

[54] **ZEOLITE SSZ-13 AND ITS METHOD OF PREPARATION**  
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 [73] Assignee: **Chevron Research Company**, San Francisco, Calif.  
 [21] Appl. No.: **519,954**  
 [22] Filed: **Aug. 3, 1983**

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**Related U.S. Application Data**

[63] Continuation-in-part of Ser. No. 397,007, Jul. 9, 1982, abandoned.

[51] Int. Cl.<sup>4</sup> ..... **C01B 33/20**

[52] U.S. Cl. .... **423/326; 423/328; 423/329; 502/60; 502/61; 502/62; 502/77**

[58] Field of Search ..... **423/328, 329, 326; 502/60-62**

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*Primary Examiner*—John Doll

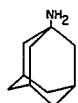
*Assistant Examiner*—Jackson Leeds

*Attorney, Agent, or Firm*—S. R. LaPaglia; W. K. Turner; V. J. Cavalieri

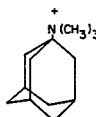
[57] **ABSTRACT**

A crystalline zeolite, SSZ-13, is prepared from organic nitrogen-containing cations derived from 1-adamantamine, 3-quinuclidinol, and 2-exo-aminonorbornane,

**10 Claims, 1 Drawing Figure**



1-ADAMANTAMINE



TEMPLATE A



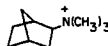
3-QUINUCLIDINOL



TEMPLATE B

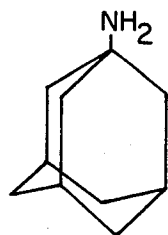


2-EXO-AMINONORBORNANE

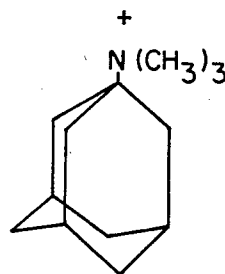


TEMPLATE C

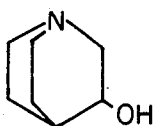
FIG. 1.



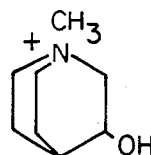
1-ADAMANTAMINE



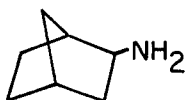
TEMPLATE A



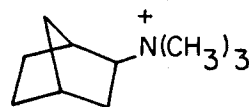
3-QUINUCLIDINOL



TEMPLATE B



2-EXO-AMINONORBORNANE



TEMPLATE C

## ZEOLITE SSZ-13 AND ITS METHOD OF PREPARATION

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation-in-part of my co-pending application Ser. No. 397,007, filed on July 9, 1982 now abandoned, the disclosure of which is incorporated herein by specific reference.

### TECHNICAL FIELD

Natural and synthetic aluminosilicates are important and useful compositions. Many of these aluminosilicates are porous and have definite, distinct crystal structures as determined by X-ray diffraction. Within the crystals are a large number of cavities and pores whose dimensions and shapes vary from zeolite to zeolite. Variations in pore dimensions and shapes cause variations in the adsorptive and catalytic properties of the zeolites. Only molecules of certain dimensions and shapes are able to fit into the pores of a particular zeolite while other molecules of larger dimensions or different shapes are unable to penetrate the zeolite crystals.

Because of their unique molecular sieving characteristics, as well as their potentially acidic nature, zeolites are especially useful in hydrocarbon processing as adsorbents, and, as catalysts, for cracking, reforming, and other hydrocarbon conversion reactions. Although many different crystalline aluminosilicates have been prepared and tested, the search for new zeolites which can be used in hydrocarbon and chemical processing continues.

I have discovered a novel family of crystalline aluminosilicate zeolites, hereinafter designated "Zeolite SSZ-13" or simply "SSZ-13", and methods for their preparation and use.

In recent years, many crystalline aluminosilicates having desirable adsorption and catalytic properties have been prepared. Typically, zeolites are prepared from reaction mixtures having sources of alkali or alkaline earth metal oxides, silica, and alumina. More recently, "nitrogenous zeolites" have been prepared from reaction mixtures containing an organic species, usually a nitrogen compound. Depending upon the reaction conditions and the composition of the reaction mixture, different zeolites can be formed even if the same organic species are used. For example, zeolites ZK-4, ZSM-4, faujasite and PHI, have all been prepared from solutions containing tetramethylammonium cations.

