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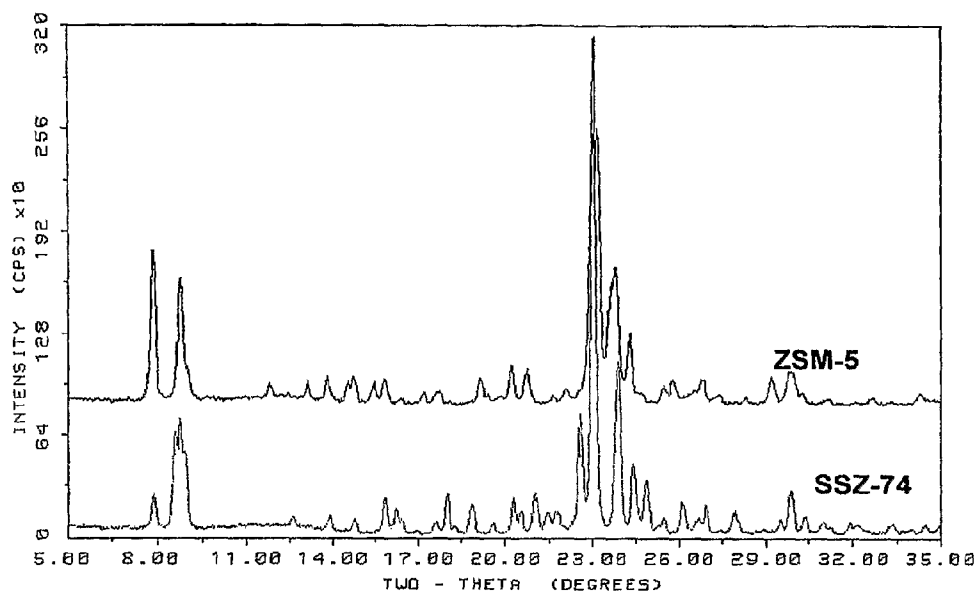
(57) Abstract: The present invention relates to new crystalline molecular sieve SSZ- 74 prepared using a hexamethylene-1 ,6-bis-(N-methyl-N-pyrrolidinium) dication as a structure-directing agent, methods for synthesizing SSZ-74, and its use in hydrocarbon conversion reactions, reduction of oxides of nitrogen in a gas stream, partial oxidation reactions, acylation reactions, oxygenate conversions, gas separations, synthesis of amines, treatment of engine exhaust (reduction of cold start emissions), and Beckmann rearrangement.

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1   **MOLECULAR SIEVE SSZ-74 COMPOSITION OF MATTER**

2   **AND SYNTHESIS THEREOF**

3

4   <u>BACKGROUND OF THE INVENTION</u>

5

6   <u>Field of the Invention</u>

7

8   The present invention relates to new crystalline molecular sieve SSZ-

9   74, a method for preparing SSZ-74 using a hexamethylene-1,6-bis-(N-methyl-

10 N-pyrrolidinium) dication as a structure directing agent ("SDA") and uses for

11 SSZ-74.

12

13 <u>State of the Art</u>

14

15 Because of their unique sieving characteristics, as well as their

16 catalytic properties, crystalline molecular sieves and zeolites are especially

17 useful in applications such as hydrocarbon conversion, gas drying and

18 separation. Although many different crystalline molecular sieves have been

19 disclosed, there is a continuing need for new molecular sieves with desirable

20 properties for gas separation and drying, hydrocarbon and chemical

21 conversions, and other applications. New molecular sieves may contain novel

22 internal pore architectures, providing enhanced selectivities in these

23 processes.

24

25 <u>SUMMARY OF THE INVENTION</u>

26

27 The present invention is directed to a family of crystalline molecular

28 sieves with unique properties, referred to herein as "molecular sieve SSZ-74"

29 or simply "SSZ-74".

30

1   <u>Composition of Matter and Synthesis</u>

2

3   In accordance with the present invention there is provided a molecular

4   sieve having a mole ratio greater than about 15 of (1) an oxide of a first

5   tetravalent element to (2) an oxide of a trivalent element, pentavalent element,

6   second tetravalent element which is different from said first tetravalent

7   element or mixture thereof and having, after calcination, the X-ray diffraction

8   lines of Table II. It should be noted that the phrase "mole ratio greater than

9   about 15" includes the case where there is no oxide (2), i.e., the mole ratio of

10   oxide (1) to oxide (2) is infinity. In that case the molecular sieve is comprised

11   of essentially all silicon oxide.

12

13   The present invention also provides a crystalline molecular sieve

14   having a mole ratio greater than about 15 of (1) silicon oxide to (2) an oxide

15   selected from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium

16   oxide, indium oxide and mixtures thereof, and having, after calcination, the

17   X-ray diffraction lines of Table II.

18

19   The present invention further provides such a crystalline molecular

20   sieve having a composition comprising, as synthesized and in the anhydrous

21   state, in terms of mole ratios the following:

22

23          $SiO_2 / X_c O_d$ greater than 100

24          $M_{2/n} / SiO_2$ 0 – 0.03

25   Q / SiO_2 0.30 – 0.70

26   F / SiO_2 0.30 – 0.70

27

28   wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures

29   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

30   c is 2 (i.e., d is 3 when W is trivalent or 5 when W is pentavalent), M is an

31   alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the

32   valence of M (i.e., 1 or 2); Q is a hexamethylene-1,6-bis-(N-methyl-N-

33   pyrrolidinium) dication and F is fluoride.

1

2   Also provided in accordance with the present invention is a method of

3   preparing a crystalline material, said method comprising contacting under

4   crystallization conditions a source(s) of (1) silicon oxide, (2) a source(s) of

5   aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium

6   oxide and mixtures thereof, (3) fluoride ions and (4) a structure directing agent

7   comprising a hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) dication. The

8   present invention includes such a method wherein the crystalline material

9   has, after calcination, the X-ray diffraction lines of Table II.

10

11   The present invention includes such a method of preparing a crystalline

12 material which uses a reaction mixture comprising (in terms of mole ratios),

13 the following:

14

15   SiO_2 / X_aO_b 100/1 and greater

16      $OH- / SiO_2$ 0.20 – 0.80

17   Q / SiO_2 0.20 – 0.80

18      $M_{2/n} / SiO_2$ 0 – 0.04

19   H_2O / SiO_2 2 - 10

20   HF / SiO_2 0.20 – 0.80

21

22 wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures

23 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

24 (i.e., W is trivalent), M is an alkali metal cation, alkaline earth metal cation or

25 mixtures thereof; n is the valence of M (i.e., 1 or 2); and Q is a

26 hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) dication.

27

28   Hydrocarbon Conversion

29

30   In accordance with the present invention there is provided a process

31 for converting hydrocarbons comprising contacting a hydrocarbonaceous feed

32 at hydrocarbon converting conditions with a catalyst comprising a crystalline

33 molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a

1   first tetravalent element to (2) an oxide of a trivalent element, pentavalent

2   element, second tetravalent element which is different from said first

3   tetravalent element or mixture thereof and having, after calcination, the X-ray

4   diffraction lines of Table II.. The molecular sieve may be predominantly in the

5   hydrogen form. It may also be substantially free of acidity.

6

7   Further provided by the present invention is a hydrocracking process

8   comprising contacting a hydrocarbon feedstock under hydrocracking

9   conditions with a catalyst comprising the molecular sieve of this invention. The

10 molecular sieve may be predominantly in the hydrogen form.

11

12   This invention also includes a dewaxing process comprising contacting

13 a hydrocarbon feedstock under dewaxing conditions with a catalyst

14 comprising the molecular sieve of this invention. The molecular sieve may be

15 predominantly in the hydrogen form.

16

17 ·   The present invention also includes a process for improving the

18 viscosity index of a dewaxed product of waxy hydrocarbon feeds comprising

19 contacting the waxy hydrocarbon feed under isomerization dewaxing

20 conditions with a catalyst comprising the molecular sieve of this invention. The

21 molecular sieve may be predominantly in the hydrogen form. ·

22   · ·

23 ·   The present invention further includes a process for producing a C_{20+}

24 lube oil from a C_{20+} olefin feed comprising isomerizing said olefin feed under

25 isomerization conditions over a catalyst comprising the molecular sieve of this

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

27 The catalyst may contain at least one Group VIII metal. ·   ·· ·

28

29   In accordance with this invention, there is also provided a process for

30 catalytically dewaxing a hydrocarbon oil feedstock boiling above about 350°F

31 (177°C) and containing straight chain and slightly branched chain   ·

32 hydrocarbons comprising contacting said hydrocarbon oil feedstock in the

33 presence of added hydrogen gas at a hydrogen pressure of about 15-3000 psi

1   (0.103 – 20.7 MPa) with a catalyst comprising the molecular sieve of this

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

3   The catalyst may contain at least one Group VIII metal. The catalyst may be a

4   combination comprising the molecular sieve of this invention, and

5   aluminosilicate zeolite which is more shape selective than the molecular

6   sieve. The combination may contain at least one Group VIII metal.

7

8   Also included in the present invention is a process for preparing a

9   lubricating oil which comprises hydrocracking in a hydrocracking zone a

10   hydrocarbonaceous feedstock to obtain an effluent comprising a

11   hydrocracked oil, and catalytically dewaxing said effluent comprising

12   hydrocracked oil at a temperature of at least about 400°F (204°C) and at a

13   pressure of from about 15 psig to about 3000 psig (0.103 – 20.7 Mpa

14   gauge)in the presence of added hydrogen gas with a catalyst comprising the

15   molecular sieve of this invention. The molecular sieve may be predominantly

16   in the hydrogen form. The catalyst may contain at least one Group VIII metal.

17

18   Further included in this invention is a process for isomerization

19   dewaxing a raffinate comprising contacting said raffinate in the presence of

20   added hydrogen with a catalyst comprising the molecular sieve of this

21   invention. The raffinate may be bright stock, and the molecular sieve may be

22   predominantly in the hydrogen form. The catalyst may contain at least one

23   Group VIII metal.

24

25   Also included in this invention is a process for increasing the octane of

26   a hydrocarbon feedstock to produce a product having an increased aromatics

27   content comprising contacting a hydrocarbonaceous feedstock which

28   comprises normal and slightly branched hydrocarbons having a boiling range

29   above about 40°C and less than about 200°C, under aromatic conversion

30   conditions with a catalyst comprising the molecular sieve of this invention

31   made substantially free of acidity by neutralizing said molecular sieve with a

32   basic metal. Also provided in this invention is such a process wherein the

33   molecular sieve contains a Group VIII metal component.

1

2   Also provided by the present invention is a catalytic cracking process

3   comprising contacting a hydrocarbon feedstock in a reaction zone under

4   catalytic cracking conditions in the absence of added hydrogen with a catalyst

5   comprising the molecular sieve of this invention. The molecular sieve may be

6   predominantly in the hydrogen form. Also included in this invention is such a

7   catalytic cracking process wherein the catalyst additionally comprises a large

8   pore crystalline cracking component.

9

10   This invention further provides an isomerization process for isomerizing

11   C_4 to C_7 hydrocarbons, comprising contacting a feed having normal and

12   slightly branched C_4 to C_7 hydrocarbons under isomerizing conditions with a

13   catalyst comprising the molecular sieve of this invention. The molecular sieve

14   may be predominantly in the hydrogen form. The molecular sieve may be

15   impregnated with at least one Group VIII metal, for example platinum. The

16   catalyst may be calcined in a steam/air mixture at an elevated temperature

17   after impregnation of the Group VIII metal.

18

19   Also provided by the present invention is a process for alkylating an

20   aromatic hydrocarbon which comprises contacting under alkylation conditions

21   at least a molar excess of an aromatic hydrocarbon with a C_2 to C_{20} olefin

22   under at least partial liquid phase conditions and in the presence of a catalyst

23   comprising the molecular sieve of this invention. The molecular sieve may be

24   predominantly in the hydrogen form. The olefin may be a C_2 to C_4 olefin, and

25   the aromatic hydrocarbon and olefin may be present in a molar ratio of about

26   4:1 to about 20:1, respectively. The aromatic hydrocarbon may be selected

27   from the group consisting of benzene, toluene, ethylbenzene, xylene,

28   naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures

29   thereof.

30

31   Further provided in accordance with this invention is a process for

32   transalkylating an aromatic hydrocarbon which comprises contacting under

33   transalkylating conditions an aromatic hydrocarbon with a polyalkyl aromatic

1   hydrocarbon under at least partial liquid phase conditions and in the presence

2   of a catalyst comprising the molecular sieve of this invention. The molecular

3   sieve may be predominantly in the hydrogen form. The aromatic hydrocarbon

4   and the polyalkyl aromatic hydrocarbon may be present in a molar ratio of

5   from about 1:1 to about 25:1, respectively.

6

7   The aromatic hydrocarbon may be selected from the group consisting

8   of benzene, toluene, ethylbenzene, xylene, or mixtures thereof, and the

9   polyalkyl aromatic hydrocarbon may be a dialkylbenzene.

10

11   Further provided by this invention is a process to convert paraffins to

12 aromatics which comprises contacting paraffins under conditions which cause

13 paraffins to convert to aromatics with a catalyst comprising the molecular

14 sieve of this invention, said catalyst comprising gallium, zinc, or a compound

15 of gallium or zinc.

16

17   In accordance with this invention there is also provided a process for

18 isomerizing olefins comprising contacting said olefin under conditions which

19 cause isomerization of the olefin with a catalyst comprising the molecular

20 sieve of this invention.

21

22   Further provided in accordance with this invention is a process for

23 isomerizing an isomerization feed comprising an aromatic C_8 stream of xylene

24 isomers or mixtures of xylene isomers and ethylbenzene, wherein a more

25 nearly equilibrium ratio of ortho-, meta- and para-xylenes is obtained, said

26 process comprising contacting said feed under isomerization conditions with a

27 catalyst comprising the molecular sieve of this invention.

28

29   The present invention further provides a process for oligomerizing

30 olefins comprising contacting an olefin feed under oligomerization conditions

31 with a catalyst comprising the molecular sieve of this invention.

32

1   This invention also provides a process for converting oxygenated

2   hydrocarbons comprising contacting said oxygenated hydrocarbon with a

3   catalyst comprising the molecular sieve of this invention under conditions to

4   produce liquid products. The oxygenated hydrocarbon may be a lower

5   alcohol.

6

7   Further provided in accordance with the present invention is a process

8   for the production of higher molecular weight hydrocarbons from lower

9   molecular weight hydrocarbons comprising the steps of:

10   (a)   introducing into a reaction zone a lower molecular weight

11   hydrocarbon-containing gas and contacting said gas in said

12   zone under C_{2+} hydrocarbon synthesis conditions with the

13   catalyst and a metal or metal compound capable of converting

14   the lower molecular weight hydrocarbon to a higher molecular

15   weight hydrocarbon; and

16   (b)   withdrawing from said reaction zone a higher molecular weight

17   hydrocarbon-containing stream.

18

19   The present invention further provides a process for hydrogenating a

20   hydrocarbon feed containing unsaturated hydrocarbons, the process

21   comprising contacting the feed and hydrogen under conditions which cause

22   hydrogenation with a catalyst comprising the molecular sieve of this invention.

23   The catalyst can also contain metals, salts or complexes wherein the metal is

24   selected from the group consisting of platinum, palladium, rhodium, iridium or

25   combinations thereof, or the group consisting of nickel, molybdenum, cobalt,

26   tungsten, titanium, chromium, vanadium, rhenium, manganese and

27   combinations thereof.

28

29   The present invention also provides a catalyst composition for

30   promoting polymerization of 1-olefins, said composition comprising

31

32   (A)   a crystalline molecular sieve having a mole ratio greater than

33   about 15 of (1) an oxide of a first tetravalent element to (2) an

-8-

1   oxide of a trivalent element, pentavalent element, second

2   tetravalent element which is different from said first tetravalent

3   element or mixture thereof and having, after calcination, the

4   X-ray diffraction lines of Table II; and

5

6   (B)   an organotitanium or organochromium compound.

7

8   Also provided is a process for polymerizing 1-olefins, which process

9   comprises contacting 1-olefin monomer with a catalytically effective amount of

10   a catalyst composition comprising

11

12   (A)   a crystalline molecular sieve having a mole ratio greater than

13   about 15 of (1) an oxide of a first tetravalent element to (2) an

14   oxide of a trivalent element, pentavalent element, second

15   tetravalent element which is different from said first tetravalent

16   element or mixture thereof and having, after calcination, the

17   X-ray diffraction lines of Table II; and

18

19   (B)   an organotitanium or organochromium compound.

20

21   under polymerization conditions which include a temperature and pressure

22   suitable for initiating and promoting the polymerization reaction. The 1-olefin

23   may be ethylene.

24

25   In accordance with this invention, there is also provided a process for

26   hydrotreating a hydrocarbon feedstock comprising contacting the feedstock

27   with a hydrotreating catalyst and hydrogen under hydrotreating conditions,

28   wherein the catalyst comprises the molecular sieve of this invention.

29

30   The present invention also provides such a process wherein the

31   molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

32   (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

33   oxide, titanium oxide, indium oxide and mixtures thereof.

1

2   <u>Reduction of Oxides of Nitrogen</u>

3

4   In accordance with this invention, there is provided a process for the

5   reduction of oxides of nitrogen contained in a gas stream wherein said

6   process comprises contacting the gas stream with a crystalline molecular

7   sieve having a mole ratio greater than about 15 of (1) an oxide of a first

8   tetravalent element to (2) an oxide of a trivalent element, pentavalent element,

9   second tetravalent element which is different from said first tetravalent

10   element or mixture thereof and having, after calcination, the X-ray diffraction

11   lines of Table II. The molecular sieve may contain a metal or metal ions (such

12   as cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc,

13   lanthanum, palladium, rhodium or mixtures thereof) capable of catalyzing the

14   reduction of the oxides of nitrogen, and the process may be conducted in the

15   presence of a stoichiometric excess of oxygen. In one embodiment, the gas

16   stream is the exhaust stream of an internal combustion engine.

17

18   The present invention also provides such a process wherein the

19   molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

20   (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

21   oxide, titanium oxide, indium oxide and mixtures thereof.

22

23   <u>Partial Oxidation</u>

24

25   In accordance with the present invention, there is provided a process

26   for oxidation of hydrocarbons comprising contacting said hydrocarbon with an

27   oxidizing agent in the presence of a catalytically effective amount of a

28   titanium-containing molecular sieve for a time and at a temperature effective

29   to oxidize said hydrocarbon, wherein the titanium-containing molecular sieve

30   is a molecular sieve having a mole ratio greater than about 15 of (1) silicon

31   oxide to (2) titanium oxide and having, after calcination, the X-ray diffraction

32   lines of Table II.

