

1 ZEOLITE SSZ-52

2 BACKGROUND OF THE INVENTION3 Field of the Invention

4 The present invention relates to new crystalline zeolite SSZ-52, a method for
5 preparing SSZ-52 using the quaternary ammonium cation templating agent N,N-
6 diethyl-5,8-dimethyl-2-azonium bicyclo[3.2.2]nonane, and processes employing SSZ-
7 52 as a catalyst.

8 State of the Art

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

17 SUMMARY OF THE INVENTION

18 The present invention is directed to a family of crystalline molecular sieves
19 with unique properties, referred to herein as "zeolite SSZ-52" or simply "SSZ-52".
20 Preferably, SSZ-52 is obtained in its aluminosilicate form. As used herein, the term
21 "aluminosilicate" refers to a zeolite containing both alumina and silica.

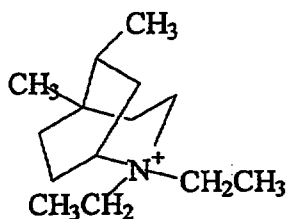
22 In accordance with this invention, there is provided a zeolite having a mole
23 ratio of about 6-50 of an oxide selected from silicon oxide, germanium oxide and
24 mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide,
25 and mixtures thereof and having, after calcination, the X-ray diffraction lines of
26 Table I below.

27 The present invention further provides such a zeolite having a composition, as
28 synthesized and in the anhydrous state, in terms of mole ratios as follows:

29	YO_2/W_2O_3	6-50
30	M_{2n}/YO_2	0.03-0.25
31	Q/YO_2	0.02-0.08

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wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium, iron, or mixtures thereof; 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 quaternary ammonium cation having the structure



X-

Template A

The zeolite has, after calcination, the X-ray diffraction lines of Table I below.

In accordance with this invention, there is also provided a zeolite prepared by thermally treating a zeolite 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, and mixtures thereof of about 6-50 at a temperature of from about 200°C to about 800°C, the thus-prepared zeolite having the X-ray diffraction lines of Table I. The present invention also includes this thus-prepared zeolite 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.

Also provided in accordance with the present invention is a method of preparing a crystalline material comprising an oxide of a first tetravalent element and an oxide of a second tetravalent element which is different from said first tetravalent element, trivalent element, pentavalent element or mixture thereof, said method comprising contacting under crystallization conditions sources of said oxides and a templating agent comprising Template A.

The present invention additionally provides a process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst comprising the zeolite of this invention. The

1 zeolite may be predominantly in the hydrogen form. It may also be substantially free
2 of acidity.

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

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

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

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

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

29 Also included in the present invention is a process for preparing a lubricating
30 oil which comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous
31 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically

1 dewaxing said effluent comprising hydrocracked oil at a temperature of at least about
2 400°F and at a pressure of from about 15 psig to about 3000 psig in the presence of
3 added hydrogen gas with a catalyst comprising at least one Group VIII metal and the
4 zeolite of this invention. The zeolite may be predominantly in the hydrogen form.

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

10 Also provided by the present invention is a catalytic cracking process
11 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic
12 cracking conditions in the absence of added hydrogen with a catalyst comprising the
13 zeolite of this invention, preferably predominantly in the hydrogen form. Also
14 included in this invention is such a catalytic cracking process wherein the catalyst
15 additionally comprises a large pore crystalline cracking component.

16 The present invention further provides a process for oligomerizing olefins
17 comprising contacting an olefin feed under oligomerization conditions with a catalyst
18 comprising the zeolite of this invention.

19 There is further provided in accordance with this invention a process for
20 isomerizing olefins comprising contacting an olefin feed under isomerization
21 conditions with a catalyst comprising the zeolite of this invention.

22 Further provided in accordance with this invention is a process for the
23 production of higher molecular weight hydrocarbons from lower molecular weight
24 hydrocarbons comprising the steps of:

25 (a) introducing into a reaction zone a lower molecular weight hydrocarbon-
26 containing gas and contacting said gas in said zone under C_{2+} hydrocarbon synthesis
27 conditions with a catalyst comprising the zeolite of this invention and a metal or metal
28 compound capable of converting the lower molecular weight hydrocarbon to a higher
29 molecular weight hydrocarbon; and

30 (b) withdrawing from said reaction zone a higher molecular weight
31 hydrocarbon-containing stream. Preferably, the metal or metal compound is a

1 lanthanide or actinide metal or metal compound and the lower molecular weight
2 hydrocarbon is methane.

3 This invention also provides a process for converting lower alcohols and other
4 oxygenated hydrocarbons comprising contacting said lower alcohol or other
5 oxygenated hydrocarbon with a catalyst comprising the zeolite of this invention under
6 conditions to produce liquid products.

7 Also provided by the present invention is an improved process for the
8 reduction of oxides of nitrogen contained in a gas stream in the presence of oxygen
9 wherein said process comprises contacting the gas stream with a zeolite, the
10 improvement comprising using as the zeolite the zeolite of this invention. The zeolite
11 may contain a metal or metal ions (such as cobalt, copper or mixtures thereof) capable
12 of catalyzing the reduction of the oxides of nitrogen, and may be conducted in the
13 presence of a stoichiometric excess of oxygen. In a preferred embodiment, the gas
14 stream is the exhaust stream of an internal combustion engine.

15 Also provided in accordance with this invention is a process for the separation
16 of nitrogen from a nitrogen-containing gas mixture comprising contacting the mixture
17 with a composition comprising the zeolite of this invention. In a preferred
18 embodiment, the gas mixture contains nitrogen and methane.

19 DETAILED DESCRIPTION OF THE INVENTION

20 SSZ-52 is prepared from a reaction mixture having the composition shown in
21 Table A below.

22 TABLE A
23 Reaction Mixture

24		
25	YO ₂ /W ₂ O ₃	15 - 60
26	OH-/YO ₂	0.30-1.0
27	Q/YO ₂	0.10 - 0.40
28	M _{2/n} /YO ₂	0.10-0.50
29	H ₂ O/YO ₂	15 - 50

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

31 In practice, SSZ-52 is prepared by a process comprising:

- 1 (a) preparing an aqueous solution containing sources of at least one oxide
- 2 capable of forming a crystalline molecular sieve and Template A;
- 3 (b) maintaining the aqueous solution under conditions sufficient to form
- 4 crystals of SSZ-52; and
- 5 (c) recovering the crystals of SSZ-52.

