

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

Disclosed herein is 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

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

In a first aspect, there is provided a molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, in its as-synthesized state, the X-ray diffraction lines of Table I.

In a second aspect, there is provided a molecular sieve having a mole ratio greater than about 15 of (1) an oxide selected from the group consisting of silicon oxide, germanium oxide and mixtures thereof to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide, vanadium oxide and mixtures thereof, and having, in its as-synthesized state, the X-ray diffraction lines of Table I.

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

$$\begin{array}{ll} \text{YO}_2/\text{W}_c\text{O}_d & 15 - \infty \\ \text{M}_{2n}/\text{YO}_2 & 0.01 - 0.03 \\ \text{Q}/\text{YO}_2 & 0.02 - 0.05 \end{array}$$

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 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. It should be noted that the mole ratio of YO_2 to W_cO_d can be infinity, i.e., there is no second oxide in the molecular sieve. In these cases, the molecular sieve is an all-silica molecular sieve or a germanosilicate.

Disclosed herein is a molecular sieve prepared by thermally treating a molecular sieve having a mole ratio of an oxide selected from silicon oxide, germanium oxide and mixtures thereof to an oxide

selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide, vanadium oxide and mixtures thereof greater than about 15 at a temperature of from about 200°C to about 800°C, the thus-prepared molecular sieve having, prior to thermal treatment, the X-ray diffraction lines of Table I. The disclosure also includes this thus-prepared molecular sieve which is predominantly in the hydrogen form, which hydrogen form is prepared by ion exchanging with an acid or with a solution of an ammonium salt followed by a second calcination. If the molecular sieve is synthesized with a high enough ratio of SDA cation to sodium ion, calcination alone may be sufficient. 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. As used herein, "predominantly in the hydrogen form" means that, after calcination, at least 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

In a fourth aspect, there is provided a method of preparing a crystalline material comprising (1) an oxide of a first tetravalent element and (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element, or mixture thereof and having a mole ratio of the first oxide to the second oxide greater than 15, said method comprising contacting under crystallization conditions sources of said oxides and a structure directing agent comprising a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation.

In a fifth aspect, there is provided a process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst comprising the molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, in its as-synthesized state, the X-ray diffraction lines of Table I.. The molecular sieve may be predominantly in the hydrogen form. It may also be substantially free of acidity.

Further disclosed herein is a hydrocracking process comprising contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst comprising the molecular sieve of this invention, preferably predominantly in the hydrogen form.

1 Disclosed herein is a dewaxing process comprising contacting a
2 hydrocarbon feedstock under dewaxing conditions with a catalyst comprising the
3 molecular sieve of this invention, preferably predominantly in the hydrogen form.

4 Disclosed herein is a process for improving the viscosity
5 index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the
6 waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst
7 comprising the molecular sieve of this invention, preferably predominantly in the
8 hydrogen form.

9 Further disclosed herein is a process for producing a C₂₀₊ lube oil
10 from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization
11 conditions over a catalyst comprising the molecular sieve of this invention. The
12 molecular sieve may be predominantly in the hydrogen form. The catalyst may
13 contain at least one Group VIII metal.

14 Disclosed herein is a process for
15 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F
16 (177°C) and containing straight chain and slightly branched chain hydrocarbons
17 comprising contacting said hydrocarbon oil feedstock in the presence of added
18 hydrogen gas at a hydrogen pressure of about 15-3000 psi (0.103 – 20.7 MPa) with a
19 catalyst comprising the molecular sieve of this invention, preferably predominantly in
20 the hydrogen form. The catalyst may contain at least one Group VIII metal. The
21 catalyst may be a layered catalyst comprising a first layer comprising the molecular
22 sieve of this invention, and a second layer comprising an aluminosilicate molecular
23 sieve which is more shape selective than the molecular sieve of said first layer. The
24 first layer may contain at least one Group VIII metal.

25 Also disclosed herein is a process for preparing a lubricating
26 oil which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous
27 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
28 dewaxing said effluent comprising hydrocracked oil at a temperature of at least about
29 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig (0.103 –
30 20.7 MPa gauge) in the presence of added hydrogen gas with a catalyst comprising the
31 molecular sieve of this invention. The molecular sieve may be predominantly in the
32 hydrogen form. The catalyst may contain at least one Group VIII metal.

1 Further disclosed herein is a process for isomerization dewaxing a
2 raffinate comprising contacting said raffinate in the presence of added hydrogen with
3 a catalyst comprising the molecular sieve of this invention. The raffinate may be
4 bright stock, and the molecular sieve may be predominantly in the hydrogen form.
5 The catalyst may contain at least one Group VIII metal.

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

14 Also disclosed herein is a catalytic cracking process
15 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic
16 cracking conditions in the absence of added hydrogen with a catalyst comprising the
17 molecular sieve of this invention, preferably predominantly in the hydrogen form.
18 Also included in this invention is such a catalytic cracking process wherein the
19 catalyst additionally comprises a large pore crystalline cracking component.

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

27 Also disclosed herein is a process for alkylating an aromatic
28 hydrocarbon which comprises contacting under alkylation conditions at least a molar
29 excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid
30 phase conditions and in the presence of a catalyst comprising the molecular sieve of
31 this invention, preferably predominantly in the hydrogen form. The olefin may be a
32 C₂ to C₄ olefin, and the aromatic hydrocarbon and olefin may be present in a molar

1 ratio of about 4:1 to about 20:1, respectively. The aromatic hydrocarbon may be
2 selected from the group consisting of benzene, toluene, ethylbenzene, xylene,
3 naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

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

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

15 Further disclosed herein is a process to convert paraffins to
16 aromatics which comprises contacting paraffins under conditions which cause
17 paraffins to convert to aromatics with a catalyst comprising the molecular sieve of this
18 invention, said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

19
20 Disclosed herein is a process for
21 isomerizing olefins comprising contacting said olefin under conditions which cause
22 isomerization of the olefin with a catalyst comprising the disclosed molecular sieve.

23
24 Further disclosed herein is a process for isomerizing an isomerization feed comprising
25 an aromatic C₈ stream of xylene isomers or mixtures of xylene isomers and ethylbenzene,
26 wherein a more nearly equilibrium ratio of ortho-, meta- and para- xylenes is obtained, said
27 process comprising contacting said feed under isomerization conditions with a catalyst
28 comprising the disclosed molecular sieve.

