

MOLECULAR SIEVE SSZ-75 COMPOSITION OF MATTER AND SYNTHESIS THEREOF

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to new crystalline molecular sieve SSZ-75, a method for preparing SSZ-75 using a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication as a structure directing agent ("SDA") and uses for SSZ-75.

STATE OF THE ART

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

SUMMARY OF THE INVENTION

In a first aspect, there is provided a crystalline molecular sieve having STI topology, a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

In a second aspect, there is provided a crystalline molecular sieve having STI topology, having a composition comprising, as synthesized and in the anhydrous state, in terms of mole ratios, the following:

$\text{SiO}_2 / \text{X}_c\text{O}_d$	at least 15
$\text{M}_{2/n} / \text{SiO}_2$	0 – 0.03
Q / SiO_2	0.02 – 0.08
F / SiO_2	0.01 – 0.04

wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, c is 1 or 2; d is 2 when c is 1, or d is 3 or 5 when c is 2, M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M; Q is a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication and F is fluoride, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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^(a) ± 0.1 .

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

In a third aspect, there is provided a method of preparing a crystalline molecular sieve having STI topology, said method comprising contacting under crystallization conditions (1) a source of silicon oxide, (2) a source of aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, (3) fluoride ions and (4) a structure directing agent comprising a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication, and said molecular sieve having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
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<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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(a) ± 0.1 .

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

In a fourth aspect, there is provided a process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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30.16	2.96	W

^(a) ± 0.1 .

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

In a fifth aspect, there is provided a process for converting oxygenated hydrocarbons comprising contacting said oxygenated hydrocarbon under conditions to produce liquid products with a catalyst comprising a molecular sieve having a mole ratio of at least 15 of an oxide of a first tetravalent element to an oxide of a second tetravalent element which is different from said first tetravalent element, trivalent element, pentavalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
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30.16	2.96	W

^(a) ± 0.1 .

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

In a sixth aspect, there is provided a catalyst composition for promoting polymerization of 1-olefins, said composition comprising

(A) a crystalline molecular sieve having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

and

(B) an organotitanium or organochromium compound.

In a seventh aspect, there is provided a dewaxing process comprising contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

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28.37	3.14	W
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(a) ± 0.1 .

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

In an eighth aspect, there is provided a process for improving the viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising contacting a waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In a ninth aspect, there is provided a process for producing a C₂₀₊ lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization conditions over a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In a tenth aspect, there is provided a process for catalytically dewaxing a 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 a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In an eleventh aspect, there is provided a process for preparing a lubricating oil which comprises:

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

(b) catalytically dewaxing said effluent comprising hydrocracked oil at a temperature of at least about 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig (0.103 to 20.7MPa gauge) in the presence of added hydrogen gas with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In a twelfth aspect, there is provided a process for isomerization dewaxing a raffinate comprising contacting said raffinate in the presence of added hydrogen under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II.
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24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In a thirteenth aspect, there is provided a process for separating gasses using a membrane containing a molecular sieve, the improvement comprising using as the molecular sieve a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2)

an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

In a fourteenth aspect, there is provided a process for producing methylamine or dimethylamine comprising reacting methanol, dimethyl ether or a mixture thereof and ammonia in the gaseous phase in the presence of a catalyst comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1

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

In a fifteenth spect, there is provided a process for the reduction of oxides of nitrogen contained in a gas stream wherein said process comprises contacting the gas stream with a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

In a sixteenth aspect, there is provided a process for treating a cold-start engine exhaust gas stream containing hydrocarbons and other pollutants consisting of flowing said engine exhaust gas stream over a molecular sieve bed which preferentially adsorbs the hydrocarbons over water to provide a first exhaust stream, and flowing the first exhaust gas stream over a catalyst to convert any residual hydrocarbons and other pollutants contained in the first exhaust gas stream to innocuous products and provide a treated exhaust stream and discharging the treated exhaust stream into the atmosphere, the molecular sieve bed comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

In a seventeenth aspect, there is provided a process for the production of light olefins from a feedstock comprising an oxygenate or mixture of oxygenates, the process comprising reacting the feedstock at effective conditions over a catalyst comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

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28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

The present disclosure is directed to a family of crystalline molecular sieves with unique properties, referred to herein as "molecular sieve SSZ-75" or simply "SSZ-75". SSZ-75 has the framework topology designated "STI" by the IZA. Materials having the STI topology include naturally occurring stilbite and the zeolite designated TNU-10. Stilbite is disclosed in Breck, Zeolite Molecular Sieves, 1984, Robert E. Krieger Publishing Company where it is reported that stilbite has a typical silica/alumina mole ratio of 5.2. TNU-10 is reported in Hong et al., J. AM. CHEM. SOC. 2004, 126, 5817-5826 as having a silica/alumina mole ratio of about 14. When attempts were made to 11`2

increase the silica/alumina mole ratio in the product, materials other than TNU-10 were produced.

In accordance with the present disclosure there is provided a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The SSZ-75 molecular sieve has, after calcination, the X-ray diffraction lines of Table II. It should be noted that the phrase "mole ratio of at least 15" includes the case where there is no oxide (2), i.e., the mole ratio of oxide (1) to oxide (2) is infinity. In that case the molecular sieve is comprised of essentially all silicon oxide.

The present disclosure also provides a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof. The SSZ-75 molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

The present disclosure further provides such a crystalline molecular sieve having a composition comprising, as synthesized and in the anhydrous state, in terms of mole ratios the following:

$\text{SiO}_2 / \text{X}_c\text{O}_d$	at least 15 (i.e., 15 - infinity)
$\text{M}_{2/n} / \text{SiO}_2$	0 – 0.03
Q / SiO_2	0.02 – 0.08
F / SiO_2	0.01 – 0.04

wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, c is 1 or 2; d is 2 when c is 1 (i.e., W is tetravalent) or d is 3 or 5 when c is 2 (i.e., d is 3 when W is trivalent or 5 when W is pentavalent), M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the

valence of M (i.e., 1 or 2); Q is a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication and F is fluoride.

Also provided in accordance with the present disclosure is a method of preparing a crystalline material, said method comprising contacting under crystallization conditions a source(s) of (1) silicon oxide, (2) a source(s) of aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, (3) fluoride ions and (4) a structure directing agent comprising a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication. The present disclosure includes such a method wherein the crystalline material has STI topology and wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

The present disclosure includes such a method of preparing a crystalline material which uses a reaction mixture comprising (in terms of mole ratios), the following:

$\text{SiO}_2 / \text{X}_a\text{O}_b$	at least 15 (i.e., 15 - infinity)
$\text{OH}^- / \text{SiO}_2$	0.20 – 0.80
Q / SiO_2	0.20 – 0.80
$\text{M}_{2/n} / \text{SiO}_2$	0 – 0.04
$\text{H}_2\text{O} / \text{SiO}_2$	2 - 10
HF / SiO_2	0.20 – 0.80

wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, a is 1 or 2, b is 2 when a is 1 (i.e., W is tetravalent); b is 3 when a is 2 (i.e., W is trivalent), M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication.

In accordance with the present disclosure there is provided a process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst comprising a crystalline

molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. SSZ-75 has, after calcination, the X-ray diffraction lines of Table II. It should be noted that the phrase "mole ratio of at least 15" includes the case where there is no oxide (2), i.e., the mole ratio of oxide (1) to oxide (2) is infinity. In that case the molecular sieve is comprised of essentially all silicon oxide. The molecular sieve may be predominantly in the hydrogen form. It may also be substantially free of acidity.

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

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

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

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

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

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

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

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

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

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

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

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

Further provided in accordance with the present disclosure is a process for the production of higher molecular weight hydrocarbons from lower molecular weight hydrocarbons comprising the steps of

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

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

The present disclosure also provides a catalyst composition for promoting polymerization of 1-olefins, said composition comprising

- (A) a crystalline molecular sieve having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II; and
- (B) an organotitanium or organochromium compound.

Also provided is a process for polymerizing 1-olefins, which process comprises contacting 1-olefin monomer with a catalytically effective amount of a catalyst composition comprising

- (A) a crystalline molecular sieve having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II; and
- (B) an organotitanium or organochromium compound.

under polymerization conditions which include a temperature and pressure suitable for initiating and promoting the polymerization reaction. The 1-olefin may be ethylene.

The present disclosure further provides a dewaxing process comprising contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve is preferably predominantly in the hydrogen form.

Also provided is a process for improving the viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising contacting a waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve is preferably predominantly in the hydrogen form

Further provided by the present disclosure is a process for producing a C₂₀₊ lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under

isomerization conditions over a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve may be predominantly in the hydrogen form. The catalyst may contain at least one Group VIII metal.

Also provided is a process for catalytically dewaxing a 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 a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve may be predominantly in the hydrogen form. The catalyst may contain at least one Group VIII metal. The catalyst may comprise a combination comprising a first catalyst comprising the molecular sieve and at least one Group VIII metal, and a second catalyst comprising an aluminosilicate zeolite which is more shape selective than the molecular sieve of said first catalyst.

The present disclosure further provides 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 pressure of from about 15 psig to about 3000 psig (0.103 to 20.7 MPa gauge) in the presence of

added hydrogen gas with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve may be predominantly in the hydrogen form. The catalyst may contain at least one Group VIII metal.

Also provided is a process for isomerization dewaxing a raffinate comprising contacting said raffinate in the presence of added hydrogen under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The raffinate may be bright stock, and the molecular sieve may be predominantly in the hydrogen form. The catalyst may contain at least one Group VIII metal.

In accordance with the present disclosure there is provided an improved process for separating gasses using a membrane containing a molecular sieve, the improvement comprising using as the molecular sieve a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve can have a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof. The molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

In accordance with the present disclosure there is provided a process for producing methylamine or dimethylamine comprising reacting methanol, dimethyl ether or a mixture thereof and ammonia in the gaseous phase in the

presence of a catalyst comprising a crystalline molecular sieve having STI topology and having a mole ratio of 15 and greater of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve can have a mole ratio of 15 and greater of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof. The molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

In accordance with this disclosure, there is provided a process for the reduction of oxides of nitrogen contained in a gas stream wherein said process comprises contacting the gas stream with a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve can have a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof. The molecular sieve has, after calcination, the X-ray diffraction lines of Table II. The molecular sieve may contain a metal or metal ions (such as cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof) capable of catalyzing the reduction of the oxides of nitrogen, and the process may be conducted in the presence of a stoichiometric excess of oxygen. In a preferred embodiment, the gas stream is the exhaust stream of an internal combustion engine.

This disclosure generally relates to a process for treating an engine exhaust stream and in particular to a process for minimizing emissions during the cold start operation of an engine. Accordingly, the present disclosure provides a process for treating a cold-start engine exhaust gas stream containing hydrocarbons and other pollutants consisting of flowing said engine exhaust

gas stream over a molecular sieve bed which preferentially adsorbs the hydrocarbons over water to provide a first exhaust stream, and flowing the first exhaust gas stream over a catalyst to convert any residual hydrocarbons and other pollutants contained in the first exhaust gas stream to innocuous products and provide a treated exhaust stream and discharging the treated exhaust stream into the atmosphere, the molecular sieve bed characterized in that it comprises a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. The molecular sieve can have a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof. The molecular sieve has the STI framework topology. It has, after calcination, the X-ray diffraction lines of Table II.