6 Accordingly, SSZ-52 may comprise the crystalline material and the templating
7 agent in combination with metallic and non-metallic oxides bonded in tetrahedral
8 coordination through shared oxygen atoms to form a cross-linked three dimensional
9 crystal structure. The metallic and non-metallic oxides comprise one or a combination
10 of oxides of a first tetravalent element(s), and one or a combination of a second
11 tetravalent element(s) different from the first tetravalent element(s), trivalent
12 element(s), pentavalent element(s) or mixture thereof. The first tetravalent element(s)
13 is preferably selected from the group consisting of silicon, germanium and
14 combinations thereof. More preferably, the first tetravalent element is silicon. The
15 second tetravalent element (which is different from the first tetravalent element),
16 trivalent element and pentavalent element is preferably selected from the group
17 consisting of aluminum, gallium, iron, and combinations thereof. More preferably,
18 the second trivalent or tetravalent element is aluminum.

19 Typical sources of aluminum oxide for the reaction mixture include
20 aluminates, alumina, aluminum colloids, aluminum oxide coated on silica sol,
21 hydrated alumina gels such as $\text{Al}(\text{OH})_3$ and aluminum compounds such as AlCl_3 and
22 $\text{Al}_2(\text{SO}_4)_3$. Typical sources of silicon oxide include silicates, silica hydrogel, silicic
23 acid, fumed silica, colloidal silica, tetra-alkyl orthosilicates, and silica hydroxides.
24 Gallium, germanium, and iron, can be added in forms corresponding to their
25 aluminum and silicon counterparts.

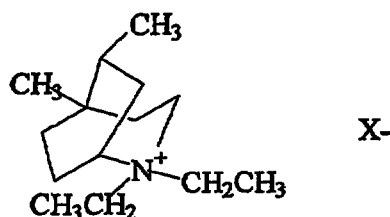
26 A source zeolite reagent may provide a source of aluminum or boron. In most
27 cases, the source zeolite also provides a source of silica. The source zeolite in its
28 dealuminated or deboronated form may also be used as a source of silica, with
29 additional silicon added using, for example, the conventional sources listed above.
30 Use of a source zeolite reagent as a source of alumina for the present process is more
31 completely described in U.S. Patent No. 4,503,024 issued on March 5, 1985 to

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1 Bourgogne et al. entitled "PROCESS FOR THE PREPARATION OF SYNTHETIC
2 ZEOLITES, AND ZEOLITES OBTAINED BY SAID PROCESS", the disclosure of
3 which is incorporated herein by reference.

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

13 The organic templating agent used to prepare SSZ-52 is an N,N-diethyl-5,8-
14 dimethyl-2-azonium bicyclo[3.2.2]nonane cation having the following structure:
15



16

17

18 where X is an anion that is not detrimental to the formation of the SSZ-52.
19 Representative anions include halogen, e.g., fluoride, chloride, bromide and iodide,
20 hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is
21 the most preferred anion.

22 The reaction mixture is maintained at an elevated temperature until the crystals
23 of the SSZ-52 zeolite are formed. The hydrothermal crystallization is usually
24 conducted under autogenous pressure, at a temperature between 120°C and 160°C.
25 The crystallization period is typically greater than 1 day and preferably from about
26 3 days to about 20 days.

27 Preferably, the zeolite is prepared using mild stirring or agitation.

During the hydrothermal crystallization step, the SSZ-52 crystals can be allowed to nucleate spontaneously from the reaction mixture. The use of SSZ-52 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-52 over any undesired phases. When used as seeds, SSZ-52 crystals are added in an amount between 0.1 and 10% of the weight of silica used in the reaction mixture.

Once the zeolite 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-52 zeolite crystals. The drying step can be performed at atmospheric pressure or under vacuum.

SSZ-52 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, and mixtures thereof of about 6-50; and has, after calcination, the X-ray diffraction lines of Table I below. SSZ-52 further has a composition, as synthesized and in the anhydrous state, in terms of mole ratios, shown in Table B below.

TABLE B

As-Synthesized SSZ-52

YO_2/W_2O_3	6-50
M_{2n}/YO_2	0.02-0.20
Q/YO_2	0.02-0.08

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

Lower silica to alumina ratios may be obtained by using methods which insert aluminum into the crystalline framework. For example, aluminum insertion may occur by thermal treatment of the zeolite 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-52 is comprised of a new framework structure or topology which is characterized by its X-ray diffraction pattern.

1 After calcination, the SSZ-52 zeolites have a crystalline structure whose X-ray
2 powder diffraction pattern include the characteristic lines shown in Table I:

3 TABLE I
4 Calcined SSZ-52

5

<u>2 Theta^(a)</u>	<u>D</u>	<u>Relative Intensity</u>
7.7	11.5	W-S
10.8	8.19	W-S
12.4	7.13	W-S
12.9	6.86	W-VS
15.1	5.86	W-S
16.9	5.24	W-S
17.85	4.97	VS
19.95	4.45	M-VS
21.35	4.16	M-VS
26.1	3.41	M-VS
30.3	2.95	M-S
31.25	2.86	W-M
34.7	2.58	W-M

6
7 ^(a) ± 0.20

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

12 Table IA below shows the X-ray powder diffraction lines for calcined SSZ-52
13 including actual relative intensities.

TABLE IA

Calcined SSZ-52

<u>2 Theta^(a)</u>	<u>D</u>	<u>Relative Intensity</u>
7.7	11.5	10-60
10.8	8.19	10-50
12.4	7.13	5-45
12.9	6.86	25-100
15.1	5.86	5-50
16.9	5.24	5-60
17.85	4.97	65-100
19.95	4.45	30-100
21.35	4.16	40-100
26.1	3.41	35-100
30.3	2.95	25-65
31.25	2.86	15-45
34.7	2.58	10-50

(a) ± 0.20

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.

