

1 **MOLECULAR SIEVE SSZ-61 COMPOSITION OF MATTER**
2 **AND SYNTHESIS THEREOF**

3
4 **BACKGROUND OF THE INVENTION**

5
6 **Field of the Invention**

7 The present invention relates to new crystalline molecular sieve SSZ-61, a
8 method for preparing SSZ-61 using a family of tetracyclic azonia cations as a
9 structure directing agent and the use of SSZ-61 as an adsorbent.

10
11 **State of the Art**

12 Because of their unique sieving characteristics, as well as their catalytic
13 properties, crystalline molecular sieves and zeolites are especially useful in
14 applications such as hydrocarbon conversion, gas drying and separation. Although
15 many different crystalline molecular sieves have been disclosed, there is a continuing
16 need for new zeolites with desirable properties for gas separation and drying,
17 hydrocarbon and chemical conversions, and other applications. New zeolites may
18 contain novel internal pore architectures, providing enhanced selectivities in these
19 processes.

20 Crystalline aluminosilicates are usually prepared from aqueous reaction
21 mixtures containing alkali or alkaline earth metal oxides, silica, and alumina.
22 Crystalline borosilicates are usually prepared under similar reaction conditions except
23 that boron is used in place of aluminum. By varying the synthesis conditions and the
24 composition of the reaction mixture, different zeolites can often be formed.

25
26 **SUMMARY OF THE INVENTION**

27
28 The present invention is directed to a family of crystalline molecular sieves
29 with unique properties, referred to herein as "molecular sieve SSZ-61" or simply
30 "SSZ-61". Preferably, SSZ-61 is obtained in its silicate, aluminosilicate,
31 titanosilicate, germanosilicate, vanadosilicate, ferrosilicate or borosilicate form. The
32 term "silicate" refers to a molecular sieve having a high mole ratio of silicon oxide
33 relative to aluminum oxide, preferably a mole ratio greater than 100, including

1 molecular sieves comprised entirely of silicon oxide. As used herein, the term
 2 "aluminosilicate" refers to a molecular sieve containing both aluminum oxide and
 3 silicon oxide and the term "borosilicate" refers to a molecular sieve containing oxides
 4 of both boron and silicon.

In a first aspect, there is provided a molecular sieve having a mole ratio greater than
 about 15 of an oxide of a first tetravalent element to an
 7 oxide of a trivalent element, pentavalent element, second tetravalent element different
 8 from said first tetravalent element or mixture thereof and having, after calcination, the
 9 X-ray diffraction lines of Table I.

In a second aspect, there is provided a molecular sieve having a mole ratio greater than
 about 15 of an oxide selected from the group consisting of silicon oxide, germanium oxide and
 mixtures thereof to an oxide selected from aluminum oxide,
 13 gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide, vanadium oxide
 14 and mixtures thereof and having, after calcination, the X-ray diffraction lines of Table
 15 I below. It should be noted that the mole ratio of the first oxide or mixture of first
 16 oxides to the second oxide can be infinity, i.e., there is no second oxide in the
 17 molecular sieve. In these cases, the molecular sieve is an all-silica molecular sieve or
 18 a germanosilicate.

Disclosed herein is a molecular sieve having a
 20 composition, as synthesized and in the anhydrous state, in terms of mole ratios as
 21 follows:

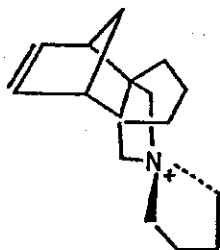
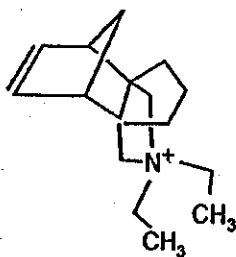
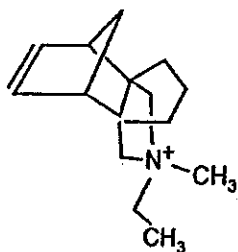
22	YO_2/W_cO_d	15 - ∞
23	$M_{2/n}/YO_2$	0 - 0.03
24	Q/YO_2	0.02 - 0.08
25	F/YO_2	0 - 0.10

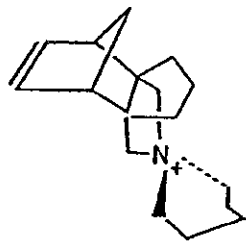
26 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium, iron,
 27 boron, titanium, indium, vanadium or mixtures thereof; c is 1 or 2; d is 2 when c is 1
 28 (i.e., W is tetravalent) or d is 3 or 5 when c is 2 (i.e., d is 3 when W is trivalent or 5
 29 when W is pentavalent); M is an alkali metal cation, alkaline earth metal cation or
 30 mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a tetracyclic azonia
 31 cation.

