]	*n*-Hexane	Cyclohexane	Water
None	6.2	...	16.0	78.0	4.9	0.375	13.8	1.4	20.7
NaCl	6.9	...	13.9	79.2	5.7	0.497	11.7	0.61	21.5
KOH	1.23	11.7 (K_2O)	15.7	71.5	4.6	0.824	9.01	0.61	13.6
$CaCl_2$	1.3	6.8 (CaO)	14.3	77.6	5.4	0.576	11.3	1.83	22.6
NH_4Cl	0.37	...	16.3	83.4	5.1	0.03	14.5	...	22.3
HCl	0.49	...	14.8	84.7	5.7	0.03	13.21	...	...

[a] M_2O is the total metallic cation oxide (does not include ammonium, quaternary ammonium, nor hydrogen).

was used in stoichiometric amounts. Some significant features of the ion-exchange data in Table II are: Sodium is readily exchanged from the zeolite by solutions containing ammonium, potassium, or calcium ions. Moreover, sodium ion is almost completely exchanged by direct treatment with dilute hydrochloric acid, without a significant loss of crystallinity. Retention of crystallinity was established by X-ray diffraction and sorptive capacity measurements. The alumina content of zeolite ZK-5 is reduced somewhat during exchange by acid or salt solutions. Similar observations have been reported for clinoptilolite on treatment with acid.[7] Treatment of zeolite ZK-5 with alkaline solution slightly reduces the silica content. Cations derived from groups I-A and II-A cannot be completely exchanged into the zeolite using salt solutions. This fact suggests that in this zeolite protons formed by the thermal decomposition of the nitrogenous cations have weak Brønsted acid activity in aqueous media. That considerable potassium ion exchanges into this zeolite as a result of treatment with potassium hydroxide solution (as compared with potassium chloride solution) supports this suggestion.

Some additional evidence that the quaternary ammonium ion on calcination yields weakly acidic hydrogen or hydronium ions emerges from two experiments: A sample of calcined zeolite ZK-5 was divided into two portions. The first was treated with sodium chloride solution, and the second was saturated with gaseous ammonia and then treated with sodium chloride solution. The compositions of the initial zeolite and the treated samples are presented in Table III. A much higher sodium content was obtained from the portion first treated with ammonia. These observations are explained as follows: weak acid sites would not readily react with salts

$$\text{HZK-5} + \text{NaCl} \rightleftharpoons \text{NaZK-5} + \text{HCl}$$

However, neutralization of the acid sites with ammonia, to yield the ammonium salt, would be expected to exchange with salt solutions.

TABLE III

EFFECT OF AMMONIA ON ION-EXCHANGE PROPERTIES OF ZEOLITE ZK-5

	Composition, mole %			Molar ratio	
Treatment	Na_2O	Al_2O_3	SiO_2	SiO_3/Al_2O_3	Na_2O_3/Al_2O_3
None	6.5	15.3	78.2	5.11	0.405
NaCl solution	6.2	15.1	78.6	5.20	0.410
NH_3 followed by NaCl solution	11.9	14.4	73.9	5.13	0.826

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(7) R. M. Barrer and M. B. Makki, *Can. J. Chem.*, **42**, 1481 (1964).