The present disclosure further provides such a process wherein the engine is an internal combustion engine, including automobile engines, which can be fueled by a hydrocarbonaceous fuel.

Also provided by the present disclosure is such a process wherein the molecular sieve has deposited on it a metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, and mixtures thereof.

The present disclosure relates to a process for the production of light olefins comprising olefins having from 2 to 4 carbon atoms per molecule from an oxygenate feedstock. The process comprises passing the oxygenate feedstock to an oxygenate conversion zone containing a molecular sieve catalyst to produce a light olefin stream.

Thus, in accordance with the present disclosure there is provided a process for the production of light olefins from a feedstock comprising an oxygenate or mixture of oxygenates, the process comprising reacting the feedstock at

1 effective conditions over a catalyst comprising a crystalline molecular sieve.
 2 having STI topology and having a mole ratio of at least 15 of (1) an oxide of a
 3 first tetravalent element to (2) an oxide of a trivalent element, pentavalent
 4 element, second tetravalent element which is different from said first
 5 tetravalent element or mixture thereof. The molecular sieve can have a mole
 6 ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum
 7 oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and
 8 mixtures thereof. The molecular sieve has, after calcination, the X-ray
 9 diffraction lines of Table II.

10

11 DETAILED DESCRIPTION OF THE INVENTION

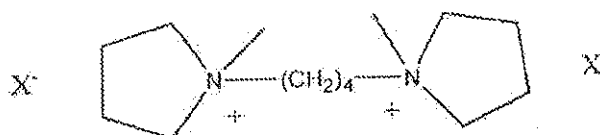
12

13 The present invention comprises a molecular sieve designated herein
 14 "molecular sieve SSZ-75" or simply "SSZ-75".

15

16 In preparing SSZ-75, a tetramethylene-1,4-bis-(N-methylpyrrolidinium)
 17 dication is used as a structure directing agent ("SDA"), also known as a
 18 crystallization template. The SDA useful for making SSZ-75 has the following
 19 structure:

20



21

22

Tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication

23

24 The SDA dication is associated with anions (X^-) which may be any anion that
 25 is not detrimental to the formation of the SSZ-75. Representative anions
 26 include halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide,
 27 acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is the
 28 most preferred anion. The structure directing agent (SDA) may be used to
 29 provide hydroxide ion. Thus, it is beneficial to ion exchange, for example, a
 30 halide to hydroxide ion.

31

The tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication SDA can be prepared by a method similar to that described in U.S. Patent No. 5,166,111, issued November 24, 1992 to Zones et al., which discloses a method for preparing a bis(1,4-diazoniabicyclo[2.2.2]alpha, omega alkane compound, or U.S. Patent No. 5,268,161, issued December 7, 1993, which discloses a method for preparing 1,3,3,8,8-pentamethyl-3-azoniabicyclo[3.2.1]octane cation. U.S. Patent No. 5,166,111 and U.S. Patent No. 5,268,161 are incorporated by reference herein in their entirety.

In general, SSZ-75 is prepared by contacting (1) an active source(s) of silicon oxide, and (2) an active source(s) of aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof with the tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication SDA in the presence of fluoride ion.

SSZ-75 is prepared from a reaction mixture comprising, in terms of mole ratios, the following:

TABLE A
Reaction Mixture

SiO ₂ / XaOb	at least 15 (i.e., 15 - infinity)
OH ⁻ / SiO ₂	0.20 - 0.80
Q / SiO ₂	0.20 - 0.80
M ₂ /n / SiO ₂	0 - 0.04
H ₂ O / SiO ₂	2 - 10
HF / SiO ₂	0.20 - 0.80

where X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, a is 1 or 2, b is 2 when a is 1 (i.e., W is tetravalent); b is 3 when a is 2 (i.e., W is trivalent), M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M (i.e., 1 or 2); Q is a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication and F is fluoride.

1 As noted above, the $\text{SiO}_2 / \text{X}_a\text{O}_b$ mole ratio in the reaction mixture is ≥ 15 .
2 This means that the $\text{SiO}_2 / \text{X}_a\text{O}_b$ mole ratio can be infinity, i.e., there is no X_aO_b
3 in the reaction mixture. This results in a version of SSZ-75 that is essentially
4 all silica. As used herein, "essentially all silicon oxide" or "essentially all-
5 silica" means that the molecular sieve's crystal structure is comprised of only
6 silicon oxide or is comprised of silicon oxide and only trace amounts of other
7 oxides, such as aluminum oxide, which may be introduced as impurities in the
8 source of silicon oxide.

9
10 In practice, SSZ-75 is prepared by a process comprising:

- 11
12 (a) preparing an aqueous solution containing (1) a source(s) of
13 silicon oxide, (2) a source(s) of aluminum oxide,
14 gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide
15 and mixtures thereof, (3) a source of fluoride ion and (4) a
16 tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication
17 having an anionic counterion which is not detrimental to the
18 formation of SSZ-75;
19 (b) maintaining the aqueous solution under conditions sufficient to
20 form crystals of SSZ-75; and
21 (c) recovering the crystals of SSZ-75.

22
23 The reaction mixture is maintained at an elevated temperature until the
24 crystals of the SSZ-75 are formed. The hydrothermal crystallization is usually
25 conducted under autogenous pressure, at a temperature between 100°C and
26 200°C, preferably between 135°C and 180°C. The crystallization period is
27 typically greater than 1 day and preferably from about 3 days to about
28 20 days. The molecular sieve may be prepared using mild stirring or
29 agitation.

30
31 During the hydrothermal crystallization step, the SSZ-75 crystals can be
32 allowed to nucleate spontaneously from the reaction mixture. The use of
33 SSZ-75 crystals as seed material can be advantageous in decreasing the time

1 necessary for complete crystallization to occur. In addition, seeding can lead
 2 to an increased purity of the product obtained by promoting the nucleation
 3 and/or formation of SSZ-75 over any undesired phases. When used as
 4 seeds, SSZ-75 crystals are added in an amount between 0.1 and 10% of the
 5 weight of the first tetravalent element oxide, e.g. silica, used in the reaction
 6 mixture.

7
 8 Once the molecular sieve crystals have formed, the solid product is separated
 9 from the reaction mixture by standard mechanical separation techniques such
 10 as filtration. The crystals are water-washed and then dried, e.g., at 90°C to
 11 150°C for from 8 to 24 hours, to obtain the as-synthesized SSZ-75 crystals.
 12 The drying step can be performed at atmospheric pressure or under vacuum.

13
 14 SSZ-75 as prepared has the X-ray diffraction lines of Table I below. SSZ-75
 15 has a composition, as synthesized (i.e., prior to removal of the SDA from the
 16 SSZ-75) and in the anhydrous state, comprising the following (in terms of
 17 mole ratios):

18		
19	$\text{SiO}_2 / \text{X}_c\text{O}_d$	at least 15 (i.e., 15 - infinity)
20	$\text{M}_{2/n} / \text{SiO}_2$	0 - 0.03
21	Q / SiO_2	0.02 - 0.08
22	F / SiO_2	0.01 - 0.04
23		

24 wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures
 25 thereof, c is 1 or 2; d is 2 when c is 1 (i.e., W is tetravalent) or d is 3 or 5 when
 26 c is 2 (i.e., d is 3 when W is trivalent or 5 when W is pentavalent), M is an
 27 alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the
 28 valence of M (i.e., 1 or 2); Q is a tetramethylene-1,4-bis-(N-methyl-
 29 pyrrolidinium) dication and F is fluoride.

30
 31 SSZ-75 (whether in the as synthesized or calcined version) has a $\text{SiO}_2 / \text{X}_c\text{O}_d$
 32 mole ratio of at least 15 (i.e., 15 - infinity), for example 20 - infinity or 40 -
 33 infinity.

SSZ-75 has the STI framework topology. It is characterized by its X-ray diffraction pattern. SSZ-75, as-synthesized, has a crystalline structure whose X-ray powder diffraction pattern exhibits the characteristic lines shown in Table I.

TABLE I
As-Synthesized SSZ-75

2 Theta	d-spacing (Angstroms)	Relative Integrated Intensity (%)
10.04	8.80	VS
17.17	5.16	W
19.44	4.56	S
21.13	4.20	W-M
22.36	3.97	VS
22.49	3.95	M
24.19	3.68	W
26.61	3.35	W
28.49	3.13	W
30.20	2.96	M

^(a) ± 0.1

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

Table IA below shows the X-ray powder diffraction lines for as-synthesized SSZ-75 including actual relative intensities.

TABLE IA
As-Synthesized SSZ-75

2 Theta	d-spacing (Angstroms)	Relative Integrated Intensity (%)
9.84	8.98	7
10.04	8.80	100
13.24	6.68	7
14.19	6.24	4
17.17	5.16	13
19.44	4.56	47
20.01	4.43	2
20.17	4.40	7
21.13	4.20	21
22.36	3.97	84
22.49	3.95	38
24.19	3.68	12
26.13	3.41	7
26.61	3.35	17
28.49	3.13	18
29.31	3.04	10
30.20	2.96	30
30.30	2.95	7
31.94	2.80	2
32.12	2.78	1
32.61	2.74	3
33.13	2.70	4
33.59	2.67	6
34.86	2.57	7
35.13	2.55	5
35.75	2.51	6
36.55	2.46	2
36.69	2.45	1
37.19	2.42	1

(a) ± 0.1

After calcination, the X-ray powder diffraction pattern for SSZ-75 exhibits the characteristic lines shown in Table II below.

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1

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

Table IIA below shows the X-ray powder diffraction lines for calcined SSZ-75 including actual relative intensities.

TABLE IIA
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	8
9.95	8.88	100
10.06	8.79	24
13.14	6.73	7
14.17	6.25	2
17.13	5.17	2
17.25	5.14	3
19.38	4.58	15
20.23	4.39	1
21.03	4.22	10
22.35	3.97	39
22.54	3.94	6
24.19	3.68	7
25.24	3.53	6
26.08	3.41	2
26.48	3.36	6

28.37	3.14	7
29.25	3.05	3
30.16	2.96	13
30.32	2.95	2
32.18	2.78	1
33.02	2.71	2
33.54	2.67	2
34.57	2.59	1
34.94	2.57	2
35.09	2.56	1
35.68	2.51	2
36.58	2.45	1
37.07	2.42	1

1
2 (a) ± 0.1

3

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

9

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

13

14 Representative peaks from the X-ray diffraction pattern of as-synthesized
15 SSZ-75 are shown in Table I. Calcination can result in changes in the
16 intensities of the peaks as compared to patterns of the "as-synthesized"
17 material, as well as minor shifts in the diffraction pattern.

18

19 Crystalline SSZ-75 can be used as-synthesized, but preferably will be
20 thermally treated (calcined). Usually, it is desirable to remove the alkali metal
21 cation (if any) by ion exchange and replace it with hydrogen, ammonium, or
22 any desired metal ion. Calcined SSZ-75 has an n-hexane adsorption capacity
23 of about 0.15 cc/g.

24

1 SSZ-75 can be formed into a wide variety of physical shapes. Generally
2 speaking, the molecular sieve can be in the form of a powder, a granule, or a
3 molded product, such as extrudate having a particle size sufficient to pass
4 through a 2-mesh (Tyler) screen and be retained on a 400-mesh (Tyler)
5 screen. In cases where the catalyst is molded, such as by extrusion with an
6 organic binder, the SSZ-75 can be extruded before drying, or, dried or
7 partially dried and then extruded.

