

[54] SILICON SUBSTITUTED ZEOLITE COMPOSITIONS AND PROCESS FOR PREPARING SAME

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 066,330, Aug. 14, 1979, abandoned.

[51] Int. Cl.³ C01B 33/28

[52] U.S. Cl. 423/328; 502/60; 502/85; 502/86

[58] Field of Search 423/328-330; 252/441, 442, 455 Z; 502/60, 78, 79, 85, 86

[56] References Cited

U.S. PATENT DOCUMENTS

- 3,130,007 4/1964 Breck 423/328
3,216,789 11/1965 Breck et al. 423/328
3,436,174 4/1969 Sand 423/328

- 3,506,400 4/1970 Eberly et al. 423/328
3,594,331 7/1971 Elliott 252/442
3,640,681 2/1972 Pickert 423/328
3,702,886 11/1972 Argauer et al. 423/328
3,929,672 12/1975 Ward 423/328
3,933,983 1/1976 Elliott 423/328
4,093,560 6/1978 Kerr 252/455 Z

FOREIGN PATENT DOCUMENTS

- 1431944 4/1976 United Kingdom .

OTHER PUBLICATIONS

Breck "Zeolite Molecular Sieves" Copyright, 1974, pp. 507-518.

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Attorney, Agent, or Firm—Richard G. Miller

[57] ABSTRACT

Aluminum from AlO4-tetrahedra of as-synthesized zeolites is extracted and substituted with silicon to form zeolite compositions having higher SiO2/Al2O3 molar ratios and exhibiting distinctive chemical and physical properties. The preparative procedure involves contact of the starting zeolite with an aqueous solution of a fluorosilicate salt using controlled proportions and temperature and pH conditions which avoid aluminum extraction without silicon substitution.

