



1 MOLECULAR SIEVE CIT-6

2 This application is a continuation-in-part of application Serial No. 09/106,598, filed June 29,
3 1998.

4 BACKGROUND OF THE INVENTION5 Field of the Invention

6 The present invention relates to new crystalline molecular sieve CIT-6, a method for
7 preparing CIT-6 using a tetraethylammonium cation templating agent, a method of using
8 CIT-6 as a precursor for making other crystalline molecular sieves, and processes employing
9 CIT-6 as a catalyst.

10 State of the Art

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

18 SUMMARY OF THE INVENTION

19 The present invention is directed to a crystalline molecular sieve with unique
20 properties, referred to herein as "molecular sieve CIT-6" or simply "CIT-6". When the CIT-
21 6 contains a metal (or non-silicon) oxide, such as aluminum oxide, boron oxide, titanium
22 oxide or iron oxide, it is referred to as "catalytically active" CIT-6.

23 The CIT-6 can be made in two forms. The first contains silicon oxide, zinc oxide
24 and optional metal (or non-silicon) oxides (such as aluminum oxide), wherein the zinc is in
25 the crystal framework of the CIT-6. This form of CIT-6 is referred to herein as "Zn-CIT-6".

26 Another form of CIT-6 is where the molecular sieve is composed only of silicon
27 oxide. This form of CIT-6 is referred to herein as "all-Si CIT-6".

28 Zn-CIT-6 and all-Si CIT-6 each have the topology of zeolite beta.

29 In accordance with this invention, there is provided a molecular sieve comprising an
30 oxide of silicon and an oxide of zinc and having the framework topology of zeolite beta,



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1 wherein the molecular sieve contains zinc in its crystal framework.

2 The present invention further provides such a molecular sieve having the topology of
3 zeolite beta, and having a composition, as synthesized and in the anhydrous state, in terms
4 of mole ratios as follows:

5	SiO_2/ZnO	10-100
6	M/SiO_2	0.01-0.1
7	Q/SiO_2	0.07-0.14

8 wherein M is lithium or a mixture of lithium and another alkali metal, and Q comprises a
9 tetraethylammonium cation, wherein the molecular sieve contains zinc in its crystal
10 framework.

11 Also in accordance with this invention there is provided a molecular sieve
12 comprising silicon oxide, zinc oxide, and an oxide selected from aluminum oxide, boron
13 oxide, gallium oxide, iron oxide, titanium oxide, vanadium oxide, zirconium oxide, tin
14 oxide or mixtures thereof and having the framework topology of zeolite beta, wherein the
15 molecular sieve contains zinc in its crystal framework.

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

19	SiO_2/ZnO	10-100
20	SiO_2/W	30-250
21	M/SiO_2	0.01-0.1
22	Q/SiO_2	0.07-0.14

23 wherein W is an oxide of aluminum, boron, gallium, vanadium, iron, titanium or mixtures
24 thereof M is lithium or a mixture of lithium and another alkali metal, and Q comprises a
25 tetraethylammonium cation, wherein the molecular sieve contains zinc in its crystal
26 framework.

27 Also provided in accordance with the present invention is a method of preparing a
28 crystalline material comprising an oxide of silicon and an oxide of zinc and having the
29 framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal
30 framework, said method comprising contacting in admixture under crystallization conditions

sources of said oxides, a source of lithium or a mixture of lithium and another alkali metal and a templating agent comprising a tetraethylammonium cation.

The present invention also provides a method of preparing a crystalline material comprising an oxide of silicon, an oxide of zinc and an oxide selected from aluminum
5 oxide, boron oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide or mixtures thereof and having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal framework, said method comprising contacting in admixture under crystallization conditions sources of said oxides, a source of lithium or a mixture of lithium and another alkali metal and a templating agent comprising a tetraethylammonium
10 cation.

Further provided by the present invention is a method of removing a tetraethylammonium organic template from the pores of a molecular sieve, said molecular sieve comprising silicon oxide and an oxide selected from zinc oxide, aluminum oxide, boron oxide, gallium oxide, iron oxide, titanium oxide, vanadium oxide, zirconium oxide,
15 tin oxide or mixture thereof, said method comprising contacting the molecular sieve with acetic acid, or a mixture of acetic acid and pyridine at elevated temperature for a time sufficient to remove tetraethylammonium organic template from the molecular sieve. In a preferred embodiment, the molecular sieve has the topology of zeolite beta.

The present invention further provides a method of removing an organic template
20 from the pores of a molecular sieve and at the same time removing zinc atoms from the framework of the molecular sieve, wherein the molecular sieve comprises an oxide of silicon, an oxide of zinc and, optionally an oxide selected from aluminum oxide, boron oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide or mixtures thereof, and has the framework topology of zeolite beta, said method comprising contacting the
25 molecular sieve with acetic acid or a mixture of acetic acid and pyridine at elevated temperature for a time sufficient to remove essentially all of the organic template and zinc from the molecular sieve. The present invention also provides the product of this method.

Also provided by the present invention is a method of making a crystalline material comprising (1) contacting in admixture under crystallization conditions a source of silicon
30 oxide, a source of zinc oxide, a source of lithium or a mixture of lithium and another alkali metal and a templating agent comprising a tetraethylammonium cation until a crystalline material comprised of oxides of silicon and zinc and having the topology of zeolite beta is

1 formed, (2) contacting the crystals with acetic acid or a mixture of acetic acid and pyridine
2 at an elevated temperature of about 60°C or less for a time sufficient to remove essentially
3 all of the organic template and zinc from the crystals, and (3) contacting the crystals with a
4 solution containing a source of aluminum, boron, gallium, iron, vanadium, titanium,
5 zirconium, tin or mixtures thereof. The present invention also provides the product of this
6 method.

7 This invention also provides a crystalline molecular sieve having the topology of
8 zeolite beta, a crystal size of less than one micron and a water adsorption capacity of less
9 than 0.05 g/g of molecular sieve.

10 Further provided by the present invention is a crystalline silicate molecular sieve
11 having the topology of zeolite beta, a crystal size of less than one micron and a water
12 adsorption capacity of less than 0.05 g/g of molecular sieve.

13 In addition, the present invention provides a method of preparing a crystalline
14 material having the topology of zeolite beta comprising impregnating a silica-containing
15 mesoporous material with an aqueous solution comprising tetraethylammonium cation in an
16 amount sufficient to form a crystalline product having the topology of zeolite beta, and
17 wherein the water to mesoporous material molar ratio is from about 0.5 to about 2, and
18 subjecting the impregnated mesoporous material to crystallizing conditions of heat and
19 pressure for a time sufficient to form crystals of a material having the topology of zeolite
20 beta.

21 The present invention additionally provides a process for converting hydrocarbons
22 comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with
23 a catalyst comprising a catalytically active molecular sieve comprising silicon oxide, zinc
24 oxide, and an oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide, vanadium oxide,
25 zirconium oxide, tin oxide or mixtures thereof and having the framework topology of zeolite
26 beta, wherein the molecular sieve contains zinc in its crystal framework. The molecular
27 sieve may be predominantly in the hydrogen form, partially acidic or substantially free of
28 acidity, depending on the process.

29 Further provided by the present invention is a hydrocracking process comprising
30 contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst

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1 comprising the catalytically active molecular sieve of this invention, preferably predominantly
2 in the hydrogen form.

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

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

10 The present invention further includes a process for producing a C_{20+} lube oil from a C_{20+}
11 olefin feed comprising isomerizing said olefin feed under isomerization conditions over a
12 catalyst comprising at least one Group VIII metal and the catalytically active molecular sieve
13 of this invention. The molecular sieve may be predominantly in the hydrogen form.

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

24 Also included in the present invention is a process for preparing a lubricating oil which
25 comprises hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an
26 effluent comprising a hydrocracked oil, and catalytically dewaxing said effluent comprising
27 hydrocracked oil at a temperature of at least about 400°F (204°C) and at a gauge pressure of
28 from about 15 psi to about 3000 psi (0.103 to 20.7 MPa) in the presence of added hydrogen gas
29 with a catalyst comprising at least one Group VIII metal and the catalytically active molecular
30 sieve of this

1 invention. The molecular sieve may be predominantly in the hydrogen form.

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

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

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

21 Also provided by the present invention is a process for alkylating an aromatic
22 hydrocarbon which comprises contacting under alkylation conditions at least a molar excess
23 of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid phase
24 conditions and in the presence of a catalyst comprising the catalytically active molecular
25 sieve of this invention, preferably predominantly in the hydrogen form. The olefin may be a
26 C₂ to C₄ olefin, and the aromatic hydrocarbon and olefin may be present in a molar ratio of
27 about 4:1 to about 20:1, respectively. The aromatic hydrocarbon may be selected from the
28 group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

29 Further provided in accordance with this invention is a process for transalkylating an
30 aromatic hydrocarbon which comprises contacting under transalkylating conditions an

1 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid
2 phase conditions and in the presence of a catalyst comprising the catalytically active
3 molecular sieve of this invention, preferably predominantly in the hydrogen form. The
4 aromatic hydrocarbon and the polyalkyl aromatic hydrocarbon may be present in a molar
5 ratio of from about 1:1 to about 25:1, respectively. The aromatic hydrocarbon may be
6 selected from the group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures
7 thereof, and the polyalkyl aromatic hydrocarbon may be a dialkylbenzene.

8 Further provided by this invention is a process to convert paraffins to aromatics
9 which comprises contacting paraffins under conditions which cause paraffins to convert to
10 aromatics with a catalyst comprising the catalytically active molecular sieve of this
11 invention, said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

12 In accordance with this invention there is also provided a process for isomerizing
13 olefins comprising contacting said olefin under conditions which cause isomerization of the
14 olefin with a catalyst comprising the catalytically active molecular sieve of this invention.

15 Further provided in accordance with this invention is a process for isomerizing an
16 isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures of
17 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta-
18 and para-xylenes is obtained, said process comprising contacting said feed under
19 isomerization conditions with a catalyst comprising the catalytically active molecular sieve
20 of this invention.

21 The present invention further provides a process for oligomerizing olefins
22 comprising contacting an olefin feed under oligomerization conditions with a catalyst
23 comprising the catalytically active molecular sieve of this invention.

24 This invention also provides a process for converting lower alcohols and other
25 oxygenated hydrocarbons comprising contacting said lower alcohol or other oxygenated
26 hydrocarbon with a catalyst comprising the catalytically active molecular sieve of this
27 invention under conditions to produce liquid products.

28 Also provided by the present invention is an improved process for the reduction of
29 oxides of nitrogen contained in a gas stream in the presence of oxygen wherein said process
30 comprises contacting the gas stream with a molecular sieve, the improvement comprising

1 using as the molecular sieve, the molecular sieve of this invention. The molecular sieve
2 may contain a metal or metal ions (such as cobalt, copper or mixtures thereof) capable of
3 catalyzing the reduction of the oxides of nitrogen, and may be conducted in the presence of
4 a stoichiometric excess of oxygen. In a preferred embodiment, the gas stream is the exhaust
5 stream of an internal combustion engine.

6 Further provided by the present invention is a method of removing liquid organic
7 compounds from a mixture of liquid organic compounds and water, comprising contacting
8 the mixture with an all-silica molecular sieve having the framework topology of zeolite beta,
9 a crystal size less than one micron and a water adsorption capacity of less than 0.05 g/g of
10 molecular sieve.