33

1   There is further provided in accordance with this invention a process

2   for epoxidation of an olefin comprising contacting said olefin with hydrogen

3   peroxide in the presence of a catalytically effective amount of a titanium-

4   containing molecular sieve for a time and at a temperature effective to

5   epoxidize said olefin, wherein the titanium-containing molecular sieve is a

6   molecular sieve having a mole ratio greater than about 15 of (1) silicon oxide

7   to (2) titanium oxide and having, after calcination, the X-ray diffraction lines of

8   Table II.

9

10   Further provided in accordance with the present invention is a process

11   for oxidizing cyclohexane comprising contacting said cyclohexane with

12   hydrogen peroxide in the presence of a catalytically effective amount of a

13   titanium-containing molecular sieve for a time and at a temperature effective

14   to oxidize said cyclohexane, wherein the titanium-containing molecular sieve

15   is a molecular sieve having a mole ratio greater than about 15 of (1) silicon

16   oxide to (2) titanium oxide and having, after calcination, the X-ray diffraction

17   lines of Table II.

18

19   The present invention also provides a catalytic oxidation process

20   comprising contacting under oxidation conditions (1) a reactant which is

21   catalytically oxidizable in the presence of hydrogen peroxide, (2) aqueous

22   hydrogen peroxide and (3) a catalytically effective amount of an oxidation

23   catalyst comprising a molecular sieve having a mole ratio greater than about

24   15 of (1) silicon oxide to (2) titanium oxide and having, after calcination, the X-

25   ray diffraction lines of Table II.

26

27   The present invention also provides a process for the epoxidation of an

28   olefin comprising contacting said olefin with hydrogen peroxide in the

29   presence of a catalytically effective amount of a catalyst comprising a

30   molecular sieve having a mole ratio greater than about 15 of (1) silicon oxide

31   to (2) titanium oxide and having, after calcination, the X-ray diffraction lines of

32   Table II.

33

1   <u>Acylation</u>

2

3   In accordance with the present invention, there is provided a method

4   for performing an acylation reaction on an aromatic substrate ArH_n to form a

5   product $ArH_{n-1}COR$, the method comprising the steps of:

6

7   · providing the aromatic substrate,

8

9   · intimately mixing the substrate and an acylating agent, wherein the

10   acylating agent is selected from the group consisting of a carboxylic acid

11   derivative, a carboxylic acid, an acid anhydride, an ester, and an acyl

12   halide, and

13

14   exposing an intimate mixture thus formed to a catalyst comprising a

15   crystalline molecular sieve having a mole ratio greater than about 15 of

16   (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

17   element, pentavalent element, second tetravalent element which is

18   different from said first tetravalent element or mixture thereof and having,

19   after calcination, the X-ray diffraction lines of Table II.

20

21   The present invention also provides such a process wherein the

22   molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

23   (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

24   oxide, titanium oxide, indium oxide and mixtures thereof.

25

26   The present invention also provides such a process wherein the

27   molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

28   (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

29   oxide, titanium oxide, indium oxide and mixtures thereof.

30

31   <u>Oxygenate Conversion</u>

32

33   The present invention relates to a process for the production of light

34   olefins comprising olefins having from 2 to 4 carbon atoms per molecule from

-12-

1   an oxygenate feedstock. The process comprises passing the oxygenate

2   feedstock to an oxygenate conversion zone containing a molecular sieve

3   catalyst to produce a light olefin stream.

4

5   Thus, in accordance with the present invention there is provided a

6   process for the production of light olefins from a feedstock comprising an

7   oxygenate or mixture of oxygenates, the process comprising reacting the

8   feedstock at effective conditions over a catalyst comprising a crystalline

9   molecular sieve having a mole ratio greater than about 15 of (1) an oxide of a

10 first tetravalent element to (2) an oxide of a trivalent element, pentavalent

11 element, second tetravalent element which is different from said first

12 tetravalent element or mixture thereof and having, after calcination, the X-ray

13 diffraction lines of Table II.

14

15   The present invention also provides such a process wherein the

16 molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

17 (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

18 oxide, titanium oxide, indium oxide and mixtures thereof.

19

20   Gas Separation

21

22   In accordance with the present invention there is provided a process

23 for separating gasses comprising contacting a mixture of gasses with a

24 membrane containing a molecular sieve wherein the molecular sieve is a

25 crystalline molecular sieve having a mole ratio greater than about 15 of (1) an

26 oxide of a first tetravalent element to (2) an oxide of a trivalent element,

27 pentavalent element, second tetravalent element which is different from said

28 first tetravalent element or mixture thereof and having, after calcination, the

29 X-ray diffraction lines of Table II. The mixture of gasses may comprise carbon

30 dioxide and methane.

31

1   the molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide

2   to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

3   oxide, titanium oxide, indium oxide and mixtures thereof.

4

5   Synthesis of Amines

6

7   In accordance with the present invention there is provided a process

8   for producing methylamine or dimethylamine comprising reacting methanol,

9   dimethyl ether or a mixture thereof and ammonia in the gaseous phase in the

10 presence of a catalyst comprising a crystalline molecular sieve having a mole

11 ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2)

12 an oxide of a trivalent element, pentavalent element, second tetravalent

13 element which is different from said first tetravalent element or mixture thereof

14 and having, after calcination, the X-ray diffraction lines of Table II.

15

16   The present invention also provides such a process wherein the

17 molecular sieve has a mole ratio greater than about 15 of (1) silicon oxide to

18 (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide, boron

19 oxide, titanium oxide, indium oxide and mixtures thereof.

20

21   Treatment of Engine Exhaust (Cold Start Emissions)

22

23   This invention generally relates to a process for treating an engine

24 exhaust stream and in particular to a process for minimizing emissions during

25 the cold start operation of an engine. Accordingly, the present invention

26 provides a process for treating a cold-start engine exhaust gas stream

27 containing hydrocarbons and other pollutants consisting of flowing said engine

28 exhaust gas stream over a molecular sieve bed which preferentially adsorbs

29 the hydrocarbons over water to provide a first exhaust stream, and flowing the

30 first exhaust gas stream over a catalyst to convert any residual hydrocarbons

31 and other pollutants contained in the first exhaust gas stream to innocuous

32 products and provide a treated exhaust stream and discharging the treated

33 exhaust stream into the atmosphere, the molecular sieve bed characterized in

1   that it comprises a crystalline molecular sieve having a mole ratio greater than

2   about 15 of (1) an oxide of a first tetravalent element to (2) an oxide of a

3   trivalent element, pentavalent element, second tetravalent element which is

4   different from said first tetravalent element or mixture thereof and having, after

5   calcination, the X-ray diffraction lines of Table II.

6

7   Also provided in accordance with the present invention is such a

8   process wherein the molecular sieve crystalline molecular sieve has a mole

9   ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected from

10   aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide, indium

11   oxide and mixtures thereof.

12

13   The present invention further provides such a process wherein the

14   engine is an internal combustion engine, including automobile engines, which

15   can be fueled by a hydrocarbonaceous fuel.

16

17   Also provided by the present invention is such a process wherein the

18   molecular sieve has deposited on it a metal selected from the group

19   consisting of platinum, palladium, rhodium, ruthenium, and mixtures thereof.

20

21   Beckmann Rearrangement

22

23   In accordance with the present invention there is provided a process

24   for the preparation of amides from oximes via Beckmann rearrangement

25   comprising contacting the oxime in the vapor phase with a catalyst comprising

26   a crystalline molecular sieve having a mole ratio greater than about 15 of (1)

27   an oxide of a first tetravalent element to (2) an oxide of a trivalent element,

28   pentavalent element, second tetravalent element which is different from said

29   first tetravalent element or mixture thereof and having, after calcination, the

30   X-ray diffraction lines of Table II. The molecular sieve typically is acidic.

31

32   The present invention also provides such a process wherein the

33   crystalline molecular sieve has a mole ratio greater than about 15 of (1) silicon

1   oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide,

2   boron oxide, titanium oxide, indium oxide and mixtures thereof, and having,

3   after calcination, the X-ray diffraction lines of Table II.

4

5   BRIEF DESCRIPTION OF THE DRAWING

6

7   Figure 1 shows a comparison of two X-ray diffraction patterns, the top

8   one being ZSM-5 and the bottom one being SSZ-74.

9

10   DETAILED DESCRIPTION OF THE INVENTION

11

12   The present invention comprises a molecular sieve designated herein

13   "molecular sieve SSZ-74" or simply "SSZ-74".

14

15   In preparing SSZ-74, a hexamethylene-1,6-bis-(N-methyl-N-

16   pyrrolidinium) dication is used as a structure directing agent ("SDA"), also

17   known as a crystallization template. The SDA useful for making SSZ-74 has

18   the following structure:

19

20

21   Hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) dication

22
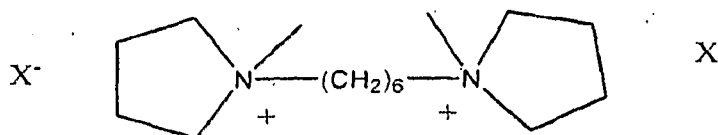
23   The SDA dication is associated with anions (X⁻) which may be any

24   anion that is not detrimental to the formation of the SSZ-74. Representative

25   anions include halogen, e.g., fluoride, chloride, bromide and iodide, hydroxide,

26   acetate, sulfate, tetrafluoroborate, carboxylate, and the like. Hydroxide is a

27   typical anion, since the structure directing agent (SDA) may be used to

28   provide hydroxide ion. Thus, it is beneficial to ion exchange, for example, a

29   halide to hydroxide ion.

30

1   In general, SSZ-74 is prepared by contacting (1) an active source(s) of

2   silicon oxide, and, optionally, (2) an active source(s) of aluminum oxide,

3   gallium oxide, iron oxide, boron oxide, titanium oxide, indium oxide and

4   mixtures thereof with the hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium)

5   dication SDA in the presence of fluoride ion.

6

7   SSZ-74 is prepared from a reaction mixture comprising, in terms of

8   mole ratios, the following:

9   TABLE A

10   Reaction Mixture

		Embodiment 1	Embodiment 2
12	SiO_2 / X_aO_b	100 and greater	
13	OH^- / SiO_2	0.20 – 0.80	0.40 – 0.60
14	Q / SiO_2	0.20 – 0.80	0.40 – 0.60
15	$M_{2/n} / SiO_2$	0 – 0.04	0 – 0.025
16	H_2O / SiO_2	2 – 10	3 – 7
17	HF / SiO_2	0.20 – 0.80	0.30 – 0.60

18

19   where X is aluminum, gallium, iron, boron, titanium, indium and mixtures

20   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

21   (i.e., W is trivalent), M is an alkali metal cation, alkaline earth metal cation or

22   mixtures thereof; n is the valence of M (i.e., 1 or 2); Q is a hexamethylene-1,6-

23   bis-(N-methyl-N-pyrrolidinium) dication and F is fluoride.

24

25   As noted above, the SiO_2 / X_aO_b mole ratio in the reaction mixture is

26   100 and greater. This means that the SiO_2 / X_aO_b mole ratio can be infinity,

27   i.e., there is no X_aO_b in the reaction mixture. This results in a version of SSZ-

28   74 that is essentially all silica. As used herein, "essentially all silicon oxide" or

29   "essentially all-silica" means that the molecular sieve's crystal structure is

30   comprised of only silicon oxide or is comprised of silicon oxide and only trace

31   amounts of other oxides, such as aluminum oxide, which may be introduced

32   as impurities in the source of silicon oxide.

33

1   An example of the source of silicon oxide is tetraethyl orthosilicate. An

2   example of the source of aluminum oxide is LZ-210 zeolite (a type of Y

3   zeolite).

4

5   In practice, SSZ-74 is prepared by a process comprising:

6   (a)   preparing an aqueous solution containing (1) a source(s) of

7   silicon oxide, (2) a source(s) of aluminum oxide, gallium oxide,

8   iron oxide, boron oxide, titanium oxide, indium oxide and

9   mixtures thereof, (3) a source of fluoride ion and (4) a

10   hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) dication

11   having an anionic counterion which is not detrimental to the

12   formation of SSZ-74;

13   (b)   maintaining the aqueous solution under conditions sufficient to

14   form crystals of SSZ-74; and

15   (c)   recovering the crystals of SSZ-74.

16

17   The reaction mixture is maintained at an elevated temperature until the

18   crystals of the SSZ-74 are formed. The hydrothermal crystallization is usually

19   conducted under autogenous pressure, at a temperature between 100°C and

20   200°C, for example between 135°C and 180°C. The crystallization period is

21   typically greater than 1 day, for example from about 3 days to about 20 days.

22   The molecular sieve may be prepared using mild stirring or agitation.

23

24   During the hydrothermal crystallization step, the SSZ-74 crystals can

25   be allowed to nucleate spontaneously from the reaction mixture. The use of

26   SSZ-74 crystals as seed material can be advantageous in decreasing the time

27   necessary for complete crystallization to occur. In addition, seeding can lead

28   to an increased purity of the product obtained by promoting the nucleation

29   and/or formation of SSZ-74 over any undesired phases. When used as seeds,

30   SSZ-74 crystals are added in an amount between 0.1 and 10% of the weight

31   of the first tetravalent element oxide, e.g. silica, used in the reaction mixture.

32

1   Once the molecular sieve crystals have formed, the solid product is

2   separated from the reaction mixture by standard mechanical separation

3   techniques such as filtration. The crystals are water-washed and then dried,

4   e.g., at 90°C to 150°C for from 8 to 24 hours, to obtain the as-synthesized

5   SSZ-74 crystals. The drying step can be performed at atmospheric pressure

6   or under vacuum.

7

8   SSZ-74 as prepared has the X-ray diffraction lines of Table I below.

9   SSZ-74 has a composition, as synthesized (i.e., prior to removal of the SDA

10   from the SSZ-74) and in the anhydrous state, comprising the following (in

11   terms of mole ratios):

12

13   SiO_2 / X_cO_d greater than 100

14                                $M_{2/n} / SiO_2$ 0 – 0.03

15   Q / SiO_2 0.30 – 0.70

16   F / SiO_2 0.30 – 0.70

17

18   wherein X is aluminum, gallium, iron, boron, titanium, indium and mixtures

19   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

20   c is 2 (i.e., d is 3 when W is trivalent or 5 when W is pentavalent), M is an

21   alkali metal cation, alkaline earth metal cation or mixtures thereof; n is the

22   valence of M (i.e., 1 or 2); Q is a hexamethylene-1,6-bis-(N-methyl-N-

23   pyrrolidinium) dication and F is fluoride.

24

25   SSZ-74 is characterized by its X-ray diffraction pattern. SSZ-74, as-

26   synthesized, has a crystalline structure whose X-ray powder diffraction pattern

27   exhibits the characteristic lines shown in Table I.

28

29   TABLE I

30   As-Synthesized SSZ-74

2 Theta[a]	d-spacing (Angstroms)	Relative Integrated Intensity (%)[b]
7.95	11.11	W

8.68	10.18	M
8.85	9.98	W-M
9.02	9.80	W
22.69	3.92	W-M
23.14	3.84	VS
24.01	3.70	M
24.52	3.63	W
24.93	3.57	W
29.95	2.98	W

1   [a] ± 0.1

2   [b] The X-ray patterns provided are based on a relative intensity scale in

3   which the strongest line in the X-ray pattern is assigned a value of 100:

4   W(weak) is less than 20; M(medium) is between 20 and 40; S(strong)

5   is between 40 and 60; VS(very strong) is greater than 60.

6

7   Table IA below shows the X-ray powder diffraction lines for as-

8   synthesized SSZ-74 including actual relative intensities.

9

10   TABLE IA

11   As-Synthesized SSZ-74

2 Theta[a]	d-spacing (Angstroms)	Intensity
7.95	11.11	7.9
8.68	10.18	21.1
8.85	9.98	18.7
9.02	9.80	11.3
11.30	7.82	0.4
12.70	6.96	1.8
13.98	6.33	2.4
14.77	5.99	0.5
14.85	5.96	2.1
15.93	5.56	6.3
16.30	5.43	4.6
16.50	5.37	1.8
17.05	5.20	0.8
17.41	5.09	0.1
17.71	5.00	2.0
18.09	4.90	7.4
18.38	4.82	0.7
18.89	4.69	0.9
18.96	4.68	4.4
19.69	4.51	1.8
20.39	4.35	5.1
20.63	4.30	4.2

21.12	4.20	7.7
21.55	4.12	5.4
21.75	4.08	0.5
21.80	4.07	1.4
21.88	4.06	2.1
21.96	4.04	1.5
22.17	4.01	0.8
22.69	3.92	18.9
23.14	3.84	100.0
23.89	3.72	9.4
24.01	3.70	25.6
24.52	3.63	13.7
24.68	3.60	2.1
24.93	3.57	11.3
25.09	3.55	0.9
25.37	3.51	1.7
25.57	3.48	2.7
26.20	3.40	5.5
26.31	3.38	0.8
26.67	3.34	2.0
26.76	3.33	1.0
26.82	3.32	0.9
27.01	3.30	3.4
27.05	3.29	0.8
27.48	3.24	0.8
27.99	3.19	4.2
28.18	3.16	0.8
28.78	3.10	0.6
29.03	3.07	0.7
29.31	3.04	0.9
29.58	3.02	2.4
29.95	2.98	9.6
30.44	2.93	3.7
31.09	2.87	3.1
31.36	2.85	0.8
31.98	2.80	2.2
32.23	2.78	1.7
32.37	2.76	0.6
32.64	2.74	1.5
33.03	2.71	0.1
33.34	2.69	1.0
33.47	2.68	1.3
34.08	2.63	0.7
34.55	2.59	1.8
34.73	2.58	0.4

[a] ± 0.1

1

2

1   After calcination, the X-ray powder diffraction pattern for SSZ-74

2   exhibits the characteristic lines shown in Table II below.

3

4   TABLE II

5   Calcined SSZ-74

2 Theta[a]	d-spacing (Angstroms)	Relative Integrated Intensity (%)
7.98	11.07	M
8.70	10.16	VS
8.89	9.93	S
9.08	9.74	S
14.02	6.31	W
14.93	5.93	M
16.03	5.52	M
23.26	3.82	VS
23.95	3.71	W
24.08	3.69	M

6   [a] ± 0.1

7

8   Table IIA below shows the X-ray powder diffraction lines for calcined

9   SSZ-74 including actual relative intensities.

10

11   TABLE IIA

12   Calcined SSZ-74

13

2 Theta[a]	d-spacing (Angstroms)	Relative Integrated Intensity (%)
7.98	11.07	34.9
8.70	10.16	86.8
8.89	9.93	40.2
9.08	9.74	47.0
9.66	9.15	1.0
11.26	7.85	0.4
11.34	7.80	0.5
12.76	6.93	1.1
13.26	6.67	4.6
14.02	6.31	13.4
14.93	5.93	20.9
16.03	5.52	23.5
16.39	5.40	4.3
16.61	5.33	4.4
17.12	5.18	3.0
17.80	4.98	2.8

18.19	4.87	7.6
19.05	4.66	1.9
19.74	4.49	0.4
20.44	4.34	3.0
20.75	4.28	3.4
21.19	4.19	7.7
21.67	4.10	4.1
21.99	4.04	5.8
22.68	3.92	3.7
22.79	3.90	9.5
23.26	3.82	100.0
23.95	3.71	14.2

1
2   (a) ± 0.1

3

4   The X-ray powder diffraction patterns were determined by standard

5   techniques. The radiation was the K-alpha/doublet of copper. The peak

6   heights and the positions, as a function of 2θ where θ is the Bragg angle, were

7   read from the relative intensities of the peaks, and d, the interplanar spacing

8   in Angstroms corresponding to the recorded lines, can be calculated.