29 Disclosed herein is a process for oligomerizing olefins comprising contacting an olefin
30 feed under oligomerization conditions with a catalyst comprising the disclosed molecular
31 sieve.

In a sixth aspect, there is provided a process for converting oxygenated hydrocarbons comprising contacting said oxygenated hydrocarbon under conditions to produce liquid products with a catalyst comprising a molecular sieve having a mole ratio greater than about 15 of an oxide of a first tetravalent element to an oxide of a second tetravalent element which is different from said first tetravalent element, trivalent element, pentavalent element or mixture thereof and having, in its as-synthesized state, the X-ray diffraction lines of Table I. The oxygenated hydrocarbon may be a lower alcohol.

Further disclosed herein is a process for the production of higher molecular weight hydrocarbons from lower molecular weight hydrocarbons comprising the steps of:

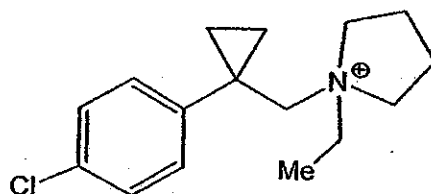
- (a) introducing into a reaction zone a lower molecular weight hydrocarbon-containing gas and contacting said gas in said zone under C_{2+} hydrocarbon synthesis conditions with the catalyst and a metal or metal compound capable of converting the lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon; and
- (b) withdrawing from said reaction zone a higher molecular weight hydrocarbon-containing stream.

In a seventh aspect, there is provided a process for the reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process comprises contacting the gas stream with a molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a second tetravalent element different from said first tetravalent element, trivalent element, pentavalent element or mixture thereof and having, in its as-synthesized state, the X-ray diffraction lines of Table I. The molecular sieve may contain a metal or metal ions (such as cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof) capable of catalyzing the reduction of the oxides of nitrogen, and the process may be conducted in the presence of a stoichiometric excess of oxygen. In a preferred embodiment, the gas stream is the exhaust stream of an internal combustion engine.

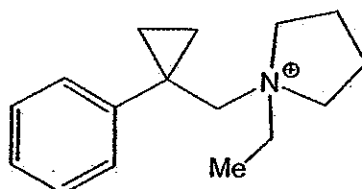
DETAILED DESCRIPTION OF THE INVENTION

The present invention comprises a family of crystalline, large pore molecular 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
4	$\text{YO}_2/\text{W}_a\text{O}_b$	> 15	30 - 70
5	OH/YO_2	0.10 - 0.50	0.20 - 0.30
6	Q/YO_2	0.05 - 0.50	0.10 - 0.20
7	$\text{M}_{2/n}/\text{YO}_2$	0.02 - 0.40	0.10 - 0.25
8	$\text{H}_2\text{O}/\text{YO}_2$	30 - 80	35 - 45

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

In practice, SSZ-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 element, pentavalent element and second tetravalent element (which is different from the first tetravalent element) is preferably selected from the group consisting of aluminum, gallium, iron, boron, titanium, indium, vanadium and combinations

1 thereof. More preferably, the second trivalent or tetravalent element is aluminum or
2 boron.

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

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

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

27 The reaction mixture is maintained at an elevated temperature until the
28 crystals of the SSZ-65 are formed. The hydrothermal crystallization is usually
29 conducted under autogenous pressure, at a temperature between 100°C and 200°C ,
30 preferably between 135°C and 160°C . The crystallization period is typically greater
31 than 1 day and preferably from about 3 days to about 20 days.

32 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, in its as-synthesized state, the X-ray diffraction lines of Table I 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_{2n}/YO_2	$0.01 - 0.03$
Q/YO_2	$0.02 - 0.05$

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

SSZ-65 can be made with a mole ratio of YO_2/W_cO_d of ∞ , i.e., there is essentially no W_cO_d present in the SSZ-65. In this case, the SSZ-65 would be an all-silica material or a germanosilicate. Thus, in a typical case where oxides of silicon and aluminum are used, SSZ-65 can be made essentially aluminum free, i.e., having a silica to alumina mole ratio of ∞ . A method of increasing the mole ratio of silica to alumina is by using standard acid leaching or chelating treatments. However,

essentially aluminum-free SSZ-65 can be synthesized using essentially aluminum-free silicon sources as the main tetrahedral metal oxide component, if boron is also present. The boron can then be removed, if desired, by treating the borosilicate SSZ-65 with acetic acid at elevated temperature (as described in Jones et al., *Chem. Mater.*, 2001, 13, 1041-1050) to produce an all-silica version of SSZ-65. SSZ-65 can also be prepared directly as a borosilicate. If desired, the boron can be removed as described above and replaced with metal atoms by techniques known in the art to make, e.g., an aluminosilicate version of SSZ-65. SSZ-65 can also be prepared directly as an aluminosilicate.

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

It is believed that SSZ-65 is comprised of a new framework structure or topology which is characterized by its X-ray diffraction pattern. SSZ-65, as-synthesized (i.e., prior to removal of the SDA), has a crystalline structure whose X-ray powder diffraction pattern exhibit the characteristic lines shown in Table I and is thereby distinguished from 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.

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

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

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

7
8 Calcination can result in changes in the intensities of the
9 peaks as compared to patterns of the "as-made" material, as well as minor shifts in the
10 diffraction pattern. The molecular sieve produced by exchanging the metal or other
11 cations present in the molecular sieve with various other cations (such as H^+ or NH_4^+)
12 yields essentially the same diffraction pattern, although again, there may be minor
13 shifts in the interplanar spacing and variations in the relative intensities of the peaks.
14 Notwithstanding these minor perturbations, the basic crystal lattice remains
15 unchanged by these treatments.

16 Crystalline SSZ-65 can be used as-synthesized, but preferably will be
17 thermally treated (calcined). Usually, it is desirable to remove the alkali metal cation
18 by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion.
19 The molecular sieve can be leached with chelating agents, e.g., EDTA or dilute acid
20 solutions, to increase the silica to alumina mole ratio. The molecular sieve can also
21 be steamed; steaming helps stabilize the crystalline lattice to attack from acids.

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

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

1 replacing metallic cations, cations of metals such as rare earth, Mn, Ca, Mg, Zn, Cd,
2 Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are particularly preferred.

