(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
21 December 2007 (21.12.2007)

PCT

(10) International Publication Number
WO 2007/146622 A2

(51) International Patent Classification:
C01B 39/00 (2006.01)

(21) International Application Number:
PCT/US2007/070210

(22) International Filing Date: 1 June 2007 (01.06.2007)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:

60/804,230	8 June 2006 (08.06.2006)	US
60/804,248	8 June 2006 (08.06.2006)	US
60/804,252	8 June 2006 (08.06.2006)	US
60/804,254	8 June 2006 (08.06.2006)	US
60/804,255	8 June 2006 (08.06.2006)	US
60/804,258	8 June 2006 (08.06.2006)	US
60/804,259	8 June 2006 (08.06.2006)	US

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(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BH, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SV, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, MT, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:
— *without international search report and to be republished upon receipt of that report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: MOLECULAR SIEVE SSZ-75 COMPOSITION OF MATTER AND SYNTHESIS THEREOF

(57) Abstract: The present invention relates to new crystalline molecular sieve SSZ-75 having STI topology prepared using a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication as a structure-directing agent, methods for synthesizing SSZ-75, and uses for SSZ-75.

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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

The present invention 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

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

In accordance with the present invention 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 invention 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 invention 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:

SiO_2 / X_cO_d	at least 15 (i.e., 15 - infinity)
$M_{2/n} / SiO_2$	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-methyl pyrrolidinium) dication and F is fluoride.

Also provided in accordance with the present invention 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 invention 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 invention includes such a method of preparing a crystalline material which uses a reaction mixture comprising (in terms of mole ratios), the following:

SiO_2 / X_aO_b	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_2O / 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 invention 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 invention is a hydrocracking process comprising contacting a hydrocarbon feedstock under hydrocracking conditions with a catalyst comprising the molecular sieve of this invention, preferably predominantly in the hydrogen form.

Also included in this invention 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 invention made substantially free of acidity by neutralizing said molecular sieve with a basic metal. Also provided in this invention is such a process wherein the molecular sieve contains a Group VIII metal component.

Also provided by the present invention 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 invention, preferably predominantly in the hydrogen form. Also included in this invention is such a catalytic cracking process wherein the catalyst additionally comprises a large pore crystalline cracking component.

This invention further provides an isomerization process for isomerizing C_4 to C_7 hydrocarbons, comprising contacting a feed having normal and slightly branched C_4 to C_7 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 invention 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 C_2 to C_{20} olefin under at least partial liquid phase conditions and in the presence of a catalyst comprising the molecular sieve of this invention, preferably predominantly in the hydrogen form. The olefin may be a C_2 to C_4 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 invention 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 invention, 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 invention 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 invention, said catalyst comprising gallium, zinc, or a compound of gallium or zinc.

In accordance with this invention 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 invention.

Further provided in accordance with this invention is a process for isomerizing an isomerization feed comprising an aromatic C_8 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 invention.

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

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

Further provided in accordance with the present invention 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 invention 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 invention. 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 invention 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 invention 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 invention is a process for producing a C_{20+} lube oil from a C_{20+} 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 invention 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 invention 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 invention 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 invention, 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 invention 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 invention 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 invention 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 invention 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 invention 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.

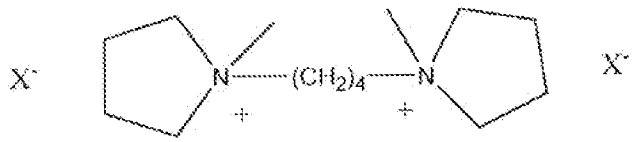
Thus, in accordance with the present invention there is provided a process for the production of light olefins from a feedstock comprising an oxygenate or mixture of oxygenates, the process comprising reacting the feedstock at

effective conditions over a catalyst comprising a crystalline molecular sieve having STI topology 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.

DETAILED DESCRIPTION OF THE INVENTION

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

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



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

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

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 / X_aO_b	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_2O / 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.