In a third aspect, there is provided a molecular sieve having a composition, as synthesized and in the anhydrous state, in terms of mole ratios as follows:

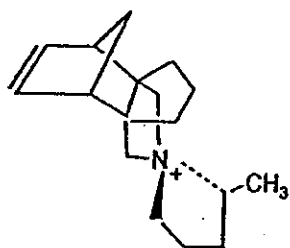
YO_2/W_cO_d	15-∞
M_{2n}/YO_2	0 - 0.03
Q/YO_2	0.02 - 0.08
F/YO_2	0 - 0.10

wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium, iron, boron, titanium, indium, vanadium or mixtures thereof; c is 1 or 2; d is 2 when c is 1 or d is 3 or 5 when c is 2; M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M; and Q is a cation selected from the group consisting of the following:





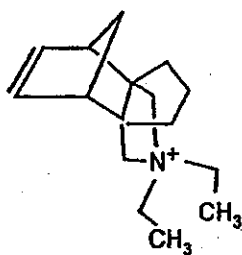
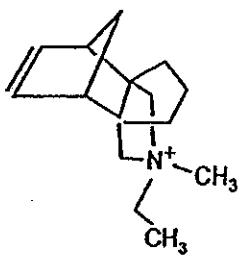
and

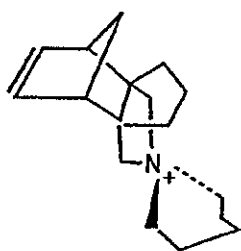
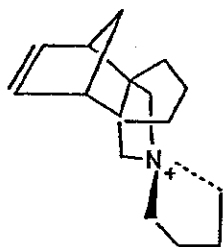


Also disclosed herein is a method of
preparing a crystalline material comprising (1) an oxide of a first tetravalent element

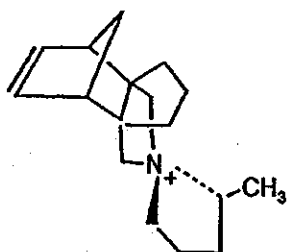
and (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element, or mixture thereof and having a mole ratio of the first oxide to the second oxide greater than 15, said method comprising contacting under crystallization conditions sources of said oxides and a structure directing agent comprising a tetracyclic azonia cation.

In a fourth aspect, there is provided a method of preparing a crystalline material comprising an oxide of a first tetravalent element and an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, said method comprising contacting under crystallization conditions sources of said oxides and a structure directing agent comprising a cation selected from the group consisting of the following:





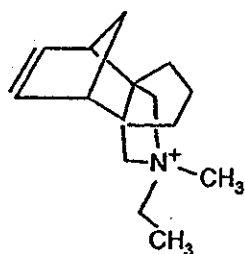
and



DETAILED DESCRIPTION OF THE INVENTION

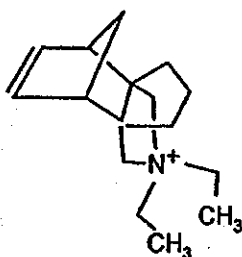
The present invention comprises a family of crystalline, large pore molecular sieves designated herein "molecular sieve SSZ-61" or simply "SSZ-61". As used herein, the term "large pore" means having an average pore size diameter greater than about 6.0 Angstroms, preferably from about 6.5 Angstroms to about 7.5 Angstroms or larger.

In preparing SSZ-61, a tetracyclic azonia cation is used as a structure directing agent ("SDA"), also known as a crystallization template. The SDA's useful for making SSZ-61 have the following structures:

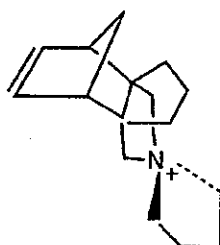


Template A

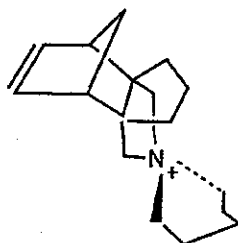
8-azonia-8-ethyl-8-methyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene



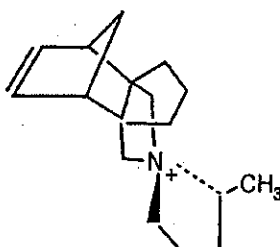
Template B

1
2
3
48-azonia-8, 8-diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene

Template C

5
6
7
81-azoniapentacyclo[8.-1.4.3^{3,8}.1^{4,7}.0^{3,8}]heptadec-5-ene

Template D

9
10
111-azoniapentacyclo[8.-1.5.3^{3,8}.1^{4,7}.0^{3,8}]octadec-5-ene

Template E

12
13
141-azonia-13-methylpentacyclo[8.-1.4.3^{3,8}.1^{4,7}.0^{3,8}]heptadec-5-ene

The SDA cation is associated with an anion (X^-) which may be any anion that is not detrimental to the formation of the zeolite. Representative anions include halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is the most preferred anion.

In general, SSZ-61 is prepared by contacting an active source of one or more oxides selected from the group consisting of monovalent element oxides, divalent element oxides, trivalent element oxides, tetravalent element oxides and/or pentavalent elements with the tetracyclic azonia cation SDA.

SSZ-61 is prepared from a reaction mixture having the composition shown in Table A below.

TABLE A

Reaction Mixture

	Typical	Preferred
YO_2/W_aO_b	> 15	-100 - ∞
$OH-/YO_2$	0.20 - 0.80	0.40 - 0.60
Q/YO_2	0.20 - 0.80	0.40 - 0.60
M_{2n}/YO_2	0 - 0.40	0 - 0.25
H_2O/YO_2	10 - 80	-15 - 25
HF/YO_2	0.20 - 0.80	0.30 - 0.60

where Y, W, Q, M and n are as defined above, and a is 1 or 2, and b is 2 when a is 1 (i.e., W is tetravalent) and b is 3 when a is 2 (i.e., W is trivalent).

