

MOLECULAR SIEVE SSZ-65

BACKGROUND OF THE INVENTIONField of the Invention

The present invention relates to new crystalline molecular sieve SSZ-65, a method for preparing SSZ-65 using a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation as a structure directing agent and the use of SSZ-65 in catalysts for, e.g., hydrocarbon conversion reactions.

State of the Art

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

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

SUMMARY OF THE INVENTION

The present invention is directed to a family of crystalline molecular sieves with unique properties, referred to herein as "molecular sieve SSZ-65" or simply "SSZ-65". Preferably, SSZ-65 is obtained in its silicate, aluminosilicate, titanosilicate, germanosilicate, vanadosilicate or borosilicate form. The term "silicate" refers to a molecular sieve having a high mole ratio of silicon oxide relative to aluminum oxide, preferably a mole ratio greater than 100, including molecular sieves comprised entirely of silicon oxide. As used herein, the term "aluminosilicate" refers to a molecular sieve containing both aluminum oxide and silicon oxide and the

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

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

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

17 The present invention also includes this molecular sieve which is
18 predominantly in the hydrogen form, which hydrogen form is prepared by ion
19 exchanging with an acid or with a solution of an ammonium salt followed by a second
20 calcination. If the molecular sieve is synthesized with a high enough ratio of SDA
21 cation to sodium ion, calcination alone may be sufficient. For high catalytic activity,
22 the SSZ-65 molecular sieve should be predominantly in its hydrogen ion form. It is
23 preferred that, after calcination, at least 80% of the cation sites are occupied by
24 hydrogen ions and/or rare earth ions. As used herein, "predominantly in the hydrogen
25 form" means that, after calcination, at least 80% of the cation sites are occupied by
26 hydrogen ions and/or rare earth ions.

27 In accordance with the present invention there is further provided a process for
28 converting hydrocarbons comprising contacting a hydrocarbonaceous feed at
29 hydrocarbon converting conditions with a catalyst comprising the molecular sieve of
30 this invention. The molecular sieve may be predominantly in the hydrogen form. It
31 may also be substantially free of acidity.

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

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

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

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

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

29 Also included in the present invention is a process for preparing a lubricating
30 oil which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous
31 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
32 dewaxing said effluent comprising hydrocracked oil at a temperature of at least about

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

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

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

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

24 This invention further provides an isomerization process for isomerizing C₄ to
25 C₇ hydrocarbons, comprising contacting a feed having normal and slightly branched
26 C₄ to C₇ hydrocarbons under isomerizing conditions with a catalyst comprising the
27 molecular sieve of this invention, preferably predominantly in the hydrogen form.
28 The molecular sieve may be impregnated with at least one Group VIII metal,
29 preferably platinum. The catalyst may be calcined in a steam/air mixture at an
30 elevated temperature after impregnation of the Group VIII metal.

31 Also provided by the present invention is a process for alkylating an aromatic
32 hydrocarbon which comprises contacting under alkylation conditions at least a molar

1 excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid
2 phase conditions and in the presence of a catalyst comprising the molecular sieve of
3 this invention, preferably predominantly in the hydrogen form. The olefin may be a
4 C₂ to C₄ olefin, and the aromatic hydrocarbon and olefin may be present in a molar
5 ratio of about 4:1 to about 20:1, respectively. The aromatic hydrocarbon may be
6 selected from the group consisting of benzene, toluene, ethylbenzene, xylene,
7 naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

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

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

19 Further provided by this invention is a process to convert paraffins to
20 aromatics which comprises contacting paraffins under conditions which cause
21 paraffins to convert to aromatics with a catalyst comprising the molecular sieve of this
22 invention, said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

23 In accordance with this invention there is also provided a process for
24 isomerizing olefins comprising contacting said olefin under conditions which cause
25 isomerization of the olefin with a catalyst comprising the molecular sieve of this
26 invention.

27 Further provided in accordance with this invention is a process for isomerizing
28 an isomerization feed comprising an aromatic C₈ stream of xylene isomers or
29 mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio
30 of ortho-, meta- and para-xylenes is obtained, said process comprising contacting said
31 feed under isomerization conditions with a catalyst comprising the molecular sieve of
32 this invention.

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

4 This invention also provides a process for converting oxygenated
5 hydrocarbons comprising contacting said oxygenated hydrocarbon with a catalyst
6 comprising the molecular sieve of this invention under conditions to produce liquid
7 products. The oxygenated hydrocarbon may be a lower alcohol.

8 Further provided in accordance with the present invention is a process for the
9 production of higher molecular weight hydrocarbons from lower molecular weight
10 hydrocarbons comprising the steps of:

11 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-
12 containing gas and contacting said gas in said zone under C_{2+} hydrocarbon
13 synthesis conditions with the catalyst and a metal or metal compound capable of
14 converting the lower molecular weight hydrocarbon to a higher molecular
15 weight hydrocarbon; and

16 (b) withdrawing from said reaction zone a higher molecular weight
17 hydrocarbon-containing stream.

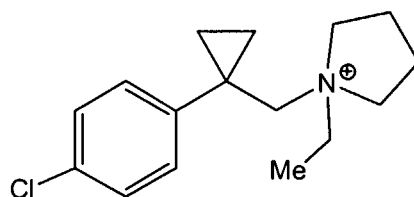
18 In accordance with this invention, there is also provided a process for the
19 reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen
20 wherein said process comprises contacting the gas stream with a molecular sieve
21 having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent element
22 to (2) an oxide of a second tetravalent element different from said first tetravalent
23 element, trivalent element, pentavalent element or mixture thereof and having, after
24 calcination, the X-ray diffraction lines of Table II. The molecular sieve may contain a
25 metal or metal ions (such as cobalt, copper, platinum, iron, chromium, manganese,
26 nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof) capable of
27 catalyzing the reduction of the oxides of nitrogen, and the process may be conducted
28 in the presence of a stoichiometric excess of oxygen. In a preferred embodiment, the
29 gas stream is the exhaust stream of an internal combustion engine.

30 DETAILED DESCRIPTION OF THE INVENTION

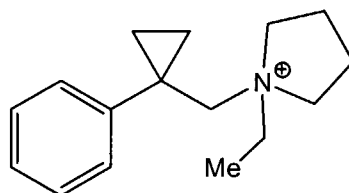
31 The present invention comprises a family of crystalline, large pore molecular
32 sieves designated herein "molecular sieve SSZ-65" or simply "SSZ-65". As used

herein, the term "large pore" means having an average pore size diameter greater than about 6.0 Angstroms, preferably from about 6.5 Angstroms to about 7.5 Angstroms.

In preparing SSZ-65, a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation is used as a structure directing agent ("SDA"), also known as a crystallization template. The SDA's useful for making SSZ-65 have the following structures:



1-[1-(4-Chloro-phenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium



1-Ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium

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

In general, SSZ-65 is prepared by contacting an active source of one or more oxides selected from the group consisting of monovalent element oxides, divalent element oxides, trivalent element oxides, tetravalent element oxides and/or pentavalent elements with the 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation SDA.

SSZ-65 is prepared from a reaction mixture having the composition shown in Table A below.

TABLE A
Reaction Mixture

	Typical	Preferred
$\text{YO}_2/\text{W}_a\text{O}_b$	> 15	30 - 70
$\text{OH-}/\text{YO}_2$	0.10 – 0.50	0.20 – 0.30
Q/YO_2	0.05 – 0.50	0.10 – 0.20
$\text{M}_{2/n}/\text{YO}_2$	0.02 – 0.40	0.10 – 0.25
$\text{H}_2\text{O}/\text{YO}_2$	30 – 80	35 - 45

wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium, iron, boron, titanium, indium, vanadium or mixtures thereof; a is 1 or 2, and b is 2 when a is 1 (i.e., W is tetravalent) and b is 3 when a is 2 (i.e., W is trivalent); M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation.

In practice, SSZ-65 is prepared by a process comprising:

- (a) preparing an aqueous solution containing sources of at least one oxide capable of forming a crystalline molecular sieve and a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation having an anionic counterion which is not detrimental to the formation of SSZ-65;
- (b) maintaining the aqueous solution under conditions sufficient to form crystals of SSZ-65; and
- (c) recovering the crystals of SSZ-65.

Accordingly, SSZ-65 may comprise the crystalline material and the SDA in combination with metallic and non-metallic oxides bonded in tetrahedral coordination through shared oxygen atoms to form a cross-linked three dimensional crystal structure. The metallic and non-metallic oxides comprise one or a combination of oxides of a first tetravalent element(s), and one or a combination of a trivalent element(s), pentavalent element(s), second tetravalent element(s) different from the first tetravalent element(s) or mixture thereof. The first tetravalent element(s) is preferably selected from the group consisting of silicon, germanium and combinations thereof. More preferably, the first tetravalent element is silicon. The trivalent

1 element, pentavalent element and second tetravalent element (which is different from
2 the first tetravalent element) is preferably selected from the group consisting of
3 aluminum, gallium, iron, boron, titanium, indium, vanadium and combinations
4 thereof. More preferably, the second trivalent or tetravalent element is aluminum or
5 boron.