Representative peaks from the X-ray diffraction pattern of calcined SSZ-52 are shown in Table I. Calcination can result in changes in the intensities of the peaks as compared to patterns of the "as-made" material, as well as minor shifts in the diffraction pattern. The zeolite produced by exchanging the metal or other cations present in the zeolite with various other cations (such as H^+ or NH_4^+) yields essentially the same diffraction pattern, although again, there may be minor shifts in the interplanar spacing and variations in the relative intensities of the peaks. Notwithstanding these minor perturbations, the basic crystal lattice remains unchanged by these treatments.

1 Crystalline SSZ-52 can be used as-synthesized, but preferably will be
2 thermally treated (calcined). Usually, it is desirable to remove the alkali metal cation
3 by ion exchange and replace it with hydrogen, ammonium, or any desired metal ion.
4 The zeolite can be leached with chelating agents, e.g., EDTA or dilute acid solutions,
5 to increase the silica to alumina mole ratio. The zeolite can also be steamed; steaming
6 helps stabilize the crystalline lattice to attack from acids.

7 The zeolite can be used in intimate combination with hydrogenating
8 components, such as tungsten, vanadium molybdenum, rhenium, nickel cobalt,
9 chromium, manganese, or a noble metal, such as palladium or platinum, for those
10 applications in which a hydrogenation-dehydrogenation function is desired.

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

19 The hydrogen, ammonium, and metal components can be ion-exchanged into
20 the SSZ-52. The zeolite can also be impregnated with the metals, or, the metals can
21 be physically and intimately admixed with the zeolite using standard methods known
22 to the art.

23 Typical ion-exchange techniques involve contacting the synthetic zeolite with
24 a solution containing a salt of the desired replacing cation or cations. Although a wide
25 variety of salts can be employed, chlorides and other halides, acetates, nitrates, and
26 sulfates are particularly preferred. The zeolite is usually calcined prior to the ion-
27 exchange procedure to remove the organic matter present in the channels and on the
28 surface, since this results in a more effective ion exchange. Representative ion
29 exchange techniques are disclosed in a wide variety of patents including U.S. Patent
30 Nos. 3,140,249 issued on July 7, 1964 to Plank et al.; 3,140,251 issued on July 7,
31 1964 to Plank et al.; and 3,140,253 issued on July 7, 1964 to Plank et al.

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

7 Regardless of the cations present in the synthesized form of SSZ-52, the
8 spatial arrangement of the atoms which form the basic crystal lattice of the zeolite
9 remains essentially unchanged.

10 SSZ-52 can be formed into a wide variety of physical shapes. Generally
11 speaking, the zeolite can be in the form of a powder, a granule, or a molded product,
12 such as extrudate having a particle size sufficient to pass through a 2-mesh (Tyler)
13 screen and be retained on a 400-mesh (Tyler) screen. In cases where the catalyst is
14 molded, such as by extrusion with an organic binder, the aluminosilicate can be
15 extruded before drying, or, dried or partially dried and then extruded.

16 SSZ-52 can be composited with other materials resistant to the temperatures
17 and other conditions employed in organic conversion processes. Such matrix
18 materials include active and inactive materials and synthetic or naturally occurring
19 zeolites as well as inorganic materials such as clays, silica and metal oxides.
20 Examples of such materials and the manner in which they can be used are disclosed in
21 U.S. Patent No. 4,910,006, issued May 20, 1990 to Zones et al., and U.S. Patent
22 No. 5,316,753, issued May 31, 1994 to Nakagawa, both of which are incorporated by
23 reference herein in their entirety.

24 Hydrocarbon Conversion Processes

25 SSZ-52 zeolites are useful in hydrocarbon conversion reactions. Hydrocarbon
26 conversion reactions are chemical and catalytic processes in which carbon containing
27 compounds are changed to different carbon containing compounds. Examples of
28 hydrocarbon conversion reactions in which SSZ-52 are expected to be useful include
29 hydrocracking, dewaxing, catalytic cracking and olefin formation reactions. The
30 catalysts are also expected to be useful in other petroleum refining and hydrocarbon
31 conversion reactions such as isomerizing n-paraffins and naphthenes, isomerizing

1 olefins, polymerizing and oligomerizing olefinic or acetylenic compounds such as
2 isobutylene and butene-1, reforming, forming higher molecular weight hydrocarbons
3 from lower molecular weight hydrocarbons (e.g., methane upgrading) and oxidation
4 reactions. The SSZ-52 catalysts may have high selectivity, and under hydrocarbon
5 conversion conditions can provide a high percentage of desired products relative to
6 total products.

7 SSZ-52 zeolites can be used in processing hydrocarbonaceous feedstocks.
8 Hydrocarbonaceous feedstocks contain carbon compounds and can be from many
9 different sources, such as virgin petroleum fractions, recycle petroleum fractions,
10 shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO, recycled plastic
11 feedstocks and, in general, can be any carbon containing feedstock susceptible to
12 zeolitic catalytic reactions. Depending on the type of processing the
13 hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals,
14 it can also have high or low nitrogen or sulfur impurities. It can be appreciated,
15 however, that in general processing will be more efficient (and the catalyst more
16 active) the lower the metal, nitrogen, and sulfur content of the feedstock.

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

21 Other reactions which can be performed using the catalyst of this invention
22 containing a metal, e.g., a Group VIII metal such platinum, include
23 hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization
24 reactions.

25 The following table indicates typical reaction conditions which may be
26 employed when using catalysts comprising SSZ-52 in the hydrocarbon conversion
27 reactions of this invention. Preferred conditions are indicated in parentheses.

28

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig (200-3000)	0.1-20 (0.2-10)
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
Condensation of alcohols	260-538	0.5-1000 psig	0.5-50 ⁵
Isomerization	93-538 (204-315)	50-1000 psig	1-10 (1-4)

1
2
3
4
5
6

¹ Several hundred atmospheres

² Gas phase reaction

³ Hydrocarbon partial pressure

⁴ Liquid phase reaction

⁵ WHSV

7

Other reaction conditions and parameters are provided below.

8

Hydrocracking

9

Using a catalyst which comprises SSZ-52, preferably predominantly in the hydrogen form, and a hydrogenation promoter, heavy petroleum residual feedstocks, cyclic stocks and other hydrocrackate charge stocks can be hydrocracked using the process conditions and catalyst components disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753.