Although most experiments reported as producing nitrogenous zeolites have used fairly simple organic species such as tetraalkylammonium cations or alkylenediamines, several experiments are reported as using more complex organic species. U.S. Pat. No. 3,692,470, Ciric, Sept. 19, 1972, discloses preparing ZSM-10 from 1,4-dimethyl-1,4-diazoniabicyclo[2.2.2]octane. U.S. Pat. No. 3,832,449, Rosinski et al., Aug. 27, 1974, discloses preparing ZSM-12 from the reaction products of alkylene dihalides with complex amines or nitrogen heterocycles. U.S. Pat. No. 3,950,496, Ciric, Apr. 13, 1976, discloses preparing ZSM-18 from "tris" ammonium hydroxide (1,3,4,6,7,9-hexahydro-2,2,5,5,8,8-hexamethyl-2H-benzo-[1,2-C:3,4-C':5,6-C'']tripyrolium trihydroxide). U.S. Pat. No. 4,018,870, Whittam, Apr. 19, 1977, discloses preparing AG5 and AG6 using nitrogenous basic dyes. And, U.S. Pat. No. 4,285,922, Audeh, Aug. 25, 1981, discloses preparing

ZSM-5 using 1-alkyl, 4 aza, 1-azonia-bicyclo(2,2,2)octane, 4-oxide halides.

Chabazite is a natural zeolite with the approximate formula  $\text{Ca}_6\text{Al}_{12}\text{Si}_{24}\text{O}_{72}$ . Three synthetic forms of chabazite are described in "Zeolite Molecular Sieves", by D. W. Breck, published in 1973 by John Wiley & Sons, the complete disclosure of which is incorporated herein by specific reference. This publication is referred to herein as "Breck". The three synthetic forms reported by Breck are: Zeolite "K-G", described in J. Chem. Soc., p. 2822 (1956), Barrer et al; Zeolite D, described in British Patent No. 868,846 (1961); and Zeolite R, described in U.S. Pat. No. 3,030,181 (1962). Chabazite is also discussed in "Atlas of Zeolite Structure Types" (1978) by W. H. Meier and D. H. Olson.

The K-G zeolite material reported in the J. Chem. Soc. article by Barrer et al is a potassium form having a silica:alumina mole ratio of 2.3:1 to 4.15:1. The zeolite D material reported in British Patent No. 868,846 is a sodium-potassium form having a silica:alumina mole ratio of 4.5:1 to 4.9:1. The zeolite R material reported in U.S. Pat. No. 3,030,181 is a sodium form which has a silica:alumina mole ratio of 3.45:1 to 3.65:1.

Citation No. 93:66052y, in Volume 93 (1980) of Chemical Abstracts, concerns a Russian Language article by Tsitsishrili et al in *Soobshch. Akad. Nauk. Gruz.*, SSR 1980, 97(3) 621-4.

This article teaches that the presence of tetramethylammonium ions in a reaction mixture containing  $\text{K}_2\text{O}-\text{Na}_2\text{O}-\text{SiO}_2-\text{Al}_2\text{O}_3-\text{H}_2\text{O}$  promotes the crystallization of chabazite. In the absence of the tetramethylammonium ion in the reaction mixture, phillipsite is obtained. The zeolite obtained by the crystallization procedure has a  $\text{SiO}_2:\text{Al}_2\text{O}_3$  mole ratio of 4.23. The article states that the tetramethylammonium ion has a great influence on the direction of crystallization of the reaction mixture, although it may not even enter into the composition of the zeolites.