As noted above, the SiO_2 / X_aO_b mole ratio in the reaction mixture is ≥ 15. This means that the SiO_2 / X_aO_b mole ratio can be infinity, i.e., there is no X_aO_b in the reaction mixture. This results in a version of SSZ-75 that is essentially all silica. As used herein, "essentially all silicon oxide" or "essentially all-silica" means that the molecular sieve's crystal structure is comprised of only silicon oxide or is comprised of silicon oxide and only trace amounts of other oxides, such as aluminum oxide, which may be introduced as impurities in the source of silicon oxide.

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

(a) preparing an aqueous solution containing (1) a source(s) of silicon oxide, (2) a source(s) of aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and mixtures thereof, (3) a source of fluoride ion and (4) a tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication having an anionic counterion which is not detrimental to the formation of SSZ-75;

(b) maintaining the aqueous solution under conditions sufficient to form crystals of SSZ-75; and

(c) recovering the crystals of SSZ-75.

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

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

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

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

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

SiO_2 / X_cO_d	at least 15 (i.e., 15 - infinity)
$M_{2/n} / SiO_2$	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-methyl-pyrrolidinium) dication and F is fluoride.

SSZ-75 (whether in the as synthesized or calcined version) has a SiO_2 / X_cO_d mole ratio of at least 15 (i.e., 15 - infinity), for example 20 - infinity or 40 - 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

2 Theta	d-spacing (Angstroms)	Relative Integrated Intensity (%)
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

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

TABLE IIA

Calcined SSZ-75

2 Theta	d-spacing (Angstroms)	Relative Integrated Intensity (%)
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

[(a)] ± 0.1

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

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

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

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

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

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

Hydrocarbon Conversion Processes

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

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

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

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

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

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

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

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

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

[1] Several hundred atmospheres

[2] Gas phase reaction

[3] Hydrocarbon partial pressure

[4] Liquid phase reaction

[5] WHSV

Other reaction conditions and parameters are provided below.

Hydrocracking

Using a catalyst which comprises SSZ-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 tpology 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

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

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

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

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

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

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

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

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

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

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

Lube oil may be prepared using SSZ-75 or TNU-10. For example, a C_{20+} lube oil may be made by isomerizing a C_{20+} olefin feed over a catalyst comprising SSZ-75 or TNU-10 in the hydrogen form and at least one Group VIII metal. Alternatively, the lubricating oil may be made by hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock to obtain an effluent comprising a hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at least about 400°F (204°C) and at a pressure of from about 15 psig to about 3000 psig (0.103-20.7 Mpa gauge) in the presence of added hydrogen gas with a catalyst comprising SSZ-75 or TNU-10F in the hydrogen form and at least one Group VIII metal.

Aromatics Formation

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

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

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

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

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

Catalytic Cracking

Hydrocarbon cracking stocks can be catalytically cracked in the absence of hydrogen using SSZ-75, preferably predominantly in the hydrogen form.

When SSZ-75 is used as a catalytic cracking catalyst in the absence of hydrogen, the catalyst may be employed in conjunction with traditional cracking catalysts, e.g., any aluminosilicate heretofore employed as a component in cracking catalysts. Typically, these are large pore, crystalline aluminosilicates. Examples of these traditional cracking catalysts are disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No 5,316,753. When a traditional cracking catalyst (TC) component is employed, the relative weight ratio of the TC to the SSZ-75 is generally between about 1:10 and about 500:1, desirably between about 1:10 and about 200:1, preferably between about 1:2 and about 50:1, and most preferably is between about 1:1 and about 20:1. The novel molecular sieve

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

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

Isomerization

The present catalyst is highly active and highly selective for isomerizing C_4 to C_7 hydrocarbons. The activity means that the catalyst can operate at relatively low temperature which thermodynamically favors highly branched paraffins. Consequently, the catalyst can produce a high octane product. The high selectivity means that a relatively high liquid yield can be achieved when the catalyst is run at a high octane.

The present process comprises contacting the isomerization catalyst, i.e., a catalyst comprising SSZ-75 in the hydrogen form, with a hydrocarbon feed under isomerization conditions. The feed is preferably a light straight run fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C) and preferably from 60°F to 200°F (16°C to 93°C). Preferably, the hydrocarbon feed for the process comprises a substantial amount of C_4 to C_7 normal and slightly branched low octane hydrocarbons, more preferably C_5 and C_6 hydrocarbons.