3 The hydrogen, ammonium, and metal components can be ion-exchanged into
4 the SSZ-65. The SSZ-65 can also be impregnated with the metals, or the metals can
5 be physically and intimately admixed with the SSZ-65 using standard methods known
6 to the art.

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

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

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

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

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

9 SSZ-65 molecular sieves are useful in hydrocarbon conversion reactions.
10 Hydrocarbon conversion reactions are chemical and catalytic processes in which
11 carbon containing compounds are changed to different carbon containing compounds.
12 Examples of hydrocarbon conversion reactions in which SSZ-65 are expected to be
13 useful include hydrocracking, dewaxing, catalytic cracking and olefin and aromatics
14 formation reactions. The catalysts are also expected to be useful in other petroleum
15 refining and hydrocarbon conversion reactions such as isomerizing n-paraffins and
16 naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds such as
17 isobutylene and butene-1, reforming, isomerizing polyalkyl substituted aromatics
18 (e.g., m-xylene), and disproportionating aromatics (e.g., toluene) to provide mixtures
19 of benzene, xylenes and higher methylbenzenes and oxidation reactions. Also
20 included are rearrangement reactions to make various naphthalene derivatives, and
21 forming higher molecular weight hydrocarbons from lower molecular weight
22 hydrocarbons (e.g., methane upgrading).

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

25 For high catalytic activity, the SSZ-65 molecular sieve should be
26 predominantly in its hydrogen ion form. Generally, the molecular sieve is converted
27 to its hydrogen form by ammonium exchange followed by calcination. If the
28 molecular sieve is synthesized with a high enough ratio of SDA cation to sodium ion,
29 calcination alone may be sufficient. It is preferred that, after calcination, at least 80%
30 of the cation sites are occupied by hydrogen ions and/or rare earth ions. As used
31 herein, "predominantly in the hydrogen form" means that, after calcination, at least
32 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

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

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

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

19 The following table indicates typical reaction conditions which may be
 20 employed when using catalysts comprising SSZ-65 in the hydrocarbon conversion
 21 reactions of this invention. Preferred conditions are indicated in parentheses.
 22

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

1

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

2

3 ¹ Several hundred atmospheres4 ² Gas phase reaction5 ³ Hydrocarbon partial pressure6 ⁴ Liquid phase reaction7 ⁵ WHSV

8 Other reaction conditions and parameters are provided below.

9

Hydrocracking

10 Using a catalyst which comprises SSZ-65, preferably predominantly in the
 11 hydrogen form, and a hydrogenation promoter, heavy petroleum residual feedstocks,
 12 cyclic stocks and other hydrocrackate charge stocks can be hydrocracked using the
 13 process conditions and catalyst components disclosed in the aforementioned U.S.
 14 Patent No. 4,910,006 and U.S. Patent No. 5,316,753.

15 The hydrocracking catalysts contain an effective amount of at least one
 16 hydrogenation component of the type commonly employed in hydrocracking
 17 catalysts. The hydrogenation component is generally selected from the group of
 18 hydrogenation catalysts consisting of one or more metals of Group VIB and
 19 Group VIII, including the salts, complexes and solutions containing such. The
 20 hydrogenation catalyst is preferably selected from the group of metals, salts and
 21 complexes thereof of the group consisting of at least one of platinum, palladium,
 22 rhodium, iridium, ruthenium and mixtures thereof or the group consisting of at least
 23 one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and mixtures
 24 thereof. Reference to the catalytically active metal or metals is intended to encompass
 25 such metal or metals in the elemental state or in some form such as an oxide, sulfide,

1 halide, carboxylate and the like. The hydrogenation catalyst is present in an effective
2 amount to provide the hydrogenation function of the hydrocracking catalyst, and
3 preferably in the range of from 0.05 to 25% by weight.

4 Dewaxing

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

10 The catalytic dewaxing conditions are dependent in large measure on the feed
11 used and upon the desired pour point. Hydrogen is preferably present in the reaction
12 zone during the catalytic dewaxing process. The hydrogen to feed ratio is typically
13 between about 500 and about 30,000 SCF/bbl (standard cubic feet per barrel) (0.089
14 to 5.34 SCM/liter (standard cubic meters/liter)), preferably about 1000 to about
15 20,000 SCF/bbl (0.178 to 3.56 SCM/liter). Generally, hydrogen will be separated
16 from the product and recycled to the reaction zone. Typical feedstocks include light
17 gas oil, heavy gas oils and reduced crudes boiling above about 350°F (177°C).

18 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil
19 feedstock boiling above about 350°F (177°C) and containing straight chain and
20 slightly branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in
21 the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi
22 (0.103-20.7 MPa) with a catalyst comprising SSZ-65 and at least one Group VIII
23 metal.

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

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

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

5 SSZ-65 may also be utilized as a dewaxing catalyst in the form of a layered
6 catalyst. That is, the catalyst comprises a first layer comprising molecular sieve SSZ-
7 65 and at least one Group VIII metal, and a second layer comprising an
8 aluminosilicate molecular sieve which is more shape selective than molecular sieve
9 SSZ-65. The use of layered catalysts is disclosed in U.S. Patent No. 5,149,421, issued
10 September 22, 1992 to Miller, which is incorporated by reference herein in its
11 entirety. The layering may also include a bed of SSZ-65 layered with a non-zeolitic
12 component designed for either hydrocracking or hydrofinishing.

13 SSZ-65 may also be used to dewax raffinates, including bright stock, under
14 conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1,
15 1980 to Gillespie et al., which is incorporated by reference herein in its entirety.

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

30 Lube oil may be prepared using SSZ-65. For example, a C₂₀₊ lube oil may be
31 made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising SSZ-65 in the
32 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil

1 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous
2 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
3 dewaxing the effluent at a temperature of at least about 400°F (204°C) and at a
4 pressure of from about 15 psig to about 3000 psig (0.103-20.7 MPa gauge) in the
5 presence of added hydrogen gas with a catalyst comprising SSZ-65 in the hydrogen
6 form and at least one Group VIII metal.

7 Aromatics Formation

8 SSZ-65 can be used to convert light straight run naphthas and similar mixtures
9 to highly aromatic mixtures. Thus, normal and slightly branched chained
10 hydrocarbons, preferably having a boiling range above about 40°C and less than about
11 200°C, can be converted to products having a substantial higher octane aromatics
12 content by contacting the hydrocarbon feed with a catalyst comprising SSZ-65. It is
13 also possible to convert heavier feeds into BTX or naphthalene derivatives of value
14 using a catalyst comprising SSZ-65.