9

10   The variation in the scattering angle (two theta) measurements, due to

11   instrument error and to differences between individual samples, is estimated

12   at ± 0.1 degrees.

13

14   Representative peaks from the X-ray diffraction pattern of calcined

15   SSZ-74 are shown in Table II. Calcination can result in changes in the

16   intensities of the peaks as compared to patterns of the "as-made" material, as

17   well as minor shifts in the diffraction pattern.

18

19   Crystalline SSZ-74 can be used as-synthesized, but typically will be

20   thermally treated (calcined). Usually, it is desirable to remove the alkali metal

21   cation (if any) by ion exchange and replace it with hydrogen, ammonium, or

22   any desired metal ion.

23

24   SSZ-74 can be formed into a wide variety of physical shapes.

25   Generally speaking, the molecular sieve can be in the form of a powder, a

1   granule, or a molded product, such as extrudate having a particle size

2   sufficient to pass through a 2-mesh (Tyler) screen and be retained on a

3   400-mesh (Tyler) screen. In cases where the catalyst is molded, such as by

4   extrusion with an organic binder, the SSZ-74 can be extruded before drying,

5   or, dried or partially dried and then extruded.

6

7   SSZ-74 can be composited with other materials resistant to the

8   temperatures and other conditions employed in organic conversion

9   processes. Such matrix materials include active and inactive materials and

10 synthetic or naturally occurring zeolites as well as inorganic materials such as

11 clays, silica and metal oxides. Examples of such materials and the manner in

12 which they can be used are disclosed in U.S. Patent No. 4,910,006, issued

13 May 20, 1990 to Zones et al., and U.S. Patent No. 5,316,753, issued May 31,

14 1994 to Nakagawa, both of which are incorporated by reference herein in their

15 entirety.

16

17   Hydrocarbon Conversion Processes

18

19   SSZ-74 molecular sieves are useful in hydrocarbon conversion

20 reactions. Hydrocarbon conversion reactions are chemical and catalytic

21 processes in which carbon containing compounds are changed to different

22 carbon containing compounds. Examples of hydrocarbon conversion

23 reactions in which SSZ-74 is expected to be useful include hydrocracking,

24 dewaxing, catalytic cracking and olefin and aromatics formation reactions.

25 The catalysts are also expected to be useful in other petroleum refining and

26 hydrocarbon conversion reactions such as isomerizing n-paraffins and

27 naphthenes, polymerizing and oligomerizing olefinic or acetylenic compounds

28 such as isobutylene and butene-1, polymerization of 1-olefins (e.g., ethylene),

29 reforming, isomerizing polyalkyl substituted aromatics (e.g., m-xylene), and

30 disproportionating aromatics (e.g., toluene) to provide mixtures of benzene,

31 xylenes and higher methylbenzenes and oxidation reactions. Also included

32 are rearrangement reactions to make various naphthalene derivatives, and

1   forming higher molecular weight hydrocarbons from lower molecular weight

2   hydrocarbons (e.g., methane upgrading).

3

4   The SSZ-74 catalysts may have high selectivity, and under

5   hydrocarbon conversion conditions can provide a high percentage of desired

6   products relative to total products.

7

8   For high catalytic activity, the SSZ-74 molecular sieve should be

9   predominantly in its hydrogen ion form. Generally, the molecular sieve is

10   converted to its hydrogen form by ammonium exchange followed by

11   calcination. If the molecular sieve is synthesized with a high enough ratio of

12   SDA cation to sodium ion, calcination alone may be sufficient. Typically, after

13   calcination at least 80% of the cation sites are occupied by hydrogen ions

14   and/or rare earth ions. As used herein, "predominantly in the hydrogen form"

15   means that, after calcination, at least 80% of the cation sites are occupied by

16   hydrogen ions and/or rare earth ions.

17

18   SSZ-74 molecular sieves can be used in processing

19   hydrocarbonaceous feedstocks. Hydrocarbonaceous feedstocks contain

20   carbon compounds and can be from many different sources, such as virgin

21   petroleum fractions, recycle petroleum fractions, shale oil, liquefied coal, tar

22   sand oil, synthetic paraffins from NAO, recycled plastic feedstocks. Other

23   feeds include synthetic feeds, such as those derived from a Fischer Tropsch

24   process, including an oxygenate-containing Fischer Tropsch process boiling

25   below about 371°C (700°F). In general, the feed can be any carbon containing

26   feedstock susceptible to zeolitic catalytic reactions. Depending on the type of

27   processing the hydrocarbonaceous feed is to undergo, the feed can contain

28   metal or be free of metals, it can also have high or low nitrogen or sulfur

29   impurities. It can be appreciated, however, that in general processing will be

30   more efficient (and the catalyst more active) the lower the metal, nitrogen, and

31   sulfur content of the feedstock.

32

1   The conversion of hydrocarbonaceous feeds can take place in any

2   convenient mode, for example, in fluidized bed, moving bed, or fixed bed

3   reactors depending on the types of process desired. The formulation of the

4   catalyst particles will vary depending on the conversion process and method

5   of operation.

6

7   Other reactions which can be performed using the catalyst of this

8   invention containing a metal, e.g., a Group VIII metal such platinum, include

9   hydrogenation-dehydrogenation reactions, denitrogenation and desulfurization

10   reactions.

11

12   The following table indicates typical reaction conditions which may be

13   employed when using catalysts comprising SSZ-74 in the hydrocarbon

14   conversion reactions of this invention. Typical conditions are indicated in

15   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.

1   Hydrocracking

2

3   Using a catalyst which comprises SSZ-74, for example predominantly

4   in the hydrogen form, and a hydrogenation promoter, heavy petroleum

5   residual feedstocks, cyclic stocks and other hydrocrackate charge stocks can

6   be hydrocracked using the process conditions and catalyst components

7   disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent

8   No. 5,316,753.

9

10   The hydrocracking catalysts contain an effective amount of at least one

11   hydrogenation component of the type commonly employed in hydrocracking

12   catalysts. The hydrogenation component is generally selected from the group

13   of hydrogenation catalysts consisting of one or more metals of Group VIB and

14   Group VIII, including the salts, complexes and solutions containing such. The

15   hydrogenation catalyst may be selected from the group of metals, salts and

16   complexes thereof of the group consisting of at least one of platinum,

17   palladium, rhodium, iridium, ruthenium and mixtures thereof or the group

18   consisting of at least one of nickel, molybdenum, cobalt, tungsten, titanium,

19   chromium and mixtures thereof. Reference to the catalytically active metal or

20   metals is intended to encompass such metal or metals in the elemental state

21   or in some form such as an oxide, sulfide, halide, carboxylate and the like.

22   The hydrogenation catalyst is present in an effective amount to provide the

23   hydrogenation function of the hydrocracking catalyst, for example in the range

24   of from 0.05 to 25% by weight.

25

26   Dewaxing

27

28   SSZ-74, for example predominantly in the hydrogen form, can be used

29   to dewax hydrocarbonaceous feeds by selectively removing straight chain

30   paraffins. Typically, the viscosity index of the dewaxed product is improved

31   (compared to the waxy feed) when the waxy feed is contacted with SSZ-74

32   under isomerization dewaxing conditions.

33

1   The catalytic dewaxing conditions are dependent in large measure on

2   the feed used and upon the desired pour point. Hydrogen is typically present

3   in the reaction zone during the catalytic dewaxing process. The hydrogen to

4   feed ratio is typically between about 500 and about 30,000 SCF/bbl (standard

5   cubic feet per barrel) (0.089 to 5.34 SCM/liter (standard cubic meters/liter)),

6   for example about 1000 to about 20,000 SCF/bbl (0.178 to 3.56 SCM/liter).

7   Generally, hydrogen will be separated from the product and recycled to the

8   reaction zone. Typical feedstocks include light gas oil, heavy gas oils and

9   reduced crudes boiling above about 350°F (177°C).

10

11   A typical dewaxing process is the catalytic dewaxing of a hydrocarbon

12 oil feedstock boiling above about 350°F (177°C) and containing straight chain

13 and slightly branched chain hydrocarbons by contacting the hydrocarbon oil

14 feedstock in the presence of added hydrogen gas at a hydrogen pressure of

15 about 15-3000 psi (0.103-20.7 Mpa) with a catalyst comprising SSZ-74 and at

16 least one Group VIII metal.

17

18   The SSZ-74 hydrodewaxing catalyst may optionally contain a

19 hydrogenation component of the type commonly employed in dewaxing

20 catalysts. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent

21 No. 5,316,753 for examples of these hydrogenation components.

22

23   The hydrogenation component is present in an effective amount to

24 provide an effective hydrodewaxing and hydroisomerization catalyst for

25 example in the range of from about 0.05 to 5% by weight. The catalyst may be

26 run in such a mode to increase isomerization dewaxing at the expense of

27 cracking reactions.

28

29   The feed may be hydrocracked, followed by dewaxing. This type of two

30 stage process and typical hydrocracking conditions are described in U.S.

31 Patent No. 4,921,594, issued May 1, 1990 to Miller, which is incorporated

32 herein by reference in its entirety.

33

1   SSZ-74 may also be utilized as a dewaxing catalyst in the form of a

2 combination of catalysts. The combination comprises a first catalyst

3 comprising molecular sieve SSZ-74 and, desirably, at least one Group VIII

4 metal, and a second catalyst comprising an aluminosilicate zeolite which is

5 more shape selective than molecular sieve SSZ-74. As used herein, the term

6 "combination" includes mixtures of the molecular sieve of this invention and

7 the aluminosilicate zeolite, layers of the molecular sieve and zeolite, or any

8 other configuration in which the feed comes in contact with both the molecular

9 sieve and the zeolite. The use of combined catalysts in the form of layers is

10 disclosed in U.S. Patent No. 5,149,421, issued September 22, 1992 to Miller,

11 which is incorporated by reference herein in its entirety. The layering may also

12 include a bed of SSZ-74 layered with a non-zeolitic component designed for

13 either hydrocracking or hydrofinishing.

14

15   SSZ-74 may also be used to dewax raffinates, including bright stock,

16 under conditions such as those disclosed in U. S. Patent No. 4,181,598,

17 issued January 1, 1980 to Gillespie et al., which is incorporated by reference

18 herein in its entirety.

19

20   It is often desirable to use mild hydrogenation (sometimes referred to

21 as hydrofinishing) to produce more stable dewaxed products. The

22 hydrofinishing step can be performed either before or after the dewaxing step,

23 typically after. Hydrofinishing is typically conducted at temperatures ranging

24 from about 190°C to about 340°C at pressures from about 400 psig to about

25 3000 psig (2.76 to 20.7 Mpa gauge) at space velocities (LHSV) between

26 about 0.1 and 20 and a hydrogen recycle rate of about 400 to 1500 SCF/bbl

27 (0.071 to 0.27 SCM/liter). The hydrogenation catalyst employed must be

28 active enough not only to hydrogenate the olefins, diolefins and color bodies

29 which may be present, but also to reduce the aromatic content. Suitable

30 hydrogenation catalyst are disclosed in U. S. Patent No. 4,921,594, issued

31 May 1, 1990 to Miller, which is incorporated by reference herein in its entirety.

32 The hydrofinishing step is beneficial in preparing an acceptably stable product

33 (e.g., a lubricating oil) since dewaxed products prepared from hydrocracked

1   stocks tend to be unstable to air and light and tend to form sludges

2   spontaneously and quickly.

3

4   Lube oil may be prepared using SSZ-74. For example, a C_{20+} lube oil may

5   be made by isomerizing a C_{20+} olefin feed over a catalyst comprising SSZ-74

6   in the hydrogen form and at least one Group VIII metal. Alternatively, the

7   lubricating oil may be made by hydrocracking in a hydrocracking zone a

8   hydrocarbonaceous feedstock to obtain an effluent comprising a

9   hydrocracked oil, and catalytically dewaxing the effluent at a temperature of at

10   least about 400°F (204°C) and at a pressure of from about 15 psig to about

11   3000 psig (0.103-20.7 Mpa gauge) in the presence of added hydrogen gas

12   with a catalyst comprising SSZ-74 in the hydrogen form and at least one

13   Group VIII metal.

14

15   Aromatics Formation

16

17   SSZ-74 can be used to convert light straight run naphthas and similar

18   mixtures to highly aromatic mixtures. Thus, normal and slightly branched

19   chained hydrocarbons, for example those having a boiling range above about

20   40°C and less than about 200°C, can be converted to products having a

21   substantial higher octane aromatics content by contacting the hydrocarbon

22   feed with a catalyst comprising SSZ-74. It is also possible to convert heavier

23   feeds into BTX or naphthalene derivatives of value using a catalyst

24   comprising SSZ-74.

25

26   The conversion catalyst typically contains a Group VIII metal

27   compound to have sufficient activity for commercial use. By Group VIII metal

28   compound as used herein is meant the metal itself or a compound thereof.

29   The Group VIII noble metals and their compounds, platinum, palladium, and

30   iridium, or combinations thereof can be used. Rhenium or tin or a mixture

31   thereof may also be used in conjunction with the Group VIII metal compound

32   (typically a noble metal compound), for example a platinum compound. The

33   amount of Group VIII metal present in the conversion catalyst should be within

1   the normal range of use in reforming catalysts, from about 0.05 to 2.0 weight

2   percent, for example 0.2 to 0.8 weight percent.

3

4   It is critical to the selective production of aromatics in useful quantities

5   that the conversion catalyst be substantially free of acidity, for example, by

6   neutralizing the molecular sieve with a basic metal, e.g., alkali metal,

7   compound. Methods for rendering the catalyst free of acidity are known in the

8   art. See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent

9   No. 5,316,753 for a description of such methods.

10

11   Typical alkali metals are sodium, potassium, rubidium and cesium. The

12   molecular sieve itself can be substantially free of acidity only at very high

13   silica:alumina mole ratios.

14

15   Catalytic Cracking

16

17   Hydrocarbon cracking stocks can be catalytically cracked in the

18   absence of hydrogen using SSZ-74, for example predominantly in the

19   hydrogen form.

20

21   When SSZ-74 is used as a catalytic cracking catalyst in the absence of

22   hydrogen, the catalyst may be employed in conjunction with traditional

23   cracking catalysts, e.g., any aluminosilicate heretofore employed as a

24   component in cracking catalysts. Typically, these are large pore, crystalline

25   aluminosilicates. Examples of these traditional cracking catalysts are

26   disclosed in the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent

27   No 5,316,753. When a traditional cracking catalyst (TC) component is

28   employed, the relative weight ratio of the TC to the SSZ-74 is generally

29   between about 1:10 and about 500:1, desirably between about 1:10 and

30   about 200:1, for example between about 1:2 and about 50:1 or between about

31   1:1 and about 20:1. The novel molecular sieve and/or the traditional cracking

32   component may be further ion exchanged with rare earth ions to modify

33   selectivity.

1

2   The cracking catalysts are typically employed with an inorganic oxide

3   matrix component. See the aforementioned U.S. Patent No. 4,910,006 and

4   U.S. Patent No. 5,316,753 for examples of such matrix components.

5

6   Isomerization

7

8   The present catalyst is highly active and highly selective for isomerizing

9   C_4 to C_7 hydrocarbons. The activity means that the catalyst can operate at

10   relatively low temperature which thermodynamically favors highly branched

11   paraffins. Consequently, the catalyst can produce a high octane product. The

12   high selectivity means that a relatively high liquid yield can be achieved when

13   the catalyst is run at a high octane.

14

15   The present process comprises contacting the isomerization catalyst,

16   i.e., a catalyst comprising SSZ-74 in the hydrogen form, with a hydrocarbon

17   feed under isomerization conditions. The feed is typically a light straight run

18   fraction, boiling within the range of 30°F to 250°F (-1°C to 121°C), for example

19   from 60°F to 200°F (16°C to 93°C). Typically, the hydrocarbon feed for the

20   process comprises a substantial amount of C_4 to C_7 normal and slightly

21   branched low octane hydrocarbons, for example C_5 and C_6 hydrocarbons.

22

23   The isomerization reaction is typically carried out in the presence of

24   hydrogen. Hydrogen may be added to give a hydrogen to hydrocarbon ratio

25   (H_2/HC) of between 0.5 and 10 H_2/HC, for example between 1 and 8 H_2/HC.

26   See the aforementioned U.S. Patent No. 4,910,006 and U.S. Patent No.

27   5,316,753 for a further discussion of isomerization process conditions.

28

29   A low sulfur feed is especially useful in the present process. The feed

30   desirably contains less than 10 ppm, for example less than 1 ppm or less than

31   0.1 ppm sulfur. In the case of a feed which is not already low in sulfur,

32   acceptable levels can be reached by hydrogenating the feed in a

33   presaturation zone with a hydrogenating catalyst which is resistant to sulfur

1   poisoning. See the aforementioned U.S. Patent No. 4,910,006 and U.S.

2   Patent No. 5,316,753 for a further discussion of this hydrodesulfurization

3   process.

4

5   It is typical to limit the nitrogen level and the water content of the feed.

6   Catalysts and processes which are suitable for these purposes are known to

7   those skilled in the art.

8

9   After a period of operation, the catalyst can become deactivated by

10   sulfur or coke. See the aforementioned U.S. Patent No. 4,910,006 and U.S.

11   Patent No. 5,316,753 for a further discussion of methods of removing this

12   sulfur and coke, and of regenerating the catalyst.

13

14   The conversion catalyst desirably contains a Group VIII metal

15   compound to have sufficient activity for commercial use. By Group VIII metal

16   compound as used herein is meant the metal itself or a compound thereof.

17   The Group VIII noble metals and their compounds, platinum, palladium, and

18   iridium, or combinations thereof can be used. Rhenium and tin may also be

19   used in conjunction with the noble metal. Typically, the metal is platinum. The

20   amount of Group VIII metal present in the conversion catalyst should be within

21   the normal range of use in isomerizing catalysts, from about 0.05 to

22   2.0 weight percent, for example 0.2 to 0.8 weight percent.

23

24   Alkylation and Transalkylation

25

26   SSZ-74 can be used in a process for the alkylation or transalkylation of

27   an aromatic hydrocarbon. The process comprises contacting the aromatic

28   hydrocarbon with a C_2 to C_{16} olefin alkylating agent or a polyalkyl aromatic

29   hydrocarbon transalkylating agent, under at least partial liquid phase

30   conditions, and in the presence of a catalyst comprising SSZ-74.

31

1   SSZ-74 can also be used for removing benzene from gasoline by

2 alkylating the benzene as described above and removing the alkylated

3 product from the gasoline.

4

5   For high catalytic activity, the SSZ-74 molecular sieve should be

6 predominantly in its hydrogen ion form. It is typical that, after calcination, at

7 least 80% of the cation sites are occupied by hydrogen ions and/or rare earth

8 ions.

9

10   Examples of suitable aromatic hydrocarbon feedstocks which may be

11 alkylated or transalkylated by the process of the invention include aromatic

12 compounds such as benzene, toluene and xylene. Benzene is especially

13 useful. There may be occasions where naphthalene or naphthalene

14 derivatives such as dimethylnaphthalene may be desirable. Mixtures of

15 aromatic hydrocarbons may also be employed.