It is preferable to carry out the isomerization reaction in the presence of hydrogen. Preferably, hydrogen is added to give a hydrogen to hydrocarbon ratio (H_2/HC) of between 0.5 and 10 H_2/HC, more preferably between 1 and 8 H_2/HC. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No. 5,316,753 for a further discussion of isomerization process conditions.

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

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

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

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

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

Alkylation and Transalkylation

SSZ-75 can be used in a process for the alkylation or transalkylation of an aromatic hydrocarbon. The process comprises contacting the aromatic hydrocarbon with a C_2 to C_{16} olefin alkylating agent or a polyalkyl aromatic hydrocarbon transalkylating agent, under at least partial liquid phase conditions, and in the presence of a catalyst comprising SSZ-75.

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

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

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

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

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

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

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

Conversion of Paraffins to Aromatics

SSZ-75 can be used to convert light gas C_2-C_6 paraffins to higher molecular weight hydrocarbons including aromatic compounds. Preferably, the molecular sieve will contain a catalyst metal or metal oxide wherein said metal is selected from the group consisting of Groups IB, IIB, VIII and IIIA of the Periodic Table. Preferably, the metal is gallium, niobium, indium or zinc in the range of from about 0.05 to 5% by weight.

Isomerization of Olefins

SSZ-75 can be used to isomerize olefins. The feed stream is a hydrocarbon stream containing at least one C_{4-6} olefin, preferably a C_{4-5} 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 C_{4-6} 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

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

Xylene Isomerization

SSZ-75 may also be useful in a process for isomerizing one or more xylene isomers in a C_8 aromatic feed to obtain ortho-, meta-, and para-xylene in a ratio approaching the equilibrium value. In particular, xylene isomerization is used in conjunction with a separate process to manufacture para-xylene. For example, a portion of the para-xylene in a mixed C_8 aromatics stream may be recovered by crystallization and centrifugation. The mother liquor from the crystallizer is then reacted under xylene isomerization conditions to restore ortho-, meta- and para-xylenes to a near equilibrium ratio. At the same time, part of the ethylbenzene in the mother liquor is converted to xylenes or to products which are easily separated by filtration. The isomerate is blended with fresh feed and the combined stream is distilled to remove heavy and light by-products. The resultant C_8 aromatics stream is then sent to the crystallizer to repeat the cycle.

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

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

Oligomerization

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

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

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

Alpha values are defined by a standard test known in the art, e.g., as shown in U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens et al. which is incorporated totally herein by reference. If required, such molecular sieves may be obtained by steaming, by use in a conversion process or by any other 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 C_{2+} hydrocarbons such as ethylene or benzene or both. Examples of useful metals and metal compounds include lanthanide and or actinide metals or metal compounds.

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

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

Polymerization of 1-Olefins

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

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

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

MY_nX_{m-n}

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Hydrogenation

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

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

encompass such metals or metals in the elemental state or in some form such as an oxide, sulfide, halide, carboxylate and the like. Examples of such metals include 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 hydrogenation component of the catalyst (i.e., the aforementioned metal) is present in an amount effective to provide the hydrogenation function of the catalyst, preferably in the range of from 0.05 to 25% by weight.

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

SSZ-75 is useful as an adsorbent for gas separations (owing to its high pore volume while maintaining diffusion control and hydrophobicity). SSZ-75 can also be used in a catalyst for converting oxygenates (such as methanol) to olefins, and for making small amines. SSZ-75 can be used to reduce oxides of nitrogen in gas streams (such as automotive exhaust). SSZ-75 can also be used as a cold start hydrocarbon trap in combustion engine pollution control systems. SSZ-75 is particularly useful for trapping C_3 fragments.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

As stated this invention 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. The engine consists of any internal or external combustion engine which generates an exhaust gas stream containing noxious components or pollutants including unburned or thermally degraded hydrocarbons or similar organics. Other noxious components usually present in the exhaust gas include nitrogen oxides and carbon monoxide. The engine may be fueled by a hydrocarbonaceous fuel. As used in this specification and in the appended claims, the term "hydrocarbonaceous fuel" includes hydrocarbons, alcohols and mixtures thereof. Examples of hydrocarbons which can be used to fuel the engine are the mixtures of hydrocarbons which make up gasoline or diesel fuel. The alcohols which may

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

The molecular sieve used in the adsorbent bed, SSZ-75, 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 present invention comprises a process for catalytic conversion of a feedstock comprising one or more oxygenates comprising alcohols and ethers to a hydrocarbon product containing light olefins, i.e., C_2, C_3 and/or C_4 olefins. The feedstock is contacted with the molecular sieve of the present invention at effective process conditions to produce light olefins.

