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(54) Titre : COMPOSITION DE TAMIS MOLECULAIRE SSZ-56 ET SYNTHÈSE DE CETTE COMPOSITION
(54) Title: MOLECULAR SIEVE SSZ-56 COMPOSITION OF MATTER AND SYNTHESIS THEREOF

(57) **Abrégé/Abstract:**

The present invention relates to new crystalline molecular sieve SSZ-56 prepared using a trans-fused ring N,N-diethyl-2-methyldecahydroquinolinium cation as a structure-directing agent, methods for synthesizing SSZ-56 and processes employing SSZ-56 in a catalyst.

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(54) Title: MOLECULAR SIEVE SSZ-56 COMPOSITION OF MATTER AND SYNTHESIS THEREOF

(57) Abstract: The present invention relates to new crystalline molecular sieve SSZ-56 prepared using a trans-fused ring N,N-di-ethyl-2-methyldecahydroquinolinium cation as a structure-directing agent, methods for synthesizing SSZ-56 and processes employ-
ing SSZ-56 in a catalyst.



WO 2007/001934 A3

1 MOLECULAR SIEVE SSZ-56 COMPOSITION OF MATTER
2 AND SYNTHESIS THEREOF
3 BACKGROUND OF THE INVENTION
4

5 Field of the Invention

6 The present invention relates to new crystalline molecular sieve SSZ-
7 56, a method for preparing SSZ-56 using a trans-fused ring N,N-diethyl-2-
8 methyldecahydroquinolinium cation as a structure directing agent and the use
9 of SSZ-56 in catalysts for, e.g., hydrocarbon conversion reactions.

10 State of the Art

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

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

25 SUMMARY OF THE INVENTION

26 The present invention is directed to a family of crystalline molecular
27 sieves with unique properties, referred to herein as "molecular sieve SSZ-56"
28 or simply "SSZ-56". Preferably, SSZ-56 is in its silicate, aluminosilicate,
29 titanosilicate, vanadosilicate or borosilicate form. The term "silicate" refers to
30 a molecular sieve having a high mole ratio of silicon oxide relative to
31 aluminum oxide, preferably a mole ratio greater than 100, including molecular
32 sieves comprised entirely of silicon oxide. As used herein, the term
33 "aluminosilicate" refers to a molecular sieve containing both aluminum oxide

1 and silicon oxide and the term "borosilicate" refers to a molecular sieve
2 containing oxides of both boron and silicon.

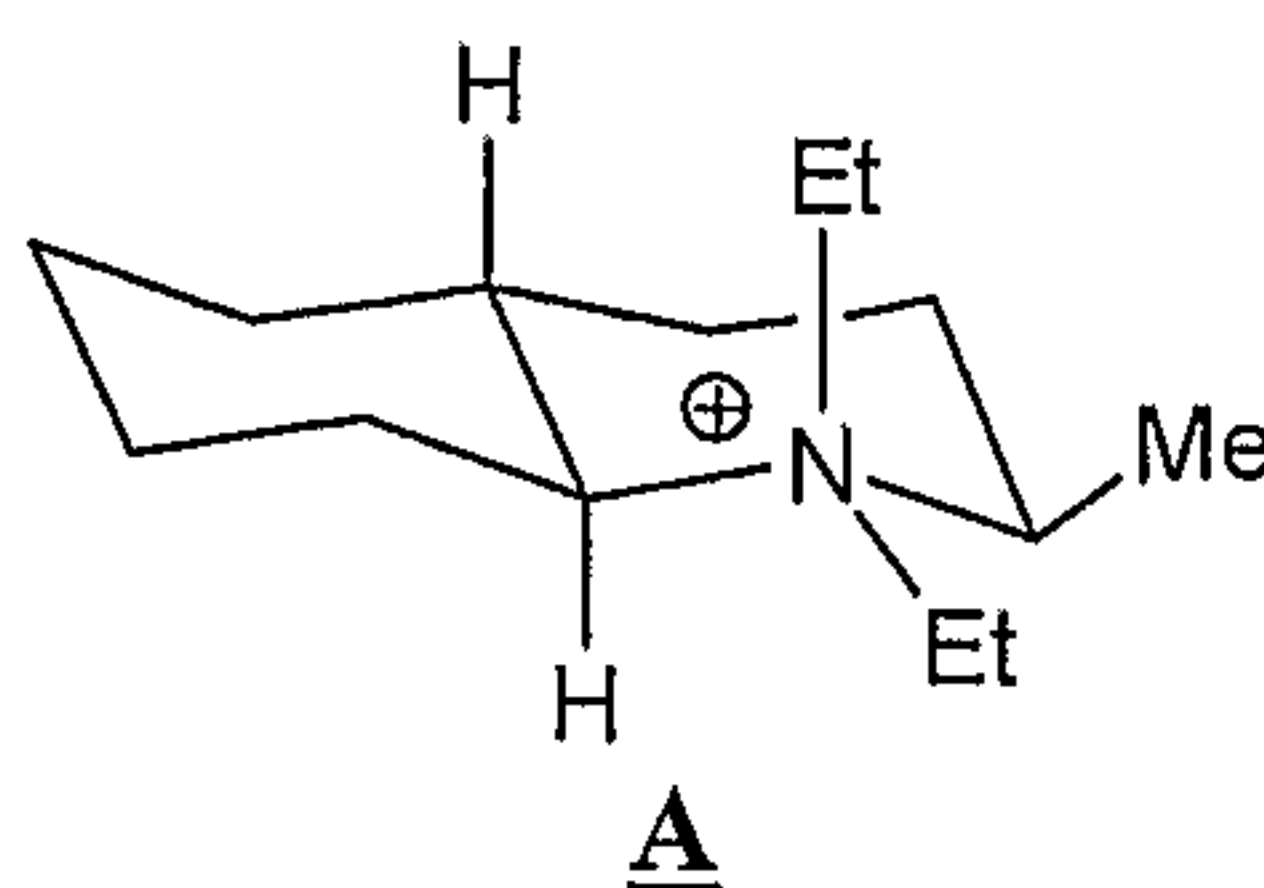
3 In accordance with this invention, there is provided a molecular sieve
4 having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent
5 element to (2) an oxide of a trivalent element, pentavalent element, second
6 tetravalent element different from said first tetravalent element or mixture
7 thereof and having, after calcination, the X-ray diffraction lines of Table 2.

8 Further, in accordance with this invention, there is provided a molecular
9 sieve having a mole ratio greater than about 15 of (1) silicon oxide to (2) an
10 oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide,
11 titanium oxide, vanadium oxide and mixtures thereof and having, after
12 calcination, the X-ray diffraction lines of Table 2 below. It should be noted
13 that the mole ratio of the first oxide to the second oxide can be infinity, i.e.,
14 there is no second oxide in the molecular sieve. In these cases, the
15 molecular sieve is an all-silica molecular sieve.

16 The present invention further provides such a molecular sieve having a
17 composition, as synthesized and in the anhydrous state, in terms of mole
18 ratios as follows:

19		
20	YO_2/W_cO_d	15 - infinity
21	$M_{2/n}/YO_2$	0 - 0.03
22	Q/YO_2	0.02 - 0.05
23		

24 wherein Y is silicon; W is aluminum, gallium, iron, boron, titanium, indium,
25 vanadium or mixtures thereof; c is 1 or 2; d is 2 when c is 1 (i.e., W is
26 tetravalent) or d is 3 or 5 when c is 2 (i.e., d is 3 when W is trivalent or 5 when
27 W is pentavalent); M is an alkali metal cation, alkaline earth metal cation or
28 mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a trans-fused
29 ring N,N-diethyl-2-methyldecahydroquinolinium cation A.



30

1 In accordance with this invention, there is also provided a
2 molecular sieve prepared by thermally treating a molecular sieve having a
3 mole ratio of silicon oxide to an oxide selected from aluminum oxide, gallium
4 oxide, iron oxide, boron oxide, titanium oxide, vanadium oxide and mixtures
5 thereof greater than about 15 at a temperature of from about 200°C to about
6 800°C, the thus-prepared molecular sieve having the X-ray diffraction lines of
7 Table 2. The present invention also includes this thus-prepared molecular
8 sieve which is predominantly in the hydrogen form, which hydrogen form is
9 prepared by ion exchanging with an acid or with a solution of an ammonium
10 salt followed by a second calcination. If the molecular sieve is synthesized
11 with a high enough ratio of SDA cation to sodium ion, calcination alone may
12 be sufficient. For high catalytic activity, the SSZ-56 molecular sieve should be
13 predominantly in its hydrogen ion form. As used herein, "predominantly in the
14 hydrogen form" means that, after calcination, at least 80% of the cation sites
15 are occupied by hydrogen ions and/or rare earth ions.

16 Also provided in accordance with the present invention is a method of
17 preparing a crystalline material comprising (1) a first oxide comprising silicon
18 oxide and (2) a second oxide comprising boron oxide, aluminum oxide,
19 gallium oxide, iron oxide, titanium oxide, vanadium oxide and mixtures thereof
20 and having a mole ratio of the first oxide to the second oxide greater than
21 about 15, said method comprising contacting under crystallization conditions
22 sources of said oxides and a structure directing agent comprising a trans-
23 fused ring N,N-diethyl-2-methyldecahydroquinolinium cation.

24 In accordance with the present invention there is provided a process
25 for converting hydrocarbons comprising contacting a hydrocarbonaceous feed
26 at hydrocarbon converting conditions with a catalyst comprising the molecular
27 sieve of this invention. The molecular sieve may be predominantly in the
28 hydrogen form. It may also be substantially free of acidity. The invention
29 includes such a process wherein the molecular sieve has a mole ratio greater
30 than about 15 of (1) silicon oxide to (2) an oxide selected from aluminum
31 oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and
32 mixtures thereof, and has, after calcination, the X-ray diffraction lines of Table
33 2.

1 Further provided by the present invention is a hydrocracking process
2 comprising contacting a hydrocarbon feedstock under hydrocracking
3 conditions with a catalyst comprising the molecular sieve of this invention,
4 preferably predominantly in the hydrogen form.

5 This invention also includes a dewaxing process comprising contacting
6 a hydrocarbon feedstock under dewaxing conditions with a catalyst
7 comprising the molecular sieve of this invention, preferably predominantly in
8 the hydrogen form.

9 The present invention also includes a process for improving the
10 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising
11 contacting the waxy hydrocarbon feed under isomerization dewaxing
12 conditions with a catalyst comprising the molecular sieve of this invention,
13 preferably predominantly in the hydrogen form.

14 The present invention further includes a process for producing a C₂₀₊
15 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under
16 isomerization conditions over a catalyst comprising the molecular sieve of this
17 invention. The molecular sieve may be predominantly in the hydrogen form.
18 The catalyst may contain at least one Group VIII metal.

19 In accordance with this invention, there is also provided a process for
20 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F
21 (177°C) and containing straight chain and slightly branched chain
22 hydrocarbons comprising contacting said hydrocarbon oil feedstock in the
23 presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi
24 (0.103 – 20.7 MPa) with a catalyst comprising the molecular sieve of this
25 invention, preferably predominantly in the hydrogen form. The catalyst may
26 contain at least one Group VIII metal. The catalyst may be a layered catalyst
27 comprising a first layer comprising the molecular sieve of this invention, and a
28 second layer comprising an aluminosilicate zeolite which is more shape
29 selective than the molecular sieve of said first layer. The first layer may
30 contain at least one Group VIII metal.

31 Also included in the present invention is a process for preparing a
32 lubricating oil which comprises hydrocracking in a hydrocracking zone a
33 hydrocarbonaceous feedstock to obtain an effluent comprising a

1 hydrocracked oil, and catalytically dewaxing said effluent comprising
2 hydrocracked oil at a temperature of at least about 400°F (204°C) and at a
3 pressure of from about 15 psig to about 3000 psig (0.103 – 20.7 Mpa
4 gauge) in the presence of added hydrogen gas with a catalyst comprising the
5 molecular sieve of this invention. The molecular sieve may be predominantly
6 in the hydrogen form. The catalyst may contain at least one Group VIII metal.

7 Further included in this invention is a process for isomerization
8 dewaxing a raffinate comprising contacting said raffinate in the presence of
9 added hydrogen with a catalyst comprising the molecular sieve of this
10 invention. The raffinate may be bright stock, and the molecular sieve may be
11 predominantly in the hydrogen form. The catalyst may contain at least one
12 Group VIII metal.

13 Also included in this invention is a process for increasing the octane of
14 a hydrocarbon feedstock to produce a product having an increased aromatics
15 content comprising contacting a hydrocarbonaceous feedstock which
16 comprises normal and slightly branched hydrocarbons having a boiling range
17 above about 40°C and less than about 200°C, under aromatic conversion
18 conditions with a catalyst comprising the molecular sieve of this invention
19 made substantially free of acidity by neutralizing said molecular sieve with a
20 basic metal. Also provided in this invention is such a process wherein the
21 molecular sieve contains a Group VIII metal component.

22 Also provided by the present invention is a catalytic cracking process
23 comprising contacting a hydrocarbon feedstock in a reaction zone under
24 catalytic cracking conditions in the absence of added hydrogen with a catalyst
25 comprising the molecular sieve of this invention, preferably predominantly in
26 the hydrogen form. Also included in this invention is such a catalytic cracking
27 process wherein the catalyst additionally comprises a large pore crystalline
28 cracking component.

29 This invention further provides an isomerization process for isomerizing
30 C₄ to C₇ hydrocarbons, comprising contacting a feed having normal and
31 slightly branched C₄ to C₇ hydrocarbons under isomerizing conditions with a
32 catalyst comprising the molecular sieve of this invention, preferably
33 predominantly in the hydrogen form. The molecular sieve may be

1 impregnated with at least one Group VIII metal, preferably platinum. The
2 catalyst may be calcined in a steam/air mixture at an elevated temperature
3 after impregnation of the Group VIII metal.

4 Also provided by the present invention is a process for alkylating an
5 aromatic hydrocarbon which comprises contacting under alkylation conditions
6 at least a molar excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin
7 under at least partial liquid phase conditions and in the presence of a catalyst
8 comprising the molecular sieve of this invention, preferably predominantly in
9 the hydrogen form. The olefin may be a C₂ to C₄ olefin, and the aromatic
10 hydrocarbon and olefin may be present in a molar ratio of about 4:1 to about
11 20:1, respectively. The aromatic hydrocarbon may be selected from the
12 group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene,
13 naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

14 Further provided in accordance with this invention is a process for
15 transalkylating an aromatic hydrocarbon which comprises contacting under
16 transalkylating conditions an aromatic hydrocarbon with a polyalkyl aromatic
17 hydrocarbon under at least partial liquid phase conditions and in the presence
18 of a catalyst comprising the molecular sieve of this invention, preferably
19 predominantly in the hydrogen form. The aromatic hydrocarbon and the
20 polyalkyl aromatic hydrocarbon may be present in a molar ratio of from about
21 1:1 to about 25:1, respectively.

22 The aromatic hydrocarbon may be selected from the group consisting
23 of benzene, toluene, ethylbenzene, xylene, or mixtures thereof, and the
24 polyalkyl aromatic hydrocarbon may be a dialkylbenzene.

25 Further provided by this invention is a process to convert paraffins to
26 aromatics which comprises contacting paraffins under conditions which cause
27 paraffins to convert to aromatics with a catalyst comprising the molecular
28 sieve of this invention, said catalyst comprising gallium, zinc, or a compound
29 of gallium or zinc.

30 In accordance with this invention there is also provided a process for
31 isomerizing olefins comprising contacting said olefin under conditions which
32 cause isomerization of the olefin with a catalyst comprising the molecular
33 sieve of this invention.

1 Further provided in accordance with this invention is a process for
2 isomerizing an isomerization feed comprising an aromatic C₈ stream of xylene
3 isomers or mixtures of xylene isomers and ethylbenzene, wherein a more
4 nearly equilibrium ratio of ortho-, meta- and para-xylenes is obtained, said
5 process comprising contacting said feed under isomerization conditions with a
6 catalyst comprising the molecular sieve of this invention.

7 The present invention further provides a process for oligomerizing
8 olefins comprising contacting an olefin feed under oligomerization conditions
9 with a catalyst comprising the molecular sieve of this invention.

10 This invention also provides a process for converting oxygenated
11 hydrocarbons comprising contacting said oxygenated hydrocarbon with a
12 catalyst comprising the molecular sieve of this invention under conditions to
13 produce liquid products. The oxygenated hydrocarbon may be a lower
14 alcohol.

15 Further provided in accordance with the present invention is a process
16 for the production of higher molecular weight hydrocarbons from lower
17 molecular weight hydrocarbons comprising the steps of:

- 18 (a) introducing into a reaction zone a lower molecular weight
19 hydrocarbon-containing gas and contacting said gas in said zone under
20 C₂₊ hydrocarbon synthesis conditions with the catalyst and a metal or
21 metal compound capable of converting the lower molecular weight
22 hydrocarbon to a higher molecular weight hydrocarbon; and
23 (b) withdrawing from said reaction zone a higher molecular weight
24 hydrocarbon-containing stream.

25 Also provided in accordance with this invention is a catalyst
26 composition for promoting polymerization of 1-olefins, said composition
27 comprising

28

29 (A) a molecular sieve having a mole ratio greater than about 15 of (1) an
30 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
31 pentavalent element, second tetravalent element which is different from said
32 first tetravalent element or mixture thereof and having, after calcination, the
33 X-ray diffraction lines of Table 2; and

1

2 (B) an organotitanium or organochromium compound.

3 Oxide (1) may be silicon oxide, and oxide (2) may be an oxide selected
4 from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide,
5 indium oxide.

