

1 PREPARATION OF MOLECULAR SIEVE SSZ-33

2
3 BACKGROUND

4
5 Crystalline molecular sieves are usually prepared from aqueous reaction
6 mixtures containing sources of alkali or alkaline earth metal oxides, sources of silicon
7 oxide, and, optionally, sources of, e.g., boron oxide and/or aluminum oxide.

8 Molecular sieves have been prepared from reaction mixtures containing an
9 organic structure directing agent ("SDA"), usually a nitrogen-containing organic
10 cation. U. S. Patent No. 4,963,337, issued October 16, 1990 to Zones, discloses that
11 the molecular sieve designated SSZ-33 can be prepared using a tricyclo[5.2.1.0^{2,6}]
12 decane quaternary ammonium cation SDA.

13 U. S. Patent No. 5,785,947, issued July 28, 1998 to Zones et al., discloses a
14 method of preparing crystalline zeolites using a small quantity of an organic
15 templating compound and a larger quantity of an amine component containing at least
16 one amine having from one to eight carbon atoms, ammonium hydroxide, or mixtures
17 thereof. It is disclosed that the amine component is preferably an aliphatic or
18 cycloaliphatic amine containing no more than eight carbon atoms. Disclosed
19 examples of the amine component are isopropylamine, isobutylamine, n-butylamine,
20 piperidine, 4-methylpiperidine, cyclohexylamine, 1,1,3,3-tetramethyl-butylamine and
21 cyclopentylamine.

22 U. S. Patent No. 5,707,600, issued January 13, 1998 to Nakagawa et al.,
23 discloses a process for preparing medium pore size zeolites using small, neutral
24 amines capable of forming the zeolite, the amine containing (a) only carbon, nitrogen
25 and hydrogen atoms, (b) one primary, secondary or tertiary, but not quaternary, amino
26 group, and (c) a tertiary nitrogen atom, at least one tertiary carbon atom, or a nitrogen
27 atom bonded directly to at least one secondary carbon atom, wherein the process is
28 conducted in the absence of a quaternary ammonium compound. Disclosed examples
29 of the small, neutral amine are isobutylamine, diisobutylamine, trimethylamine,
30 cyclopentylamine, diisopropylamine, sec-butylamine, 2,5-dimethylpyrrolidine and 2,6-
31 dimethylpiperidine.

1 U. S. Patent No. 5,707,601, issued January 13, 1998 to Nakagawa, discloses a
2 process for preparing zeolites having the MTT crystal structure using small, neutral
3 amines capable of forming the zeolite, the amine containing (a) only carbon, nitrogen
4 and hydrogen atoms, (b) one primary, secondary or tertiary, but not quaternary, amino
5 group, and (c) a tertiary nitrogen atom, at least one tertiary carbon atom, or a nitrogen
6 atom bonded directly to at least one secondary carbon atom, wherein the process is
7 conducted in the absence of a quaternary ammonium compound. Disclosed examples
8 of the small, neutral amine are isobutylamine, diisobutylamine, diisopropylamine and
9 trimethylamine.

10 11 SUMMARY OF THE INVENTION

12
13 In a first aspect, there is provided a method for preparing a
14 molecular sieve having a mole ratio of greater than about 15:1 of (1) silicon oxide,
15 germanium oxide and mixtures thereof to (2) boron oxide or a mixture of boron oxide
16 with aluminum oxide, gallium oxide, titanium oxide or iron oxide and mixtures
17 thereof, and having, after calcination, the X-ray diffraction lines of Table II, said
18 method comprising:

- 19
20 A. forming an aqueous reaction mixture comprising (1) a source of silicon oxide,
21 germanium oxide and mixtures thereof; (2) a source of boron oxide or a
22 mixture of boron oxide with aluminum oxide, gallium oxide, titanium oxide or
23 iron oxide and mixtures thereof; (3) a source of alkali metal or alkaline earth
24 metal; (4) an N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane
25 quaternary ammonium cation, and (5) an N,N-dialkyl-8-amino-
26 tricyclo[5.2.1.0^{2,6}]decane compound; and
27 B. maintaining said aqueous mixture under sufficient crystallization conditions
28 until crystals are formed.