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

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

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

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

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

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

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

EXAMPLES

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

Example 1
Synthesis of Al-Containing SSZ-75

1.5 mM of tetramethylene-1,4-bis-(N-methylpyrrolidinium) dication SDA (3 mM OH^-) was mixed in a Teflon cup (for a Parr 23 ml reactor) with 1.26 grams of tetraethylorthosilicate and the cup was placed in a hood to evaporate (as ethanol is formed from hydrolysis) over several days. When all of the visible liquid was gone, the Teflon cup was reweighed and water was added to bring the H_2O/SiO_2 mole ratio to about four. Then, 12 mg of Reheiss F2000 (50% Al_2O_3) was added and dissolved into the reaction mixture. This represents a starting synthesis mole ratio of SiO_2/ Al_2O_3 of 100. Lastly, 0.135

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 SiO_2/ Al_2O_3 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 All-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.

Ex.	SDA/ SiO_2	NH_4F/ SiO_2	HF/ SiO_2	H_2O/ 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

Example 8

Calcination of SSZ-75

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

Example 9

Conversion of Methanol

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

Methanol conversion = 100%

No dimethylether detected

C_2-C_4 is about 70% of the product

C_{5+} showed a mixture of olefins and saturates

Aromatics were made with ethylbenzene the most abundant single product

Trimethylbenzene isomers were observed as the heaviest products

At 100 minutes on stream the SSZ-75 was fouling, but still produced the same products (although very few aromatics were observed).

WHAT IS CLAIMED IS:

1. A crystalline molecular sieve 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.

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. The molecular sieve of claim 1 having, after calcination, the X-ray diffraction lines of Table II.

4. The molecular sieve of claim 2 having, after calcination, the X-ray diffraction lines of Table II.

5. A crystalline molecular sieve having a composition comprising, as synthesized and in the anhydrous state, in terms of mole ratios, the following:

SiO_2 / X_cO_d	at least 15
$M_{2/n} / SiO_2$	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.

6. A method of preparing a crystalline material, 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.

7. The method of claim 6 wherein the crystalline material is prepared from a reaction mixture comprising silicon oxide and, in terms of mole ratios, the following:

SiO_2 / X_aO_b	at least 15
OH^- / SiO_2	0.20 – 0.80
Q / SiO_2	0.20 – 0.80
$M_{2/n}$ / SiO_2	0 – 0.04
H_2O / 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, 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.

8. 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 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.

9. The process of Claim 8 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.

10. The process of Claim 9 wherein the molecular sieve is predominantly in the hydrogen form.

11. The process of Claim 9 wherein the molecular sieve is substantially free of acidity.

12. The process of Claim 9 wherein the process is a hydrocracking process comprising contacting the catalyst with a hydrocarbon feedstock under hydrocracking conditions.

13. The process of Claim 9 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.

14. The process of Claim 13 wherein the molecular sieve is substantially free of acid.

15. The process of Claim 13 wherein the molecular sieve contains a Group VIII metal component.

16. The process of Claim 9 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.

17. The process of Claim 16 wherein the catalyst additionally comprises a large pore crystalline cracking component.

18. The process of Claim 9 wherein the process is an isomerization process for isomerizing C_4 to C_7 hydrocarbons, comprising contacting a feed having normal and slightly branched C_4 to C_7 hydrocarbons under isomerizing conditions with the catalyst.

19. The process of Claim 18 wherein the molecular sieve has been impregnated with at least one Group VIII metal.

20. The process of Claim 18 wherein the catalyst has been calcined in a steam/air mixture at an elevated temperature after impregnation of the Group VIII metal.

21. The process of Claim 19 wherein the Group VIII metal is platinum.

22. The process of Claim 9 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 C_2 to C_{20} olefin under at least partial liquid phase conditions and in the presence of the catalyst.