6 Typical sources of aluminum oxide for the reaction mixture include
7 aluminates, alumina, aluminum colloids, aluminum oxide coated on silica sol,
8 hydrated alumina gels such as $\text{Al}(\text{OH})_3$ and aluminum compounds such as AlCl_3 and
9 $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include silicates, silica hydrogel, silicic
10 acid, fumed silica, colloidal silica, tetra-alkyl orthosilicates, and silica hydroxides.
11 Boron, as well as gallium, germanium, titanium, indium, vanadium and iron, can be
12 added in forms corresponding to their aluminum and silicon counterparts.

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

21 Typically, an alkali metal hydroxide and/or an alkaline earth metal hydroxide,
22 such as the hydroxide of sodium, potassium, lithium, cesium, rubidium, calcium, and
23 magnesium, is used in the reaction mixture; however, this component can be omitted
24 so long as the equivalent basicity is maintained. The SDA may be used to provide
25 hydroxide ion. Thus, it may be beneficial to ion exchange, for example, the halide to
26 hydroxide ion, thereby reducing or eliminating the alkali metal hydroxide quantity
27 required. The alkali metal cation or alkaline earth cation may be part of the
28 as-synthesized crystalline oxide material, in order to balance valence electron charges
29 therein.

30 The reaction mixture is maintained at an elevated temperature until the
31 crystals of the SSZ-65 are formed. The hydrothermal crystallization is usually
32 conducted under autogenous pressure, at a temperature between 100°C and 200°C,

preferably between 135°C and 160°C. The crystallization period is typically greater than 1 day and preferably from about 3 days to about 20 days.

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

During the hydrothermal crystallization step, the SSZ-65 crystals can be allowed to nucleate spontaneously from the reaction mixture. The use of SSZ-65 crystals as seed material can be advantageous in decreasing the time necessary for complete crystallization to occur. In addition, seeding can lead to an increased purity of the product obtained by promoting the nucleation and/or formation of SSZ-65 over any undesired phases. When used as seeds, SSZ-65 crystals are added in an amount between 0.1 and 10% of the weight of first tetravalent element oxide, e.g. silica, used in the reaction mixture.

Once the molecular sieve crystals have formed, the solid product is separated from the reaction mixture by standard mechanical separation techniques such as filtration. The crystals are water-washed and then dried, e.g., at 90°C to 150°C for from 8 to 24 hours, to obtain the as-synthesized SSZ-65 crystals. The drying step can be performed at atmospheric pressure or under vacuum.

SSZ-65 as prepared has a mole ratio of an oxide selected from silicon oxide, germanium oxide and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide, vanadium oxide and mixtures thereof greater than about 15; and has, after calcination, the X-ray diffraction lines of Table II below. SSZ-65 further has a composition, as synthesized (i.e., prior to removal of the SDA from the SSZ-65) and in the anhydrous state, in terms of mole ratios, shown in Table B below.

TABLE B

As-Synthesized SSZ-65

YO_2/W_cO_d	> 15
$M_{2/n}/YO_2$	0.01 – 0.03
Q/YO_2	0.02 – 0.05

wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium, iron, boron, titanium, indium, vanadium or mixtures thereof; c is 1 or 2; d is 2 when c is 1 (i.e., W is tetravalent) or d is 3 or 5 when c is 2 (i.e., d is 3 when W is trivalent or 5 when W is pentavalent); M is an alkali metal cation, alkaline earth metal cation or

1 mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a 1-[1-(4-chlorophenyl)-
2 cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-
3 cyclopropylmethyl)-pyrrolidinium cation.

4 SSZ-65 can be made with a mole ratio of $\text{YO}_2/\text{W}_c\text{O}_d$ of ∞ , i.e., there is
5 essentially no W_cO_d present in the SSZ-65. In this case, the SSZ-65 would be an all-
6 silica material or a germanosilicate. Thus, in a typical case where oxides of silicon
7 and aluminum are used, SSZ-65 can be made essentially aluminum free, i.e., having a
8 silica to alumina mole ratio of ∞ . A method of increasing the mole ratio of silica to
9 alumina is by using standard acid leaching or chelating treatments. However,
10 essentially aluminum-free SSZ-65 can be synthesized using essentially aluminum-free
11 silicon sources as the main tetrahedral metal oxide component, if boron is also
12 present. The boron can then be removed, if desired, by treating the borosilicate SSZ-
13 65 with acetic acid at elevated temperature (as described in Jones et al., *Chem.*
14 *Mater.*, 2001, 13, 1041-1050) to produce an all-silica version of SSZ-65. SSZ-65 can
15 also be prepared directly as a borosilicate. If desired, the boron can be removed as
16 described above and replaced with metal atoms by techniques known in the art to
17 make, e.g., an aluminosilicate version of SSZ-65. SSZ-65 can also be prepared
18 directly as an aluminosilicate.

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

24 It is believed that SSZ-65 is comprised of a new framework structure or
25 topology which is characterized by its X-ray diffraction pattern. SSZ-65,
26 as-synthesized, has a crystalline structure whose X-ray powder diffraction pattern
27 exhibit the characteristic lines shown in Table I and is thereby distinguished from
28 other molecular sieves.

TABLE I
As-Synthesized SSZ-65

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)^(b)</u>
6.94	12.74	M
9.18	9.63	M
16.00	5.54	W
17.48	5.07	M
21.02	4.23	VS
21.88	4.06	S
22.20	4.00	M
23.02	3.86	M
26.56	3.36	M
28.00	3.19	M

^(a) ± 0.1

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

Table IA below shows the X-ray powder diffraction lines for as-synthesized SSZ-65 including actual relative intensities.

TABLE IA

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
7.17	12.32	5.1
7.46	11.84	13.5
7.86	11.24	10.2
8.32	10.62	4.7
13.38	6.61	1.7
17.20	5.15	1.4
18.21	4.87	2.0
19.29	4.60	1.5
21.42	4.15	15.7
22.46	3.96	100.0
22.85	3.89	6.9
25.38	3.51	6.7
26.02	3.42	1.8
27.08	3.29	12.3
28.80	3.10	3.2
29.62	3.01	8.5
30.50	2.93	2.9
32.88	2.72	1.4
33.48	2.67	5.7

	34.76	2.58	1.8
	36.29	2.47	1.6
	37.46	2.40	1.3
1	(a) ± 0.1		

2 After calcination, the SSZ-65 molecular sieves have a crystalline structure
 3 whose X-ray powder diffraction pattern include the characteristic lines shown in
 4 Table II:

5 TABLE II
 6 Calcined SSZ-65

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
6.08	14.54	M
6.98	12.66	VS
9.28	9.53	S
17.58	5.04	M
21.14	4.20	VS
21.98	4.04	S
22.26	3.99	M
23.14	3.84	M
26.68	3.34	M
28.10	3.18	M

7 (a) ± 0.1

8 Table IIA below shows the X-ray powder diffraction lines for calcined SSZ-65
 9 including actual relative intensities.

10 TABLE IIA

<u>2 Theta^(a)</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Intensity (%)</u>
6.08	14.54	37.7
6.98	12.66	82.8
9.28	9.53	50.7
17.58	5.04	28.2
21.14	4.20	100.0
21.98	4.04	47.8
22.26	3.99	19.6

23.14	3.84	28.3
26.68	3.34	20.4
28.10	3.18	26.8

1 ^(a) ± 0.1

2

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

8 The variation in the scattering angle (two theta) measurements, due to
9 instrument error and to differences between individual samples, is estimated at
10 ± 0.1 degrees.

11 The X-ray diffraction pattern of Table I is representative of "as-synthesized"
12 or "as-made" SSZ-65 molecular sieves. Minor variations in the diffraction pattern
13 can result from variations in the silica-to-alumina or silica-to-boron mole ratio of the
14 particular sample due to changes in lattice constants. In addition, sufficiently small
15 crystals will affect the shape and intensity of peaks, leading to significant peak
16 broadening.

17 Representative peaks from the X-ray diffraction pattern of calcined SSZ-65
18 are shown in Table II. Calcination can also result in changes in the intensities of the
19 peaks as compared to patterns of the "as-made" material, as well as minor shifts in the
20 diffraction pattern. The molecular sieve produced by exchanging the metal or other
21 cations present in the molecular sieve with various other cations (such as H^+ or NH_4^+)
22 yields essentially the same diffraction pattern, although again, there may be minor
23 shifts in the interplanar spacing and variations in the relative intensities of the peaks.
24 Notwithstanding these minor perturbations, the basic crystal lattice remains
25 unchanged by these treatments.

26 Crystalline SSZ-65 can be used as-synthesized, but preferably will be
27 thermally treated (calcined). Usually, it is desirable to remove the alkali metal cation
28 by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion.
29 The molecular sieve can be leached with chelating agents, e.g., EDTA or dilute acid

1 solutions, to increase the silica to alumina mole ratio. The molecular sieve can also
2 be steamed; steaming helps stabilize the crystalline lattice to attack from acids.