6 The present invention further provides a for polymerizing 1-olefins,
7 which process comprises contacting 1-olefin monomer with a catalytically
8 effective amount of a catalyst composition comprising

9

10 (A) a molecular sieve having a mole ratio greater than about 15 of (1) an
11 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
12 pentavalent element, second tetravalent element which is different from
13 said first tetravalent element or mixture thereof and having, after
14 calcination, the X-ray diffraction lines of Table 2; and

15

16 (B) an organotitanium or organochromium compound

17

18 under polymerization conditions which include a temperature and pressure
19 suitable for initiating and promoting the polymerization reaction.

20 Oxide (1) may be silicon oxide, and oxide (2) may be an oxide selected
21 from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide,
22 indium oxide.

23 The present invention further provides a process for hydrogenating a
24 hydrocarbon feed containing unsaturated hydrocarbons, the process
25 comprising contacting the feed and hydrogen under conditions which cause
26 hydrogenation with a catalyst comprising the molecular sieve of this invention.
27 The catalyst can also contain metals, salts or complexes wherein the metal is
28 selected from the group consisting of platinum, palladium, rhodium, iridium or
29 combinations thereof, or the group consisting of nickel, molybdenum, cobalt,
30 tungsten, titanium, chromium, vanadium, rhenium, manganese and
31 combinations thereof.

32 In accordance with this invention, there is also provided a process for
33 hydrotreating a hydrocarbon feedstock comprising contacting the feedstock

1 with a hydrotreating catalyst and hydrogen under hydrotreating conditions,
2 wherein the catalyst comprises the molecular sieve of this invention.

3 In accordance with this invention, there is provided a process for the
4 reduction of oxides of nitrogen contained in a gas stream wherein said
5 process comprises contacting the gas stream with a molecular sieve, the
6 molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a
7 first tetravalent element to (2) an oxide of a trivalent element, pentavalent
8 element, second tetravalent element different from said first tetravalent
9 element or mixture thereof and having, after calcination, the X-ray diffraction
10 lines of Table 2. There is also provided a process for the reduction of oxides
11 of nitrogen contained in a gas stream wherein said process comprises
12 contacting the gas stream with a molecular sieve, the molecular sieve having
13 a mole ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected
14 from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide,
15 indium oxide and mixtures thereof, and having, after calcination, the X-ray
16 diffraction lines of Table 2. The molecular sieve may contain a metal or metal
17 ions (such as cobalt, copper, platinum, iron, chromium, manganese, nickel,
18 zinc, lanthanum, palladium, rhodium or mixtures thereof) capable of catalyzing
19 the reduction of the oxides of nitrogen, and the process may be conducted in
20 the presence of a stoichiometric excess of oxygen. In a preferred
21 embodiment, the gas stream is the exhaust stream of an internal combustion
22 engine.

23 The present invention provides a process for treating a cold-start
24 engine exhaust gas stream containing hydrocarbons and other pollutants
25 consisting of flowing said engine exhaust gas stream over a molecular sieve
26 bed which preferentially adsorbs the hydrocarbons over water to provide a
27 first exhaust stream, and flowing the first exhaust gas stream over a catalyst
28 to convert any residual hydrocarbons and other pollutants contained in the
29 first exhaust gas stream to innocuous products and provide a treated exhaust
30 stream and discharging the treated exhaust stream into the atmosphere, the
31 molecular sieve bed characterized in that it comprises a molecular sieve
32 having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent
33 element to (2) an oxide of a trivalent element, pentavalent element, second
34 tetravalent element which is different from said first tetravalent element or

1 mixture thereof and having, after calcination, the X-ray diffraction lines of Table
2 2.

3 Further provided in accordance with this invention is the above process
4 for treatment of cold-start engine exhaust wherein the molecular sieve has a
5 mole ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected from
6 aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium
7 oxide and mixtures thereof, and having, after calcination, the X-ray diffraction
8 lines of Table 2. The present invention further provides such a process wherein
9 the engine is an internal combustion engine, including automobile engines,
10 which can be fueled by a hydrocarbonaceous fuel. Also provided by the present
11 invention is such a process wherein the molecular sieve has deposited on it a
12 metal selected from the group consisting of platinum, palladium, rhodium,
13 ruthenium, and mixtures thereof.

14 According to another aspect, there is provided a molecular sieve having a
15 mole ratio greater than about 15 of (1) an oxide of a first tetravalent element to
16 (2) an oxide of a trivalent element, pentavalent element, second tetravalent
17 element which is different from said first tetravalent element or mixture thereof
18 and having, after calcination, the X-ray diffraction lines of Table 2.

19 According to a further aspect, there is provided a molecular sieve having
20 a mole ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected
21 from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide,
22 indium oxide and mixtures thereof, and having, after calcination, the X-ray
23 diffraction lines of Table 2.

24 According to another aspect, there is provided a process for converting
25 hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon
26 converting conditions with a catalyst comprising a molecular sieve having a mole
27 ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an
28 oxide of a trivalent element, pentavalent element, second tetravalent element
29 which is different from said first tetravalent element or mixture thereof and
30 having, after calcination, the X-ray diffraction lines of Table 2.

31 According to a further aspect, there is provided a process for converting
32 oxygenated hydrocarbons comprising contacting said oxygenated hydrocarbon
33 under conditions to produce liquid products with a catalyst comprising a
34 molecular sieve having a mole ratio greater than about 15 of an oxide of a first
35 tetravalent element to an oxide of a second tetravalent element which is different

1 from said first tetravalent element, trivalent element, pentavalent element or
2 mixture thereof and having, after calcination, the X-ray diffraction lines of Table
3 2.

4 According to another aspect, there is provided a catalyst composition for
5 promoting polymerization of 1-olefins, said composition comprising:

6 (A) a molecular sieve having a mole ratio greater than about 15 of (1) an
7 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
8 pentavalent element, second tetravalent element which is different from said first
9 tetravalent element or mixture thereof and having, after calcination, the X-ray
10 diffraction lines of Table 2; and

11 (B) an organotitanium or organochromium compound.

12 According to a further aspect, there is provided a process for
13 hydrotreating a hydrocarbon feedstock comprising contacting the feedstock with
14 a hydrotreating catalyst and hydrogen under hydrotreating conditions, wherein
15 the catalyst comprises a molecular sieve having a mole ratio greater than about
16 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent
17 element, pentavalent element, second tetravalent element which is different from
18 said first tetravalent element or mixture thereof and having, after calcination, the
19 X-ray diffraction lines of Table 2.

20 According to another aspect, there is provided a process for
21 hydrotreating a hydrocarbon feedstock comprising contacting the feedstock with
22 a hydrotreating catalyst and hydrogen under hydrotreating conditions, wherein
23 the catalyst comprises a molecular sieve having a mole ratio greater than about
24 15 of (1) an silicon oxide (2) an oxide selected from aluminum oxide, gallium
25 oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof,
26 and having, after calcination, the X-ray diffraction lines of Table 2.

27 According to a further aspect, there is provided a process for converting
28 hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon
29 converting conditions with a catalyst comprising a molecular sieve having a mole
30 ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected from
31 aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium
32 oxide and mixtures thereof, and having, after calcination, the X-ray diffraction
33 lines of Table 2.

34 According to another aspect, there is provided a process for the reduction
35 of oxides of nitrogen contained in a gas stream wherein said process comprises

1 contacting the gas stream with a molecular sieve, the molecular sieve having a
2 mole ratio greater than about 15 of (1) an oxide of a first tetravalent element to
3 (2) an oxide of a trivalent element, pentavalent element, second tetravalent
4 element which is different from said first tetravalent element or mixture thereof
5 and having, after calcination, the X-ray diffraction lines of Table 2.

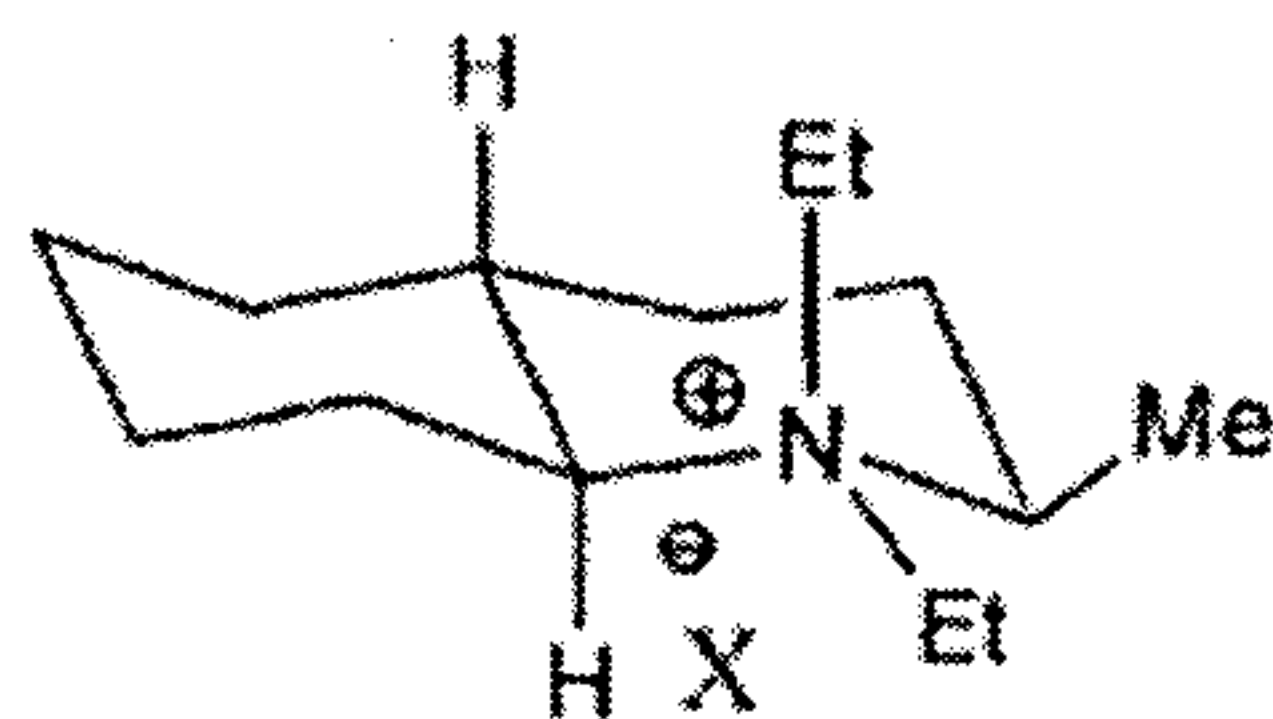
6 According to a further aspect, there is provided a process for the
7 reduction of oxides of nitrogen contained in a gas stream wherein said process
8 comprises contacting the gas stream with a molecular sieve, the molecular sieve
9 having a mole ratio greater than about 15 of (1) silicon oxide to (2) an oxide
10 selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium
11 oxide, indium oxide and mixtures thereof, and having, after calcination, the X-ray
12 diffraction lines of Table 2.

13 According to another aspect, there is provided a process for treating a
14 cold-start engine exhaust gas stream containing hydrocarbons and other
15 pollutants consisting of flowing said engine exhaust gas stream over a molecular
16 sieve bed which preferentially adsorbs the hydrocarbons over water to provide a
17 first exhaust stream, and flowing the first exhaust gas stream over a catalyst to
18 convert any residual hydrocarbons and other pollutants contained in the first
19 exhaust gas stream to innocuous products and provide a treated exhaust stream
20 and discharging the treated exhaust stream into the atmosphere, the molecular
21 sieve bed characterized in that it comprises a molecular sieve having a mole
22 ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an
23 oxide of a trivalent element, pentavalent element, second tetravalent element
24 which is different from said first tetravalent element or mixture thereof and
25 having, after calcination, the X-ray diffraction lines of Table 2.

26 DETAILED DESCRIPTION OF THE INVENTION

27 The present invention comprises a family of crystalline molecular sieves
28 designated herein "molecular sieve SSZ-56" or simply "SSZ-56". In preparing
29 SSZ-56, a N,N-diethyl-2-methyldecahydroquinolinium cation (the trans-fused ring
30 isomer) is used as a structure directing agent ("SDA"), also known as a
31 crystallization template. The SDA useful for making SSZ-56 has the following
32 structure:

1



2

- 3 The SDA cation is associated with an anion (X⁻) which may be any anion
4 that is not detrimental to the formation of the molecular sieve.
5 Representative anions include halogen, e.g., fluoride, chloride, bromide and

1 iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like.
 2 Hydroxide is the most preferred anion.

3 SSZ-56 is prepared from a reaction mixture having the composition
 4 shown in Table A below.

5		TABLE A	
6		Reaction Mixture	
7		Typical	Preferred
8	YO_2/W_aO_b	≥ 15	30 - 60
9	OH-/YO ₂	0.10 – 0.50	0.20 – 0.30
10	Q/YO ₂	0.05 – 0.50	0.10 – 0.30
11	$M_{2/n}/YO_2$	0 – 0.40	0.10 – 0.25
12	H ₂ O/YO ₂	20 – 80	30 – 45

13
 14 where Y is silicon; W is aluminum, gallium, iron, boron, titanium, indium,
 15 vanadium or mixtures thereof; a is 1 or 2, b is 2 when a is 1 (i.e., W is
 16 tetravalent); b is 3 when a is 2 (i.e., W is trivalent); M is an alkali metal cation,
 17 alkaline earth metal cation or mixtures thereof; n is the valence of M (i.e., 1 or
 18 2); and Q is a trans-fused ring N,N-diethyl-2-methyldecahydroquinolinium
 19 cation;.

20 In practice, SSZ-56 is prepared by a process comprising:

- 21 (a) preparing an aqueous solution containing sources of
 22 oxides capable of forming a crystalline molecular sieve and a trans-fused ring
 23 N,N-diethyl-2-methyldecahydroquinolinium cation having an anionic
 24 counterion which is not detrimental to the formation of SSZ-56;
 25 (b) maintaining the aqueous solution under conditions
 26 sufficient to form crystals of SSZ-56; and
 27 (c) recovering the crystals of SSZ-56.

28 Accordingly, SSZ-56 may comprise the crystalline material and the
 29 SDA in combination with metallic and non-metallic oxides bonded in
 30 tetrahedral coordination through shared oxygen atoms to form a cross-linked
 31 three dimensional crystal structure. Typical sources of silicon oxide
 32 include silicates, silica hydrogel, silicic acid, fumed silica, colloidal silica,
 33 tetra-alkyl orthosilicates, and silica hydroxides. Boron can be added in forms
 34 corresponding to its silicon counterpart, such as boric acid.

1 A source zeolite reagent may provide a source of boron. In most
2 cases, the source zeolite also provides a source of silica. The source zeolite
3 in its deboronated form may also be used as a source of silica, with additional
4 silicon added using, for example, the conventional sources listed above. Use
5 of a source zeolite reagent for the present process is more completely
6 described in U.S. Patent No. 5,225,179, issued July 6, 1993 to Nakagawa
7 entitled "Method of Making Molecular Sieves", the disclosure of which is
8 incorporated herein by reference.

9 Typically, an alkali metal hydroxide and/or an alkaline earth metal
10 hydroxide, such as the hydroxide of sodium, potassium, lithium, cesium,
11 rubidium, calcium, and magnesium, is used in the reaction mixture; however,
12 this component can be omitted so long as the equivalent basicity is
13 maintained. The SDA may be used to provide hydroxide ion. Thus, it may be
14 beneficial to ion exchange, for example, the halide to hydroxide ion, thereby
15 reducing or eliminating the alkali metal hydroxide quantity required. The alkali
16 metal cation or alkaline earth cation may be part of the as-synthesized
17 crystalline oxide material, in order to balance valence electron charges
18 therein.

19 The reaction mixture is maintained at an elevated temperature until the
20 crystals of the SSZ-56 are formed. The hydrothermal crystallization is usually
21 conducted under autogenous pressure, at a temperature between 100°C and
22 200°C, preferably between 135°C and 160°C. The crystallization period is
23 typically greater than 1 day and preferably from about 3 days to about
24 20 days.

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

27 During the hydrothermal crystallization step, the SSZ-56 crystals can
28 be allowed to nucleate spontaneously from the reaction mixture. The use of
29 SSZ-56 crystals as seed material can be advantageous in decreasing the time
30 necessary for complete crystallization to occur. In addition, seeding can lead
31 to an increased purity of the product obtained by promoting the nucleation
32 and/or formation of SSZ-56 over any undesired phases. When used as
33 seeds, SSZ-56 crystals are added in an amount between 0.1 and 10% of the

1 weight of first tetravalent element oxide, e.g. silica, used in the reaction
2 mixture.

3 Once the molecular sieve crystals have formed, the solid product is
4 separated from the reaction mixture by standard mechanical separation
5 techniques such as filtration. The crystals are water-washed and then dried,
6 e.g., at 90°C to 150°C for from 8 to 24 hours, to obtain the as-synthesized
7 SSZ-56 crystals. The drying step can be performed at atmospheric pressure
8 or under vacuum.

9 SSZ-56 as prepared has a mole ratio of silicon oxide to boron oxide
10 greater than about 15; and has, after calcination, the X-ray diffraction lines of
11 Table 2 below. SSZ-56 further has a composition, as synthesized (i.e., prior
12 to removal of the SDA from the SSZ-56) and in the anhydrous state, in terms
13 of mole ratios, shown in Table B below.

14 TABLE B

15 As-Synthesized SSZ-56

16	YO_2/W_cO_d	15 - infinity
17	$M_{2/n}/YO_2$	0 - 0.03
18	Q/YO_2	0.02 - 0.05

19
20 where Y, W, M, n, and Q are as defined above and c is 1 or 2; d is 2 when c is
21 1 (i.e., W is tetravalent) or d is 3 or 5 when c is 2 (i.e., d is 3 when W is
22 trivalent or 5 when W is pentavalent).