11 The present invention further provides a method of removing liquid organic
12 compounds from a mixture of liquid organic compounds and water, comprising contacting
13 the mixture with a molecular sieve comprising an oxide of silicon, an oxide of zinc and,
14 optionally, an oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide,
15 vanadium oxide, titanium oxide, zirconium oxide, tin oxide and mixtures thereof, and
16 having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in
17 its crystal framework.

18 BRIEF DESCRIPTION OF THE DRAWINGS

19 Figures 1 and 2 show the results of water adsorption isotherms at 25°C of the molecular
20 sieves of this invention and beta zeolite.

21 DETAILED DESCRIPTION OF THE INVENTION

22 In preparing CIT-6 molecular sieves, a tetraethylammonium cation ("TEA") is used
23 as a crystallization template (also known as a structure directing agent, or SDA). The anion
24 associated with the cation may be any anion which is not detrimental to the formation of the
25 molecular sieve. Representative anions include halogen, e.g., fluoride, chloride, bromide
26 and iodide, hydroxide, acetate, sulfate, tetrafluoroborate, carboxylate, and the like.
27 Hydroxide is the most preferred anion.

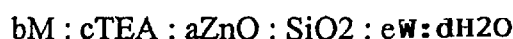
28 In general, Zn-CIT-6 is prepared by contacting an active source of silicon oxide, an
29 active source of zinc oxide, an active source of lithium or mixture of lithium and another
30 alkali metal with the TEA templating agent.

1 Zn-CIT-6 is prepared from a reaction mixture having the following composition:



5 where M is lithium or a mixture of lithium and another alkali metal, $b = 0.05-0.1$; $c = 0.55-$
6 0.7 ; $a = 0.03-0.05$; $d = 30-40$. It is believed the concentrations of Li^+ , Zn^{2+} and TEAOH are
7 critical to the formation of Zn-CIT-6.

8 When it is desired to prepare Zn-CIT-6 containing zinc oxide in combination with
9 another metal oxide, such as aluminum oxide, a reaction mixture having the following
10 composition:



14 where M is lithium or a mixture of lithium and another alkali metal, W is an oxide of
15 aluminum, boron, gallium, vanadium, iron, titanium or mixtures thereof; b, c, a and d are as
16 defined above and $e = 0.005-0.1$.

17 In practice, Zn-CIT-6 is prepared by a process comprising:

18 (a) preparing an aqueous solution containing sources of silicon oxide, zinc oxide,
19 lithium or a mixture of lithium and another alkali metal, TEA having an anionic
20 counterion which is not detrimental to the formation of Zn-CIT-6, and, optionally, an
21 oxide selected from aluminum oxide, boron oxide, gallium oxide, vanadium oxide,
22 iron oxide, titanium oxide or mixtures thereof;

23 (b) maintaining the aqueous solution under conditions sufficient to form crystals
24 of Zn-CIT-6; and

25 (c) recovering the crystals of Zn-CIT-6.

26 The aqueous solution prepared in step (a) should be a clear solution. In some cases, heating
27 a reaction mixture that is a white, cloudy mixture at room temperature will convert the
28 mixture to a clear solution from which Zn-CIT-6 will form.

29 It has been discovered that higher amounts of TEA and lower reaction temperatures
30 favor the formation of Zn-CIT-6.

1 Typical sources of silicon oxide include silicates, silica hydrogel, silicic acid, fumed
2 silica, colloidal silica, tetra-alkyl orthosilicates, and silica hydroxides. Typical sources of
3 zinc oxide include water-soluble zinc salts, such as zinc acetate. Typical sources of
4 aluminum oxide for the reaction mixture include aluminates, alumina, aluminum colloids,
5 aluminum oxide coated on silica sol, and hydrated alumina gels such as $\text{Al}(\text{OH})_3$. Sources
6 of boron, gallium, vanadium, iron and titanium compounds analogous to those listed for
7 silicon and aluminum, and are known in the art.

8 Lithium or a mixture of lithium and another alkali metal is added to the reaction
9 mixture. A variety of sources can be used, such as alkali metal hydroxides and alkali metal
10 carbonates, with lithium hydroxide being particularly preferred. The lithium cation may be
11 part of the as-synthesized crystalline oxide material, in order to balance valence electron
12 charges therein. Other alkali metals which can be used in combination with the lithium
13 include sodium and potassium, with the hydroxides being preferred, provided that lithium is
14 the predominant alkali metal in the combination. The alkali metal (i.e., lithium or mixture
15 of lithium and another alkali metal) may be employed in an amount of from about 0.05 to
16 about 0.1 mole of alkali metal per mole of silica.

17 The reaction mixture is maintained at an elevated temperature until the crystals of
18 the Zn-CIT-6 molecular sieve are formed. The hydrothermal crystallization is usually
19 conducted under autogenous pressure, at about 100°C to less than about 150°C. It has been
20 discovered that higher reaction temperatures, e.g., 150°C and higher, favor the formation of
21 a molecular sieve having the topology of zeolite VPI-8 rather than the desired molecular
22 sieve with the topology of zeolite beta. Preferably, the reaction temperature should be about
23 135°C to 150°C.

24 The crystallization period is typically greater than 1 day to less than 7 days. The Zn-
25 CIT-6 crystals should be recovered from the reaction mixture as soon as they form, since it
26 has been discovered that under some circumstances if they remain in the reaction mixture
27 for too long after formation, they can convert to a molecular sieve having the topology of
28 VPI-8.

29 During the hydrothermal crystallization step, the Zn-CIT-6 crystals can be allowed
30 to nucleate spontaneously from the reaction mixture. The use of Zn-CIT-6 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 Zn-CIT-6 over any undesired phases. When used as seeds, Zn-CIT-6 crystals are added in an amount between 0.1 and 10% of the weight of 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 Zn-CIT-6 molecular sieve crystals. The drying step can be performed at atmospheric pressure or under vacuum.

Zn-CIT-6 has a composition, as synthesized and in the anhydrous state, in terms of mole ratios, shown in Table B below.

TABLE B

As-Synthesized Zn-CIT-6

SiO ₂ /ZnO	10-100
M/SiO ₂	0.01-0.1
Q/SiO ₂	0.07-0.14

where M and Q are as defined above.

Zn-CIT-6 can also have a composition, as synthesized and in the anhydrous state, in terms of mole ratios, shown in Table C below.

TABLE C

As-Synthesized Zn-CIT-6

SiO ₂ /ZnO	10-100
SiO ₂ /W	30-250
M/SiO ₂	0.01-0.1
Q/SiO ₂	0.07-0.14

where W, M and Q are as defined above.

Solid state ²⁹Si NMR analysis and acidity measurements have shown that at least part of the zinc is in the framework of the Zn-CIT-6 crystals. Indeed, in one embodiment, the Zn-CIT-6 crystal framework contains only silicon, zinc and oxygen atoms, i.e., there are no

1 other metals in this form of Zn-CIT-6.

2 Once the Zn-CIT-6 crystals have been formed and recovered, the organic template
3 should be removed. This is typically done by calcining the crystals at high temperature until
4 the organic template is removed. However, it has been discovered that calcination can be
5 avoided by extracting the organic template from the molecular sieve. This extraction
6 technique has advantages over calcination. For example, no calcination equipment is
7 needed. Also, the organic template is not destroyed by the extraction, so it may be possible
8 to recycle it, thereby reducing the cost of making the molecular sieve.

9 The organic template can be removed by contacting the Zn-CIT-6 crystals with
10 acetic acid or a mixture of acetic acid and pyridine at a temperature of about 80°C to about
11 135°C for a period sufficient to remove essentially all of the organic template from the
12 crystals (typically about two days). At the same time, the zinc is removed from the crystals,
13 and they convert to all-Si CIT-6, i.e., an all-silica crystal having the framework topology of
14 zeolite beta. As shown by water adsorption isotherms, all-Si CIT-6 is highly hydrophobic.
15 ²⁹Si NMR analysis further shows that the crystal lattice has virtually no defects.

16 It has quite surprisingly been found that CIT-6 prepared as described above, i.e., the
17 CIT-6 is prepared and then contacted with acetic acid or a mixture of acetic acid and
18 pyridine at a temperature of about 80°C to about 135°C (referred to herein as "extraction"),
19 is highly hydrophobic. This is in marked contrast to CIT-6 or beta zeolite in which the
20 organic template has been removed by calcination.

21 This phenomenon is illustrated in the Figure 1. Five water adsorption isotherms are
22 shown for the following materials:

- 23 (a) All-Si-CIT-6 prepared by extraction at 135°C.
- 24 (b) Zn-CIT-6 prepared using calcination
- 25 (c) Silicoalumino-CIT-6 extracted at 60°C followed by insertion of
26 aluminum
- 27 (d) Silicoalumino-CIT-6 prepared using aluminum oxide in the reaction
28 mixture with the product extracted at 135°C
- 29 (e) Calcined all-silica beta zeolite

30 The data indicate that the extracted aluminum-containing CIT-6 (sample d) is more

1 hydrophobic than the sample prepared via aluminum insertion (sample c) and far more
2 hydrophobic than the calcined zeolite beta (sample e). Calcined Zn-CIT-6 (sample b)
3 likewise is far more hydrophobic than calcined zeolite beta, with extracted all-Si-CIT-6
4 (sample a) exhibiting the highest degree of hydrophobicity.

5 Alternatively, the extraction or removal of the organic template from Zn-CIT-6 can
6 be accomplished by contacting the Zn-CIT-6 crystal with acetic acid or a mixture of acetic
7 acid and pyridine at an elevated temperature of about 60°C or less for a period sufficient to
8 remove essentially all of the organic template from the crystals.

9 It has also been found that this latter extraction technique also removes some or all
10 of the zinc atoms from the crystal framework. However, in this case the resultant molecular
11 sieve contains internal silanol groups and other metals (or non-silicon atoms), such as
12 aluminum, boron, gallium, vanadium, iron, titanium, zirconium, tin or mixtures thereof can
13 be inserted into the crystal framework, replacing the zinc.

14 The metal can be inserted into the crystal framework by contacting the molecular
15 sieve with a solution containing a source, such as a salt, of the desired metal. Although a
16 wide variety of sources can be employed, chlorides and other halides, acetates, nitrates, and
17 sulfates are particularly preferred. The preferred metals (or non-silicon atoms) are
18 aluminum, boron, gallium, iron, titanium, vanadium, zirconium, tin, zinc and mixtures
19 thereof. Representative techniques for inserting the metal are disclosed in a wide variety of
20 patents including U. S. Patent No. 3,140,249, issued July 7, 1964 to Plank et al.; U. S.
21 Patent No. 3,140,251, issued on July 7, 1964 to Plank et al.; and U. S. Patent No. 3,140,253,
22 issued on July 7, 1964 to Plank et al., each of which is incorporated by reference herein. By
23 way of example, aluminum can be inserted into the molecular sieve in place of some or all
24 of the zinc by extracting the zinc (at about 60°C) as described above, and then contacting the
25 molecular sieve with an aluminum nitrate solution in about a 1 : 2 : 50 weight ratio of sieve :
26 aluminum nitrate : water at about 80°C for about one day.