14

The hydrocracking catalysts contain an effective amount of at least one hydrogenation component of the type commonly employed in hydrocracking catalysts. The hydrogenation component is generally selected from the group of hydrogenation catalysts consisting of one or more metals of Group VIB and Group VIII, including the salts, complexes and solutions containing such. The hydrogenation catalyst is preferably selected from the group of metals, salts and complexes thereof of the group consisting of at least one of platinum, palladium, rhodium, iridium, ruthenium and mixtures thereof or the group consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium, chromium and mixtures thereof. Reference to the catalytically active metal or metals is intended to encompass such metal or metals in the elemental

23

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1 state or in some form such as an oxide, sulfide, halide, carboxylate and the like. The
2 hydrogenation catalyst is present in an effective amount to provide the hydrogenation
3 function of the hydrocracking catalyst, and preferably in the range of from 0.05 to
4 25% by weight.

5 Dewaxing

6 SSZ-52, preferably predominantly in the hydrogen form, can be used to dewax
7 hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically,
8 the viscosity index of the dewaxed product is improved (compared to the waxy feed)
9 when the waxy feed is contacted with SSZ-52 under isomerization dewaxing
10 conditions.

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

18 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil
19 feedstock boiling above about 350°F and containing straight chain and slightly
20 branched chain hydrocarbons by contacting the hydrocarbon oil feedstock in the
21 presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi with a
22 catalyst comprising SSZ-52 and at least one Group VIII metal.

23 The SSZ-52 hydrodewaxing catalyst may optionally contain a hydrogenation
24 component of the type commonly employed in dewaxing catalysts. See the
25 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for
26 examples of these hydrogenation components.

27 The hydrogenation component is present in an effective amount to provide an
28 effective hydrodewaxing and hydroisomerization catalyst preferably in the range of
29 from about 0.05 to 5% by weight. The catalyst may be run in such a mode to increase
30 isodewaxing 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-52 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 zeolite SSZ-52 and at
7 least one Group VIII metal, and a second layer comprising an aluminosilicate zeolite
8 which has a shape selectivity different from zeolite SSZ-52. The use of layered
9 catalysts is disclosed in U.S. Patent No. 5,149,421, issued September 22, 1992 to
10 Miller, which is incorporated by reference herein in its entirety. The layering may
11 also include a bed of SSZ-52 layered with a non-zeolitic component designed for
12 either hydrocracking or hydrofinishing.

13 SSZ-52 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 at space velocities
21 (LHSV) between about 0.1 and 20 and a hydrogen recycle rate of about 400 to
22 1500 SCF/bbl. The hydrogenation catalyst employed must be active enough not only
23 to hydrogenate the olefins, diolefins and color bodies which may be present, but also
24 to reduce the aromatic content. Suitable hydrogenation catalyst are disclosed in U. S.
25 Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated by
26 reference herein in its entirety. The hydrofinishing step is beneficial in preparing an
27 acceptably stable product (e.g., a lubricating oil) since dewaxed products prepared
28 from hydrocracked stocks tend to be unstable to air and light and tend to form sludges
29 spontaneously and quickly.

30 Lube oil may be prepared using SSZ-52. For example, a C₂₀₊ lube oil may be
31 made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising SSZ-52 in the

1 hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil
2 may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous
3 feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically
4 dewaxing the effluent at a temperature of at least about 400°F and at a pressure of
5 from about 15 psig to about 3000 psig in the presence of added hydrogen gas with a
6 catalyst comprising SSZ-52 in the hydrogen form and at least one Group VIII metal.

7 Catalytic Cracking

8 Hydrocarbon cracking stocks can be catalytically cracked in the absence of
9 hydrogen using SSZ-52, preferably predominantly in the hydrogen form.

10 When SSZ-52 is used as a catalytic cracking catalyst in the absence of
11 hydrogen, the catalyst may be employed in conjunction with traditional cracking
12 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking
13 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of
14 these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent
15 No. 4,910,006 and U.S. Patent No 5,316,753. When a traditional cracking catalyst
16 (TC) component is employed, the relative weight ratio of the TC to the SSZ-52 is
17 generally between about 1:10 and about 500:1, desirably between about 1:10 and
18 about 200:1, preferably between about 1:2 and about 50:1, and most preferably is
19 between about 1:1 and about 20:1. The novel zeolite and/or the traditional cracking
20 component may be further ion exchanged with rare earth ions to modify selectivity.

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

24 Oligomerization

25 It is expected that SSZ-52 can also be used to oligomerize straight and
26 branched chain olefins having from about 2 to 21 and preferably 2-5 carbon atoms.
27 The oligomers which are the products of the process are medium to heavy olefins
28 which are useful for both fuels, i.e., gasoline or a gasoline blending stock and
29 chemicals.

30 The oligomerization process comprises contacting the olefin feedstock in the
31 gaseous or liquid phase with a catalyst comprising SSZ-52.

1 The process is carried out under isomerization conditions. The hydrocarbon
2 feed is contacted in a vapor phase with a catalyst comprising the SSZ-52. The
3 process may be carried out generally at a temperature from about 625°F to about
4 950°F (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-
5 482°C), and about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The
6 pressure ranges from subatmospheric to about 200 psig, preferably from about 15 psig
7 to about 200 psig, and more preferably from about 1 psig to about 150 psig.

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

19 Methane Upgrading

20 Higher molecular weight hydrocarbons can be formed from lower molecular
21 weight hydrocarbons by contacting the lower molecular weight hydrocarbon with a
22 catalyst comprising SSZ-52 and a metal or metal compound capable of converting the
23 lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon.
24 Examples of such reactions include the conversion of methane to C₂+ hydrocarbons
25 such as ethylene or benzene or both. Examples of useful metals and metal compounds
26 include lanthanide and or actinide metals or metal compounds.

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

1 issued April 14, 1992 to Washecheck; 5,238,898, issued August 24, 1993 to Han et
2 al.; 5,321,185, issued June 14, 1994 to van der Vaart; and 5,336,825, issued August 9,
3 1994 to Choudhary et al., each of which is incorporated herein by reference in its
4 entirety.