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

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

15 The hydrogen, ammonium, and metal components can be ion-exchanged into
16 the SSZ-65. The SSZ-65 can also be impregnated with the metals, or the metals can
17 be physically and intimately admixed with the SSZ-65 using standard methods known
18 to the art.

19 Typical ion-exchange techniques involve contacting the synthetic molecular
20 sieve with a solution containing a salt of the desired replacing cation or cations.
21 Although a wide variety of salts can be employed, chlorides and other halides,
22 acetates, nitrates, and sulfates are particularly preferred. The molecular sieve is
23 usually calcined prior to the ion-exchange procedure to remove the organic matter
24 present in the channels and on the surface, since this results in a more effective ion
25 exchange. Representative ion exchange techniques are disclosed in a wide variety of
26 patents including U.S. Patent Nos. 3,140,249 issued on July 7, 1964 to Plank et al.;
27 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964
28 to Plank et al.

29 Following contact with the salt solution of the desired replacing cation, the
30 molecular sieve is typically washed with water and dried at temperatures ranging from
31 65°C to about 200°C. After washing, the molecular sieve can be calcined in air or
32 inert gas at temperatures ranging from about 200°C to about 800°C for periods of

1 time ranging from 1 to 48 hours, or more, to produce a catalytically active product
2 especially useful in hydrocarbon conversion processes.

3 Regardless of the cations present in the synthesized form of SSZ-65, the
4 spatial arrangement of the atoms which form the basic crystal lattice of the molecular
5 sieve remains essentially unchanged.

6 SSZ-65 can be formed into a wide variety of physical shapes. Generally
7 speaking, the molecular sieve can be in the form of a powder, a granule, or a molded
8 product, such as extrudate having a particle size sufficient to pass through a 2-mesh
9 (Tyler) screen and be retained on a 400-mesh (Tyler) screen. In cases where the
10 catalyst is molded, such as by extrusion with an organic binder, the SSZ-65 can be
11 extruded before drying, or, dried or partially dried and then extruded.

12 SSZ-65 can be composited with other materials resistant to the temperatures
13 and other conditions employed in organic conversion processes. Such matrix
14 materials include active and inactive materials and synthetic or naturally occurring
15 molecular sieves as well as inorganic materials such as clays, silica and metal oxides.
16 Examples of such materials and the manner in which they can be used are disclosed in
17 U.S. Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S. Patent
18 No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are incorporated by
19 reference herein in their entirety.

20 SSZ-65 molecular sieves are useful in hydrocarbon conversion reactions.
21 Hydrocarbon conversion reactions are chemical and catalytic processes in which
22 carbon containing compounds are changed to different carbon containing compounds.
23 Examples of hydrocarbon conversion reactions in which SSZ-65 are expected to be
24 useful include hydrocracking, dewaxing, catalytic cracking and olefin and aromatics
25 formation reactions. The catalysts are also expected to be useful in other petroleum
26 refining and hydrocarbon conversion reactions such as isomerizing n-paraffins and
27 naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds such as
28 isobutylene and butene-1, reforming, isomerizing polyalkyl substituted aromatics
29 (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide mixtures
30 of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also
31 included are rearrangement reactions to make various naphthalene derivatives, and

1 forming higher molecular weight hydrocarbons from lower molecular weight
2 hydrocarbons (e.g., methane upgrading).

3 The SSZ-65 catalysts may have high selectivity, and under hydrocarbon conversion
4 conditions can provide a high percentage of desired products relative to total products.

5 For high catalytic activity, the SSZ-65 molecular sieve should be
6 predominantly in its hydrogen ion form. Generally, the molecular sieve is converted
7 to its hydrogen form by ammonium exchange followed by calcination. If the
8 molecular sieve is synthesized with a high enough ratio of SDA cation to sodium ion,
9 calcination alone may be sufficient. It is preferred that, after calcination, at least 80%
10 of the cation sites are occupied by hydrogen ions and/or rare earth ions. As used
11 herein, "predominantly in the hydrogen form" means that, after calcination, at least
12 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

13 SSZ-65 molecular sieves can be used in processing hydrocarbonaceous
14 feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and can be
15 from many different sources, such as virgin petroleum fractions, recycle petroleum
16 fractions, shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO,
17 recycled plastic feedstocks and, in general, can be any carbon containing feedstock
18 susceptible to zeolitic catalytic reactions. Depending on the type of processing the
19 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals,
20 it can also have high or low nitrogen or sulfur impurities. It can be appreciated,
21 however, that in general processing will be more efficient (and the catalyst more
22 active) the lower the metal, nitrogen, and sulfur content of the feedstock.

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

27 Other reactions which can be performed using the catalyst of this invention
28 containing a metal, e.g., a Group VIII metal such platinum, include
29 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization
30 reactions.

1 The following table indicates typical reaction conditions which may be
 2 employed when using catalysts comprising SSZ-65 in the hydrocarbon conversion
 3 reactions of this invention. Preferred conditions are indicated in 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 Several hundred atmospheres

² Gas phase reaction

³ Hydrocarbon partial pressure

⁴ Liquid phase reaction

⁵ WHSV

Other reaction conditions and parameters are provided below.

Hydrocracking

Using a catalyst which comprises SSZ-65, preferably predominantly in the hydrogen form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other hydrocrackate charge stocks can be hydrocracked using the

1 process conditions and catalyst components disclosed in the aforementioned U.S.
2 Patent No. 4,910,006 and U.S. Patent No. 5,316,753.

3 The hydrocracking catalysts contain an effective amount of at least one
4 hydrogenation component of the type commonly employed in hydrocracking
5 catalysts. The hydrogenation component is generally selected from the group of
6 hydrogenation catalysts consisting of one or more metals of Group VIB and
7 Group VIII, including the salts, complexes and solutions containing such. The
8 hydrogenation catalyst is preferably selected from the group of metals, salts and
9 complexes thereof of the group consisting of at least one of platinum, palladium,
10 rhodium, iridium, ruthenium and mixtures thereof or the group consisting of at least
11 one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and mixtures
12 thereof. Reference to the catalytically active metal or metals is intended to encompass
13 such metal or metals in the elemental state or in some form such as an oxide, sulfide,
14 halide, carboxylate and the like. The hydrogenation catalyst is present in an effective
15 amount to provide the hydrogenation function of the hydrocracking catalyst, and
16 preferably in the range of from 0.05 to 25% by weight.

17 Dewaxing

18 SSZ-65, preferably predominantly in the hydrogen form, can be used to dewax
19 hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically,
20 the viscosity index of the dewaxed product is improved (compared to the waxy feed)
21 when the waxy feed is contacted with SSZ-65 under isomerization dewaxing
22 conditions.

23 The catalytic dewaxing conditions are dependent in large measure on the feed
24 used and upon the desired pour point. Hydrogen is preferably present in the reaction
25 zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically
26 between about 500 and about 30,000 SCF/bbl (standard cubic feet per barrel) (0.089
27 to 5.34 SCM/liter (standard cubic meters/liter)), preferably about 1000 to about
28 20,000 SCF/bbl (0.178 to 3.56 SCM/liter). Generally, hydrogen will be separated
29 from the product and recycled to the reaction zone. Typical feedstocks include light
30 gas oil, heavy gas oils and reduced crudes boiling above about 350°F (177°C).

31 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil
32 feedstock boiling above about 350°F (177°C) and containing straight chain and

1 slightly branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in
2 the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi
3 (0.103-20.7 MPa) with a catalyst comprising SSZ-65 and at least one Group VIII
4 metal.

5 The SSZ-65 hydrodewaxing catalyst may optionally contain a hydrogenation
6 component of the type commonly employed in dewaxing catalysts. See the
7 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for
8 examples of these hydrogenation components.

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

13 The feed may be hydrocracked, followed by dewaxing. This type of two stage
14 process and typical hydrocracking conditions are described in U.S. Patent
15 No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated herein by
16 reference in its entirety.

17 SSZ-65 may also be utilized as a dewaxing catalyst in the form of a layered
18 catalyst. That is, the catalyst comprises a first layer comprising molecular sieve SSZ-
19 65 and at least one Group VIII metal, and a second layer comprising an
20 aluminosilicate molecular sieve which is more shape selective than molecular sieve
21 SSZ-65. The use of layered catalysts is disclosed in U.S. Patent No. 5,149,421, issued
22 September 22, 1992 to Miller, which is incorporated by reference herein in its
23 entirety. The layering may also include a bed of SSZ-65 layered with a non-zeolitic
24 component designed for either hydrocracking or hydrofinishing.

25 SSZ-65 may also be used to dewax raffinates, including bright stock, under
26 conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1,
27 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.

28 It is often desirable to use mild hydrogenation (sometimes referred to as
29 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing step
30 can be performed either before or after the dewaxing step, and preferably after.
31 Hydrofinishing is typically conducted at temperatures ranging from about 190°C to
32 about 340°C at pressures from about 400 psig to about 3000 psig (2.76 to 20.7 MPa

1 gauge) at space velocities (LHSV) between about 0.1 and 20 and a hydrogen recycle
2 rate of about 400 to 1500 SCF/bbl (0.071 to 0.27 SCM/liter). The hydrogenation
3 catalyst employed must be active enough not only to hydrogenate the olefins,
4 diolefins and color bodies which may be present, but also to reduce the aromatic
5 content. Suitable hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594,
6 issued May 1, 1990 to Miller, which is incorporated by reference herein in its entirety.
7 The hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a
8 lubricating oil) since dewaxed products prepared from hydrocracked stocks tend to be
9 unstable to air and light and tend to form sludges spontaneously and quickly.