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

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

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

Catalytic Cracking

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

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

The cracking catalysts are typically employed with an inorganic oxide matrix component. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent 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.

1 For high catalytic activity, the SSZ-65 molecular sieve should be
2 predominantly in its hydrogen ion form. It is preferred that, after calcination, at least
3 80% of the cation sites are occupied by hydrogen ions and/or rare earth ions.

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

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

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

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

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

Conversion of Paraffins to Aromatics

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

Isomerization of Olefins

SSZ-65 can be used to isomerize olefins. The feed stream is a hydrocarbon stream containing at least one C₄₋₆ olefin, preferably a C₄₋₆ normal olefin, more preferably normal butene. Normal butene as used in this specification means all forms of normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons other than normal butene or other C₄₋₆ normal olefins will be present in the feed stream. These other hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and inert gases.

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

The process is carried out under isomerization conditions. The hydrocarbon feed is contacted in a vapor phase with a catalyst comprising the SSZ-65. The

1 process may be carried out generally at a temperature from about 625°F to about
2 950°F (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-
3 482°C), and about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The
4 pressure ranges from subatmospheric to about 200 psig (1.38 MPa gauge), preferably
5 from about 15 psig to about 200 psig (0.103 to 1.38 MPa gauge), and more preferably
6 from about 1 psig to about 150 psig (0.00689 to 1.03 MPa gauge).

7 The liquid hourly space velocity during contacting is generally from about 0.1
8 to about 50 hr⁻¹, based on the hydrocarbon feed, preferably from about 0.1 to about
9 20 hr⁻¹, more preferably from about 0.2 to about 10 hr⁻¹, most preferably from about 1
10 to about 5 hr⁻¹. A hydrogen/hydrocarbon molar ratio is maintained from about 0 to
11 about 30 or higher. The hydrogen can be added directly to the feed stream or directly
12 to the isomerization zone. The reaction is preferably substantially free of water,
13 typically less than about two weight percent based on the feed. The process can be
14 carried out in a packed bed reactor, a fixed bed, fluidized bed reactor, or a moving bed
15 reactor. The bed of the catalyst can move upward or downward. The mole percent
16 conversion of, e.g., normal butene to iso-butene is at least 10, preferably at least 25,
17 and more preferably at least 35.

18 Xylene Isomerization

19 SSZ-65 may also be useful in a process for isomerizing one or more xylene
20 isomers in a C₈ aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio
21 approaching the equilibrium value. In particular, xylene isomerization is used in
22 conjunction with a separate process to manufacture para-xylene. For example, a
23 portion of the para-xylene in a mixed C₈ aromatics stream may be recovered by
24 crystallization and centrifugation. The mother liquor from the crystallizer is then
25 reacted under xylene isomerization conditions to restore ortho-, meta- and
26 para-xylenes to a near equilibrium ratio. At the same time, part of the ethylbenzene in
27 the mother liquor is converted to xylenes or to products which are easily separated by
28 filtration. The isomerate is blended with fresh feed and the combined stream is
29 distilled to remove heavy and light by-products. The resultant C₈ aromatics stream is
30 then sent to the crystallizer to repeat the cycle.

31 Optionally, isomerization in the vapor phase is conducted in the presence of
32 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene). If

1 hydrogen is used, the catalyst should comprise about 0.1 to 2.0 wt.% of a
2 hydrogenation/dehydrogenation component selected from Group VIII (of the Periodic
3 Table) metal component, especially platinum or nickel. By Group VIII metal
4 component is meant the metals and their compounds such as oxides and sulfides.

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

7 Oligomerization

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

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

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

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

31 Condensation of Alcohols

32 SSZ-65 can be used to condense lower aliphatic alcohols having 1 to
33 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed

aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent No. 3,894,107, issued July 8, 1975 to Butter et al., describes the process conditions used in this process, which patent is incorporated totally herein by reference.

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

Methane Upgrading

Higher molecular weight hydrocarbons can be formed from lower molecular weight hydrocarbons by contacting the lower molecular weight hydrocarbon with a catalyst comprising SSZ-65 and a metal or metal compound capable of converting the lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon. Examples of such reactions include the conversion of methane to C₂₊ hydrocarbons such as ethylene or benzene or both. Examples of useful metals and metal compounds include lanthanide and or actinide metals or metal compounds.

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

Reduction of Oxides of Nitrogen in a Gas Stream

SSZ-65 may be used for the catalytic reduction of the oxides of nitrogen in a gas stream. Typically, the gas stream also contains oxygen, often a stoichiometric excess thereof. Also, the SSZ-65 may contain a metal or metal ions within or on it which are capable of catalyzing the reduction of the nitrogen oxides. Examples of

such metals or metal ions include copper, cobalt, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium and mixtures thereof.

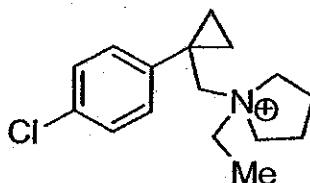
One example of such a process for the catalytic reduction of oxides of nitrogen in the presence of a molecular sieve is disclosed in U.S. Patent No. 4,297,328, issued October 27, 1981 to Ritscher et al., which is incorporated by reference herein. There, the catalytic process is the combustion of carbon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

EXAMPLES

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

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.

1 Then, 39 gm (0.25 mol.) of ethyl iodide is added and the mixture is heated at reflux
2 for 3 hours. The reaction mixture is cooled down and excess ethyl iodide and the
3 solvent are removed at reduced pressure on a rotary evaporator. The obtained dark
4 tan-colored solids (162 gm) are further purified by dissolving in acetone (500 ml)
5 followed by precipitation by adding diethyl ether. Filtration and air-drying the
6 obtained solids gives 153 gm (93% yield) of the desired 1-[1-(4-chloro-phenyl)-
7 cyclopropylmethyl]-1-ethyl-pyrrolidinium iodide as a white powder. The product is
8 pure by ^1H and ^{13}C -NMR analysis.