In practice, SSZ-61 is prepared by a process comprising:

(a) preparing an aqueous solution containing sources of at least one oxide capable of forming a crystalline molecular sieve and a tetracyclic azonia cation capable of forming SSZ-61 having an anionic counterion which is not detrimental to the formation of SSZ-61;

(b) maintaining the aqueous solution under conditions sufficient to form crystals of SSZ-61; and

(c) recovering the crystals of SSZ-61.

Accordingly, SSZ-61 may comprise the crystalline material and the SDA in combination with metallic and non-metallic oxides bonded in tetrahedral coordination through shared oxygen atoms to form a cross-linked three dimensional crystal structure. The metallic and non-metallic oxides comprise one or a combination of

1 oxides of a first tetravalent element(s), and one or a combination of a trivalent
2 element(s), pentavalent element(s), second tetravalent element(s) different from the
3 first tetravalent element(s) or mixture thereof. The first tetravalent element(s) is
4 preferably selected from the group consisting of silicon, germanium and combinations
5 thereof. More preferably, the first tetravalent element is silicon. The trivalent
6 element, pentavalent element and second tetravalent element (which is different from
7 the first tetravalent element) is preferably selected from the group consisting of
8 aluminum, gallium, iron, boron, titanium, indium, vanadium and combinations
9 thereof. More preferably, the second trivalent or tetravalent element is aluminum or
10 boron.

11 Typical sources of aluminum oxide for the reaction mixture include
12 aluminates, alumina, aluminum colloids, aluminum oxide coated on silica sol,
13 hydrated alumina gels such as $\text{Al}(\text{OH})_3$ and aluminum compounds such as $\text{Al}(\text{NO}_3)_3$,
14 AlCl_3 and $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include silicates, silica
15 hydrogel, silicic acid, fumed silica, colloidal silica, tetra-alkyl orthosilicates, and
16 silica hydroxides. Boron, as well as gallium, germanium, titanium, indium, vanadium
17 and iron, can be added in forms corresponding to their aluminum and silicon
18 counterparts.

19 A source zeolite reagent may provide a source of aluminum or boron. In most
20 cases, the source zeolite also provides a source of silica. The source zeolite in its
21 dealuminated or deboronated form may also be used as a source of silica, with
22 additional silicon added using, for example, the conventional sources listed above.
23 Use of a source zeolite reagent as a source of alumina for the present process is more
24 completely described in U.S. Patent No. 5,225,179, issued July 6, 1993 to Nakagawa
25 entitled "Method of Making Molecular Sieves", the disclosure of which is
26 incorporated herein by reference.

27 Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide,
28 such as the hydroxide of sodium, potassium, lithium, cesium, rubidium, calcium, and
29 magnesium, is used in the reaction mixture; however, this component can be omitted
30 so long as the equivalent basicity is maintained. The SDA may be used to provide
31 hydroxide ion. Thus, it may be beneficial to ion exchange, for example, the halide to
32 hydroxide ion, thereby reducing or eliminating the alkali metal hydroxide quantity
33 required. The alkali metal cation or alkaline earth cation may be part of the

1 as-synthesized crystalline oxide material, in order to balance valence electron charges
2 therein.

3 The reaction mixture is maintained at an elevated temperature until the
4 crystals of the SSZ-61 are formed. The hydrothermal crystallization is usually
5 conducted under autogenous pressure, at a temperature between 100°C and 200°C,
6 preferably between 135°C and 160°C. The crystallization period is typically greater
7 than 1 day and preferably from about 3 days to about 20 days.

8 Preferably, the molecular sieve is prepared using mild stirring or agitation.

9 During the hydrothermal crystallization step, the SSZ-61 crystals can be
10 allowed to nucleate spontaneously from the reaction mixture. The use of SSZ-61
11 crystals as seed material can be advantageous in decreasing the time necessary for
12 complete crystallization to occur. In addition, seeding can lead to an increased purity
13 of the product obtained by promoting the nucleation and/or formation of SSZ-61 over
14 any undesired phases. When used as seeds, SSZ-61 crystals are added in an amount
15 between 0.1 and 10% of the weight of first tetravalent element oxide, e.g. silica, used
16 in the reaction mixture.

17 Once the molecular sieve crystals have formed, the solid product is separated
18 from the reaction mixture by standard mechanical separation techniques such as
19 filtration. The crystals are water-washed and then dried, e.g., at 90°C to 150°C for
20 from 8 to 24 hours, to obtain the as-synthesized SSZ-61 crystals. The drying step can
21 be performed at atmospheric pressure or under vacuum.

22 SSZ-61 as prepared has a mole ratio of an oxide selected from silicon oxide,
23 germanium oxide and mixtures thereof to an oxide selected from aluminum oxide,
24 gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide, vanadium oxide
25 and mixtures thereof greater than about 15; and has, after calcination, the X-ray
26 diffraction lines of Table I below. SSZ-61 further has a composition, as synthesized
27 (i.e., prior to removal of the SDA from the SSZ-61) and in the anhydrous state, in
28 terms of mole ratios, shown in Table B below.

29 TABLE B

30 As-Synthesized SSZ-61

31	YO_2/W_cO_d	15 - ∞
32	$M_{2/n}/YO_2$	0 - 0.03
33	Q/YO_2	0.02 - 0.08

1 F/YO_2 0 – 0.10

2 where Y, W, c, d, M, n and Q are as defined above.