10 Lube oil may be prepared using SSZ-65. For example, a C₂₀₊ lube oil may be
11 made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising SSZ-65 in the
12 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil
13 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous
14 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
15 dewaxing the effluent at a temperature of at least about 400°F (204°C) and at a
16 pressure of from about 15 psig to about 3000 psig (0.103-20.7 MPa gauge) in the
17 presence of added hydrogen gas with a catalyst comprising SSZ-65 in the hydrogen
18 form and at least one Group VIII metal.

19 Aromatics Formation

20 SSZ-65 can be used to convert light straight run naphthas and similar mixtures
21 to highly aromatic mixtures. Thus, normal and slightly branched chained
22 hydrocarbons, preferably having a boiling range above about 40°C and less than about
23 200°C, can be converted to products having a substantial higher octane aromatics
24 content by contacting the hydrocarbon feed with a catalyst comprising SSZ-65. It is
25 also possible to convert heavier feeds into BTX or naphthalene derivatives of value
26 using a catalyst comprising SSZ-65.

27 The conversion catalyst preferably contains a Group VIII metal compound to
28 have sufficient activity for commercial use. By Group VIII metal compound as used
29 herein is meant the metal itself or a compound thereof. The Group VIII noble metals
30 and their compounds, platinum, palladium, and iridium, or combinations thereof can
31 be used. Rhenium or tin or a mixture thereof may also be used in conjunction with
32 the Group VIII metal compound and preferably a noble metal compound. The most

1 preferred metal is platinum. The amount of Group VIII metal present in the
2 conversion catalyst should be within the normal range of use in reforming catalysts,
3 from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

4 It is critical to the selective production of aromatics in useful quantities that
5 the conversion catalyst be substantially free of acidity, for example, by neutralizing
6 the molecular sieve with a basic metal, e.g., alkali metal, compound. Methods for
7 rendering the catalyst free of acidity are known in the art. See the aforementioned
8 U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a description of such
9 methods.

10 The preferred alkali metals are sodium, potassium, rubidium and cesium. The
11 molecular sieve itself can be substantially free of acidity only at very high
12 silica:alumina mole ratios.

13 Catalytic Cracking

14 Hydrocarbon cracking stocks can be catalytically cracked in the absence of
15 hydrogen using SSZ-65, preferably predominantly in the hydrogen form.

16 When SSZ-65 is used as a catalytic cracking catalyst in the absence of
17 hydrogen, the catalyst may be employed in conjunction with traditional cracking
18 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking
19 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of
20 these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent
21 No. 4,910,006 and U.S. Patent No 5,316,753. When a traditional cracking catalyst
22 (TC) component is employed, the relative weight ratio of the TC to the SSZ-65 is
23 generally between about 1:10 and about 500:1, desirably between about 1:10 and
24 about 200:1, preferably between about 1:2 and about 50:1, and most preferably is
25 between about 1:1 and about 20:1. The novel molecular sieve and/or the traditional
26 cracking component may be further ion exchanged with rare earth ions to modify
27 selectivity.

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

Isomerization

The present catalyst is highly active and highly selective for isomerizing C₄ to C₇ hydrocarbons. The activity means that the catalyst can operate at relatively low temperature which thermodynamically favors highly branched paraffins.

Consequently, the catalyst can produce a high octane product. The high selectivity means that a relatively high liquid yield can be achieved when the catalyst is run at a high octane.

The present process comprises contacting the isomerization catalyst, i.e., a catalyst comprising SSZ-65 in the hydrogen form, with a hydrocarbon feed under isomerization conditions. The feed is preferably a light straight run fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C) and preferably from 60°F to 200°F (16°C to 93°C). Preferably, the hydrocarbon feed for the process comprises a substantial amount of C₄ to C₇ normal and slightly branched low octane hydrocarbons, more preferably C₅ and C₆ hydrocarbons.

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

A low sulfur feed is especially preferred in the present process. The feed preferably contains less than 10 ppm, more preferably less than 1 ppm, and most preferably less than 0.1 ppm sulfur. In the case of a feed which is not already low in sulfur, acceptable levels can be reached by hydrogenating the feed in a presaturation zone with a hydrogenating catalyst which is resistant to sulfur poisoning. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of this hydrodesulfurization process.

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

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

The conversion catalyst preferably contains a Group VIII metal compound to have sufficient activity for commercial use. By Group VIII metal compound as used

herein is meant the metal itself or a compound thereof. The Group VIII noble metals and their compounds, platinum, palladium, and iridium, or combinations thereof can be used. Rhenium and tin may also be used in conjunction with the noble metal. The most preferred metal is platinum. The amount of Group VIII metal present in the conversion catalyst should be within the normal range of use in isomerizing catalysts, from about 0.05 to 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

Alkylation and Transalkylation

SSZ-65 can be used in a process for the alkylation or transalkylation of an aromatic hydrocarbon. The process comprises contacting the aromatic hydrocarbon with a C₂ to C₁₆ olefin alkylating agent or a polyalkyl aromatic hydrocarbon transalkylating agent, under at least partial liquid phase conditions, and in the presence of a catalyst comprising SSZ-65.

SSZ-65 can also be used for removing benzene from gasoline by alkylating the benzene as described above and removing the alkylated product from the gasoline.

For high catalytic activity, the SSZ-65 molecular sieve should be predominantly in its hydrogen ion form. It is preferred that, after calcination, at least 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

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

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

When transalkylation is desired, the transalkylating agent is a polyalkyl aromatic hydrocarbon containing two or more alkyl groups that each may have from 2 to about 4 carbon atoms. For example, suitable polyalkyl aromatic hydrocarbons include di-, tri- and tetra-alkyl aromatic hydrocarbons, such as diethylbenzene, triethylbenzene, diethylmethylbenzene (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene, dibutylbenzene, and the like. Preferred polyalkyl aromatic

1 hydrocarbons are the dialkyl benzenes. A particularly preferred polyalkyl aromatic
2 hydrocarbon is di-isopropylbenzene.

3 When alkylation is the process conducted, reaction conditions are as follows.
4 The aromatic hydrocarbon feed should be present in stoichiometric excess. It is
5 preferred that molar ratio of aromatics to olefins be greater than four-to-one to prevent
6 rapid catalyst fouling. The reaction temperature may range from 100°F to 600°F
7 (38°C to 315°C), preferably 250°F to 450°F (121°C to 232°C). The reaction pressure
8 should be sufficient to maintain at least a partial liquid phase in order to retard
9 catalyst fouling. This is typically 50 psig to 1000 psig (0.345 to 6.89 MPa gauge)
10 depending on the feedstock and reaction temperature. Contact time may range from
11 10 seconds to 10 hours, but is usually from 5 minutes to an hour. The weight hourly
12 space velocity (WHSV), in terms of grams (pounds) of aromatic hydrocarbon and
13 olefin per gram (pound) of catalyst per hour, is generally within the range of about 0.5
14 to 50.

15 When transalkylation is the process conducted, the molar ratio of aromatic
16 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from about
17 2:1 to 20:1. The reaction temperature may range from about 100°F to 600°F (38°C to
18 315°C), but it is preferably about 250°F to 450°F (121°C to 232°C). The reaction
19 pressure should be sufficient to maintain at least a partial liquid phase, typically in the
20 range of about 50 psig to 1000 psig (0.345 to 6.89 MPa gauge), preferably 300 psig to
21 600 psig (2.07 to 4.14 MPa gauge). The weight hourly space velocity will range from
22 about 0.1 to 10. U.S. Patent No. 5,082,990 issued on January 21, 1992 to Hsieh, et al.
23 describes such processes and is incorporated herein by reference.

24 Conversion of Paraffins to Aromatics

25 SSZ-65 can be used to convert light gas C₂-C₆ paraffins to higher molecular
26 weight hydrocarbons including aromatic compounds. Preferably, the molecular sieve
27 will contain a catalyst metal or metal oxide wherein said metal is selected from the
28 group consisting of Groups IB, IIB, VIII and IIIA of the Periodic Table. Preferably,
29 the metal is gallium, niobium, indium or zinc in the range of from about 0.05 to 5%
30 by weight.

31 Isomerization of Olefins

32 SSZ-65 can be used to isomerize olefins. The feed stream is a hydrocarbon
33 stream containing at least one C₄₋₆ olefin, preferably a C₄₋₆ normal olefin, more
34 preferably normal butene. Normal butene as used in this specification means all

1 forms of normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically,
2 hydrocarbons other than normal butene or other C₄₋₆ normal olefins will be present in
3 the feed stream. These other hydrocarbons may include, e.g., alkanes, other olefins,
4 aromatics, hydrogen, and inert gases.