### TECHNICAL DISCLOSURE

My invention is a zeolite having a mole ratio of an oxide selected from silicon oxide, germanium oxide, and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, and mixtures thereof greater than about 5:1 and having the X-ray diffraction lines of Table 1. The zeolite further has a composition, as synthesized and in the anhydrous state, in terms of mole ratios of oxides as follows:  $(0.5 \text{ to } 1.4)\text{R}_2\text{O}:(0 \text{ to } 0.50)\text{M}_2\text{O}:\text{W}_2\text{O}_3$ : (greater than 5) $\text{YO}_2$  wherein M is an alkali metal cation, W is selected from aluminum, gallium, and mixtures thereof, Y is selected from silicon, germanium and mixtures thereof, and R is an organic cation. SSZ-13 zeolites can have a  $\text{YO}_2:\text{W}_2\text{O}_3$  mole ratio greater than about 5:1. As prepared, the silica:alumina mole ratio is typically in the range of 8:1 to about 50:1; higher mole ratios can be obtained by varying the relative ratios of reactants. Higher mole ratios can also be obtained by treating the zeolite with chelating agents or acids to extract aluminum from the zeolite lattice. The silica:alumina mole ratio can also be increased by using silicon and carbon halides and similar compounds. Preferably, SSZ-13 is an aluminosilicate wherein W is aluminum and Y is silicon.

My invention also involves a method for preparing SSZ-13 zeolites, comprising preparing an aqueous mixture containing sources of an organic nitrogen-containing compound, an oxide selected from aluminum oxide,

Exhibit 2035.003

gallium oxide, and mixtures thereof, and an oxide selected from silicon oxide, germanium oxide, and mixtures thereof, and having a composition, in terms of mole ratios of oxides, falling within the following ranges:  $YO_2/W_2O_3$ , 5:1 to 350:1; and  $R_2O/W_2O_3$  0.5:1 to 40:1; wherein Y is selected from silicon, germanium, and mixtures thereof, W is selected from aluminum, gallium and mixtures thereof, and R is an organic cation; maintaining the mixture at a temperature of at least 100° C. until the crystals of said zeolite are formed; and recovering said crystals.

In a preferred embodiment, the SSZ-13 contains silica, and is prepared from a reaction mixture which includes colloidal silica. I have found that use of an aqueous colloidal suspension of silica in the reaction mixture to provide a silica source allows production of SSZ-13 having a relatively high silica:alumina mole ratio, and that use of colloidal silica in the reaction mixture also allows a relatively smaller concentration of hydroxide ion to be present in the reaction mixture. Preferably, the silica source is an aqueous silica suspension such as Ludox AS-30, a commercially available colloidal silica suspension.

Uncalcined SSZ-13 zeolites, as prepared (with the organic templating component present in the crystal structure), have a crystalline structure whose X-ray powder diffraction pattern shows the characteristic lines shown in Table 1 below:

TABLE 1

$2\theta$	d(A)	100 I/I <sub>0</sub>
9.57	9.24	61
14.06	6.30	21
16.23	5.46	80
17.82	4.98	24
20.87	4.26	100
22.14	4.01	9
22.72	3.91	8
25.01	3.56	69
26.30	3.589	18
31.00	2.885	47
31.29	2.859	21

The X-ray diffraction pattern of SSZ-13 is completely indexed on a rhombohedral lattice. SSZ-13 has been found to possess the crystal structure of chabazite. The rhombohedral unit cell of SSZ-13 shows significant change between the as-prepared condition (with the organic templating component present in the structure) and the condition after calcination. The rhombohedral lattice provides appreciable flexibility. With the organic templating species present in the crystal structure, the volume of the unit cell is 7 cubic Angstroms (one percent) larger than the volume of the unit cell after calcination. Calcined SSZ-13 zeolites have a crystal structure whose X-ray diffraction pattern shows the characteristic lines shown in Table 2 below:

TABLE 2

$2\theta$	d(A)	100 I/I <sub>0</sub>
9.62	9.19	100
13.04	6.79	32
16.22	5.46	18
18.00	4.93	16
20.87	4.26	50
23.36	3.808	6
25.23	3.530	18
26.26	3.394	11
31.02	2.883	27
31.44	2.846	13