23 SSZ-56 can be an all-silica. SSZ-56 is made as a borosilicate and then
24 the boron can be removed, if desired, by treating the borosilicate SSZ-56 with
25 acetic acid at elevated temperature (as described in Jones et al., *Chem.*
26 *Mater.*, 2001, 13, 1041-1050) to produce an all-silica version of SSZ-56 (i.e.,
27 YO_2/W_cO_d is ∞).

28 If desired, SSZ-56 can be made as a borosilicate and then the boron
29 can be removed as described above and replaced with metal atoms by
30 techniques known in the art. Aluminum, gallium, iron, titanium, vanadium and
31 mixtures thereof can be added in this manner.

32 It is believed that SSZ-56 is comprised of a new framework structure or
33 topology which is characterized by its X-ray diffraction pattern. SSZ-56,

1 as-synthesized, has a crystalline structure whose X-ray powder diffraction
 2 pattern exhibit the characteristic lines shown in Table 1 and is thereby
 3 distinguished from other molecular sieves.

4 TABLE 1

5 X-ray data for the as-synthesized Boron-SSZ-56

<u>$2\theta^{(a)}$</u>	<u>d</u>	<u>Relative Intensity^(b)</u>
6.58	13.43	M
7.43	11.88	M
7.93	11.14	S
8.41	10.51	M
13.22	6.69	M
13.93	5.95	M
14.86	5.95	M
22.59	3.93	VS
23.26	3.82	VS
24.03	3.70	S

6 ^(a) ± 0.10

7 ^(b) The X-ray patterns provided are based on a relative intensity
 8 scale in which the strongest line in the X-ray pattern is assigned
 9 a value of 100: W(weak) is less than 20; M(medium) is between
 10 20 and 40; S(strong) is between 40 and 60; VS(very strong) is
 11 greater than 60.

12 Table 1A below shows the X-ray powder diffraction lines for as-
 13 synthesized SSZ-56 including actual relative intensities.

14 TABLE 1A

15 As-Synthesized SSZ-56

<u>$2\theta^{(a)}$</u>	<u>d</u>	<u>I/I_o x100</u> <u>Relative Intensity</u>
6.58	13.42	36.3
7.43	11.88	25.2
7.93	11.14	58.5
8.41	10.51	30.9
8.84	10.00	18.0
9.5	9.30	4.9
11.04	8.00	11.1
11.29	7.83	4.5
11.56	7.64	12.6
12.15	7.27	18.7
13.22	6.70	34.3

	<u>2θ^(a)</u>	<u>d</u>	<u>I/I₀ x100</u> <u>Relative Intensity</u>
	13.93	6.35	21.6
	14.86	5.96	20.4
	15.94	5.56	5.7
	17.02	5.20	10.8
	17.45	5.07	8.2
	17.77	4.99	5.8
	18.04	4.91	13.6
	18.79	4.72	8.4
	19.72	4.50	2.1
	19.90	4.46	2.2
	20.11	4.41	4.4
	20.42	4.35	8.8
	21.22	4.18	19.8
	21.57	4.12	3.2
	22.58	3.93	73.1
	23.26	3.82	100.0
	24.03	3.70	48.9
	25.04	3.55	5.7
	25.32	3.51	4.1
	25.49	3.49	3.5
	25.99	3.42	12.9
	26.58	3.35	10.2
	26.86	3.32	7.2
	28.33	3.15	6.6
	28.86	3.09	13.3
	29.41	3.03	3.5
	29.68	3.00	5.1
	30.07	2.97	9.4
	31.07	2.88	2.2
	32.08	2.79	5.9
	32.82	2.73	2.7
	34.13	2.62	4.9
	34.97	2.56	3.4
	37.49	2.39	2.9
1	^(a) ± 0.10		

2 After calcination, the SSZ-56 molecular sieves have a crystalline
3 structure whose X-ray powder diffraction pattern include the characteristic
4 lines shown in Table 2:

5 TABLE 2
6 X-ray data for calcined SSZ-56

<u>2θ</u>	<u>d</u>	<u>Relative Intensity</u>
6.54	13.51	VS
7.36	11.97	VS
7.89	11.20	VS

	8.35	10.58	VS
	8.81	10.03	S
	13.16	6.72	M
	14.83	5.96	M
	22.48	3.95	VS
	23.24	3.82	VS
	23.99	3.70	S
1	(a) ± 0.10		

2 Table 2A below shows the X-ray powder diffraction lines for calcined
3 SSZ-56 including actual relative intensities.

4 TABLE 2A
5 Calcined SSZ-56

<u>$2\theta^{(a)}$</u>	<u>d</u>	<u>I/I₀ x 100</u> <u>Relative Intensity</u>
6.54	13.51	70.0
7.38	11.97	69.3
7.89	11.20	85.2
8.35	10.58	68.7
8.81	10.03	43.2
11.23	7.87	14.7
11.52	7.68	5.6
12.09	7.31	9.9
13.16	6.72	23.3
13.89	6.37	11.1
14.42	6.14	9.3
14.83	5.97	38.5
15.89	5.57	8.1
16.95	5.22	6.0
17.41	5.09	5.4
17.75	5.00	6.7
17.96	4.93	6.3
18.75	4.73	7.7
19.05	4.66	3.3
20.00	4.44	7.5
20.36	4.36	5.0
21.15	4.19	16.9
21.55	4.12	4.5
22.48	3.95	63.0
23.24	3.82	100.0
23.99	3.71	44.8
25.15	3.54	4.4
25.41	3.50	2.6
25.96	3.43	15.6
26.51	3.36	10.2
26.83	3.32	6.5
28.19	3.16	10.6

	$2\theta^{(a)}$	d	$\frac{I/I_0 \times 100}{\text{Relative Intensity}}$
	28.80	3.10	15.7
	29.28	3.05	2.7
	30.02	2.97	11.3
	30.98	2.88	3.0
	31.99	2.80	5.5
	32.72	2.73	4.3
	34.04	2.63	5.9
	34.42	2.60	2.6
	34.70	2.58	4.1
	35.34	2.54	2.1
	36.05	2.49	2.7
	37.41	2.40	2.8
	39.76	2.26	1.8
1	$^{(a)} \pm 0.10$		

2 The X-ray powder diffraction patterns were determined by standard
3 techniques. The radiation was the K-alpha/doublet of copper. The peak
4 heights and the positions, as a function of 2θ where θ is the Bragg angle, were
5 read from the relative intensities of the peaks, and d , the interplanar spacing
6 in Angstroms 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
9 at ± 0.10 degrees.

10 The X-ray diffraction pattern of Table 1 is representative of "as-
11 synthesized" or "as-made" SSZ-56 molecular sieves. Minor variations in the
12 diffraction pattern can result from variations in the silica-to-boron mole ratio of
13 the particular sample due to changes in lattice constants. In addition,
14 sufficiently small crystals will affect the shape and intensity of peaks, leading
15 to significant peak broadening.

16 Representative peaks from the X-ray diffraction pattern of calcined
17 SSZ-56 are shown in Table 2. Calcination can also result in changes in the
18 intensities of the peaks as compared to patterns of the "as-made" material, as
19 well as minor shifts in the diffraction pattern. The molecular sieve produced
20 by exchanging the metal or other cations present in the molecular sieve with
21 various other cations (such as H^+ or NH_4^+) yields essentially the same
22 diffraction pattern, although again, there may be minor shifts in the interplanar
23 spacing and variations in the relative intensities of the peaks. Notwithstanding

1 these minor perturbations, the basic crystal lattice remains unchanged by
2 these treatments.

3 Crystalline SSZ-56 can be used as-synthesized, but preferably will be
4 thermally treated (calcined). Usually, it is desirable to remove the alkali metal
5 cation by ion exchange and replace it with hydrogen, ammonium, or any
6 desired metal ion. The molecular sieve can be leached with chelating agents,
7 e.g., EDTA or dilute acid solutions, to increase the silica to alumina mole ratio.
8 The molecular sieve can also be steamed; steaming helps stabilize the
9 crystalline lattice to attack from acids.

10 The molecular sieve can be used in intimate combination with
11 hydrogenating components, such as tungsten, vanadium, molybdenum,
12 rhenium, nickel, cobalt, chromium, manganese, or a noble metal, such as
13 palladium or platinum, for those applications in which a hydrogenation-
14 dehydrogenation function is desired.

15 Metals may also be introduced into the molecular sieve by replacing
16 some of the cations in the molecular sieve with metal cations via standard ion
17 exchange techniques (see, for example, U.S. Patent Nos. 3,140,249 issued
18 July 7, 1964 to Plank et al.; 3,140,251 issued July 7, 1964 to Plank et al.; and
19 3,140,253 issued July 7, 1964 to Plank et al.). Typical replacing cations can
20 include metal cations, e.g., rare earth, Group IA, Group IIA and Group VIII
21 metals, as well as their mixtures. Of the replacing metallic cations, cations of
22 metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and
23 Fe are particularly preferred.

24 The hydrogen, ammonium, and metal components can be
25 ion-exchanged into the SSZ-56. The SSZ-56 can also be impregnated with
26 the metals, or the metals can be physically and intimately admixed with the
27 SSZ-56 using standard methods known to the art.

28 Typical ion-exchange techniques involve contacting the synthetic
29 molecular sieve with a solution containing a salt of the desired replacing
30 cation or cations. Although a wide variety of salts can be employed, chlorides
31 and other halides, acetates, nitrates, and sulfates are particularly preferred.
32 The molecular sieve is usually calcined prior to the ion-exchange procedure to
33 remove the organic matter present in the channels and on the surface, since
34 this results in a more effective ion exchange. Representative ion exchange

1 techniques are disclosed in a wide variety of patents including U.S. Patent
2 Nos. 3,140,249 issued on July 7, 1964 to Plank et al.; 3,140,251 issued on
3 July 7, 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964 to Plank
4 et al.

5 Following contact with the salt solution of the desired replacing cation,
6 the molecular sieve is typically washed with water and dried at temperatures
7 ranging from 65°C to about 200°C. After washing, the molecular sieve can be
8 calcined in air or inert gas at temperatures ranging from about 200°C to about
9 800°C for periods of time ranging from 1 to 48 hours, or more, to produce a
10 catalytically active product especially useful in hydrocarbon conversion
11 processes.

12 Regardless of the cations present in the synthesized form of SSZ-56,
13 the spatial arrangement of the atoms which form the basic crystal lattice of the
14 molecular sieve remains essentially unchanged.

15 SSZ-56 can be formed into a wide variety of physical shapes.
16 Generally speaking, the molecular sieve can be in the form of a powder, a
17 granule, or a molded product, such as extrudate having a particle size
18 sufficient to pass through a 2-mesh (Tyler) screen and be retained on a
19 400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by
20 extrusion with an organic binder, the SSZ-56 can be extruded before drying,
21 or, dried or partially dried and then extruded.

22 SSZ-56 can be composited with other materials resistant to the
23 temperatures and other conditions employed in organic conversion
24 processes. Such matrix materials include active and inactive materials and
25 synthetic or naturally occurring zeolites as well as inorganic materials such as
26 clays, silica and metal oxides. Examples of such materials and the manner in
27 which they can be used are disclosed in U.S. Patent No. 4,910,006, issued
28 May 20, 1990 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31,
29 1994 to Nakagawa.

30

31 SSZ-56 is useful in catalysts for a variety of hydrocarbon conversion
32 reactions such as hydrocracking, dewaxing, isomerization and the like, for the

1 reduction of oxides of nitrogen in a gas stream, and for treating a cold-start
2 engine exhaust stream.

3 Hydrocarbon Conversion Processes

4 SSZ-56 zeolites are useful in hydrocarbon conversion reactions.

5 Hydrocarbon conversion reactions are chemical and catalytic processes in
6 which carbon containing compounds are changed to different carbon
7 containing compounds. Examples of hydrocarbon conversion reactions in
8 which SSZ-56 are expected to be useful include hydrocracking, dewaxing,
9 catalytic cracking and olefin and aromatics formation reactions. The catalysts
10 are also expected to be useful in other petroleum refining and hydrocarbon
11 conversion reactions such as isomerizing n-paraffins and naphthenes,
12 polymerizing and oligomerizing olefinic or acetylenic compounds such as
13 isobutylene and butene-1, polymerization of 1-olefins (e.g., ethylene),
14 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and
15 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene,
16 xylenes and higher methylbenzenes and oxidation reactions. Also included
17 are rearrangement reactions to make various naphthalene derivatives, and
18 forming higher molecular weight hydrocarbons from lower molecular weight
19 hydrocarbons (e.g., methane upgrading).

20 The SSZ-56 catalysts may have high selectivity, and under
21 hydrocarbon conversion conditions can provide a high percentage of desired
22 products relative to total products.

23 For high catalytic activity, the SSZ-56 zeolite should be predominantly
24 in its hydrogen ion form. Generally, the zeolite is converted to its hydrogen
25 form by ammonium exchange followed by calcination. If the zeolite is
26 synthesized with a high enough ratio of SDA cation to sodium ion, calcination
27 alone may be sufficient. It is preferred that, after calcination, at least 80% of
28 the cation sites are occupied by hydrogen ions and/or rare earth ions. As
29 used herein, "predominantly in the hydrogen form" means that, after
30 calcination, at least 80% of the cation sites are occupied by hydrogen ions
31 and/or rare earth ions.

32 SSZ-56 zeolites can be used in processing hydrocarbonaceous
33 feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and
34 can be from many different sources, such as virgin petroleum fractions,

1 recycle petroleum fractions, shale oil, liquefied coal, tar sand oil, synthetic
2 paraffins from NAO, recycled plastic feedstocks and, in general, can be any
3 carbon containing feedstock susceptible to zeolitic catalytic reactions.
4 Depending on the type of processing the hydrocarbonaceous feed is to
5 undergo, the feed can contain metal or be free of metals, it can also have high
6 or low nitrogen or sulfur impurities. It can be appreciated, however, that in
7 general processing will be more efficient (and the catalyst more active) the
8 lower the metal, nitrogen, and sulfur content of the feedstock.

9 The conversion of hydrocarbonaceous feeds can take place in any
10 convenient mode, for example, in fluidized bed, moving bed, or fixed bed
11 reactors depending on the types of process desired. The formulation of the
12 catalyst particles will vary depending on the conversion process and method
13 of operation.

14 Other reactions which can be performed using the catalyst of this
15 invention containing a metal, e.g., a Group VIII metal such platinum, include
16 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization
17 reactions.

18 The following table indicates typical reaction conditions which may be
19 employed when using catalysts comprising SSZ-56 in the hydrocarbon
20 conversion reactions of this invention. Preferred conditions are indicated in
21 parentheses.

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig, 0.103-20.7 Mpa gauge (200-3000, 1.38- 20.7 Mpa gauge)	0.1-20 (0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar	0.1-15
Cat. Cracking	127-885	subatm. ¹ (atm.-5 atm.)	0.5-50
Oligomerization	232-649 ² 10-232 ⁴ (27-204) ⁴	0.1-50 atm. ^{2,3} - -	0.2-50 ² 0.05-20 ⁵ (0.1-10) ⁵
Paraffins to aromatics	100-700	0-1000 psig	0.5-40 ⁵
Condensation of alcohols	260-538	0.5-1000 psig, 0.00345-6.89 Mpa gauge	0.5-50 ⁵
Isomerization	93-538 (204-315)	50-1000 psig, 0.345-6.89 Mpa gauge	1-10 (1-4)
Xylene isomerization	260-593 ² (315-566) ² 38-371 ⁴	0.5-50 atm. ² (1-5 atm) ² 1-200 atm. ⁴	0.1-100 ⁵ (0.5-50) ⁵ 0.5-50

1

2 ¹ Several hundred atmospheres3 ² Gas phase reaction4 ³ Hydrocarbon partial pressure5 ⁴ Liquid phase reaction6 ⁵ WHSV

7 Other reaction conditions and parameters are provided below.

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1 (0.178 to 3.56 SCM/liter). Generally, hydrogen will be separated from the
2 product and recycled to the reaction zone. Typical feedstocks include light
3 gas oil, heavy gas oils and reduced crudes boiling above about 350°F
4 (177°C).

5 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon
6 oil feedstock boiling above about 350°F (177°C) and containing straight chain
7 and slightly branched chain hydrocarbons by contacting the hydrocarbon oil
8 feedstock in the presence of added hydrogen gas at a hydrogen pressure of
9 about 15-3000 psi (0.103-20.7 Mpa) with a catalyst comprising SSZ-56 and at
10 least one Group VIII metal.

11 The SSZ-56 hydrodewaxing catalyst may optionally contain a
12 hydrogenation component of the type commonly employed in dewaxing
13 catalysts. See the aforementioned U.S. Patent No. 4,910,006 and U.S.
14 Patent No. 5,316,753 for examples of these hydrogenation components.

15 The hydrogenation component is present in an effective amount to
16 provide an effective hydrodewaxing and hydroisomerization catalyst
17 preferably in the range of from about 0.05 to 5% by weight. The catalyst may
18 be run in such a mode to increase isomerization dewaxing at the expense of
19 cracking reactions.

20 The feed may be hydrocracked, followed by dewaxing. This type of
21 two stage process and typical hydrocracking conditions are described in U.S.
22 Patent No. 4,921,594, issued May 1, 1990 to Miller.