5 The feed stream typically may be the effluent from a fluid catalytic cracking
6 unit or a methyl-tert-butyl ether unit. A fluid catalytic cracking unit effluent typically
7 contains about 40-60 weight percent normal butenes. A methyl-tert-butyl ether unit
8 effluent typically contains 40-100 weight percent normal butene. The feed stream
9 preferably contains at least about 40 weight percent normal butene, more preferably at
10 least about 65 weight percent normal butene. The terms iso-olefin and methyl
11 branched iso-olefin may be used interchangeably in this specification.

12 The process is carried out under isomerization conditions. The hydrocarbon
13 feed is contacted in a vapor phase with a catalyst comprising the SSZ-65. The
14 process may be carried out generally at a temperature from about 625°F to about
15 950°F (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-
16 482°C), and about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The
17 pressure ranges from subatmospheric to about 200 psig (1.38 MPa gauge), preferably
18 from about 15 psig to about 200 psig (0.103 to 1.38 MPa gauge), and more preferably
19 from about 1 psig to about 150 psig (0.00689 to 1.03 MPa gauge).

20 The liquid hourly space velocity during contacting is generally from about 0.1
21 to about 50 hr⁻¹, based on the hydrocarbon feed, preferably from about 0.1 to about
22 20 hr⁻¹, more preferably from about 0.2 to about 10 hr⁻¹, most preferably from about 1
23 to about 5 hr⁻¹. A hydrogen/hydrocarbon molar ratio is maintained from about 0 to
24 about 30 or higher. The hydrogen can be added directly to the feed stream or directly
25 to the isomerization zone. The reaction is preferably substantially free of water,
26 typically less than about two weight percent based on the feed. The process can be
27 carried out in a packed bed reactor, a fixed bed, fluidized bed reactor, or a moving bed
28 reactor. The bed of the catalyst can move upward or downward. The mole percent
29 conversion of, e.g., normal butene to iso-butene is at least 10, preferably at least 25,
30 and more preferably at least 35.

Xylene Isomerization

1
2 SSZ-65 may also be useful in a process for isomerizing one or more xylene
3 isomers in a C₈ aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio
4 approaching the equilibrium value. In particular, xylene isomerization is used in
5 conjunction with a separate process to manufacture para-xylene. For example, a
6 portion of the para-xylene in a mixed C₈ aromatics stream may be recovered by
7 crystallization and centrifugation. The mother liquor from the crystallizer is then
8 reacted under xylene isomerization conditions to restore ortho-, meta- and
9 para-xylenes to a near equilibrium ratio. At the same time, part of the ethylbenzene in
10 the mother liquor is converted to xylenes or to products which are easily separated by
11 filtration. The isomerate is blended with fresh feed and the combined stream is
12 distilled to remove heavy and light by-products. The resultant C₈ aromatics stream is
13 then sent to the crystallizer to repeat the cycle.

14 Optionally, isomerization in the vapor phase is conducted in the presence of
15 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If
16 hydrogen is used, the catalyst should comprise about 0.1 to 2.0 wt.% of a
17 hydrogenation/dehydrogenation component selected from Group VIII (of the Periodic
18 Table) metal component, especially platinum or nickel. By Group VIII metal
19 component is meant the metals and their compounds such as oxides and sulfides.

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

Oligomerization

22
23 It is expected that SSZ-65 can also be used to oligomerize straight and
24 branched chain olefins having from about 2 to 21 and preferably 2-5 carbon atoms.
25 The oligomers which are the products of the process are medium to heavy olefins
26 which are useful for both fuels, i.e., gasoline or a gasoline blending stock and
27 chemicals.

28 The oligomerization process comprises contacting the olefin feedstock in the
29 gaseous or liquid phase with a catalyst comprising SSZ-65.

30 The molecular sieve can have the original cations associated therewith
31 replaced by a wide variety of other cations according to techniques well known in the
32 art. Typical cations would include hydrogen, ammonium and metal cations including

1 mixtures of the same. Of the replacing metallic cations, particular preference is given
2 to cations of metals such as rare earth metals, manganese, calcium, as well as metals
3 of Group II of the Periodic Table, e.g., zinc, and Group VIII of the Periodic Table,
4 e.g., nickel. One of the prime requisites is that the molecular sieve have a fairly low
5 aromatization activity, i.e., in which the amount of aromatics produced is not more
6 than about 20% by weight. This is accomplished by using a molecular sieve with
7 controlled acid activity [alpha value] of from about 0.1 to about 120, preferably from
8 about 0.1 to about 100, as measured by its ability to crack n-hexane.

9 Alpha values are defined by a standard test known in the art, e.g., as shown in
10 U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens et al. which is
11 incorporated totally herein by reference. If required, such molecular sieves may be
12 obtained by steaming, by use in a conversion process or by any other method which
13 may occur to one skilled in this art.

14 Condensation of Alcohols

15 SSZ-65 can be used to condense lower aliphatic alcohols having 1 to
16 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed
17 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent
18 No. 3,894,107, issued July 8, 1975 to Butter et al., describes the process conditions
19 used in this process, which patent is incorporated totally herein by reference.

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

28 Methane Upgrading

29 Higher molecular weight hydrocarbons can be formed from lower molecular
30 weight hydrocarbons by contacting the lower molecular weight hydrocarbon with a
31 catalyst comprising SSZ-65 and a metal or metal compound capable of converting the
32 lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon.
33 Examples of such reactions include the conversion of methane to C₂₊ hydrocarbons

1 such as ethylene or benzene or both. Examples of useful metals and metal
2 compounds include lanthanide and or actinide metals or metal compounds.

3 These reactions, the metals or metal compounds employed and the conditions
4 under which they can be run are disclosed in U.S. Patents No. 4,734,537, issued
5 March 29, 1988 to Devries et al.; 4,939,311, issued July 3, 1990 to Washecheck et al.;
6 4,962,261, issued October 9, 1990 to Abrevaya et al.; 5,095,161, issued March 10,
7 1992 to Abrevaya et al.; 5,105,044, issued April 14, 1992 to Han et al.; 5,105,046,
8 issued April 14, 1992 to Washecheck; 5,238,898, issued August 24, 1993 to Han et
9 al.; 5,321,185, issued June 14, 1994 to van der Vaart; and 5,336,825, issued August 9,
10 1994 to Choudhary et al., each of which is incorporated herein by reference in its
11 entirety.

12 SSZ-65 may be used for the catalytic reduction of the oxides of nitrogen in a
13 gas stream. Typically, the gas stream also contains oxygen, often a stoichiometric
14 excess thereof. Also, the SSZ-65 may contain a metal or metal ions within or on it
15 which are capable of catalyzing the reduction of the nitrogen oxides. Examples of
16 such metals or metal ions include copper, cobalt, platinum, iron, chromium,
17 manganese, nickel, zinc, lanthanum, palladium, rhodium and mixtures thereof.

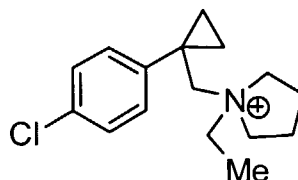
18 One example of such a process for the catalytic reduction of oxides of nitrogen
19 in the presence of a molecular sieve is disclosed in U.S. Patent No. 4,297,328, issued
20 October 27, 1981 to Ritscher et al., which is incorporated by reference herein. There,
21 the catalytic process is the combustion of carbon monoxide and hydrocarbons and the
22 catalytic reduction of the oxides of nitrogen contained in a gas stream, such as the
23 exhaust gas from an internal combustion engine. The molecular sieve used is metal
24 ion-exchanged, doped or loaded sufficiently so as to provide an effective amount of
25 catalytic copper metal or copper ions within or on the molecular sieve. In addition,
26 the process is conducted in an excess of oxidant, e.g., oxygen.

27 EXAMPLES

28 The following examples demonstrate but do not limit the present invention.
29

Example 1

Synthesis of SDA 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium
Cation



1-[1-(4-Chloro-phenyl)-
cyclopropylmethyl]-1-ethyl-pyrrolidinium

The structure directing agent is synthesized according to the synthetic scheme shown below (Scheme 1).

1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium iodide is prepared from the reaction of the parent amine 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine with ethyl iodide. A 100 gm (0.42 mole) of the amine, 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine, is dissolved in 1000 ml anhydrous methanol in a 3-litre 3-necked reaction flask (equipped with a mechanical stirrer and a reflux condenser). To this solution, 98 gm (0.62 mole) of ethyl iodide is added, and the mixture is stirred at room temperature for 72 hours. Then, 39 gm (0.25 mol.) of ethyl iodide is added and the mixture is heated at reflux for 3 hours. The reaction mixture is cooled down and excess ethyl iodide and the solvent are removed at reduced pressure on a rotary evaporator. The obtained dark tan-colored solids (162 gm) are further purified by dissolving in acetone (500 ml) followed by precipitation by adding diethyl ether. Filtration and air-drying the obtained solids gives 153 gm (93% yield) of the desired 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium iodide as a white powder. The product is pure by ^1H and ^{13}C -NMR analysis.