16

17   Suitable olefins for the alkylation of the aromatic hydrocarbon are those

18 containing 2 to 20, for example 2 to 4, carbon atoms, such as ethylene,

19 propylene, butene-1, trans-butene-2 and cis-butene-2, or mixtures thereof.

20 There may be instances where pentenes are desirable. Typical olefins are

21 ethylene and propylene. Longer chain alpha olefins may be used as well.

22

23   When transalkylation is desired, the transalkylating agent is a polyalkyl

24 aromatic hydrocarbon containing two or more alkyl groups that each may

25 have from 2 to about 4 carbon atoms. For example, suitable polyalkyl

26 aromatic hydrocarbons include di-, tri- and tetra-alkyl aromatic hydrocarbons,

27 such as diethylbenzene, triethylbenzene, diethylmethylbenzene

28 (diethyltoluene), di-isopropylbenzene, di-isopropyltoluene, dibutylbenzene,

29 and the like. Typical polyalkyl aromatic hydrocarbons are the dialkyl

30 benzenes. A particularly desirable polyalkyl aromatic hydrocarbon is

31 di-isopropylbenzene.

32

1   When alkylation is the process conducted, reaction conditions are as

2   follows. The aromatic hydrocarbon feed should be present in stoichiometric

3   excess. It is typical that the molar ratio of aromatics to olefins be greater than

4   four-to-one to prevent rapid catalyst fouling. The reaction temperature may

5   range from 100°F to 600°F (38°C to 315°C), for example 250°F to 450°F

6   (121°C to 232°C). The reaction pressure should be sufficient to maintain at

7   least a partial liquid phase in order to retard catalyst fouling. This is typically

8   50 psig to 1000 psig (0.345 to 6.89 Mpa gauge) depending on the feedstock

9   and reaction temperature. Contact time may range from 10 seconds to 10

10   hours, but is usually from 5 minutes to an hour. The weight hourly space

11   velocity (WHSV), in terms of grams (pounds) of aromatic hydrocarbon and

12   olefin per gram (pound) of catalyst per hour, is generally within the range of

13   about 0.5 to 50.

14

15   When transalkylation is the process conducted, the molar ratio of

16   aromatic hydrocarbon will generally range from about 1:1 to 25:1, and for

17   example from about 2:1 to 20:1. The reaction temperature may range from

18   about 100°F to 600°F (38°C to 315°C), but it is typically about 250°F to 450°F

19   (121°C to 232°C). The reaction pressure should be sufficient to maintain at

20   least a partial liquid phase, typically in the range of about 50 psig to 1000 psig

21   (0.345 to 6.89 Mpa gauge), for example 300 psig to 600 psig (2.07 to 4.14

22   Mpa gauge). The weight hourly space velocity will range from about 0.1 to 10.

23   U.S. Patent No. 5,082,990 issued on January 21, 1992 to Hsieh, et al.

24   describes such processes and is incorporated herein by reference.

25

26   Conversion of Paraffins to Aromatics

27

28   SSZ-74 can be used to convert light gas C_2-C_6 paraffins to higher

29   molecular weight hydrocarbons including aromatic compounds. Typically, the

30   molecular sieve will contain a catalyst metal or metal oxide wherein said metal

31   is selected from the group consisting of Groups IB, IIB, VIII and IIIA of the

32   Periodic Table, for example gallium, niobium, indium or zinc, in the range of

33   from about 0.05 to 5% by weight.

1

2   <u>Isomerization of Olefins</u>

3

4   SSZ-74 can be used to isomerize olefins. The feed stream is a

5   hydrocarbon stream containing at least one C_{4-6} olefin, for example a C_{4-6}

6   normal olefin such as normal butene. Normal butene as used in this

7   specification means all forms of normal butene, e.g., 1-butene, cis-2-butene,

8   and trans-2-butene. Typically, hydrocarbons other than normal butene or

9   other C_{4-6} normal olefins will be present in the feed stream. These other

10 hydrocarbons may include, e.g., alkanes, other olefins, aromatics, hydrogen,

11 and inert gases.

12

13   The feed stream typically may be the effluent from a fluid catalytic

14 cracking unit or a methyl-tert-butyl ether unit. A fluid catalytic cracking unit

15 effluent typically contains about 40-60 weight percent normal butenes. A

16 methyl-tert-butyl ether unit effluent typically contains 40-100 weight percent

17 normal butene. The feed stream typically contains at least about 40 weight

18 percent normal butene, for example at least about 65 weight percent normal

19 butene. The terms iso-olefin and methyl branched iso-olefin may be used

20 interchangeably in this specification.

21

22   The process is carried out under isomerization conditions. The

23 hydrocarbon feed is contacted in a vapor phase with a catalyst comprising the

24 SSZ-74. The process may be carried out generally at a temperature from

25 about 625°F to about 950°F (329-510°C), for butenes, for example from about

26 700°F to about 900°F (371-482°C) or from about 350°F to about 650°F (177-

27 343°C) for pentenes and hexenes. The pressure ranges from subatmospheric

28 to about 200 psig (1.38 Mpa gauge), for example from about 15 psig to about

29 200 psig (0.103 to 1.38 Mpa gauge) or from about 1 psig to about 150 psig

30 (0.00689 to 1.03 Mpa gauge).

31

32   The liquid hourly space velocity during contacting is generally from

33 about 0.1 to about 50 hr^{-1}, based on the hydrocarbon feed, for example from

1   about 0.1 to about 20 hr⁻¹, from about 0.2 to about 10 hr⁻¹, or from about 1 to

2   about 5 hr⁻¹. A hydrogen/hydrocarbon molar ratio is maintained from about 0

3   to about 30 or higher. The hydrogen can be added directly to the feed stream

4   or directly to the isomerization zone. The reaction is typically substantially free

5   of water, typically less than about two weight percent based on the feed. The

6   process can be carried out in a packed bed reactor, a fixed bed, fluidized bed

7   reactor, or a moving bed reactor. The bed of the catalyst can move upward or

8   downward. The mole percent conversion of, e.g., normal butene to iso-butene

9   is at least 10, for example at least 25 or at least 35.

10

11   Xylene Isomerization

12

13   SSZ-74 may also be useful in a process for isomerizing one or more

14   xylene isomers in a C_8 aromatic feed to obtain ortho-, meta-, and para-xylene

15   in a ratio approaching the equilibrium value. In particular, xylene isomerization

16   is used in conjunction with a separate process to manufacture para-xylene.

17   For example, a portion of the para-xylene in a mixed C_8 aromatics stream may

18   be recovered by crystallization and centrifugation. The mother liquor from the

19   crystallizer is then reacted under xylene isomerization conditions to restore

20   ortho-, meta- and para-xylenes to a near equilibrium ratio. At the same time,

21   part of the ethylbenzene in the mother liquor is converted to xylenes or to

22   products which are easily separated by filtration. The isomerate is blended

23   with fresh feed and the combined stream is distilled to remove heavy and light

24   by-products. The resultant C_8 aromatics stream is then sent to the crystallizer

25   to repeat the cycle.

26

27   Optionally, isomerization in the vapor phase is conducted in the

28   presence of 3.0 to 30.0 moles of hydrogen per mole of alkylbenzene (e.g.,

29   ethylbenzene). If hydrogen is used, the catalyst should comprise about 0.1 to

30   2.0 wt.% of a hydrogenation/dehydrogenation component selected from

31   Group VIII (of the Periodic Table) metal component, especially platinum or

32   nickel. By Group VIII metal component is meant the metals and their

33   compounds such as oxides and sulfides.

1

2   Optionally, the isomerization feed may contain 10 to 90 wt. of a diluent

3   such as toluene, trimethylbenzene, naphthenes or paraffins.

4

5   Oligomerization

6

7   It is expected that SSZ-74 can also be used to oligomerize straight and

8   branched chain olefins having from about 2 to 21, for example 2-5 carbon

9   atoms. The oligomers which are the products of the process are medium to

10   heavy olefins which are useful for both fuels, i.e., gasoline or a gasoline

11   blending stock and chemicals.

12

13   The oligomerization process comprises contacting the olefin feedstock

14   in the gaseous or liquid phase with a catalyst comprising SSZ-74.

15

16   The molecular sieve can have the original cations associated therewith

17   replaced by a wide variety of other cations according to techniques well

18   known in the art. Typical cations would include hydrogen, ammonium and

19   metal cations including mixtures of the same. Of the replacing metallic

20   cations, cations of metals such as rare earth metals, manganese, calcium, as

21   well as metals of Group II of the Periodic Table, e.g., zinc, and Group VIII of

22   the Periodic Table, e.g., nickel are particularly desirable. One of the prime

23   requisites is that the molecular sieve have a fairly low aromatization activity,

24   i.e., in which the amount of aromatics produced is not more than about 20%

25   by weight. This is accomplished by using a molecular sieve with controlled

26   acid activity [alpha value] of from about 0.1 to about 120, for example from

27   about 0.1 to about 100, as measured by its ability to crack n-hexane.

28

29   Alpha values are defined by a standard test known in the art, e.g., as

30   shown in U.S. Patent No. 3,960,978 issued on June 1, 1976 to Givens et al.

31   which is incorporated totally herein by reference. If required, such molecular

32   sieves may be obtained by steaming, by use in a conversion process or by

33   any other method which may occur to one skilled in this art.

1

2   <u>Condensation of Alcohols</u>

3

4   SSZ-74 can be used to condense lower aliphatic alcohols having 1 to

5   10 carbon atoms to a gasoline boiling point hydrocarbon product comprising

6   mixed aliphatic and aromatic hydrocarbon. The process disclosed in U.S.

7   Patent No. 3,894,107, issued July 8, 1975 to Butter et al., describes the

8   process conditions used in this process, which patent is incorporated totally

9   herein by reference.

10

11   The catalyst may be in the hydrogen form or may be base exchanged

12   or impregnated to contain ammonium or a metal cation complement, typically

13   in the range of from about 0.05 to 5% by weight. The metal cations that may

14   be present include any of the metals of the Groups I through VIII of the

15   Periodic Table. However, in the case of Group IA metals, the cation content

16   should in no case be so large as to effectively inactivate the catalyst, nor

17   should the exchange be such as to eliminate all acidity. There may be other

18   processes involving treatment of oxygenated substrates where a basic

19   catalyst is desired.

20

21   <u>Methane Upgrading</u>

22

23   Higher molecular weight hydrocarbons can be formed from lower

24   molecular weight hydrocarbons by contacting the lower molecular weight

25   hydrocarbon with a catalyst comprising SSZ-74 and a metal or metal

26   compound capable of converting the lower molecular weight hydrocarbon to a

27   higher molecular weight hydrocarbon. Examples of such reactions include the

28   conversion of methane to C_{2+} hydrocarbons such as ethylene or benzene or

29   both. Examples of useful metals and metal compounds include lanthanide and

30   or actinide metals or metal compounds.

31

32   These reactions, the metals or metal compounds employed and the

33   conditions under which they can be run are disclosed in U.S. Patents No.

1   4,734,537, issued March 29, 1988 to Devries et al.; 4,939,311, issued July 3,

2   1990 to Washecheck et al.; 4,962,261, issued October 9, 1990 to Abrevaya et

3   al.; 5,095,161, issued March 10, 1992 to Abrevaya et al.; 5,105,044, issued

4   April 14, 1992 to Han et al.; 5,105,046, issued April 14, 1992 to Washecheck;

5   5,238,898, issued August 24, 1993 to Han et al.; 5,321,185, issued June 14,

6   1994 to van der Vaart; and 5,336,825, issued August 9, 1994 to Choudhary et

7   al., each of which is incorporated herein by reference in its entirety.

8

9   Polymerization of 1-Olefins

10

11   The molecular sieve of the present invention may be used in a catalyst

12   for the polymerization of 1-olefins, e.g., the polymerization of ethylene. To

13   form the olefin polymerization catalyst, the molecular sieve as hereinbefore

14   described is reacted with a particular type of organometallic compound.

15   Organometallic compounds useful in forming the polymerization catalyst

16   include trivalent and tetravalent organotitanium and organochromium

17   compounds having alkyl moieties and, optionally, halo moieties. In the context

18   of the present invention the term "alkyl" includes both straight and branched

19   chain alkyl, cycloalkyl and alkaryl groups such as benzyl.

20

21   Examples of trivalent and tetravalent organochromium and

22   organotitanium compounds are disclosed in U.S. Patent No. 4,376,722,

23   issued March 15, 1983 to Chester et al., U.S. Patent No. 4,377,497, issued

24   March 22, 1983 to Chester et al.; U.S. Patent No. 4,446,243, issued May 1,

25   1984 to Chester et al., and U.S. Patent No. 4,526,942, issued July 2, 1985 to

26   Chester et al. The disclosure of the aforementioned patents are incorporated

27   herein by reference in their entirety.

28

29   Examples of the organometallic compounds used to form the

30   polymerization catalyst include, but are not limited to, compounds

31   corresponding to the general formula:

32

1

2    $MAlk_xHal_{m-x}$

3
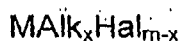
4   wherein M is a metal selected from titanium and chromium; Alk is alkyl; Hal is

5   halogen (e.g., Cl or Br); x is 1-4; and m is greater than or equal to x and is 3

6   or 4.

7

8   Examples of organotitanium and organochromium compounds

9   encompassed by such a formula include compounds of the formula $CrAlk_4$,

10   $CrAlk_3$, $CrAlk_3Hal$, $CrAlk_2Hal$, $CrAlk_2Hal_2$, $CrAlkHal_2$, $CrAlkHal_3$, $TiAlk_4$, $TiAlk_3$,

11   $TiAlk_3Hal$, $TiAlk_2Hal$, $TiAlk_2Hal_2$, $TiAlkHal_2$, $TiAlkHal_3$, wherein Hal can be Cl

12   or Br and Alk can be methyl, ethyl, propyl, isopropyl, butyl, isobutyl, sec-butyl,

13   tert-butyl, pentyl, isopentyl, neopentyl, hexyl, isohexyl, neohexyl, 2-ethybutyl,

14   octyl, 2-ethylhexyl, 2,2-diethylbutyl, 2-isopropyl-3-methylbutyl, etc.,

15   cyclohexylalkyls such as, for example, cyclohexylmethyl, 2-cyclohexylethyl, 3-

16   cyclyhexylpropyl, 4-cyclohexylbutyl, and the corresponding alkyl-substituted

17   cyclohexyl radicals as, for example, (4-methylcyclohexyl)methyl, neophyl, i.e.,

18   beta, beta-dimethyl-phenethyl, benzyl, ethylbenzyl, and p-isopropylbenzyl.

19   Desirable examples of Y include C_{1-5} alkyl, especially butyl.

20

21   The organotitanium and organochromium materials employed in the

22   catalyst can be prepared by techniques well known in the art. See, for

23   example the aforementioned Chester et al. patents.

24

25   The organotitanium or organochromium compounds can be with the

26   molecular sieve of the present invention, such as by reacting the

27   organometallic compound and the molecular sieve, in order to form the olefin

28   polymerization catalyst. Generally, such a reaction takes place in the same

29   reaction medium used to prepare the organometallic compound under

30   conditions which promote formation of such a reaction product. The molecular

31   sieve can simply be added to the reaction mixture after formation of the

32   organometallic compound has been completed. Molecular sieve is added in

33   an amount sufficient to provide from about 0.1 to 10 parts by weight, for

1   example from about 0.5 to 5 parts by weight, of organometallic compound in

2   the reaction medium per 100 parts by weight of molecular sieve.

3

4   Temperature of the reaction medium during reaction of organometallic

5   compound with molecular sieve is also maintained at a level which is low

6   enough to ensure the stability of the organometallic reactant. Thus,

7   temperatures in the range of from about -150° C. to 50° C., for example from

8   about -80° C. to 0° C. can be usefully employed. Reaction times of from about

9   0.01 to 10 hours, more for example from about 0.1 to 1 hour, can be

10   employed in reacting the organotitanium or organochromium compound with

11   the molecular sieve.

12

13   Upon completion of the reaction, the catalyst material so formed may

14   be recovered and dried by evaporating the reaction medium solvent under a

15   nitrogen atmosphere. Alternatively, olefin polymerization reactions can be

16   conducted in this same solvent based reaction medium used to form the

17   catalyst.

18

19   The polymerization catalyst can be used to catalyze polymerization of

20   1-olefins. The polymers produced using the catalysts of this invention are

21   normally solid polymers of at least one mono-1-olefin containing from 2 to 8

22   carbon atoms per molecule. These polymers are normally solid

23   homopolymers of ethylene or copolymers of ethylene with another mono-1-

24   olefin containing 3 to 8 carbon atoms per molecule. Exemplary copolymers

25   include those of ethylene/propylene, ethylene/1-butene, ethylene/1-hexane,

26   and ethylene/1-octene and the like. The major portion of such copolymers is

27   derived from ethylene and generally consists of about 80-99, for example 95-

28   99 mole percent of ethylene. These polymers are well suited for extrusion,

29   blow molding, injection molding and the like.

30

31   The polymerization reaction can be conducted by contacting monomer

32   or monomers, e.g., ethylene, alone or with one or more other olefins, and in

33   the substantial absence of catalyst poisons such as moisture and air, with a

1   catalytic amount of the supported organometallic catalyst at a temperature

2   and at a pressure sufficient to initiate the polymerization reaction. If desired,

3   an inert organic solvent may be used as a diluent and to facilitate materials

4   handling if the polymerization reaction is conducted with the reactants in the

5   liquid phase, e.g. in a particle form (slurry) or solution process. The reaction

6   may also be conducted with reactants in the vapor phase, e.g., in a fluidized

7   bed arrangement in the absence of a solvent but, if desired, in the presence of

8   an inert gas such as nitrogen.

9

10   The polymerization reaction is carried out at temperatures of from

11   about 30° C. or less, up to about 200° C. or more, depending to a great extent

12   on the operating pressure, the pressure of the olefin monomers, and the

13   particular catalyst being used and its concentration. Naturally, the selected

14   operating temperature is also dependent upon the desired polymer melt index

15   since temperature is definitely a factor in adjusting the molecular weight of the

16   polymer. Typically, the temperature used is from about 30° C. to about 100°

17   C. in a conventional slurry or "particle forming" process or from 100° C. to

18   150° C. in a "solution forming" process. A temperature of from about 70° C to

19   110° C. can be employed for fluidized bed processes.

20

21   The pressure to be used in the polymerization reactions can be any

22   pressure sufficient to initiate the polymerization of the monomer(s) to high

23   molecular weight polymer. The pressure, therefore, can range from

24   subatmospheric pressures, using an inert gas as diluent, to superatmospheric

25   pressures of up to about 30,000 psig or more, for example from atmospheric

26   (0 psig) up to about 1000 psig. As a general rule, a pressure of 20 to 800 psig

27   is desirable.

