

1 **EXTREMELY LOW ACIDITY USY AND HOMOGENEOUS,**
2 **AMORPHOUS SILICA-ALUMINA HYDROCRACKING**
3 **CATALYST AND PROCESS**

4
5 FIELD OF THE INVENTION

6
7 The present invention relates to catalysts and processes using the catalysts
8 for converting hydrocarbonaceous oils to products of an average lower
9 molecular weight and an average lower boiling point.

10
11 BACKGROUND OF THE INVENTION

12
13 Modern hydrocracking catalysts are generally based on zeolitic materials due
14 to their advantages over earlier refractory oxide based materials such as
15 silica-alumina, magnesia, and alumina. Amorphous catalysts have relatively
16 poor activity but higher selectivity for production of distillate range product
17 while zeolite catalysts provide higher activity but poorer selectivity for
18 distillate, particularly for the heavy-distillate fraction. Among other things, the
19 present invention provides a hydrocracking process with superior overall
20 catalytic performance over amorphous silica-alumina cogel catalyst while
21 maintaining the excellent heavy-distillate selectivity and unconverted oil
22 quality of the amorphous cogel catalyst.

23
24 In state-of-the-art cogel hydroprocessing catalysts, various combination of
25 metals, their oxides and sulfides, from Group VI-B and Group VIII of the
26 Periodic Table, were precipitated or cogelled with the base. Therefore, the
27 deposition of metals by cogellation was considered superior to impregnation
28 of the metals on the base (post-metal impregnation), since the latter method
29 tended to produce non-uniform deposits of active metals. The increased costs
30 of production inherent in cogellation or precipitation were simply borne in
31 order to obtain more uniform catalyst which had better distillate selectivity and
32 produced a superior quality product.

1 The present invention provides, among other things, a novel
2 post-metal-impregnated, hydrocracking catalyst made with homogeneous
3 silica-alumina and highly dealuminated ultrastable Y zeolite (USY) which
4 produces a number of unexpected benefits including: the catalyst activity is
5 improved significantly over the state-of-the-art amorphous cogel catalyst, and
6 at the same time the total distillate yield increased. The catalysts of the
7 invention are very stable and showed significantly lower fouling rates than the
8 cogel catalyst.

9
10 It is well known that addition of USY to a cogel hydrocracking catalyst
11 generally lowers the distillate yield, particularly the heavy-distillate fraction
12 with 550°-700°F boiling point range. The catalyst of the present invention is
13 particularly effective with respect to maintaining the yield of a heavy-distillate
14 fraction. The hydrocracked heavy-distillate fraction from vacuum gas oil
15 typically exhibits very high Cetane Numbers of 60-80, while a light-distillate
16 fraction with 250°-550 °F boiling point range exhibits Cetane Numbers of 40-
17 55. In order to achieve a high Cetane Number for the combined diesel fuel, it
18 is desirable to increase the heavy-distillate content in the combined distillate
19 pool. Moreover, the unconverted 700 °F⁺ fraction in a process according to
20 the invention exhibits high viscosity index indicating that a high quality
21 lubricating oil bas stock can be produced from that fraction.

22
23 An early synthetic zeolite Y was described in U.S. Patent No. 3,130,007
24 issued April 21, 1964, which is incorporated herein by reference. A number of
25 modifications have been reported for this material, one of which is ultrastable
26 Y zeolite as described in U.S. Patent No. 3,536,605 issued October 27, 1970,
27 which is incorporated herein by reference. Zeolite Y has been constantly
28 improved by techniques like ammonium ion exchange and acid extraction,
29 and various forms of calcination in order to improve the performance of the
30 hydrocracking catalysts.

1 To further enhance the utility of synthetic Y zeolite and depending upon the
2 hydroprocessing problem sought to be solved, additional components have
3 been added by means known in the art. U.S. Patent No. 3,835,027 to
4 Ward et al., which is incorporated herein by reference, describes a catalyst
5 containing at least one amorphous refractory oxide, a crystalline zeolitic
6 aluminosilicate and a hydrogenation component selected from the Group VI
7 and VIII metals and their sulfides and oxides. Ward et al. teach that the added
8 materials enhance the catalytic and denitrogenation activity of the catalyst.

