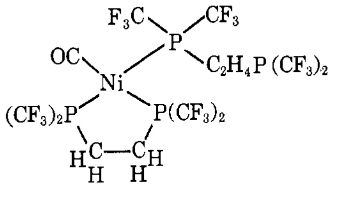
experiments on the subject, 0.12 mmole of the perfluoro chelate and 0.36 mmole of $(CF_3)_2PC_2H_4P(CF_3)_2$ were heated in a 10-ml sealed tube for 2 weeks at 36°. The displaced CO was measured as 0.13 mmole—essentially one per molecule of the original chelate compound, none of which could be recovered. The volatile material was a mixture of the two bis phosphines. The 96-mg weight of this mixture indicated 0.12 mmole of each bis phosphine (calcd weight, 96.5 mg), meaning that the nonvolatile product was 0.12 mmole of the compound



The second experiment, employing 0.1284 mmole of $(CF_3)_2PC_2H_4P(CF_3)_2$ and 0.0639 mmole of $(CF_3)_2PC_2F_4P(CF_3)_2Ni(CO)_2$, during 12 hr at 25° produced 0.017 mmole of CO, rising to 0.0547 during a further 25 hr at 40°. Now the free-ligand mixture amounted to 0.0655 mmole, with an infrared spectrum showing roughly an equimolar proportion of the two bis phosphines; thus the displacement was less advanced than in the first experiment. At this stage it was possible to isolate 0.006 mmole of a chelate–nickel dicarbonyl fraction, the infrared spectrum of which showed C=O stretching only at 2092 and 2060 cm^{-1}, identifying pure $(CF_3)_2PC_2H_4P(CF_3)_2Ni(CO)_2$. Thus it appears that the displacement of one chelating ligand by the other can precede the displacement of CO, although we cannot exclude a parallel mechanism whereby one CO is displaced before $(CF_3)_2PC_2F_4P(CF_3)_2$ is detached.

Nuclear Magnetic Resonance Results

The F^{19} magnetic resonance spectra of the two NiP_4 compounds were explored by Dr. S. L. Manatt at the Jet Propulsion Laboratory in Pasadena, Calif. The number and arrangement of the peaks agreed with the assumed tetrahedral structures, with some subtle distortions which might be ascribed either to nonbonding contacts within each molecule or to intermolecular contacts in the "neat" liquid samples. With Cl_3CF as an internal standard, the following parameters were measured.

For $(CF_3PF_2)_4Ni$ the chemical shifts were +82.14 ppm for F in CF_3 and +60.59 ppm for F on P; coupling constants, $J_{P-F} = 1190$ cps, $J_{F-C-P} = 119$ cps, and $J_{P-P-F} = 38$ cps.

For $[(CF_3)_2PF]_4Ni$ the chemical shifts were +68.53 ppm for F in CF_3 and +158.95 ppm for F on P; coupling constants, $J_{P-F} = 998$ cps, $J_{F-C-P} = 106$ cps, and $J_{P-P-F} = 40$ cps.

Attempts to relate these preliminary results to bond character would be premature. A more thorough study, including P^{31} spectra and the effects of temperature and dilution, is planned for the future.

CONTRIBUTION FROM THE MOBIL OIL CORPORATION, RESEARCH DEPARTMENT,
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Chemistry of Crystalline Aluminosilicates.
II. The Synthesis and Properties of Zeolite ZK-4[1]

BY GEORGE T. KERR

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A new zeolite, designated zeolite ZK-4, has been synthesized using aqueous solutions of sodium aluminate and tetramethylammonium silicate as reagents. For ZK-4, sodium and tetramethylammonium ions occupy cation sites in the zeolite lattice. This zeolite is isostructural with zeolite A. Unlike zeolite A, however, it has a ratio of silicon to aluminum occupying tetrahedral positions in the crystal lattice that exceeds 1.0, and ratios as high as 1.7 have been obtained. This increased silicon content of the new zeolite results in a smaller unit cell parameter than that of zeolite A. Because the sodium form of zeolite ZK-4 contains fewer sodium ions per unit cell than does sodium zeolite A, it is capable of adsorbing straight-chain hydrocarbons; sodium zeolite A is not.