28

29   The selection of an inert organic solvent medium to be employed in the

30   solution or slurry process embodiments of this invention is not too critical, but

31   the solvent should be inert to the supported organometallic catalyst and olefin

32   polymer produced, and be stable at the reaction temperature used. It is not

33   necessary, however, that the inert organic solvent medium also serve as a

1   solvent for the polymer to be produced. Among the inert organic solvents

2   applicable for such purposes may be mentioned saturated aliphatic

3   hydrocarbons having from about 3 to 12 carbon atoms per molecule such as

4   hexane, heptane, pentane, isooctane, purified kerosene and the like,

5   saturated cycloaliphatic hydrocarbons having from about 5 to 12 carbon

6   atoms per molecule such as cyclohexane, cyclopentane,

7   dimethylcyclopentane and methylcyclohexane and the like and aromatic

8   hydrocarbons having from about 6 to 12 carbon atoms per molecule such as

9   benzene, toluene, xylene, and the like. Particularly desirable solvent media

10   are cyclohexane, pentane, hexane and heptane.

11

12   Hydrogen can be introduced into the polymerization reaction zone in

13   order to decrease the molecular weight of the polymers produced (i.e., give a

14   much higher Melt Index, MI). Partial pressure of hydrogen when hydrogen is

15   used can be within the range of 5 to 100 psig, for example 25 to 75 psig. The

16   melt indices of the polymers produced in accordance with the instant invention

17   can range from about 0.1 to about 70 or even higher.

18

19   More detailed description of suitable polymerization conditions

20   including examples of particle form, solution and fluidized bed polymerization

21   arrangements are found in Karapinka; U.S. Pat. No. 3,709,853; Issued Jan. 9,

22   1973 and Karol et al; U.S. Pat. No. 4,086,408; Issued Apr. 25, 1978. Both of

23   these patents are incorporated herein by reference.

24

25   Hydrotreating

26

27   SSZ-74 is useful in a hydrotreating catalyst. During hydrotreatment,

28   oxygen, sulfur and nitrogen present in the hydrocarbonaceous feed is reduced

29   to low levels. Aromatics and olefins, if present in the feed, may also have their

30   double bonds saturated. In some cases, the hydrotreating catalyst and

31   hydrotreating conditions are selected to minimize cracking reactions, which

32   can reduce the yield of the most desulfided product (typically useful as a fuel).

33

1   Hydrotreating conditions typically include a reaction temperature

2   between 400-900°F (204-482°C), for example 650-850°F (343-454°C); a

3   pressure between 500 and 5000 psig (3.5-34.6 Mpa), for example 1000 to

4   3000 psig (7.0-20.8 MPa); a feed rate (LHSV) of 0.5 hr^{-1} to 20 hr^{-1} (v/v); and

5   overall hydrogen consumption 300 to 2000 scf per barrel of liquid hydrocarbon

6   feed (53.4-356 m^3 H$_2$/m^3 feed). The hydrotreating catalyst will typically be a

7   composite of a Group VI metal or compound thereof, and a Group VIII metal

8   or compound thereof supported on the molecular sieve of this invention..

9   Typically, such hydrotreating catalyst are presulfided.

10

11   Catalysts useful for hydrotreating hydrocarbon feeds are disclosed in

12   U.S. Patents No. 4,347,121, issued August 31,1982 to Mayer et al, and

13   4,810,357, issued March 7, 1989 to Chester et al, both of which are

14   incorporated herein by reference in their entirety. Suitable catalysts include

15   noble metals from Group VIII, such as Fe, Co, Ni, Pt or Pd, and/or Group VI

16   metals, such as Cr, Mo, Sn or W. Examples of combinations of Group VIII and

17   Group VI metals include Ni-Mo or Ni-Sn. Other suitable catalysts are

18   described in U. S. Patents No. 4,157,294, issued June 5, 1979 to Iwao et al,

19   and 3,904,513, issued September 9, 1975 to Fischer et al. U. S. Patent No.

20   3,852,207, issued December 3, 1974 to Strangeland et al, describes suitable

21   noble metal catalysts and mild hydrotreating conditions. The contents of these

22   patents are hereby incorporated by reference.

23

24   The amount of hydrogenation component(s) in the catalyst suitably

25   range from about 0.5% to about 10% by weight of Group VIII component(s)

26   and from 5% to about 25% by weight of Group VI metal component(s),

27   calculated as metal oxide(s) per 100 parts by weight of total catalyst., where

28   the percentages by weight are based on the weight of the catalyst before

29   sulfiding. The hydrogenation component(s) in the catalyst may be in the oxidic

30   and/or sulfidic form.

31

Hydrogenation

SSZ-74 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-74. 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, for example 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.

Reduction of Oxides of Nitrogen

SSZ-74 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

1   include cobalt, copper, platinum, iron, chromium, manganese, nickel, zinc,

2   lanthanum, palladium, rhodium and mixtures thereof.

3

4   One example of such a process for the catalytic reduction of oxides of

5   nitrogen in the presence of a zeolite is disclosed in U.S. Patent No. 4,297,328,

6   issued October 27, 1981 to Ritscher et al., which is incorporated by reference

7   herein. There, the catalytic process is the combustion of carbon monoxide

8   and hydrocarbons and the catalytic reduction of the oxides of nitrogen

9   contained in a gas stream, such as the exhaust gas from an internal

10   combustion engine. The zeolite used is metal ion-exchanged, doped or

11   loaded sufficiently so as to provide an effective amount of catalytic copper

12   metal or copper ions within or on the zeolite. In addition, the process is

13   conducted in an excess of oxidant, e.g., oxygen.

14

15   Partial Oxidation

16

17   The partial oxidation of low value hydrocarbons such as alkanes and

18   alkenes into high value products such as alcohols and epoxides is of great

19   commercial interest. These oxidation products are not only valuable as is, but

20   also as intermediates for specialty chemicals including pharmaceuticals and

21   pesticides.

22

23   U.S. Patent No. 4,410,501, issued October 18, 1983 to Esposito et al.,

24   discloses a titanium-containing analogue of the all-silica ZSM-5 molecular

25   sieve. This material (known as "TS-1") has been found to be useful in

26   catalyzing a wide range of partial oxidation chemistries, for example the

27   production of catechol and hydroquinone from phenol and hydrogen peroxide

28   (H_2O_2) and the manufacture of propylene oxide and cyclohexanone oxime

29   from propylene and cyclohexanone, respectively. In addition, TS-1 can be

30   used to catalyze the reaction of alkanes and aqueous H_2O_2 to form alcohols

31   and ketones. (See Huybrechts, D.R.C. et al., *Nature* 1990, 345; 240-242 and

32   Tatsumi, T. et al., *J.C.S. Chem. Commun.* 1990, 476-477.)

33

1   TS-1 has many salient features, other than its catalytic abilities, which

2   make it attractive as a commercial catalyst. Most importantly, it is a solid. This

3   allows for easy separation from the reactants and products (typically liquids)

4   by simple, inexpensive filtration. Moreover, this solid has high thermal stability

5   and a very long lifetime. Calcination in air at moderate temperatures (550°C)

6   restores the material to its original catalytic ability. TS-1 performs best at mild

7   temperatures (<100°C) and pressures (1 atm). The oxidant used for reactions

8   catalyzed by TS-1 is aqueous H_2O_2, which is important because aqueous

9   H_2O_2 is relatively inexpensive and its by-product is water. Hence, the choice

10   of oxidant is favorable from both a commercial and environmental point of

11   view.

12

13   While a catalyst system based on TS-1 has many useful features, it

14   has one serious drawback. The zeolite structure of TS-1 includes a regular

15   system of pores which are formed by nearly circular rings of ten silicon atoms

16   (called 10-membered rings, or simply "10 rings") creating pore diameters of

17   approximately 5.5 Å. This small size results in the exclusion of molecules

18   larger than 5.5 Å. Because the catalytically active sites are located within the

19   pores of the zeolite, any exclusion of molecules from the pores results in poor

20   catalytic activity.

21

22   SSZ-74 containing titanium oxide (Ti-SSZ-74) is useful as a catalyst in

23   oxidation reactions, particularly in the oxidation of hydrocarbons. Examples of

24   such reactions include, but are not limited to, the epoxidation of olefins, the

25   oxidation of alkanes, and the oxidation of sulfur-containing, nitrogen-

26   containing or phosphorus-containing compounds.

27

28   The amount of Ti-SSZ-74 catalyst employed is not critical, but should

29   be sufficient so as to substantially accomplish the desired oxidation reaction in

30   a practicably short period of time (i.e., a catalytically effective amount). The

31   optimum quantity of catalyst will depend upon a number of factors including

32   reaction temperature, the reactivity and concentration of the substrate,

33   hydrogen peroxide concentration, type and concentration of organic solvent,

1   as well as the activity of the catalyst. Typically, however, the amount of

2   catalyst will be from about 0.001 to 10 grams per mole of substrate.

3

4   Typically, the Ti-SSZ-74 is thermally treated (calcined) prior to use as a

5   catalyst.

6

7   The oxidizing agent employed in the oxidation processes of this

8   invention is a hydrogen peroxide source such as hydrogen peroxide (H_2O_2) or

9   a hydrogen peroxide precursor (i.e., a compound which under the oxidation

10   reaction conditions is capable of generating or liberating hydrogen peroxide).

11

12   The amount of hydrogen peroxide relative to the amount of substrate is

13   not critical, but must be sufficient to cause oxidation of at least some of the

14   substrate. Typically, the molar ratio of hydrogen peroxide to substrate is from

15   about 100:1 to about 1:100, for example 10:1 to about 1:10. When the

16   substrate is an olefin containing more than one carbon-carbon double bond,

17   additional hydrogen peroxide may be required. Theoretically, one equivalent

18   of hydrogen peroxide is required to oxidize one equivalent of a mono-

19   unsaturated substrate, but it may be desirable to employ an excess of one

20   reactant to optimize selectivity to the epoxide. In particular, the use of a

21   moderate to large excess (e.g., 50 to 200%) of olefin relative to hydrogen

22   peroxide may be advantageous for certain substrates.

23

24   If desired, a solvent may additionally be present during the oxidation

25   reaction in order to dissolve the reactants other than the Ti-SSZ-74, to provide

26   better temperature control, or to favorably influence the oxidation rates and

27   selectivities. The solvent, if present, may comprise from 1 to 99 weight

28   percent of the total oxidation reaction mixture and is desirably selected such

29   that it is a liquid at the oxidation reaction temperature. Organic compounds

30   having boiling points at atmospheric pressure of from about 50°C to about

31   150°C are generally desirable for use. Excess hydrocarbon may serve as a

32   solvent or diluent. Illustrative examples of other suitable solvents include, but

33   are not limited to, ketones (e.g., acetone, methyl ethyl ketone, acetophenone),

1   ethers (e.g., tetrahydrofuran, butyl ether), nitriles (e.g., acetonitrile), aliphatic

2   and aromatic hydrocarbons, halogenated hydrocarbons, and alcohols (e.g.,

3   methanol, ethanol, isopropyl alcohol, t-butyl alcohol, alpha-methyl benzyl

4   alcohol, cyclohexanol). More than one type of solvent may be utilized. Water

5   may also be employed as a solvent or diluent.

6

7   The reaction temperature is not critical, but should be sufficient to

8   accomplish substantial conversion of the substrate within a reasonably short

9   period of time. It is generally advantageous to carry out the reaction to

10   achieve as high a hydrogen peroxide conversion as possible, typically at least

11   about 50%, for example at least about 90% or at least about 95%, consistent

12   with reasonable selectivities. The optimum reaction temperature will be

13   influenced by catalyst activity, substrate reactivity, reactant concentrations,

14   and type of solvent employed, among other factors, but typically will be in a .

15   range of from about 0°C to about 150°C (for example from about 25°C to

16   about 120°C). Reaction or residence times from about one minute to about 48

17   hours (for example from about ten minutes to about eight hours) will typically

18   be appropriate, depending upon the above-identified variables. Although

19   subatmospheric pressures can be employed, the reaction is typically

20   performed at atmospheric or at elevated pressure (typically, between one and

21   100 atmospheres), especially when the boiling point of the substrate is below

22   the oxidation reaction temperature. Generally, it is desirable to pressurize the

23   reaction vessel sufficiently to maintain the reaction components as a liquid

24   phase mixture. Most (over 50%) of the substrate should desirably be present

25   in the liquid phase.

26

27   The oxidation process of this invention may be carried out in a batch,

28   continuous, or semi-continuous manner using any appropriate type of reaction

29   vessel or apparatus such as a fixed bed, transport bed, fluidized bed, stirred

30   slurry, or CSTR reactor. The reactants may be combined all at once or

31   sequentially. For example, the hydrogen peroxide or hydrogen peroxide

32   precursor may be added incrementally to the reaction zone. The hydrogen

1   peroxide could also be generated in situ within the same reactor zone where

2   oxidation is taking place.

3

4   Once the oxidation has been carried out to the desired degree of

5   conversion, the oxidized product may be separated and recovered from the

6   reaction mixture using any appropriate technique such as fractional

7   distillation, extractive distillation, liquid-liquid extraction, crystallization, or the

8   like.

9

10   Olefin Epoxidation

11

12   One of the oxidation reactions for which Ti-SSZ-74 is useful as a

13   catalyst is the epoxidation of olefins. The olefin substrate epoxidized in the

14   process of this invention may be any organic compound having at least one

15   ethylenically unsaturated functional group (i.e., a carbon-carbon double bond)

16   and may be a cyclic, branched or straight-chain olefin. The olefin may contain

17   aryl groups (e.g., phenyl, naphthyl). Typically, the olefin is aliphatic in

18   character and contains from 2 to about 20 carbon atoms. The use of light

19   (low-boiling) C_2 to C_{10} mono-olefins is especially advantageous.

20

21   More than one carbon-carbon double bond may be present in the

22   olefin, i.e., dienes, trienes and other polyunsaturated substrates may be used.

23   The double bond may be in a terminal or internal position in the olefin or may

24   alternatively form part of a cyclic structure (as in cyclooctene, for example).

25

26   Other examples of suitable substrates include unsaturated fatty acids

27   or fatty acid derivatives such as esters.

28

29   The olefin may contain substituents other than hydrocarbon

30   substituents such as halide, carboxylic acid, ether, hydroxy, thiol, nitro, cyano,

31   ketone, acyl, ester, anhydride, amino; and the like.

32

1   Exemplary olefins suitable for use in the process of this invention

2   include ethylene, propylene, the butenes (i.e., 1,2-butene, 2,3-butene,

3   isobutylene), butadiene, the pentenes, isoprene, 1-hexene, 3-hexene, 1-

4   heptene, 1-octene, diisobutylene, 1-nonene, 1-tetradecene, pentamyrcene,

5   camphene, 1-undecene, 1-dodecene, 1-tridecene, 1-tetradecene, 1-

6   pentadecene, 1-hexadecene, 1-heptadecene, 1-octadecene, 1-nonadecene,

7   1-eicosene, the trimers and tetramers of propylene, cyclopentene,

8   cyclohexene, cycloheptene, cyclooctene, cyclooctadiene, dicyclopentadiene,

9   methylenecyclopropane, methylenecyclopentane, methylenecyclohexane,

10   vinyl cyclohexane, vinyl cyclohexene, methallyl ketone, allyl chloride, the

11   dichlorobutenes, allyl alcohol, allyl carbonate, allyl acetate, alkyl acrylates and

12   methacrylates, diallyl maleate, diallyl phthalate, and unsaturated fatty acids,

13   such as oleic acid, linolenic acid, linoleic acid, erucic acid, palmitoleic acid,

14   and ricinoleic acid and their esters (including mono-, di-, and triglyceride

15   esters) and the like.

16

17   Olefins which are especially useful for epoxidation are the C_2-C_{20}

18   olefins having the general structure

19

20                              $R^3R^4C=CR^5R^6$

21
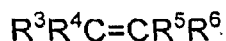
22   wherein R^3, R^4, R^5 and R^6 are the same or different and are selected from the

23   group consisting of hydrogen and C_1-C_{18} alkyl.

24

25   Mixtures of olefins may be epoxidized and the resulting mixtures of

26   epoxides either employed in the mixed form or separated into the different

27   component epoxides.

28

29   The present invention further provides a process for oxidation of

30   hydrocarbons comprising contacting said hydrocarbon with hydrogen peroxide

31   in the presence of a catalytically effective amount of Ti-SSZ-74 for a time and

32   at a temperature effective to oxidize said hydrocarbon.

33

1   Acylation

2

3   The molecular sieve of the present invention can be used in a catalyst for

4   acylating an aromatic substrate ArH_n, where n is at least 1, by reacting the

5   aromatic substrate with an acylating agent in the presence of the catalyst. The

6   product of the acylation reaction is $ArH_{n-1}COR$ where R is an organic radical.

7

8   Examples of the aromatic substrate include, but are not limited to,

9   benzene, toluene, anisole and 2-naphthol. Examples of the acylating agent

10 included, but are not limited to, carboxylic acid derivatives, carboxylic acids,

11 acid anhydrides, esters, and acyl halides.

12

13   Reaction conditions are known in the art (see, for example, U. S.

14 Patent No. 6,630,606, issued October 7, 2003 to Poliakoff et al., U. S. Patent

15 No. 6,459,000, issued October 1, 2002 to Choudhary et al., and U. S. Patent

16 No. 6,548,722, issued April 15, 2003 to Choudhary et al., all of which are

17 incorporated herein by reference in their entirety). Typically, the acylation

18 reaction is conducted with a weight ratio of the catalyst to the acylating agent

19 of about 0.03 to about 0.5, a mole ratio of aromatic substrate to acylating

20 agent of about 1.0 to about 20, a reaction temperature in the range of about

21 20°C to about 200°C, a reaction pressure in the range of about 1 atm to about

22 5 atm, and a reaction time of about 0.05 hours to about 20 hours.

23

24   Oxygenate Conversion

25

26   The present invention comprises a process for catalytic conversion of a

27 feedstock comprising one or more oxygenates comprising alcohols and ethers

28 to a hydrocarbon product containing light olefins, i.e., C_2, C_3 and/or C_4 olefins.

29 The feedstock is contacted with the molecular sieve of the present invention

30 at effective process conditions to produce light olefins.

31

1   The term "oxygenate" as used herein designates compounds such as

2   alcohols, ethers and mixtures thereof. Examples of oxygenates include, but

3   are not limited to, methanol and dimethyl ether.

4

5   The process of the present invention may be conducted in the

6   presence of one or more diluents which may be present in the oxygenate feed

7   in an amount between about 1 and about 99 molar percent, based on the total

8   number of moles of all feed and diluent components. Diluents include, but are

9   not limited to, helium, argon, nitrogen, carbon monoxide, carbon dioxide,

10 hydrogen, water, paraffins, hydrocarbons (such as methane and the like),

11 aromatic compounds, or mixtures thereof. U. S. Patents No. 4,861,938 and

12 4,677,242, which are incorporated by reference herein in their entirety,

13 emphasize the use of a diluent to maintain catalyst selectivity toward the

14 production of light olefins, particularly ethylene.

15

16   The oxygenate conversion is desirably conducted in the vapor phase

17 such that the oxygenate feedstock is contacted in a vapor phase in a reaction

18 zone with the molecular sieve of this invention at effective process conditions

19 to produce hydrocarbons, i.e., an effective temperature, pressure, weight

20 hourly space velocity (WHSV) and, optionally, an effective amount of diluent.