23
24 SSZ-56 may also be utilized as a dewaxing catalyst in the form of a
25 layered catalyst. That is, the catalyst comprises a first layer comprising
26 zeolite SSZ-56 and at least one Group VIII metal, and a second layer
27 comprising an aluminosilicate zeolite which is more shape selective than
28 zeolite SSZ-56. The use of layered catalysts is disclosed in U.S. Patent
29 No. 5,149,421, issued September 22, 1992 to Miller. The layering may also
30 include a bed of SSZ-56 layered with a non-zeolitic component designed for
31 either hydrocracking or hydrofinishing.

32

1 SSZ-56 may also be used to dewax raffinates, including bright stock,
2 under conditions such as those disclosed in U. S. Patent No. 4,181,598, issued
3 January 1, 1980 to Gillespie *et al.*

4 It is often desirable to use mild hydrogenation (sometimes referred to as
5 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing
6 step can be performed either before or after the dewaxing step, and preferably
7 after. Hydrofinishing is typically conducted at temperatures ranging from about
8 190°C to about 340°C at pressures from about 400 psig to about 3000 psig (2.76
9 to 20.7 Mpa gauge) at space velocities (LHSV) between about 0.1 and 20 and a
10 hydrogen recycle rate of about 400 to 1500 SCF/bbl (0.071 to 0.27 SCM/liter).
11 The hydrogenation catalyst employed must be active enough not only to
12 hydrogenate the olefins, diolefins and color bodies which may be present, but
13 also to reduce the aromatic content. Suitable hydrogenation catalyst are
14 disclosed in U. S. Patent No. 4,921,594, issued May 1, 1990 to Miller. The
15 hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a
16 lubricating oil) since dewaxed products prepared from hydrocracked stocks tend
17 to be unstable to air and light and tend to form sludges spontaneously and
18 quickly.

19 Lube oil may be prepared using SSZ-56. For example, a C₂₀₊ lube oil
20 may be made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising SSZ-
21 56 in the hydrogen form and at least one Group VIII metal. Alternatively, the
22 lubricating oil may be made by hydrocracking in a hydrocracking zone a
23 hydrocarbonaceous feedstock to obtain an effluent comprising a hydrocracked
24 oil, and catalytically dewaxing the effluent at a temperature of at least about
25 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig
26 (0.103-20.7 Mpa gauge) in the presence of added hydrogen gas with a catalyst
27 comprising SSZ-56 in the hydrogen form and at least one Group VIII metal.

28 Aromatics Formation

29 SSZ-56 can be used to convert light straight run naphthas and similar
30 mixtures to highly aromatic mixtures. Thus, normal and slightly branched

1 disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
2 No 5,316,753. When a traditional cracking catalyst (TC) component is
3 employed, the relative weight ratio of the TC to the SSZ-56 is generally
4 between about 1:10 and about 500:1, desirably between about 1:10 and
5 about 200:1, preferably between about 1:2 and about 50:1, and most
6 preferably is between about 1:1 and about 20:1. The novel zeolite and/or the
7 traditional cracking component may be further ion exchanged with rare earth
8 ions to modify selectivity.

9 The cracking catalysts are typically employed with an inorganic oxide
10 matrix component. See the aforementioned U.S. Patent No. 4,910,006 and
11 U.S. Patent No. 5,316,753 for examples of such matrix components.

12 Isomerization

13 The present catalyst is highly active and highly selective for isomerizing
14 C₄ to C₇ hydrocarbons. The activity means that the catalyst can operate at
15 relatively low temperature which thermodynamically favors highly branched
16 paraffins. Consequently, the catalyst can produce a high octane product.
17 The high selectivity means that a relatively high liquid yield can be achieved
18 when the catalyst is run at a high octane.

19 The present process comprises contacting the isomerization catalyst,
20 i.e., a catalyst comprising SSZ-56 in the hydrogen form, with a hydrocarbon
21 feed under isomerization conditions. The feed is preferably a light straight run
22 fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C) and
23 preferably from 60°F to 200°F (16°C to 93°C). Preferably, the hydrocarbon
24 feed for the process comprises a substantial amount of C₄ to C₇ normal and
25 slightly branched low octane hydrocarbons, more preferably C₅ and C₆
26 hydrocarbons.

27 It is preferable to carry out the isomerization reaction in the presence of
28 hydrogen. Preferably, hydrogen is added to give a hydrogen to hydrocarbon
29 ratio (H₂/HC) of between 0.5 and 10 H₂/HC, more preferably between 1 and
30 8 H₂/HC. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
31 No. 5,316,753 for a further discussion of isomerization process conditions.

32 A low sulfur feed is especially preferred in the present process. The
33 feed preferably contains less than 10 ppm, more preferably less than 1 ppm,
34 and most preferably less than 0.1 ppm sulfur. In the case of a feed which is

1 not already low in sulfur, acceptable levels can be reached by hydrogenating
2 the feed in a presaturation zone with a hydrogenating catalyst which is
3 resistant to sulfur poisoning. See the aforementioned U.S. Patent
4 No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of this
5 hydrodesulfurization process.

6 It is preferable to limit the nitrogen level and the water content of the
7 feed. Catalysts and processes which are suitable for these purposes are
8 known to those skilled in the art.

9 After a period of operation, the catalyst can become deactivated by
10 sulfur or coke. See the aforementioned U.S. Patent No. 4,910,006 and U.S.
11 Patent No. 5,316,753 for a further discussion of methods of removing this
12 sulfur and coke, and of regenerating the catalyst.

13 The conversion catalyst preferably contains a Group VIII metal
14 compound to have sufficient activity for commercial use. By Group VIII metal
15 compound as used herein is meant the metal itself or a compound thereof.
16 The Group VIII noble metals and their compounds, platinum, palladium, and
17 iridium, or combinations thereof can be used. Rhenium and tin may also be
18 used in conjunction with the noble metal. The most preferred metal is
19 platinum. The amount of Group VIII metal present in the conversion catalyst
20 should be within the normal range of use in isomerizing catalysts, from about
21 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

22 Alkylation and Transalkylation

23 SSZ-56 can be used in a process for the alkylation or transalkylation of
24 an aromatic hydrocarbon. The process comprises contacting the aromatic
25 hydrocarbon with a C₂ to C₁₆ olefin alkylating agent or a polyalkyl aromatic
26 hydrocarbon transalkylating agent, under at least partial liquid phase
27 conditions, and in the presence of a catalyst comprising SSZ-56.

28 SSZ-56 can also be used for removing benzene from gasoline by
29 alkylating the benzene as described above and removing the alkylated
30 product from the gasoline.

31 For high catalytic activity, the SSZ-56 zeolite should be predominantly
32 in its hydrogen ion form. It is preferred that, after calcination, at least 80% of
33 the cation sites are occupied by hydrogen ions and/or rare earth ions.

1 Examples of suitable aromatic hydrocarbon feedstocks which may be
2 alkylated or transalkylated by the process of the invention include aromatic
3 compounds such as benzene, toluene and xylene. The preferred aromatic
4 hydrocarbon is benzene. There may be occasions where naphthalene or
5 naphthalene derivatives such as dimethylnaphthalene may be desirable.
6 Mixtures of aromatic hydrocarbons may also be employed.

7 Suitable olefins for the alkylation of the aromatic hydrocarbon are those
8 containing 2 to 20, preferably 2 to 4, carbon atoms, such as ethylene,
9 propylene, butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof.
10 There may be instances where pentenes are desirable. The preferred olefins
11 are ethylene and propylene. Longer chain alpha olefins may be used as well.

12 When transalkylation is desired, the transalkylating agent is a polyalkyl
13 aromatic hydrocarbon containing two or more alkyl groups that each may
14 have from 2 to about 4 carbon atoms. For example, suitable polyalkyl
15 aromatic hydrocarbons include di-, tri- and tetra-alkyl aromatic hydrocarbons,
16 such as diethylbenzene, triethylbenzene, diethylmethylbenzene
17 (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene, dibutylbenzene,
18 and the like. Preferred polyalkyl aromatic hydrocarbons are the dialkyl
19 benzenes. A particularly preferred polyalkyl aromatic hydrocarbon is
20 di-isopropylbenzene.

21 When alkylation is the process conducted, reaction conditions are as
22 follows. The aromatic hydrocarbon feed should be present in stoichiometric
23 excess. It is preferred that molar ratio of aromatics to olefins be greater than
24 four-to-one to prevent rapid catalyst fouling. The reaction temperature may
25 range from 100°F to 600°F (38°C to 315°C), preferably 250°F to 450°F (121°C
26 to 232°C). The reaction pressure should be sufficient to maintain at least a
27 partial liquid phase in order to retard catalyst fouling. This is typically 50 psig
28 to 1000 psig (0.345 to 6.89 Mpa gauge) depending on the feedstock and
29 reaction temperature. Contact time may range from 10 seconds to 10 hours,
30 but is usually from 5 minutes to an hour. The weight hourly space velocity
31 (WHSV), in terms of grams (pounds) of aromatic hydrocarbon and olefin per
32 gram (pound) of catalyst per hour, is generally within the range of about 0.5 to
33 50.

1 When transalkylation is the process conducted, the molar ratio of
2 aromatic hydrocarbon will generally range from about 1:1 to 25:1, and
3 preferably from about 2:1 to 20:1. The reaction temperature may range from
4 about 100°F to 600°F (38°C to 315°C), but it is preferably about 250°F to
5 450°F (121°C to 232°C). The reaction pressure should be sufficient to
6 maintain at least a partial liquid phase, typically in the range of about 50 psig
7 to 1000 psig (0.345 to 6.89 Mpa gauge), preferably 300 psig to 600 psig (2.07
8 to 4.14 Mpa gauge). The weight hourly space velocity will range from about
9 0.1 to 10. U.S. Patent No. 5,082,990 issued on January 21, 1992 to Hsieh, et
10 al. describes such processes and is incorporated herein by reference.

11 Conversion of Paraffins to Aromatics

12 SSZ-56 can be used to convert light gas C₂-C₆ paraffins to higher
13 molecular weight hydrocarbons including aromatic compounds. Preferably,
14 the zeolite will contain a catalyst metal or metal oxide wherein said metal is
15 selected from the group consisting of Groups IB, IIB, VIII and IIIA of the
16 Periodic Table. Preferably, the metal is gallium, niobium, indium or zinc in the
17 range of from about 0.05 to 5% by weight.

18 Isomerization of Olefins

19 SSZ-56 can be used to isomerize olefins. The feed stream is a
20 hydrocarbon stream containing at least one C₄₋₆ olefin, preferably a C₄₋₆
21 normal olefin, more preferably normal butene. Normal butene as used in this
22 specification means all forms of normal butene, e.g., 1-butene, cis-2-butene,
23 and trans-2-butene. Typically, hydrocarbons other than normal butene or
24 other C₄₋₆ normal olefins will be present in the feed stream. These other
25 hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen,
26 and inert gases.

27 The feed stream typically may be the effluent from a fluid catalytic
28 cracking unit or a methyl-tert-butyl ether unit. A fluid catalytic cracking unit
29 effluent typically contains about 40-60 weight percent normal butenes. A
30 methyl-tert-butyl ether unit effluent typically contains 40-100 weight percent
31 normal butene. The feed stream preferably contains at least about 40 weight
32 percent normal butene, more preferably at least about 65 weight percent
33 normal butene. The terms iso-olefin and methyl branched iso-olefin may be
34 used interchangeably in this specification.

The liquid hourly space velocity during contacting is generally from about 0.1 to about 50 hr^{-1} , based on the hydrocarbon feed, preferably from about 0.1 to about 20 hr^{-1} , more preferably from about 0.2 to about 10 hr^{-1} , most preferably from about 1 to about 5 hr^{-1} . A hydrogen/hydrocarbon molar ratio is maintained from about 0 to about 30 or higher. The hydrogen can be added directly to the feed stream or directly to the isomerization zone. The reaction is preferably substantially free of water, typically less than about two weight percent based on the feed. The process can be carried out in a packed bed reactor, a fixed bed, fluidized bed reactor, or a moving bed reactor. The bed of the catalyst can move upward or downward. The mole percent conversion of, e.g., normal butene to iso-butene is at least 10, preferably at least 25, and more preferably at least 35.

SSZ-56 may also be useful in a process for isomerizing one or more xylene isomers in a C₈ aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio approaching the equilibrium value. In particular, xylene isomerization is used in conjunction with a separate process to manufacture para-xylene. For example, a portion of the para-xylene in a mixed C₈ aromatics stream may be recovered by crystallization and centrifugation. The mother liquor from the crystallizer is then reacted under xylene isomerization conditions to restore ortho-, meta- and para-xylenes to a near equilibrium ratio. At the same time, part of the ethylbenzene in the mother liquor is converted to xylenes or to products which are easily separated by filtration. The isomerate is blended with fresh feed and the combined stream is distilled

1 to remove heavy and light by-products. The resultant C₈ aromatics stream is
2 then sent to the crystallizer to repeat the cycle.

3 Optionally, isomerization in the vapor phase is conducted in the
4 presence of 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g.,
5 ethylbenzene). If hydrogen is used, the catalyst should comprise about 0.1 to
6 2.0 wt.% of a hydrogenation/dehydrogenation component selected from
7 Group VIII (of the Periodic Table) metal component, especially platinum or
8 nickel. By Group VIII metal component is meant the metals and their
9 compounds such as oxides and sulfides.

10 Optionally, the isomerization feed may contain 10 to 90 wt. of a diluent
11 such as toluene, trimethylbenzene, naphthenes or paraffins.

12 Oligomerization

13 It is expected that SSZ-56 can also be used to oligomerize straight and
14 branched chain olefins having from about 2 to 21 and preferably 2-5 carbon
15 atoms. The oligomers which are the products of the process are medium to
16 heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline
17 blending stock and chemicals.

18 The oligomerization process comprises contacting the olefin feedstock
19 in the gaseous or liquid phase with a catalyst comprising SSZ-56.

20 The zeolite can have the original cations associated therewith replaced
21 by a wide variety of other cations according to techniques well known in the
22 art. Typical cations would include hydrogen, ammonium and metal cations
23 including mixtures of the same. Of the replacing metallic cations, particular
24 preference is given to cations of metals such as rare earth metals,
25 manganese, calcium, as well as metals of Group II of the Periodic Table, e.g.,
26 zinc, and Group VIII of the Periodic Table, e.g., nickel. One of the prime
27 requisites is that the zeolite have a fairly low aromatization activity, i.e., in
28 which the amount of aromatics produced is not more than about 20% by
29 weight. This is accomplished by using a zeolite with controlled acid activity
30 [alpha value] of from about 0.1 to about 120, preferably from about 0.1 to
31 about 100, as measured by its ability to crack n-hexane.

32 Alpha values are defined by a standard test known in the art, e.g., as
33 shown in U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens et al.
34 If required, such zeolites

1 may be obtained by steaming, by use in a conversion process or by any other
2 method which may occur to one skilled in this art.

3 Condensation of Alcohols

4 SSZ-56 can be used to condense lower aliphatic alcohols having 1 to
5 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising
6 mixed aliphatic and aromatic hydrocarbon. The process disclosed in U.S.
7 Patent No. 3,894,107, issued July 8, 1975 to Butter et al., describes the
8 process conditions used in this process.

9
10 The catalyst may be in the hydrogen form or may be base exchanged
11 or impregnated to contain ammonium or a metal cation complement,
12 preferably in the range of from about 0.05 to 5% by weight. The metal cations
13 that may be present include any of the metals of the Groups I through VIII of
14 the Periodic Table. However, in the case of Group IA metals, the cation
15 content should in no case be so large as to effectively inactivate the catalyst,
16 nor should the exchange be such as to eliminate all acidity. There may be
17 other processes involving treatment of oxygenated substrates where a basic
18 catalyst is desired.

19 Methane Upgrading

20 Higher molecular weight hydrocarbons can be formed from lower
21 molecular weight hydrocarbons by contacting the lower molecular weight
22 hydrocarbon with a catalyst comprising SSZ-56 and a metal or metal
23 compound capable of converting the lower molecular weight hydrocarbon to a
24 higher molecular weight hydrocarbon. Examples of such reactions include the
25 conversion of methane to C₂₊ hydrocarbons such as ethylene or benzene or
26 both. Examples of useful metals and metal compounds include lanthanide
27 and or actinide metals or metal compounds.

28 These reactions, the metals or metal compounds employed and the
29 conditions under which they can be run are disclosed in U.S. Patents No.
30 4,734,537, issued March 29, 1988 to Devries et al.; 4,939,311, issued July 3,
31 1990 to Washecheck et al.; 4,962,261, issued October 9, 1990 to Abrevaya et
32 al.; 5,095,161, issued March 10, 1992 to Abrevaya et al.; 5,105,044, issued
33 April 14, 1992 to Han et al.; 5,105,046, issued April 14, 1992 to Washecheck;
34 5,238,898, issued August 24, 1993 to Han et al.; 5,321,185, issued June 14,

1 1994 to van der Vaart; and 5,336,825, issued August 9, 1994 to Choudhary et
2 al.

3 Polymerization of 1-Olefins

4 The molecular sieve of the present invention may be used in a catalyst
5 for the polymerization of 1-olefins, e.g., the polymerization of ethylene. To
6 form the olefin polymerization catalyst, the molecular sieve as hereinbefore
7 described is reacted with a particular type of organometallic compound.
8 Organometallic compounds useful in forming the polymerization catalyst
9 include trivalent and tetravalent organotitanium and organochromium
10 compounds having alkyl moieties and, optionally, halo moieties. In the
11 context of the present invention the term "alkyl" includes both straight and
12 branched chain alkyl, cycloalkyl and alkaryl groups such as benzyl.