Introduction

The work reported in the present study is concerned with the use of tetramethylammonium and sodium ions to produce a new crystalline aluminosilicate, designated zeolite ZK-4,[2] which is isostructural with zeolite A.[3] A substance similar to zeolite ZK-4 was probably synthesized by Barrer and Denny when they prepared a variety of zeolites in which only nitrogenous bases were used for crystallizing silica–alumina gels.[4] The use of quaternary ammonium ions in conjunction with ions of group I-A in the synthesis of zeolite was suggested by an earlier study,[1] which showed that zeolite growth probably proceeds from

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(1) Part I: G. T. Kerr, *J. Phys. Chem.*, **70**, 1047 (1966).

(2) G. T. Kerr and G. T. Kokotailo, *J. Am. Chem. Soc.*, **83**, 4675 (1961).

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

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

strongly alkaline solutions containing active species derived from an amorphous aluminosilicate substrate.

Experimental Section

Apparatus and Reagents.—Descriptions of reaction vessels used for zeolite syntheses were reported previously.[1] Reagent grade sodium aluminate, consisting of 36–37 wt % Na_2O and 41–42 wt % Al_2O_3, and Eastman Kodak White Label tetramethylammonium hydroxide and tetramethylammonium iodide were used. Some hydroxide was also obtained from reaction of the iodide with moist silver oxide. The concentration of the hydroxide solutions used in this study ranged from 2 to 3 *M*. Davison silica gel, the source of silica, was dissolved in the tetramethylammonium hydroxide solution. Two moles of the hydroxide were used per gram formula weight of silica. The resulting solution probably consists of tetramethylammonium trihydrogen silicate tetrahydrate, $(CH_3)_4N(H_3SiO)_4 \cdot 4H_2O$, and tetramethylammonium hydroxide in equimolar ratios. The former compound was first isolated and characterized by Merrill and Spencer[5] and was prepared in this study using their method.

Analyses.—Sodium and potassium were determined by conventional flame spectrophotometry. Silica was determined gravimetrically, and alumina was analyzed by a complexometric titration.[6] Nitrogen was determined by the Kjeldahl method and carbon by the conventional microtechnique.

Typical Syntheses of Zeolite ZK-4.—Sodium aluminate, 21.5 g (0.126 mole of Na_2O and 0.086 mole of Al_2O_3), was dissolved in 250 ml of water. Meanwhile 20.25 g (0.35 mole of SiO_2) of silica gel was dissolved by heating with 285 ml of 2.49 *M* solution (0.71 mole) of tetramethylammonium hydroxide. The silicate solution was filtered to remove traces of insoluble solid. Both the aluminate and silicate solutions were heated to boiling, and the silicate was added rapidly to the aluminate with stirring. A precipitate appeared immediately. After 2 min, stirring was stopped, and the mixture was heated to reflux temperature, approximately 100°, for 24 hr. The solid product was collected on a Büchner funnel and was washed with 1 l. of water. This product will be identified as "sample 1."

To a solution of 3.45 g of sodium aluminate (0.0203 mole of Na_2O and 0.0138 mole of Al_2O_3) and 10 ml of water was added 0.3 g of zeolite ZK-4 as seed. A solution of 36.75 g (0.15 mole) of tetramethylammonium trihydrogen silicate tetrahydrate $[(CH_3)_4N(H_3SiO_4) \cdot 4H_2O]$ in 59 ml of a 2.47 *M* (0.15 mole) solution of tetramethylammonium hydroxide was added with stirring to the mixture of sodium aluminate and zeolite ZK-4. When the voluminous precipitate was smooth, the vessel containing the mixture was surrounded by a glycerol bath heated to 100°, and stirring was stopped. After 39 hr, the crystallization of the amorphous precipitate was complete. The solid was collected on a Büchner funnel and rinsed with 100 ml of water. This material will be referred to as "sample 2."

On completion of crystallization of zeolite ZK-4, both solid and liquid phases are obtained. It has been repeatedly observed that all of the alumina present in the reaction mixture will be found in the solid phase, which is essentially pure crystalline zeolite.