21 The process is conducted for a period of time sufficient to produce the desired

22 light olefins. In general, the residence time employed to produce the desired

23 product can vary from seconds to a number of hours. It will be readily

24 appreciated that the residence time will be determined to a significant extent

25 by the reaction temperature , the molecular sieve catalyst, the WHSV, the

26 phase (liquid or vapor) and process design characteristics. The oxygenate

27 feedstock flow rate affects olefin production. Increasing the feedstock flow

28 rate increases WHSV and enhances the formation of olefin production relative

29 to paraffin production. However, the enhanced olefin production relative to

30 paraffin production is offset by a diminished conversion of oxygenate to

31 hydrocarbons.

32

1   The oxygenate conversion process is effectively carried out over a

2   wide range of pressures, including autogenous pressures. At pressures

3   between about 0.01 atmospheres (0.1 kPa) and about 1000 atmospheres

4   (101.3 kPa), the formation of light olefins will be affected although the

5   optimum amount of product will not necessarily be formed at all pressures. A

6   typical pressure is between about 0.01 atmospheres (0.1 kPa) and about 100

7   atmospheres (10.13 kPa), for example from about 1 to about 10 atmospheres

8   (101.3 kPa to 1.013 Mpa). The pressures referred to herein are exclusive of

9   the diluent, if any, that is present and refer to the partial pressure of the

10   feedstock as it relates to oxygenate compounds.

11

12   The temperature which may be employed in the oxygenate conversion

13   process may vary over a wide range depending, at least in part, on the

14   molecular sieve catalyst. In general, the process can be conducted at an

15   effective temperature between about 200°C and about 700°C. At the lower

16   end of the temperature range, and thus generally at a lower rate of reaction,

17   the formation of the desired light olefins may become low. At the upper end of

18   the range, the process may not form an optimum amount of light olefins and

19   catalyst deactivation may be rapid.

20

21   The molecular sieve catalyst can be incorporated into solid particles in

22   which the catalyst is present in an amount effective to promote the desired

23   conversion of oxygenates to light olefins. In one aspect, the solid particles

24   comprise a catalytically effective amount of the catalyst and at least one

25   matrix material selected from the group consisting of binder materials, filler

26   materials and mixtures thereof to provide a desired property or properties,

27   e.g., desired catalyst dilution, mechanical strength and the like to the solid

28   particles. Such matrix materials are often, to some extent, porous in nature

29   and may or may not be effective to promote the desired reaction. Filler and

30   binder materials include, for example, synthetic and naturally occurring

31   substances such as metal oxides, clays, silicas, aluminas, silica-aluminas,

32   silica-magnesias, silica-zirconias, silica-thorias and the like. If matrix materials

33   are included in the catalyst composition, the molecular sieve desirably

1   comprises about 1 to 99%, for example about 5 to 90% or about 10 to 80%

2   by weight of the total composition.

3

4   Gas Separation

5

6   The molecular sieve of the present invention can be used to separate

7   gasses. For example, it can be used to separate carbon dioxide from natural

8   gas. Typically, the molecular sieve is used as a component in a membrane

9   that is used to separate the gasses. Examples of such membranes are

10 disclosed in U. S. Patent No. 6,508,860, issued January 21, 2003 to Kulkarni

11 et al., which is incorporated by reference herein in its entirety.

12

13   Synthesis of Amines

14

15   The molecular sieve of the present invention can be used in a catalyst

16 to prepare methylamine or dimethylamine. Dimethylamine is generally

17 prepared in industrial quantities by continuous reaction of methanol (and/or

18 dimethylether) and ammonia in the presence of a silica-alumina catalyst. The

19 reactants are typically combined in the vapor phase, at temperatures in the

20 range of 300°C to 500°C, and at elevated pressures. Such a process is

21 disclosed in U. S. Patent No. 4,737,592, issued April 12, 1988 to Abrams et

22 al., which is incorporated by reference in its entirety.

23

24   The catalyst is used in its acid form. Acid forms of molecular sieves can

25 be prepared by a variety of techniques. Desirably, the molecular sieve used to

26 prepare dimethylamine will be in the hydrogen form, or have an alkali or

27 alkaline earth metal, such as Na, K, Rb, or Cs, ion-exchanged into it.

28

29   The process of the present invention involves reacting methanol,

30 dimethylether or a mixture thereof and ammonia in amounts sufficient to

31 provide a carbon/nitrogen (C/N) ratio from about 0.2 to about 1.5, for example

32 about 0.5 to about 1.2. The reaction is conducted at a temperature from about

33 250°C to about 450°C, for example about 300°C to about 400°C. Reaction

1   pressures can vary from about 7-7000 kPa (1-1000 psi), for example about

2   70-3000 kPa (10-500 psi). A methanol and/or dimethylether space time of

3   about 0.01-80 hours, for example 0.10-1.5 hours, is typically used. This space

4   time is calculated as the mass of catalyst divided by the mass flow rate of

5   methanol/dimethylether introduced into the reactor.

6

7   Treatment of Engine Exhaust (Cold Start Emissions)

8

9   Gaseous waste products resulting from the combustion of

10   hydrocarbonaceous fuels, such as gasoline and fuel oils, comprise carbon

11   monoxide, hydrocarbons and nitrogen oxides as products of combustion or

12   incomplete combustion, and pose a serious health problem with respect to

13   pollution of the atmosphere. While exhaust gases from other carbonaceous

14   fuel-burning sources, such as stationary engines, industrial furnaces, etc.,

15   contribute substantially to air pollution, the exhaust gases from automotive

16   engines are a principal source of pollution. Because of these health problem

17   concerns, the Environmental Protection Agency (EPA) has promulgated strict

18   controls on the amounts of carbon monoxide, hydrocarbons and nitrogen

19   oxides which automobiles can emit. The implementation of these controls has

20   resulted in the use of catalytic converters to reduce the amount of pollutants

21   emitted from automobiles.

22

23   In order to achieve the simultaneous conversion of carbon monoxide,

24   hydrocarbon and nitrogen oxide pollutants, it has become the practice to

25   employ catalysts in conjunction with air-to-fuel ratio control means which

26   functions in response to a feedback signal from an oxygen sensor in the

27   engine exhaust system. Although these three component control catalysts

28   work quite well after they have reached operating temperature of about 300°

29   C., at lower temperatures they are not able to convert substantial amounts of

30   the pollutants. What this means is that when an engine and in particular an

31   automobile engine is started up, the three component control catalyst is not

32   able to convert the hydrocarbons and other pollutants to innocuous

33   compounds.

1

2   Adsorbent beds have been used to adsorb the hydrocarbons during the

3   cold start portion of the engine. Although the process typically will be used

4   with hydrocarbon fuels, the instant invention can also be used to treat exhaust

5   streams from alcohol fueled engines. The adsorbent bed is typically placed

6   immediately before the catalyst. Thus, the exhaust stream is first flowed

7   through the adsorbent bed and then through the catalyst. The adsorbent bed

8   preferentially adsorbs hydrocarbons over water under the conditions present

9   in the exhaust stream. After a certain amount of time, the adsorbent bed has

10 reached a temperature (typically about 150° C.) at which the bed is no longer

11 able to remove hydrocarbons from the exhaust stream. That is, hydrocarbons

12 are actually desorbed from the adsorbent bed instead of being adsorbed. This

13 regenerates the adsorbent bed so that it can adsorb hydrocarbons during a

14 subsequent cold start.

15

16   The prior art reveals several references dealing with the use of

17 adsorbent beds to minimize hydrocarbon emissions during a cold start engine

18 operation. One such reference is U.S. Pat. No. 3,699,683 in which an

19 adsorbent bed is placed after both a reducing catalyst and an oxidizing

20 catalyst. The patentees disclose that when the exhaust gas stream is below

21 200° C. the gas stream is flowed through the reducing catalyst then through

22 the oxidizing catalyst and finally through the adsorbent bed, thereby adsorbing

23 hydrocarbons on the adsorbent bed. When the temperature goes above 200°

24 C. the gas stream which is discharged from the oxidation catalyst is divided

25 into a major and minor portion, the major portion being discharged directly into

26 the atmosphere and the minor portion passing through the adsorbent bed

27 whereby unburned hydrocarbon is desorbed and then flowing the resulting

28 minor portion of this exhaust stream containing the desorbed unburned

29 hydrocarbons into the engine where they are burned.

30

31   Another reference is U.S. Pat. No. 2,942,932 which teaches a process

32 for oxidizing carbon monoxide and hydrocarbons which are contained in

33 exhaust gas streams. The process disclosed in this patent consists of flowing

1   an exhaust stream which is below 800° F. into an adsorption zone which

2   adsorbs the carbon monoxide and hydrocarbons and then passing the

3   resultant stream from this adsorption zone into an oxidation zone. When the

4   temperature of the exhaust gas stream reaches about 800° F. the exhaust

5   stream is no longer passed through the adsorption zone but is passed directly

6   to the oxidation zone with the addition of excess air.

7

8   U. S. Patent No. 5,078,979, issued January 7, 1992 to Dunne, which is

9   incorporated herein by reference in its entirety, discloses treating an exhaust

10   gas stream from an engine to prevent cold start emissions using a molecular

11   sieve adsorbent bed. Examples of the molecular sieve include faujasites,

12   clinoptilolites, mordenites, chabazite, silicalite, zeolite Y, ultrastable zeolite Y,

13   and ZSM-5.

14

15   Canadian Patent No. 1,205,980 discloses a method of reducing

16   exhaust emissions from an alcohol fueled automotive vehicle. This method

17   consists of directing the cool engine startup exhaust gas through a bed of

18   zeolite particles and then over an oxidation catalyst and then the gas is

19   discharged to the atmosphere. As the exhaust gas stream warms up it is

20   continuously passed over the adsorption bed and then over the oxidation bed.

21

22   As stated, this invention generally relates to a process for treating an

23   engine exhaust stream and in particular to a process for minimizing emissions

24   during the cold start operation of an engine. The engine consists of any

25   internal or external combustion engine which generates an exhaust gas

26   stream containing noxious components or pollutants including unburned or

27   thermally degraded hydrocarbons or similar organics. Other noxious

28   components usually present in the exhaust gas include nitrogen oxides and

29   carbon monoxide. The engine may be fueled by a hydrocarbonaceous fuel.

30   As used in this specification and in the appended claims, the term

31   "hydrocarbonaceous fuel" includes hydrocarbons, alcohols and mixtures

32   thereof. Examples of hydrocarbons which can be used to fuel the engine are

33   the mixtures of hydrocarbons which make up gasoline or diesel fuel. The

1   alcohols which may be used to fuel engines include ethanol and methanol.

2   Mixtures of alcohols and mixtures of alcohols and hydrocarbons can also be

3   used. The engine may be a jet engine, gas turbine, internal combustion

4   engine, such as an automobile, truck or bus engine, a diesel engine or the

5   like. The process of this invention is particularly suited for hydrocarbon,

6   alcohol, or hydrocarbon-alcohol mixture, internal combustion engine mounted

7   in an automobile. For convenience the description will use hydrocarbon as the

8   fuel to exemplify the invention. The use of hydrocarbon in the subsequent

9   description is not to be construed as limiting the invention to hydrocarbon

10 fueled engines.

11

12   When the engine is started up, it produces a relatively high

13 concentration of hydrocarbons in the engine exhaust gas stream as well as

14 other pollutants. Pollutants will be used herein to collectively refer to any

15 unburned fuel components and combustion byproducts found in the exhaust

16 stream. For example, when the fuel is a hydrocarbon fuel, hydrocarbons,

17 nitrogen oxides, carbon monoxide and other combustion byproducts will be

18 found in the engine exhaust gas stream. The temperature of this engine

19 exhaust stream is relatively cool, generally below 500° C. and typically in the

20 range of 200° to 400° C. This engine exhaust stream has the above

21 characteristics during the initial period of engine operation, typically for the

22 first 30 to 120 seconds after startup of a cold engine. The engine exhaust

23 stream will typically contain, by volume, about 500 to 1000 ppm

24 hydrocarbons.

25

26   The engine exhaust gas stream which is to be treated is flowed over a

27 molecular sieve bed comprising molecular sieve SSZ-74 a first exhaust

28 stream. Molecular sieve SSZ-74 is described herein. The first exhaust stream

29 which is discharged from the molecular sieve bed is now flowed over a

30 catalyst to convert the pollutants contained in the first exhaust stream to

31 innocuous components and provide a treated exhaust stream which is

32 discharged into the atmosphere. It is understood that prior to discharge into

1   the atmosphere, the treated exhaust stream may be flowed through a muffler

2   or other sound reduction apparatus well known in the art.

3

4   The catalyst which is used to convert the pollutants to innocuous

5   components is usually referred to in the art as a three-component control

6   catalyst because it can simultaneously oxidize any residual hydrocarbons

7   present in the first exhaust stream to carbon dioxide and water, oxidize any

8   residual carbon monoxide to carbon dioxide and reduce any residual nitric

9   oxide to nitrogen and oxygen. In some cases the catalyst may not be required

10   to convert nitric oxide to nitrogen and oxygen, e.g., when an alcohol is used

11   as the fuel. In this case the catalyst is called an oxidation catalyst. Because of

12   the relatively low temperature of the engine exhaust stream and the first

13   exhaust stream, this catalyst does not function at a very high efficiency,

14   thereby necessitating the molecular sieve bed.

15

16   When the molecular sieve bed reaches a sufficient temperature,

17   typically about 150-200° C., the pollutants which are adsorbed in the bed

18   begin to desorb and are carried by the first exhaust stream over the catalyst.

19   At this point the catalyst has reached its operating temperature and is

20   therefore capable of fully converting the pollutants to innocuous components.

21

22   The adsorbent bed used in the instant invention can be conveniently

23   employed in particulate form or the adsorbent can be deposited onto a solid

24   monolithic carrier. When particulate form is desired, the adsorbent can be

25   formed into shapes such as pills, pellets, granules, rings, spheres, etc. In the

26   employment of a monolithic form, it is usually most convenient to employ the

27   adsorbent as a thin film or coating deposited on an inert carrier material which

28   provides the structural support for the adsorbent. The inert carrier material

29   can be any refractory material such as ceramic or metallic materials. It is

30   desirable that the carrier material be unreactive with the adsorbent and not be

31   degraded by the gas to which it is exposed. Examples of suitable ceramic

32   materials include sillimanite, petalite, cordierite, mullite, zircon, zircon mullite,

33   spondumene, alumina-titanate, etc. Additionally, metallic materials which are

-62-

1   within the scope of this invention include metals and alloys as disclosed in

2   U.S. Pat. No. 3,920,583 which are oxidation resistant and are otherwise

3   capable of withstanding high temperatures.

4

5   The carrier material can best be utilized in any rigid unitary

6   configuration which provides a plurality of pores or channels extending in the

7   direction of gas flow. The configuration may be a honeycomb configuration.

8   The honeycomb structure can be used advantageously in either unitary form,

9   or as an arrangement of multiple modules. The honeycomb structure is

10   usually oriented such that gas flow is generally in the same direction as the

11   cells or channels of the honeycomb structure. For a more detailed discussion

12   of monolithic structures, refer to U.S. Pat. Nos. 3,785,998 and 3,767,453.

13

14   The molecular sieve is deposited onto the carrier by any convenient

15   way well known in the art. A desirable method involves preparing a slurry

16   using the molecular sieve and coating the monolithic honeycomb carrier with

17   the slurry. The slurry can be prepared by means known in the art such as

18   combining the appropriate amount of the molecular sieve and a binder with

19   water. This mixture is then blended by using means such as sonification,

20   milling, etc. This slurry is used to coat a monolithic honeycomb by dipping the

21   honeycomb into the slurry, removing the excess slurry by draining or blowing

22   out the channels, and heating to about 100° C. If the desired loading of

23   molecular sieve is not achieved, the above process may be repeated as many

24   times as required to achieve the desired loading.

25

26   Instead of depositing the molecular sieve onto a monolithic honeycomb

27   structure, one can take the molecular sieve and form it into a monolithic

28   honeycomb structure by means known in the art.

29

30   The adsorbent may optionally contain one or more catalytic metals

31   dispersed thereon. The metals which can be dispersed on the adsorbent are

32   the noble metals which consist of platinum, palladium, rhodium, ruthenium,

33   and mixtures thereof. The desired noble metal may be deposited onto the

1 adsorbent, which acts as a support, in any suitable manner well known in the

2 art. One example of a method of dispersing the noble metal onto the

3 adsorbent support involves impregnating the adsorbent support with an

4 aqueous solution of a decomposable compound of the desired noble metal or

5 metals, drying the adsorbent which has the noble metal compound dispersed

6 on it and then calcining in air at a temperature of about 400° to about 500° C.

7 for a time of about 1 to about 4 hours. By decomposable compound is meant

8 a compound which upon heating in air gives the metal or metal oxide.

9 Examples of the decomposable compounds which can be used are set forth

10 in U.S. Pat. No. 4,791,091 which is incorporated by reference. Examples of

11 decomposable compounds are chloroplatinic acid, rhodium trichloride,

12 chloropalladic acid, hexachloroiridate (IV) acid and hexachlororuthenate. It is

13 typical that the noble metal be present in an amount ranging from about 0.01

14 to about 4 weight percent of the adsorbent support. Specifically, in the case of

15 platinum and palladium the range is 0.1 to 4 weight percent, while in the case

16 of rhodium and ruthenium the range is from about 0.01 to 2 weight percent.

17

18   These catalytic metals are capable of oxidizing the hydrocarbon and

19 carbon monoxide and reducing the nitric oxide components to innocuous

20 products. Accordingly, the adsorbent bed can act both as an adsorbent and

21 as a catalyst.

22

23   The catalyst which is used in this invention is selected from any three

24 component control or oxidation catalyst well known in the art. Examples of

25 catalysts are those described in U.S. Pat. Nos. 4,528,279; 4,791,091;

26 4,760,044; 4,868,148; and 4,868,149, which are all incorporated by reference.

27 Desirable catalysts well known in the art are those that contain platinum and

28 rhodium and optionally palladium, while oxidation catalysts usually do not

29 contain rhodium. Oxidation catalysts usually contain platinum and/or

30 palladium metal. These catalysts may also contain promoters and stabilizers

31 such as barium, cerium, lanthanum, nickel, and iron. The noble metals

32 promoters and stabilizers are usually deposited on a support such as alumina,

33 silica, titania, zirconia, alumino silicates, and mixtures thereof with alumina

1   being desirable. The catalyst can be conveniently employed in particulate

2   form or the catalytic composite can be deposited on a solid monolithic carrier

3   with a monolithic carrier being desirable. The particulate form and monolithic

4   form of the catalyst are prepared as described for the adsorbent above.

5

6   The molecular sieve used in the adsorbent bed is SSZ-74.

7

8   Beckmann Rearrangement

9

10   The present invention relates to a process for the preparation of

11   amides from oximes. The present invention further relates to the use of SSZ-

12   74 in the catalytic transformation of oximes, such as cyclohexanone oxime, to

13   amides, such as epsilon-caprolactam (caprolactam), also known as

14   Beckmann catalytic rearrangement. The Beckmann rearrangement is shown

15   below (where sulfuric acid is used instead of a molecular sieve catalyst).