20 Claims, 3 Drawing Figures

FIG. 1a

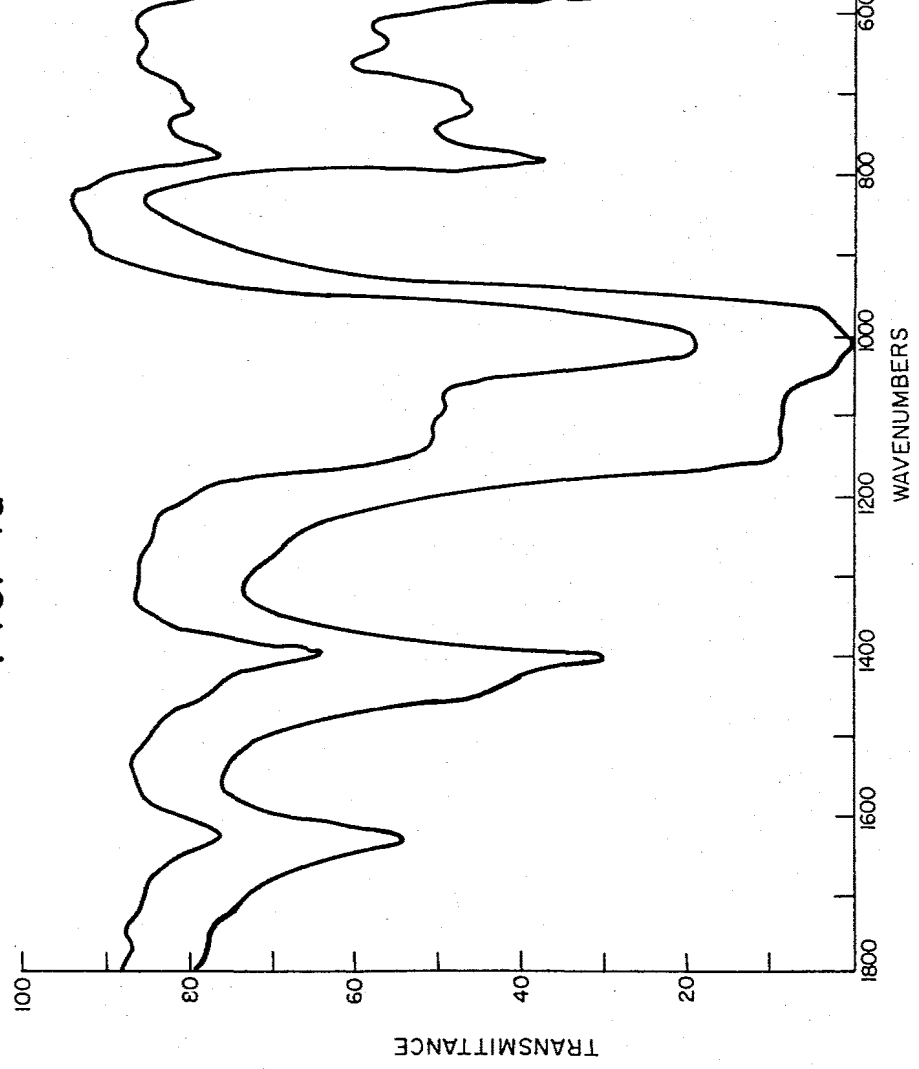


FIG. 1b

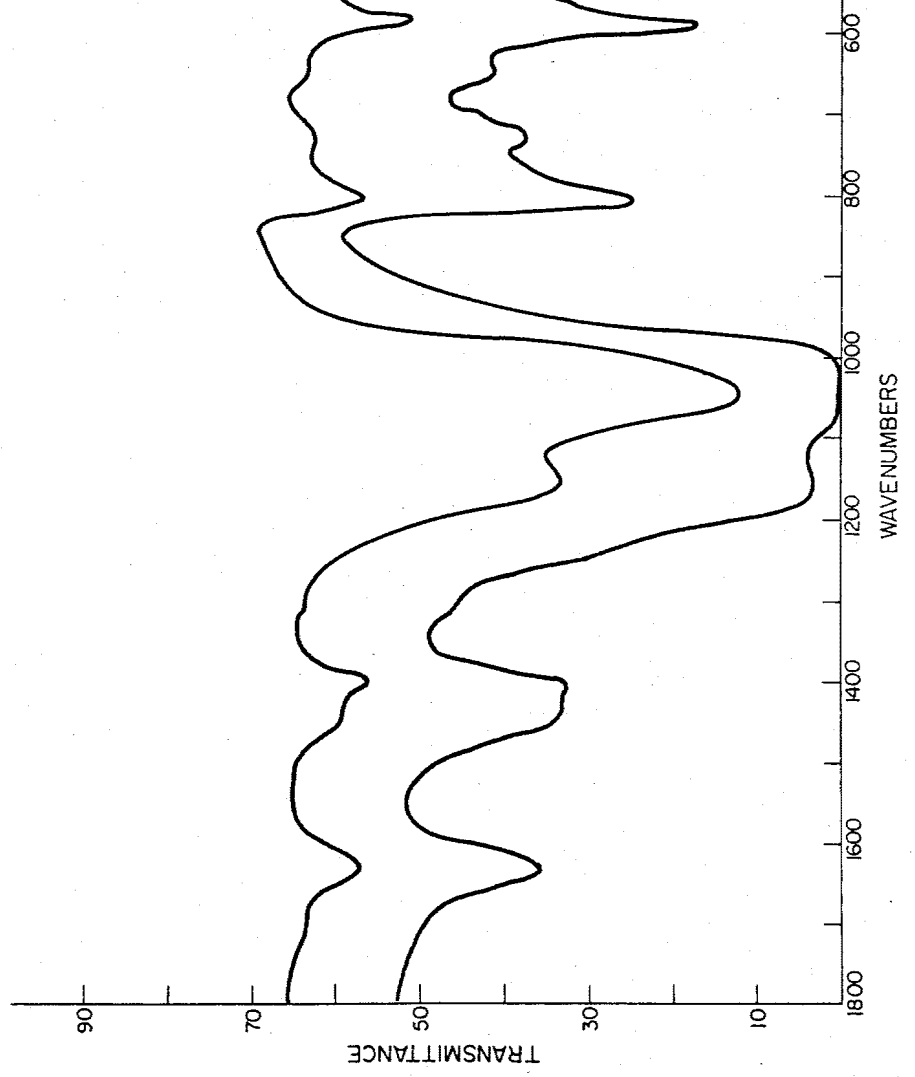
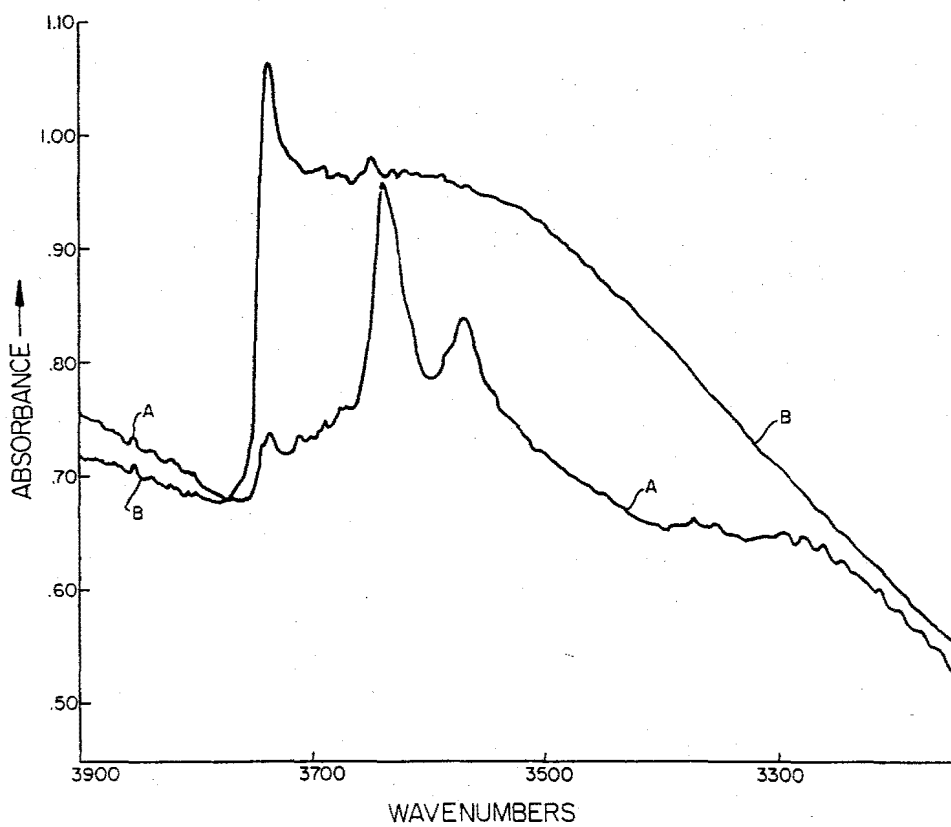