29
30 The reaction mixture should have a composition in terms of mole ratios falling within
31 the ranges shown in Table A below:
32

TABLE A

	Broad	Preferred
YO_2/W_aO_b	10-200	30-60
OH/YO_2	0.10-1.0	0.20-0.30
Q/YO_2	0.05-0.50	0.10-0.25
M^{n+}/YO_2	0.05-0.30	0.05-0.15
H_2O/YO_2	15-300	25-60
$Q/Q+M^{n+}$	0.30-0.70	0.40-0.60

where Y is silicon, germanium or a mixture thereof, W is boron, or a mixture of boron, aluminum, gallium, titanium, iron or mixtures thereof, a is 1 or 2, b is 2 when a is 1 (i.e., W is tetravalent), b is 3 when a is 2 (i.e., W is trivalent), M is an alkali metal or alkaline earth metal, n is the valence of M (i.e., 1 or 2), and Q is a mixture of a N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.

In one embodiment, the disclosure provides these processes wherein the N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation is used in an amount less than that required to fill all of the micropore volume of the molecular sieve, i.e., an amount less than that required to crystallize the molecular sieve in the absence of the N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound. Typically, the mole ratio of N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher, for example about 1:4 to about 4:1.

In one embodiment, there is also provided a molecular sieve having a composition, as-synthesized and in the anhydrous state, in terms of mole ratios as follows:

$$(1 \text{ to } 5) Q : (0.1 \text{ to } 1) M^{n+} : W_aO_b : (\text{greater than } 15) YO_2$$

where Q, M, n, W, a, b and Y are as defined above.

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

(1 to 5) Q : (0.1 to 1) Mⁿ⁺ : W_aO_b : (greater than 15) YO₂

where Y is silicon, germanium or a mixture thereof, W is boron, or a mixture of boron, aluminum, gallium, titanium, iron or mixtures thereof, a is 1 or 2, b is 2 when a is 1, b is 3 when a is 2, M is an alkali metal or alkaline earth metal, n is the valence of M, and Q is a mixture of a N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.

The as-synthesized molecular sieve can have a boron content of greater than 100 parts per million by weight.

1 In one embodiment, the disclosure provides the as-synthesized
2 molecular sieve wherein the N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane
3 quaternary ammonium cation is used in an amount less than that required to fill all of
4 the micropore volume of the molecular sieve, i.e., an amount less than that required to
5 crystallize the molecular sieve in the absence of the N,N-dialkyl-8-amino-
6 tricyclo[5.2.1.0^{2,6}]decane compound. Typically, the mole ratio of N,N,N-trialkyl-8-
7 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-
8 amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher, for example about
9 1:4 to about 4:1.

10 In a third aspect, there is further provided an improved
11 method for preparing a molecular sieve from source materials for said molecular sieve
12 and an organic structure directing agent, the improvement comprising employing a
13 structure directing agent comprising a mixture of an N,N,N-trialkyl-8-ammonium-
14 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation, and an N,N-dialkyl-8-amino-
15 tricyclo[5.2.1.0^{2,6}]decane compound.

16 In one embodiment, the disclosure provides this improved method
17 wherein the N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary
18 ammonium cation is used in an amount less than that required to fill all of the
19 micropore volume of the molecular sieve, i.e., an amount less than that required to
20 crystallize the molecular sieve in the absence of the N,N-dialkyl-8-amino-
21 tricyclo[5.2.1.0^{2,6}]decane compound. Typically, the mole ratio of N,N,N-trialkyl-8-
22 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-
23 amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher, for example about
24 1:4 to about 4:1.

25 DETAILED DESCRIPTION

26
27
28 Molecular sieve SSZ-33 can be prepared by a method comprising preparing an
29 aqueous mixture that contains a N,N,N-trialkyl-8-ammonium-
30 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation, and a N,N-dialkyl-8-amino-
31 tricyclo[5.2.1.0^{2,6}]decane compound. Typically, the mole ratio of N,N,N-trialkyl-8-
32 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-

1 amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher, for example about
2 1:4 to about 4:1. Preferably, seeds of SSZ-33 are used in the preparation.

3 This invention provides considerable cost improvement over the use of a
4 N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation
5 SDA alone.