5 Condensation of Alcohols

6 SSZ-52 can be used to condense lower aliphatic alcohols having 1 to
7 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed
8 aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent
9 No. 3,894,107, issued July 8, 1975 to Butter et al., describes the process conditions
10 used in this process, which patent is incorporated totally herein by reference.

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

19 Other Uses for SSZ-52

20 SSZ-52 can also be used as an adsorbent with high selectivities based on
21 molecular sieve behavior and also based upon preferential hydrocarbon packing
22 within the pores.

23 SSZ-52 may also be used for the catalytic reduction of the oxides of nitrogen
24 in a gas stream. Typically, the gas stream also contains oxygen, often a stoichiometric
25 excess thereof. Also, the SSZ-52 may contain a metal or metal ions within or on it
26 which are capable of catalyzing the reduction of the nitrogen oxides. Examples of
27 such metals or metal ions include copper, cobalt and mixtures thereof.

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

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

6 SSZ-52 may also be used in the separation of gases, such as the separation of
7 nitrogen from a nitrogen-containing gas mixture. One example of such separation is
8 the separation of nitrogen from methane (e.g., the separation of nitrogen from natural
9 gas).

10 EXAMPLES

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

12 Example 1

13 Synthesis of N,N-diethyl-5,8-dimethyl-2-azonium bicyclo[3.2.2]nonane cation

14 (Template A)

15 A three-neck, 5-liter flask is set up with additional funnel with equalization
16 arm. A septum is place over the funnel. Nitrogen is passed through the system. First
17 an in-situ reagent is developed by placing 104.55 grams of diisopropylamine in
18 1859 ml of tetrahydrofuran (THF) and then slowly adding 401.7 ml of n-butyl lithium
19 (2.5 M in hexane) while keeping the temperature near -70°C. The n-butyl lithium is
20 charged to the addition funnel by use of a cannula. The addition into THF takes about
21 1.25 hours after which the resulting mixture is stirred for another hour. 104.53 grams
22 of 3-methyl-2- cyclohexene-1 one in 1117 ml THF is added dropwise over a 0.75 hour
23 period. Lastly, 161.73 grams of methyl acrylate is added over a period of 0.25 hour.
24 Gradually, the reaction is allowed to warm to room temperature and its progress is
25 followed by TLC. The reaction appears to go overnight.

26 Recovery of the product is begun by adding 1N HCl until the solution becomes
27 acidic. The reaction product is transferred to separatory funnel and the aqueous phase
28 is recovered to subsequently treat with methylene chloride (2 x 250 ml). The
29 combined organic phase is dried over sodium sulfate and then strip solvent. The
30 residue is taken up in ether to free it from a little gummy material. The ether is

1 removed and the resulting oil is distilled; a Vigreux column (30 cm) is set up and run
2 at 2-4 mm Hg. The bulk of the product comes over between 123-137°C.

3 The resulting product is reduced using lithium aluminum hydride. The
4 reduction produces a diol, 1-methyl-2-methanol-7-hydroxy bicyclo[2.2.2]octane. The
5 side methanol group is tosylated by reaction of tosyl chloride (96.92 grams) with the
6 diol (85.68 grams) in anhydrous pyridine (500 ml). The tosyl chloride is added to the
7 other two components, under nitrogen, using a powder addition funnel while cooling
8 the reaction to -5°C. The addition is carried out over 0.75 hour and the reaction
9 mixture is warmed to room temperature and the reaction is allowed to run overnight.
10 500 ml of methylene chloride is added, the resulting mixture transferred to a
11 separatory funnel, and washed with water (2 x 250 ml). The resulting product is
12 dried over sodium sulfate, filtered, and stripped to yield 150 grams of oil.

13 The product is purified by column chromatography. A kilogram of silica gel
14 (230-400 mesh) is slurried in hexane, and the oil is loaded on top in 50 ml methylene
15 chloride. The elution is carried out using 25/75 ethyl acetate (ETOAC); hexane and
16 fractions are monitored by TLC. Eighty-three grams of product is collected. The
17 tosylate is then reduced using LAH (as above) to yield 1,2-dimethyl-7-hydroxy
18 bicyclo[2.2.2]octane. Next, the alcohol is reoxidized to the ketone. 37.84 grams of
19 the alcohol is reacted in a three-neck, 2-liter flask as follows: 34.60 grams of oxalyl
20 chloride and 604 ml of methylene chloride are loaded in and blanketed under nitrogen.
21 With an addition funnel with side arm, 46 grams of anhydrous dimethylsulfoxide
22 (DMSO) in 122.7 ml of methylene chloride is added. The bath is cooled to -60°C
23 using a dry ice/acetone bath, and the addition takes 0.5 hour. The alcohol, in 53.4 ml
24 methylene chloride, is added at this temperature over 0.5 hour followed by stirring for
25 another 0.5 hour. 126.65 Grams of triethylamine is then placed in the addition funnel
26 and addition begun and continued over 0.25 hour. All of the additions produce
27 exothermic response, so cooling is continued. The reaction mixture is slowly warmed
28 to room temperature and the reaction continued to run overnight.

29 Work-up of the reaction product begins with addition of 500 ml water. The
30 separated aqueous phase is then extracted with methylene chloride (2 x 250 ml). The
31 combined organic phases are then dried over magnesium sulfate and stripped. The

1 resulting oil is triturated with ether to separate a small amount of insoluble material.
2 Stripping off ether yields 37 grams of product.

3 Thirty-seven grams of ketone and 240 ml of 96 % formic acid are placed into a
4 1 liter round bottom flask connected to an addition funnel. These components are
5 stirred using a magnetic stir bar. 125 Ml of formic acid with 43 grams of
6 hydroxylamine-O-sulfonic acid dissolved and suspended in it , are added to the funnel.
7 The addition is carried out over a 20 minute period with stirring. The solution
8 darkens. The addition funnel is replaced with a reflux condenser, and the reaction is
9 refluxed for 15-20 hours with samples taken to follow by TLC.