FIG. 2



**SILICON SUBSTITUTED ZEOLITE
COMPOSITIONS AND PROCESS FOR
PREPARING SAME**

RELATED APPLICATIONS

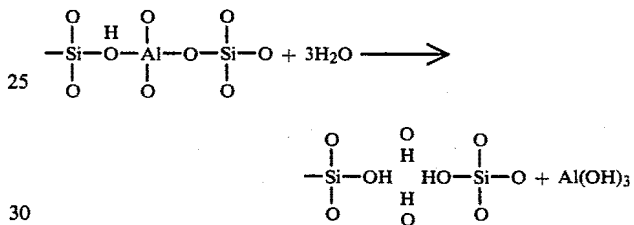
This is a continuation-in-part of application Ser. No. 066,330 filed Aug. 14, 1979, now abandoned.

The present invention relates in general to novel zeolite compositions and to the method for their preparation. More particularly it relates to zeolite compositions topologically related to prior known zeolites but which have substantially greater SiO₂/Al₂O₃ molar ratios than the heretofore known zeolite species and characterized by containing framework silicon atoms from an extraneous source, and preferably a very low content of defect sites in the structure. In general the preparative process involves contacting the starting zeolite under controlled conditions with an aqueous solution of a fluorosilicate salt, preferably one which does not form insoluble salts with aluminum.