3 SSZ-61 can be made with a mole ratio of YO_2/W_cO_d of ∞ , i.e., there is
 4 essentially no W_cO_d present in the SSZ-61. In this case, the SSZ-61 would be an all-
 5 silica material or a germanosilicate. Thus, in a typical case where oxides of silicon
 6 and, optionally, germanium are used, SSZ-61 can be made essentially aluminum free,
 7 i.e., having a silica to alumina mole ratio of ∞ . A method of increasing the mole ratio
 8 of silica to alumina is by using standard acid leaching or chelating treatments.
 9 However, essentially aluminum-free SSZ-61 can be synthesized using essentially
 10 aluminum-free silicon sources as the main tetrahedral metal oxide component, if
 11 boron is also present. The boron can then be removed, if desired, by treating the
 12 borosilicate SSZ-61 with acetic acid at elevated temperature (as described in Jones et
 13 al., *Chem. Mater.*, 2001, 13, 1041-1050) to produce an all-silica version of SSZ-61.
 14 SSZ-61 can also be prepared directly as a borosilicate. If desired, the boron can be
 15 removed as described above and replaced with metal atoms by techniques known in
 16 the art.

17 Lower silica to alumina ratios may also be obtained by using methods which
 18 insert aluminum into the crystalline framework. For example, aluminum insertion
 19 may occur by thermal treatment of the zeolite in combination with an alumina binder
 20 or dissolved source of alumina. Such procedures are described in U.S. Patent
 21 No. 4,559,315, issued on December 17, 1985 to Chang et al.

22 It is believed that SSZ-61 is comprised of a new framework structure or
 23 topology which is characterized by its X-ray diffraction pattern. SSZ-61, after
 24 calcination, has a crystalline structure whose X-ray powder diffraction pattern exhibit
 25 the characteristic lines shown in Table I and is thereby distinguished from other
 26 molecular sieves.

27 TABLE I

28 Calcined SSZ-61

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)^(b)</u>
4.48	19.7	S
7.24	12.2	VS
9.23	9.6	W

10.08	8.8	W-M
13.94	6.4	W
17.90	4.96	W
20.68	4.30	VS
21.70	4.10	W
23.37	3.80	W
25.40	3.51	W-M
35.48	2.53	W

^(a) ± 0.1

^(b) The X-ray patterns provided are based on a relative intensity scale in which the strongest line in the X-ray pattern is assigned a value of 100: W(weak) is less than 20; M(medium) is between 20 and 40; S(strong) is between 40 and 60; VS(very strong) is greater than 60.

Table IA below shows the X-ray powder diffraction lines for calcined SSZ-61 including actual relative intensities.

TABLE IA
Calcined SSZ-61

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
4.48	19.7	47
7.24	12.2	100
9.23	9.6	13
10.08	8.8	21
13.94	6.4	7
17.90	4.96	11
18.28	4.85	12
18.68	4.75	7
19.72	4.5	12
20.68	4.30	84
21.70	4.10	18
23.37	3.80	12
24.13	3.69	6
25.40	3.51	19

25.62	3.48	17
26.64	3.35	17
35.48	2.53	10

1 ^(a) ± 0.1

2 The X-ray powder diffraction patterns were determined by standard
3 techniques. The radiation was the K-alpha/doublet of copper. The peak heights and
4 the positions, as a function of 2θ where θ is the Bragg angle, were read from the
5 relative intensities of the peaks, and d, the interplanar spacing in Angstroms
6 corresponding to the recorded lines, can be calculated.

7 The variation in the scattering angle (two theta) measurements, due to
8 instrument error and to differences between individual samples, is estimated at
9 ± 0.1 degrees.

10 Representative peaks from the X-ray diffraction pattern of calcined SSZ-61
11 are shown in Table I. Calcination can result in changes in the intensities of the peaks
12 as compared to patterns of the "as-made" material, as well as minor shifts in the
13 diffraction pattern. The molecular sieve produced by exchanging the metal or other
14 cations present in the molecular sieve with various other cations (such as H^+ or NH_4^+)
15 yields essentially the same diffraction pattern, although again, there may be minor
16 shifts in the interplanar spacing and variations in the relative intensities of the peaks.
17 Notwithstanding these minor perturbations, the basic crystal lattice remains
18 unchanged by these treatments.

19 Crystalline SSZ-61 can be used as-synthesized, but preferably will be
20 thermally treated (calcined). Usually, it is desirable to remove the alkali metal cation
21 by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion.
22 The molecular sieve can be leached with chelating agents, e.g., EDTA or dilute acid
23 solutions, to increase the silica to alumina mole ratio. The molecular sieve can also
24 be steamed; steaming helps stabilize the crystalline lattice to attack from acids.

25 Metals may be introduced into the molecular sieve by replacing some of the
26 cations in the molecular sieve with metal cations via standard ion exchange
27 techniques (see, for example, U.S. Patent Nos. 3,140,249 issued July 7, 1964 to Plank
28 et al.; 3,140,251 issued July 7, 1964 to Plank et al.; and 3,140,253 issued July 7, 1964
29 to Plank et al.). Typical replacing cations can include metal cations, e.g., rare earth,

1 Group IA, Group IIA and Group VIII metals, as well as their mixtures. Of the
2 replacing metallic cations, cations of metals such as rare earth, Mn, Ca, Mg, Zn, Cd,
3 Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are particularly preferred.