The X-ray powder diffraction patterns were determined by standard techniques. The radiation was the K-alpha/doublet of copper and a scintillation counter spectrometer with a strip-chart pen recorder was used. The peak heights I and their positions, in degrees,  $2\theta$ , where  $\theta$  is the Bragg angle, were read from the spectrometer chart. From these measured values, the relative intensities,  $100 I/I_0$ , where  $I_0$  is the intensity of the strongest line or peak, and d, the interplanar spacing in Angstroms corresponding to the recorded lines, can be calculated. The X-ray diffraction pattern of Tables 1 and 2 is characteristic of all species of SSZ-13 family compositions. The zeolite produced by exchanging the metal or other cations present in the zeolite with various other cations yields substantially the same diffraction pattern as is given in Table 2, although there can be minor shifts in interplanar spacing and variations in relative intensity. Minor variations in the diffraction pattern given in Tables 1 and 2 can also result from variations in the organic compound used in the preparation and from variations in the silica-to-alumina mole ratio from sample to sample. Notwithstanding these minor perturbations, the basic crystal structures for the as-prepared condition and the calcined condition remain substantially unchanged.

SSZ-13 zeolites can be suitably prepared from an aqueous solution containing sources of an alkali metal oxide, an organic compound, an oxide of aluminum or gallium, or mixture of the two, and an oxide of silicon or germanium, or mixture of the two. The reaction mixture should have a composition in terms of mole ratios of oxides falling within the following ranges:

	Broad	Preferred
$YO_2/W_2O_3$	5-350	12-200
$M_2O/W_2O_3$	0.5-20	1-17
$R_2O/W_2O_3$	0.5-40	5-25
$MCl/W_2O_3$	20-200	50-150

wherein R is as disclosed below, Y is silicon, germanium or both, and W is aluminum, gallium or both. M is an alkali metal, preferably sodium or potassium. Typically, an alkali metal hydroxide or alkali metal halide is used in the reaction mixture; however, these components can be omitted so long as the equivalent basicity is maintained. The organic compound can provide hydroxide ion. The  $OH^-/YO_2$  mole ratio to produce SSZ-13 having silica:alumina mole ratios of less than about 20:1 is above about 0.95 and is preferably in the range of 0.95 to 1.10. To prepare high silica content SSZ-13, the  $OH^-/YO_2$  mole ratio is below about 0.95.

The organic component of the crystallization mixture is typically a bicyclo heteroatom compound. The heteroatom is preferably nitrogen. The preferred organic species are derivatives of either 1-adamantamine, 3-quinuclidinol, or 2-exo-aminonorborene. The quaternary lower alkylammonium cation derivatives of these compounds are especially preferred. Methyl and other lower alkyl derivatives can be made using standard synthetic procedures.

The reaction mixture is prepared using standard zeolitic preparation techniques. Typical sources of aluminum oxide for the reaction mixture include aluminates, alumina, and aluminum compounds such as  $AlCl_3$  and  $Al_2(SO_4)_3$ . Typical sources of silicon oxide include silicates, silica hydrogel, silicic acid, colloidal silica, tetraalkyl orthosilicates, and silica hydroxides. Gallium

and germanium can be added in forms corresponding to their aluminum and silicon counterparts. Salts, particularly alkali metal halides such as sodium chloride, can be added to or formed in the reaction mixture. They are disclosed in the literature as facilitating the crystallization of zeolites while preventing silica occlusion in the lattice.

The reaction mixture is maintained at an elevated temperature until the crystals of the zeolite are formed. The temperatures during the hydrothermal crystallization step are typically maintained from about 100° C. to about 235° C., preferably from about 120° C. to about 200° C. and most preferably from about 130° C. to about 165° C. The crystallization period is typically greater than 3 days and preferably from about 7 days to about 50 days.

The hydrothermal crystallization is conducted under pressure and usually in an autoclave so that the reaction mixture is subject to autogenous pressure. The reaction mixture can be stirred during crystallization.

Once the zeolite crystals have formed, the solid product is separated from the reaction mixture by standard mechanical separation techniques such as filtration. The crystals are water-washed and then dried, e.g., at 90° C. to 150° C. for from 8 to 24 hours, to obtain the as synthesized, SSZ-13 zeolite crystals. The drying step can be performed at atmospheric or subatmospheric pressures.

During the hydrothermal crystallization step, the SSZ-13 crystals can be allowed to nucleate spontaneously from the reaction mixture. The reaction mixture can also be seeded with SSZ-13 crystals both to direct, and accelerate the crystallization, as well as to minimize the formation of undesired aluminosilicate contaminants. If the reaction mixture is seeded with SSZ-13 crystals, the concentration of the organic compound can be greatly reduced or eliminated, but it is preferred to have some organic compound present, e.g., an alcohol.