Results

Synthesis.—In the preparation of zeolite ZK-4, the following mole ratios of reaction mixture compositions were used: $SiO_2:Al_2O_3$, 4–11; $Na_2O:Al_2O_3 + [(CH_3)_4N]_2O:Al_2O_3$, 9–30; $Na_2O:Al_2O_3$, 1.0–1.5; $H_2O:Al_2O_3$, 100–350. For complete conversion of amorphous substrate to crystalline solid, 24–72 hr was usually necessary. However, crystallization times have been reduced to as little as 13 hr upon seeding with preformed zeolite ZK-4. Similar seeding of zeolite A preparations has also been reported.[1] Nevertheless, the formation of zeolite ZK-4 is always markedly slower than that of zeolite A, which is complete in 1–4 hr.[1] At present, the cause and the nature of the relative rates of growth of zeolite ZK-4 and zeolite A are not understood. Our observations indicate that silica-rich zeolites crystallize more slowly than do less siliceous ones with the same structure.

Composition.—The compositions of samples 1 and 2, the preparation of which has been described, were typical of ZK-4 zeolites. After being calcined at 550°, with an air purge, the analyses were: Sample 1: 17.0% Na_2O, 30.5% Al_2O_3, 51.0% SiO_2 (total 98.5%); atom ratios: Si:Al, 1.42; Na:Al, 0.915. Sample 2: 13.9% Na_2O, 28.3% Al_2O_3, 56.7% SiO_2 (total 98.9%); atom ratios: Si:Al, 1.70; Na:Al, 0.807. For comparison, the atom ratios of zeolite A are: Si:Al, 0.92–1.04; Na:Al, 0.92–1.00.[3] The data show that the composition of zeolite ZK-4 is more variable than that of zeolite A, that zeolite ZK-4 is more siliceous than zeolite A, and that the ratio of sodium to aluminum in zeolite ZK-4 is significantly less than 1.0. Analyses for an air-dried sample of uncalcined zeolite ZK-4 were: 2.8% C, 0.83% N, 11.2% Na_2O, 21.6% Al_2O_3, 40.3% SiO_2, 23.3% H_2O (by difference, indicating that samples contained sorbed water), and 25.8% loss on ignition. Atom ratios were: Si:Al, 1.59; Na:Al, 0.853; N:Al, 0.140; C:N, 3.94. These data show that the sum of the ratios, Na:Al and N:Al, is close to 1.00, the expected value if sodium and quaternary ammonium ions together occupy all of the cation sites. The atom ratio of C:N is close to 4.00, the calculated ratio for tetramethylammonium ion. Upon calcination with an air purge at 550°, the quaternary ammonium ion is probably decomposed to produce a hydrogen ion, thus compensating for anionic sites not satisfied by sodium.

Ion Exchange.—The crystal structure and adsorptive properties of zeolite ZK-4 show that the intracrystalline channels in this zeolite have ports (or windows) not more than about 5 A in diameter.[2] The tetramethylammonium ion, occupying between 5 and 20% of the cation sites in uncalcined zeolite ZK-4, is about 6.0–6.5 A in diameter.[7] It was expected that this ion would be too large to undergo cation exchange from the crystal. Experimental data support this expectation.

Three portions of a freshly prepared sample of zeolite ZK-4 were taken: Portion 1 was calcined by purging with air at 550° to serve as a reference for the Na_2O–Al_2O_3 balance. Portion 2 was calcined along with portion 1 and then treated with sodium hydroxide to base exchange it, washed with water, and calcined. Portion 3 was treated with sodium hydroxide solution in an attempt to base exchange it and then washed with water and calcined.

The compositions by mole per cent of the three products are: Portion 1: Na_2O, 17.0; Al_2O_3, 19.6;

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

(6) K. E. Burke and C. M. Davis, *Anal. Chem.*, **36**, 172 (1964).

(7) R. M. Barrer, W. Buser, and W. F. Grütter, *Helv. Chim. Acta*, **39**, 518 (1956).

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

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

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Chemistry of Crystalline Aluminosilicates.
III. The Synthesis and Properties of Zeolite ZK-5[1]

BY GEORGE T. KERR

Received March 18, 1966

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).