4 The hydrogen, ammonium, and metal components can be ion-exchanged into
5 the SSZ-61. The SSZ-61 can also be impregnated with the metals, or the metals can
6 be physically and intimately admixed with the SSZ-61 using standard methods known
7 to the art.

8 Typical ion-exchange techniques involve contacting the synthetic molecular
9 sieve with a solution containing a salt of the desired replacing cation or cations.
10 Although a wide variety of salts can be employed, chlorides and other halides,
11 acetates, nitrates, and sulfates are particularly preferred. The molecular sieve is
12 usually calcined prior to the ion-exchange procedure to remove the organic matter
13 present in the channels and on the surface, since this results in a more effective ion
14 exchange. Representative ion exchange techniques are disclosed in a wide variety of
15 patents including U.S. Patent Nos. 3,140,249 issued on July 7, 1964 to Plank et al.;
16 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964
17 to Plank et al.

18 Following contact with the salt solution of the desired replacing cation, the
19 molecular sieve is typically washed with water and dried at temperatures ranging from
20 65°C to about 200°C. After washing, the molecular sieve can be calcined in air or
21 inert gas at temperatures ranging from about 200°C to about 800°C for periods of
22 time ranging from 1 to 48 hours, or more, to produce a catalytically active product
23 especially useful in hydrocarbon conversion processes.

24 Regardless of the cations present in the synthesized form of SSZ-61, the
25 spatial arrangement of the atoms which form the basic crystal lattice of the molecular
26 sieve remains essentially unchanged.

27 SSZ-61 can be formed into a wide variety of physical shapes. Generally
28 speaking, the molecular sieve can be in the form of a powder, a granule, or a molded
29 product, such as extrudate having a particle size sufficient to pass through a 2-mesh
30 (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the
31 catalyst is molded, such as by extrusion with an organic binder, the SSZ-61 can be
32 extruded before drying, or, dried or partially dried and then extruded.

1 SSZ-61 can be composited with other materials resistant to the temperatures
 2 and other conditions employed in organic conversion processes. Such matrix
 3 materials include active and inactive materials and synthetic or naturally occurring
 4 zeolites as well as inorganic materials such as clays, silica and metal oxides.
 5 Examples of such materials and the manner in which they can be used are disclosed in
 6 U.S. Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S. Patent
 7 No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are incorporated by
 8 reference herein in their entirety.

9 SSZ-61 is useful as an adsorbent.

10

11 EXAMPLES

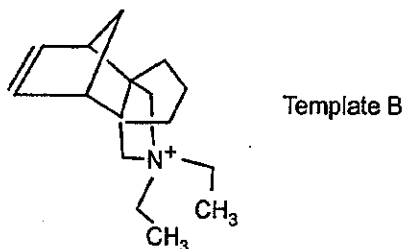
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13 The following examples demonstrate but do not limit the present invention.

14 Example 1

15 Synthesis of Template B

16



17

18

19 8-azonia-8,8-diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene

20

21 An anion (X⁻) is associated with the cation and may be any anion which is not
 22 detrimental to the formation of SSZ-61. Representative anions include halogen, e.g.,
 23 fluoride, chloride, bromide and iodide, hydroxide, acetate, sulfate, tetrafluoroborate,
 24 carboxylate, and the like. Hydroxide is the most preferred anion.

25 The structure-directing agent (SDA) 8-azonia-8,8-
 26 diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene cation is synthesized according to the
 27 procedure described below. To a solution of freshly cracked cyclopentadiene (40

grams) in 1200 ml of dichloromethane is added 1-cyclopentene-1,2-dicarboxylic acid anhydride (30 grams). The reaction is stirred at room temperature for several days. The desired product, 8-oxa-tetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene-7,9-dione, is isolated by recrystallization (after stripping off solvent) from 2/1 ethyl ether, dichloromethane with refrigeration.

Next the product is reacted with a primary amine in water at 85°C for 3 days in a closed system. For example, 4.5 grams of the tetracyclic anhydride is placed in the Teflon cup of a 125 cc Parr reactor with 10 ml of ethylamine (70% in H₂O) and 0.30 grams of 4-dimethylaminopyridine as catalyst. After heating for three days, the reaction is cooled, and upon gentle agitation the desired imide precipitates. The precipitate is collected by filtration and dried under vacuum.

Reduction of the precursor imide to the corresponding amine.

To a suspension of lithium aluminum hydride (2.52.) in tetrahydrofuran (55 mL) at 0 °C (by means of an ice-bath) in a 250 ml three-necked flask, the imide (5 gm) dissolved in 40 ml THF is added drop-wise (via an addition funnel) with mechanical stirring. Once the imide is all added, the ice-bath is replaced with a heating mantle, and the reaction mixture is heated to reflux overnight. The heating mantle is replaced with an ice-bath and the reaction mixture is diluted with 50 mL diethyl ether. The reaction is worked up by adding 15 ml of 15% NaOH solution drop-wise under vigorous stirring. Once the addition of the NaOH solution is completed, the gray reaction mixture turned to a colorless liquid with a white precipitate. The mixture is filtered and the filtrate is dried over MgSO₄. Filtration and concentration of the filtrate at reduced pressure on a rotary evaporator gives 4.12 gm of the desired amine.