16

17
18
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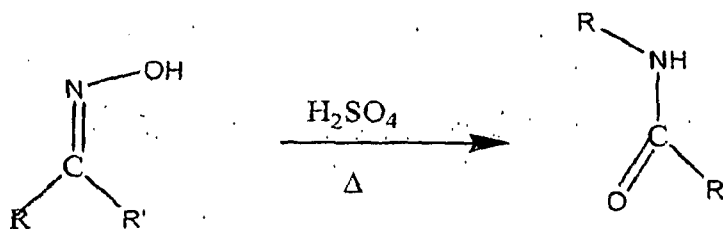
20   Amides, and in particular caprolactam, are known in literature as

21   important intermediates for chemical syntheses and as raw materials for the

22   preparation of polyamide resins.

23

24   Caprolactam is produced industrially by cyclohexanone oxime

25   rearrangement in liquid phase using sulfuric acid or oleum. The rearranged

26   product is neutralized with ammonia causing the joint formation of ammonium

27   sulfate. This technology has numerous problems linked to the use of sulfuric

28   acid, to the formation of high quantities of ammonium sulfate, with relative

29   problems of disposal, corrosion of the equipment owing to the presence of

30   acid vapors, etc.

1

2   Alternative processes have been proposed in the literature for the

3   catalytic rearrangement of cyclohexanone oxime into caprolactam, in which

4   solids of an acid nature are used, as catalysts, selected from derivatives of

5   boric acid, zeolites, non-zeolitic molecular sieves, solid phosphoric acid,

6   mixed metal oxides, etc.

7

8   In particular, European patent 234.088 describes a method for

9   preparing caprolactam which comprises putting cyclohexanone oxime in

10   gaseous state in contact with alumino-silicates of the zeolitic type such as

11   ZSM-5, ZSM-11 or ZSM-23 having a "Constraint Index" of between 1 and 12,

12   an atomic ratio Si/Al of at least 500 (SiO_2/Al_2O_3 mole ratio of at least 1,000)

13   and an external acid functionality of less than 5 micro equivalents/g.

14

15   Zeolites, as described in "Zeolite Molecular Sieves" D. W. Breck, John

16   Wiley & Sons, (1974) or in "Nature" 381 (1996), 295, are crystalline products

17   characterized by the presence of a regular microporosity, with channels

18   having dimensions of between 3 and 10 Angstroms. In some particular zeolitic

19   structures there can be cavities with greater dimensions, of up to about 13

20   Angstroms.

21

22   With the aim of providing another method for the preparation of

23   amides, and in particular of caprolactam, a new process has now been found

24   which uses a catalyst comprising SSZ-74. The present invention therefore

25   relates to a process for the preparation of amides via the catalytic

26   rearrangement of oximes which comprises putting an oxime in vapor phase in

27   contact with a catalyst comprising a crystalline molecular sieve having a mole

28   ratio greater than about 15 of (1) an oxide of a first tetravalent element to (2)

29   an oxide of a trivalent element, pentavalent element, second tetravalent

30   element which is different from said first tetravalent element or mixture thereof

31   and having, after calcination, the X-ray diffraction lines of Table II. The

32   molecular sieve may have a mole ratio greater than about 15 of (1) silicon

1   oxide to (2) an oxide selected from aluminum oxide, gallium oxide, iron oxide,

2   boron oxide, titanium oxide, indium oxide and mixtures thereof.

3

4   Other methods for converting oximes to amides via Beckmann

5   rearrangement are disclosed in U.S. Patent No. $,883,915,issued November

6   28, 1989 to McMahon, which uses a crystalline borosilicate molecular sieve in

7   the catalyst and U.S. Patent No. 5,942,613, issued August 24, 1999 to Carati

8   et al., which uses a mesoporous silica-alumina in the catalyst. Both patents

9   are incorporated by reference herein in their entirety.

10

11   According to the present invention a desirable amide is epsilon-

12   caprolactam (caprolactam) and the desirable oxime is cyclohexanone oxime

13   (CEOX). In particular, the catalytic rearrangement of the cyclohexanone

14   oxime takes place at a pressure of between 0.05 and 10 bars and at a

15   temperature of between 250°C and 500°C., for example between 300°C and

16   450°C. More specifically, the cyclohexanone oxime, in vapor phase, is fed to

17   the reactor containing the catalyst in the presence of a solvent and optionally

18   an incondensable gas. The cyclohexanone oxime is dissolved in the solvent

19   and the mixture thus obtained is then vaporized and fed to the reactor. The

20   solvent should be essentially inert to the oxime and the amide, as well as the

21   catalyst. Useful solvents include, but are not limited to, lower boiling

22   hydrocarbons, alcohols and ethers.

23

24   Desirable solvents are of the type $R^1 - O - R^2$ wherein R^1 is a $C_1 - C_4$ alkyl

25   chain and R^2 can be a hydrogen atom or an alkyl chain containing a number

26   of carbon atoms less than or equal to R^1. These solvents can be used alone

27   or mixed with each other or combined with an aromatic hydrocarbon such as

28   benzene or toluene. Alcohols with a $C_1 - C_2$ alkyl chain are particularly

29   desirable.

30

31   The cyclohexanone oxime is fed to the rearrangement reactor with a weight

32   ratio with respect to the catalyst which is such as to give a WHSV (Weight

1   Hourly Space Velocity), expressed as Kg of cyclohexanone oxime/kg of

2   catalyst/time, of between 0.1 and 50 hr.$^{-1}$, for example between 0.5 and 20

3   hr.$^{-1}$.

4

5   The deterioration of the catalyst is due to the formation of organic residues

6   which obstruct the pores of the catalyst and poison its active sites. The

7   deterioration process is slow and depends on the operating conditions and in

8   particular the space velocity, solvent, temperature, composition of the feeding.

9   The catalytic activity however can be efficiently reintegrated by the

10 combustion of the residues, by treatment in a stream of air and nitrogen at a

11 temperature of between 450°C and 600°C.

12

13   EXAMPLES

14

15   The following examples demonstrate but do not limit the present

16 invention.

17

18   Example 1

19 Synthesis of Hexamethylene-1,6-bis-(N-methyl-N-pyrrolidinium) dication SDA

20

21   In 50 ml of acetone was dissolved 5ml (48 mmoles) of N-methyl

22 pyrrolidine. 4.9 Grams of 1,6 dibromohexane (20 mmoles) were added and

23 the resulting mixture was stirred at room temperature for three days. Solids

24 formed and were collected by filtration and washed with ether and kept in a

25 vacuum oven. Then 3.71 grams of the dried solid was mixed into 18.7 grams

26 of water and 9.57 grams of AG1-X8 resin for exchange to the OH form. The

27 exchange was run overnight and then the solution was collected and titrated.

28

29   Example 2

30   Synthesis of All-Silica SSZ-74

31

32   6.4 Grams of the solution from Example 1 (3 mmoles) was mixed in a

33 tared Teflon cup with 1.26 grams of tetraethyl orthosilicate and then allowed

1   to evaporate (in a hood) for several days as hydrolysis occurred. A second

2   reaction was set up the same way. After evaporation to the appearance of

3   dryness, one reaction was given 0.20 gram of water and mixed. The second

4   was given 0.60 gram of water and the same treatment ensued. 0.125 Gram of

5   about 50% HF was carefully added to each reaction mixture and the contents

6   were stirred with a plastic spatula and a thick gel formed. In the first case the

7   H2O/SiO2 ratio was now roughly 3.5 and it was 7.0 in the second case. The

8   materials were heated to 150° C and at 43 RPM in tumbled Parr reactors

9   placed in a Blue M convection heating oven. The reactions were cooled and

10   opened in 6 day periods with a small amount examined by Scanning Electron

11   Microscopy to determine if crystals had formed. After 22 days there was

12   crystalline material in both and the solids were collected (filtration) and

13   washed with copious amounts of water, air dried and then examined by X-ray

14   diffraction (XRD). The product in both cases was SSZ-74.

15

16   Example 3

17   Calcination of SSZ-74

18

19   The products from both reactions in Example 2 were calcined in stages

20   and in air to 595° C to remove the organic content. The materials were found

21   to be stable and the XRD patterns showed the relationship to the as-made

22   SSZ-74.

23

24   Example 4

25   Adsorption of 2,2-Dimethylbutane

26

27   The calcined material of Example 3 was then tested for the uptake of

28   the hydrocarbon 2,2-dimethylbutane. This adsorbate does not enter small

29   pore zeolites (8-ring portals) and sometimes is hindered in entering

30   intermediate pore zeolites like ZSM-5. The SSZ-74 showed a profile more

31   characteristic of intermediate pore materials (as contrasted to Y zeolite, a

32   large pore material), showing steady gradual uptake of the adsorbate.

33

1   SSZ-74 was shown to adsorb about 0.08 cc/gram after 3 hours of

2   exposure to the 2,2 dimethyl butane adsorbate using a pulsed mode. This

3   value compares with an analysis for ZSM-5 zeolite which gives a value closer

4   to 0.07cc/gm at the same point in time under the same experimental

5   conditions. This would indicate that the pores of SSZ-74 are at least 10-rings

6

7   Example 5

8   Synthesis of Aluminosilicate SSZ-74

9

10   The synthesis parameters of Example 2 were repeated except for the

11   following changes. (1) 0.04 gram of Y zeolite material LZ-210 was added as a

12   potential contributor of Al; (2) the initial H_2O/SiO_2 ratio for the synthesis was

13   adjusted to 5; (3) seeds of a successful SSZ-74 product were added; and (4)

14   the reaction was run at 170° C. After 9 days there was crystalline material

15   which was SSZ-74 when worked up and analyzed by XRD. The solids were

16   calcined then as in Example 3.

17

18   Example 6

19   Constraint Index

20

21   0.12 grams of the material from Example 5, in a 20-40 pelleted and

22   meshed range, was loaded into a stainless steel reactor and run in a

23   Constraint Index test (50/50 n-hexane/3-methylpentane). The normal feed

24   rate was used (8 µl/min.) and the test was run at 700° F after the catalyst had

25   been dried in the reactor to near 1000° F. Helium flow was used. At 10

26   minutes on-stream nearly 30% of the feed was being converted with about

27   equal amounts of each reactant. The selectivity did not change as the catalyst

28   fouled to half the conversion at 100 minutes. The pores of the active SSZ-74

29   were at least intermediate in size.

30

1   Example 7

2   Synthesis of Aluminosilicate SSZ-74

3

4   . . Three mMoles of SDA solution and 1.26 grams (6 mMoles) of

5   tetraethylorthosilicate were combined in a Teflon cup for a Parr reactor. The

6   contents were allowed to react and then most of the water and then the

7   ethanol by-product were allowed to evaporate in a hood over several days.

8   Once the H2O/SiO2 ratio was about 5, from the evaporation, 0.04 grams of

9   LZ-210 zeolite were added (LZ-210 is a Y zeolite which has been treated with

10     $(NH_4^+)_2SiF_6$ to provide some de-alumination). A few mg of seeds of SSZ-74

11   were added in the as-made state. Lastly, 0.132 gram of 50% HF was added

12   and the reactor was closed up and heated at 170°C, 43 RPM, for six days. A

13   sample of the cooled reaction product showed nicely crystalline material in an

14   electron microscope. The reaction contents were worked up and dried.

15   Analysis by X-ray diffraction showed the product to be molecular sieve SSZ-

16   74.

17   The sample was calcined (in air to 595°C) and then pelleted and

18   meshed (20-40) and run in a standard Constraint Index test. At 700°F the

19   initial conversion was 28% with a CI value of 1.1. With time-on-stream the

20   catalyst showed a steady deactivation while the CI value did not change

21   much.

1   WHAT IS CLAIMED IS:

2

3   1.   A crystalline molecular sieve having a mole ratio greater than about 15 of

4   (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

5   element, pentavalent element, second tetravalent element which is

6   different from said first tetravalent element or mixture thereof and having,

7   after calcination, the X-ray diffraction lines of Table II.

8

9   2.   The molecular sieve of claim 1 wherein the molecular sieve has a mole

10   ratio greater than about 15 of (1) silicon oxide to (2) an oxide selected

11   from aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium

12   oxide, indium oxide and mixtures thereof.

13

14 3.   A crystalline molecular sieve having a composition comprising, as

15   synthesized and in the anhydrous state, in terms of mole ratios, the

16   following:

17   SiO_2 / X_cO_d greater than 100

18                              $M_{2/n} / SiO_2$ 0 − 0.03

19   Q / SiO_2 0.30 − 0.70

20   F / SiO_2 0.30 − 0.70

21

22   wherein X is aluminum, gallium, iron, boron, titanium, indium and

23   mixtures thereof, c is 1 or 2; d is 2 when c is 1, or d is 3 or 5 when c is 2,

24   M is an alkali metal cation, alkaline earth metal cation or mixtures

25   thereof; n is the valence of M; Q is a hexamethylene-1,6-bis-(N-methyl-

26   N-pyrrolidinium) dication and F is fluoride.

27

28 4.   A method of preparing a crystalline material; said method comprising

29   contacting under crystallization conditions (1) a source of silicon oxide,

30   (2) a source of aluminum oxide, gallium oxide, iron oxide, boron oxide,

31   titanium oxide, indium oxide and mixtures thereof, (3) fluoride ions and

32   (4) a structure directing agent comprising a hexamethylene-1,6-bis-(N-

33   methyl-N-pyrrolidinium) dication.

1

2   5.   The method of claim 4 wherein the crystalline material is prepared from a

3   reaction mixture comprising silicon oxide and, in terms of mole ratios, the

4   following:

5   SiO_2 / X_aO_b 100 and greater

6   OH^- / SiO_2 0.20 – 0.80

7   Q / SiO_2 0.20 – 0.80

8          $M_{2/n} / SiO_2$ 0 – 0.04

9   H_2O / SiO_2 2 – 10

10   HF / SiO_2 0.20 – 0.80

11

12   wherein X is aluminum, gallium, iron, boron, titanium, indium and

13   mixtures thereof, a is 1 or 2, b is 2 when a is 1, b is 3 when a is 2, M is

14   an alkali metal cation, alkaline earth metal cation or mixtures thereof; n is

15   the valence of M and Q is a hexamethylene-1,6-bis-(N-methyl-N-

16   pyrrolidinium) dication.

17

18   6.   The method of claim 5 wherein the reaction mixture comprises

19

20   SiO_2 / X_aO_b 100 and greater

21   OH^- / SiO_2 0.40 – 0.60

22   Q / SiO_2 0.40 – 0.60

23          $M_{2/n} / SiO_2$ 0 – 0.025

24   H_2O / SiO_2 3 - 7

25   HF / SiO_2 0.30 – 0.60.

26

27   7.   A process for converting hydrocarbons comprising contacting a

28   hydrocarbonaceous feed at hydrocarbon converting conditions with a

29   catalyst comprising a crystalline molecular sieve having a mole ratio

30   greater than about 15 of (1) an oxide of a first tetravalent element to (2)

31   an oxide of a trivalent element, pentavalent element, second tetravalent

32   element which is different from said first tetravalent element or mixture

1   thereof and having, after calcination, the X-ray diffraction lines of

2   Table II.

3

4   8.   The process of Claim 1 wherein the molecular sieve has a mole ratio

5   greater than about 15 of (1) silicon oxide to (2) an oxide selected from

6   aluminum oxide, gallium oxide, iron oxide, boron oxide, titanium oxide,

7   indium oxide and mixtures thereof.

8

9   9.   The process of Claim 8 wherein the molecular sieve is substantially free

10   of acidity.

11

12   10.   The process of Claim 8 wherein the process is a hydrocracking process

13   comprising contacting the catalyst with a hydrocarbon feedstock under

14   hydrocracking conditions.

15

16   11.   The process of Claim 8 wherein the process is a dewaxing process

17   comprising contacting the catalyst with a hydrocarbon feedstock under

18   dewaxing conditions.

19

20   12.   The process of Claim 8 wherein the process is a process for improving

21   the viscosity index of a dewaxed product of waxy hydrocarbon feeds

22   comprising contacting the catalyst with a waxy hydrocarbon feed under

23   isomerization dewaxing conditions.

24

25   13.   The process of Claim 8 wherein the process is a process for producing a

26   C_{20+} lube oil from a C_{20+} olefin feed comprising isomerizing said olefin

27   feed under isomerization conditions over the catalyst.

28

29   14.   The process of Claim 13 wherein the catalyst further comprises at least

30   one Group VIII metal.

31

32   15.   The process of Claim 8 wherein the process is a process for catalytically

33   dewaxing a hydrocarbon oil feedstock boiling above about 350°F (177°C)

1   and containing straight chain and slightly branched chain hydrocarbons

2   comprising contacting said hydrocarbon oil feedstock in the presence of

3   added hydrogen gas at a hydrogen pressure of about 15-3000 psi

4   (0.103-20.7 MPa) under dewaxing conditions with the catalyst.

5

6   16.   The process of Claim 15 wherein the catalyst further comprises at least

7   one Group VIII metal.

8

9   17.   The process of Claim 15 wherein said catalyst comprises a layered

10   catalyst comprising a first layer comprising the molecular sieve and at

11   least one Group VIII metal, and a second layer comprising an

12   aluminosilicate zeolite which is more shape selective than the molecular

13   sieve of said first layer.

14

15   18.   The process of Claim 8 wherein the process is a process for preparing a

16   lubricating oil which comprises:

17

18   hydrocracking in a hydrocracking zone a hydrocarbonaceous feedstock

19   to obtain an effluent comprising a hydrocracked oil; and

20

21   catalytically dewaxing said effluent comprising hydrocracked oil at a

22   temperature of at least about 400°F (204°C) and at a pressure of from

23   about 15 psig to about 3000 psig (0.103 to 20.7 MPa gauge) in the

24   presence of added hydrogen gas with the catalyst.

25

26   19.   The process of Claim 18 wherein the catalyst further comprises at least

27   one Group VIII metal.

28

29   20.   The process of Claim 8 wherein the process is a process for

30   isomerization dewaxing a raffinate comprising contacting said raffinate in

31   the presence of added hydrogen under isomerization dewaxing

32   conditions with the catalyst.

33

1   21.   The process of Claim 20 wherein the catalyst further comprises at least
2   one Group VIII metal.
3
4   22.   The process of Claim 20 wherein the raffinate is bright stock.
5
6   23.   The process of Claim 8 wherein the process is a process for increasing
7   the octane of a hydrocarbon feedstock to produce a product having an
8   increased aromatics content comprising contacting a hydrocarbonaceous
9   feedstock which comprises normal and slightly branched hydrocarbons
10   having a boiling range above about 40°C and less than about 200°C
11   under aromatic conversion conditions with the catalyst.
12
13   24.   The process of Claim 23 wherein the molecular sieve is substantially free
14   of acidity.
15
16   25.   The process of Claim 23 wherein the molecular sieve contains a
17   Group VIII metal component.
18
19   26.   The process of Claim 8 wherein the process is a catalytic cracking
20   process comprising contacting a hydrocarbon feedstock in a reaction
21   zone under catalytic cracking conditions in the absence of added
22   hydrogen with the catalyst.
23
24   27.   The process of Claim 26 wherein the catalyst additionally comprises a
25   large pore crystalline cracking component.
26
27   28.   The process of Claim 8 wherein the process is an isomerization process
28   for isomerizing C_4 to C_7 hydrocarbons, comprising contacting a feed
29   having normal and slightly branched C_4 to C_7 hydrocarbons under
30   isomerizing conditions with the catalyst.
31
32   29.   The process of Claim 28 wherein the molecular sieve has been
33   impregnated with at least one Group VIII metal.