10 The mixture is carefully poured into 2 kg of ice. After cooling in the ice, the
11 mixture is slowly brought to pH =12 with the addition of 50% NaOH. Three
12 extractions are carried out using 500 cc units of methylene chloride. These extracts
13 are dried over sodium sulfate. After drying, the solvent is stripped off leaving a black
14 oil of about 45 grams.

15 This oil is dissolved in a minimum of chloroform and loaded onto a column
16 (750 grams of 230-400 mesh silica gel, already slurried in chloroform). The elution
17 progresses using chloroform with 2 vol. % methanol. The elution fractions are
18 followed by TLC (fractions 7-21 give the same product). The similar fractions are
19 combined and removing the eluting solvent yields about 30 grams of lactam.

20 25 Grams of this lactam is used in the reduction step. Using a 2 liter 3-neck
21 round bottom flask, nitrogen gas is run into the system and vented up through the
22 reflux condenser and into a bubbler. The system has an addition funnel. 460 Ml of
23 anhydrous ether are added into the flask. Carefully, 18 grams of lithium aluminum
24 hydride are also admitted into the flask. There is some gas evolution. The lactam is
25 dissolved in 230 ml of methylene chloride (also anhydrous). After cooling the flask
26 down in an acetone/dry ice bath, the lactam is added dropwise. The reaction is
27 exothermic so periodically more ice needs to be added as temperature rises. The
28 reduction can be followed by change in TLC data (monitored by iodine and eluted on
29 silica with 98/2 chloroform/methanol). The reaction is allowed to come to room
30 temperature overnight.

1 18 Grams of water are slowly added with the expected exothermic evolution of
2 gas occurring. The ether is removed and its volume replaced with dichloromethane.
3 18 Grams of 15% NaOH solution and then 55 grams of water are added. The solids
4 which form are filtered off, washed with additional dichloromethane, and combined
5 with the organic fractions and dry over sodium sulfate (Caution : Do not let the NaOH
6 solution sit in contact with dichloromethane overnight.). The solvent is stripped off to
7 recover about 15 grams of oil/solid mix. This is the crude amine.

8 10 grams of this amine is quaternized as follows : In a 250 ml flask equipped
9 with stir bar and reflux condenser add the amine, 10 grams of KHCO_3 , 65 ml of
10 methanol and lastly, 30 grams of ethyl iodide. The mixture is brought to reflux and
11 maintained in that state for 48 hours. Upon cooling, the solvent is removed. The
12 solids are treated with chloroform. In turn the chloroform-soluble fractions are
13 stripped to yield another solid which is recrystallized from a minimum of hot acetone
14 and methanol. Recrystallization in the cold yields 3 separate crops of product, totaling
15 11 grams of the salt. The melting points for these crops are all in the range of 252-256
16 °C.

18 The salt is converted to the hydroxide form by ion-exchange over a BioRad
19 AG1-X8 resin.

Example 2

Synthesis of SSZ-52

3.36 Grams of Template A (0.596 M) is placed in the Teflon cup of a 23 ml Parr reactor. Next, 0.20 gram of 1.0 N NaOH and 2.26 grams of water are added. 2.5 Grams of Banco N silicate is added ($\text{NaOH}/\text{SiO}_2 = 0.59$ and SiO_2 is about 28 weight percent). 0.25 Grams of sodium Y zeolite is added as a source of aluminum. The reaction vessel is closed and heated at 135°C with 43 RPM tumbling. The reaction is run for seven days. Upon cooling the reaction mixture to room temperature, the pH is 12.36 indicating that crystallization has occurred. A crystalline product is recovered and determined by X-ray diffraction to be SSZ-52. The XRD data appears in Table II below.

-25-

1

TABLE II

<u>2 Theta</u>	<u>D</u>	<u>I/I₀ x 100</u>
7.7	11.47	46
8.46	10.44	8
10.75	8.22	20
12.41	7.13	28
12.94	6.84	37
15.11	5.86	4
15.49	5.72	16
16.86	5.25	46
17.78	4.99	94
19.97	4.44	78
21.33	4.16	100
22.14	4.01	17
22.53	3.94	22
26.09	3.41	77
26.84	3.32	17
27.2	3.28	12
28.26	3.16	8
28.97	3.08	14
30.29	2.95	47
31.24	2.86	34
31.81	2.81	12
32.73	2.73	19
34.72	2.58	37
38.88	2.31	5
39.44	2.28	8

2

Example 3Synthesis of SSZ-52

A reaction is carried out as described in Example 2. A new solution of Template A is used with a 0.527 M value as the hydroxide salt. 3.80 Grams of Template A is used and the other reagents are the same as in Example 2. Eleven days are required to crystallize a product that is identified as SSZ-52.

Example 4Calcination of SSZ-52

The material from Example 2 is calcined in the following manner. A thin bed of material is heated in a muffle furnace from room temperature to 120°C at a rate of 1°C per minute and held at 120°C for three hours. The temperature is then ramped up to 540°C at the same rate and held at this temperature for 5 hours. A 50/50 mixture of air and nitrogen is passed over the zeolite at a rate of 20 standard cubic feet per minute during heating. The X-ray diffraction data for the product is provided in Table III below.

TABLE III

<u>2 Theta</u>	<u>D</u>	<u>I/I₀ x 100</u>
7.74	11.41	21
8.43	10.48	6
10.80	8.19	37
12.47	7.09	15
12.92	6.85	100
15.09	5.87	17
15.41	5.75	7
15.67	5.65	2
16.88	5.25	18
17.91	4.95	77
19.95	4.45	45
20.17	4.40	25
21.33	4.16	67
22.21	4.00	29
26.05	3.42	47

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27.06	3.29	13
28.29	3.15	6
29.08	3.07	9
29.41	3.04	3
30.26	2.95	32
31.22	2.86	29
31.85	2.81	15
32.82	2.73	11
33.22	2.70	3
34.69	2.58	21
38.86	2.32	3
39.46	2.28	4

1 Example 5

2 NH₄ Exchange of SSZ-52

3 Ion exchange of calcined SSZ-52 material (prepared in Example 4) is
 4 performed using NH₄NO₃ to convert the zeolite from its Na⁺ form to the NH₄⁺ form,
 5 and, ultimately, the H⁺ form. The same mass of NH₄NO₃ as zeolite is slurried in
 6 water at a weight ratio of 20:1 water to zeolite. The exchange solution is heated at
 7 90°C for 2 hours and then filtered. This procedure can be repeated up to three times.
 8 Following the final exchange, the zeolite is washed several times with water and
 9 dried. This NH₄⁺ form of SSZ-52 can then be converted to the H⁺ form by calcination
 10 (as described in Example 4) to 540°C.