The hydroxide form of 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium cation is obtained by an ion exchange treatment of the iodide salt with Ion-Exchange Resin-OH (BIO RAD[®] AH1-X8). In a 1-liter volume plastic bottle, 100 gm (255 mmol) of 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium iodide is dissolved in 300 ml de-ionized water. Then, 320 gm of the ion exchange resin is added and the solution is allowed to gently stir overnight. The

1 mixture is then filtered, and the resin cake is rinsed with minimal amount of de-
2 ionized water. The filtrate is analyzed for hydroxide concentration by titration
3 analysis on a small sample of the solution with 0.1N HCl. The reaction yields 96% of
4 (245 mmol) of the desired 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-
5 pyrrolidinium hydroxide (hydroxide concentration of 0.6 M).

6 The parent amine 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine is
7 obtained from the LiAlH_4 -reduction of the precursor amide [1-(4-chloro-phenyl)-
8 cyclopropyl]-pyrrolidin-1-yl-methanone. In a 3-neck 3-liter reaction flask equipped
9 with a mechanical stirrer and reflux condenser, 45.5 gm (1.2 mol.) of LiAlH_4 is
10 suspended in 750 ml anhydrous tetrahydrofuran (THF). The suspension is cooled
11 down to 0°C (ice-bath), and 120 gm (0.48 mole) of [1-(4-chloro-phenyl)-
12 cyclopropyl]-pyrrolidin-1-yl-methanone dissolved in 250 ml THF is added (to the
13 suspension) drop-wise via an addition funnel. Once all the amide solution is added,
14 the ice-bath is replaced with a heating mantle and the reaction mixture is heated at
15 reflux overnight. Then, the reaction solution is cooled down to 0°C (the heating
16 mantle was replaced with an ice-bath), and the mixture is diluted with 500 ml diethyl
17 ether. The reaction is worked up by adding 160 ml of 15% wt. of an aqueous NaOH
18 solution drop-wise (via an addition funnel) with vigorous stirring. The starting gray
19 reaction solution changes to a colorless liquid with a white powdery precipitate. The
20 solution mixture is filtered and the filtrate is dried over anhydrous magnesium sulfate.
21 Filtration and concentration of the filtrate gives 106 gm (94% yield) of the desired
22 amine 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine as a pale yellow oily
23 substance. The amine is pure as indicated by the clean ^1H and ^{13}C -NMR spectral
24 analysis.

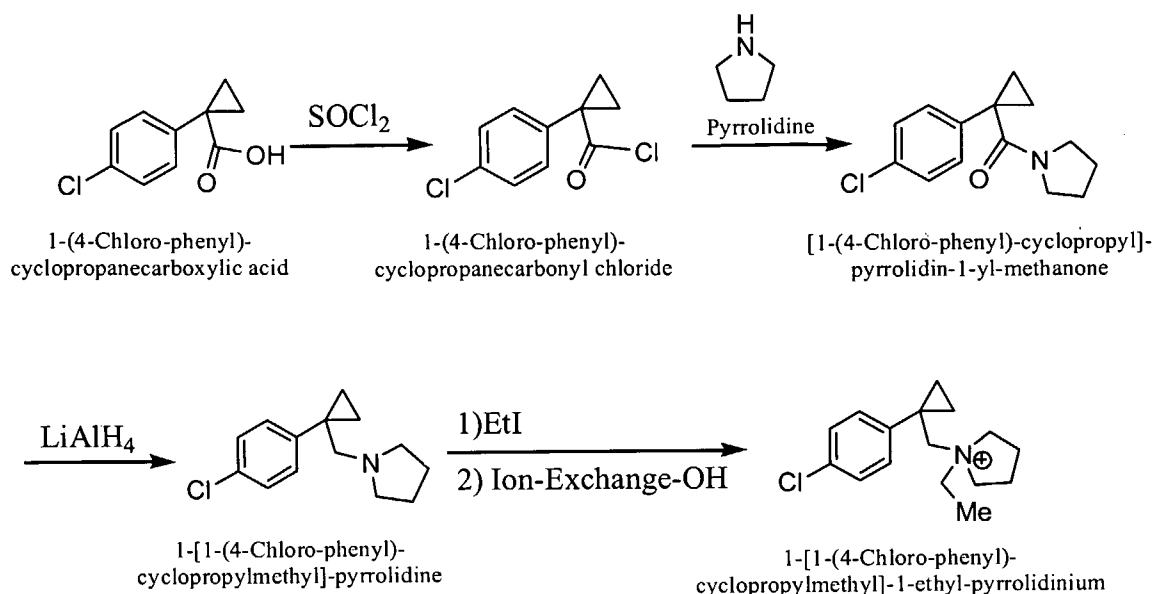
25 The parent amide [1-(4-chloro-phenyl)-cyclopropyl]-pyrrolidin-1-yl-
26 methanone is prepared by reacting pyrrolidine with 1-(4-chloro-phenyl)-
27 cyclopropanecarbonyl chloride. A 2-Liter reaction flask equipped with a mechanical
28 stirrer is charged with 1000 ml of dry benzene, 53.5 gm (0.75 mol.) of pyrrolidine and
29 76 gm (0.75 mol.) of triethyl amine. To this mixture (at 0°C), 108 1-(4-chloro-
30 phenyl)-cyclopropanecarbonyl chloride gm (0.502 mol.) of (dissolved 100 ml
31 benzene) is added drop-wise (via an addition funnel). Once the addition is completed,
32 the resulting mixture is allowed to stir at room temperature overnight. The reaction

1 mixture (a biphasic mixture: liquid and tan-colored precipitate) is concentrated on a
2 rotary evaporator at reduced pressure to strip off excess pyrrolidine and the solvent
3 (usually hexane or benzene). The remaining residue is diluted with 750 ml water and
4 extracted with 750 ml chloroform in a separatory funnel. The organic layer is washed
5 twice with 500 ml water and once with brine. Then, the organic layer is dried over
6 anhydrous sodium sulfate, filtered and concentrated on a rotary evaporator at reduced
7 pressure to give 122 gm (0.49 mol, 97% yield) of the amide as a tan-colored solid
8 substance.

9 The 1-(4-chloro-phenyl)-cyclopropanecarbonyl chloride used in the synthesis
10 of the amide is synthesized by treatment of the parent acid 1-(4-chloro-phenyl)-
11 cyclopropanecarboxylic acid with thionyl chloride (SOCl_2) as described below. To
12 200 gms of thionyl chloride and 200 ml dichloromethane in a 3-necked reaction flask,
13 equipped with a mechanical stirrer and a reflux condenser, 100 gm (0.51 mol.) of the
14 1-(4-chloro-phenyl)-cyclopropanecarboxylic acid is added in small increments (5 gm
15 at a time) over 15 minutes period. Once all the acid is added, the reaction mixture is
16 then heated at reflux. The reaction vessel is equipped with a trap (filled with water) to
17 collect and trap the acidic gaseous byproducts, and used in monitoring the reaction.
18 The reaction is usually done once the evolution of the gaseous byproducts is ceased.
19 The reaction mixture is then cooled down and concentrated on a rotary evaporator at
20 reduced pressure to remove excess thionyl chloride and dichloromethane. The
21 reaction yields 109 gm (98%) of the desired 1-(4-chloro-phenyl)-
22 cyclopropanecarbonyl chloride as reddish viscous oil.

23

1

Scheme 1

2

3

4

Example 2Synthesis of SDA 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation

SDA 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation is synthesized using the synthesis procedure of Example 1, except that the synthesis starts from 1-phenyl-cyclopropanecarbonyl chloride and pyrrolidine.

9

Example 3Synthesis of SSZ-65

A 23 cc Teflon liner is charged with 5.4 gm of 0.6M aqueous solution of 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium hydroxide (3 mmol SDA), 1.2 gm of 1M aqueous solution of NaOH (1.2 mmol NaOH) and 5.4 gm of de-ionized water. To this mixture, 0.06 gm of sodium borate decahydrate (0.157 mmol of $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$; ~ 0.315 mmol B_2O_3) is added and stirred until completely dissolved. Then, 0.9 gm of CAB-O-SIL[®] M-5 fumed silica (~ 14.7 mmol SiO_2) is added to the solution and the mixture is thoroughly stirred. The resulting gel is capped off and placed in a Parr bomb steel reactor and heated in an oven at 160° C while rotating at 43 rpm. The reaction is monitored by checking the gel's pH, and by looking for crystal formation using Scanning Electron Microscopy (SEM). The reaction is usually complete after heating 9-12 days at the conditions described above. Once the crystallization is completed, the starting reaction gel turns to a mixture comprised of a

1 clear liquid and powdery precipitate. The mixture is filtered through a fritted-glass
2 funnel. The collected solids are thoroughly washed with water and, then, rinsed with
3 acetone (10 ml) to remove any organic residues. The solids are allowed to air-dry
4 overnight and, then, dried in an oven at 120° C for 1 hour. The reaction affords 0.85
5 gram of a very fine powder. SEM shows the presence of only one crystalline phase.
6 The product is determined by powder XRD data analysis to be SSZ-65.