30. The process of Claim 28 wherein the catalyst has been calcined in a steam/air mixture at an elevated temperature after impregnation of the Group VIII metal.

31. The process of Claim 29 wherein the Group VIII metal is platinum.

32. The process of Claim 8 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.

33. The process of Claim 32 wherein the olefin is a C_2 to C_4 olefin.

34. The process of Claim 33 wherein the aromatic hydrocarbon and olefin are present in a molar ratio of about 4:1 to about 20:1, respectively.

35. The process of Claim 33 wherein the aromatic hydrocarbon is selected from the group consisting of benzene, toluene, ethylbenzene, xylene, naphthalene, naphthalene derivatives, dimethylnaphthalene or mixtures thereof.

36. The process of Claim 8 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.

37. The process of Claim 7, 10, 11, 12, 13, 15, 18, 20, 26, 28, 32 or 36 wherein the molecular sieve is predominantly in the hydrogen form.

1   38. The process of Claim 36 wherein the aromatic hydrocarbon and the

2   polyalkyl aromatic hydrocarbon are present in a molar ratio of from about

3   1:1 to about 25:1, respectively.

4

5   39. The process of Claim 36 wherein the aromatic hydrocarbon is selected

6   from the group consisting of benzene, toluene, ethylbenzene, xylene, or

7   mixtures thereof.

8

9   40. The process of Claim 36 wherein the polyalkyl aromatic hydrocarbon is a

10   dialkylbenzene.

11

12 41. The process of Claim 8 wherein the process is a process to convert

13   paraffins to aromatics which comprises contacting paraffins under

14   conditions which cause paraffins to convert to aromatics with a catalyst

15   comprising the molecular sieve and gallium, zinc, or a compound of

16   gallium or zinc.

17

18 42. The process of Claim 8 wherein the process is a process for isomerizing

19   olefins comprising contacting said olefin under conditions which cause

20   isomerization of the olefin with the catalyst.

21

22 43. The process of Claim 8 wherein the process is a process for isomerizing

23   an isomerization feed comprising an aromatic C_8 stream of xylene

24   isomers or mixtures of xylene isomers and ethylbenzene, wherein a

25   more nearly equilibrium ratio of ortho-, meta and para-xylenes is

26   obtained, said process comprising contacting said feed under

27   isomerization conditions with the catalyst.

28

29 44. The process of Claim 8 wherein the process is a process for

30   oligomerizing olefins comprising contacting an olefin feed under

31   oligomerization conditions with the catalyst.

32

1   45. The process of Claim 8 wherein the process is a process for the

2   production of higher molecular weight hydrocarbons from lower

3   molecular weight hydrocarbons comprising the steps of:

4

5   (a) introducing into a reaction zone a lower molecular weight

6   hydrocarbon-containing gas and contacting said gas in said zone under

7   C_{2+} hydrocarbon synthesis conditions with the catalyst and a metal or

8   metal compound capable of converting the lower molecular weight

9   hydrocarbon to a higher molecular weight hydrocarbon; and

10

11   (b) withdrawing from said reaction zone a higher molecular weight

12   hydrocarbon-containing stream.

13

14   46. The process of Claim 45 wherein the metal or metal compound

15   comprises a lanthanide or actinide metal or metal compound.

16

17   47. The process of Claim 45 wherein the lower molecular weight

18   hydrocarbon is methane.

19

20   48. A catalyst composition for promoting polymerization of 1-olefins; said

21   composition comprising

22

23   (A) a crystalline molecular sieve having a mole ratio greater than about

24   15 of (1) an oxide of a first tetravalent element to (2) an oxide of a

25   trivalent element, pentavalent element, second tetravalent element which

26   is different from said first tetravalent element or mixture thereof and

27   having, after calcination, the X-ray diffraction lines of Table II; and

28

29   (B) an organotitanium or organochromium compound.

30

31   49. The process of Claim 8 wherein the process is a process for

32   polymerizing 1-olefins, which process comprises contacting 1-olefin

1   monomer with a catalytically effective amount of a catalyst composition

2   comprising

3

4   (A)   a crystalline molecular sieve having a mole ratio greater than

5   about 15 of (1) an oxide of a first tetravalent element to (2) an

6   oxide of a trivalent element, pentavalent element, second

7   tetravalent element which is different from said first tetravalent

8   element or mixture thereof and having, after calcination, the

9   X-ray diffraction lines of Table II; and

10

11   (B)   an organotitanium or organochromium compound.

12   under polymerization conditions which include a temperature

13   and pressure suitable for initiating and promoting the

14   polymerization reaction.

15

16   50. The process of Claim 49 wherein the 1-olefin monomer is ethylene.

17

18   51. The process of Claim 8 wherein the process is a process for

19   hydrogenating a hydrocarbon feed containing unsaturated hydrocarbons,

20   the process comprising contacting the feed with hydrogen under

21   conditions which cause hydrogenation with the catalyst.

22

23   52. The process of Claim 51 wherein the catalyst contains metals, salts or

24   complexes wherein the metal is selected from the group consisting of

25   platinum, palladium, rhodium, iridium or combinations thereof, or the

26   group consisting of nickel, molybdenum, cobalt, tungsten, titanium,

27   chromium, vanadium, rhenium, manganese and combinations thereof.

28

29   53. A process for converting oxygenated hydrocarbons comprising

30   contacting said oxygenated hydrocarbon under conditions to produce

31   liquid products with a catalyst comprising a molecular sieve having a

32   mole ratio greater than about 15 of an oxide of a first tetravalent element

33   to an oxide of a second tetravalent element which is different from said

-80-

first tetravalent element, trivalent element, pentavalent element or

mixture thereof and having, after calcination, the X-ray diffraction lines of

Table II.

54. The process of Claim 53 wherein the oxygenated hydrocarbon is a lower

alcohol.

55. The process of Claim 54 wherein the lower alcohol is methanol.

56. A process for hydrotreating a hydrocarbon feedstock comprising

contacting the feedstock with a hydrotreating catalyst and hydrogen

under hydrotreating conditions, wherein the catalyst comprises a

crystalline molecular sieve having a mole ratio greater than about 15 of

(1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

element, pentavalent element, second tetravalent element which is

different from said first tetravalent element or mixture thereof and having,

after calcination, the X-ray diffraction lines of Table II.

57. The process of Claim 56 wherein the catalyst contains a Group VIII metal

or compound, a Group VI metal or compound or combinations thereof.

58. 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 a mole ratio greater than about 15 of

(1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

element, pentavalent element, second tetravalent element which is

different from said first tetravalent element or mixture thereof and having,

after calcination, the X-ray diffraction lines of Table II.

59. The process of Claim 58 conducted in the presence of oxygen.

1   60. The process of Claim 58 wherein said molecular sieve contains a metal

2   or metal ions capable of catalyzing the reduction of the oxides of

3   nitrogen.

4

5   61. The process of Claim 60 wherein the metal is cobalt, copper, platinum,

6   iron, chromium, manganese, nickel, zinc, lanthanum, palladium, rhodium

7   or mixtures thereof.

8

9   62. The process of Claim 58 wherein the gas stream is the exhaust stream

10   of an internal combustion engine.

11

12   63. The process of Claim 61 wherein the gas stream is the exhaust stream

13   of an internal combustion engine.

14

15   64. A process for oxidation of hydrocarbons comprising contacting said

16   hydrocarbon with an oxidizing agent in the presence of a catalytically

17   effective amount of a titanium-containing molecular sieve for a time and

18   at a temperature effective to oxidize said hydrocarbon, wherein the

19   titanium-containing molecular sieve is a molecular sieve having a mole

20   ratio greater than about 15 of (1) silicon oxide to (2) titanium oxide and

21   having, after calcination, the X-ray diffraction lines of Table II.

22

23   65. A process for epoxidation of an olefin comprising contacting said olefin

24   with hydrogen peroxide in the presence of a catalytically effective

25   amount of a titanium-containing molecular sieve for a time and at a

26   temperature effective to epoxidize said olefin, wherein the titanium-

27   containing molecular sieve is a molecular sieve having a mole ratio

28   greater than about 15 of (1) silicon oxide to (2) titanium oxide and

29   having, after calcination, the X-ray diffraction lines of Table II.

30

31   66. A process for oxidizing cyclohexane comprising contacting said

32   cyclohexane with hydrogen peroxide in the presence of a catalytically

33   effective amount of a titanium-containing molecular sieve for a time and

1   at a temperature effective to oxidize said cyclohexane, wherein the

2   titanium-containing molecular sieve is a molecular sieve having a mole

3   ratio greater than about 15 of (1) silicon oxide to (2) titanium oxide and

4   having, after calcination, the X-ray diffraction lines of Table II.

5

6   67.   A catalytic oxidation process comprising contacting under oxidation

7   conditions (1) a reactant which is catalytically oxidizable in the presence

8   of hydrogen peroxide, (2) aqueous hydrogen peroxide and (3) a

9   catalytically effective amount of an oxidation catalyst comprising a

10   molecular sieve having a mole ratio greater than about 15 of (1) silicon

11   oxide to (2) titanium oxide and having, after calcination, the X-ray

12   diffraction lines of Table II.

13

14 68.   The process of Claim 67 wherein the oxidizable reactant is a

15   hydrocarbon.

16

17 69.   A process for the epoxidation of an olefin comprising contacting said

18   olefin with hydrogen peroxide in the presence of a catalytically effective

19   amount of a catalyst comprising a molecular sieve having a mole ratio

20   greater than about 15 of (1) silicon oxide to (2) titanium oxide and

21   having, after calcination, the X-ray diffraction lines of Table II.

22

23 70.   A method for performing an acylation reaction on an aromatic substrate

24   ArH_n to form a product $ArH_{n-1}COR$, the method comprising the steps of:

25

26   providing the aromatic substrate,

27

28   intimately mixing the substrate and an acylating agent, wherein the

29   acylating agent is selected from the group consisting of a carboxylic acid

30   derivative, a carboxylic acid, an acid anhydride, an ester, and an acyl

31   halide, and

32

33   exposing an intimate mixture thus formed to a catalyst comprising a

34   crystalline molecular sieve having a mole ratio greater than about 15 of

1   (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

2   element, pentavalent element, second tetravalent element which is

3   different from said first tetravalent element or mixture thereof and having,

4   after calcination, the X-ray diffraction lines of Table II.

5

6   71.   The method of Claim 70 wherein the organic substrate is selected from

7   the group consisting of benzene, toluene, anisole and 2-naphthol.

8

9   72.   The method of Claim 71 wherein the organic substrate is anisole.

10

11   73.   The method of Claim 70 wherein the acylating agent is selected from the

12   group consisting of carboxylic acid derivatives, carboxylic acids, acid

13   anhydrides, esters, and acyl halides.

14

15   74.   A process for the production of light olefins from a feedstock comprising

16   an oxygenate or mixture of oxygenates, the process comprising reacting

17   the feedstock at effective conditions over a catalyst comprising a

18   crystalline molecular sieve having a mole ratio greater than about 15 of

19   (1) an oxide of a first tetravalent element to (2) an oxide of a trivalent

20   element, pentavalent element, second tetravalent element which is

21   different from said first tetravalent element or mixture thereof and having,

22   after calcination, the X-ray diffraction lines of Table II.

23

24   75.   The process of Claim 74 wherein the light olefins are ethylene,

25   propylene, butylene or mixtures thereof.

26

27   76.   The process of Claim 75 wherein the light olefin is ethylene.

28

29   77.   The process of Claim 74 wherein the oxygenate is methanol, dimethyl

30   ether or a mixture thereof.

31

32   78.   The process of Claim 77 wherein the oxygenate is methanol.

33

1 79. A process for separating gasses comprising contacting a mixture of

2   gasses with a membrane containing a molecular sieve wherein the

3   molecular sieve comprises a crystalline molecular sieve having a mole

4   ratio greater than about 15 of (1) an oxide of a first tetravalent element to

5   (2) an oxide of a trivalent element, pentavalent element, second

6   tetravalent element which is different from said first tetravalent element

7   or mixture thereof and having, after calcination, the X-ray diffraction lines

8   of Table II.

9

10 80. The process of Claim 79 wherein the mixture of gasses comprises

11   carbon dioxide and methane.

12

13 81. A process for producing methylamine or dimethylamine comprising

14   reacting methanol, dimethyl ether or a mixture thereof and ammonia in

15   the gaseous phase in the presence of a catalyst comprising a crystalline

16   molecular sieve having a mole ratio greater than about 15 of (1) an oxide

17   of a first tetravalent element to (2) an oxide of a trivalent element,

18   pentavalent element, second tetravalent element which is different from

19   said first tetravalent element or mixture thereof and having, after

20   calcination, the X-ray diffraction lines of Table II.

21

22 82. The process of Claim 81 wherein the methanol, dimethylether or mixture

23   thereof and ammonia are present in amounts sufficient to provide a

24   carbon/nitrogen ratio from about 0.2 to about 1.5.

25

26 83. The process of Claim 81 conducted at a temperature of from about

27   250°C to about 450°C.

28

29 84. A process for treating a cold-start engine exhaust gas stream containing

30   hydrocarbons and other pollutants consisting of flowing said engine

31   exhaust gas stream over a molecular sieve bed which preferentially

32   adsorbs the hydrocarbons over water to provide a first exhaust stream,

33   and flowing the first exhaust gas stream over a catalyst to convert any

1   residual hydrocarbons and other pollutants contained in the first exhaust

2   gas stream to innocuous products and provide a treated exhaust stream

3   and discharging the treated exhaust stream into the atmosphere, the

4   molecular sieve bed comprising a crystalline molecular sieve having a

5   mole ratio greater than about 15 of (1) an oxide of a first tetravalent

6   element to (2) an oxide of a trivalent element, pentavalent element,

7   second tetravalent element which is different from said first tetravalent

8   element or mixture thereof and having, after calcination, the X-ray

9   diffraction lines of Table II.

10

11   85.   The process of Claim 84 wherein the engine is an internal combustion

12   engine.

13

14   86.   The process of Claim 85 wherein the internal combustion engine is an

15   automobile engine.

16

17   87.   The process of Claim 84 wherein the engine is fueled by a

18   hydrocarbonaceous fuel.

19

20   88.   The process of Claim 84 wherein the molecular sieve has deposited on it

21   a metal selected from the group consisting of platinum, palladium,

22   rhodium, ruthenium, and mixtures thereof.

23

24   89.   The process of Claim 88 wherein the metal is platinum.

25

26   90.   The process of Claim 88 wherein the metal is palladium.

27

28   91.   The process of Claim 88 wherein the metal is a mixture of platinum and

29   palladium.

30

31   92.   A process for the preparation of amides from oximes via Beckmann

32   rearrangement comprising contacting the oxime in the vapor phase with

33   a catalyst comprising a crystalline molecular sieve having a mole ratio

1   greater than about 15 of (1) an oxide of a first tetravalent element to (2)

2   an oxide of a trivalent element, pentavalent element, second tetravalent

3   element which is different from said first tetravalent element or mixture

4   thereof and having, after calcination, the X-ray diffraction lines of

5   Table II.

6

7 93. The process of Claim 92 wherein the oxime is cyclohexanone oxime and

8   the amide is caprolactam.

9

10 94. The process of Claim 93 wherein the rearrangement takes place in the

11   presence of a solvent.

12

13 95. The process of Claim 94 wherein the solvent is of the type $R^1 - O - R^2$

14   wherein R^1 is a $C_1 - C_4$ alkyl chain and R^2 can be a hydrogen atom or an

15   alkyl chain containing a number of carbon atoms less than or equal to

16   R^1.

17

18 96. The process of Claim 48, 53, 54, 55, 56, 58, 59, 60, 61, 62, 63, 70, 71,

19   72, 73, 74, 75, 76, 77, 78, 79, 80, 91, 82, 83, 84, 85, 86, 87, 88, 89, 90,

20   91, 91, 93, 94 or 95 wherein the molecular sieve has a mole ratio greater

21   than about 15 of (1) silicon oxide to (2) an oxide selected from aluminum

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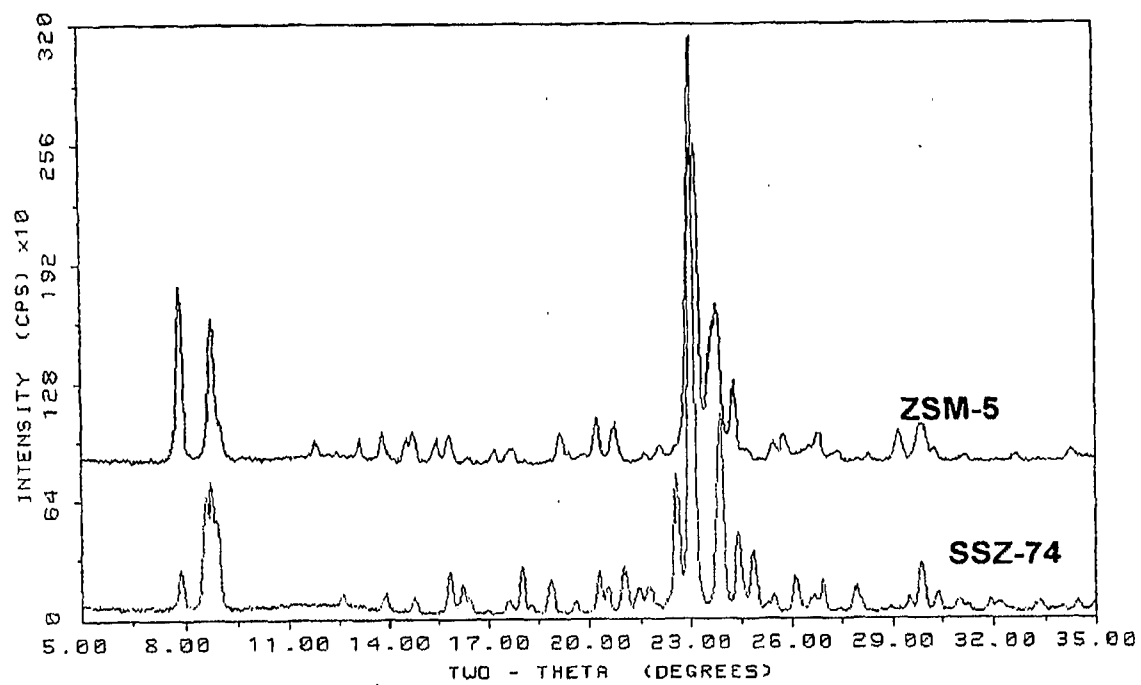
23   and mixtures thereof.

FIG. 1