11 Example 6

12 Micropore Volume of SSZ-52

13 The argon adsorption capacity of the SSZ-52 is measured using an Omnisorp
 14 100CX instrument. Fifty mg samples of SSZ52 are used. After evacuation of the
 15 sample in the cell at room temperature, the temperature is raised to 300°C while
 16 keeping the cell under vacuum. These conditions are held for two hours. The cell and
 17 sample are then cooled to 87 Kelvin in a reservoir of liquid argon. In a static
 18 micropore filling measurement, doses of argon from a calibrated volume are admitted
 19 to the cell at successively higher pressures. The amounts that adsorb from each dose
 20 are calculated from the pressure changes. Micropore filling is detected as a step

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1 increase in a plot of amount adsorbed versus pressure. The position of the step
2 defines a P/P_0 for micropore filling and its size indicates the adsorption capacity of the
3 micropores.

4 Two peaks are found for calcined SSZ-52 (from Example 4) using argon and
5 static uptake measurements. Both peaks are in the range of 20-30 microbars. The
6 combined micropore volume is quite high and equals 0.34 cc/gm of micropore
7 volume.

8 Example 7

9 Use of SSZ-52 To Convert Methanol

10 130 Milligrams of SSZ-52, as prepared in Example 2, 4 and 5 is pressed in a
11 Carver press to 3 KPSI. The material is slightly chipped to maintain a +40 mesh
12 fraction. The material is calcined in air to 1100°F (593°C) and then packed into a 3/8
13 inch stainless steel reactor. The catalyst is supported on glass wool and the bed is
14 preceded by a zone of acid-washed alundum. The reactor is loaded into a Lindberg
15 furnace and the catalyst is equilibrated at 400°C in a stream of nitrogen (20cc/min.).
16 The feed is then introduced by syringe pump (1.31 cc/hr) and is 22.1 wt. % methanol
17 in water.

18 A first sample is taken at 10 minutes on stream, via a Valco sampling valve.
19 The conversion of methanol is 95% with almost all the products consisting of C₂-C₅
20 hydrocarbons. No aromatics are detected. The catalyst loses activity with time-on-
21 stream, dropping to about 5% conversion over a 3 hour period. The test reaction
22 demonstrates that SSZ-52 can be used for the conversion of methanol to olefins
23 (MTO). The data is also consistent with a view that SSZ-52 could be an 8-ring, small
24 pore zeolite.



1 WHAT IS CLAIMED IS:

2

- 3 1. A zeolite having a mole ratio of about 6-50 of an oxide selected from the group
4 consisting of silicon oxide, germanium oxide and mixtures thereof to an oxide
5 selected from aluminum oxide, gallium oxide, iron oxide and mixtures thereof,
6 and having, after calcination, the X-ray diffraction lines of Table I.

7

- 8 2. A zeolite according to Claim 1 wherein the oxides comprise silicon oxide and
9 aluminum oxide.

10

- 11 3. A zeolite according to Claim 1 wherein said zeolite is predominantly in the
12 hydrogen form.

13

- 14 4. A zeolite according to Claim 1 wherein said zeolite is substantially free of
15 acidity.

16

- 17 5. A zeolite having a composition, as synthesized and in the anhydrous state, in
18 terms of mole ratios as follows:

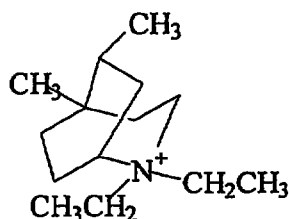
19

20	YO_2/W_2O_3	6-50
21	$M_{2/n}/YO_2$	0.03-0.25
22	Q/YO_2	0.02 - 0.08

23

24 wherein Y is silicon, germanium or a mixture thereof; W is aluminum, gallium,
25 iron or mixtures thereof; M is an alkali metal cation, alkaline earth metal cation
26 or mixtures thereof; n is the valence of M; and Q is a quaternary ammonium
27 cation having the structure

-30-

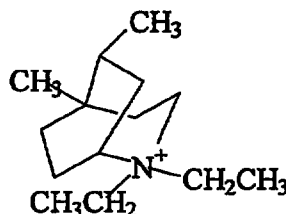


X-

where X- is an anion which is not detrimental to the formation of the zeolite.

6. A zeolite according to Claim 5 wherein W is aluminum and Y is silicon.

7. A method of preparing a crystalline material comprising an oxide selected from silicon oxide, germanium oxide and mixtures thereof to an oxide selected from aluminum oxide, gallium oxide, iron oxide, and mixtures thereof, said method comprising contacting under crystallization conditions sources of said oxides and a templating agent comprising a quaternary ammonium cation having the structure



X-

where X- is an anion which is not detrimental to the formation of the crystalline material.

8. The method according to Claim 7 wherein the oxides are silicon oxide and aluminum oxide.

9. The method of Claim 7 wherein the crystalline material has, after calcination, the X-ray diffraction lines of Table I.