Quaternization with ethyl iodide (Synthesis of the 8-azonia-8,8-diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene iodide, Template B)

To a solution of 5 gm of 8-aza-8-ethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene in 60 ml anhydrous methanol, 9.4 gm of ethyl iodide is added. The reaction is mechanically stirred for 48 hours at room temperature. Then, an additional equivalent of ethyl iodide (4.7 gm) is added and the reaction is further stirred at room temperature for an additional 48 hours. The reaction mixture is concentrated under reduced pressure on a rotary evaporator to give the iodide salt as an off-white-colored solid material. This iodide salt is purified by recrystallization. This is done by

1 completely dissolving the iodide salt in acetone and then precipitating by the addition
 2 of ethyl ether to the acetone solution. The procedure gives a white powder with very
 3 clean ^1H and ^{13}C NMR spectra, and correct elemental analysis for the product.

4 Ion Exchange

5 8-Azonias-8,8-diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene iodide (4.10gm) is
 6 dissolved in 12 ml water in a 100-ml volume plastic bottle. To the solution, 8.4 gm of
 7 Ion-Exchange Resin-OH (Bio Rad® AG1-X8) is added and the mixture is stirred at
 8 room temperature overnight. The product is collected by filtration removal of the
 9 resin after 3-4 days of exchange. A sample of the solution is titrated to determine the
 10 OH molarity for subsequent use in zeolite synthesis.

11 Examples 2-5

12 Synthesis of Templates A, C, D and E

13 Template A is synthesized by quaternization of 8-aza-8-
 14 ethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene with methyl iodide. Templates C-E are all
 15 made using the methodology described above. The parent imide, 8-aza-
 16 tetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene-7,9-dione, is synthesized by reacting the
 17 tetracyclic anhydride with ammonia, which upon LiAlH_4 -reduction yields the
 18 unsubstituted secondary cyclic amine, 8-aza-tetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene.
 19 Quaternization of this amine with the appropriate dihalide in the presence of KHCO_3
 20 yields the desired template (Template C from 1,4-diiodobutane, Template D from 1,5-
 21 diiodobutane, and Template E from 2-methyl-1,4-diiodobutane). It is to be anticipated
 22 that other derivatives can be prepared by the choice of the imide forming reagent
 23 coupled with choices for the alkylation step.

24 Example 6

25 Representative Synthesis of SSZ-61

26 A 23 cc Teflon liner (tared) is charged with a solution of 8-azonias-8,8-
 27 diethyltetracyclo[4.3.3.1^{2,5}.0^{1,6}]tridec-3-ene hydroxide (4 mmol Template B), and 1.66
 28 grams of tetraethyl orthosilicate (8mM of SiO_2). This material is placed in a hood and
 29 allowed to evaporate (ethanol) for several days and then the $\text{H}_2\text{O}/\text{SiO}_2$ ratio is
 30 adjusted to 20. 0.148 Grams of 50% HF is added with stirring using a plastic spatula.
 31 The resulting gel is capped off and placed in a Parr steel autoclave reactor and heated
 32 in an oven at 150°C while rotating at 43 rpm. The reaction is monitored by checking
 33 the gel's pH, and by looking for crystal formation using Scanning Electron

1 Microscopy (SEM) at six day intervals. The reaction is completed after heating for 18
2 days at the conditions described above. Once the crystallization is complete, the
3 mixture is filtered through a fritted-glass funnel. The collected solids are thoroughly
4 washed with water and then rinsed with acetone (~20 ml) to remove any organic
5 residues. The solids are allowed to air-dry over night and then dried in an oven at
6 120°C for one hour. The reaction afforded 0.38 gram of SSZ-61. X-ray and IR
7 analysis of the powder indicated the product to be SSZ-61.

8 Example 7

9 Calcination of SSZ-61

10 The material from Example 6 is calcined in the following manner. A thin bed
11 of material is heated in a muffle furnace from room temperature to 120°C at a rate of
12 1°C per minute and held at 120°C for three hours. The temperature is then ramped up
13 to 540°C at the same rate and held at this temperature for five hours, after which it is
14 increased to 594°C and held there for another five hours. A 50/50 mixture of air and
15 nitrogen is passed over the SSZ-61 at a rate of 20 standard cubic feet (0.57 standard
16 cubic meters) per minute during heating.

17 Example 8

18 Synthesis of SSZ-61

19 SSZ-61 is synthesized as described in Example 6 using SDA B.

20 Example 9

21 Synthesis of SSZ-61

22 SSZ-61 is synthesized as described in Example 6 using SDA C.

23 Example 10

24 Synthesis of SSZ-61

25 SSZ-61 is synthesized as described in Example 6 using SDA D.

26 Example 11

27 Synthesis of SSZ-61

28 SSZ-61 is synthesized as described in Example 6 except that the reaction is
29 conducted at 170°C.

30 Example 12

31 Synthesis of SSZ-61

32 SSZ-61 is synthesized as described in Example 10 except that the reaction is
33 conducted at 170°C.

Example 13

Synthesis of SSZ-61

SSZ-61 is synthesized as described in Example 6 except that the $\text{SiO}_2/\text{Al}_2\text{O}_3$ mole ratio is 150 and $\text{Al}(\text{NO}_3)_3$ is used as the source of aluminum.