27 As an alternative to making Zn-CIT-6, extracting the zinc and inserting, e.g.,
28 aluminum, an aluminosilicate can be made directly by synthesizing aluminozincosilicate
29 CIT-6 as described above and in **Example 27**, and then extracting the zinc at the higher
30 extraction temperature (135°C). This removes the zinc from the CIT-6 and leaves an

1 aluminosilicate molecular sieve with the topology of zeolite beta. ²⁷Al NMR analysis of
2 aluminosilicates made in this manner shows that the aluminum remains in the crystal
3 framework.

4 All-Si CIT-6 can be made by preparing Zn-CIT-6 as described above, followed by
5 extraction of the zinc. It has surprisingly been found that all-Si CIT-6 made by this method
6 has a much lower water adsorption capacity than all-silica zeolite beta made by traditional
7 methods. The all-Si CIT-6 made by this method also has a crystal size of less than about
8 one micron, whereas all-silica zeolite beta made by traditional method has a crystal size of
9 greater than one micron, e.g., on the order of five microns. Furthermore, the all-Si CIT-6
10 made by this method has essentially no defect (i.e., Si-OH instead of Si-O-Si) sites, whereas
11 all-silica zeolite beta made by traditional methods does contain defect sites that adsorb
12 water.

13 A series of silica-containing mesoporous materials denoted M41S have been
14 reported. These materials have been further classified, e.g., MCM-41 (hexagonal), MCM-
15 48 (cubic) and others. These materials have uniform pores of 1.5 – 10 nm diameters, and
16 are made by using a variety of surfactants as structure-directing agents. Non-silicon atom,
17 e.g., Al, B, Ga, Ti, V, Zr, Fe, Mn, Sn, Zn, Cu and Nb, containing mesoporous materials have
18 also been prepared.

19 The inorganic portion of MCM-41 resembles amorphous silicas rather than
20 crystalline molecular sieves in terms of the local structure and bonding, but has many
21 peculiar properties. It possesses uniformly sized mesopores with thin walls (around 10
22 Angstroms) and shows hydrophobic adsorption behavior.

23 It has now been discovered that zeolites having the topology of zeolite beta, in either
24 all-silica form or in a form containing silica and metal (or non-silicon) oxide(s), can be
25 made using the inorganic portion of ordered, mesoporous materials as reagents. The
26 mesoporous materials may be all-silica, or they may contain silica and metal (or non-
27 silicon) oxide(s), e.g., aluminum oxide. Examples of such mesoporous materials include,
28 but are not limited to, MCM-41 and MCM-48.

29 The mesoporous materials are used in combination with tetraethylammonium cation
30 organic templating agent, e.g., tetraethylammonium hydroxide (TEAOH). It has been found

1 that, in order to assure the zeolite beta has essentially no defect sites, the reaction mixture
2 containing the mesoporous material and TEAOH should be in the form of a "dry gel". The
3 dry gel is made by impregnating the mesoporous material with an aqueous solution of
4 TEAOH, allowing the resulting impregnated material to dry for about one day at room
5 temperature. The thus-impregnated product should have a molar ratio of water to
6 mesoporous material of about 0.5 to about 2, and contain sufficient TEAOH to cause
7 formation of the beta structure. The impregnated material is then subject to crystallization
8 conditions in an autoclave. The resulting crystalline product can either be calcined to
9 remove the TEAOH, or it can be subjected to the extraction technique described above, thus
10 assuring the product will be essentially defect-free.

11 If it is desired that the final product contain silicon oxide and a metal (or non-silicon)
12 oxide, the mesoporous starting material can contain silicon oxide and the desired metal (or
13 non-silicon) oxide. Metal oxides such as aluminum oxide, titanium oxide, vanadium oxide,
14 zinc oxide, zirconium oxide, and magnesium oxide, as well as non-silicon oxides such as
15 boron oxide, can be incorporated into the zeolite beta structure in this manner.

16 The molecular sieves made by either of these two techniques are highly
17 hydrophobic. Figure 2 shows the results of water adsorption isotherms for calcined all-silica
18 beta zeolite (line 1), all-Si CIT-6 made from MCM-41 and subjected to extraction rather
19 than calcination (line 2), and Zn-CIT-6 made by extraction (line 3). As can be seen, the
20 water adsorption capacities of both the all-Si CIT-6 and Zn-CIT-6 are substantially lower
21 than that of calcined all-silica beta zeolite.

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

26 Metals may also be introduced into the molecular sieve by replacing some of the
27 cations in the molecular sieve with metal cations via standard ion exchange techniques (see,
28 for example, U.S. Patent Nos. 3,140,249 issued July 7, 1964 to Plank et al.; 3,140,251
29 issued July 7, 1964 to Plank et al.; and 3,140,253 issued July 7, 1964 to Plank et al.).

30 Typical replacing cations can include metal cations, e.g., rare earth, Group IA, Group IIA

1 and Group VIII metals, as well as their mixtures. Of the replacing metallic cations, cations
2 of metals such as rare earth, Mn, Ca, Mg, Zn, Cd, Pt, Pd, Ni, Co, Ti, Al, Sn, and Fe are
3 particularly preferred.

4 The hydrogen, ammonium, and metal components can be ion-exchanged into the
5 catalytically active CIT-6. The molecular sieve can also be impregnated with the metals, or,
6 the metals can be physically and intimately admixed with the molecular sieve using standard
7 methods known to the art.

8 Typical ion-exchange techniques involve contacting the synthetic molecular sieve
9 with a solution containing a salt of the desired replacing cation or cations. Although a wide
10 variety of salts can be employed, chlorides and other halides, acetates, nitrates, and sulfates
11 are particularly preferred. The molecular sieve is usually calcined prior to the ion-exchange
12 procedure to remove the organic matter present in the channels and on the surface, since this
13 results in a more effective ion exchange. Representative ion exchange techniques are
14 disclosed in a wide variety of patents including U.S. Patent Nos. 3,140,249 issued on July 7,
15 1964 to Plank et al.; 3,140,251 issued on July 7, 1964 to Plank et al.; and 3,140,253 issued
16 on July 7, 1964 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 65°C
19 to about 200°C. After washing, the molecular sieve can be calcined in air or inert gas at
20 temperatures ranging from about 200°C to about 800°C for periods of time ranging from 1
21 to 48 hours, or more, to produce a catalytically active product especially useful in
22 hydrocarbon conversion processes.

23 Regardless of the cations present in the synthesized form of CIT-6, the spatial
24 arrangement of the atoms which form the basic crystal lattice of the molecular sieve remains
25 essentially unchanged.

26 Catalytically active CIT-6 can be formed into a wide variety of physical shapes.
27 Generally speaking, the molecular sieve can be in the form of a powder, a granule, or a
28 molded 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 catalyst is
30 molded, such as by extrusion with an organic binder, the molecular sieve can be extruded

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1 before drying, or, dried or partially dried and then extruded.

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

10 Hydrocarbon Conversion Processes

11 The catalytically active CIT-6 molecular sieves are useful in hydrocarbon conversion
12 reactions. Hydrocarbon conversion reactions are chemical and catalytic processes in which
13 carbon containing compounds are changed to different carbon containing compounds.
14 Examples of hydrocarbon conversion reactions in which catalytically active CIT-6 is
15 expected to be useful include hydrocracking, dewaxing, catalytic cracking and olefin and
16 aromatics formation reactions. The catalysts are also expected to be useful in other
17 petroleum refining and hydrocarbon conversion reactions such as polymerizing and
18 oligomerizing olefinic or acetylenic compounds such as isobutylene and butene-1,
19 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and
20 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene, xylenes and
21 higher methylbenzenes and oxidation reactions. Also included are rearrangement reactions
22 to make various naphthalene derivatives. The catalytically active CIT-6 catalysts may have
23 high selectivity, and under hydrocarbon conversion conditions can provide a high
24 percentage of desired products relative to total products.

25 The catalytically active CIT-6 molecular sieves can be used in processing
26 hydrocarbonaceous feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds
27 and can be from many different sources, such as virgin petroleum fractions, recycle
28 petroleum fractions, shale oil, liquefied coal, tar sand oil, synthetic paraffins from NAO,
29 recycled plastic feedstocks and, in general, can be any carbon containing feedstock
30 susceptible to zeolitic catalytic reactions. Depending on the type of processing the

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hydrocarbonaceous feed is to undergo, the feed can contain metal or be free of metals, it can also have high or low nitrogen or sulfur impurities. It can be appreciated, however, that in general processing will be more efficient (and the catalyst more active) the lower the metal, nitrogen, and sulfur content of the feedstock.

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

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

Depending upon the type of reaction which is catalyzed, the molecular sieve may be predominantly in the hydrogen form, partially acidic or substantially free of acidity. 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.

The following table indicates typical reaction conditions which may be employed when using catalysts comprising catalytically active CIT-6 in the hydrocarbon conversion reactions of this invention. Preferred conditions are indicated in parentheses. Metric equivalents for the pressure values are shown in italics.

Process	Temp., °C	Pressure	LHSV
Hydrocracking	175-485	0.5-350 bar <i>0.05-35MPa</i>	0.1-30
Dewaxing	200-475 (250-450)	15-3000 psig <i>0.103-20.7MPa</i> (200-3000psig <i>1.38-20.7MPa</i>)	0.1-20 (0.2-10)
Aromatics formation	400-600 (480-550)	atm.-10 bar <i>0.101-1.0MPa</i>	0.1-15
Cat. cracking	127-885	Subatm. ⁻¹ (atm.-5 atm. <i>0.103-0.51MPa</i>)	0.5-50
Oligomerization	232-649 ² 10-232 ⁴ (27-204) ⁴	0.1-50 atm. <i>0.01-5.1MPa</i> ^{2,3} - -	0.2-50 ² 0.05-20 ⁵ (0.1-10) ⁵
Paraffins to aromatics	100-700	0-1000 psig <i>0-6.89MPa</i>	0.5-40 ⁵
Condensation of alcohols	260-538	0.5-1000 psig <i>3.4kPa-6.89MPa</i>	0.5-50 ⁵

isomerization	(315-566) ² 38-371 ⁴	(1-5 atm) ² 1-200 atm. ⁴	(0.5-50) ⁵ 0.5-50
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¹ Several hundred atmospheres

² Gas phase reaction

³ Hydrocarbon partial pressure

⁴ Liquid phase reaction

⁵ WHSV

Other reaction conditions and parameters are provided below.

Hydrocracking

Using a catalyst which comprises catalytically active CIT-6, 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.

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

Dewaxing

Catalytically active CIT-6, preferably predominantly in the hydrogen form, can be used to dewax hydrocarbonaceous feeds by selectively removing straight chain paraffins. Typically, the viscosity index of the dewaxed product is improved (compared to the waxy

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1 feed) when the waxy feed is contacted with catalytically active CIT-6 under isomerization
2 dewaxing conditions.

3 The catalytic dewaxing conditions are dependent in large measure on the feed used and
4 upon the desired pour point. Hydrogen is preferably present in the reaction zone during the
5 catalytic dewaxing process. The hydrogen to feed ratio in standard cubic feet per barrel
6 (SCF/bbl) is typically between about 500 and about 30,000 SCF/bbl (89 to 5340m³ hydrogen
7 per m³ of feed), preferably about 1000 to about 20,000 SCF/bbl (178-3560m³ hydrogen per m³
8 of feed). Generally, hydrogen will be separated from the product and recycled to the reaction
9 zone. Typical feedstocks include light gas oil, heavy gas oils and reduced crudes boiling above
10 about 350°F (177°C).