6 SSZ-33 molecular sieves can be suitably prepared from an aqueous reaction
7 mixture containing sources of an alkali metal or alkaline earth metal oxide, sources of
8 an oxide of silicon, germanium or mixtures thereof, sources of boron oxide or boron
9 oxide and aluminum oxide, gallium oxide, titanium oxide or iron oxide and mixtures
10 thereof, a N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary
11 ammonium cation and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.
12 The mixture should have a composition in terms of mole ratios falling within the
13 ranges shown in Table A below:

14

15

TABLE A

	Broad	Preferred
YO ₂ /W _a O _b	10-200	30-60
OH/YO ₂	0.10-1.0	0.20-0.30
Q/YO ₂	0.05-0.50	0.10-0.25
M ⁿ⁺ /YO ₂	0.05-0.30	0.05-0.15
H ₂ O/YO ₂	15-300	25-60
Q/Q+M ⁿ⁺	0.30-0.70	0.40-0.60

16

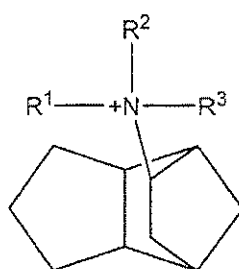
17 where Y is silicon, germanium or a mixture thereof; W is boron, or a mixture of
18 boron, aluminum, gallium, titanium, iron or mixtures thereof; a is 1 or 2, b is 2 when a
19 is 1 (i.e., W is tetravalent), b is 3 when a is 2 (i.e., W is trivalent), M is an alkali metal
20 or alkaline earth metal; n is the valence of M (i.e., 1 or 2); and Q is a mixture of a
21 N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation
22 and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.

23 The reaction mixture is prepared using standard molecular sieve preparation
24 techniques. Sources of boron for the reaction mixture include borosilicate glasses and
25 other reactive boron oxides. These include borates, boric acid and borate esters.

1 Typical sources of silicon oxide include fumed silica, silicates, silica hydrogel, silicic
 2 acid, colloidal silica, tetra-alkyl orthosilicates, and silica hydroxides. Sources of other
 3 oxides, such as aluminum oxide, gallium oxide, titanium oxide or iron oxide are
 4 analogous to those for boron oxide and silicon oxide.

5 Mixture Q comprises a N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane
 6 quaternary ammonium cation and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane
 7 compound. The N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary
 8 ammonium cation has the formula

9



A⁻

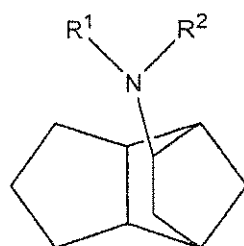
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11

12 where R¹, R² and R³ are each independently a lower alkyl, for example methyl. The
 13 cation is associated with an anion, A⁻, which is not detrimental to the formation of the
 14 SSZ-33. Representative of such anions include halogens, such as fluoride, chloride,
 15 bromide and iodide; hydroxide; acetate; sulfate and carboxylate. Hydroxide is the
 16 preferred anion. It may be beneficial to ion exchange, for example, a halide for
 17 hydroxide ion, thereby reducing or eliminating the alkali metal or alkaline earth metal
 18 hydroxide required.

19 The N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary
 20 ammonium cation can be synthesized in the manner described in Example 1 of
 21 aforementioned U. S. Patent No. 4,963,337 which is incorporated herein by reference
 22 in its entirety.

23 The N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound has the formula
 24



1

2

3 where R¹ and R² are as defined above. Synthesis of the N,N-dialkyl-8-amino-
4 tricyclo[5.2.1.0^{2,6}]decane compound is also described in U. S. Patent No. 4,963,337,
5 the N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound being an intermediate
6 for the N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium
7 cation.

8

9 Mixture Q typically has a mole ratio of N,N,N-trialkyl-8-
10 ammoniumtricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-
11 amino-tricyclo[5.2.1.0^{2,6}]decane compound of about 1:4 and higher, for example
12 about 1:4 to about 4:1.

13 Use of a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound in mixture
14 Q permits a reduction in the amount of N,N,N-trialkyl-8-ammonium-
15 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation used in mixture Q, which
16 results in significant cost savings. In fact, it has been found that, by using a N,N-
17 dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound in mixture Q, the amount of
18 N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation
19 can be reduced to a level below that which is required to fill the micropore volume of
20 SSZ-33, i.e., an amount less than that required to crystallize SSZ-33 in the absence of
21 the N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.

22 The reaction mixture can be seeded with SSZ-33 crystals both to direct and
23 accelerate the crystallization, as well as to minimize the formation of undesired
24 contaminants. Typically, when seeds are employed they are used in an amount which
25 is about 2-3 weight percent based on the weight of silicon oxide in the reaction
26 mixture.

27 The reaction mixture is maintained at an elevated temperature until crystals of
28 SSZ-33 are formed. The temperatures during the hydrothermal crystallization step are
typically maintained from about 140°C to about 200°C, preferably from about 150°C

1 to about 170°C, and most preferably from about 155°C to about 165°C. The
2 crystallization period is typically greater than 1 day and preferably from about 3 days
3 to about 7 days.