Example 14

Argon Adsorption Analysis

SSZ-61 has a micropore volume of at least 0.06 cc/gm based on argon adsorption isotherm at 87.3°K (-186°C) recorded on ASAP 2010 equipment from Micromeritics. The low-pressure dose was 2.00 cm^3/g (STP) with 15-s equilibration interval. The argon adsorption isotherm was analyzed using the density function theory (DFT) formalism and parameters developed for activated carbon slits by Olivier (*Porous Mater.* 1995, 2, 9) using the Saito Foley adaptation of the Horvath-Kawazoe formalism (*Microporous Materials*, 1995, 3, 531) and the conventional t-plot method (*J. Catalysis*, 1965, 4, 319). The analysis indicated a large pore molecular sieve.

Example 15

1,3,5-Triisopropylbenzene Adsorption

The adsorption capacity of SSZ-61 for vapor phase hydrocarbons is measured at room temperature using a Cahn C-2000 balance coupled with a computer via an ATI-Cahn digital interface. 1,3,5-Triisopropylbenzene is used as a "plug gauge" adsorbate molecule. The 1,3,5-triisopropylbenzene (liquid) is 99.5+% pure as determined with GC analysis and used as supplied by the manufacturer (Aldrich). The vapor of the adsorbate is delivered from the liquid phase. The relative vapor pressure P/P_0 is maintained at ~0.3 by controlling the temperature of the liquid adsorbate using a cooling circulator. Prior to the adsorption experiments, the calcined SSZ-61 is degassed at 350 °C in a vacuum of at least 10^{-3} Torr for 5 hours. The adsorption capacity is reported in milliliters of liquid per gram of dry SSZ-61, assuming bulk liquid density for the adsorbate adsorbed in the sample pores. Data for 1,3,5-triisopropylbenzene adsorption is collected after 5 days.

SSZ-61 has an adsorption capacity for 1,3,5-triisopropylbenzene of 0.079 ml/g for the product of Example 7. This value places SSZ-61 in the group of zeolites that are usually larger than 12 ring (certainly for the high silica, one dimensional systems).

1 WHAT IS CLAIMED IS:

2

3 1. A molecular sieve having a mole ratio greater than about 15 of an oxide of a
 4 first tetravalent element to an oxide of a second tetravalent element which is
 5 different from said first tetravalent element, trivalent element, pentavalent
 6 element or mixture thereof and having, after calcination, the X-ray diffraction
 7 lines of Table I.

8

9 2. A molecular sieve having a mole ratio greater than about 15 of an oxide selected
 10 from the group consisting of silicon oxide, germanium oxide and mixtures
 11 thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide,
 12 boron oxide, titanium oxide, indium oxide, vanadium oxide and mixtures
 13 thereof, and having, after calcination, the X-ray diffraction lines of Table I.

14

15 3. A molecular sieve according to Claim 2 wherein the oxides comprise silicon
 16 oxide and aluminum oxide.

17

18 4. A molecular sieve according to Claim 2 wherein the oxides comprise silicon
 19 oxide and boron oxide.

20

21 5. A molecular sieve according to Claim 1 wherein said molecular sieve is
 22 predominantly in the hydrogen form.

23

24 6. A molecular sieve according to Claim 1 wherein said molecular sieve is
 25 substantially free of acidity.

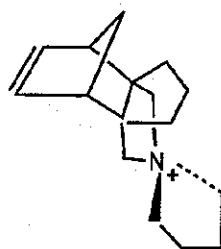
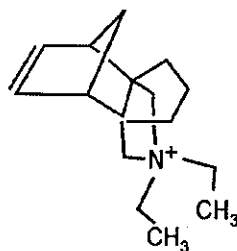
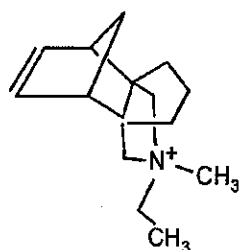
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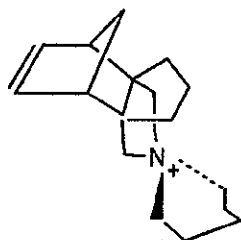
27 7. A molecular sieve having a composition, as synthesized and in the anhydrous
 28 state, in terms of mole ratios as follows:

29

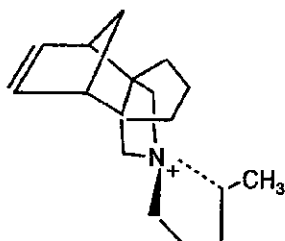
30	YO_2/W_cO_d	15- ∞
31	$M_{2/h}/YO_2$	0 - 0.03
32	Q/YO_2	0.02 - 0.08
33	F/YO_2	0 - 0.10

1
2 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium,
3 iron, boron, titanium, indium, vanadium or mixtures thereof; c is 1 or 2; d is 2
4 when c is 1 or d is 3 or 5 when c is 2; M is an alkali metal cation, alkaline earth
5 metal cation or mixtures thereof; n is the valence of M; and Q is a cation
6 selected from the group consisting of the following:





1
2 and
3



4
5

6 8. A molecular sieve according to Claim 7 wherein W is aluminum and Y is
7 silicon.