11 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil feedstock
12 boiling above about 350°F (177°C) and containing straight chain and slightly branched chain
13 hydrocarbons by contacting the hydrocarbon oil feedstock in the presence of added hydrogen
14 gas at a hydrogen pressure of about 15-3000 psi (0.103-20.7MPa) with a catalyst comprising
15 catalytically active CIT-6 and at least one Group VIII metal.

16 The catalytically active CIT-6 hydrodewaxing catalyst may optionally contain a
17 hydrogenation component of the type commonly employed in dewaxing catalysts. See the
18 aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for examples of these
19 hydrogenation components.

20 The hydrogenation component is present in an effective amount to provide an effective
21 hydrodewaxing and hydroisomerization catalyst preferably in the range of from about 0.05 to
22 5% by weight. The catalyst may be run in such a mode to increase isodewaxing at the expense
23 of cracking reactions.

24 The feed may be hydrocracked, followed by dewaxing. This type of two stage process
25 and typical hydrocracking conditions are described in U.S. Patent No. 4,921,594, issued May 1,
26 1990 to Miller, which is incorporated herein by reference in its entirety.

27 Catalytically active CIT-6 may also be utilized as a dewaxing catalyst in the form of a
28 layered catalyst. That is, the catalyst comprises a first layer comprising catalytically active
29 molecular sieve CIT-6 and at least one Group VIII metal, and a second layer comprising an
30 aluminosilicate zeolite which is more shape selective than catalytically active molecular sieve
31 CIT-6. The use of layered catalysts is disclosed in U.S. Patent No. 5,149,421, issued

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1 September 22, 1992 to Miller, which is incorporated by reference herein in its entirety. The
2 layering may also include a bed of catalytically active CIT-6 layered with a non-zeolitic
3 component designed for either hydrocracking or hydrofinishing.

4 Catalytically active CIT-6 may also be used to dewax raffinates, including bright stock,
5 under conditions such as those disclosed in U. S. Patent No. 4,181,598, issued January 1, 1980
6 to Gillespie et al., which is incorporated by reference herein in its entirety.

7 It is often desirable to use mild hydrogenation (sometimes referred to as hydrofinishing)
8 to produce more stable dewaxed products. The hydrofinishing step can be performed either
9 before or after the dewaxing step, and preferably after. Hydrofinishing is typically conducted at
10 temperatures ranging from about 190°C to about 340°C at gauge pressures of from about
11 400 psi (2.76MPa) to about 3000 psi (206.8MPa) at space velocities (LHSV) between about 0.1
12 and 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl (71.2-267m³ hydrogen per m³
13 of feed). The hydrogenation catalyst employed must be active enough not only to hydrogenate
14 the olefins, diolefins and color bodies which may be present, but also to reduce the aromatic
15 content. Suitable hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued
16 May 1, 1990 to Miller, which is incorporated by reference herein in its entirety. The
17 hydrofinishing step is beneficial in preparing an acceptably stable product (e.g., a lubricating
18 oil) since dewaxed products prepared from hydrocracked stocks tend to be unstable to air and
19 light and tend to form sludges spontaneously and quickly.

20 Lube oil may be prepared using catalytically active CIT-6. For example, a C₂₀₊ lube oil
21 may be made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising catalytically active
22 CIT-6 in the hydrogen form and at least one Group VIII metal. Alternatively, the lubricating
23 oil may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to
24 obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing the effluent at a
25 temperature of at least about 400°F (204°C) and at a gauge pressure of from about 15 psi to
26 about 3000 psi (0.103-20.7MPa) in the presence of added hydrogen gas with a catalyst
27 comprising catalytically active CIT-6 in the hydrogen form and at least one Group VIII metal.

28 Aromatics Formation

29 Catalytically active CIT-6 can be used to convert light straight run naphthas and similar
30 mixtures to highly aromatic mixtures. Thus, normal and slightly branched chained

1 hydrocarbons, preferably having a boiling range above about 40°C and less than about
2 200°C, can be converted to products having a substantial higher octane aromatics content by
3 contacting the hydrocarbon feed with a catalyst comprising catalytically active CIT-6. It is
4 also possible to convert heavier feeds into BTX or naphthalene derivatives of value using a
5 catalyst comprising catalytically active CIT-6.

6 The conversion catalyst preferably contains a Group VIII metal compound to have
7 sufficient activity for commercial use. By Group VIII metal compound as used herein is
8 meant the metal itself or a compound thereof. The Group VIII noble metals and their
9 compounds, platinum, palladium, and iridium, or combinations thereof can be used.
10 Rhenium or tin or a mixture thereof may also be used in conjunction with the Group VIII
11 metal compound and preferably a noble metal compound. The most preferred metal is
12 platinum. The amount of Group VIII metal present in the conversion catalyst should be
13 within the normal range of use in reforming catalysts, from about 0.05 to 2.0 weight percent,
14 preferably 0.2 to 0.8 weight percent.

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

20 The preferred alkali metals are sodium, potassium, rubidium and cesium.

21 Catalytic Cracking

22 Hydrocarbon cracking stocks can be catalytically cracked in the absence of hydrogen
23 using catalytically active CIT-6, preferably predominantly in the hydrogen form.

24 When catalytically active CIT-6 is used as a catalytic cracking catalyst in the
25 absence of hydrogen, the catalyst may be employed in conjunction with traditional cracking
26 catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking
27 catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of these
28 traditional cracking catalysts are disclosed in the aforementioned U.S. Patent No. 4,910,006
29 and U.S. Patent No 5,316,753. When a traditional cracking catalyst (TC) component is
30 employed, the relative weight ratio of the TC to the catalytically active CIT-6 is generally

1 between about 1:10 and about 500:1, desirably between about 1:10 and about 200:1,
2 preferably between about 1:2 and about 50:1, and most preferably is between about 1:1 and
3 about 20:1. The novel molecular sieve and/or the traditional cracking component may be
4 further ion exchanged with rare earth ions to modify selectivity.

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

8 Alkylation and Transalkylation

9 Catalytically active CIT-6 can be used in a process for the alkylation or
10 transalkylation of an aromatic hydrocarbon. The process comprises contacting the aromatic
11 hydrocarbon with a C₂ to C₁₆ olefin alkylating agent or a polyalkyl aromatic hydrocarbon
12 transalkylating agent, under at least partial liquid phase conditions, and in the presence of a
13 catalyst comprising catalytically active CIT-6.

14 Catalytically active CIT-6 can also be used for removing benzene from gasoline by
15 alkylating the benzene as described above and removing the alkylated product from the
16 gasoline.

17 For high catalytic activity, the catalytically active CIT-6 molecular sieve should be
18 predominantly in its hydrogen ion form. It is preferred that, after calcination, at least 80% of
19 the cation sites are occupied by hydrogen ions and/or rare earth ions.

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

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

30 When transalkylation is desired, the transalkylating agent is a polyalkyl aromatic

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1 hydrocarbon containing two or more alkyl groups that each may have from 2 to about 4 carbon
2 atoms. For example, suitable polyalkyl aromatic hydrocarbons include di-, tri- and tetra-alkyl
3 aromatic hydrocarbons, such as diethylbenzene, triethylbenzene, diethylmethylbenzene
4 (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene, dibutylbenzene, and the like.
5 Preferred polyalkyl aromatic hydrocarbons are the dialkyl benzenes. A particularly preferred
6 polyalkyl aromatic hydrocarbon is di-isopropylbenzene.

7 When alkylation is the process conducted, reaction conditions are as follows. The
8 aromatic hydrocarbon feed should be present in stoichiometric excess. It is preferred that molar
9 ratio of aromatics to olefins be greater than four-to-one to prevent rapid catalyst fouling. The
10 reaction temperature may range from 100°F to 600°F (38°C to 316°C), preferably 250°F to
11 450°F (121°C to 232°C). The reaction pressure should be sufficient to maintain at least a
12 partial liquid phase in order to retard catalyst fouling. This is typically a gauge pressure of
13 50 psi to 1000 psi (0.344-6.9MPa) depending on the feedstock and reaction temperature.
14 Contact time may range from 10 seconds to 10 hours, but is usually from 5 minutes to an hour.
15 The weight hourly space velocity (WHSV), in terms of grams (pounds) of aromatic
16 hydrocarbon and olefin per gram (pound) of catalyst per hour, is generally within the range of
17 about 0.5 to 50.

18 When transalkylation is the process conducted, the molar ratio of aromatic hydrocarbon
19 will generally range from about 1:1 to 25:1, and preferably from about 2:1 to 20:1. The
20 reaction temperature may range from about 100°F to 600°F (38°C to 316°C), but it is
21 preferably about 250°F to 450°F (121°C to 232°C). The reaction pressure should be sufficient
22 to maintain at least a partial liquid phase, typically a gauge pressure in the range of about 50 psi
23 to 1000 psi (0.344-6.9MPa), preferably 300 psi to 600 psi (2.07-4.14MPa). The weight hourly
24 space velocity will range from about 0.1 to 10. U.S. Patent No. 5,082,990 issued on January
25 21, 1992 to Hsieh, et al. describes such processes and is incorporated herein by reference.

26 Isomerization of Olefins

27 Catalytically active CIT-6 can be used to isomerize olefins. The feed stream is a
28 hydrocarbon stream containing at least one C₄₋₆ olefin, preferably a C₄₋₆ normal olefin, more
29 preferably normal butene. Normal butene as used in this specification means all forms of
30 normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons
31 other than normal butene or other C₄₋₆ normal olefins will be present in the feed stream.

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1 These other hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and
2 inert gases.

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

10 The process is carried out under isomerization conditions. The hydrocarbon feed is
11 contacted in a vapor phase with a catalyst comprising the catalytically active CIT-6. The
12 process may be carried out generally at a temperature from about 625°F to about 950°F (329-
13 510°C), for butenes, preferably from about 700°F to about 900°F (371-482°C), and about
14 350°F to about 650°F (177-343°C) for pentenes and hexenes. The pressure ranges from
15 subatmospheric to a gauge pressure of about 200 psi (1.38MPa), preferably a gauge pressure of
16 from about 15 psi (0.103MPa) to about 200 psi (1.38MPa), and more preferably from about
17 1 psi (6.9kPa) to about 150 psi (1.03MPa).

18 The liquid hourly space velocity during contacting is generally from about 0.1 to about
19 50 hr⁻¹, based on the hydrocarbon feed, preferably from about 0.1 to about 20 hr⁻¹, more
20 preferably from about 0.2 to about 10 hr⁻¹, most preferably from about 1 to about 5 hr⁻¹. A
21 hydrogen/hydrocarbon molar ratio is maintained from about 0 to about 30 or higher. The
22 hydrogen can be added directly to the feed stream or directly to the isomerization zone. The
23 reaction is preferably substantially free of water, typically less than about two weight percent
24 based on the feed. The process can be carried out in a packed bed reactor, a fixed bed, fluidized
25 bed reactor, or a moving bed reactor. The bed of the catalyst can move upward or downward.
26 The mole percent conversion of, e.g., normal butene to iso-butene is at least 10, preferably at
27 least 25, and more preferably at least 35.