4 The hydrothermal crystallization is conducted under pressure and usually in an
5 autoclave so that the reaction mixture is subject to autogenous pressure. The reaction
6 mixture can be stirred, such as by rotating the reactor, during crystallization. During
7 the hydrothermal crystallization step, the SSZ-33 crystals can be allowed to nucleate
8 spontaneously from the reaction mixture.

9 Once the SSZ-33 crystals have formed, the solid product can be separated
10 from the reaction mixture by standard mechanical separation techniques such as
11 filtration. The crystals can be water-washed and then dried, e.g., at 90°C to 150°C for
12 from 8 to 24 hours, to obtain the as-synthesized SSZ-33 crystals. The drying step can
13 be performed at atmospheric or subatmospheric pressures.

14 As used herein, the term "as-synthesized" means that the molecular sieve
15 crystals have been recovered from the reaction mixture and still contain the SDA in
16 their pores, i.e., the SDA has not been removed from the molecular sieve crystals by
17 (typically) calcination. SSZ-33 molecular sieve has a composition, as-synthesized and
18 in the anhydrous state, in terms of mole ratios as indicated in Table B below:

19 As-Synthesized SSZ-33 Composition

20 TABLE B

21 (1 to 5) Q : (0.1 to 1) Mⁿ⁺ : W_aO_b : (greater than 15) YO₂

22
23 where Q, M, n, W, a, b and Y are as defined above.

24 As-synthesized SSZ-33 can have a boron content of greater than 100 parts per
25 million.

1 SSZ-33 molecular sieves, as-synthesized, have a crystalline structure whose X-
 2 ray powder diffraction pattern shows the following characteristic lines:

3 As-Synthesized SSZ-33

4 TABLE I

<u>2 Theta^a</u>	<u>d spacing (Angstroms)</u>	<u>Intensity^b</u>
7.86	11.25	VS
20.48	4.336	VS
21.47	4.139	M-S
22.03	4.035	VS
23.18	3.837	S-VS
26.83	3.323	M-S

5 ^a ±0.1

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

10 Table IA below shows the characteristic X-ray powder diffraction lines of as-
 11 synthesized SSZ-33 including actual relative intensities.

12 As-Synthesized SSZ-33

13 Table IA

<u>2 Theta^a</u>	<u>d spacing (Angstroms)</u>	<u>Rel. Intensity (100 x I/I₀)</u>
7.86	11.25	90
20.48	4.336	100
21.47	4.139	40
22.03	4.035	90
23.18	3.837	64
26.83	3.323	40

14 ^a ±0.1

15 SSZ-33 molecular sieves can be used as-synthesized or can be thermally
 16 treated (calcined). By "thermal treatment" is meant heating to a temperature from
 17 about 200°C to about 820°C, either with or without the presence of steam. Usually, it
 18 is desirable to remove the alkali metal or alkaline earth metal cation by ion exchange

1 and replace it with hydrogen, ammonium, or any desired metal ion. Thermal
2 treatment including steam helps to stabilize the crystalline lattice from attack by acids.

3 After calcination, SSZ-33 molecular sieves have a crystalline structure whose
4 X-ray powder diffraction pattern shows the characteristic lines as indicated in Table II
5 below.

6 Calcined SSZ-33

7 Table II

<u>2 Theta^a</u>	<u>d spacing (Angstroms)</u>	<u>Intensity</u>
7.81	11.32	VS
20.43	4.347	M-S
21.44	4.144	W
22.02	4.037	M
23.18	3.837	M
26.80	3.326	M

8 ^a ±0.1

9 Table IIA below shows the characteristic X-ray powder diffraction lines of
10 calcined SSZ-33 including actual relative intensities.

11 Calcined SSZ-33

12 Table IIA

<u>2 Theta^a</u>	<u>d spacing (Angstroms)</u>	<u>Rel. Intensity (100 x I/I₀)</u>
7.81	11.32	100
20.43	4.347	46
21.44	4.144	9
22.02	4.037	41
23.18	3.837	28
26.80	3.326	31

13 ^a ±0.1

14 The X-ray powder diffraction patterns were determined by standard
15 techniques. The radiation was the K-alpha/doublet of copper and a scintillation
16 counter spectrometer with a strip-chart pen recorder was used. The peak heights I and
17 the positions, as a function of 2 Theta where Theta is the Bragg angle, were read from
18 the spectrometer chart. From these measured values, the relative intensities, 100 x

1 I/I_0 , where I_0 is the intensity of the strongest line or peak, and d , the interplanar
2 spacing in Angstroms corresponding to the recorded lines, can be calculated.