7 Example 4

8 Seeded Synthesis of Borosilicate SSZ-65

9 The synthesis of borosilicate SSZ-65 (B-SSZ-65) described in Example 3
10 above is repeated with the exception of adding 0.04 gm of SSZ-65 as seeds to speed
11 up the crystallization process. The reaction conditions are exactly the same as for the
12 previous example. The crystallization is complete in four days and affords 0.9 gm of
13 B-SSZ-65.

14 Example 5

15 Synthesis of Aluminosilicate SSZ-65

16 A 23 cc Teflon liner is charged with 4 gm of 0.6M aqueous solution of 1-
17 ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium hydroxide (2.25 mmol SDA),
18 1.5 gm of 1M aqueous solution of NaOH (1.5 mmol NaOH) and 2 gm of de-ionized
19 water. To this mixture, 0.25 gm of Na-Y molecular sieve (Union Carbide's LZY-52;
20 $\text{SiO}_2/\text{Al}_2\text{O}_3=5$) is added and stirred until completely dissolved. Then, 0.85 gm of
21 CAB-O-SIL® M-5 fumed silica (~14. mmol SiO_2) is added to the solution and the
22 mixture is thoroughly stirred. The resulting gel is capped off and placed in a Parr
23 bomb steel reactor and heated in an oven at 160° C while rotating at 43 rpm. The
24 reaction is monitored by checking the gel's pH (increase in the pH usually results
25 from condensation of the silicate species during crystallization, and decrease in pH
26 often indicates decomposition of the SDA), and by checking for crystal formation by
27 scanning electron microscopy. The reaction is usually complete after heating for 12
28 days at the conditions described above. Once the crystallization is completed, the
29 starting reaction gel turns to a mixture comprised of a liquid and powdery precipitate.
30 The mixture is filtered through a fritted-glass funnel. The collected solids are
31 thoroughly washed with water and, then, rinsed with acetone (10 ml) to remove any

1 organic residues. The solids are allowed to air-dry overnight and, then, dried in an
2 oven at 120° C for 1 hour. The reaction affords 0.8 gram of SSZ-65.

3 Examples 6-15

4 Syntheses of SSZ-65 at Varying SiO₂/B₂O₃ Ratios

5 SSZ-65 is synthesized at varying SiO₂/B₂O₃ mole ratios in the starting
6 synthesis gel. This is accomplished using the synthetic conditions described in
7 Example 3 keeping everything the same while changing the SiO₂/B₂O₃ mole ratios in
8 the starting gel. This is done by keeping the amount of CAB-O-SIL[®] M-5 (98% SiO₂
9 and 2% H₂O) the same while varying the amount of sodium borate in each synthesis.
10 Consequently, varying the amount of sodium borate leads to varying the SiO₂/Na
11 mole ratios in the starting gels. Table 1 below shows the results of a number of
12 syntheses with varying SiO₂/B₂O₃ in the starting synthesis gel.

13 Table 1

Example No.	SiO ₂ /B ₂ O ₃	SiO ₂ /Na	Crystallization Time(days)	Products
6	140	13.3	15	SSZ-65
7	93	12.7	12	SSZ-65
8	70	12.1	12	SSZ-65
9	56	11.6	12	SSZ-65
10	47	11.2	12	SSZ-65
11	40	10.7	12	SSZ-65
12	31	10	12	SSZ-65
13	23	9	12	SSZ-65
14	19	8.2	6	SSZ-65
15	14	7.1	6	SSZ-65

14 OH/SiO₂=0.28, R⁺/SiO₂=0.2, H₂O/SiO₂=44

15 (R⁺= organic cation (SDA))

16 Example 16

17 Calcination of SSZ-65

18 SSZ-65 as synthesized in Example 3 is calcined to remove the structure
19 directing agent (SDA) as described below. A thin bed of SSZ-65 in a calcination dish
20 is heated in a muffle furnace from room temperature to 120°C at a rate of 1°C/minute

1 and held for 2 hours. Then, the temperature is ramped up to 540°C at a rate of
2 1°C/minute and held for 5 hours. The temperature is ramped up again at 1°C/minute
3 to 595°C and held there for 5 hours. A 50/50 mixture of air and nitrogen passes
4 through the muffle furnace at a rate of 20 standard cubic feet (0.57 standard cubic
5 meters) per minute during the calcination process.

6 Example 17

7 Conversion of Borosilicate-SSZ-65 to Aluminosilicate SSZ-65

8 The calcined version of borosilicate SSZ-65 (as synthesized in Example 3 and
9 calcined in Example 16) is easily converted to the aluminosilicate SSZ-65 version by
10 suspending borosilicate SSZ-65 in 1M solution of aluminum nitrate nonahydrate (15
11 ml of 1M $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ soln./1 gm SSZ-65). The suspension is heated at reflux
12 overnight. The resulting mixture is then filtered and the collected solids are
13 thoroughly rinsed with de-ionized water and air-dried overnight. The solids are
14 further dried in an oven at 120°C for 2 hours.

15 Example 18

16 Ammonium- Ion Exchange of SSZ-65

17 The Na^+ form of SSZ-65 (prepared as in Example 3 or as in Example 5 and
18 calcined as in Example 16) is converted to NH_4^+ -SSZ-65 form by heating the material
19 in an aqueous solution of NH_4NO_3 (typically 1gm NH_4NO_3 /1 gm SSZ-65 in 20 ml
20 H_2O) at 90°C for 2-3 hours. The mixture is then filtered and the obtained NH_4 -
21 exchanged-product is washed with de-ionized water and dried. The NH_4^+ form of
22 SSZ-65 can be converted to the H^+ form by calcination (as described in Example 16)
23 to 540°C.

24 Example 19

25 Argon Adsorption Analysis

26 SSZ-65 has a micropore volume of 0.16 cc/gm based on argon adsorption isotherm at
27 87.5° K (-186°C) recorded on ASAP 2010 equipment from Micromeritics. The
28 sample is first degassed at 400°C for 16 hours prior to argon adsorption. The low-
29 pressure dose is 6.00 cm^3/g (STP). A maximum of one hour equilibration time per
30 dose is used and the total run time is 35 hours. The argon adsorption isotherm is
31 analyzed using the density function theory (DFT) formalism and parameters
32 developed for activated carbon slits by Olivier (*Porous Mater.* 1995, 2, 9) using the

1 Saito Foley adaptation of the Horvarth-Kawazoe formalism (*Microporous Materials*,
2 1995, 3, 531) and the conventional t-plot method (*J. Catalysis*, 1965, 4, 319).

3 Example 20

4 Constraint Index

5 The hydrogen form of SSZ-65 of Example 3 (after treatment according to
6 Examples 16, 17 and 18) is pelletized at 3 KPSI, crushed and granulated to 20-40
7 mesh. A 0.6 gram sample of the granulated material is calcined in air at 540°C for 4
8 hours and cooled in a desiccator to ensure dryness. Then, 0.5 gram is packed into a
9 3/8 inch stainless steel tube with alundum on both sides of the molecular sieve bed. A
10 Lindburg furnace is used to heat the reactor tube. Helium is introduced into the
11 reactor tube at 10 cc/min. and at atmospheric pressure. The reactor is heated to about
12 315°C, and a 50/50 feed of n-hexane and 3-methylpentane is introduced into the
13 reactor at a rate of 8 µl/min. The feed is delivered by a Brownlee pump. Direct
14 sampling into a GC begins after 10 minutes of feed introduction. The Constraint
15 Index (CI) value is calculated from the GC data using methods known in the art.
16 SSZ-65 has a CI of 0.67 and a conversion of 92% after 20 minutes on stream. The
17 material fouls rapidly and at 218 minutes the CI is 0.3 and the conversion is 15.7%.
18 The data suggests a large pore molecular sieve with perhaps large cavities.

19 Example 21

20 Hydrocracking of n-Hexadecane

21 A 1 gm sample of SSZ-65 (prepared as in Example 3 and treated as in
22 Examples 16, 17 and 18) is suspended in 10 gm de-ionized water. To this suspension,
23 a solution of $\text{Pd}(\text{NH}_3)_4(\text{NO}_3)_2$ at a concentration which would provide 0.5 wt. % Pd
24 with respect to the dry weight of the molecular sieve sample is added. The pH of the
25 solution is adjusted to pH of ~9 by a drop-wise addition of dilute ammonium
26 hydroxide solution. The mixture is then heated in an oven at 75°C for 48 hours. The
27 mixture is then filtered through a glass frit, washed with de-ionized water, and air-
28 dried. The collected Pd-SSZ-65 sample is slowly calcined up to 482°C in air and held
29 there for three hours.

30 The calcined Pd/SSZ-65 catalyst is pelletized in a Carver Press and granulated
31 to yield particles with a 20/40 mesh size. Sized catalyst (0.5 g) is packed into a ¼
32 inch OD tubing reactor in a micro unit for n-hexadecane hydroconversion. The table

1 below gives the run conditions and the products data for the hydrocracking test on n-
2 hexadecane.