8
9 SSZ-75 can be composited with other materials resistant to the temperatures
10 and other conditions employed in organic conversion processes. Such matrix
11 materials include active and inactive materials and synthetic or naturally
12 occurring zeolites as well as inorganic materials such as clays, silica and
13 metal oxides. Examples of such materials and the manner in which they can
14 be used are disclosed in U.S. Patent No. 4,910,006, issued May 20, 1990 to
15 Zones et al., and U.S. Patent No. 5,316,753, issued May 31, 1994 to
16 Nakagawa, both of which are incorporated by reference herein in their
17 entirety.

18 19 Hydrocarbon Conversion Processes

20
21 SSZ-75 molecular sieves are useful in hydrocarbon conversion reactions.
22 Hydrocarbon conversion reactions are chemical and catalytic processes in
23 which carbon containing compounds are changed to different carbon
24 containing compounds. Examples of hydrocarbon conversion reactions in
25 which SSZ-75 is expected to be useful include hydrocracking, dewaxing,
26 catalytic cracking and olefin and aromatics formation reactions. The catalysts
27 are also expected to be useful in other petroleum refining and hydrocarbon
28 conversion reactions such as isomerizing n-paraffins and naphthenes,
29 polymerizing and oligomerizing olefinic or acetylenic compounds such as
30 isobutylene and butene-1, polymerization of 1-olefins (e.g., ethylene),
31 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and
32 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene,
33 xylenes and higher methylbenzenes and oxidation reactions. Also included

1 are rearrangement reactions to make various naphthalene derivatives, and
2 forming higher molecular weight hydrocarbons from lower molecular weight
3 hydrocarbons (e.g., methane upgrading).
4

5 The SSZ-75 catalysts may have high selectivity, and under hydrocarbon
6 conversion conditions can provide a high percentage of desired products
7 relative to total products.
8

9 For high catalytic activity, the SSZ-75 molecular sieve should be
10 predominantly in its hydrogen ion form. Generally, the molecular sieve is
11 converted to its hydrogen form by ammonium exchange followed by
12 calcination. If the molecular sieve is synthesized with a high enough ratio of
13 SDA cation to sodium ion, calcination alone may be sufficient. It is preferred
14 that, after calcination, at least 80% of the cation sites are occupied by
15 hydrogen ions and/or rare earth ions. As used herein, "predominantly in the
16 hydrogen form" means that, after calcination, at least 80% of the cation sites
17 are occupied by hydrogen ions and/or rare earth ions.
18

19 SSZ-75 molecular sieves can be used in processing hydrocarbonaceous
20 feedstocks. Hydrocarbonaceous feedstocks contain carbon compounds and
21 can be from many different sources, such as virgin petroleum fractions,
22 recycle petroleum fractions, shale oil, liquefied coal, tar sand oil, synthetic
23 paraffins from NAO, recycled plastic feedstocks. Other feeds include
24 synthetic feeds, such as those derived from a Fischer Tropsch process,
25 including an oxygenate-containing Fischer Tropsch process boiling below
26 about 371°C (700°F). In general, the feed can be any carbon containing
27 feedstock susceptible to zeolitic catalytic reactions. Depending on the type of
28 processing the hydrocarbonaceous feed is to undergo, the feed can contain
29 metal or be free of metals, it can also have high or low nitrogen or sulfur
30 impurities. It can be appreciated, however, that in general processing will be
31 more efficient (and the catalyst more active) the lower the metal, nitrogen, and
32 sulfur content of the feedstock.
33

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

6

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

11

12 The following table indicates typical reaction conditions which may be
13 employed when using catalysts comprising SSZ-75 in the hydrocarbon
14 conversion reactions of this invention. Preferred conditions are indicated in
15 parentheses.

16

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

1

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

7 Other reaction conditions and parameters are provided below.

Hydrocracking

Using a catalyst which comprises SSZ-75, 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

For dewaxing processes, the catalyst comprises a molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof. Thus, the molecular sieve may be SSZ-75 or

1 TNU-10, preferably predominantly in the hydrogen form. The catalyst can be
2 used to dewax hydrocarbonaceous feeds by selectively removing straight
3 chain paraffins. Typically, the viscosity index of the dewaxed product is
4 improved (compared to the waxy feed) when the waxy feed is contacted with
5 SSZ-75 or TNU-10 under isomerization dewaxing conditions.

6
7 The catalytic dewaxing conditions are dependent in large measure on the
8 feed used and upon the desired pour point. Hydrogen is preferably present in
9 the reaction zone during the catalytic dewaxing process. The hydrogen to
10 feed ratio is typically between about 500 and about 30,000 SCF/bbl (standard
11 cubic feet per barrel) (0.089 to 5.34 SCM/liter (standard cubic meters/liter)),
12 preferably about 1000 to about 20,000 SCF/bbl (0.178 to 3.56 SCM/liter).
13 Generally, hydrogen will be separated from the product and recycled to the
14 reaction zone. Typical feedstocks include light gas oil, heavy gas oils and
15 reduced crudes boiling above about 350°F (177°C).

16
17 A typical dewaxing process is the catalytic dewaxing of a hydrocarbon oil
18 feedstock boiling above about 350°F (177°C) and containing straight chain
19 and slightly branched chain hydrocarbons by contacting the hydrocarbon oil
20 feedstock in the presence of added hydrogen gas at a hydrogen pressure of
21 about 15-3000 psi (0.103-20.7 Mpa) with a catalyst comprising SSZ-75 and at
22 least one Group VIII metal.

23
24 The SSZ-75 or TNU-10 hydrodewaxing catalyst may optionally contain a
25 hydrogenation component of the type commonly employed in dewaxing
26 catalysts. See the aforementioned U.S. Patent No. 4,910,006 and U.S.
27 Patent No. 5,316,753 for examples of these hydrogenation components.

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

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

6
7 SSZ-75 or TNU-10 may also be utilized as a combination of catalysts. That
8 is, the catalyst comprises a combination comprising molecular sieve SSZ-75
9 or TNU-10 and at least one Group VIII metal, and a second catalyst
10 comprising an aluminosilicate zeolite which is more shape selective than
11 molecular sieve SSZ-75 or TNU-10. The combination may be comprised of
12 layers. The use of layered catalysts is disclosed in U.S. Patent
13 No. 5,149,421, issued September 22, 1992 to Miller, which is incorporated by
14 reference herein in its entirety. The layering may also include a bed of SSZ-
15 75 or TNU-10 layered with a non-zeolitic component designed for either
16 hydrocracking or hydrofinishing.

17
18 SSZ-75 or TNU-10 may also be used to dewax raffinates, including bright
19 stock, under conditions such as those disclosed in U. S. Patent
20 No. 4,181,598, issued January 1, 1980 to Gillespie et al., which is
21 incorporated by reference herein in its entirety.

22
23 It is often desirable to use mild hydrogenation (sometimes referred to as
24 hydrofinishing) to produce more stable dewaxed products. The hydrofinishing
25 step can be performed either before or after the dewaxing step, and
26 preferably after. Hydrofinishing is typically conducted at temperatures ranging
27 from about 190°C to about 340°C at pressures from about 400 psig to about
28 3000 psig (2.76 to 20.7 Mpa gauge) at space velocities (LHSV) between
29 about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl
30 (0.071 to 0.27 SCM/liter). The hydrogenation catalyst employed must be
31 active enough not only to hydrogenate the olefins, diolefins and color bodies
32 which may be present, but also to reduce the aromatic content. Suitable
33 hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued

1 May 1, 1990 to Miller, which is incorporated by reference herein in its entirety.
2 The hydrofinishing step is beneficial in preparing an acceptably stable product
3 (e.g., a lubricating oil) since dewaxed products prepared from hydrocracked
4 stocks tend to be unstable to air and light and tend to form sludges
5 spontaneously and quickly.

6
7 Lube oil may be prepared using SSZ-75 or TNU-10. For example, a C₂₀₊ lube
8 oil may be made by isomerizing a C₂₀₊ olefin feed over a catalyst comprising
9 SSZ-75 or TNU-10 in the hydrogen form and at least one Group VIII metal.
10 Alternatively, the lubricating oil may be made by hydrocracking in a
11 hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent
12 comprising a hydrocracked oil, and catalytically dewaxing the effluent at a
13 temperature of at least about 400°F (204°C) and at a pressure of from about
14 15 psig to about 3000 psig (0.103-20.7 Mpa gauge) in the presence of added
15 hydrogen gas with a catalyst comprising SSZ-75 or TNU-10F in the hydrogen
16 form and at least one Group VIII metal.

17

18 Aromatics Formation

19

20 SSZ-75 can be used to convert light straight run naphthas and similar
21 mixtures to highly aromatic mixtures. Thus, normal and slightly branched
22 chained hydrocarbons, preferably having a boiling range above about 40°C
23 and less than about 200°C, can be converted to products having a substantial
24 higher octane aromatics content by contacting the hydrocarbon feed with a
25 catalyst comprising SSZ-75. It is also possible to convert heavier feeds into
26 BTX or naphthalene derivatives of value using a catalyst comprising SSZ-75.

27

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

1 preferably a noble metal compound. The most preferred metal is platinum.
2 The amount of Group VIII metal present in the conversion catalyst should be
3 within the normal range of use in reforming catalysts, from about 0.05 to
4 2.0 weight percent, preferably 0.2 to 0.8 weight percent.
5
6 It is critical to the selective production of aromatics in useful quantities that the
7 conversion catalyst be substantially free of acidity, for example, by
8 neutralizing the molecular sieve with a basic metal, e.g., alkali metal,
9 compound. Methods for rendering the catalyst free of acidity are known in the
10 art. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
11 No. 5,316,753 for a description of such methods.
12
13 The preferred alkali metals are sodium, potassium, rubidium and cesium. The
14 molecular sieve itself can be substantially free of acidity only at very high
15 silica:alumina mole ratios.

17 Catalytic Cracking

18
19 Hydrocarbon cracking stocks can be catalytically cracked in the absence of
20 hydrogen using SSZ-75, preferably predominantly in the hydrogen form.
21
22 When SSZ-75 is used as a catalytic cracking catalyst in the absence of
23 hydrogen, the catalyst may be employed in conjunction with traditional
24 cracking catalysts, e.g., any aluminosilicate heretofore employed as a
25 component in cracking catalysts. Typically, these are large pore, crystalline
26 aluminosilicates. Examples of these traditional cracking catalysts are
27 disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent
28 No 5,316,753. When a traditional cracking catalyst (TC) component is
29 employed, the relative weight ratio of the TC to the SSZ-75 is generally
30 between about 1:10 and about 500:1, desirably between about 1:10 and
31 about 200:1, preferably between about 1:2 and about 50:1, and most
32 preferably is between about 1:1 and about 20:1. The novel molecular sieve

1 and/or the traditional cracking component may be further ion exchanged with
2 rare earth ions to modify selectivity.

3

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

7

8

Isomerization

9

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

16

17 The present process comprises contacting the isomerization catalyst, i.e., a
18 catalyst comprising SSZ-75 in the hydrogen form, with a hydrocarbon feed
19 under isomerization conditions. The feed is preferably a light straight run
20 fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C) and
21 preferably from 60°F to 200°F (16°C to 93°C). Preferably, the hydrocarbon
22 feed for the process comprises a substantial amount of C₄ to C₇ normal and
23 slightly branched low octane hydrocarbons, more preferably C₅ and C₆
24 hydrocarbons.