The synthetic SSZ-13 zeolites can be used as synthesized or can be thermally treated (calcined). Usually, it is desirable to remove the alkali metal cation by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion. The zeolite can be leached with chelating agents, e.g., EDTA, or dilute acid solutions to increase the silica:alumina mole ratio. I have found that SSZ-13 synthesized with a relatively high silica:alumina mole ratio is more active for a cracking activity micro-test than SSZ-13 synthesized with a relatively lower silica:alumina mole ratio and subsequently acid leached with HCl to raise its silica:alumina mole ratio to the same relatively high level. The zeolite can also be steamed; steaming stabilizes the crystalline lattice to attack from acids. The zeolite can be used in intimate combination with hydrogenating components, such as tungsten, vanadium, molybdenum, rhenium, nickel, cobalt, chromium, manganese, or a noble metal, such as palladium or platinum, for those applications in which a hydrogenation-dehydrogenation function is desired. Typical replacing cations can include metal cations, e.g., rare earth, Group IIA and Group VIII metals, as well as their mixtures. Of the replacing metallic cations, cations of metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, Fe and Co are particularly preferred.

The hydrogen, ammonium, and metal components can be exchanged into the zeolite. The zeolite can also be impregnated with the metals, or, the metals can be

physically intimately admixed with the zeolite using standard methods known to the art. And, the metals can be occluded in the crystal lattice by having the desired metals present as ions in the reaction mixture from which the SSZ-13 zeolite is prepared.

Typical ion exchange techniques involve contacting the synthetic zeolite with a solution containing a salt of the desired replacing cation or cations. Although a wide variety of salts can be employed, chlorides and other halides, nitrates, and sulfates are particularly preferred. Representative ion exchange techniques are disclosed in a wide variety of patents including U.S. Pat. Nos. 3,140,249; 3,140,251; and 3,140,253. Ion exchange can take place either before or after the zeolite is calcined.

Following contact with the salt solution of the desired replacing cation, the zeolite is typically washed with water and dried at temperatures ranging from 65° C. to about 315° C. After washing, the zeolite can be calcined in air or inert gas at temperatures ranging from about 200° C. to 820° C. for periods of time ranging from 1 to 48 hours, or more, to produce a catalytically active product especially useful in hydrocarbon conversion processes.

Regardless of the cations present in the synthesized form of the zeolite, the spatial arrangement of the atoms which form the basic crystal lattice of the zeolite remains essentially unchanged. The exchange of cations has little, if any, effect on the zeolite lattice structure.

The SSZ-13 aluminosilicate can be formed into a wide variety of physical shapes. Generally speaking, the zeolite can be in the form of a powder, a granule, or a molded product, such as extrudate having particle size sufficient to pass through a 2-mesh (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by extrusion with an organic binder, the aluminosilicate can be extruded before drying, or, dried or partially dried and then extruded.

The zeolite can be composited with other materials resistant to the temperatures and other conditions employed in organic conversion processes. Such matrix materials include active and inactive materials and synthetic or naturally occurring zeolites as well as inorganic materials such as clays, silica and metal oxides. The latter may occur naturally or may be in the form of gelatinous precipitates, sols or gels including mixtures of silica and metal oxides. Use of an active material in conjunction with the synthetic zeolite, i.e., combined therewith, tends to improve the conversion and selectivity of the catalyst in certain organic conversion processes. Inactive materials can serve as diluents to control the amount of conversion in a given process so that products can be obtained economically without using other means for controlling the rate of reaction. Frequently, zeolite materials have been incorporated into naturally occurring clays, e.g., bentonite and kaolin. These materials, i.e., clays, oxides, etc., function, in part, as binders for the catalyst. It is desirable to provide a catalyst having good crush strength, because in petroleum refining the catalyst is often subjected to rough handling. This tends to break the catalyst down into powder-like materials which cause problems in processing.

Naturally occurring clays which can be composited with the synthetic zeolites of this invention include the montmorillonite and kaolin families, which families include the sub-bentonites, and the kaolins, in which the main mineral constituent is halloysite, kaolinite, dickite,

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