9 The hydroxide form of 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-
10 pyrrolidinium cation is obtained by an ion exchange treatment of the iodide salt with
11 Ion-Exchange Resin-OH (BIO RAD[®] AH1-X8). In a 1-liter volume plastic bottle,
12 100 gm (255 mmol) of 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-
13 pyrrolidinium iodide is dissolved in 300 ml de-ionized water. Then, 320 gm of the
14 ion exchange resin is added and the solution is allowed to gently stir overnight. The
15 mixture is then filtered, and the resin cake is rinsed with minimal amount of de-
16 ionized water. The filtrate is analyzed for hydroxide concentration by titration
17 analysis on a small sample of the solution with 0.1N HCl. The reaction yields 96% of
18 (245 mmol) of the desired 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-1-ethyl-
19 pyrrolidinium hydroxide (hydroxide concentration of 0.6 M).

20 The parent amine 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine is
21 obtained from the LiAlH_4 -reduction of the precursor amide [1-(4-chloro-phenyl)-
22 cyclopropyl]-pyrrolidin-1-yl-methanone. In a 3-neck 3-liter reaction flask equipped
23 with a mechanical stirrer and reflux condenser, 45.5 gm (1.2 mol.) of LiAlH_4 is
24 suspended in 750 ml anhydrous tetrahydrofuran (THF). The suspension is cooled
25 down to 0°C (ice-bath), and 120 gm (0.48 mole) of [1-(4-chloro-phenyl)-
26 cyclopropyl]-pyrrolidin-1-yl-methanone dissolved in 250 ml THF is added (to the
27 suspension) drop-wise via an addition funnel. Once all the amide solution is added,
28 the ice-bath is replaced with a heating mantle and the reaction mixture is heated at
29 reflux overnight. Then, the reaction solution is cooled down to 0°C (the heating
30 mantle was replaced with an ice-bath), and the mixture is diluted with 500 ml diethyl
31 ether. The reaction is worked up by adding 160 ml of 15% wt. of an aqueous NaOH
32 solution drop-wise (via an addition funnel) with vigorous stirring. The starting gray

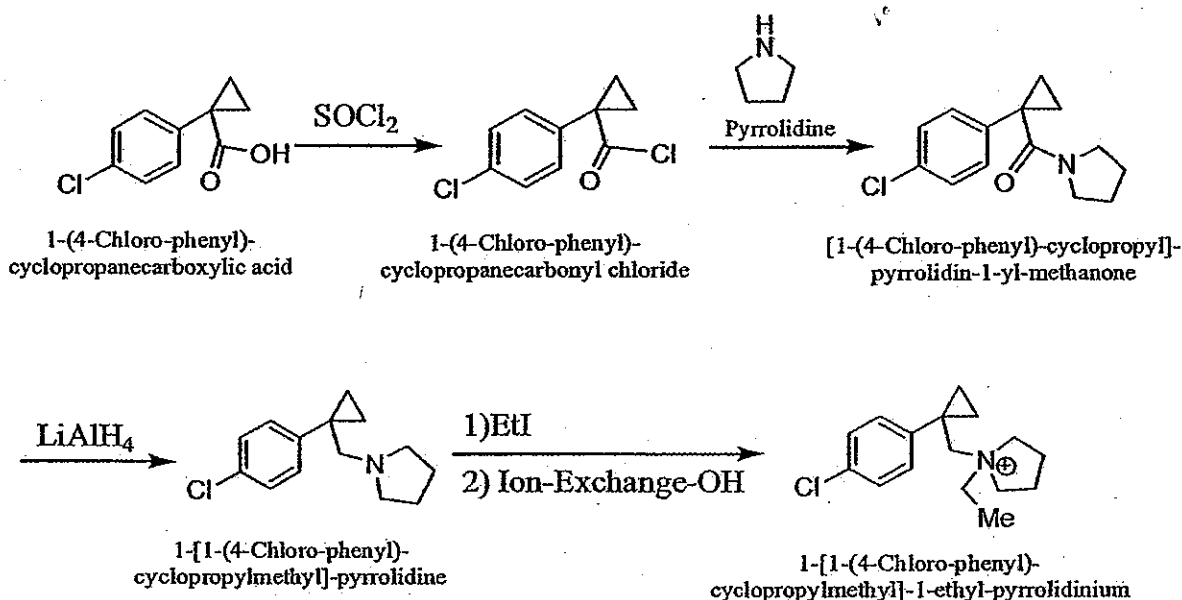
1 reaction solution changes to a colorless liquid with a white powdery precipitate. The
2 solution mixture is filtered and the filtrate is dried over anhydrous magnesium sulfate.
3 Filtration and concentration of the filtrate gives 106 gm (94% yield) of the desired
4 amine 1-[1-(4-chloro-phenyl)-cyclopropylmethyl]-pyrrolidine as a pale yellow oily
5 substance. The amine is pure as indicated by the clean ^1H and ^{13}C -NMR spectral
6 analysis.

7 The parent amide [1-(4-chloro-phenyl)-cyclopropyl]-pyrrolidin-1-yl-
8 methanone is prepared by reacting pyrrolidine with 1-(4-chloro-phenyl)-
9 cyclopropanecarbonyl chloride. A 2-Liter reaction flask equipped with a mechanical
10 stirrer is charged with 1000 ml of dry benzene, 53.5 gm (0.75 mol.) of pyrrolidine and
11 76 gm (0.75 mol.) of triethyl amine. To this mixture (at 0°C), 108 1-(4-chloro-
12 phenyl)-cyclopropanecarbonyl chloride gm (0.502 mol.) of (dissolved 100 ml
13 benzene) is added drop-wise (via an addition funnel). Once the addition is completed,
14 the resulting mixture is allowed to stir at room temperature overnight. The reaction
15 mixture (a biphasic mixture: liquid and tan-colored precipitate) is concentrated on a
16 rotary evaporator at reduced pressure to strip off excess pyrrolidine and the solvent
17 (usually hexane or benzene). The remaining residue is diluted with 750 ml water and
18 extracted with 750 ml chloroform in a separatory funnel. The organic layer is washed
19 twice with 500 ml water and once with brine. Then, the organic layer is dried over
20 anhydrous sodium sulfate, filtered and concentrated on a rotary evaporator at reduced
21 pressure to give 122 gm (0.49 mol, 97% yield) of the amide as a tan-colored solid
22 substance.