25

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

31

32 A low sulfur feed is especially preferred in the present process. The feed
33 preferably contains less than 10 ppm, more preferably less than 1 ppm, and

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

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

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

16
17 The conversion catalyst preferably contains a Group VIII metal compound to
18 have sufficient activity for commercial use. By Group VIII metal compound as
19 used herein is meant the metal itself or a compound thereof. The Group VIII
20 noble metals and their compounds, platinum, palladium, and iridium, or
21 combinations thereof can be used. Rhenium and tin may also be used in
22 conjunction with the noble metal. The most preferred metal is platinum. The
23 amount of Group VIII metal present in the conversion catalyst should be within
24 the normal range of use in isomerizing catalysts, from about 0.05 to
25 2.0 weight percent, preferably 0.2 to 0.8 weight percent.

26 27 Alkylation and Transalkylation

28
29 SSZ-75 can be used in a process for the alkylation or transalkylation of an
30 aromatic hydrocarbon. The process comprises contacting the aromatic
31 hydrocarbon with a C₂ to C₁₆ olefin alkylating agent or a polyalkyl aromatic
32 hydrocarbon transalkylating agent, under at least partial liquid phase
33 conditions, and in the presence of a catalyst comprising SSZ-75.

1
2 SSZ-75 can also be used for removing benzene from gasoline by alkylating
3 the benzene as described above and removing the alkylated product from the
4 gasoline.

5
6 For high catalytic activity, the SSZ-75 molecular sieve should be
7 predominantly in its hydrogen ion form. It is preferred that, after calcination, at
8 least 80% of the cation sites are occupied by hydrogen ions and/or rare earth
9 ions.

10
11 Examples of suitable aromatic hydrocarbon feedstocks which may be
12 alkylated or transalkylated by the process of the invention include aromatic
13 compounds such as benzene, toluene and xylene. The preferred aromatic
14 hydrocarbon is benzene. There may be occasions where naphthalene or
15 naphthalene derivatives such as dimethylnaphthalene may be desirable.
16 Mixtures of aromatic hydrocarbons may also be employed.

17
18 Suitable olefins for the alkylation of the aromatic hydrocarbon are those
19 containing 2 to 20, preferably 2 to 4, carbon atoms, such as ethylene,
20 propylene, butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof.
21 There may be instances where pentenes are desirable. The preferred olefins
22 are ethylene and propylene. Longer chain alpha olefins may be used as well.

23
24 When transalkylation is desired, the transalkylating agent is a polyalkyl
25 aromatic hydrocarbon containing two or more alkyl groups that each may
26 have from 2 to about 4 carbon atoms. For example, suitable polyalkyl
27 aromatic hydrocarbons include di-, tri- and tetra-alkyl aromatic hydrocarbons,
28 such as diethylbenzene, triethylbenzene, diethylmethylbenzene
29 (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene, dibutylbenzene,
30 and the like. Preferred polyalkyl aromatic hydrocarbons are the dialkyl
31 benzenes. A particularly preferred polyalkyl aromatic hydrocarbon is
32 di-isopropylbenzene.

33

1 When alkylation is the process conducted, reaction conditions are as follows.
2 The aromatic hydrocarbon feed should be present in stoichiometric excess. It
3 is preferred that molar ratio of aromatics to olefins be greater than four-to-one
4 to prevent rapid catalyst fouling. The reaction temperature may range from
5 100°F to 600°F (38°C to 315°C), preferably 250°F to 450°F (121°C to 232°C).
6 The reaction pressure should be sufficient to maintain at least a partial liquid
7 phase in order to retard catalyst fouling. This is typically 50 psig to 1000 psig
8 (0.345 to 6.89 Mpa gauge) depending on the feedstock and reaction
9 temperature. Contact time may range from 10 seconds to 10 hours, but is
10 usually from 5 minutes to an hour. The weight hourly space velocity (WHSV),
11 in terms of grams (pounds) of aromatic hydrocarbon and olefin per gram
12 (pound) of catalyst per hour, is generally within the range of about 0.5 to 50.
13
14 When transalkylation is the process conducted, the molar ratio of aromatic
15 hydrocarbon will generally range from about 1:1 to 25:1, and preferably from
16 about 2:1 to 20:1. The reaction temperature may range from about 100°F to
17 600°F (38°C to 315°C), but it is preferably about 250°F to 450°F (121°C to
18 232°C). The reaction pressure should be sufficient to maintain at least a
19 partial liquid phase, typically in the range of about 50 psig to 1000 psig (0.345
20 to 6.89 Mpa gauge), preferably 300 psig to 600 psig (2.07 to 4.14 Mpa
21 gauge). The weight hourly space velocity will range from about 0.1 to 10.
22 U.S. Patent No. 5,082,990 issued on January 21, 1992 to Hsieh, et al.
23 describes such processes and is incorporated herein by reference.

24

25 Conversion of Paraffins to Aromatics

26

27 SSZ-75 can be used to convert light gas C₂-C₆ paraffins to higher molecular
28 weight hydrocarbons including aromatic compounds. Preferably, the
29 molecular sieve will contain a catalyst metal or metal oxide wherein said metal
30 is selected from the group consisting of Groups IB, IIB, VIII and IIIA of the
31 Periodic Table. Preferably, the metal is gallium, niobium, indium or zinc in the
32 range of from about 0.05 to 5% by weight.

33

Isomerization of Olefins

SSZ-75 can be used to isomerize olefins. The feed stream is a hydrocarbon stream containing at least one C₄₋₆ olefin, preferably a C₄₋₅ normal olefin, more preferably normal butene. Normal butene as used in this specification means all forms of normal butene, e.g., 1-butene, cis-2-butene, and trans-2-butene. Typically, hydrocarbons other than normal butene or other C₄₋₆ normal olefins will be present in the feed stream. These other hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen, and inert gases.

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

The process is carried out under isomerization conditions. The hydrocarbon feed is contacted in a vapor phase with a catalyst comprising the SSZ-75. The process may be carried out generally at a temperature from about 625°F to about 950°F (329-510°C), for butenes, preferably from about 700°F to about 900°F (371-482°C), and about 350°F to about 650°F (177-343°C) for pentenes and hexenes. The pressure ranges from subatmospheric to about 200 psig (1.38 Mpa gauge), preferably from about 15 psig to about 200 psig (0.103 to 1.38 Mpa gauge), and more preferably from about 1 psig to about 150 psig (0.00689 to 1.03 Mpa gauge).

The liquid hourly space velocity during contacting is generally from about 0.1 to about 50 hr⁻¹, based on the hydrocarbon feed, preferably from about 0.1 to about 20 hr⁻¹, more preferably from about 0.2 to about 10 hr⁻¹, most preferably from about 1 to about 5 hr⁻¹. A hydrogen/hydrocarbon molar ratio is

1 maintained from about 0 to about 30 or higher. The hydrogen can be added
2 directly to the feed stream or directly to the isomerization zone. The reaction
3 is preferably substantially free of water, typically less than about two weight
4 percent based on the feed. The process can be carried out in a packed bed
5 reactor, a fixed bed, fluidized bed reactor, or a moving bed reactor. The bed
6 of the catalyst can move upward or downward. The mole percent conversion
7 of, e.g., normal butene to iso-butene is at least 10, preferably at least 25, and
8 more preferably at least 35.

9 10 Xylene Isomerization

11
12 SSZ-75 may also be useful in a process for isomerizing one or more xylene
13 isomers in a C₈ aromatic feed to obtain ortho-, meta-, and para-xylene in a
14 ratio approaching the equilibrium value. In particular, xylene isomerization is
15 used in conjunction with a separate process to manufacture para-xylene. For
16 example, a portion of the para-xylene in a mixed C₈ aromatics stream may be
17 recovered by crystallization and centrifugation. The mother liquor from the
18 crystallizer is then reacted under xylene isomerization conditions to restore
19 ortho-, meta- and para-xylenes to a near equilibrium ratio. At the same time,
20 part of the ethylbenzene in the mother liquor is converted to xylenes or to
21 products which are easily separated by filtration. The isomerate is blended
22 with fresh feed and the combined stream is distilled to remove heavy and light
23 by-products. The resultant C₈ aromatics stream is then sent to the crystallizer
24 to repeat the cycle.

25
26 Optionally, isomerization in the vapor phase is conducted in the presence of
27 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g., ethylbenzene).
28 If hydrogen is used, the catalyst should comprise about 0.1 to 2.0 wt.% of a
29 hydrogenation/dehydrogenation component selected from Group VIII (of the
30 Periodic Table) metal component, especially platinum or nickel. By Group VIII
31 metal component is meant the metals and their compounds such as oxides
32 and sulfides.

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

3 4 Oligomerization

5
6 It is expected that SSZ-75 can also be used to oligomerize straight and
7 branched chain olefins having from about 2 to 21 and preferably 2-5 carbon
8 atoms. The oligomers which are the products of the process are medium to
9 heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline
10 blending stock and chemicals.

11
12 The oligomerization process comprises contacting the olefin feedstock in the
13 gaseous or liquid phase with a catalyst comprising SSZ-75.

14
15 The molecular sieve can have the original cations associated therewith
16 replaced by a wide variety of other cations according to techniques well
17 known in the art. Typical cations would include hydrogen, ammonium and
18 metal cations including mixtures of the same. Of the replacing metallic
19 cations, particular preference is given to cations of metals such as rare earth
20 metals, manganese, calcium, as well as metals of Group II of the Periodic
21 Table, e.g., zinc, and Group VIII of the Periodic Table, e.g., nickel. One of the
22 prime requisites is that the molecular sieve have a fairly low aromatization
23 activity, i.e., in which the amount of aromatics produced is not more than
24 about 20% by weight. This is accomplished by using a molecular sieve with
25 controlled acid activity [alpha value] of from about 0.1 to about 120, preferably
26 from about 0.1 to about 100, as measured by its ability to crack n-hexane.

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

Condensation of Alcohols

SSZ-75 can be used to condense lower aliphatic alcohols having 1 to 10 carbon atoms to a gasoline boiling point hydrocarbon product comprising mixed aliphatic and aromatic hydrocarbon. The process disclosed in U.S. Patent No. 3,894,107, issued July 8, 1975 to Butter et al., describes the process conditions used in this process, which patent is incorporated totally herein by reference.

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

Methane Upgrading

Higher molecular weight hydrocarbons can be formed from lower molecular weight hydrocarbons by contacting the lower molecular weight hydrocarbon with a catalyst comprising SSZ-75 and a metal or metal compound capable of converting the lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon. Examples of such reactions include the conversion of methane to C₂₊ hydrocarbons such as ethylene or benzene or both. Examples of useful metals and metal compounds include lanthanide and or actinide metals or metal compounds.

These reactions, the metals or metal compounds employed and the conditions under which they can be run are disclosed in U.S. Patents No. 4,734,537, issued March 29, 1988 to Devries et al.; 4,939,311, issued July 3,

1 1990 to Washecheck et al.; 4,962,261, issued October 9, 1990 to Abrevaya et
2 al.; 5,095,161, issued March 10, 1992 to Abrevaya et al.; 5,105,044, issued
3 April 14, 1992 to Han et al.; 5,105,046, issued April 14, 1992 to Washecheck;
4 5,238,898, issued August 24, 1993 to Han et al.; 5,321,185, issued June 14,
5 1994 to van der Vaart; and 5,336,825, issued August 9, 1994 to Choudhary et
6 al., each of which is incorporated herein by reference in its entirety.