13 Examples of trivalent and tetravalent organochromium and
14 organotitanium compounds are disclosed in U. S. Patent No. 4,376,722,
15 issued March 15, 1983 to Chester et al., U. S. Patent No. 4,377,497, issued
16 March 22, 1983 to Chester et al., U. S. Patent No. 4,446,243, issued May 1,
17 1984 to Chester et al., and U. S. Patent No. 4,526,942, issued July 2, 1985 to
18 Chester et al.

19
20 Examples of the organometallic compounds used to form the
21 polymerization catalyst include, but are not limited to, compounds
22 corresponding to the general formula:



25
26 wherein M is a metal selected from titanium and chromium; Y is alkyl; X is
27 halogen (e.g., Cl or Br); n is 1-4; and m is greater than or equal to n and is 3
28 or 4.

29 Examples of organotitanium and organochromium compounds
30 encompassed by such a formula include compounds of the formula CrY_4 ,
31 CrY_3 , CrY_3X , CrY_2X , CrY_2X_2 , $CrYX_2$, $CrYX_3$, TiY_4 , TiY_3 , TiY_3X , TiY_2X , TiY_2X_2 ,
32 $TiYX_2$, $TiYX_3$, wherein X can be Cl or Br and Y can be methyl, ethyl, propyl,
33 isopropyl, butyl, isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl,
34 hexyl, isohexyl, neohexyl, 2-ethylbutyl, octyl, 2-ethylhexyl, 2,2-diethylbutyl, 2-

1 isopropyl-3-methylbutyl, etc., cyclohexylalkyls such as, for example,
2 cyclohexylmethyl, 2-cyclohexylethyl, 3-cyclohexylpropyl, 4-cyclohexylbutyl,
3 and the corresponding alkyl-substituted cyclohexyl radicals as, for example,
4 (4-methylcyclohexyl)methyl, neophyl, i.e., beta, beta-dimethyl-phenethyl,
5 benzyl, ethylbenzyl, and p-isopropylbenzyl. Preferred examples of Y include
6 C₁₋₅ alkyl, especially butyl.

7 The organotitanium and organochromium materials employed in the
8 catalyst can be prepared by techniques well known in the art. See, for
9 example the aforementioned Chester et al. patents.

10 The organotitanium or organochromium compounds can be with the
11 molecular sieve of the present invention, such as by reacting the
12 organometallic compound and the molecular sieve, in order to form the olefin
13 polymerization catalyst. Generally, such a reaction takes place in the same
14 reaction medium used to prepare the organometallic compound under
15 conditions which promote formation of such a reaction product. The
16 molecular sieve can simply be added to the reaction mixture after formation of
17 the organometallic compound has been completed. Molecular sieve is added
18 in an amount sufficient to provide from about 0.1 to 10 parts by weight,
19 preferably from about 0.5 to 5 parts by weight, of organometallic compound in
20 the reaction medium per 100 parts by weight of molecular sieve.

21 Temperature of the reaction medium during reaction of organometallic
22 compound with molecular sieve is also maintained at a level which is low
23 enough to ensure the stability of the organometallic reactant. Thus,
24 temperatures in the range of from about -150° C. to 50° C., preferably from
25 about -80° C. to 0° C. can be usefully employed. Reaction times of from
26 about 0.01 to 10 hours, more preferably from about 0.1 to 1 hour, can be
27 employed in reacting the organotitanium or organochromium compound with
28 the molecular sieve.

29 Upon completion of the reaction, the catalyst material so formed may
30 be recovered and dried by evaporating the reaction medium solvent under a
31 nitrogen atmosphere. Alternatively, olefin polymerization reactions can be
32 conducted in this same solvent based reaction medium used to form the
33 catalyst.

34 The polymerization catalyst can be used to catalyze polymerization of

1 1-olefins. The polymers produced using the catalysts of this invention are
2 normally solid polymers of at least one mono-1-olefin containing from 2 to 8
3 carbon atoms per molecule. These polymers are normally solid
4 homopolymers of ethylene or copolymers of ethylene with another mono-1-
5 olefin containing 3 to 8 carbon atoms per molecule. Exemplary copolymers
6 include those of ethylene/propylene, ethylene/1-butene, ethylene/1-hexane,
7 and ethylene/1-octene and the like. The major portion of such copolymers is
8 derived from ethylene and generally consists of about 80-99, preferably 95-99
9 mole percent of ethylene. These polymers are well suited for extrusion, blow
10 molding, injection molding and the like.

11 The polymerization reaction can be conducted by contacting monomer
12 or monomers, e.g., ethylene, alone or with one or more other olefins, and in
13 the substantial absence of catalyst poisons such as moisture and air, with a
14 catalytic amount of the supported organometallic catalyst at a temperature
15 and at a pressure sufficient to initiate the polymerization reaction. If desired,
16 an inert organic solvent may be used as a diluent and to facilitate materials
17 handling if the polymerization reaction is conducted with the reactants in the
18 liquid phase, e.g. in a particle form (slurry) or solution process. The reaction
19 may also be conducted with reactants in the vapor phase, e.g., in a fluidized
20 bed arrangement in the absence of a solvent but, if desired, in the presence of
21 an inert gas such as nitrogen.

22 The polymerization reaction is carried out at temperatures of from
23 about 30° C. or less, up to about 200° C. or more, depending to a great extent
24 on the operating pressure, the pressure of the olefin monomers, and the
25 particular catalyst being used and its concentration. Naturally, the selected
26 operating temperature is also dependent upon the desired polymer melt index
27 since temperature is definitely a factor in adjusting the molecular weight of the
28 polymer. Preferably, the temperature used is from about 30° C. to about 100°
29 C. in a conventional slurry or "particle forming" process or from 100° C. to
30 150° C. in a "solution forming" process. A temperature of from about 70° C to
31 110° C. can be employed for fluidized bed processes.

32 The pressure to be used in the polymerization reactions can be any
33 pressure sufficient to initiate the polymerization of the monomer(s) to high
34 molecular weight polymer. The pressure, therefore, can range from

1 subatmospheric pressures, using an inert gas as diluent, to superatmospheric
2 pressures of up to about 30,000 psig or more. The preferred pressure is from
3 atmospheric (0 psig) up to about 1000 psig. As a general rule, a pressure of
4 20 to 800 psig is most preferred.

5 The selection of an inert organic solvent medium to be employed in the
6 solution or slurry process embodiments of this invention is not too critical, but
7 the solvent should be inert to the supported organometallic catalyst and olefin
8 polymer produced, and be stable at the reaction temperature used. It is not
9 necessary, however, that the inert organic solvent medium also serve as a
10 solvent for the polymer to be produced. Among the inert organic solvents
11 applicable for such purposes may be mentioned saturated aliphatic
12 hydrocarbons having from about 3 to 12 carbon atoms per molecule such as
13 hexane, heptane, pentane, isooctane, purified kerosene and the like,
14 saturated cycloaliphatic hydrocarbons having from about 5 to 12 carbon
15 atoms per molecule such as cyclohexane, cyclopentane,
16 dimethylcyclopentane and methylcyclohexane and the like and aromatic
17 hydrocarbons having from about 6 to 12 carbon atoms per molecule such as
18 benzene, toluene, xylene, and the like. Particularly preferred solvent media
19 are cyclohexane, pentane, hexane and heptane.

20 Hydrogen can be introduced into the polymerization reaction zone in
21 order to decrease the molecular weight of the polymers produced (i.e., give a
22 much higher Melt Index, MI). Partial pressure of hydrogen when hydrogen is
23 used can be within the range of 5 to 100 psig, preferably 25 to 75 psig. The
24 melt indices of the polymers produced in accordance with the instant invention
25 can range from about 0.1 to about 70 or even higher.

26 More detailed description of suitable polymerization conditions
27 including examples of particle form, solution and fluidized bed polymerization
28 arrangements are found in Karapinka; U.S. Pat. No. 3,709,853; Issued Jan. 9,
29 1973 and Karol et al; U.S. Pat. No. 4,086,408; Issued Apr. 25, 1978.

30

31 Hydrotreating

32 SSZ-56 is useful in a hydrotreating catalyst. During hydrotreatment,
33 oxygen, sulfur and nitrogen present in the hydrocarbonaceous feed is reduced
34 to low levels. Aromatics and olefins, if present in the feed, may also have

1 their double bonds saturated. In some cases, the hydrotreating catalyst and
2 hydrotreating conditions are selected to minimize cracking reactions, which can
3 reduce the yield of the most desulfided product (typically useful as a fuel).
4 Hydrotreating conditions typically include a reaction temperature between 400-
5 900°F (204-482°C), preferably 650-850°F (343-454°C); a pressure between 500
6 and 5000 psig (3.5-34.6 Mpa), preferably 1000 to 3000 psig (7.0-20.8 MPa); a
7 feed rate (LHSV) of 0.5 hr⁻¹ to 20 hr⁻¹ (v/v); and overall hydrogen consumption
8 300 to 2000 scf per barrel of liquid hydrocarbon feed (53.4-356 m³ H₂/m³ feed).
9 The hydrotreating catalyst will typically be a composite of a Group VI metal or
10 compound thereof, and a Group VIII metal or compound thereof supported on
11 the molecular sieve of this invention. Typically, such hydrotreating catalyst are
12 presulfided.

13 Catalysts useful for hydrotreating hydrocarbon feeds are disclosed in
14 U.S. Patent Nos. 4,347,121, issued August 31, 1982 to Mayer *et al*, and
15 4,810,357, issued March 7, 1989 to Chester *et al*. Suitable catalysts include
16 noble metals from Group VIII, such as Fe, Co, Ni, Pt or Pd, and/or Group VI
17 metals, such as Cr, Mo, Sn or W. Examples of combinations of Group VIII and
18 Group VI metals include Ni-Mo or Ni-Sn. Other suitable catalysts are described
19 in U.S. Patent Nos. 4,157,294, issued June 5, 1979 to Iwao *et al*, and 3,904,513,
20 issued September 9, 1975 to Fischer *et al*. U. S. Patent No. 3,852,207, issued
21 December 3, 1974 to Strangeland *et al*, describes suitable noble metal catalysts
22 and mild hydrotreating conditions.

23 The amount of hydrogenation component(s) in the catalyst suitably range
24 from about 0.5% to about 10% by weight of Group VIII component(s) and from
25 5% to about 25% by weight of Group VI metal component(s), calculated as metal
26 oxide(s) per 100 parts by weight of total catalyst., where the percentages by
27 weight are based on the weight of the catalyst before sulfiding. The
28 hydrogenation component(s) in the catalyst may be in the oxidic and/or sulfidic
29 form.

30 Hydrogenation

31 SSZ-56 can be used in a catalyst to catalyze hydrogenation of a
32 hydrocarbon feed containing unsaturated hydrocarbons. The unsaturated

1 hydrocarbons can comprise olefins, dienes, polyenes, aromatic compounds
2 and the like.

3 Hydrogenation is accomplished by contacting the hydrocarbon feed
4 containing unsaturated hydrocarbons with hydrogen in the presence of a
5 catalyst comprising SSZ-56. The catalyst can also contain one or more
6 metals of Group VIB and Group VIII, including salts, complexes and solutions
7 thereof. Reference to these catalytically active metals is intended to
8 encompass such metals or metals in the elemental state or in some form such
9 as an oxide, sulfide, halide, carboxylate and the like. Examples of such
10 metals include metals, salts or complexes wherein the metal is selected from
11 the group consisting of platinum, palladium, rhodium, iridium or combinations
12 thereof, or the group consisting of nickel, molybdenum, cobalt, tungsten,
13 titanium, chromium, vanadium, rhenium, manganese and combinations
14 thereof.

15 The hydrogenation component of the catalyst (i.e., the aforementioned
16 metal) is present in an amount effective to provide the hydrogenation function
17 of the catalyst, preferably in the range of from 0.05 to 25% by weight.

18 Hydrogenation conditions, such as temperature, pressure, space
19 velocities, contact time and the like are well known in the art.

20

21 Reduction of Oxides of Nitrogen In a Gas Stream

22

23 SSZ-56 may be used for the catalytic reduction of the oxides of
24 nitrogen in a gas stream. Typically, the gas stream also contains oxygen,
25 often a stoichiometric excess thereof. Also, the SSZ-56 may contain a metal
26 or metal ions within or on it which are capable of catalyzing the reduction of
27 the nitrogen oxides. Examples of such metals or metal ions include cobalt,
28 copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum,
29 palladium, rhodium and mixtures thereof.

30 One example of such a process for the catalytic reduction of oxides of
31 nitrogen in the presence of a zeolite is disclosed in U.S. Patent No. 4,297,328,
32 issued October 27, 1981 to Ritscher et al. There, the catalytic process
33 is the combustion of carbon monoxide and hydrocarbons and the catalytic
34 reduction of the oxides of nitrogen

1 contained in a gas stream, such as the exhaust gas from an internal
2 combustion engine. The zeolite used is metal ion-exchanged, doped or
3 loaded sufficiently so as to provide an effective amount of catalytic copper
4 metal or copper ions within or on the zeolite. In addition, the process is
5 conducted in an excess of oxidant, e.g., oxygen.

6 7 Cold-Start Emissions

8
9 Gaseous waste products resulting from the combustion of
10 hydrocarbonaceous fuels, such as gasoline and fuel oils, comprise carbon
11 monoxide, hydrocarbons and nitrogen oxides as products of combustion or
12 incomplete combustion, and pose a serious health problem with respect to
13 pollution of the atmosphere. While exhaust gases from other carbonaceous
14 fuel-burning sources, such as stationary engines, industrial furnaces, etc.,
15 contribute substantially to air pollution, the exhaust gases from automotive
16 engines are a principal source of pollution. Because of these health problem
17 concerns, the Environmental Protection Agency (EPA) has promulgated strict
18 controls on the amounts of carbon monoxide, hydrocarbons and nitrogen
19 oxides which automobiles can emit. The implementation of these controls has
20 resulted in the use of catalytic converters to reduce the amount of pollutants
21 emitted from automobiles.

22 In order to achieve the simultaneous conversion of carbon monoxide,
23 hydrocarbon and nitrogen oxide pollutants, it has become the practice to
24 employ catalysts in conjunction with air-to-fuel ratio control means which
25 functions in response to a feedback signal from an oxygen sensor in the
26 engine exhaust system. Although these three component control catalysts
27 work quite well after they have reached operating temperature of about 300°
28 C., at lower temperatures they are not able to convert substantial amounts of
29 the pollutants. What this means is that when an engine and in particular an
30 automobile engine is started up, the three component control catalyst is not
31 able to convert the hydrocarbons and other pollutants to innocuous
32 compounds.

33 Adsorbent beds have been used to adsorb the hydrocarbons during the
34 cold start portion of the engine. Although the process typically will be used

1 with hydrocarbon fuels, the instant invention can also be used to treat exhaust
2 streams from alcohol fueled engines. The adsorbent bed is typically placed
3 immediately before the catalyst. Thus, the exhaust stream is first flowed
4 through the adsorbent bed and then through the catalyst. The adsorbent bed
5 preferentially adsorbs hydrocarbons over water under the conditions present
6 in the exhaust stream. After a certain amount of time, the adsorbent bed has
7 reached a temperature (typically about 150° C.) at which the bed is no longer
8 able to remove hydrocarbons from the exhaust stream. That is, hydrocarbons
9 are actually desorbed from the adsorbent bed instead of being adsorbed. This
10 regenerates the adsorbent bed so that it can adsorb hydrocarbons during a
11 subsequent cold start.

12 The prior art reveals several references dealing with the use of
13 adsorbent beds to minimize hydrocarbon emissions during a cold start engine
14 operation. One such reference is U.S. Pat. No. 3,699,683 in which an
15 adsorbent bed is placed after both a reducing catalyst and an oxidizing
16 catalyst. The patentees disclose that when the exhaust gas stream is below
17 200° C. the gas stream is flowed through the reducing catalyst then through
18 the oxidizing catalyst and finally through the adsorbent bed, thereby adsorbing
19 hydrocarbons on the adsorbent bed. When the temperature goes above 200°
20 C. the gas stream which is discharged from the oxidation catalyst is divided
21 into a major and minor portion, the major portion being discharged directly into
22 the atmosphere and the minor portion passing through the adsorbent bed
23 whereby unburned hydrocarbon is desorbed and then flowing the resulting
24 minor portion of this exhaust stream containing the desorbed unburned
25 hydrocarbons into the engine where they are burned.

26 Another reference is U.S. Pat. No. 2,942,932 which teaches a process
27 for oxidizing carbon monoxide and hydrocarbons which are contained in
28 exhaust gas streams. The process disclosed in this patent consists of flowing
29 an exhaust stream which is below 800° F. into an adsorption zone which
30 adsorbs the carbon monoxide and hydrocarbons and then passing the
31 resultant stream from this adsorption zone into an oxidation zone. When the
32 temperature of the exhaust gas stream reaches about 800° F. the exhaust
33 stream is no longer passed through the adsorption zone but is passed directly
34 to the oxidation zone with the addition of excess air.

1 U. S. Patent No. 5,078,979, issued January 7, 1992 to Dunne, discloses
2 treating an exhaust gas stream from an engine to prevent cold start emissions
3 using a molecular sieve adsorbent bed. Examples of the molecular sieve include
4 faujasites, clinoptilolites, mordenites, chabazite, silicalite, zeolite Y, ultrastable
5 zeolite Y, and ZSM-5.

6 Canadian Patent No. 1,205,980 discloses a method of reducing exhaust
7 emissions from an alcohol fueled automotive vehicle. This method consists of
8 directing the cool engine startup exhaust gas through a bed of zeolite particles
9 and then over an oxidation catalyst and then the gas is discharged to the
10 atmosphere. As the exhaust gas stream warms up it is continuously passed over
11 the adsorption bed and then over the oxidation bed.