3 Variations in the diffraction pattern can result from variations in the
4 silica-to-boron mole ratio from sample to sample. The molecular sieve produced by
5 exchanging the metal or other cations present in the molecular sieve with various
6 other cations yields a similar diffraction pattern, although there can be shifts in
7 interplanar spacing as well as variations in relative intensity. Calcination can also
8 cause shifts in the X-ray diffraction pattern. Notwithstanding these perturbations, the
9 basic crystal lattice structure remains unchanged.

10 SSZ-33 molecular sieves are useful in hydrocarbon conversion reactions.
11 Examples of these uses are described in U.S. Patent No. 4,963,337, issued October 16,
12 1990 to Zones, which is incorporated herein by reference.

14 EXAMPLES

15 Examples 1-8

16 In the following examples, "SDA 1" represents N,N,N-trimethyl-8-
17 ammonium-tricyclo[5.2.1.0^{2,6}]decane hydroxide, and "SDA 2" is N,N-dimethyl-8-
18 amino-tricyclo[5.2.1.0^{2,6}]decane. The following components were held constant: SiO₂
19 (Cabosil M-5 fumed silica, 97%), 1N NaOH, and boric acid. All runs shown were at
20 the following mole ratios: H₂O/SiO₂ = 44, Na/SiO₂ = 0.10 and SiO₂/B₂O₃ = 12.
21 Reactions were carried out at 160° C, 43 RPM tumbling on a spit within an enclosed,
22 convection heated oven. Runs were 6-12 days.

24	<u>Ex. #</u>	<u>mM SDA 1</u>	<u>mM SDA 2</u>	<u>SiO₂</u>	<u>XRD RESULT</u>
25	1	2.6	0	12	SSZ-33
26	2	2.1	0.50	12	SSZ-33
27	3	1.56	1.0	12	SSZ-33
28	4	1.04	1.5	12	SSZ-33
29	5	0.77	1.8	12	SSZ-33, MIN. AMO
30	6	0.52	2.0	12	AMO > SSZ-33
31	7	0.26	2.22	12	AMO > SSZ-33
32	8	0.00	2.5	12	ONLY TRACE 33

1

2 Examples 1-8 demonstrate that as much as 75% of SDA 1 can be replaced
3 with SDA 2 with some optimization of the conditions.

4

5

Example 9

6

7 The synthesis of SSZ-33 was carried out in a 1 gallon reactor using an
8 overhead motor driven stirrer within the reactor. The following amounts of reagent
9 were used in the preparation :

9

10 130 grams of 0.73M solution of SDA 1 (95 mM)

11 72 grams of SDA 2 (381 mM)

12 H₂O = 1485 grams

13 Boric Acid = 23.4 grams (189 mM B₂O₃)

14 1 N NaOH = 234 grams (234 mM)

15 Cabosil M-5, fumed silica (97%) = 140 grams (2.33 moles)

16 Seeds of SSZ-33 = 3.90 grams

17

18 The reaction was brought to 160° C using a 12 hour ramp up. The reactor was
19 stirred at 75 RPM and allowed to run for 11 days. The reactor was cooled, a sample
20 initially taken and washed and dried. The XRD data of the product showed it to be
21 SSZ-33. The entire batch was then washed and dried and the same XRD data was
22 obtained.

1 WHAT IS CLAIMED IS:

2

3 1. A method for preparing a molecular sieve having a mole ratio of greater than
4 about 15:1 of (1) silicon oxide, germanium oxide and mixtures thereof to (2)
5 boron oxide or a mixture of boron oxide with aluminum oxide, gallium oxide,
6 titanium oxide or iron oxide and mixtures thereof, and having, after
7 calcination, the X-ray diffraction lines of Table II, said method comprising:

8

9 A. forming an aqueous reaction mixture comprising (1) a source of silicon
10 oxide, germanium oxide and mixtures thereof; (2) a source of boron
11 oxide or a mixture of boron oxide with aluminum oxide, gallium
12 oxide, titanium oxide or iron oxide and mixtures thereof; (3) a source
13 of alkali metal or alkaline earth metal; (4) an N,N,N-trialkyl-8-
14 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation,
15 and (5) an N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound;
16 and