7

8

Polymerization of 1-Olefins

9

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

19

20 Examples of trivalent and tetravalent organochromium and organotitanium
21 compounds are disclosed in U. S. Patent No. 4,376,722, issued March 15,
22 1983 to Chester et al., U. S. Patent No. 4,377,497, issued March 22, 1983 to
23 Chester et al., U. S. Patent No. 4,446,243, issued May 1, 1984 to Chester et
24 al., and U. S. Patent No. 4,526,942, issued July 2, 1985 to Chester et al. The
25 disclosure of the aforementioned patents are incorporated herein by reference
26 in their entirety.

27

28 Examples of the organometallic compounds used to form the polymerization
29 catalyst include, but are not limited to, compounds corresponding to the
30 general formula:

31

32 MY_nX_{m-n}

33

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

4
5 Examples of organotitanium and organochromium compounds encompassed
6 by such a formula include compounds of the formula CrY_4 , CrY_3 , CrY_3X ,
7 CrY_2X , CrY_2X_2 , $CrYX_2$, $CrYX_3$, TiY_4 , TiY_3 , TiY_3X , TiY_2X , TiY_2X_2 , $TiYX_2$, $TiYX_3$,
8 wherein X can be Cl or Br and Y can be methyl, ethyl, propyl, isopropyl, butyl,
9 isobutyl, sec-butyl, tert-butyl, pentyl, isopentyl, neopentyl, hexyl, isohexyl,
10 neohexyl, 2-ethylbutyl, octyl, 2-ethylhexyl, 2,2-diethylbutyl, 2-isopropyl-3-
11 methylbutyl, etc., cyclohexylalkyls such as, for example, cyclohexylmethyl, 2-
12 cyclohexylethyl, 3-cyclohexylpropyl, 4-cyclohexylbutyl, and the corresponding
13 alkyl-substituted cyclohexyl radicals as, for example, (4-
14 methylcyclohexyl)methyl, neophyl, i.e., beta, beta-dimethyl-phenethyl, benzyl,
15 ethylbenzyl, and p-isopropylbenzyl. Preferred examples of Y include C_{1-5} alkyl,
16 especially butyl.

17
18 The organotitanium and organochromium materials employed in the catalyst
19 can be prepared by techniques well known in the art. See, for example the
20 aforementioned Chester et al. patents.

21
22 The organotitanium or organochromium compounds can be with the
23 molecular sieve of the present invention, such as by reacting the
24 organometallic compound and the molecular sieve, in order to form the olefin
25 polymerization catalyst. Generally, such a reaction takes place in the same
26 reaction medium used to prepare the organometallic compound under
27 conditions which promote formation of such a reaction product. The
28 molecular sieve can simply be added to the reaction mixture after formation of
29 the organometallic compound has been completed. Molecular sieve is added
30 in an amount sufficient to provide from about 0.1 to 10 parts by weight,
31 preferably from about 0.5 to 5 parts by weight, of organometallic compound in
32 the reaction medium per 100 parts by weight of molecular sieve.

1
2 Temperature of the reaction medium during reaction of organometallic
3 compound with molecular sieve is also maintained at a level which is low
4 enough to ensure the stability of the organometallic reactant. Thus,
5 temperatures in the range of from about -150° C. to 50° C., preferably from
6 about -80° C. to 0° C. can be usefully employed. Reaction times of from
7 about 0.01 to 10 hours, more preferably from about 0.1 to 1 hour, can be
8 employed in reacting the organotitanium or organochromium compound with
9 the molecular sieve.

10
11 Upon completion of the reaction, the catalyst material so formed may be
12 recovered and dried by evaporating the reaction medium solvent under a
13 nitrogen atmosphere. Alternatively, olefin polymerization reactions can be
14 conducted in this same solvent based reaction medium used to form the
15 catalyst.

16
17 The polymerization catalyst can be used to catalyze polymerization of 1-
18 olefins. The polymers produced using the catalysts of this invention are
19 normally solid polymers of at least one mono-1-olefin containing from 2 to 8
20 carbon atoms per molecule. These polymers are normally solid
21 homopolymers of ethylene or copolymers of ethylene with another mono-1-
22 olefin containing 3 to 8 carbon atoms per molecule. Exemplary copolymers
23 include those of ethylene/propylene, ethylene/1-butene, ethylene/1-hexene,
24 and ethylene/1-octene and the like. The major portion of such copolymers is
25 derived from ethylene and generally consists of about 80-99, preferably 95-99
26 mole percent of ethylene. These polymers are well suited for extrusion, blow
27 molding, injection molding and the like.

28
29 The polymerization reaction can be conducted by contacting monomer or
30 monomers, e.g., ethylene, alone or with one or more other olefins, and in the
31 substantial absence of catalyst poisons such as moisture and air, with a
32 catalytic amount of the supported organometallic catalyst at a temperature
33 and at a pressure sufficient to initiate the polymerization reaction. If desired,

1 an inert organic solvent may be used as a diluent and to facilitate materials
2 handling if the polymerization reaction is conducted with the reactants in the
3 liquid phase, e.g. in a particle form (slurry) or solution process. The reaction
4 may also be conducted with reactants in the vapor phase, e.g., in a fluidized
5 bed arrangement in the absence of a solvent but, if desired, in the presence of
6 an inert gas such as nitrogen.

7
8 The polymerization reaction is carried out at temperatures of from about 30°
9 C. or less, up to about 200° C. or more, depending to a great extent on the
10 operating pressure, the pressure of the olefin monomers, and the particular
11 catalyst being used and its concentration. Naturally, the selected operating
12 temperature is also dependent upon the desired polymer melt index since
13 temperature is definitely a factor in adjusting the molecular weight of the
14 polymer. Preferably, the temperature used is from about 30° C. to about 100°
15 C. in a conventional slurry or "particle forming" process or from 100° C. to
16 150° C. in a "solution forming" process. A temperature of from about 70° C to
17 110° C. can be employed for fluidized bed processes.

18
19 The pressure to be used in the polymerization reactions can be any pressure
20 sufficient to initiate the polymerization of the monomer(s) to high molecular
21 weight polymer. The pressure, therefore, can range from subatmospheric
22 pressures, using an inert gas as diluent, to superatmospheric pressures of up
23 to about 30,000 psig or more. The preferred pressure is from atmospheric (0
24 psig) up to about 1000 psig. As a general rule, a pressure of 20 to 800 psig is
25 most preferred.

26
27 The selection of an inert organic solvent medium to be employed in the
28 solution or slurry process embodiments of this invention is not too critical, but
29 the solvent should be inert to the supported organometallic catalyst and olefin
30 polymer produced, and be stable at the reaction temperature used. It is not
31 necessary, however, that the inert organic solvent medium also serve as a
32 solvent for the polymer to be produced. Among the inert organic solvents
33 applicable for such purposes may be mentioned saturated aliphatic

1 hydrocarbons having from about 3 to 12 carbon atoms per molecule such as
2 hexane, heptane, pentane, isooctane, purified kerosene and the like,
3 saturated cycloaliphatic hydrocarbons having from about 5 to 12 carbon
4 atoms per molecule such as cyclohexane, cyclopentane,
5 dimethylcyclopentane and methylcyclohexane and the like and aromatic
6 hydrocarbons having from about 6 to 12 carbon atoms per molecule such as
7 benzene, toluene, xylene, and the like. Particularly preferred solvent media
8 are cyclohexane, pentane, hexane and heptane.

9
10 Hydrogen can be introduced into the polymerization reaction zone in order to
11 decrease the molecular weight of the polymers produced (i.e., give a much
12 higher Melt Index, MI). Partial pressure of hydrogen when hydrogen is used
13 can be within the range of 5 to 100 psig, preferably 25 to 75 psig. The melt
14 indices of the polymers produced in accordance with the instant invention can
15 range from about 0.1 to about 70 or even higher.

16
17 More detailed description of suitable polymerization conditions including
18 examples of particle form, solution and fluidized bed polymerization
19 arrangements are found in Karapinka; U.S. Pat. No. 3,709,853; Issued Jan. 9,
20 1973 and Karol et al; U.S. Pat. No. 4,086,408; Issued Apr. 25, 1978. Both of
21 these patents are incorporated herein by reference.

22 23 Hydrogenation

24
25 SSZ-75 can be used in a catalyst to catalyze hydrogenation of a hydrocarbon
26 feed containing unsaturated hydrocarbons. The unsaturated hydrocarbons
27 can comprise olefins, dienes, polyenes, aromatic compounds and the like.

28
29 Hydrogenation is accomplished by contacting the hydrocarbon feed
30 containing unsaturated hydrocarbons with hydrogen in the presence of a
31 catalyst comprising SSZ-75. The catalyst can also contain one or more
32 metals of Group VIB and Group VIII, including salts, complexes and solutions
33 thereof. Reference to these catalytically active metals is intended to

1 encompass such metals or metals in the elemental state or in some form such
2 as an oxide, sulfide, halide, carboxylate and the like. Examples of such
3 metals include metals, salts or complexes wherein the metal is selected from
4 the group consisting of platinum, palladium, rhodium, iridium or combinations
5 thereof, or the group consisting of nickel, molybdenum, cobalt, tungsten,
6 titanium, chromium, vanadium, rhenium, manganese and combinations
7 thereof.

8
9 The hydrogenation component of the catalyst (i.e., the aforementioned metal)
10 is present in an amount effective to provide the hydrogenation function of the
11 catalyst, preferably in the range of from 0.05 to 25% by weight.

12
13 Hydrogenation conditions, such as temperature, pressure, space velocities,
14 contact time and the like are well known in the art.

15
16 SSZ-75 is useful as an adsorbent for gas separations (owing to its high pore
17 volume while maintaining diffusion control and hydrophobicity). SSZ-75 can
18 also be used in a catalyst for converting oxygenates (such as methanol) to
19 olefins, and for making small amines. SSZ-75 can be used to reduce oxides
20 of nitrogen in gas streams (such as automotive exhaust). SSZ-75 can also be
21 used as a cold start hydrocarbon trap in combustion engine pollution control
22 systems. SSZ-75 is particularly useful for trapping C₃ fragments.

23
24 The molecular sieve of the present invention can be used to separate gasses.
25 For example, it can be used to separate carbon dioxide from natural gas.
26 Typically, the molecular sieve is used as a component in a membrane that is
27 used to separate the gasses. Examples of such membranes are disclosed in
28 U. S. Patent No. 6,508,860, issued January 21, 2003 to Kulkarni et al., which
29 is incorporated by reference herein in its entirety.

30
31 The molecular sieve of the present invention can be used in a catalyst to
32 prepare methylamine or dimethylamine. Dimethylamine is generally prepared
33 in industrial quantities by continuous reaction of methanol (and/or

1 dimethylether) and ammonia in the presence of a silica-alumina catalyst. The
2 reactants are typically combined in the vapor phase, at temperatures in the
3 range of 300°C to 500°C, and at elevated pressures. Such a process is
4 disclosed in U. S. Patent No. 4,737,592, issued April 12, 1988 to Abrams et
5 al., which is incorporated by reference in its entirety.