23 The 1-(4-chloro-phenyl)-cyclopropanecarbonyl chloride used in the synthesis
24 of the amide is synthesized by treatment of the parent acid 1-(4-chloro-phenyl)-
25 cyclopropanecarboxylic acid with thionyl chloride (SOCl_2) as described below. To
26 200 gms of thionyl chloride and 200 ml dichloromethane in a 3-necked reaction flask,
27 equipped with a mechanical stirrer and a reflux condenser, 100 gm (0.51 mol.) of the
28 1-(4-chloro-phenyl)-cyclopropanecarboxylic acid is added in small increments (5 gm
29 at a time) over 15 minutes period. Once all the acid is added, the reaction mixture is
30 then heated at reflux. The reaction vessel is equipped with a trap (filled with water) to
31 collect and trap the acidic gaseous byproducts, and used in monitoring the reaction.
32 The reaction is usually done once the evolution of the gaseous byproducts is ceased.

The reaction mixture is then cooled down and concentrated on a rotary evaporator at reduced pressure to remove excess thionyl chloride and dichloromethane. The reaction yields 109 gm (98%) of the desired 1-(4-chloro-phenyl)-cyclopropanecarbonyl chloride as reddish viscous oil.

Scheme 1



Example 2

Synthesis 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.

Example 3

Synthesis 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

1 placed in a Parr bomb steel reactor and heated in an oven at 160° C while rotating at
2 43 rpm. The reaction is monitored by checking the gel's pH, and by looking for
3 crystal formation using Scanning Electron Microscopy (SEM). The reaction is
4 usually complete after heating 9-12 days at the conditions described above. Once the
5 crystallization is completed, the starting reaction gel turns to a mixture comprised of a
6 clear liquid and powdery precipitate. The mixture is filtered through a fritted-glass
7 funnel. The collected solids are thoroughly washed with water and, then, rinsed with
8 acetone (10 ml) to remove any organic residues. The solids are allowed to air-dry
9 overnight and, then, dried in an oven at 120° C for 1 hour. The reaction affords 0.85
10 gram of a very fine powder. SEM shows the presence of only one crystalline phase.
11 The product is determined by powder XRD data analysis to be SSZ-65.

12 Example 4

13 Seeded Synthesis of Borosilicate SSZ-65

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

19 Example 5

20 Synthesis of Aluminosilicate SSZ-65

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

days at the conditions described above. Once the crystallization is completed, the starting reaction gel turns to a mixture comprised of a liquid and powdery precipitate. The mixture is filtered through a fritted-glass funnel. The collected solids are thoroughly washed with water and, then, rinsed with acetone (10 ml) to remove any organic residues. The solids are allowed to air-dry overnight and, then, dried in an oven at 120° C for 1 hour. The reaction affords 0.8 gram of SSZ-65.

Examples 6-15

Syntheses of SSZ-65 at Varying SiO₂/B₂O₃ Ratios

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

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

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

(R⁺= organic cation (SDA))

Example 16

Calcination of SSZ-65

SSZ-65 as synthesized in Example 3 is calcined to remove the structure directing agent (SDA) as described below. A thin bed of SSZ-65 in a calcination dish is heated in a muffle furnace from room temperature to 120°C at a rate of 1°C/minute and held for 2 hours. Then, the temperature is ramped up to 540°C at a rate of 1°C/minute and held for 5 hours. The temperature is ramped up again at 1°C/minute to 595°C and held there for 5 hours. A 50/50 mixture of air and nitrogen passes through the muffle furnace at a rate of 20 standard cubic feet (0.57 standard cubic meters) per minute during the calcination process.

Example 17

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

The calcined version of borosilicate SSZ-65 (as synthesized in Example 3 and calcined in Example 16) is easily converted to the aluminosilicate SSZ-65 version by suspending borosilicate SSZ-65 in 1M solution of aluminum nitrate nonahydrate (15 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 overnight. The resulting mixture is then filtered and the collected solids are thoroughly rinsed with de-ionized water and air-dried overnight. The solids are further dried in an oven at 120°C for 2 hours.

Example 18

Ammonium- Ion Exchange of SSZ-65

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

Example 19

Argon Adsorption Analysis

SSZ-65 has a micropore volume of 0.16 cc/gm based on argon adsorption isotherm at 87.5° K (-186°C) recorded on ASAP 2010 equipment from Micromeritics. The

1 sample is first degassed at 400°C for 16 hours prior to argon adsorption. The low-
2 pressure dose is 6.00 cm³/g (STP). A maximum of one hour equilibration time per
3 dose is used and the total run time is 35 hours. The argon adsorption isotherm is
4 analyzed using the density function theory (DFT) formalism and parameters
5 developed for activated carbon slits by Olivier (*Porous Mater.* 1995, 2, 9) using the
6 Saito Foley adaptation of the Horvarth-Kawazoe formalism (*Microporous Materials*,
7 1995, 3, 531) and the conventional t-plot method (*J. Catalysis*, 1965, 4, 319).

8 Example 20

9 Constraint Index

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

24 Example 21

25 Hydrocracking of n-Hexadecane

26 A 1 gm sample of SSZ-65 (prepared as in Example 3 and treated as in
27 Examples 16, 17 and 18) is suspended in 10 gm de-ionized water. To this suspension,
28 a solution of Pd(NH₃)₄(NO₃)₂ at a concentration which would provide 0.5 wt. % Pd
29 with respect to the dry weight of the molecular sieve sample is added. The pH of the
30 solution is adjusted to pH of ~9 by a drop-wise addition of dilute ammonium
31 hydroxide solution. The mixture is then heated in an oven at 75°C for 48 hours. The
32 mixture is then filtered through a glass frit, washed with de-ionized water, and air-

1 dried. The collected Pd-SSZ-65 sample is slowly calcined up to 482°C in air and held
2 there for three hours.

3 The calcined Pd/SSZ-65 catalyst is pelletized in a Carver Press and granulated
4 to yield particles with a 20/40 mesh size. Sized catalyst (0.5 g) is packed into a ¼
5 inch OD tubing reactor in a micro unit for n-hexadecane hydroconversion. The table
6 below gives the run conditions and the products data for the hydrocracking test on n-
7 hexadecane.