12 As stated this invention generally relates to a process for treating an
13 engine exhaust stream and in particular to a process for minimizing emissions
14 during the cold start operation of an engine. The engine consists of any internal
15 or external combustion engine which generates an exhaust gas stream
16 containing noxious components or pollutants including unburned or thermally
17 degraded hydrocarbons or similar organics. Other noxious components usually
18 present in the exhaust gas include nitrogen oxides and carbon monoxide. The
19 engine may be fueled by a hydrocarbonaceous fuel. As used in this specification
20 and in the appended claims, the term "hydrocarbonaceous fuel" includes
21 hydrocarbons, alcohols and mixtures thereof. Examples of hydrocarbons which
22 can be used to fuel the engine are the mixtures of hydrocarbons which make up
23 gasoline or diesel fuel. The alcohols which may be used to fuel engines include
24 ethanol and methanol. Mixtures of alcohols and mixtures of alcohols and
25 hydrocarbons can also be used. The engine may be a jet engine, gas turbine,
26 internal combustion engine, such as an automobile, truck or bus engine, a diesel
27 engine or the like. The process of this invention is particularly suited for
28 hydrocarbon, alcohol, or hydrocarbon-alcohol mixture, internal combustion
29 engine mounted in an automobile. For convenience the description will use
30 hydrocarbon as the fuel to exemplify the invention. The use of hydrocarbon in
31 the subsequent description is not to be construed as limiting the invention to
32 hydrocarbon fueled engines.

1 When the engine is started up, it produces a relatively high
2 concentration of hydrocarbons in the engine exhaust gas stream as well as
3 other pollutants. Pollutants will be used herein to collectively refer to any
4 unburned fuel components and combustion byproducts found in the exhaust
5 stream. For example, when the fuel is a hydrocarbon fuel, hydrocarbons,
6 nitrogen oxides, carbon monoxide and other combustion byproducts will be
7 found in the engine exhaust gas stream. The temperature of this engine
8 exhaust stream is relatively cool, generally below 500° C. and typically in the
9 range of 200° to 400° C. This engine exhaust stream has the above
10 characteristics during the initial period of engine operation, typically for the
11 first 30 to 120 seconds after startup of a cold engine. The engine exhaust
12 stream will typically contain, by volume, about 500 to 1000 ppm
13 hydrocarbons.

14 The engine exhaust gas stream which is to be treated is flowed over a
15 molecular sieve bed comprising molecular sieve SSZ-56 a first exhaust
16 stream. Molecular sieve SSZ-56 is described below. The first exhaust stream
17 which is discharged from the molecular sieve bed is now flowed over a
18 catalyst to convert the pollutants contained in the first exhaust stream to
19 innocuous components and provide a treated exhaust stream which is
20 discharged into the atmosphere. It is understood that prior to discharge into
21 the atmosphere, the treated exhaust stream may be flowed through a muffler
22 or other sound reduction apparatus well known in the art.

23 The catalyst which is used to convert the pollutants to innocuous
24 components is usually referred to in the art as a three-component control
25 catalyst because it can simultaneously oxidize any residual hydrocarbons
26 present in the first exhaust stream to carbon dioxide and water, oxidize any
27 residual carbon monoxide to carbon dioxide and reduce any residual nitric
28 oxide to nitrogen and oxygen. In some cases the catalyst may not be required
29 to convert nitric oxide to nitrogen and oxygen, e.g., when an alcohol is used
30 as the fuel. In this case the catalyst is called an oxidation catalyst. Because of
31 the relatively low temperature of the engine exhaust stream and the first
32 exhaust stream, this catalyst does not function at a very high efficiency,
33 thereby necessitating the molecular sieve bed.

1 When the molecular sieve bed reaches a sufficient temperature,
2 typically about 150-200° C., the pollutants which are adsorbed in the bed
3 begin to desorb and are carried by the first exhaust stream over the catalyst.
4 At this point the catalyst has reached its operating temperature and is
5 therefore capable of fully converting the pollutants to innocuous components.

6 The adsorbent bed used in the instant invention can be conveniently
7 employed in particulate form or the adsorbent can be deposited onto a solid
8 monolithic carrier. When particulate form is desired, the adsorbent can be
9 formed into shapes such as pills, pellets, granules, rings, spheres, etc. In the
10 employment of a monolithic form, it is usually most convenient to employ the
11 adsorbent as a thin film or coating deposited on an inert carrier material which
12 provides the structural support for the adsorbent. The inert carrier material
13 can be any refractory material such as ceramic or metallic materials. It is
14 desirable that the carrier material be unreactive with the adsorbent and not be
15 degraded by the gas to which it is exposed. Examples of suitable ceramic
16 materials include sillimanite, petalite, cordierite, mullite, zircon, zircon mullite,
17 spondumene, alumina-titanate, etc. Additionally, metallic materials which are
18 within the scope of this invention include metals and alloys as disclosed in
19 U.S. Pat. No. 3,920,583 which are oxidation resistant and are otherwise
20 capable of withstanding high temperatures.

21 The carrier material can best be utilized in any rigid unitary
22 configuration which provides a plurality of pores or channels extending in the
23 direction of gas flow. It is preferred that the configuration be a honeycomb
24 configuration. The honeycomb structure can be used advantageously in either
25 unitary form, or as an arrangement of multiple modules. The honeycomb
26 structure is usually oriented such that gas flow is generally in the same
27 direction as the cells or channels of the honeycomb structure. For a more
28 detailed discussion of monolithic structures, refer to U.S. Pat. Nos. 3,785,998
29 and 3,767,453.

30 The molecular sieve is deposited onto the carrier by any convenient
31 way well known in the art. A preferred method involves preparing a slurry
32 using the molecular sieve and coating the monolithic honeycomb carrier with
33 the slurry. The slurry can be prepared by means known in the art such as
34 combining the appropriate amount of the molecular sieve and a binder with

1 water. This mixture is then blended by using means such as sonification, milling,
2 etc. This slurry is used to coat a monolithic honeycomb by dipping the
3 honeycomb into the slurry, removing the excess slurry by draining or blowing out
4 the channels, and heating to about 100°C. If the desired loading of molecular
5 sieve is not achieved, the above process may be repeated as many times as
6 required to achieve the desired loading.

7 Instead of depositing the molecular sieve onto a monolithic honeycomb
8 structure, one can take the molecular sieve and form it into a monolithic
9 honeycomb structure by means known in the art.

10 The adsorbent may optionally contain one or more catalytic metals
11 dispersed thereon. The metals which can be dispersed on the adsorbent are the
12 noble metals which consist of platinum, palladium, rhodium, ruthenium, and
13 mixtures thereof. The desired noble metal may be deposited onto the adsorbent,
14 which acts as a support, in any suitable manner well known in the art. One
15 example of a method of dispersing the noble metal onto the adsorbent support
16 involves impregnating the adsorbent support with an aqueous solution of a
17 decomposable compound of the desired noble metal or metals, drying the
18 adsorbent which has the noble metal compound dispersed on it and then
19 calcining in air at a temperature of about 400° to about 500°C for a time of about
20 1 to about 4 hours. By decomposable compound is meant a compound which
21 upon heating in air gives the metal or metal oxide. Examples of the
22 decomposable compounds which can be used are set forth in U.S. Pat. No.
23 4,791,091. Preferred decomposable compounds are chloroplatinic acid, rhodium
24 trichloride, chloropalladic acid, hexachloroiridate (IV) acid and
25 hexachlororuthenate. It is preferable that the noble metal be present in an
26 amount ranging from about 0.01 to about 4 weight percent of the adsorbent
27 support. Specifically, in the case of platinum and palladium the range is 0.1 to 4
28 weight percent, while in the case of rhodium and ruthenium the range is from
29 about 0.01 to 2 weight percent.

30 These catalytic metals are capable of oxidizing the hydrocarbon and
31 carbon monoxide and reducing the nitric oxide components to innocuous
32 products. Accordingly, the adsorbent bed can act both as an adsorbent and as a
33 catalyst.

34 The catalyst which is used in this invention is selected from any three
35 component control or oxidation catalyst well known in the art. Examples of
36 catalysts are those described in U.S. Pat. Nos. 4,528,279; 4,791,091; 4,760,044;

1 4,868,148; and 4,868,149. Preferred catalysts well known in the art are those
2 that contain platinum and rhodium and optionally palladium, while oxidation
3 catalysts usually do not contain rhodium. Oxidation catalysts usually contain
4 platinum and/or palladium metal. These catalysts may also contain promoters
5 and stabilizers such as barium, cerium, lanthanum, nickel, and iron. The noble
6 metals promoters and stabilizers are usually deposited on a support such as
7 alumina, silica, titania, zirconia, alumino silicates, and mixtures thereof with
8 alumina being preferred. The catalyst can be conveniently employed in
9 particulate form or the catalytic composite can be deposited on a solid monolithic
10 carrier with a monolithic carrier being preferred. The particulate form and
11 monolithic form of the catalyst are prepared as described for the adsorbent
12 above.

13 EXAMPLES

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

16 Example 1

17 Synthesis of the directing agent N,N-Diethyl-2-Methyldecahydroquinolinium 18 Hydroxide

19 The parent amine 2-Methyldecahydroquinoline was obtained by
20 hydrogenation of 2-methylquinoline (quinaldine) as described below. A 1000-ml
21 stainless steel hydrogenation vessel was charged with 200 gm (1.4 mol) of 2-
22 methylquinoline (quinaldine), purchased from Aldrich Chemical Company, and
23 300 ml glacial acetic acid, 10 gm of PtO₂ and 15 ml concentrated H₂SO₄. The
24 mixture was purged twice with nitrogen (the vessel was pressurized with nitrogen
25 to 1000 psi and evacuated). Then, the reaction vessel was pressurized to 1500-
26 psi of hydrogen gas and allowed to stir at 50°C overnight. The pressure dropped
27 overnight and the vessel was pressurized back to 1500 psi (with H₂ gas) and let
28 to stir until no further drop in the pressure was observed. Once the reaction was
29 complete, the mixture was filtered and the
30

1 filtrate was treated with 50wt% aqueous sodium hydroxide solution until a pH
2 of ~9 was achieved. The treated filtrate was diluted with 1000 ml diethyl
3 ether. The organic layer was separated, washed with water and brine, and
4 dried over anhydrous MgSO_4 . Concentration under vacuum (using rotary
5 evaporator) gave the amine as a pair of isomers (cis-fused and trans-fused
6 ring system with the methyl group in the equatorial position in both isomers) in
7 97% yield (208 gm) in a ratio of 1.1:0.9 trans-fused:cis-fused. The
8 authenticity of the product was established by spectral data analysis including
9 NMR, IR and GCMS spectroscopy. In principle, there are four likely isomers,
10 but only two isomers were produced.

11 N-Ethyl-2-methyldecahydroquinolinium hydroiodide was prepared
12 according to the method described below. To a solution 100 gm (0.65 mol) of
13 2-methyldecahydroquinoline (trans and cis) in 350 ml acetonitrile, 111 gm
14 (0.72 mole) of ethyl iodide was added. The mixture was stirred (using an
15 overhead stirrer) at room temperature for 96 hours. Then, an additional 1/2
16 mole equivalent of ethyl iodide was added and the mixture was heated at
17 reflux for 6 hours. The reaction mixture was concentrated on a rotary
18 evaporator at reduced pressure and the obtained solids were rinsed with 500
19 ml ethyl ether to remove any unreactive amines and excess iodide. The
20 reaction afforded a mixture of two N-ethyl-2-methyl-decahydroquinolinium
21 hydroiodide salts (mono-ethyl derivatives) and a small mixture of the
22 quaternized derivatives. The products were isolated by recrystallization from
23 isopropyl alcohol several times to give the pure trans-fused ring N-ethyl-2-
24 methyl-decahydroquinolinium hydroiodide and the pure cis-fused ring N-ethyl-
25 2-methyl-decahydroquinolinium hydroiodide (see the scheme below).

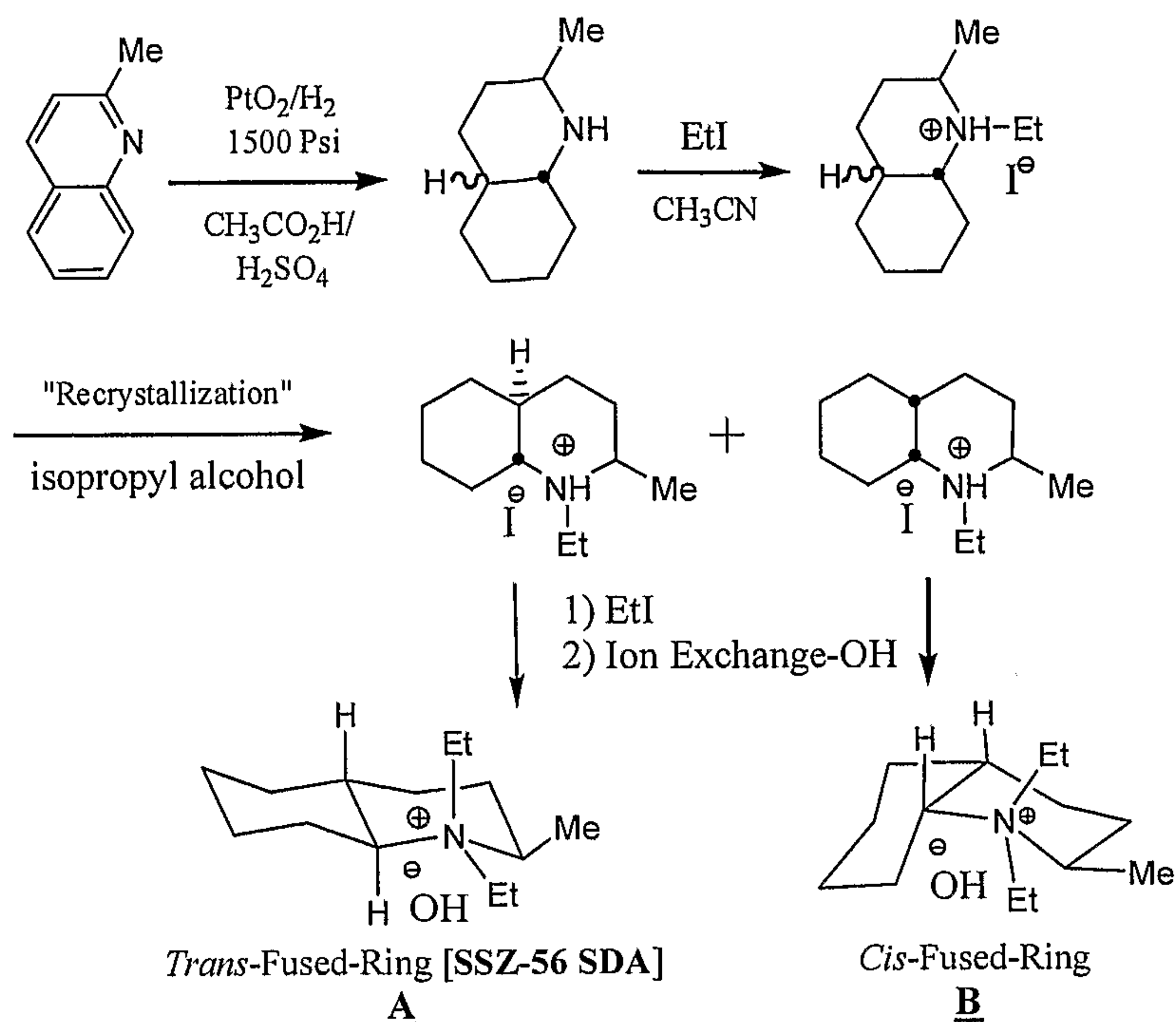
26 N,N-Diethyl-2-methyldecahydroquinolinium iodide was prepared
27 according to the procedure shown below. The procedure below is typical for
28 making the N,N-diethyl-2-methyl-decahydro-quinolinium iodide. The obtained
29 trans-fused ring N-ethyl-2-methyl-decahydroquinolinium hydroiodide (28 gm,
30 0.09 mol) was added to an acetonitrile (150 ml) and KHCO_3 (14 gm, 0.14 mol)
31 solution. To this solution, 30 gm (0.19 mol) of ethyl iodide was added and the
32 resulting mixture was stirred (with an overhead stirrer) at room temperature
33 for 72 hours. Then, one more mole equivalent of ethyl iodide was added and

1 the reaction was heated to reflux and allowed to stir at the reflux temperature
2 for 6 hours. Heating was stopped and the reaction was allowed to further stir
3 at room temperature overnight. The reaction was worked up by removing the
4 excess ethyl iodide and the solvent at reduced pressure on a rotary
5 evaporator. The resulting solids were suspended in 500 ml chloroform, which
6 dissolves the desired product and leaves behind the unwanted KHCO_3 and its
7 salt by-products. The solution was filtered, and the filtrate was dried over
8 anhydrous MgSO_4 . Filtration followed by concentration at reduced pressure
9 on a rotary evaporator, gave the desired N,N-diethyl-2-methyl-
10 decahydroquinolinium iodide as a pale tan-colored solid. The solid was
11 further purified by recrystallization in isopropyl alcohol. The reaction afforded
12 26.8 gm (87% yield). The N,N-diethyl-2-methyl-decahydro-quinolinium iodide
13 of the cis-fused ring isomer was made according to the procedure described
14 above. The trans-fused ring derivative A (see the scheme 1 below) is the
15 templating agent (SDA) useful for making SSZ-56.