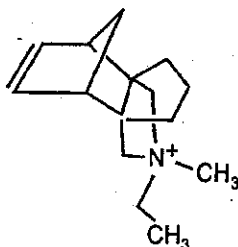
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9 9. A molecular sieve according to Claim 7 wherein W is boron and Y is silicon.

10

11 10. A molecular sieve according to Claim 7 wherein Q is

12

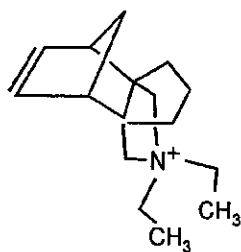


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1 11. A molecular sieve according to Claim 7 wherein Q is

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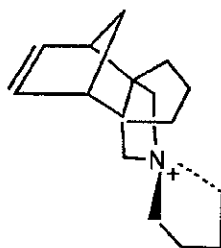


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5 12. A molecular sieve according to Claim 7 wherein Q is

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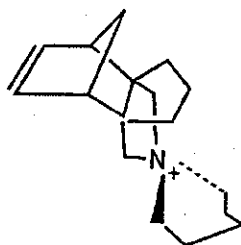


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9 13. A molecular sieve according to Claim 7 wherein Q is

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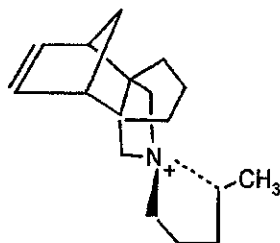
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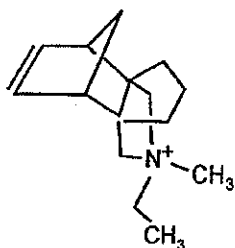
- 1 14. A molecular sieve according to Claim 7 wherein Q is

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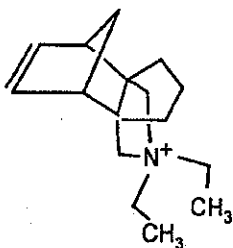
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- 4 15. A method of preparing a crystalline material comprising (1) an oxide of a first
 5 tetravalent element and (2) an oxide of a trivalent element, pentavalent element,
 6 second tetravalent element which is different from said first tetravalent element
 7 or mixture thereof, said method comprising contacting under crystallization
 8 conditions sources of said oxides and a structure directing agent comprising a
 9 cation selected from the group consisting of the following:



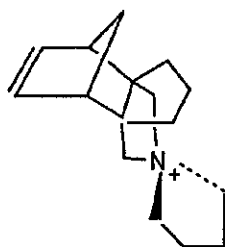
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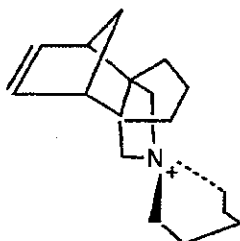


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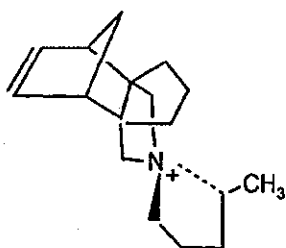
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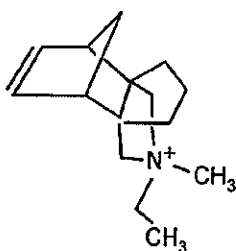
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11 16. The method according to Claim 15 wherein the first tetravalent element is
 12 selected from the group consisting of silicon, germanium and combinations
 13 thereof.

14

- 1 17. The method according to Claim 15 wherein the second trivalent element,
2 pentavalent element or tetravalent element is selected from the group consisting
3 of aluminum, gallium, iron, boron, titanium, indium, vanadium and
4 combinations thereof.
5
6 18. The method according to Claim 17 wherein the second trivalent element or
7 tetravalent element is selected from the group consisting of aluminum, boron,
8 titanium and combinations thereof.
9
10 19. The method according to Claim 16 wherein the first tetravalent element is
11 silicon.
12
13 20. The method of Claim 15 wherein the structure directing agent is
14

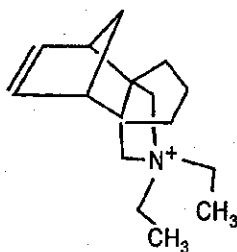


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- 17 21. The method of Claim 15 wherein the structure directing agent is

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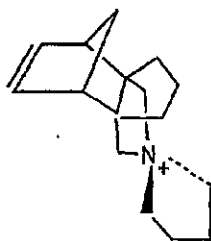
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1 22. The method of Claim 15 wherein the structure directing agent is

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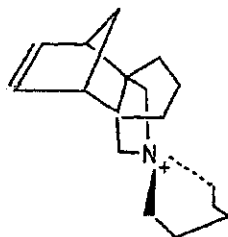


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5 23. The method of Claim 15 wherein the structure directing agent is

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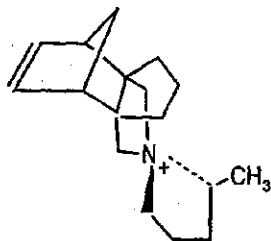


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9 24. The method of Claim 15 wherein the structure directing agent is

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13 25. The method of Claim 15 wherein the crystalline material has, after calcination,
14 the X-ray diffraction lines of Table I.