28 Conversion of Paraffins to Aromatics

29 Catalytically active CIT-6 can be used to convert light gas C₂-C₆ paraffins to higher
30 molecular weight hydrocarbons including aromatic compounds. Preferably, the molecular
31 sieve will contain a catalyst metal or metal oxide wherein said metal is selected from the

1 group consisting of Groups IB, IIB, VIII and IIIA of the Periodic Table. Preferably, the
2 metal is gallium, niobium, indium or zinc in the range of from about 0.05 to 5% by weight.

3 Xylene Isomerization

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

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

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

23 Oligomerization

24 It is expected that catalytically active CIT-6 can also be used to oligomerize straight
25 and branched chain olefins having from about 2 to 21 and preferably 2-5 carbon atoms. The
26 oligomers which are the products of the process are medium to heavy olefins which are
27 useful for both fuels, i.e., gasoline or a gasoline blending stock and chemicals.

28 The oligomerization process comprises contacting the olefin feedstock in the
29 gaseous or liquid phase with a catalyst comprising catalytically active CIT-6.

30 The molecular sieve can have the original cations associated therewith replaced by a

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

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

14 Condensation of Alcohols

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

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

27 Other Uses for CIT-6

28 CIT-6 can also be used as an adsorbent with high selectivities based on molecular
29 sieve behavior and also based upon preferential hydrocarbon packing within the pores.

30 CIT-6 is a hydrophobic material that can be used to remove some organic

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1 compounds from water.

2 CIT-6 may also be used for the catalytic reduction of the oxides of nitrogen in a gas
3 stream. Typically, the gas stream also contains oxygen, often a stoichiometric excess
4 thereof. Also, the CIT-6 may contain a metal or metal ions within or on it which are capable
5 of catalyzing the reduction of the nitrogen oxides. Examples of such metals or metal ions
6 include copper, cobalt and mixtures thereof.

7 One example of such a process for the catalytic reduction of oxides of nitrogen in the
8 presence of a molecular sieve is disclosed in U.S. Patent No. 4,297,328, issued October 27,
9 1981 to Ritscher et al., which is incorporated by reference herein. There, the catalytic
10 process is the combustion of carbon monoxide and hydrocarbons and the catalytic reduction
11 of the oxides of nitrogen contained in a gas stream, such as the exhaust gas from an internal
12 combustion engine. The molecular sieve used is metal ion-exchanged, doped or loaded
13 sufficiently so as to provide an effective amount of catalytic copper metal or copper ions
14 within or on the molecular sieve. In addition, the process is conducted in an excess of
15 oxidant, e.g., oxygen.

16 Oxidation

17 Titanium-containing CIT-6 may be used as a catalyst in oxidation reactions.

18 The oxidizing agent employed in the oxidation processes of this invention is a
19 hydrogen peroxide source such as hydrogen peroxide (H_2O_2) or a hydrogen peroxide
20 precursor (i.e., a compound which under the oxidation reaction conditions is capable of
21 generating or liberating hydrogen peroxide).

22 The amount of hydrogen peroxide relative to the amount of substrate is not critical,
23 but must be sufficient to cause oxidation of at least some of the substrate. Typically, the
24 molar ratio of hydrogen peroxide to substrate is from about 100:1 to about 1:100, preferably
25 10:1 to about 1:10. When the substrate is an olefin containing more than one carbon-carbon
26 double bond, additional hydrogen peroxide may be required. Theoretically, one equivalent
27 of hydrogen peroxide is required to oxidize one equivalent of a mono-unsaturated substrate,
28 but it may be desirable to employ an excess of one reactant to optimize selectivity to the
29 epoxide. In particular, the use of a moderate to large excess (e.g., 50 to 200%) of olefin
30 relative to hydrogen peroxide may be advantageous for certain substrates.

1 If desired, a solvent may additionally be present during the oxidation reaction in
2 order to dissolve the reactants other than the Ti-containing CIT-6, to provide better
3 temperature control, or to favorably influence the oxidation rates and selectivities. The
4 solvent, if present, may comprise from 1 to 99 weight percent of the total oxidation reaction
5 mixture and is preferably selected such that it is a liquid at the oxidation reaction
6 temperature. Organic compounds having boiling points at atmospheric pressure of from
7 about 50°C to about 150°C are generally preferred for use. Excess hydrocarbon may serve
8 as a solvent or diluent. Illustrative examples of other suitable solvents include, but are not
9 limited to, ketones (e.g., acetone, methyl ethyl ketone, acetophenone), ethers (e.g.,
10 tetrahydrofuran, butyl ether), nitriles (e.g., acetonitrile), aliphatic and aromatic
11 hydrocarbons, halogenated hydrocarbons, and alcohols (e.g., methanol, ethanol, isopropyl
12 alcohol, t-butyl alcohol, alpha-methyl benzyl alcohol, cyclohexanol). More than one type of
13 solvent may be utilized. Water may also be employed as a solvent or diluent.

14 The reaction temperature is not critical, but should be sufficient to accomplish
15 substantial conversion of the substrate within a reasonably short period of time. It is
16 generally advantageous to carry out the reaction to achieve as high a hydrogen peroxide
17 conversion as possible, preferably at least about 50%, more preferably at least about 90%,
18 most preferably at least about 95%, consistent with reasonable selectivities. The optimum
19 reaction temperature will be influenced by catalyst activity, substrate reactivity, reactant
20 concentrations, and type of solvent employed, among other factors, but typically will be in a
21 range of from about 0°C to about 150°C (more preferably from about 25°C to about 120°C).
22 Reaction or residence times from about one minute to about 48 hours (more desirably from
23 about ten minutes to about eight hours) will typically be appropriate, depending upon the
24 above-identified variables. Although subatmospheric pressures can be employed, the
25 reaction is preferably performed at atmospheric or at elevated pressure (typically, between
26 one and 100 atmospheres), especially when the boiling point of the substrate is below the
27 oxidation reaction temperature. Generally, it is desirable to pressurize the reaction vessel
28 sufficiently to maintain the reaction components as a liquid phase mixture. Most (over
29 50%) of the substrate should preferably be present in the liquid phase.

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1 The oxidation process of this invention may be carried out in a batch, continuous, or
2 semi-continuous manner using any appropriate type of reaction vessel or apparatus such as a
3 fixed bed, transport bed, fluidized bed, stirred slurry, or CSTR reactor. The reactants may
4 be combined all at once or sequentially. For example, the hydrogen peroxide or hydrogen
5 peroxide precursor may be added incrementally to the reaction zone. The hydrogen
6 peroxide could also be generated in situ within the same reactor zone where oxidation is
7 taking place.

8 Once the oxidation has been carried out to the desired degree of conversion, the
9 oxidized product may be separated and recovered from the reaction mixture using any
10 appropriate technique such as fractional distillation, extractive distillation, liquid-liquid
11 extraction, crystallization, or the like.

12 Additional details for oxidation reactions are disclosed in U. S. Patent No.
13 5,869,706, issued February 9, 1999 to Dartt and Davis, which is incorporated herein by
14 reference in its entirety.

15 Vanadium-containing CIT-6 may be used as a catalyst in the
16 oxidation/dehydrogenation of hydrocarbons. For example, vanadium-containing CIT-6 may
17 be used to partially (or completely) oxidize hydrocarbons in the presence of oxygen (air) or
18 hydrogen peroxide. The oxidation may either be complete, i.e., oxidizing the hydrocarbon
19 to carbon dioxide, or partial, as in the oxidation of propane to propylene. The reaction is
20 conducted under conditions that yield the desired degree of oxidation, and are known in the
21 art.

22 EXAMPLES

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

24 Example 1-25

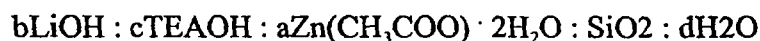
25 Synthesis of Zn-CIT-6

26 Zn-CIT-6 reaction mixtures are prepared by the following method. After the organic
27 and inorganic cations are dissolved in distilled water, zinc acetate dihydrate is added. Next,
28 silica is added and the mixture is stirred for two hours.

29 The starting mixtures are each charged into Teflon-lined, stainless autoclaves and
30 heated statically in convection ovens. The products are collected by vacuum filtration,

washed with distilled water, and dried in air at room temperature. In order to remove the occluded organic molecules, the product is heated in air to 540°C within six hours and maintained at this temperature for six hours. An as-made Zn-CIT-6 is treated with 1 M aqueous ammonium nitrate solution at 80°C for ten hours. The treated sample is recovered by vacuum filtration and washed with distilled water. This procedure is repeated four times. The final material is dried in air at room temperature.

Using the above procedure, the products indicated below are made from a reaction mixture having the following composition:



Example No.	b	c	a	D	Temp. (°C)	Days	Product
1	0.05	0.55	0.03	30	150	3	CIT-6
2	0.05	0.55	0.03	30	150	5	CIT-6 + VPI-8
3	0.05	0.55	0.03	30	150	7	VPI-8
4	0.2	0.4	0.03	30	150	3	VPI-8
5	0.05	0.55	0.03	30	175	2	Amorph.
6	0.05	0.55	0.03	30	175	3	VPI-8
7	0.05	0.55	0.03	30	135	9	CIT-6
8	0.05	0.55	0.03	30	135	15	CIT-6
9	0.05	0.55	0.03	30	135	18	VPI-8
10	0.05	0.45	0.03	30	150	6	VPI-8
11	0.05	0.55	0.03	30	150	4	CIT-6
12	0.05	0.55	0.03	30	150	6	VPI-8
13	0.05	0.6	0.03	30	150	4	CIT-6

1

14	0.05	0.6	0.03	30	150	29	VPI-8 + small amnt. CIT-6
15	0.05	0.65	0.03	30	150	4	CIT-6
16	0.05	0.65	0.03	30	150	17	CIT-6 + small amnt. VPI-8
17	0.05	0.65	0.03	40	150	4	CIT-6
18	0.05 ¹	0.65	0.03	30	150	14	Amorph.
19	0.05	0.6	0.01	30	150	11	Amorph. + small amnt. MFI
20	0.05	0.6	0.01	30	150	18	MFI
21	0.05	0.55	-	30	150	5	MTW
22	0.05	0.65	0.05	30	150	4	CIT-6 + small amnt. VPI-8
23	0.02	0.6	0.03	30	150	17	Amorph.
24	0.1	0.6	0.03	30	150	4	Unknown + CIT- 6
25 ^{2,3}	0.05	0.7	0.03	30	150	4	CIT-6

2

3

¹NaOH used instead of LiOH.

4

²Silica source is Cab-O-Sil M5 fumed silica. All others are HS-30.

5

³Milky white mixture heated at 80°C for three hours to get a clear solution.

14 03 05 00
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1 The results above demonstrate that (1) too long a reaction time can produce VPI-8
2 instead of Zn-CIT-6 (Ex. 3,9, 12, 14 and 17); (2) too high a reaction temperature may not
3 produce Zn-CIT-6 (Ex. 5 and 6); (3) the presence and concentration of lithium is critical to
4 formation of Zn-CIT-6 (Ex. 4, 18 and 22); and the presence and concentration of zinc is critical
5 to formation of Zn-CIT-6 (Ex. 19, 20 and 21).