16 N,N-Diethyl-2-methyldecahydroquinolinium hydroxide

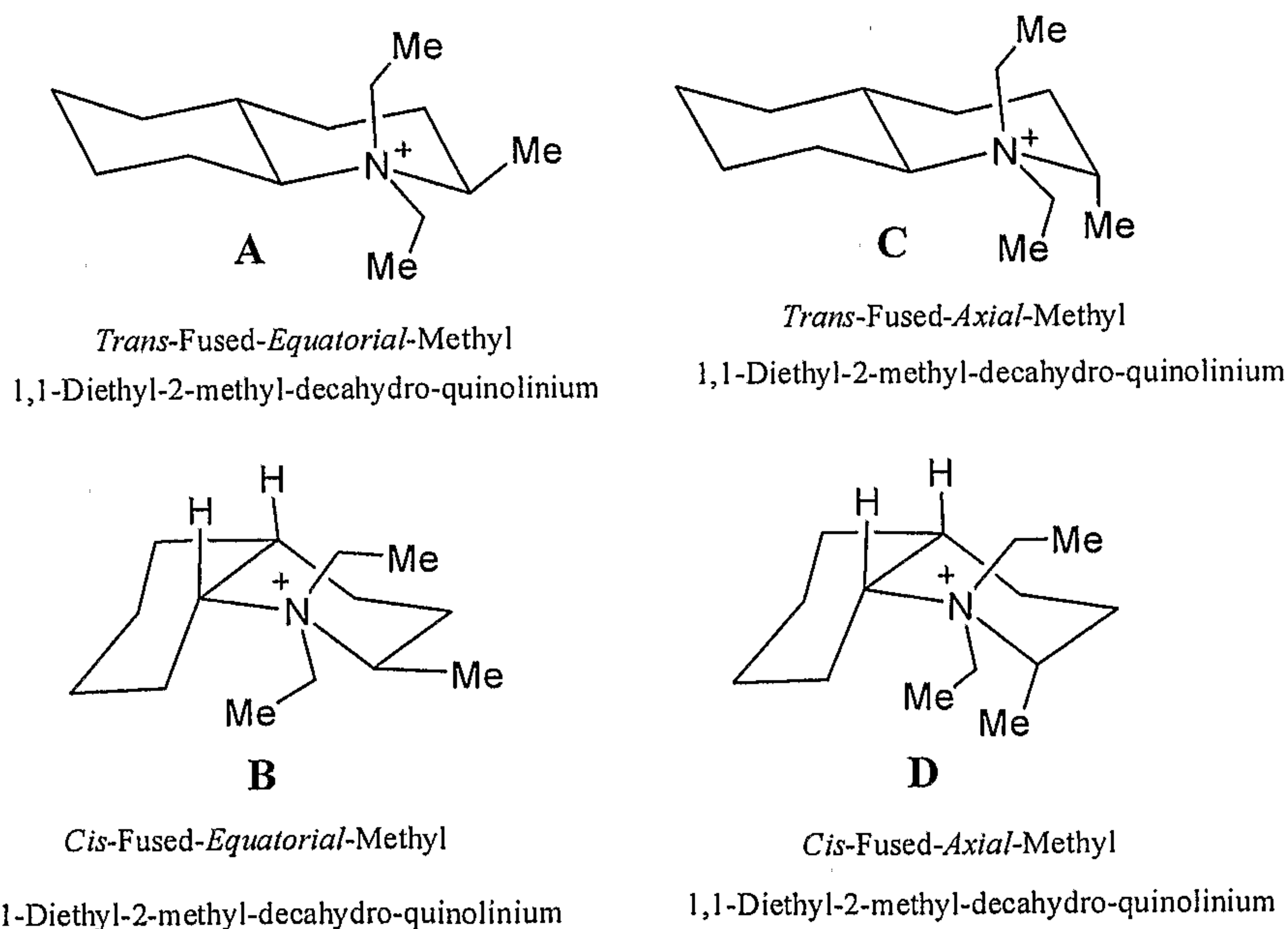
17 The hydroxide version of N,N-diethyl-2-methyldecahydro-quinolinium
18 cation was prepared by ion exchange as described in the procedure below.
19 To a solution of 20 gm (0.06 mol) of N,N-diethyl-2-methyldecahydro-
20 quinolinium iodide in 80 ml water, 80 gm of OH-ion exchange resin (BIO
21 RAD® AGI-X8) was added, and the resulting mixture was allowed to gently
22 stir at room temperature for few hours. The mixture was filtered and the ion
23 exchange resin was rinsed with additional 30 ml water (to ensure removing all
24 the cations from the resin). The rinse and the original filtrate were combined
25 and titration analysis on a small sample of the filtrate with 0.1N HCl indicated
26 a 0.5M OH ions concentration (0.055 mol cations). Scheme 1 below depicts
27 the synthesis of the templating agent.

28



Scheme 1

There are 4 possible isomers (depicted below) from the synthesis, but only two isomers were produced: trans-fused-equatorial methyl **A** and cis-fused-equatorial methyl **B**.



Example 2

Synthesis of Borosilicate SSZ-56 from Calcined Boron-BETA Zeolite

In a 23 cc Teflon liner, 3 gm of 0.5M solution (1.5 mmol) of N,N-diethyl-

1 2-methyldecahydroquinolinium hydroxide (the trans-fused ring isomer), 0.5
2 gm of 1.0N solution of aqueous NaOH (0.5 mmol), 4.5 gm of de-ionized water,
3 and 0.65 gm of calcined boron-BETA zeolite were all mixed. The Teflon liner
4 was capped and placed in a Parr reactor and heated in an oven at 150°C
5 while tumbling at about 43 rpm. The reaction progress was checked by
6 monitoring the gel's pH and by looking for crystal formation using Scanning
7 Electron Microscopy (SEM) at 3-6 days intervals. The reaction was usually
8 completed after heating for 18-24 days (shorter crystallization periods were
9 achieved at 160 °C). The final pH at the end of the reaction ranged from 10.8-
10 11.6. Once the crystallization was completed (by SEM analysis), the reaction
11 mixture (usually a white fine powdery precipitate with clear liquid) was filtered.
12 The collected solids were rinsed a few times with de-ionized water (~1000 ml),
13 and then let to air-dry overnight followed by drying in an oven at 120 °C for 15-
14 20 minutes. The reaction yielded about 0.55 -0.6 gm of pure boron-SSZ-56 as
15 determined by XRD analysis.

16 Example 3

17 Seeded Preparation of Borosilicate SSZ-56

18 In a 23 cc Teflon liner, 3 gm of 0.5M solution (1.5 mmol) of N,N-diethyl-
19 2-methyldecahydroquinolinium hydroxide (the trans-fused ring isomer), 0.5
20 gm of 1.0N solution of aqueous NaOH (0.5 mmol), 4.5 gm of de-ionized water,
21 0.65 gm of calcined boron-BETA zeolite and 0.03 gm of SSZ-56 (made as
22 described above) were mixed. The Teflon liner was capped and placed in a
23 Parr reactor and heated in an oven at 150°C while tumbling at about 43 rpm.
24 The reaction progress was checked by monitoring the gel's pH and by looking
25 for crystal formation using Scanning Electron Microscopy (SEM) at 3 day
26 intervals. The crystallization was complete (SEM analysis) after heating for 6
27 days. The final pH at the end of the reaction was usually 11.2. Once
28 completed, the reaction mixture was filtered, and the collected solids were
29 rinsed with de-ionized water (~1000 ml), and then let to air-dry overnight
30 followed by drying in an oven at 120 °C for 15-20 minutes. The reaction
31 yielded 0.6 gm of pure boron-SSZ-56. Identity and characterization of the
32 material was determined by XRD analysis.

Direct Synthesis of Borosilicate SSZ-56 from Sodium Borate Decahydrate as the Boron Sources and CAB-O-SIL M-5 as the Silicon Source

In a 23 cc Teflon liner, 6 gm of 0.5M solution (3 mmol) of N,N-diethyl-2-methyldecahydroquinolinium hydroxide (the trans-fused ring isomer), 1.2 gm of 1.0N solution of aqueous NaOH (1.2 mmol), 4.8 gm of de-ionized water, and 0.065 gm of sodium borate decahydrate were mixed and stirred until the sodium borate was completely dissolved. Then, 0.9 gm of Cab-O-Sil M-5 (~98% SiO₂) was added and thoroughly mixed. The resulting gel was capped and placed in a Parr reactor and heated in an oven at 160°C while tumbling at about 43 rpm. The reaction progress was checked by monitoring the gel's pH and by looking for crystal formation using Scanning Electron Microscopy (SEM) at 6 days intervals. The reaction was usually completed after heating for 18-24 days. The final pH at the end of the reaction ranged from 11.5-12.3. Once the crystallization was completed (by SEM analysis), the reaction mixture, a white fine powdery precipitate with clear liquid, was filtered. The collected solids were rinsed few times with de-ionized water (~1000 ml), and then air-dried overnight followed by drying in an oven at 120°C for 15 minutes. The reaction usually yields about 0.75-0.9 gm of pure boron-SSZ-56.

Seeded Synthesis of Borosilicate SSZ-56 from Sodium Borate Decahydrate as the Boron Source and CAB-O-SIL M-5 as the Silicon Source

In a 23 cc Teflon liner, 6 gm of 0.5M solution (3 mmol) of N,N-diethyl-2-methyldecahydroquinolinium hydroxide (the trans-fused ring isomer), 1.2 gm of 1.0N solution of aqueous NaOH (1.2 mmol), 4.8 gm of de-ionized water, and 0.062 gm of sodium borate decahydrate were mixed and stirred until the sodium borate was completely dissolved. Then, 0.9 gm of Cab-O-Sil M-5 (~98% SiO₂) and 0.04 gm of B-SSZ-56 made as in Example 4 were added and thoroughly mixed. The resulting gel was capped and placed in a Parr reactor and heated in an oven at 160°C while tumbling at about 43 rpm. The reaction progress was checked by monitoring the gel's pH and by looking for

1 crystal formation using Scanning Electron Microscopy (SEM) at 3-5 days
2 intervals. The reaction was completed after heating for 7 days. The final pH
3 at the end of the reaction was about 12.2. Once the crystallization was
4 completed (by SEM analysis), the reaction mixture, a white fine powdery
5 precipitate with clear liquid, was filtered. The collected solids were rinsed few
6 times with de-ionized water (~1000 ml), and then air-dried overnight followed
7 by drying in an oven at 120°C for 15 minutes. The reaction yielded 0.88 gm of
8 pure boron-SSZ-56.

9 Example 6

10 Calcination of SSZ-56

11 Removing the templating agent molecules (structure-directing agents:
12 SDAs) from zeolite SSZ-56 to free its channels and cavities was
13 accomplished by the calcination method described below. A sample of the
14 as-made SSZ-56 synthesized according to the procedures of Examples 2, 3,
15 4 or 5 discussed above is calcined by preparing a thin bed of SSZ-56 in a
16 calcination dish which was heated in a muffle furnace from room temperature
17 to 595°C in three stages. The sample was heated to 120°C at a rate of
18 1°C/minute and held for 2 hours. Then, the temperature was ramped up to
19 540°C at a rate of 1°C/minute and held for 5 hours. The temperature was
20 then ramped up again at 1°C/minute to 595°C and held there for 5 hours. A
21 nitrogen stream with a slight bleed of air was passed over the zeolite at a rate
22 of 20 standard cubic feet (0.57 standard cubic meters) per minute during
23 heating the calcination process.

24 Example 7

25 Ammonium- Ion Exchange of SSZ-56

26
27
28
29 The Na⁺ form of SSZ-56 prepared as in Examples 2, 3, 4 or 5 and
30 calcined as in Example 6 was converted to NH₄⁺-SSZ-56 form by heating the
31 material in an aqueous solution of NH₄NO₃ (typically 1gm NH₄NO₃/1 gm SSZ-
32 56 in 20 ml H₂O) at 90°C for 2-3 hours. The mixture was then filtered and the
33 step was repeated as many times as desired (usually done 2-3 times). After

1 filtration, the obtained NH_4 -exchanged-product was washed with de-ionized
2 water and air dried. The NH_4^+ form of SSZ-56 can be converted to the H^+
3 form by calcination to 540°C (as described in Example 6 above stopping at
4 the end of the second stage).

5

6

Example 8

7

Preparation of Aluminosilicate SSZ-56 by Aluminum Exchange of Boron-SSZ-

8

56

9 The aluminosilicate version of SSZ-56 was prepared by way of
10 exchanging borosilicate SSZ-56 with aluminum nitrate according to the
11 procedure described below. The H^+ version of calcined borosilicate SSZ-56
12 (prepared as in Examples 2, 3, 4 or 5 and treated with ammonium nitrate and
13 calcined as Example 6) was easily converted to the aluminosilicate SSZ-56 by
14 suspending the zeolite (H^+ /borosilicate SSZ-56) in 1M solution of aluminum
15 nitrate nonahydrate (10 ml of $1\text{M Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ soln./1 gm SSZ-56). The
16 suspension was heated at reflux overnight. The resulting mixture was then
17 filtered and the collected solids were thoroughly rinsed with de-ionized water
18 and air-dried overnight. The solids were further dried in an oven at 120°C for
19 2 hours. The exchange can also be done on the Na^+ version of SSZ-56 (as
20 prepared in Examples 2, 3, 4 or 5 and calcined as in Example 6).

21

22

Example 9

23

Nitrogen Adsorption (MicroPore Volume Analysis)

24

25 The Na^+ and H^+ forms of SSZ-56 as synthesized in Examples 2 and 4
26 above and treated as in Examples 6 and 7 was subjected to a surface area
27 and micropore volume analysis using N_2 as adsorbate and via the BET
28 method. The zeolite exhibited a considerable void volume with a micropore
29 volume of 0.18 cc/g for Na^+ form, and 0.19 cc/gm for the H^+ form.

30

Argon Adsorption (MicroPore Volume Analysis)

Constraint Index Test

The hydrogen form of SSZ-56 synthesized as in Example 2 was calcined and ammonium exchanged as in Examples 6 and 7 was aluminum exchanged as in Example 8. The obtained aluminum-exchanged sample of SSZ-56 was then ammonium exchanged as in Example 7 followed by calcination to 540 °C as in Example 6. The H-Al-SSZ-56 was pelletized at 4 KPSI, crushed and granulated to 20-40 mesh. A 0.6 gram sample of the granulated material was calcined in air at 540°C for 4 hours and cooled in a desiccator to ensure dryness. Then, 0.5 gram was packed into a 3/8 inch stainless steel tube with alundum on both sides of the molecular sieve bed. A Lindburg furnace was used to heat the reactor tube. Helium was introduced into the reactor tube at 10 cc/min. and at atmospheric pressure. The reactor was heated to about 315°C, and a 50/50 feed of n-hexane and 3-methylpentane is introduced into the reactor at a rate of 8 µl/min. The feed was delivered by a Brownlee pump. Direct sampling into a GC began after 10 minutes of feed introduction. The Constraint Index (CI) value was calculated

1 from the GC data using methods known in the art. SSZ-56 had a CI of 0.76
2 and a conversion of 79% after 15 minutes on stream. The material fouled
3 rapidly and at 105 minutes the CI was 0.35 and the conversion was 25.2%.
4 The CI test showed the material was very active catalytic material.
5

6 Example 12

7 n-Hexadecane Hydrocracking Test

8
9 A 1 gm sample of SSZ-56 (prepared as described for the Constraint
10 Index test in Example 11) was suspended in 10 gm de-ionized water. To this
11 suspension, a solution of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ at a concentration which would
12 provide 0.5 wt. % Pd with respect to the dry weight of the molecular sieve
13 sample was added. The pH of the solution was adjusted to pH of 9.2 by a
14 drop-wise addition of 0.15N solution of ammonium hydroxide. The mixture
15 was then heated in an oven at 75°C for 48 hours. The mixture was then
16 filtered through a glass frit, washed with de-ionized water, and air-dried. The
17 collected Pd-SSZ-56 sample was slowly calcined up to 482°C in air and held
18 there for three hours.

19 The calcined Pd/SSZ-56 catalyst was pelletized in a Carver Press and
20 granulated to yield particles with a 20/40 mesh size. Sized catalyst (0.5 g)
21 was packed into a ¼ inch OD tubing reactor in a micro unit for n-hexadecane
22 hydroconversion. The table below gives the run conditions and the products
23 data for the hydrocracking test on n-hexadecane.

24 As the results show in the table below, SSZ-56 is a very active and
25 isomerisation selective catalyst at 96.5% n-C₁₆ conversion at 256°C.
26

Temperature	256°C (496°F)
Time-on-Stream (hrs.)	71.4-72.9
WHSV	1.55
PSIG	1200
Titrated?	NO
n-16, % Conversion	96.5
Hydrocracking Conv.	35.2

Isomerization Selectivity, %	63.5
Cracking Selectivity, %	36.5
C ₄ - %	2.3
C ₅ /C ₄	15.2
C ₅ +C ₆ /C ₅ , %	19.3
DMB/MP	0.05
C ₄ -C ₁₃ i/n	3.7
C ₇ -C ₁₃ yield	27.7

1

2

1 **WHAT IS CLAIMED IS:**

2 1. A molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a
3 first tetravalent element to (2) an oxide of a trivalent element, pentavalent
4 element, second tetravalent element which is different from said first tetravalent
5 element or mixture thereof and having, after calcination, the X-ray diffraction
6 lines of Table 2.

7 2. A molecular sieve having a mole ratio greater than about 15 of (1) silicon oxide
8 to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron
9 oxide, titanium oxide, indium oxide and mixtures thereof, and having, after
10 calcination, the X-ray diffraction lines of Table 2.

11 3. A molecular sieve according to Claim 2 wherein the oxide of (2) is aluminum
12 oxide.

13 4. A molecular sieve according to Claim 2 wherein the oxide of (2) is boron oxide.

14 5. A molecular sieve according to Claim 1 or 2 wherein said molecular sieve is
15 predominantly in the hydrogen form.