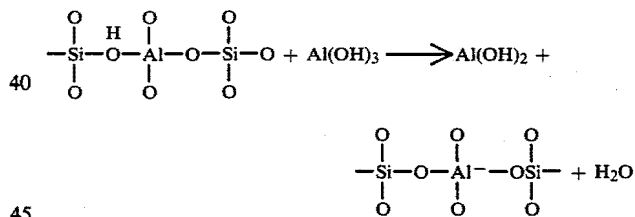
The crystal structures of naturally occurring and as-synthesized zeolitic aluminosilicates are composed of AlO₄⁻ and SiO₄ tetrahedra which are cross-linked by the sharing of oxygen atoms. The electrovalence of each tetrahedron containing an aluminum atom is balanced by association with a cation. Most commonly this cation is a metal cation such as Na⁺ or K⁺ but organic species such as quaternary ammonium ions are also employed in zeolite synthesis and in some instances appear as cations in the synthesized product zeolite. In general the metal cations are, to a considerable extent at least, replaceable with other cations including H⁺ and NH₄⁺. In many instances the organic cation species are too large to pass through the pore system of the zeolite and hence cannot be directly replaced by ion exchange techniques. Thermal treatments can reduce these organic cations to H⁺ or NH₄⁺ cations which can be directly ion-exchanged. Thermal treatment of the H⁺ or NH₄⁺ cationic forms of the zeolites can result in the substantial removal of these cations from their normal association with the AlO₄⁻ tetrahedra thereby creating an electrovalent imbalance in the zeolite structure which must be accompanied by structural rearrangements to restore the electrovalent balance. Commonly when the AlO₄⁻ tetrahedra constitute about 40% or more of the total framework tetrahedra, the necessary structural rearrangements cannot be accommodated and the crystal structure collapses. In more siliceous zeolites, the structural integrity is substantially maintained but the resulting "decaionized" form has certain significantly different properties from its fully cationized precursor.

The relative instability of aluminum in zeolites, particularly in the non-metallic cationic or the decaionized form, is well recognized in the art. For example, in U.S. Pat. No. 3,640,681, issued to P. E. Pickert on Feb. 3, 1972, there is disclosed a process for extracting framework aluminum from zeolites which involves dehydroxylating a partially cation deficient form of the zeolite and then contacting it with acetylacetone or a metal derivative thereof to chelate and solubilize aluminum atoms. Ethylenediaminetetraacetic acid has been proposed as an extractant for aluminum from a zeolite framework in a process which is in some respects similar to the Pickert process. It is also known that calcining the H⁺ or NH₄⁺ cation forms of zeolites such as zeolite Y is an environment of water vapor, either extraneous

or derived from dehydroxylation of the zeolite itself, is effective in removing framework aluminum by hydrolysis. Evidence of this phenomenon is set forth in U.S. Pat. No. 3,506,400, issued Apr. 14, 1970 to P. E. Eberly, Jr. et al.; U.S. Pat. No. 3,493,519, issued Feb. 3, 1970 to G. T. Kerr et al.; and U.S. Pat. No. 3,513,108, issued May 19, 1970 to G. T. Kerr. In those instances in which the crystal structure of the product composition is retained after the rigorous hydrothermal treatment involved, infrared analysis indicated the presence of substantial hydroxyl groups exhibiting a stretching frequency in the area of about 3740, 3640 and 3550 cm⁻¹. The infrared analytical data of U.S. Pat. No. 3,506,400 is especially instructive in this regard. An explanation of the mechanism of the creation of these hydroxyl groups is provided by Kerr et al. in U.S. Pat. No. 3,493,519 wherein the patentees state that the aluminum atoms in the lattice framework of hydrogen zeolites can react with water resulting in the removal of aluminum from the lattice in accordance with the following equation:



The aluminum removed from its original lattice position is capable of further reaction with cationic hydrogen, according to Kerr et al. to yield aluminum-containing i.e. hydroxoaluminum, cations by the equation:



It has been suggested that stabilization of NH₄Y occurs through hydrolysis of sufficient framework aluminum to form stable clusters of these hydroxoaluminum cations within the sodalite cages, thereby holding the zeolite structure together while the framework anneals itself through the migration of some of the framework silicon atoms.

It is alleged in U.S. Pat. No. 3,594,331, issued July 20, 1971 to C. H. Elliott, that fluoride ions in aqueous media, particularly under conditions in which the pH is less than about 7, are quite effective in extracting framework aluminum from zeolite lattices, and in fact when the fluoride concentration exceeds about 15 grams active fluoride per 10,000 grams of zeolite, destruction of the crystal lattice by the direct attack on the framework silicon as well as on the framework aluminum, can result. A fluoride treatment of this type using from 2 to 22 grams of available fluoride per 10,000 grams of zeolite (anhydrous) in which the fluorine is provided by ammonium fluorosilicate is also described therein. The treatment is carried out for the purpose of improving the thermal stability of the zeolite. It is theorized by the

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