6
7 The catalyst is used in its acid form. Acid forms of molecular sieves can be
8 prepared by a variety of techniques. Preferably, the molecular sieve used to
9 prepare dimethylamine will be in the hydrogen form, or have an alkali or
10 alkaline earth metal, such as Na, K, Rb, or Cs, ion-exchanged into it.

11
12 The process of the present invention involves reacting methanol,
13 dimethylether or a mixture thereof and ammonia in amounts sufficient to
14 provide a carbon/nitrogen (C/N) ratio from about 0.2 to about 1.5, preferably
15 about 0.5 to about 1.2. The reaction is conducted at a temperature from
16 about 250°C to about 450°C, preferably about 300°C to about 400°C.
17 Reaction pressures can vary from about 7-7000 kPa (1-1000 psi), preferably
18 about 70-3000 kPa (10-500 psi). A methanol and/or dimethylether space time
19 of about 0.01-80 hours, preferably 0.10-1.5 hours, is typically used. This
20 space time is calculated as the mass of catalyst divided by the mass flow rate
21 of methanol/dimethylether introduced into the reactor.

22
23 SSZ-75 may be used for the catalytic reduction of the oxides of nitrogen in a
24 gas stream. Typically, the gas stream also contains oxygen, often a
25 stoichiometric excess thereof. Also, the molecular sieve may contain a metal
26 or metal ions within or on it which are capable of catalyzing the reduction of
27 the nitrogen oxides. Examples of such metals or metal ions include cobalt,
28 copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum,
29 palladium, rhodium and mixtures thereof.

30
31 One example of such a process for the catalytic reduction of oxides of
32 nitrogen in the presence of a zeolite is disclosed in U.S. Patent No. 4,297,328,
33 issued October 27, 1981 to Ritscher et al., which is incorporated by reference

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

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

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

1

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

15

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

30

31 Another reference is U.S. Pat. No. 2,942,932 which teaches a process for
32 oxidizing carbon monoxide and hydrocarbons which are contained in exhaust
33 gas streams. The process disclosed in this patent consists of flowing an

1 exhaust stream which is below 800° F. into an adsorption zone which adsorbs
2 the carbon monoxide and hydrocarbons and then passing the resultant
3 stream from this adsorption zone into an oxidation zone. When the
4 temperature of the exhaust gas stream reaches about 800° F. the exhaust
5 stream is no longer passed through the adsorption zone but is passed directly
6 to the oxidation zone with the addition of excess air.

7
8 U. S. Patent No. 5,078,979, issued January 7, 1992 to Dunne, which is
9 incorporated herein by reference in its entirety, discloses treating an exhaust
10 gas stream from an engine to prevent cold start emissions using a molecular
11 sieve adsorbent bed. Examples of the molecular sieve include faujasites,
12 clinoptilolites, mordenites, chabazite, silicalite, zeolite Y, ultrastable zeolite Y,
13 and ZSM-5.

14
15 Canadian Patent No. 1,205,980 discloses a method of reducing exhaust
16 emissions from an alcohol fueled automotive vehicle. This method consists of
17 directing the cool engine startup exhaust gas through a bed of zeolite particles
18 and then over an oxidation catalyst and then the gas is discharged to the
19 atmosphere. As the exhaust gas stream warms up it is continuously passed
20 over the adsorption bed and then over the oxidation bed.

21
22 As stated this invention generally relates to a process for treating an engine
23 exhaust stream and in particular to a process for minimizing emissions during
24 the cold start operation of an engine. The engine consists of any internal or
25 external combustion engine which generates an exhaust gas stream
26 containing noxious components or pollutants including unburned or thermally
27 degraded hydrocarbons or similar organics. Other noxious components
28 usually present in the exhaust gas include nitrogen oxides and carbon
29 monoxide. The engine may be fueled by a hydrocarbonaceous fuel. As used
30 in this specification and in the appended claims, the term "hydrocarbonaceous
31 fuel" includes hydrocarbons, alcohols and mixtures thereof. Examples of
32 hydrocarbons which can be used to fuel the engine are the mixtures of
33 hydrocarbons which make up gasoline or diesel fuel. The alcohols which may

1 be used to fuel engines include ethanol and methanol. Mixtures of alcohols
2 and mixtures of alcohols and hydrocarbons can also be used. The engine
3 may be a jet engine, gas turbine, internal combustion engine, such as an
4 automobile, truck or bus engine, a diesel engine or the like. The process of
5 this invention is particularly suited for hydrocarbon, alcohol, or hydrocarbon-
6 alcohol mixture, internal combustion engine mounted in an automobile. For
7 convenience the description will use hydrocarbon as the fuel to exemplify the
8 invention. The use of hydrocarbon in the subsequent description is not to be
9 construed as limiting the invention to hydrocarbon fueled engines.

10

11 When the engine is started up, it produces a relatively high concentration of
12 hydrocarbons in the engine exhaust gas stream as well as other pollutants.
13 Pollutants will be used herein to collectively refer to any unburned fuel
14 components and combustion byproducts found in the exhaust stream. For
15 example, when the fuel is a hydrocarbon fuel, hydrocarbons, nitrogen oxides,
16 carbon monoxide and other combustion byproducts will be found in the engine
17 exhaust gas stream. The temperature of this engine exhaust stream is
18 relatively cool, generally below 500° C. and typically in the range of 200° to
19 400° C. This engine exhaust stream has the above characteristics during the
20 initial period of engine operation, typically for the first 30 to 120 seconds after
21 startup of a cold engine. The engine exhaust stream will typically contain, by
22 volume, about 500 to 1000 ppm hydrocarbons.

23

24 The engine exhaust gas stream which is to be treated is flowed over a
25 molecular sieve bed comprising molecular sieve SSZ-56 a first exhaust
26 stream. Molecular sieve SSZ-56 is described below. The first exhaust stream
27 which is discharged from the molecular sieve bed is now flowed over a
28 catalyst to convert the pollutants contained in the first exhaust stream to
29 innocuous components and provide a treated exhaust stream which is
30 discharged into the atmosphere. It is understood that prior to discharge into
31 the atmosphere, the treated exhaust stream may be flowed through a muffler
32 or other sound reduction apparatus well known in the art.

1
2 The catalyst which is used to convert the pollutants to innocuous components
3 is usually referred to in the art as a three-component control catalyst because
4 it can simultaneously oxidize any residual hydrocarbons present in the first
5 exhaust stream to carbon dioxide and water, oxidize any residual carbon
6 monoxide to carbon dioxide and reduce any residual nitric oxide to nitrogen
7 and oxygen. In some cases the catalyst may not be required to convert nitric
8 oxide to nitrogen and oxygen, e.g., when an alcohol is used as the fuel. In this
9 case the catalyst is called an oxidation catalyst. Because of the relatively low
10 temperature of the engine exhaust stream and the first exhaust stream, this
11 catalyst does not function at a very high efficiency, thereby necessitating the
12 molecular sieve bed.

13
14 When the molecular sieve bed reaches a sufficient temperature, typically
15 about 150-200° C., the pollutants which are adsorbed in the bed begin to
16 desorb and are carried by the first exhaust stream over the catalyst. At this
17 point the catalyst has reached its operating temperature and is therefore
18 capable of fully converting the pollutants to innocuous components.

19
20 The adsorbent bed used in the instant invention can be conveniently
21 employed in particulate form or the adsorbent can be deposited onto a solid
22 monolithic carrier. When particulate form is desired, the adsorbent can be
23 formed into shapes such as pills, pellets, granules, rings, spheres, etc. In the
24 employment of a monolithic form, it is usually most convenient to employ the
25 adsorbent as a thin film or coating deposited on an inert carrier material which
26 provides the structural support for the adsorbent. The inert carrier material
27 can be any refractory material such as ceramic or metallic materials. It is
28 desirable that the carrier material be unreactive with the adsorbent and not be
29 degraded by the gas to which it is exposed. Examples of suitable ceramic
30 materials include sillimanite, petalite, cordierite, mullite, zircon, zircon mullite,
31 spondumene, alumina-titanate, etc. Additionally, metallic materials which are
32 within the scope of this invention include metals and alloys as disclosed in

1 U.S. Pat. No. 3,920,583 which are oxidation resistant and are otherwise
2 capable of withstanding high temperatures.

3

4 The carrier material can best be utilized in any rigid unitary configuration
5 which provides a plurality of pores or channels extending in the direction of
6 gas flow. It is preferred that the configuration be a honeycomb configuration.
7 The honeycomb structure can be used advantageously in either unitary form,
8 or as an arrangement of multiple modules. The honeycomb structure is
9 usually oriented such that gas flow is generally in the same direction as the
10 cells or channels of the honeycomb structure. For a more detailed discussion
11 of monolithic structures, refer to U.S. Pat. Nos. 3,785,998 and 3,767,453.

12

13 The molecular sieve is deposited onto the carrier by any convenient way well
14 known in the art. A preferred method involves preparing a slurry using the
15 molecular sieve and coating the monolithic honeycomb carrier with the slurry.
16 The slurry can be prepared by means known in the art such as combining the
17 appropriate amount of the molecular sieve and a binder with water. This
18 mixture is then blended by using means such as sonification, milling, etc. This
19 slurry is used to coat a monolithic honeycomb by dipping the honeycomb into
20 the slurry, removing the excess slurry by draining or blowing out the channels,
21 and heating to about 100° C. If the desired loading of molecular sieve is not
22 achieved, the above process may be repeated as many times as required to
23 achieve the desired loading.

24

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

28

29 The adsorbent may optionally contain one or more catalytic metals dispersed
30 thereon. The metals which can be dispersed on the adsorbent are the noble
31 metals which consist of platinum, palladium, rhodium, ruthenium, and
32 mixtures thereof. The desired noble metal may be deposited onto the
33 adsorbent, which acts as a support, in any suitable manner well known in the

1 art. One example of a method of dispersing the noble metal onto the
2 adsorbent support involves impregnating the adsorbent support with an
3 aqueous solution of a decomposable compound of the desired noble metal or
4 metals, drying the adsorbent which has the noble metal compound dispersed
5 on it and then calcining in air at a temperature of about 400° to about 500° C.
6 for a time of about 1 to about 4 hours. By decomposable compound is meant
7 a compound which upon heating in air gives the metal or metal oxide.
8 Examples of the decomposable compounds which can be used are set forth
9 in U.S. Pat. No. 4,791,091 which is incorporated by reference. Preferred
10 decomposable compounds are chloroplatinic acid, rhodium trichloride,
11 chloropalladic acid, hexachloroiridate (IV) acid and hexachlororuthenate. It is
12 preferable that the noble metal be present in an amount ranging from about
13 0.01 to about 4 weight percent of the adsorbent support. Specifically, in the
14 case of platinum and palladium the range is 0.1 to 4 weight percent, while in
15 the case of rhodium and ruthenium the range is from about 0.01 to 2 weight
16 percent.

17

18 These catalytic metals are capable of oxidizing the hydrocarbon and carbon
19 monoxide and reducing the nitric oxide components to innocuous products.
20 Accordingly, the adsorbent bed can act both as an adsorbent and as a
21 catalyst.