17 B. maintaining said aqueous mixture under sufficient crystallization
18 conditions until crystals are formed.

19

20 2. The method of Claim 1 wherein the reaction mixture has a composition in
21 terms of mole ratios falling within the ranges shown below:

YO_2/W_aO_b	10-200
OH/YO_2	0.10-1.0
Q/YO_2	0.05-0.50
M^{n+}/YO_2	0.05-0.30
H_2O/YO_2	15-300
$Q/Q+M^{n+}$	0.30-0.70

22

23 where Y is silicon, germanium or a mixture thereof, W is boron, or a mixture
24 of boron, aluminum, gallium, titanium, iron or mixtures thereof, a is 1 or 2, b
25 is 2 when a is 1, b is 3 when a is 2, M is an alkali metal or alkaline earth metal,

1 n is the valence of M, and Q is a mixture of a N,N,N-trialkyl-8-ammonium-
 2 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation and a N,N-dialkyl-8-
 3 amino-tricyclo[5.2.1.0^{2,6}]decane compound.

4
 5 3. The method of Claim 2 wherein the reaction mixture has a composition in
 6 terms of mole ratios falling within the ranges shown below:
 7

YO ₂ /W _a O _b	30-60
OH/YO ₂	0.20-0.30
Q/YO ₂	0.10-0.25
M ⁿ⁺ /YO ₂	0.05-0.15
H ₂ O/YO ₂	25-60
Q/Q+M ⁿ⁺	0.40-0.60

- 8
 9 4. The method of Claim 1 wherein the N,N,N-trialkyl-8-ammonium-
 10 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation is used in an amount
 11 less than that required to fill all of the micropore volume of the molecular
 12 sieve.
 13
 14 5. The method of Claim 1 wherein the mole ratio of N,N,N-trialkyl-8-
 15 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-
 16 dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher.
 17
 18 6. The method of Claim 5 wherein the mole ratio of N,N,N-trialkyl-8-
 19 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-
 20 dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 to about 4:1.
 21
 22 7. The method of Claim 1 wherein the amount of boron in the molecular sieve is
 23 greater than 100 parts per million.
 24
 25 8. A molecular sieve having a composition, as-synthesized and in the anhydrous
 26 state, in terms of mole ratios as follows:

1

2

 $(1 \text{ to } 5) Q : (0.1 \text{ to } 1) M^{n+} : W_a O_b : (\text{greater than } 15) Y O_2$

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where Y is silicon, germanium or a mixture thereof, W is boron, or a mixture of boron, aluminum, gallium, titanium, iron or mixtures thereof, a is 1 or 2, b is 2 when a is 1, b is 3 when a is 2, M is an alkali metal or alkaline earth metal, n is the valence of M, and Q is a mixture of a N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation and a N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.

9. The molecular sieve of Claim 8 wherein the N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation is used in an amount less than that required to fill all of the micropore volume of the molecular sieve.

10. The molecular sieve of Claim 8 wherein the mole ratio of N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher.

11. The molecular sieve of Claim 10 wherein the mole ratio of N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 to about 4:1.

12. The molecular sieve of Claim 8 wherein the amount of boron in the molecular sieve is greater than 100 parts per million.

13. The molecular sieve of Claim 8 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

14. An improved method for preparing a molecular sieve from source materials for said molecular sieve and an organic structure directing agent, the improvement comprising employing a structure directing agent comprising a mixture of an

- 1 N,N,N-trialkyl-8-ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium
2 cation, and an N,N-dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound.
3
- 4 15. The method of Claim 14 wherein the N,N,N-trialkyl-8-ammonium-
5 tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation is used in an amount
6 less than that required to fill all of the micropore volume of the molecular
7 sieve
8
- 9 16. The method of Claim 14 wherein the mole ratio of N,N,N-trialkyl-8-
10 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-
11 dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 and higher. .
12
- 13 17. The method of Claim 16 wherein the mole ratio of N,N,N-trialkyl-8-
14 ammonium-tricyclo[5.2.1.0^{2,6}]decane quaternary ammonium cation to N,N-
15 dialkyl-8-amino-tricyclo[5.2.1.0^{2,6}]decane compound is about 1:4 to about 4:1.
16
- 17 18. The method of Claim 14 wherein the amount of boron in the molecular sieve
18 is greater than 100 parts per million.
19
- 20 19. The method of Claim 14 wherein the molecular sieve has, after calcination, the
21 X-ray diffraction lines of Table II.