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

12

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

13

14

Example 22

15

Synthesis of SSZ-65

16

17

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, in its as-synthesized state, the X-ray
7 diffraction lines of Table I.
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, in its as-synthesized state, the X-ray diffraction
14 lines of Table I.
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 molecular sieve having a composition, as synthesized and in the anhydrous
6 state, in terms of mole ratios as follows:

7

8

$$YO_2/W_cO_d > 15$$

9

$$M_{2n}/YO_2 \quad 0.01 - 0.03$$

10

$$Q/YO_2 \quad 0.02 - 0.05$$

11

12 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium,
13 iron, boron, titanium, indium, vanadium or mixtures thereof; c is 1 or 2; d is 2
14 when c is 1 or d is 3 or 5 when c is 2; M is an alkali metal cation, alkaline earth
15 metal cation or mixtures thereof; n is the valence of M; and Q is a 1-[1-(4-
16 chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-
17 phenyl-cyclopropylmethyl)-pyrrolidinium cation.

18

19

20 11. A molecular sieve according to Claim 10 wherein W is aluminum and Y is silicon.

21

22 12. A molecular sieve according to Claim 10 wherein W is boron and Y is silicon.

23

24 13. A molecular sieve according to Claim 10 wherein Q is a 1-[1-(4-chlorophenyl)
25 cyclopropylmethyl]-1-ethyl-pyrrolidinium cation.

26

27 14. A molecular sieve according to Claim 10 wherein Q is a 1-ethyl-1-(1-phenyl
28 cyclopropylmethyl)-pyrrolidinium cation.

28

29

30 15. A method of preparing a crystalline material comprising (1) an oxide of a first
31 tetravalent element and (2) an oxide of a trivalent element, pentavalent element,
32 second tetravalent element which is different from said first tetravalent element

1 or mixture thereof and having mole ratio of the first oxide to the second oxide
2 greater than 15, said method comprising contacting under crystallization
3 conditions sources of said oxides and a structure directing agent comprising a 1-
4 [1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium or 1-ethyl-1-(1-
5 phenyl-cyclopropylmethyl)-pyrrolidinium cation.

6
7 16. The method according to Claim 15 wherein the first tetravalent element is
8 selected from the group consisting of silicon, germanium and combinations
9 thereof.

10
11 17. The method according to Claim 15 wherein the trivalent element, pentavalent
12 element or second tetravalent element is selected from the group consisting of
13 aluminum, gallium, iron, boron, titanium, indium, vanadium and combinations
14 thereof.

15
16 18. The method according to Claim 17 wherein the trivalent element, pentavalent
17 element or second tetravalent element is selected from the group consisting of
18 aluminum, boron, titanium and combinations thereof.

19
20 19. The method according to Claim 16 wherein the first tetravalent element is
21 silicon.

22
23 20. The method according to Claim 15 wherein the structure directing agent
24 comprises a 1-[1-(4-chlorophenyl)-cyclopropylmethyl]-1-ethyl-pyrrolidinium
25 cation.

26
27 21. The method according to Claim 15 wherein the structure directing agent
28 comprises a 1-ethyl-1-(1-phenyl-cyclopropylmethyl)-pyrrolidinium cation.

29
30 22. The method of Claim 15 wherein the crystalline material has, in its as-
31 synthesized state, the X-ray diffraction lines of Table I.

- 1 23. A process for converting hydrocarbons comprising contacting a
2 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
3 comprising a molecular sieve having a mole ratio greater than about 15 of (1) an
4 oxide of a first tetravalent element to (2) an oxide of a trivalent element,
5 pentavalent element, second tetravalent element which is different from said
6 first tetravalent element or mixture thereof and having, in its as-synthesized
7 state, the X-ray diffraction lines of Table I.
8
- 9 24. The process of Claim 23 wherein the molecular sieve is substantially free of
10 acidity.
11
- 12 25. The process of Claim 23 wherein the process is a hydrocracking process
13 comprising contacting the catalyst with a hydrocarbon feedstock under
14 hydrocracking conditions.
15
- 16 26. The process of Claim 23 wherein the process is a dewaxing process comprising
17 contacting the catalyst with a hydrocarbon feedstock under dewaxing
18 conditions.
19
- 20 27. The process of Claim 23 wherein the process is a process for improving the
21 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising
22 contacting the catalyst with a waxy hydrocarbon feed under isomerization
23 dewaxing conditions.
24
- 25 28. The process of Claim 23 wherein the process is a process for producing a C₂₀₊
26 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under
27 isomerization conditions over the catalyst.
28
- 29 29. The process of Claim 28 wherein the catalyst further comprises at least one
30 Group VIII metal.
31
- 32 30. The process of Claim 23 wherein the process is a process for catalytically
33 dewaxing a hydrocarbon oil feedstock boiling above about 350°F (177°C) and

- 1 containing straight chain and slightly branched chain hydrocarbons comprising
2 contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas
3 at a hydrogen pressure of about 15-3000 psi (0.103-20.7 MPa) under dewaxing
4 conditions with the catalyst.
5
- 6 31. The process of Claim 30 wherein the catalyst further comprises at least one
7 Group VIII metal.
8
- 9 32. The process of Claim 30 wherein said catalyst comprises a layered catalyst
10 comprising a first layer comprising the molecular sieve and at least one Group
11 VIII metal, and a second layer comprising an aluminosilicate molecular sieve
12 which is more shape selective than the molecular sieve of said first layer.
13
- 14 33. The process of Claim 23 wherein the process is a process for preparing a
15 lubricating oil which comprises:
16
17 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain
18 an effluent comprising a hydrocracked oil; and
19
20 catalytically dewaxing said effluent comprising hydrocracked oil at a
21 temperature of at least about 400°F (204°C) and at a pressure of from about
22 15 psig to about 3000 psig (0.103 to 20.7 MPa gauge) in the presence of added
23 hydrogen gas with the catalyst.
24
- 25 34. The process of Claim 33 wherein the catalyst further comprises at least one
26 Group VIII metal.
27
- 28 35. The process of Claim 23 wherein the process is a process for isomerization
29 dewaxing a raffinate comprising contacting said raffinate in the presence of
30 added hydrogen under isomerization dewaxing conditions with the catalyst.
31
- 32 36. The process of Claim 35 wherein the catalyst further comprises at least one
33 Group VIII metal.