- 1
- 2 10. A process for converting hydrocarbons comprising contacting a
- 3 hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst
- 4 comprising a zeolite having a mole ratio of about 6-50 of an oxide selected from
- 5 silicon oxide, germanium oxide and mixtures thereof to an oxide selected from
- 6 aluminum oxide, gallium oxide, iron oxide, and mixtures thereof and having,
- 7 after calcination, the X-ray diffraction lines of Table I.
- 8
- 9 11. The process of Claim 10 wherein the zeolite is predominantly in the hydrogen
- 10 form.
- 11
- 12 12. The process of Claim 10 wherein the zeolite is substantially free of acidity.
- 13
- 14 13. The process of Claim 10 wherein the process is a hydrocracking process
- 15 comprising contacting the catalyst with a hydrocarbon feedstock under
- 16 hydrocracking conditions.
- 17
- 18 14. The process of Claim 13 wherein the zeolite is predominantly in the hydrogen
- 19 form.
- 20
- 21 15. The process of Claim 10 wherein the process is a dewaxing process comprising
- 22 contacting the catalyst with a hydrocarbon feedstock under dewaxing conditions.
- 23
- 24 16. The process of Claim 15 wherein the zeolite is predominantly in the hydrogen
- 25 form.
- 26
- 27 17. The process of Claim 10 wherein the process is a process for improving the
- 28 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising
- 29 contacting the catalyst with a waxy hydrocarbon feed under isomerization
- 30 dewaxing conditions.
- 31



- 1 18. The process of Claim 17 wherein the zeolite is predominantly in the hydrogen
2 form.
3
- 4 19. The process of Claim 10 wherein the process is a process for producing a C₂₀₊
5 lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under
6 isomerization conditions over the catalyst.
7
- 8 20. The process of Claim 19 wherein the zeolite is predominantly in the hydrogen
9 form.
10
- 11 21. The process of Claim 19 wherein the catalyst further comprises at least one
12 Group VIII metal.
13
- 14 22. The process of Claim 10 wherein the process is a process for catalytically
15 dewaxing a hydrocarbon oil feedstock boiling above about 350°F and containing
16 straight chain and slightly branched chain hydrocarbons comprising contacting
17 said hydrocarbon oil feedstock in the presence of added hydrogen gas at a
18 hydrogen pressure of about 15-3000 psi under dewaxing conditions with the
19 catalyst.
20
- 21 23. The process of Claim 22 wherein the zeolite is predominantly in the hydrogen
22 form.
23
- 24 24. The process of Claim 22 wherein the catalyst further comprises at least one
25 Group VIII metal.
26
- 27 25. The process of Claim 22 wherein said catalyst comprises a layered catalyst
28 comprising a first layer comprising the zeolite and at least one Group VIII metal,
29 and a second layer comprising an aluminosilicate zeolite which has different
30 shape selectivity than the zeolite of said first layer.
31



- 1 26. The process of Claim 10 wherein the process is a process for preparing a
2 lubricating oil which comprises:
3
4 hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain
5 an effluent comprising a hydrocracked oil; and
6
7 catalytically dewaxing said effluent comprising hydrocracked oil at a
8 temperature of at least about 400°F and at a pressure of from about 15 psig to
9 about 3000 psig in the presence of added hydrogen gas with the catalyst.
10
- 11 27. The process of Claim 26 wherein the zeolite is predominantly in the hydrogen
12 form.
13
- 14 28. The process of Claim 26 wherein the catalyst further comprises at least one
15 Group VIII metal.
16
- 17 29. The process of Claim 10 wherein the process is a process for isomerization
18 dewaxing a raffinate comprising contacting said raffinate in the presence of
19 added hydrogen under isomerization dewaxing conditions with the catalyst.
20
- 21 30. The process of Claim 29 wherein the zeolite is predominantly in the hydrogen
22 form.
23
- 24 31. The process of Claim 29 wherein the catalyst further comprises at least one
25 Group VIII metal.
26
- 27 32. The process of Claim 29 wherein the raffinate is bright stock.
28
- 29 33. The process of Claim 10 wherein the process is a catalytic cracking process
30 comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic
31 cracking conditions in the absence of added hydrogen with the catalyst.



- 1
2 34. The process of Claim 33 wherein the zeolite is predominantly in the hydrogen
3 form.
4
5 35. The process of Claim 33 wherein the catalyst additionally comprises a large pore
6 crystalline cracking component.
7
8 36. The process of Claim 10 wherein the process is a process for oligomerizing
9 olefins comprising contacting an olefin feed under oligomerization conditions
10 with the catalyst.
11
12 37. The process of Claim 10 wherein the process is a process for isomerizing olefins
13 comprising contacting an olefin feed under isomerization conditions with the
14 catalyst.
15
16 38. The process of Claim 37 wherein the olefin feed comprises at least one C₄-C₆
17 normal olefin.
18
19 39. The process of Claim 10 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 40. The process of Claim 39 wherein the metal or metal compound comprises a
2 lanthanide or actinide metal or metal compound.
3
- 4 41. The process of Claim 39 wherein the lower molecular weight hydrocarbon is
5 methane.
6
- 7 42. A process for converting lower alcohols and other oxygenated hydrocarbons
8 comprising contacting said lower alcohol or other oxygenated hydrocarbon
9 under conditions to produce liquid products with a catalyst comprising a zeolite
10 having a mole ratio of about 6-50 of an oxide selected from silicon oxide,
11 germanium oxide and mixtures thereof to an oxide selected from aluminum
12 oxide, gallium oxide, iron oxide, and mixtures thereof and having, after
13 calcination, the X-ray diffraction lines of Table I.
14
- 15 43. In a process for the reduction of oxides of nitrogen contained in a gas stream in
16 the presence of oxygen wherein said process comprises contacting the gas
17 stream with a zeolite, the improvement comprising using as the zeolite a zeolite
18 having a mole ratio of about 6-50 of an oxide selected from silicon oxide,
19 germanium oxide and mixtures thereof to an oxide selected from aluminum
20 oxide, gallium oxide, iron oxide, and mixtures thereof and having, after
21 calcination, the X-ray diffraction lines of Table I.
22
- 23 44. The process of Claim 43 wherein said zeolite contains a metal or metal ions
24 capable of catalyzing the reduction of the oxides of nitrogen.
25
- 26 45. The process of Claim 44 wherein the metal is copper, cobalt or mixtures thereof.
27
- 28 46. The process of Claim 44 wherein the gas stream is the exhaust stream of an
29 internal combustion engine.
30



- 1 47. A process for the separation of nitrogen from a nitrogen-containing gas mixture
2 comprising contacting the mixture with a composition comprising a zeolite
3 having a mole ratio of about 6-50 of an oxide selected from silicon oxide,
4 germanium oxide and mixtures thereof to an oxide selected from aluminum
5 oxide, gallium oxide, iron oxide, and mixtures thereof and having, after
6 calcination, the X-ray diffraction lines of Table I.
7
- 8 48. The process of Claim 47 wherein the gas mixture contains methane.