6 Example 26

7 Synthesis of Zincoaluminosilicate CIT-6

8 A solution of tetraethylammonium hydroxide (4.10 grams of a 35 wt.% solution) is
9 added to 3.34 grams of water. To this is added 0.018 gram of LiOH, 0.098 gram of zinc acetate
10 dihydrate, and 0.056 gram of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ and the resulting mixture stirred. Three grams
11 of Ludox HS-30 silica is added and the resulting mixture stirred for two hours. The resulting
12 solution is charged into a Teflon-lined autoclave, and heated (statically) at 150°C for four days.
13 The product was CIT-6 containing both zinc and aluminum in the crystal framework.

14 Example 27

15 Extraction of TEA and Zinc

16 The TEA and zinc are extracted from the CIT-6 prepared in Example 26 by contacting 0.1 gram
17 of the aluminosilicate CIT-6 with a solution containing 6 ml acetic acid, 1 ml pyridine and
18 10 ml water at 135°C for two days. The TEA and zinc are extracted from the CIT-6, but the
19 aluminum remains in the crystal framework, as shown by ^{27}Al NMR.

20 Example 28

21 Cyclohexane Adsorption

22 The adsorption amount of vapor-phase cyclohexane (99.5%, EM) for Zn-CIT-6 is measured at
23 25°C using a McBaine-Bakr balance. Prior to the adsorption experiment, calcined samples of
24 CIT-6 are dehydrated at 350°C under vacuum for five hours. The saturation pressure, P_0 , of
25 cyclohexane is 97.5 mm Hg (13.0 kPa). The adsorption is performed at a cyclohexane pressure
26 of 30 mm Hg (3.0 kPa). The amount of adsorbed cyclohexane of the Zn-CIT-6 sample is 0.16
27 ml/g. This value is slightly smaller than that of aluminosilicate beta (0.22 ml/g).

11 03 05 00
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Example 29

Extraction of TEA and Zinc

The TEA and zinc are extracted from Zn-CIT-6 by contacting 0.1 gram of CIT-6 with a solution containing 6 ml acetic acid, 0.1 ml pyridine and 10 ml water at 60°C for three days.

Example 30

Insertion of Aluminum

Aluminum is inserted into the product of Example 29 by contacting the product with an aqueous solution of aluminum nitrate at a 1 : 2 : 50 weight ratio of Zn-CIT-6 : aluminum nitrate : water at 80°C for one day.

Example 31

Insertion of Titanium

Titanium is inserted into the product of Example 29 by contacting the product with 1.5 ml 1M TiCl₄ toluene solution and 10 ml toluene at 80°C for 12 hours under nitrogen atmosphere. After treatment, the sample is filtrated, washed with acetone and dried. UV analysis of the resultant product shows that titanium is inserted in the product.

Example 32

Preparation of Pd-Zn-CIT-6

2.84 grams of Zn-CIT-6 synthesized as in Example 1 is calcined to 540°C in a mixture of air and nitrogen, and subsequently ion-exchanged once with ammonium nitrate at 85°C for two hours, recovered and dried to 300°C. Pd acetylacetonate (0.0286 gms) in toluene (2.25 ml) is admitted into a sealed bottle in which the heated Zn-CIT-6 has been placed. This provides for some vacuum at room temperature. The bottle is manually shaken while the solution is admitted by syringe. The wetted solid is allowed to stand overnight. Next the material is calcined to 425°C in air.

Example 33

Catalytic Activity

The Pd-Zn-CIT-6 prepared in Example 30 is loaded as 24-40 mesh particles into a stainless steel reactor. 0.50 Gram is packed into a 3/8 inch (9.53mm) stainless steel tube with alundum on both sides of the zeolite bed. A Lindburg furnace is used to heat the reactor tube.

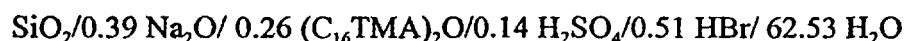
-35-

Helium is introduced into the reactor tube at 10 cc/min. and at atmospheric pressure. The reactor is heated to about 372°C, and a 50/50 (w/w) feed of n-hexane and 3-methylpentane is introduced into the reactor at a rate of 8 µl/min. Feed delivery is made via a Brownlee pump. Direct sampling into a gas chromatograph begins after 10 minutes of feed introduction. At 800°F (427°C) and 10 minutes on stream the catalyst gives 47% conversion with the products being about 1/3 aromatics, 1/3 isomerized C₆ and a third olefins from dehydrogenation. There is a few percent cracked product. There is no preference for reaction of either isomer.

Example 34

Synthesis of All-Si CIT-6 From All-silica Mesoporous Material

MCM-41 is prepared using the following gel composition where C₁₆TMA is hexadecyltrimethylammonium:



The gel is placed in an autoclave at 120°C for three days. The resulting MCM-41 crystals are recovered and calcined at 540°C for ten hours.

The calcined MCM-41 (0.1 gram) is impregnated with 0.3 gram of 35 wt.% TEAOH aqueous solution and dried at room temperature for one day (TEAOH/Si = 0.4, H₂O/Si = ~2). The resulting powder is charged into an autoclave and heated at 150°C for seven days. The product is all-silica zeolite beta.

0.1 Gram of the all-silica zeolite beta (still containing TEAOH) is treated with a mixture of 6 ml acetic acid and 10 ml water at 135°C for two days. Almost all of the TEAOH is removed from the material, and it retains the beta zeolite structure. The resulting product is highly hydrophobic.

Example 35

Synthesis of Si-MCM-41

Si-MCM-41 materials (Si-1-MCM-41) are prepared by adding 2.4 grams of 29 wt.% NH₄OH solution (EM) to 26.4 grams of 29 wt.% hexadecyltrimethylammonium chloride (C₁₆TMACl) solution. This solution is combined with 2.3 grams of tetramethylammonium hydroxide pentahydrate (TMAOH·5H₂O), 20 grams of tetramethylammonium silicate (10 wt.% SiO₂, TMA/Si = 0.5) and 4.5 grams of fumed silica (Cab-O-Sil M-5 from Cabot)

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1 under stirring. The composition of the resulting gel is:

2 $\text{SiO}_2 : 0.11 (\text{C}_{16}\text{TMA})_2\text{O} : 0.09 (\text{NH}_4)_2\text{O} : 0.11 \text{HCl} : 19.3 \text{H}_2\text{O}.$

3 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated
4 statically at 140°C for three days. The product is collected by vacuum filtration, washed
5 with water and dried in air at room temperature. In order to remove occluded molecules, the
6 as-made sample is calcined in air at 550°C within six hours and maintained at this
7 temperature for six hours. The product is identified as MCM-41 and designated Si-1-MCM-
8 41.

9 Example 36

10 Synthesis of Si-MCM-41

11 Concentrated H_2SO_4 (1.2 grams) is added dropwise to 20 grams of sodium silicate (10.8
12 wt.% Na_2O , 27.0 wt.% SiO_2 and 62.2 wt.% H_2O) in 42.8 grams of water under stirring.
13 Next, 16.8 grams of $\text{C}_{16}\text{TMABr}$ in 50.3 grams of water is added to the solution and the
14 resulting mixture is stirred for two hours. The resulting gel has the composition:

15 $\text{SiO}_2 : 0.26 (\text{C}_{16}\text{TMA})_2\text{O} : 0.39 \text{Na}_2\text{O} : 0.14 \text{H}_2\text{SO}_4 : 0.51 \text{HBr} : 62.5 \text{H}_2\text{O}.$

16 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated
17 statically at 120°C for three days. The product is collected by vacuum filtration, washed
18 with water and dried in air at room temperature and calcined in air at 550°C within six hours
19 and maintained at this temperature for six hours to remove the organic molecules. The
20 organic molecules occluded in the pores of the material are also removed by contacting the
21 as-made sample with 1M HCl solution in diethyl ether at room temperature. The product is
22 identified as MCM-41 and designated Si-2-MCM-41.

23 Example 37

24 Synthesis of MCM-48

25 NaOH (0.8 gram) is dissolved in 44 grams of water. To this solution is added 8.89
26 grams of $\text{C}_{16}\text{TMABr}$ and finally 8.33 grams of TEOS is added to it. The resulting mixture is
27 stirred at room temperature for two hours. The mixture has the following composition:

28 $\text{SiO}_2 : 0.61 \text{C}_{16}\text{TMABr} : 60 \text{H}_2\text{O} : 0.5 \text{NaOH} : 4 \text{EtOH}.$

29 The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated
30 statically at 105°C for three days. The product is collected by vacuum filtration, washed

with water and dried in air at room temperature and calcined in air at 550°C within six hours and maintained at this temperature for six hours to remove the organic molecules. The product is identified as MCM-48.

Example 38

Synthesis of Al-Containing MCM-41

2.4 Grams of 29 wt.% NH_4OH solution is added to 26.4 grams of 29 wt.% $\text{C}_{16}\text{TMACl}$ solution. To this, 0.37 gram of sodium aluminate (54 wt.% Al_2O_3 , 41 wt.% Na_2O , 5 wt.% H_2O) is added and the solution is combined with 2.3 grams of $\text{TMAOH} \cdot 5\text{H}_2\text{O}$, 20 grams of tetramethylammonium silicate (10 wt.% SiO_2 , $\text{TMA/Si} = 0.5$) and 4.5 grams of fumed silica (Cab-O-Sil M-5) under stirring. The resulting gel composition is:

$\text{SiO}_2 : 0.02 \text{ Al}_2\text{O}_3 : 0.02 \text{ Na}_2\text{O} : 0.11 (\text{C}_{16}\text{TMA})_2\text{O} : 0.13 (\text{TMA})_2\text{O} : 0.09 (\text{NH}_4)_2\text{O} : 0.22 \text{ HCl} : 19.3 \text{ H}_2\text{O}$.

The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated statically at 135°C for three days. The product is collected by vacuum filtration, washed with water and dried in air at room temperature. In order to remove the occluded molecules, the as-made sample is calcined in air at 550°C within six hours and maintained at this temperature for six hours. The product is identified as MCM-41 containing aluminum in its framework, and is designated Al-MCM-41.

Example 39

Synthesis of B-Containing MCM-41

A mixture of 1 gram of fumed silica (Cab-O-Sil M5) and 6.4 grams of water are mixed under vigorous stirring. After ten minutes of mixing, a solution of 3.3 grams of $\text{C}_{16}\text{TMABr}$ in 21.7 grams of water is added to this slurry. After another ten minutes of stirring, a third solution containing 2.9 grams of tetramethylammonium silicate solution (10 wt.% SiO_2 , $\text{TMA/Si} = 0.5$) and 1.4 grams of sodium silicate is added to the slurry. H_3BO_3 (0.034 gram) is added and the mixing continued for 30 minutes. The resulting gel has the composition:

$\text{SiO}_2 : 0.02 \text{ H}_3\text{BO}_3 : 0.16 \text{ C}_{16} \text{ TMABr} : 0.085 \text{ Na}_2\text{O} : 63 \text{ H}_2\text{O}$.