3 After the catalyst is tested with n-hexadecane, it is titrated using a solution of
4 butylamine in hexane. The temperature is increased and the conversion and product
5 data evaluated again under titrated conditions. The results shown in the table below
6 show that SSZ-65 is effective as a hydrocracking catalyst.

7

Temperature	260°C (550°F)
Time-on-Stream (hrs.)	342.4-343.4
WHSV	1.55
PSIG	1200
Titrated?	Yes
n-16, % Conversion	96.9
Hydrocracking Conv.	47.9
Isomerization Selectivity, %	50.5
Cracking Selectivity, %	49.5
C ₄ -, %	2.7
C ₅ /C ₄	16.9
C ₅ +C ₆ /C ₅ , %	16.74
DMB/MP	0.06
C ₄ -C ₁₃ i/n	3.83
C ₇ -C ₁₃ yield	38.35

8

9

Example 22

10

Synthesis of SSZ-65

11

12

SSZ-65 is synthesized in a manner similar to that of Example 3 using a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium cation as the SDA.

1 WHAT IS CLAIMED IS:

2

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

8

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

15

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

18

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

21

22 5. A molecular sieve according to Claim 2 wherein the oxide comprises silicon
23 oxide.

24

25 6. A molecular sieve according to Claim 1 wherein said molecular sieve is
26 predominantly in the hydrogen form.

27

28 7. A molecular sieve according to Claim 1 wherein said molecular sieve is
29 substantially free of acidity.

30

31 8. A molecular sieve according to Claim 2 wherein said molecular sieve is
32 predominantly in the hydrogen form.

- 1
- 2 9. A molecular sieve according to Claim 2 wherein said molecular sieve is
- 3 substantially free of acidity.
- 4
- 5 10. A process for converting hydrocarbons comprising contacting a
- 6 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
- 7 comprising a molecular sieve having a mole ratio greater than about 15 of (1) an
- 8 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
- 9 pentavalent element, second tetravalent element which is different from said
- 10 first tetravalent element or mixture thereof and having, after calcination, the
- 11 X-ray diffraction lines of Table II.
- 12
- 13 11. The process of Claim 10 wherein the molecular sieve is substantially free of
- 14 acidity.
- 15
- 16 12. The process of Claim 10 wherein the process is a hydrocracking process
- 17 comprising contacting the catalyst with a hydrocarbon feedstock under
- 18 hydrocracking conditions.
- 19
- 20 13. The process of Claim 10 wherein the process is a dewaxing process comprising
- 21 contacting the catalyst with a hydrocarbon feedstock under dewaxing
- 22 conditions.
- 23
- 24 14. The process of Claim 10 wherein the process is a process for improving the
- 25 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising
- 26 contacting the catalyst with a waxy hydrocarbon feed under isomerization
- 27 dewaxing conditions.
- 28
- 29 15. The process of Claim 10 wherein the process is a process for producing a C₂₀₊
- 30 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under
- 31 isomerization conditions over the catalyst.
- 32

- 1 16. The process of Claim 15 wherein the catalyst further comprises at least one
2 Group VIII metal.
3
- 4 17. The process of Claim 10 wherein the process is a process for catalytically
5 dewaxing a hydrocarbon oil feedstock boiling above about 350°F (177°C) and
6 containing straight chain and slightly branched chain hydrocarbons comprising
7 contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas
8 at a hydrogen pressure of about 15-3000 psi (0.103-20.7 MPa) under dewaxing
9 conditions with the catalyst.
10
- 11 18. The process of Claim 17 wherein the catalyst further comprises at least one
12 Group VIII metal.
13
- 14 19. The process of Claim 17 wherein said catalyst comprises a layered catalyst
15 comprising a first layer comprising the molecular sieve and at least one Group
16 VIII metal, and a second layer comprising an aluminosilicate molecular sieve
17 which is more shape selective than the molecular sieve of said first layer.
18
- 19 20. The process of Claim 10 wherein the process is a process for preparing a
20 lubricating oil which comprises:
21
- 22 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain
23 an effluent comprising a hydrocracked oil; and
24
- 25 catalytically dewaxing said effluent comprising hydrocracked oil at a
26 temperature of at least about 400°F (204°C) and at a pressure of from about
27 15 psig to about 3000 psig (0.103 to 20.7 MPa gauge) in the presence of added
28 hydrogen gas with the catalyst.
29
- 30 21. The process of Claim 20 wherein the catalyst further comprises at least one
31 Group VIII metal.
32

- 1 22. The process of Claim 10 wherein the process is a process for isomerization
2 dewaxing a raffinate comprising contacting said raffinate in the presence of
3 added hydrogen under isomerization dewaxing conditions with the catalyst.
4
- 5 23. The process of Claim 22 wherein the catalyst further comprises at least one
6 Group VIII metal.
7
- 8 24. The process of Claim 22 wherein the raffinate is bright stock.
9
- 10 25. The process of Claim 10 wherein the process is a process for increasing the
11 octane of a hydrocarbon feedstock to produce a product having an increased
12 aromatics content comprising contacting a hydrocarbonaceous feedstock which
13 comprises normal and slightly branched hydrocarbons having a boiling range
14 above about 40°C and less than about 200°C under aromatic conversion
15 conditions with the catalyst.
16
- 17 26. The process of Claim 25 wherein the molecular sieve is substantially free of
18 acid.
19
- 20 27. The process of Claim 25 wherein the molecular sieve contains a Group VIII
21 metal component.
22
- 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 catalyst.
26
- 27 29. The process of Claim 28 wherein the catalyst additionally comprises a large
28 pore crystalline cracking component.
29
- 30 30. The process of Claim 10 wherein the process is an isomerization process for
31 isomerizing C₄ to C₇ hydrocarbons, comprising contacting a feed having normal

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

- 1 40. The process of Claim 38 wherein the aromatic hydrocarbon is selected from the
2 group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.
3
- 4 41. The process of Claim 38 wherein the polyalkyl aromatic hydrocarbon is a
5 dialkylbenzene.
6
- 7 42. The process of Claim 10 wherein the process is a process to convert paraffins to
8 aromatics which comprises contacting paraffins under conditions which cause
9 paraffins to convert to aromatics with a catalyst comprising the molecular sieve
10 and gallium, zinc, or a compound of gallium or zinc.
11
- 12 43. The process of Claim 10 wherein the process is a process for isomerizing olefins
13 comprising contacting said olefin under conditions which cause isomerization of
14 the olefin with the catalyst.
15
- 16 44. 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
- 23 45. The process of Claim 10 wherein the process is a process for oligomerizing
24 olefins comprising contacting an olefin feed under oligomerization conditions
25 with the catalyst.
26
- 27 46. The process of Claim 10 wherein the process is a process for the production of
28 higher molecular weight hydrocarbons from lower molecular weight
29 hydrocarbons comprising the steps of:
30
- 31 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-
32 containing gas and contacting said gas in said zone under C₂₊ hydrocarbon
33 synthesis conditions with the catalyst and a metal or metal compound capable of

- 1 converting the lower molecular weight hydrocarbon to a higher molecular
2 weight hydrocarbon; and
3
- 4 (b) withdrawing from said reaction zone a higher molecular weight
5 hydrocarbon-containing stream.
6
- 7 47. The process of Claim 46 wherein the metal or metal compound comprises a
8 lanthanide or actinide metal or metal compound.
9
- 10 48. The process of Claim 46 wherein the lower molecular weight hydrocarbon is
11 methane.
12
- 13 49. The process of Claim 10, 12, 13, 14, 15, 17, 20, 22, 28, 30, 34 or 38 wherein the
14 molecular sieve is predominantly in the hydrogen form.
15
- 16 50. A process for converting oxygenated hydrocarbons comprising contacting said
17 oxygenated hydrocarbon under conditions to produce liquid products with a
18 catalyst comprising a molecular sieve having a mole ratio greater than about 15
19 of an oxide of a first tetravalent element to an oxide of a second tetravalent
20 element which is different from said first tetravalent element, trivalent element,
21 pentavalent element or mixture thereof and having, after calcination, the X-ray
22 diffraction lines of Table II.
23
- 24 51. The process of Claim 50 wherein the oxygenated hydrocarbon is a lower
25 alcohol.
26
- 27 52. The process of Claim 51 wherein the lower alcohol is methanol.
28
- 29 53. A process for the reduction of oxides of nitrogen contained in a gas stream in the
30 presence of oxygen wherein said process comprises contacting the gas stream
31 with a molecular sieve having a mole ratio greater than about 15 of (1) an oxide
32 of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent

- 1 element, second tetravalent element which is different from said first tetravalent
2 element or mixture thereof and having, after calcination, the X-ray diffraction
3 lines of Table II
4
- 5 54. The process of Claim 53 wherein said molecular sieve contains a metal or metal
6 ions capable of catalyzing the reduction of the oxides of nitrogen.
7
- 8 55. The process of Claim 54 wherein the metal is copper, cobalt, platinum, iron,
9 chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures
10 thereof.
11
- 12 56. The process of Claim 54 wherein the gas stream is the exhaust stream of an
13 internal combustion engine.