23. The process of Claim 22 wherein the olefin is a C_2 to C_4 olefin.

24. The process of Claim 23 wherein the aromatic hydrocarbon and olefin are present in a molar ratio of about 4:1 to about 20:1, respectively.

25. The process of Claim 23 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

26. The process of Claim 9 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.

27. The process of Claim 26 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.

28. The process of Claim 26 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, or mixtures thereof.

29. The process of Claim 26 wherein the polyalkyl aromatic hydrocarbon is a dialkylbenzene.

30. The process of Claim 9 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.

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

32. The process of Claim 9 wherein the process is a process for isomerizing an isomerization feed comprising an aromatic C_8 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.

33. The process of Claim 9 wherein the process is a process for oligomerizing olefins comprising contacting an olefin feed under oligomerization conditions with the catalyst.

34. 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.

35. The process of Claim 34 wherein the oxygenated hydrocarbon is a lower alcohol.

36. The process of Claim 35 wherein the lower alcohol is methanol.

37. The process of Claim 9 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 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.

38. The process of Claim 37 wherein the metal or metal compound comprises a lanthanide or actinide metal or metal compound.

39. The process of Claim 37 wherein the lower molecular weight hydrocarbon is methane.

40. 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.

41. The process of Claim 9 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.

42. The process of Claim 41 wherein the 1-olefin monomer is ethylene.

43. The process of Claim 9 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.

44. The process of Claim 43 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.

45. 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.

46. 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..

47. A process for producing a C_{20+} lube oil from a C_{20+} 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.

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

49. 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.

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

51. The process of Claim 49 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.

52. 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.

53. The process of Claim 52 wherein the catalyst further comprises at least one Group VIII metal.

54. 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.

55. The process of Claim 54 wherein the catalyst further comprises at least one Group VIII metal.

56. The process of Claim 54 wherein the raffinate is bright stock.

57. The process of Claim 46, 47, 48, 49, 50, 51, 52, 53, 54, 55 or 56 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.

58. The process of Claim 12, 16, 18, 22, 26, 45, 46, 47, 49, 52 or 54 wherein the molecular sieve is predominantly in the hydrogen form.

59. 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 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.

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

61 The process of Claim 59 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

62. The process of Claim 60 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

63. 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 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.

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 63 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

66. The process of Claim 64 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II

67. The process of Claim 64 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.

68. The process of Claim 64 conducted at a temperature of from about 250°C to about 450°C.

69. 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.

70. The process of Claim 69 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.

71. The process of Claim 69 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

72. The process of Claim 70 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

73. The process of Claim 70 conducted in the presence of oxygen.

74. The process of Claim 70 wherein said molecular sieve contains a metal or metal ions capable of catalyzing the reduction of the oxides of nitrogen.

75. The process of Claim 74 wherein the metal is cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium or mixtures thereof.

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

77. The process of Claim 75 wherein the gas stream is the exhaust stream of an internal combustion engine.

78. 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 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.

79. The process of Claim 78 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.

80. The process of Claim 78 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

81. The process of Claim 79 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

82. The process of Claim 79 wherein the engine is an internal combustion engine.

83. The process of Claim 82 wherein the internal combustion engine is an automobile engine.

84. The process of Claim 79 wherein the engine is fueled by a hydrocarbonaceous fuel.

85. The process of Claim 79 wherein the molecular sieve has deposited on it a metal selected from the group consisting of platinum, palladium, rhodium, ruthenium, and mixtures thereof.

86. The process of Claim 85 wherein the metal is platinum.

87. The process of Claim 85 wherein the metal is palladium.

88. The process of Claim 85 wherein the metal is a mixture of platinum and palladium.

89. 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 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.

90. The process of Claim 89 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.

91. The process of Claim 89 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

92. The process of Claim 90 wherein the molecular sieve has, after calcination, the X-ray diffraction lines of Table II.

93. The process of Claim 90 wherein the light olefins are ethylene, propylene, butylene or mixtures thereof.

94. The process of Claim 93 wherein the light olefin is ethylene.

95. The process of Claim 90 wherein the oxygenate is methanol, dimethyl ether or a mixture thereof.

96. The process of Claim 95 wherein the oxygenate is methanol.