22

23 The catalyst which is used in this invention is selected from any three
24 component control or oxidation catalyst well known in the art. Examples of
25 catalysts are those described in U.S. Pat. Nos. 4,528,279; 4,791,091;
26 4,760,044; 4,868,148; and 4,868,149, which are all incorporated by reference.
27 Preferred catalysts well known in the art are those that contain platinum and
28 rhodium and optionally palladium, while oxidation catalysts usually do not
29 contain rhodium. Oxidation catalysts usually contain platinum and/or
30 palladium metal. These catalysts may also contain promoters and stabilizers
31 such as barium, cerium, lanthanum, nickel, and iron. The noble metals
32 promoters and stabilizers are usually deposited on a support such as alumina,
33 silica, titania, zirconia, alumino silicates, and mixtures thereof with alumina

1 being preferred. The catalyst can be conveniently employed in particulate
2 form or the catalytic composite can be deposited on a solid monolithic carrier
3 with a monolithic carrier being preferred. The particulate form and monolithic
4 form of the catalyst are prepared as described for the adsorbent above.

5
6 The molecular sieve used in the adsorbent bed, SSZ-75, comprises a
7 crystalline molecular sieve having STI topology and having a mole ratio of at
8 least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a
9 trivalent element, pentavalent element, second tetravalent element which is
10 different from said first tetravalent element or mixture thereof.

11
12 The present invention comprises a process for catalytic conversion of a
13 feedstock comprising one or more oxygenates comprising alcohols and ethers
14 to a hydrocarbon product containing light olefins, i.e., C₂, C₃ and/or C₄ olefins.
15 The feedstock is contacted with the molecular sieve of the present invention
16 at effective process conditions to produce light olefins.

17
18 The term "oxygenate" as used herein designates compounds such as
19 alcohols, ethers and mixtures thereof. Examples of oxygenates include, but
20 are not limited to, methanol and dimethyl ether.

21
22 The process of the present invention may be conducted in the presence of
23 one or more diluents which may be present in the oxygenate feed in an
24 amount between about 1 and about 99 molar percent, based on the total
25 number of moles of all feed and diluent components. Diluents include, but are
26 not limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide,
27 hydrogen, water, paraffins, hydrocarbons (such as methane and the like),
28 aromatic compounds, or mixtures thereof. U. S. Patents No. 4,861,938 and
29 4,677,242, which are incorporated by reference herein in their entirety,
30 emphasize the use of a diluent to maintain catalyst selectivity toward the
31 production of light olefins, particularly ethylene.

32

1 The oxygenate conversion is preferably conducted in the vapor phase such
2 that the oxygenate feedstock is contacted in a vapor phase in a reaction zone
3 with the molecular sieve of this invention at effective process conditions to
4 produce hydrocarbons, i.e., an effective temperature, pressure, weight hourly
5 space velocity (WHSV) and, optionally, an effective amount of diluent. The
6 process is conducted for a period of time sufficient to produce the desired light
7 olefins. In general, the residence time employed to produce the desired
8 product can vary from seconds to a number of hours. It will be readily
9 appreciated that the residence time will be determined to a significant extent
10 by the reaction temperature, the molecular sieve catalyst, the WHSV, the
11 phase (liquid or vapor) and process design characteristics. The oxygenate
12 feedstock flow rate affects olefin production. Increasing the feedstock flow
13 rate increases WHSV and enhances the formation of olefin production relative
14 to paraffin production. However, the enhanced olefin production relative to
15 paraffin production is offset by a diminished conversion of oxygenate to
16 hydrocarbons.

17

18 The oxygenate conversion process is effectively carried out over a wide range
19 of pressures, including autogenous pressures. At pressures between about
20 0.01 atmospheres (0.1 kPa) and about 1000 atmospheres (101.3 kPa), the
21 formation of light olefins will be affected although the optimum amount of
22 product will not necessarily be formed at all pressures. The preferred
23 pressure is between about 0.01 atmospheres (0.1 kPa) and about 100
24 atmospheres (10.13 kPa). More preferably, the pressure will range from
25 about 1 to about 10 atmospheres (101.3 kPa to 1.013 Mpa). The pressures
26 referred to herein are exclusive of the diluent, if any, that is present and refer
27 to the partial pressure of the feedstock as it relates to oxygenate compounds.

28

29 The temperature which may be employed in the oxygenate conversion
30 process may vary over a wide range depending, at least in part, on the
31 molecular sieve catalyst. In general, the process can be conducted at an
32 effective temperature between about 200°C and about 700°C. At the lower
33 end of the temperature range, and thus generally at a lower rate of reaction,

1 the formation of the desired light olefins may become low. At the upper end of
2 the range, the process may not form an optimum amount of light olefins and
3 catalyst deactivation may be rapid.

4
5 The molecular sieve catalyst preferably is incorporated into solid particles in
6 which the catalyst is present in an amount effective to promote the desired
7 conversion of oxygenates to light olefins. In one aspect, the solid particles
8 comprise a catalytically effective amount of the catalyst and at least one
9 matrix material selected from the group consisting of binder materials, filler
10 materials and mixtures thereof to provide a desired property or properties,
11 e.g., desired catalyst dilution, mechanical strength and the like to the solid
12 particles. Such matrix materials are often, to some extent, porous in nature
13 and may or may not be effective to promote the desired reaction. Filler and
14 binder materials include, for example, synthetic and naturally occurring
15 substances such as metal oxides, clays, silicas, aluminas, silica-aluminas,
16 silica-magnesias, silica-zirconias, silica-thorias and the like. If matrix
17 materials are included in the catalyst composition, the molecular sieve
18 preferably comprises about 1 to 99%, more preferably about 5 to 90%, and
19 still more preferably about 10 to 80% by weight of the total composition.

21 EXAMPLES

22
23 The following examples demonstrate but do not limit the present invention.

25 Example 1

26 Synthesis of Al-Containing SSZ-75

27
28 1.5 mM of tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication SDA
29 (3 mM OH⁻) was mixed in a Teflon cup (for a Parr 23 ml reactor) with 1.26
30 grams of tetraethylorthosilicate and the cup was placed in a hood to
31 evaporate (as ethanol is formed from hydrolysis) over several days. When all
32 of the visible liquid was gone, the Teflon cup was reweighed and water was
33 added to bring the H₂O/SiO₂ mole ratio to about four. Then, 12 mg of Reheiss
34 F2000 (50% Al₂O₃) was added and dissolved into the reaction mixture. This
35 represents a starting synthesis mole ratio of SiO₂/ Al₂O₃ of 100. Lastly, 0.135

1 gram of 50% HF was added using a plastic pipette. The gel was mixed with a plastic spatula and then the resulting reaction mixture was heated in a closed vessel rotating at 43 RPM at 150°C for 16 days. A crystalline product formed which was recovered and found by X-ray diffraction analysis to be molecular sieve SSZ-75.

Example 2

Synthesis of Al-Containing SSZ-75

The procedure described in Example 1 was repeated, except that the source of aluminum was LZ-210 zeolite (a form of dealuminated FAU) and the SiO₂/Al₂O₃ mole ratio was 70. The reaction formed SSZ-75 in 10 days.

Example 3

Synthesis of Al-Containing SSZ-75

The procedure described in Example 1 was repeated, except that the source of aluminum was Catapal B (a form of pseudoboehmite alumina). The reaction formed SSZ-75 in 10 days.

Examples 4-7

Synthesis of Al-Silica SSZ-75

A procedure similar to that of Example 1 was repeated using the reaction mixture (expressed as mole ratios) and conditions shown in the table below. The reactions were run until a crystalline product was observed by SEM, and then the product was recovered. The products are also shown in the table.

1

Ex.	SDA/ SiO ₂	NH ₄ F/ SiO ₂	HF/ SiO ₂	H ₂ O/ SiO ₂	°C/RPM	Prod.
4	0.50	0.0	0.50	5.0	150/43	SSZ-75
5	0.40	0.1	0.40	5.0	150/43	SSZ-75
6	0.30	0.2	0.30	5.0	150/43	MTW
7	0.20	0.3	0.20	5.0	150/43	Amor. ZSM- 48

2

3

Example 8

4

Calcination of SSZ-75

5

6 The product from Example 1 was calcined in the following manner. A thin bed
7 of material was heated in a flowing bed of air in a muffle furnace from room
8 temperature to 120°C at a rate of 1°C per minute and held at 120°C for two
9 hours. The temperature is then ramped up to 540°C at the same rate and
10 held at this temperature for three hours, after which it was increased to 594°C
11 and held there for another three hours.

12

13

Example 9

14

Conversion of Methanol

15

16 The calcined material of Example 8 (0.10) gram) was pelleted and meshed
17 (with recycling) to 20-40 mesh and packed into a 3/8 inch stainless steel
18 reactor. After sufficient purge with nitrogen carrier gas (20 cc/min), the
19 catalyst was heated to 750°F (399°C). A feed of 22.5% methanol in water
20 was introduced into the reactor via syringe pump at a rate of 1.59 cc/hr. A
21 sample of the effluent stream was diverted to an on-line gas chromatograph at
22 ten minute point of feed introduction. SSZ-75 showed the following behavior:

23

24 Methanol conversion = 100%

25 No dimethylether detected

26 C₂-C₄ is about 70% of the product

- 1 C₅₊ showed a mixture of olefins and saturates
- 2 Aromatics were made with ethylbenzene the most abundant single product
- 3 Trimethylbenzene isomers were observed as the heaviest products
- 4
- 5 At 100 minutes on stream the SSZ-75 was fouling, but still produced the same
- 6 products (although very few aromatics were observed).
- 7

WHAT IS CLAIMED IS:

1. A crystalline molecular sieve having STI topology, a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

2. The molecular sieve of claim 1 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.
3. A crystalline molecular sieve having STI topology, having a composition comprising, as synthesized and in the anhydrous state, in terms of mole ratios, the following:

$\text{SiO}_2 / \text{X}_c\text{O}_d$	at least 15
$\text{M}_{2/n} / \text{SiO}_2$	0 – 0.03
Q / SiO_2	0.02 – 0.08
F / SiO_2	0.01 – 0.04

wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, c is 1 or 2; d is 2 when c is 1, or d is 3 or 5 when c is 2, M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M; Q is a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication and F is fluoride, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

4. A method of preparing a crystalline molecular sieve having STI topology, said method comprising contacting under crystallization conditions (1) a source of silicon oxide, (2) a source of aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, (3) fluoride ions and (4) a structure directing agent comprising a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication, and said molecular sieve having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

5. The method of claim 4 wherein the crystalline molecular sieve is prepared from a reaction mixture comprising silicon oxide and, in terms of mole ratios, the following:

SiO₂ / XaOb at least 15

OH- / SiO₂ 0.20 – 0.80

Q / SiO₂ 0.20 – 0.80

M₂/n / SiO₂ 0 – 0.04

H₂O / SiO₂ 2 - 10

HF / SiO₂ 0.20 – 0.80

wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures thereof, a is 1 or 2, b is 2 when a is 1, b is 3 when a is 2, M is an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the valence of M and Q is a tetramethylene-1,4-bis-(N methylpyrrolidinium) dication.