- 1
- 2 37. The process of Claim 35 wherein the raffinate is bright stock.
- 3
- 4 38. The process of Claim 23 wherein the process is a process for increasing the
- 5 octane of a hydrocarbon feedstock to produce a product having an increased
- 6 aromatics content comprising contacting a hydrocarbonaceous feedstock which
- 7 comprises normal and slightly branched hydrocarbons having a boiling range
- 8 above about 40°C and less than about 200°C under aromatic conversion
- 9 conditions with the catalyst.
- 10
- 11 39. The process of Claim 38 wherein the molecular sieve is substantially free of
- 12 acid.
- 13
- 14 40. The process of Claim 38 wherein the molecular sieve contains a Group VIII
- 15 metal component.
- 16
- 17 41. The process of Claim 23 wherein the process is a catalytic cracking process
- 18 comprising contacting a hydrocarbon feedstock in a reaction zone under
- 19 catalytic cracking conditions in the absence of added hydrogen with the catalyst.
- 20
- 21 42. The process of Claim 41 wherein the catalyst additionally comprises a large
- 22 pore crystalline cracking component.
- 23
- 24 43. The process of Claim 23 wherein the process is an isomerization process for
- 25 isomerizing C₄ to C₇ hydrocarbons, comprising contacting a feed having normal
- 26 and slightly branched C₄ to C₇ hydrocarbons under isomerizing conditions with
- 27 the catalyst.
- 28
- 29 44. The process of Claim 43 wherein the molecular sieve has been impregnated with
- 30 at least one Group VIII metal.
- 31
- 32 45. The process of Claim 43 wherein the catalyst has been calcined in a steam/air
- 33 mixture at an elevated temperature after impregnation of the Group VIII metal.

- 1
2 46. The process of Claim 44 wherein the Group VIII metal is platinum.
3
- 4 47. The process of Claim 23 wherein the process is a process for alkylating an
5 aromatic hydrocarbon which comprises contacting under alkylation conditions
6 at least a molar excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under
7 at least partial liquid phase conditions and in the presence of the catalyst.
8
- 9 48. The process of Claim 47 wherein the olefin is a C₂ to C₄ olefin.
10
- 11 49. The process of Claim 48 wherein the aromatic hydrocarbon and olefin are
12 present in a molar ratio of about 4:1 to about 20:1, respectively.
13
- 14 50. The process of Claim 48 wherein the aromatic hydrocarbon is selected from the
15 group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene,
16 naphthalene derivatives, dimethylnaphthalene or mixtures thereof.
17
- 18 51. The process of Claim 23 wherein the process is a process for transalkylating an
19 aromatic hydrocarbon which comprises contacting under transalkylating
20 conditions an aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon
21 under at least partial liquid phase conditions and in the presence of the catalyst.
22
- 23 52. The process of Claim 51 wherein the aromatic hydrocarbon and the polyalkyl
24 aromatic hydrocarbon are present in a molar ratio of from about 1:1 to about
25 25:1, respectively.
26
- 27 53. The process of Claim 51 wherein the aromatic hydrocarbon is selected from the
28 group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.
29
- 30 54. The process of Claim 51 wherein the polyalkyl aromatic hydrocarbon is a
31 dialkylbenzene.
32
- 33 55. The process of Claim 23 wherein the process is a process to convert paraffins to
34 aromatics which comprises contacting paraffins under conditions which cause

- 1 paraffins to convert to aromatics with a catalyst comprising the molecular sieve
2 and gallium, zinc, or a compound of gallium or zinc.
3
- 4 56. The process of Claim 23 wherein the process is a process for isomerizing olefins
5 comprising contacting said olefin under conditions which cause isomerization of
6 the olefin with the catalyst.
7
- 8 57. The process of Claim 23 wherein the process is a process for isomerizing an
9 isomerization feed comprising an aromatic C₈ stream of xylene isomers or
10 mixtures of xylene isomers and ethylbenzene, wherein a more nearly
11 equilibrium ratio of ortho-, meta and para-xylenes is obtained, said process
12 comprising contacting said feed under isomerization conditions with the
13 catalyst.
14
- 15 58. The process of Claim 23 wherein the process is a process for oligomerizing
16 olefins comprising contacting an olefin feed under oligomerization conditions
17 with the catalyst.
18
- 19 59. The process of Claim 23 wherein the process is a process for the production of
20 higher molecular weight hydrocarbons from lower molecular weight
21 hydrocarbons comprising the steps of:
22
- 23 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-
24 containing gas and contacting said gas in said zone under C₂₊ hydrocarbon
25 synthesis conditions with the catalyst and a metal or metal compound capable of
26 converting the lower molecular weight hydrocarbon to a higher molecular
27 weight hydrocarbon; and
28
- 29 (b) withdrawing from said reaction zone a higher molecular weight
30 hydrocarbon-containing stream.
31

- 1 60. The process of Claim 59 wherein the metal or metal compound comprises a
2 lanthanide or actinide metal or metal compound.
3
- 4 61. The process of Claim 59 wherein the lower molecular weight hydrocarbon is
5 methane.
6
- 7 62. The process of Claim 23, 25, 26, 27, 28, 30, 33, 35, 41, 43, 47 or 51 wherein the
8 molecular sieve is predominantly in the hydrogen form.
9
- 10 63. A process for converting oxygenated hydrocarbons comprising contacting said
11 oxygenated hydrocarbon under conditions to produce liquid products with a
12 catalyst comprising a molecular sieve having a mole ratio greater than about 15
13 of an oxide of a first tetravalent element to an oxide of a second tetravalent
14 element which is different from said first tetravalent element, trivalent element,
15 pentavalent element or mixture thereof and having, in its as-synthesized state,
16 the X-ray diffraction lines of Table I.
17
- 18 64. The process of Claim 63 wherein the oxygenated hydrocarbon is a lower
19 alcohol.
20
- 21 65. The process of Claim 64 wherein the lower alcohol is methanol.
22
- 23 66. A process for the reduction of oxides of nitrogen contained in a gas stream in the
24 presence of oxygen wherein said process comprises contacting the gas stream
25 with a molecular sieve having a mole ratio greater than about 15 of (1) an oxide
26 of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent
27 element, second tetravalent element which is different from said first tetravalent
28 element or mixture thereof and having, in its as-synthesized state, the X-ray
29 diffraction lines of Table I.
30
- 31 67. The process of Claim 66 wherein said molecular sieve contains a metal or metal
32 ions capable of catalyzing the reduction of the oxides of nitrogen.

1

2 68. The process of Claim 67 wherein the metal is copper, cobalt, platinum, iron,
3 chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures
4 thereof.

5

6 69. The process of Claim 67 wherein the gas stream is the exhaust stream of an
7 internal combustion engine.