16 6. A molecular sieve according to Claim 1 or 2 wherein said molecular sieve is
17 substantially free of acidity.

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

20	YO_2 / W_cO_d	15 - infinity
21	$M_{2/n} / YO_2$	0.01 - 0.03
22	Q / YO_2	0.02 - 0.05

23 wherein Y is silicon; W is aluminum, gallium, iron, boron, titanium, indium,
24 vanadium or mixtures thereof; c is 1 or 2; d is 2 when c is 1 or d is 3 or 5 when
25 c is 2; M is an alkali metal cation, alkaline earth metal cation or mixtures
26 thereof; n is the valence of M; and Q is a trans-fused ring
27 N,N-diethyl-2-methyldecahydroquinolinium cation.

28 8. A method of preparing a crystalline material comprising (1) a first oxide
29 comprising silicon oxide and (2) a second oxide comprising boron oxide and

1 having a mole ratio of the first oxide to the second oxide greater than about 15
 2 and having, after calcination, the X-ray diffraction lines of Table 2, said method
 3 comprising contacting under crystallization conditions sources of said oxides
 4 and a structure directing agent comprising a trans-fused ring
 5 N,N-diethyl-2-methyldecahydroquinolinium cation.

6 9. The method according to Claim 8 wherein the molecular sieve is prepared from
 7 a reaction mixture comprising, in term of mole ratios:

8	YO_2/W_aO_b	≥ 15
9	$OH-/YO_2$	0.10 - 0.50
10	Q/YO_2	0.05 - 0.50
11	$M_{2/n}/YO_2$	0.02 - 0.40
12	H_2O/YO_2	30 - 80

13 where Y is silicon; W is aluminum, gallium, iron, boron, titanium, indium,
 14 vanadium or mixtures thereof; a is 1 or 2, b is 2 when a is 1; b is 3 when a is 2;
 15 M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is
 16 the valence of M; and Q is a trans-fused ring
 17 N,N-diethyl-2-methyldecahydroquinolinium cation.

18 10. A process for converting hydrocarbons comprising contacting a
 19 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
 20 comprising a molecular sieve having a mole ratio greater than about 15 of (1)
 21 an oxide of a first tetravalent element to (2) an oxide of a trivalent element,
 22 pentavalent element, second tetravalent element which is different from said
 23 first tetravalent element or mixture thereof and having, after calcination, the X-
 24 ray diffraction lines of Table 2.

25 11. The process of Claim 10 wherein the molecular sieve is substantially free of
 26 acidity.

27 12. The process of Claim 10 wherein the process is a hydrocracking process
 28 comprising contacting the catalyst with a hydrocarbon feedstock under
 29 hydrocracking conditions.

- 1 13. The process of Claim 10 wherein the process is a dewaxing process
2 comprising contacting the catalyst with a hydrocarbon feedstock under
3 dewaxing conditions.
- 4 14. The process of Claim 10 wherein the process is a process for improving the
5 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising
6 contacting the catalyst with a waxy hydrocarbon feed under isomerization
7 dewaxing conditions.
- 8 15. The process of Claim 10 wherein the process is a process for producing a C₂₀₊
9 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under
10 isomerization conditions over the catalyst.
- 11 16. The process of Claim 15 wherein the catalyst further comprises at least one
12 Group VIII metal.
- 13 17. The process of Claim 10 wherein the process is a process for catalytically
14 dewaxing a hydrocarbon oil feedstock boiling above about 350°F (177°C) and
15 containing straight chain and slightly branched chain hydrocarbons comprising
16 contacting said hydrocarbon oil feedstock in the presence of added hydrogen
17 gas at a hydrogen pressure of about 15-3000 psi (0.103-20.7 MPa) under
18 dewaxing conditions with the catalyst.
- 19 18. The process of Claim 17 wherein the catalyst further comprises at least one
20 Group VIII metal.
- 21 19. The process of Claim 17 wherein said catalyst comprises a layered catalyst
22 comprising a first layer comprising the molecular sieve and at least one Group
23 VIII metal, and a second layer comprising an aluminosilicate zeolite which is
24 more shape selective than the molecular sieve of said first layer.
- 25 20. The process of Claim 10 wherein the process is a process for preparing a
26 lubricating oil which comprises:

27 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to
28 obtain an effluent comprising a hydrocracked oil; and

- 1 catalytically dewaxing said effluent comprising hydrocracked oil at a
 2 temperature of at least about 400°F (204°C) and at a pressure of from about 15
 3 psig to about 3000 psig (0.103 to 20.7 MPa gauge) in the presence of added
 4 hydrogen gas with the catalyst.
- 5 21. The process of Claim 20 wherein the catalyst further comprises at least one
 6 Group VIII metal.
- 7 22. The process of Claim 10 wherein the process is a process for isomerization
 8 dewaxing a raffinate comprising contacting said raffinate in the presence of
 9 added hydrogen under isomerization dewaxing conditions with the catalyst.
- 10 23. The process of Claim 22 wherein the catalyst further comprises at least one
 11 Group VIII metal.
- 12 24. The process of Claim 22 wherein the raffinate is bright stock.
- 13 25. The process of Claim 10 wherein the process is a process for increasing the
 14 octane of a hydrocarbon feedstock to produce a product having an increased
 15 aromatics content comprising contacting a hydrocarbonaceous feedstock which
 16 comprises normal and slightly branched hydrocarbons having a boiling range
 17 above about 40°C and less than about 200°C under aromatic conversion
 18 conditions with the catalyst.
- 19 26. The process of Claim 25 wherein the molecular sieve is substantially free of
 20 acid.
- 21 27. The process of Claim 25 wherein the molecular sieve contains a Group VIII
 22 metal component.
- 23 28. The process of Claim 10 wherein the process is a catalytic cracking process
 24 comprising contacting a hydrocarbon feedstock in a reaction zone under
 25 catalytic cracking conditions in the absence of added hydrogen with the
 26 catalyst.
- 27 29. The process of Claim 28 wherein the catalyst additionally comprises a large
 28 pore crystalline cracking component.

- 1 30. The process of Claim 10 wherein the process is an isomerization process for
2 isomerizing C₄ to C₇ hydrocarbons, comprising contacting a feed having normal
3 and slightly branched C₄ to C₇ hydrocarbons under isomerizing conditions with
4 the catalyst.
- 5 31. The process of Claim 30 wherein the molecular sieve has been impregnated
6 with at least one Group VIII metal.
- 7 32. The process of Claim 30 wherein the catalyst has been calcined in a steam/air
8 mixture at an elevated temperature after impregnation of the Group VIII metal.
- 9 33. The process of Claim 31 wherein the Group VIII metal is platinum.
- 10 34. The process of Claim 10 wherein the process is a process for alkylating an
11 aromatic hydrocarbon which comprises contacting under alkylation conditions
12 at least a molar excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin
13 under at least partial liquid phase conditions and in the presence of the
14 catalyst.
- 15 35. The process of Claim 34 wherein the olefin is a C₂ to C₄ olefin.
- 16 36. The process of Claim 35 wherein the aromatic hydrocarbon and olefin are
17 present in a molar ratio of about 4:1 to about 20:1, respectively.
- 18 37. The process of Claim 35 wherein the aromatic hydrocarbon is selected from
19 the group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene,
20 naphthalene derivatives, dimethylnaphthalene or mixtures thereof.
- 21 38. The process of Claim 10 wherein the process is a process for transalkylating
22 an aromatic hydrocarbon which comprises contacting under transalkylating
23 conditions an aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon
24 under at least partial liquid phase conditions and in the presence of the
25 catalyst.
- 26 39. The process of any one of Claims 10, 12 to 15, 17, 20, 22, 28, 30, 34 and 38,
27 wherein the molecular sieve is predominantly in the hydrogen form.

- 1 40. The process of Claim 38 wherein the aromatic hydrocarbon and the polyalkyl
2 aromatic hydrocarbon are present in a molar ratio of from about 1:1 to about
3 25:1, respectively.
- 4 41. The process of Claim 38 wherein the aromatic hydrocarbon is selected from
5 the group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures
6 thereof.
- 7 42. The process of Claim 38 wherein the polyalkyl aromatic hydrocarbon is a
8 dialkylbenzene.
- 9 43. The process of Claim 10 wherein the process is a process to convert paraffins
10 to aromatics which comprises contacting paraffins under conditions which
11 cause paraffins to convert to aromatics with a catalyst comprising the molecular
12 sieve and gallium, zinc, or a compound of gallium or zinc.
- 13 44. The process of Claim 10 wherein the process is a process for isomerizing
14 olefins comprising contacting said olefin under conditions which cause
15 isomerization of the olefin with the catalyst.
- 16 45. The process of Claim 10 wherein the process is a process for isomerizing an
17 isomerization feed comprising an aromatic C₈ stream of xylene isomers or
18 mixtures of xylene isomers and ethylbenzene, wherein a more nearly
19 equilibrium ratio of ortho-, meta and para-xylenes is obtained, said process
20 comprising contacting said feed under isomerization conditions with the
21 catalyst.
- 22 46. The process of Claim 10 wherein the process is a process for oligomerizing
23 olefins comprising contacting an olefin feed under oligomerization conditions
24 with the catalyst.
- 25 47. A process for converting oxygenated hydrocarbons comprising contacting said
26 oxygenated hydrocarbon under conditions to produce liquid products with a
27 catalyst comprising a molecular sieve having a mole ratio greater than about 15
28 of an oxide of a first tetravalent element to an oxide of a second tetravalent
29 element which is different from said first tetravalent element, trivalent element,
30 pentavalent element or mixture thereof and having, after calcination, the X-ray
31 diffraction lines of Table 2.

- 1 48. The process of Claim 47 wherein the oxygenated hydrocarbon is a lower
2 alcohol.
- 3 49. The process of Claim 48 wherein the lower alcohol is methanol.
- 4 50. The process of Claim 10 wherein the process is a process for the production of
5 higher molecular weight hydrocarbons from lower molecular weight
6 hydrocarbons comprising the steps of:
- 7 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-
8 containing gas and contacting said gas in said zone under C₂₊ hydrocarbon
9 synthesis conditions with the catalyst and a metal or metal compound capable
10 of converting the lower molecular weight hydrocarbon to a higher molecular
11 weight hydrocarbon; and
- 12 (b) withdrawing from said reaction zone a higher molecular weight
13 hydrocarbon-containing stream.
- 14 51. The process of Claim 50 wherein the metal or metal compound comprises a
15 lanthanide or actinide metal or metal compound.
- 16 52. The process of Claim 50 wherein the lower molecular weight hydrocarbon is
17 methane.
- 18 53. A catalyst composition for promoting polymerization of 1-olefins, said
19 composition comprising:
- 20 (A) a molecular sieve having a mole ratio greater than about 15 of (1) an oxide
21 of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent
22 element, second tetravalent element which is different from said first tetravalent
23 element or mixture thereof and having, after calcination, the X-ray diffraction
24 lines of Table 2; and
- 25 (B) an organotitanium or organochromium compound.
- 26 54. The catalyst composition of Claim 53 wherein oxide (1) is silicon oxide, and
27 oxide (2) is an oxide selected from aluminum oxide, gallium oxide, iron oxide,
28 boron oxide, titanium oxide, indium oxide.

- 1 55. The process of Claim 10 wherein the process is a process for polymerizing
 2 1-olefins, which process comprises contacting 1-olefin monomer with a
 3 catalytically effective amount of a catalyst composition comprising:
- 4 (A) a molecular sieve having a mole ratio greater than about 15 of (1) an oxide
 5 of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent
 6 element, second tetravalent element which is different from said first tetravalent
 7 element or mixture thereof and having, after calcination, the X-ray diffraction
 8 lines of Table 2; and
- 9 (B) an organotitanium or organochromium compound
- 10 under polymerization conditions which include a temperature and pressure
 11 suitable for initiating and promoting the polymerization reaction.
- 12 56. The process of Claim 55 wherein oxide (1) is silicon oxide, and oxide (2) is an
 13 oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide,
 14 titanium oxide, indium oxide.
- 15 57. The process of Claim 55 wherein the 1-olefin monomer is ethylene.
- 16 58. The process of Claim 56 wherein the 1-olefin monomer is ethylene.
- 17 59. The process of Claim 10 wherein the process is a process for hydrogenating a
 18 hydrocarbon feed containing unsaturated hydrocarbons, the process
 19 comprising contacting the feed with hydrogen under conditions which cause
 20 hydrogenation with the catalyst.
- 21 60. The process of Claim 59 wherein the catalyst contains metals, salts or
 22 complexes wherein the metal is selected from the group consisting of platinum,
 23 palladium, rhodium, iridium or combinations thereof, or the group consisting of
 24 nickel, molybdenum, cobalt, tungsten, titanium, chromium, vanadium, rhenium,
 25 manganese and combinations thereof.
- 26 61. A process for hydrotreating a hydrocarbon feedstock comprising contacting the
 27 feedstock with a hydrotreating catalyst and hydrogen under hydrotreating
 28 conditions, wherein the catalyst comprises a molecular sieve having a mole
 29 ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an

- 1 oxide of a trivalent element, pentavalent element, second tetravalent element
2 which is different from said first tetravalent element or mixture thereof and
3 having, after calcination, the X-ray diffraction lines of Table 2.
- 4 62. The process of Claim 61 wherein the catalyst contains a Group VIII metal or
5 compound, a Group VI metal or compound or combinations thereof.
- 6 63. A process for hydrotreating a hydrocarbon feedstock comprising contacting the
7 feedstock with a hydrotreating catalyst and hydrogen under hydrotreating
8 conditions, wherein the catalyst comprises a molecular sieve having a mole
9 ratio greater than about 15 of (1) an silicon oxide (2) an oxide selected from
10 aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium
11 oxide and mixtures thereof, and having, after calcination, the X-ray diffraction
12 lines of Table 2.
- 13 64. The process of Claim 63 wherein the oxide of (2) is aluminum oxide.
- 14 65. The process of Claim 63 wherein the oxide of (2) is boron oxide.
- 15 66. The process of Claim 63 wherein the catalyst contains a Group VIII metal or
16 compound, a Group VI metal or compound or combinations thereof.
- 17 67. A process for converting hydrocarbons comprising contacting a
18 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
19 comprising a molecular sieve having a mole ratio greater than about 15 of (1)
20 silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron
21 oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, and
22 having, after calcination, the X-ray diffraction lines of Table 2.
- 23 68. A process for the reduction of oxides of nitrogen contained in a gas stream
24 wherein said process comprises contacting the gas stream with a molecular
25 sieve, the molecular sieve having a mole ratio greater than about 15 of (1) an
26 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
27 pentavalent element, second tetravalent element which is different from said
28 first tetravalent element or mixture thereof and having, after calcination, the X-
29 ray diffraction lines of Table 2.

- 1 69. A process for the reduction of oxides of nitrogen contained in a gas stream
 2 wherein said process comprises contacting the gas stream with a molecular
 3 sieve, the molecular sieve having a mole ratio greater than about 15 of (1)
 4 silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron
 5 oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, and
 6 having, after calcination, the X-ray diffraction lines of Table 2.
- 7 70. The process of Claim 68 or 69 conducted in the presence of oxygen.
- 8 71. The process of Claim 68 or 69 wherein said molecular sieve contains a metal
 9 or metal ions capable of catalyzing the reduction of the oxides of nitrogen.
- 10 72. The process of Claim 71 wherein the metal is cobalt, copper, platinum, iron,
 11 chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures
 12 thereof.
- 13 73. The process of Claim 68 or 69 wherein the gas stream is the exhaust stream of
 14 an internal combustion engine.
- 15 74. The process of Claim 71 wherein the gas stream is the exhaust stream of an
 16 internal combustion engine.
- 17 75. A process for treating a cold-start engine exhaust gas stream containing
 18 hydrocarbons and other pollutants consisting of flowing said engine exhaust
 19 gas stream over a molecular sieve bed which preferentially adsorbs the
 20 hydrocarbons over water to provide a first exhaust stream, and flowing the first
 21 exhaust gas stream over a catalyst to convert any residual hydrocarbons and
 22 other pollutants contained in the first exhaust gas stream to innocuous products
 23 and provide a treated exhaust stream and discharging the treated exhaust
 24 stream into the atmosphere, the molecular sieve bed characterized in that it
 25 comprises a molecular sieve having a mole ratio greater than about 15 of (1)
 26 an oxide of a first tetravalent element to (2) an oxide of a trivalent element,
 27 pentavalent element, second tetravalent element which is different from said
 28 first tetravalent element or mixture thereof and having, after calcination, the X-
 29 ray diffraction lines of Table 2.
- 30 76. The process of Claim 75 wherein the molecular sieve has a mole ratio greater
 31 than about 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide,

1 gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and
2 mixtures thereof, and having, after calcination, the X-ray diffraction lines of
3 Table 2.

4 77. The process of Claim 76 wherein the oxide of (2) is aluminum oxide.

5 78. The process of Claim 76 wherein the oxide of (2) is boron oxide.

6 79. The process of Claim 75 wherein the engine is an internal combustion engine.

7 80. The process of Claim 79 wherein the internal combustion engine is an
8 automobile engine.

9 81. The process of Claim 75 wherein the engine is fueled by a hydrocarbonaceous
10 fuel.

11 82. The process of Claim 75 wherein the molecular sieve has deposited on it a
12 metal selected from the group consisting of platinum, palladium, rhodium,
13 ruthenium, and mixtures thereof.

14 83. The process of Claim 82 wherein the metal is platinum.

15 84. The process of Claim 82 wherein the metal is palladium.

16 85. The process of Claim 82 wherein the metal is a mixture of platinum and
17 palladium.