6. A process for converting hydrocarbons comprising contacting a hydrocarbonaceous feed at hydrocarbon converting conditions with a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

7. The process of Claim 6 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.
8. The process of Claim 7 wherein the molecular sieve is predominantly in the hydrogen form.
9. The process of Claim 7 wherein the molecular sieve is substantially free of acidity.
10. The process of Claim 7 wherein the process is a hydrocracking process comprising contacting the catalyst with a hydrocarbon feedstock under hydrocracking conditions.
11. The process of Claim 7 wherein the process is a process for increasing the octane of a hydrocarbon feedstock to produce a product having an increased aromatics content comprising contacting a hydrocarbonaceous feedstock which comprises normal and slightly branched hydrocarbons having a boiling range above about 40°C and less than about 200°C under aromatic conversion conditions with the catalyst.
12. The process of Claim 11 wherein the molecular sieve is substantially free of acid.
13. The process of Claim 11 wherein the molecular sieve contains a Group VIII metal component.
14. The process of Claim 7 wherein the process is a catalytic cracking process comprising contacting a hydrocarbon feedstock in a reaction zone under catalytic cracking conditions in the absence of added hydrogen with the catalyst.

15. The process of Claim 14 wherein the catalyst additionally comprises a large pore crystalline cracking component.
16. The process of Claim 7 wherein the process is an isomerization process for isomerizing C₄ to C₇ hydrocarbons, comprising contacting a feed having normal and slightly branched C₄ to C₇ hydrocarbons under isomerizing conditions with the catalyst.
17. The process of Claim 16 wherein the molecular sieve has been impregnated with at least one Group VIII metal.
18. The process of Claim 16 wherein the catalyst has been calcined in a steam/air mixture at an elevated temperature after impregnation of the Group VIII metal.
19. The process of Claim 17 wherein the Group VIII metal is platinum.
20. The process of Claim 7 wherein the process is a process for alkylating an aromatic hydrocarbon which comprises contacting under alkylation conditions at least a molar excess of an aromatic hydrocarbon with a C₂ to C₂₀ olefin under at least partial liquid phase conditions and in the presence of the catalyst.
21. The process of Claim 20 wherein the olefin is a C₂ to C₄ olefin.
22. The process of Claim 21 wherein the aromatic hydrocarbon and olefin are present in a molar ratio of about 4:1 to about 20:1, respectively.
23. The process of Claim 21 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

24. The process of Claim 7 wherein the process is a process for transalkylating an aromatic hydrocarbon which comprises contacting under transalkylating conditions an aromatic hydrocarbon with a polyalkyl aromatic hydrocarbon under at least partial liquid phase conditions and in the presence of the catalyst.
25. The process of Claim 24 wherein the aromatic hydrocarbon and the polyalkyl aromatic hydrocarbon are present in a molar ratio of from about 1:1 to about 25:1, respectively.
26. The process of Claim 24 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.
27. The process of Claim 24 wherein the polyalkyl aromatic hydrocarbon is a dialkylbenzene.
28. The process of Claim 7 wherein the process is a process to convert paraffins to aromatics which comprises contacting paraffins under conditions which cause paraffins to convert to aromatics with a catalyst comprising the molecular sieve and gallium, zinc, or a compound of gallium or zinc.
29. The process of Claim 7 wherein the process is a process for isomerizing olefins comprising contacting said olefin under conditions which cause isomerization of the olefin with the catalyst.
30. The process of Claim 7 wherein the process is a process for isomerizing an isomerization feed comprising an aromatic C₈ stream of xylene isomers or mixtures of xylene isomers and ethylbenzene, wherein a more nearly equilibrium ratio of ortho-, meta and para-xylenes is obtained, said process comprising contacting said feed under isomerization conditions with the catalyst.

31. The process of Claim 7 wherein the process is a process for oligomerizing olefins comprising contacting an olefin feed under oligomerization conditions with the catalyst.
32. A process for converting oxygenated hydrocarbons comprising contacting said oxygenated hydrocarbon under conditions to produce liquid products with a catalyst comprising a molecular sieve having a mole ratio of at least 15 of an oxide of a first tetravalent element to an oxide of a second tetravalent element which is different from said first tetravalent element, trivalent element, pentavalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

33. The process of Claim 32 wherein the oxygenated hydrocarbon is a lower alcohol.
34. The process of Claim 33 wherein the lower alcohol is methanol.
35. The process of Claim 7 wherein the process is a process for the production of higher molecular weight hydrocarbons from lower molecular weight hydrocarbons comprising the steps of:

(a) introducing into a reaction zone a lower molecular weight hydrocarbon-containing gas and contacting said gas in said zone under C₂+ hydrocarbon synthesis conditions with the catalyst and a metal or metal compound capable of converting the lower molecular weight hydrocarbon to a higher molecular weight hydrocarbon; and

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

36. The process of Claim 35 wherein the metal or metal compound comprises a lanthanide or actinide metal or metal compound.
37. The process of Claim 35 wherein the lower molecular weight hydrocarbon is methane.
38. A catalyst composition for promoting polymerization of 1-olefins, said composition comprising

(A) a crystalline molecular sieve having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

and

(B) an organotitanium or organochromium compound.

39. The process of Claim 7 wherein the process is a process for polymerizing 1-olefins, which process comprises contacting 1-olefin monomer with a catalytically effective amount of a catalyst composition comprising
- (A) a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof; and
 - (B) an organotitanium or organochromium compound,
- under polymerization conditions which include a temperature and pressure suitable for initiating and promoting the polymerization reaction.
40. The process of Claim 39 wherein the 1-olefin monomer is ethylene.

41. The process of Claim 7 wherein the process is a process for hydrogenating a hydrocarbon feed containing unsaturated hydrocarbons, the process comprising contacting the feed with hydrogen under conditions which cause hydrogenation with the catalyst.
42. The process of Claim 41 wherein the catalyst contains metals, salts or complexes wherein the metal is selected from the group consisting of platinum, palladium, rhodium, iridium or combinations thereof, or the group consisting of nickel, molybdenum, cobalt, tungsten, titanium, chromium, vanadium, rhenium, manganese and combinations thereof.
43. A dewaxing process comprising contacting a hydrocarbon feedstock under dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

44. A process for improving the viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising contacting a waxy hydrocarbon feed under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

45. A process for producing a C₂₀₊ lube oil from a C₂₀₊ olefin feed comprising isomerizing said olefin feed under isomerization conditions over a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

46. The process of Claim 45 wherein the catalyst further comprises at least one Group VIII metal.
47. A process for catalytically dewaxing a 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 a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

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19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

48. The process of Claim 47 wherein the catalyst further comprises at least one Group VIII metal.
49. The process of Claim 47 wherein said catalyst comprises a combination comprising a first catalyst comprising the molecular sieve and at least one Group VIII metal, and a second catalyst comprising an aluminosilicate zeolite which is more shape selective than the molecular sieve of said first catalyst.

50. A process for preparing a lubricating oil which comprises:

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

(b) catalytically dewaxing said effluent comprising hydrocracked oil at a temperature of at least about 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig (0.103 to 20.7MPa gauge) in the presence of added hydrogen gas with a catalyst comprising a crystalline

molecular sieve having STI topology and a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
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13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

51. The process of Claim 50 wherein the catalyst further comprises at least one Group VIII metal.
52. A process for isomerization dewaxing a raffinate comprising contacting said raffinate in the presence of added hydrogen under isomerization dewaxing conditions with a catalyst comprising a crystalline molecular sieve having STI topology, a mole ratio of at least about 14 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

53. The process of Claim 52 wherein the catalyst further comprises at least one Group VIII metal.
54. The process of Claim 52 wherein the raffinate is bright stock.
55. The process of Claim 44, 45, 46, 47, 48, 49, 50, 51, 52, 53 or 54 wherein the molecular sieve has a mole ratio of at least about 14 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.
56. The process of Claim 10, 14, 16, 20, 24, 44, 44, 45, 47, 50 or 52 wherein the molecular sieve is predominantly in the hydrogen form.
57. In a process for separating gasses using a membrane containing a molecular sieve, the improvement comprising using as the molecular sieve a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2)

an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

58. The process of Claim 57 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.
59. A process for producing methylamine or dimethylamine comprising reacting methanol, dimethyl ether or a mixture thereof and ammonia in the gaseous phase in the presence of a catalyst comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1

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

60. The process of Claim 59 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.

61. The process of Claim 60 wherein the methanol, dimethylether or mixture thereof and ammonia are present in amounts sufficient to provide a carbon/nitrogen ratio from about 0.2 to about 1.5.
62. The process of Claim 60 conducted at a temperature of from about 250°C to about 450°C.
63. A process for the reduction of oxides of nitrogen contained in a gas stream wherein said process comprises contacting the gas stream with a crystalline molecular sieve having STI topology and having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

64. The process of Claim 63 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.

65. The process of Claim 64 conducted in the presence of oxygen.
66. The process of Claim 64 wherein said molecular sieve contains a metal or metal ions capable of catalyzing the reduction of the oxides of nitrogen.

67. The process of Claim 66 wherein the metal is cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof.
68. The process of Claim 63 wherein the gas stream is the exhaust stream of an internal combustion engine.
69. The process of Claim 67 wherein the gas stream is the exhaust stream of an internal combustion engine.
70. A process for treating a cold-start engine exhaust gas stream containing hydrocarbons and other pollutants consisting of flowing said engine exhaust gas stream over a molecular sieve bed which preferentially adsorbs the hydrocarbons over water to provide a first exhaust stream, and flowing the first exhaust gas stream over a catalyst to convert any residual hydrocarbons and other pollutants contained in the first exhaust gas stream to innocuous products and provide a treated exhaust stream and discharging the treated exhaust stream into the atmosphere, the molecular sieve bed comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
9.95	8.88	VS
10.06	8.79	M
13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

^(a) ± 0.1 .

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

71. The process of Claim 70 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.

72. The process of Claim 71 wherein the engine is an internal combustion engine.
73. The process of Claim 72 wherein the internal combustion engine is an automobile engine.
74. The process of Claim 71 wherein the engine is fueled by a hydrocarbonaceous fuel.
75. The process of Claim 71 wherein the molecular sieve has deposited on it a metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, and mixtures thereof.
76. The process of Claim 75 wherein the metal is platinum.
77. The process of Claim 75 wherein the metal is palladium.
78. The process of Claim 75 wherein the metal is a mixture of platinum and palladium.
79. A process for the production of light olefins from a feedstock comprising an oxygenate or mixture of oxygenates, the process comprising reacting the feedstock at effective conditions over a catalyst comprising a crystalline molecular sieve having STI topology, having a mole ratio of at least 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent element, pentavalent element, second tetravalent element which is different from said first

tetravalent element or mixture thereof, and having, after calcination, the X-ray diffraction lines of Table II, as follows:

TABLE II
Calcined SSZ-75

<u>2 Theta</u>	<u>d-spacing (Angstroms)</u>	<u>Relative Integrated Intensity (%)</u>
9.64	9.17	W
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13.14	6.73	W
19.38	4.58	W
21.03	4.22	W
22.35	3.97	M-S
24.19	3.68	W
28.37	3.14	W
30.16	2.96	W

(a) ± 0.1 .

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

80. The process of Claim 79 wherein the molecular sieve has a mole ratio of at least 15 of (1) silicon oxide to (2) an oxide selected from aluminum

oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof.

81. The process of Claim 80 wherein the light olefins are ethylene, propylene, butylene or mixtures thereof.
82. The process of Claim 81 wherein the light olefin is ethylene.
83. The process of Claim 80 wherein the oxygenate is methanol, dimethyl ether or a mixture thereof.
84. The process of Claim 83 wherein the oxygenate is methanol.