The reaction mixture is charged into a Teflon-lined, stainless steel autoclave and heated statically at 100°C for one day. The product is collected by vacuum filtration, washed with

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1 water and dried in air at room temperature and calcined under nitrogen for temperatures up
2 to 550°C within six hours and maintained at this temperature for two hours before slowly
3 switching from nitrogen to air. After an additional four hours at 500°C, the sample is cooled
4 to room temperature. The product is identified as MCM-41 containing boron in its
5 framework, and is designated B-MCM-41.

6 Example 40

7 Synthesis of V-Containing MCM-41

8 6.24 Grams of tetraethyl orthosilicate (TEOS), 0.16 gram of vanadyl acetylacetonate,
9 9 grams of ethanol, and 1.8 of isopropyl alcohol are mixed together (Solution A). A second
10 solution (B) contains 1.5 grams of dodecylamine ($C_{12}A$), 0.6 gram of 1 N HCl and 19 grams
11 of water. Solution A is added slowly to Solution B under vigorous stirring. The resulting
12 reaction mixture has the following composition:

13 $SiO_2 : 0.02 VO(acac)_2 : 0.27 C_{12}A : 0.02 HCl : 36 H_2O : 10.5 EtOH : 1 iPrOH$.

14 The mixture is stirred at room temperature for 12 hours. The product is collected by
15 vacuum filtration, washed with water and dried in air at room temperature and calcined in
16 air at 550°C within six hours and maintained at this temperature for six hours to remove
17 organic molecules. The product is identified as MCM-41 containing vanadium in its
18 framework, and is designated V-MCM-41.

19 Example 41

20 Synthesis of Zr-Containing MCM-41

21 Solution A is prepared by mixing 10.42 grams of TEOS, 0.47 gram of zirconium
22 propoxide (70 wt.% solution in 1-propanol). A second solution (B) contains 4 grams of
23 octadecylamine ($C_{18}A$), 15 grams of ethanol and 27 grams of water. Solution A is added
24 slowly to Solution B under vigorous stirring. The resulting reaction mixture has the
25 following composition:

26 $SiO_2 : 0.02 ZrO_2 : 0.3 C_{18}A : 30 H_2O : 10.5 EtOH : 2.5 PrOH$.

27 The mixture is stirred at room temperature for 12 hours. The product is collected by
28 vacuum filtration, washed with water and dried in air at room temperature and calcined in
29 air at 550°C within six hours and maintained at this temperature for six hours to remove
30 organic molecules. The product is identified as MCM-41 containing zirconium in its

framework, and is designated Zr-MCM-41.

Example 42

Synthesis of Zn-Containing MCM-41

0.18 Gram of zinc acetate dihydrate ($\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$) and 0.8 gram of NaOH are dissolved in 44 grams of water. 8.89 Grams of $\text{C}_{16}\text{TMABr}$ is added to this solution and finally 8.33 grams of TEOS is added. The resulting mixture is stirred at room temperature for two hours. The reaction mixture has the following composition:

$\text{SiO}_2 : 0.02 \text{ Zn}(\text{OAc})_2 : 0.61 \text{ C}_{16}\text{TMABr} : 60 \text{ H}_2\text{O} : 0.5 \text{ NaOH} : 4 \text{ EtOH}$

The reaction mixture was charged into a Teflon-line, stainless steel autoclave and heated statically at 105°C for three days. The product is collected by vacuum filtration, washed with water and dried in air at room temperature and calcined in air at 550°C within six hours and maintained at this temperature for six hours to remove organic molecules. The product is identified as MCM-41 containing zinc in its framework, and is designated Zn-MCM-41.

Examples 43-49

Synthesis of CIT-6 from Mesoporous Materials

Calcined, mesoporous materials are each in turn impregnated with 35 wt.% TEAOH aqueous solution and dried at room temperature for 12 hours. The resulting powder is charged into a Teflon-lined autoclave and heated at 150°C statically. The product is washed with distilled water and dried in air at room temperature. In order to remove the occluded molecules, the as-made sample is calcined in air at 550°C within six hours and maintained at this temperature for six hours. The organic molecules occluded in the pores of the as-made sample are also removed by contacting the as-made sample with acetic acid at 135°C for two days.

A typical procedure is as follows: 0.1 gram of calcined Si-MCM-41 is impregnated with 0.3 gram of 35 wt.% TEAOH aqueous solution ($\text{TEAOH}/\text{Si} = 0.4$) and dried at room temperature for 12 hours ($\text{H}_2\text{O}/\text{SiO}_2$ molar ratio is about 1.5). The resulting powder is heated at 150°C for one week in an autoclave. The yield of crystalline solid after calcination is about 80%. Conditions for specific materials are shown in the table below.

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Example Number	Non-Si Atom Containing Mesoporous Material ^(a)	Impregnated TEAOH/Si Ratio	Conditions	Result ^(a)
43	Al-MCM-41 (26)	0.4	150°C x 7 days	Al-Beta (26)
44	B-MCM-41 (54)	0.4	150°C x 7 days	B-Beta (62)
45	Ti-MCM-41 (47)	0.4	150°C x 7 days	Ti-Beta (47)
46	Si-MCM-41	0.4 + Ti (0.02)	150°C x 7 days	Si-Beta (63)
47	V-MCM-41 (59)	0.4	150°C x 7 days	V-Beta (148)
48	Zr-MCM-41 (47)	0.4	150°C x 7 days	Zr-Beta (73)
49	Zn-MCM-41 (33)	0.4	150°C x 7 days	Zn-Beta (30)

(a) Values in parentheses are the Si/Y molar ratios (Y = Al, B, Ti, V, Zr or Zn) in the as-made product, measured by elemental analysis.

The as-made materials are then calcined to remove the TEA cations.

Example 50

Synthesis of Ti-Containing CIT-6

Calcined Si-MCM-41 is impregnated with a solution containing titanium tetraisopropoxide (Ti/Si = 0.02) and a 35 wt.% aqueous solution of TEAOH (TEA/Si = 0.4). The impregnated solid is treated as described above in Examples 43-49. The resulting product is CIT-6 containing titanium in its framework.

The results above clearly indicate that a highly crystalline all-Si-CIT-6 is formed from Si-MCM-41 using TEAOH as the organic template (or structure directing agent).

When Na⁺ was added to the reaction mixture, it was found that all-Si-CIT-6 is formed faster

1 than in the absence of Na^+ . It was also found that when fumed silica was used as the silica
2 source, only amorphous phases were obtained, even if Na^+ is added. Conventional
3 hydrothermal reaction ($\text{H}_2\text{O}/\text{Si} = 20$) yields only amorphous products as well. When using
4 MCM-48 as a silica source, all-Si-CIT-6 is also formed. These data indicate that
5 mesoporous silicas such as MCM-41 and MCM-48 can be used to synthesize all-Si-CIT-6,
6 that Na^+ cations promote the conversion to all-Si-CIT-6 and that the mesoporous materials
7 can also be used to prepare CIT-6.

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WHAT IS CLAIMED IS:

1. A molecular sieve comprising an oxide of silicon and an oxide of zinc and having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal framework.

2. The molecular sieve of claim 1 wherein the oxides of silicon and zinc are the only oxides in the framework of the molecular sieve.

3. A molecular sieve having the topology of zeolite beta, and having a composition, as synthesized and in the anhydrous state, in terms of mole ratios as follows:

SiO_2/ZnO 10-100

M/SiO_2 0.01-0.1

Q/SiO_2 0.07-0.14

wherein M is lithium or a mixture of lithium and another alkali metal; and Q comprises a tetraethylammonium cation, wherein the molecular sieve contains zinc in its crystal framework.

4. A molecular sieve comprising silicon oxide, zinc oxide, and an oxide selected from aluminum oxide, boron oxide, gallium oxide, iron oxide, titanium oxide, vanadium oxide, zirconium oxide, tin oxide or mixtures thereof and having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal framework.

5. The molecular sieve of claim 4 comprising silicon oxide, zinc oxide and aluminum oxide.

6. The molecular sieve of claim 4 comprising silicon oxide, zinc oxide and boron oxide.

1 7. The molecular sieve of claim 4 comprising silicon oxide, zinc oxide and gallium
2 oxide.

3
4 8. The molecular sieve of claim 4 comprising silicon oxide, zinc oxide and titanium
5 oxide.

6
7 9. A molecular sieve having the topology of zeolite beta, and having a composition, as
8 synthesized and in the anhydrous state, in terms of mole ratios as follows:

9 SiO_2/ZnO 10-100

10 SiO_2/W 30-250

11 M/SiO_2 0.01-0.1

12 Q/SiO_2 0.07-0.14

13
14 wherein W is an oxide of aluminum, boron, gallium, vanadium, iron, titanium or
15 mixtures thereof, M is lithium or a mixture of lithium and another alkali metal; and Q
16 comprises a tetraethylammonium cation, wherein the molecular sieve contains zinc in
17 its crystal framework.

18
19 10. A method of preparing a crystalline material comprising an oxide of silicon and an
20 oxide of zinc and having the framework topology of zeolite beta, wherein the
21 molecular sieve contains zinc in its crystal framework, said method comprising
22 contacting in admixture under crystallization conditions sources of said oxides, a
23 source of lithium or a mixture of lithium and another alkali metal and a templating
24 agent comprising a tetraethylammonium cation.

25
26 11. The method of claim 10 wherein the source of the alkali metal contains no alkali metal
27 other than lithium.

28
29 12. The method of claim 10 wherein the source of alkali metal contains lithium and
30 another alkali metal.

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13. A method of preparing a crystalline material comprising an oxide of silicon, an oxide of zinc and an oxide selected from aluminum oxide, boron oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide or mixtures thereof and having the framework topology of zeolite beta, wherein the molecular sieve contains zinc in its crystal framework, said method comprising contacting in admixture under crystallization conditions sources of said oxides, a source of lithium or a mixture of lithium and another alkali metal and a templating agent comprising a tetraethylammonium cation.
14. A method of removing a tetraethylammonium organic template from the pores of a molecular sieve, said molecular sieve comprising silicon oxide and an oxide selected from zinc oxide, aluminum oxide, boron oxide, gallium oxide, iron oxide, titanium oxide, vanadium oxide, zirconium oxide, tin oxide, or mixtures thereof, said method comprising contacting the molecular sieve with acetic acid or a mixture of acetic acid and pyridine at elevated temperature for a time sufficient to remove tetraethylammonium organic template from the molecular sieve.
15. The method of claim 14 wherein the molecular sieve has the topology of zeolite beta.
16. The method of claim 14 wherein the elevated temperature is 60°C or less.
17. The method of claim 14 wherein the elevated temperature is from about 80°C to about 135°C.
18. A method of removing an organic template from the pores of a molecular sieve and at the same time removing zinc atoms from the framework of the molecular sieve, wherein the molecular sieve comprises an oxide of silicon, an oxide of zinc and, optionally, an oxide selected from aluminum oxide, boron oxide, gallium oxide, vanadium oxide, iron oxide, titanium oxide and mixtures thereof, and having the framework topology of zeolite beta, said method comprising contacting the molecular sieve with acetic acid or a mixture of acetic acid and pyridine at elevated temperature

1 for a time sufficient to remove essentially all of the organic template and zinc from the
2 molecular sieve.

3
4 19. The method of claim 18 wherein the elevated temperature is about 60°C or less.

5
6 20. The method of claim 18 wherein the elevated temperature is from about 80°C to about
7 135°C.

8
9 21. A method of making a crystalline material comprising (1) contacting in admixture
10 under crystallization conditions a source of silicon oxide, a source of zinc oxide, a
11 source of lithium or a mixture of lithium and another alkali metal and a templating
12 agent comprising a tetraethylammonium cation until a crystalline material comprised
13 of oxides of silicon and zinc and having the topology of zeolite beta are formed, (2)
14 contacting the crystals with acetic acid or a mixture of acetic acid and pyridine at an
15 elevated temperature of about 60°C or less for a time sufficient to remove essentially
16 all of the organic template and zinc from the crystals, and (3) contacting the crystals
17 with a solution containing a source of aluminum, boron, gallium, iron, titanium,
18 vanadium, zirconium, tin or mixtures thereof.

19
20 22. The product produced by the method of claim 18.

21
22 23. The product produced by the method of claim 21.

23
24 24. A crystalline molecular sieve having the topology of zeolite beta, a crystal size of less
25 than one micron and a water adsorption capacity of less than 0.05 g/g of molecular
26 sieve.

27
28 25. A crystalline silicate molecular sieve having the topology of zeolite beta, a crystal size
29 of less than one micron and a water adsorption capacity of less than 0.05 g/g of
30 molecular sieve.

1

2 26. A method of preparing a crystalline material having the topology of zeolite beta
3 comprising impregnating a silica-containing mesoporous material with an aqueous
4 solution of tetraethylammonium cation in an amount sufficient to form a crystalline
5 product having the topology of zeolite beta, and wherein the water to mesoporous
6 material molar ratio is from about 0.5 to about 2, and subjecting the impregnated
7 mesoporous material to crystallizing conditions of heat and pressure for a time
8 sufficient to form crystals of a material having the topology of zeolite beta.

9

10 27. The method of claim 26 wherein the mesoporous material is an all-silica material.

11

12 28. The method of claim 26 wherein the mesoporous material comprises, in addition to
13 silica, an oxide selected from the group consisting of aluminum oxide, boron oxide,
14 titanium oxide, vanadium oxide, zirconium oxide, zinc oxide and mixtures thereof.

15

16 29. The method of claim 27 wherein the mesoporous material is MCM-41 or MCM-48.

17

18 30. The method of claim 28 wherein the mesoporous material is MCM-41 or MCM-48.

19

20 31. A process for converting hydrocarbons comprising contacting a hydrocarbonaceous
21 feed at hydrocarbon converting conditions with a catalyst comprising a molecular
22 sieve comprising an silicon oxide, zinc oxide, and an oxide selected from aluminum
23 oxide, boron oxide, gallium oxide, iron oxide, vanadium oxide, zirconium oxide, tin
24 oxide or mixtures thereof and having the framework topology of zeolite beta.

25

26 32. The process of claim 31 wherein the molecular sieve is predominantly in the hydrogen
27 form.

28

29 33. The process of claim 31 wherein the molecular sieve is substantially free of acidity.

30

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- 1 34. The process of claim 31 wherein the process is a hydrocracking process comprising
2 contacting the catalyst with a hydrocarbon feedstock under hydrocracking conditions.
3
- 4 35. The process of claim 34 wherein the molecular sieve is predominantly in the hydrogen
5 form.
6
- 7 36. The process of claim 31 wherein the process is a dewaxing process comprising contacting
8 the catalyst with a hydrocarbon feedstock under dewaxing conditions.
9
- 10 37. The process of claim 36 wherein the molecular sieve is predominantly in the hydrogen
11 form.
12
- 13 38. The process of claim 31 wherein the process is a process for improving the viscosity
14 index of a dewaxed product of waxy hydrocarbon feeds comprising contacting the catalyst
15 with a waxy hydrocarbon feed under isomerization dewaxing conditions.
16
- 17 39. The process of claim 38 wherein the molecular sieve is predominantly in the hydrogen
18 form.
19
- 20 40. The process of claim 31 wherein the process is a process for producing a C₂₀₊ lube oil
21 from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization
22 conditions over the catalyst.
23
- 24 41. The process of claim 40 wherein the molecular sieve is predominantly in the hydrogen
25 form.
26
- 27 42. The process of claim 40 wherein the catalyst further comprises at least one Group VIII
28 metal.
29
- 30 43. The process of claim 31 wherein the process is a process for catalytically dewaxing a

14 03 05 00
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hydrocarbon oil feedstock boiling above about 350°F (177°C) and containing straight chain and slightly branched chain hydrocarbons comprising contacting said hydrocarbon oil feedstock in the presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi (0.103-20.7 MPa) under dewaxing conditions with the catalyst.

44. The process of claim 43 wherein the molecular sieve is predominantly in the hydrogen form.

45. The process of claim 43 wherein the catalyst further comprises at least one Group VIII metal.

46. The process of claim 43 wherein said catalyst comprises a layered catalyst comprising a first layer comprising the molecular sieve and at least one Group VIII metal, and a second layer comprising an aluminosilicate zeolite which is more shape selective than the molecular sieve of said first layer.

47. The process of claim 31 wherein the process is a process for preparing a lubricating oil which comprises:

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

catalytically dewaxing said effluent comprising hydrocracked oil at a temperature of at least about 400°F (204°C) and at a gauge pressure of from about 15 psi (103kPa) to about 3000 psi (20.7MPa) in the presence of added hydrogen gas with the catalyst.

48. The process of claim 47 wherein the molecular sieve is predominantly in the hydrogen form.

49. The process of claim 47 wherein the catalyst further comprises at least one Group VIII metal.

- 1 50. The process of claim 31 wherein the process is a process for isomerization dewaxing a
2 raffinate comprising contacting said raffinate in the presence of added hydrogen under
3 isomerization dewaxing conditions with the catalyst.
4
- 5 51. The process of claim 50 wherein the molecular sieve is predominantly in the hydrogen
6 form.
7
- 8 52. The process of claim 50 wherein the catalyst further comprises at least one Group VIII
9 metal.
10
- 11 53. The process of claim 50 wherein the raffinate is bright stock.
12
- 13 54. The process of claim 31 wherein the process is a process for increasing the octane of a
14 hydrocarbon feedstock to produce a product having an increased aromatics content
15 comprising contacting a hydrocarbonaceous feedstock which comprises normal and
16 slightly branched hydrocarbons having a boiling range above about 40°C and less than
17 about 200°C under aromatic conversion conditions with the catalyst.
18
- 19 55. The process of claim 54 wherein the molecular sieve is substantially free of acid.
20
- 21 56. The process of claim 54 wherein the molecular sieve contains a Group VIII metal
22 component.
23
- 24 57. The process of claim 31 wherein the process is a catalytic cracking process comprising
25 contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking
26 conditions in the absence of added hydrogen with the catalyst.
27
- 28 58. The process of claim 57 wherein the molecular sieve is predominantly in the hydrogen
29 form.
30

- 1 59. The process of claim 57 wherein the catalyst additionally comprises a large pore
2 crystalline cracking component.
3
- 4 60. The process of claim 31 wherein the process is a process for alkylating an aromatic
5 hydrocarbon which comprises contacting under alkylation conditions at least a molar
6 excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid
7 phase conditions and in the presence of the catalyst.
8
- 9 61. The process of claim 60 wherein the molecular sieve is predominantly in the hydrogen
10 form.
11
- 12 62. The process of claim 60 wherein the olefin is a C₂ to C₄ olefin.
13
- 14 63. The process of claim 62 wherein the aromatic hydrocarbon and olefin are present in a
15 molar ratio of about 4:1 to about 20:1, respectively.
16
- 17 64. The process of claim 62 wherein the aromatic hydrocarbon is selected from the group
18 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.
19
- 20 65. The process of claim 31 wherein the process is a process for transalkylating an
21 aromatic hydrocarbon which comprises contacting under transalkylating conditions an
22 aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial
23 liquid phase conditions and in the presence of the catalyst.
24
- 25 66. The process of claim 65 wherein the molecular sieve is predominantly in the hydrogen
26 form.
27
- 28 67. The process of claim 65 wherein the aromatic hydrocarbon and the polyalkyl aromatic
29 hydrocarbon are present in a molar ratio of from about 1:1 to about 25:1, respectively.
30
- 31 68. The process of claim 65 wherein the aromatic hydrocarbon is selected from the group
32 consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.
33
- 34 69. The process of claim 65 wherein the polyalkyl aromatic hydrocarbon is a

1 dialkylbenzene.

2
3 70. The process of claim 31 wherein the process is a process to convert paraffins to
4 aromatics which comprises contacting paraffins under conditions which cause
5 paraffins to convert to aromatics with a catalyst comprising the molecular sieve and
6 gallium, zinc, or a compound of gallium or zinc.

7
8 71. The process of claim 31 wherein the process is a process for isomerizing olefins
9 comprising contacting said olefin under conditions which cause isomerization of the
10 olefin with the catalyst.

11
12 72. The process of claim 31 wherein the process is a process for isomerizing an
13 isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures of
14 xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-,
15 meta and para-xylenes is obtained, said process comprising contacting said feed under
16 isomerization conditions with the catalyst.

17
18 73. The process of claim 31 wherein the process is a process for oligomerizing olefins
19 comprising contacting an olefin feed under oligomerization conditions with the
20 catalyst.

21
22 74. A process for converting lower alcohols and other oxygenated hydrocarbons
23 comprising contacting said lower alcohol or other oxygenated hydrocarbon under
24 conditions to produce liquid products with a catalyst comprising a molecular sieve
25 comprising silicon oxide, zinc oxide, and an oxide selected from aluminum oxide,
26 boron oxide, gallium oxide, iron oxide or mixtures thereof and having the framework
27 topology of zeolite beta.

28
29 75. In a process for the reduction of oxides of nitrogen contained in a gas stream in the
30 presence of oxygen wherein said process comprises contacting the gas stream with a

1 molecular sieve, the improvement comprising using as the molecular sieve a molecular
2 sieve comprising silicon oxide, zinc oxide, and an oxide selected from aluminum
3 oxide, boron oxide, gallium oxide, iron oxide, vanadium oxide, zirconium oxide, tin
4 oxide or mixtures thereof and having the framework topology of zeolite beta, wherein
5 the molecular sieve contains zinc in its crystal framework.

6

7 76. The process of claim 75 wherein said molecular sieve contains a metal or metal ions
8 capable of catalyzing the reduction of the oxides of nitrogen.

9

10 77. The process of claim 76 wherein the metal is copper, cobalt or mixtures thereof.

11

12 78. The process of claim 76 wherein the gas stream is the exhaust stream of an internal
13 combustion engine.

14

15 79. A method of removing liquid organic compounds from a mixture of liquid organic
16 compounds and water, comprising contacting the mixture with an all-silica molecular
17 sieve having the framework topology of zeolite beta, a crystal size less than one
18 micron and a water adsorption capacity of less than 0.05 g/g of molecular sieve.

19

20 80. A method of removing liquid organic compounds from a mixture of liquid organic
21 compounds and water, comprising contacting the mixture with a molecular sieve
22 comprising an oxide of silicon, an oxide of zinc and, optionally, an oxide selected
23 from aluminum oxide, boron oxide, gallium oxide, iron oxide and mixtures thereof,
24 and having the framework topology of zeolite beta, wherein the molecular sieve
25 contains zinc in its crystal framework.

26