9
10 U.S. Patent No. 3,897,327 to Ward, which is incorporated herein by reference,
11 describes a hydrocracking process using a sodium Y zeolite wherein the
12 Y zeolite has a preliminary ammonium ion exchange to replace most of the
13 sodium ion with ammonium ions. This product is then calcined in the presence
14 of at least 0.2 psi of water vapor for a sufficient time to reduce the cell size to
15 a range between 24.40-24.64 Å. The patent teaches that the catalyst has
16 increased hydrothermal stability by maintaining crystallinity and surface area
17 after calcination, exposure to water vapor or water vapor at
18 high temperatures.

19
20 In addition to various catalyst compositions, preparation techniques have
21 been discovered to also affect catalytic selectivity. U.S. Patent No. 3,867,277
22 to Ward, which is incorporated herein by reference, discloses the use of a
23 Y type zeolite catalyst in a low pressure hydrocracking process. The catalyst
24 described in the patent requires the Y zeolite to be double-exchanged and
25 double-calcined wherein the first calcination step uses a relatively
26 high temperature (950°-1800 °F) and the second calcination step uses
27 relatively low temperatures (750°-1300 °F) to yield a catalyst that is stable in
28 ammonia environments.

29
30 U.S. Patent No. 3,853,747 to Young, which is incorporated herein by
31 reference, teaches that hydrocracking activity of the catalyst is greater when
32 the hydrogenating component is incorporated in the zeolite in such a manner
33 as to avoid impregnation into the inner adsorption area of the zeolite

1 crystallites or particles. For example, the mixing may consist of stirring,
2 mulling, grinding, or any conventional procedure for obtaining an intimate
3 mixture of solid material. The dispersion of the Group VIB metal
4 hydrogenation component is achieved by adding it to the zeolite in a finely
5 divided but essentially undissolved form. The patent teaches that in some
6 cases the soluble molybdenum or tungsten compounds added to the zeolite
7 by impregnation tends to destroy the zeolite crystal structure and acidity
8 during the subsequent drying and calcination steps. Young teaches, however,
9 that the particle size should range from 0.5 microns to 5 microns.

10

11 U.S. Patent No. 4,857,171 to Hoek et al., which is incorporated herein by
12 reference, teaches a process for converting hydrocarbon oils comprising
13 contacting the oil with a catalyst consisting essentially of a Y zeolite having a
14 unit cell size less than 24.40 Å, a silica based amorphous cracking
15 component, a binder and at least one hydrogenation component selected
16 from the group consisting of a Group VI metal, and/or a Group VIII metal and
17 mixtures thereof.

18

19 U.S. Patent No. 4,419,271 to Ward, which is incorporated herein by reference,
20 discloses a composition matter useful as a catalyst base for supporting active
21 hydrogenation metal components or for catalyzing acid catalyzed hydrocarbon
22 conversion reactions comprising in intimate heterogeneous mixture
23 (1) a modified hydrogen crystalline aluminosilicate Y zeolite having activity for
24 catalytically cracking hydrocarbons and having a unit cell size between
25 24.25 and 24.35 Å and a water absorption capacity, at 4.6 mm water vapor
26 partial pressure and 25° C., less than 8% by weight of zeolite and
27 (2) a dispersion of silica-alumina in a gamma alumina matrix.

28

29 U.S. Patent No. 4,820,402 to Partridge et al., which is incorporated herein by
30 reference, discloses the use of a highly siliceous large pore zeolite as the
31 acidic component of a catalyst in a process for improved distillate selectivity.

1 U.S. Patent No. 5,171,422 to Kirker et al., which is incorporated herein by
2 reference, discloses a process for producing a high quality lube base stock
3 with a USY catalyst with greater than 50:1 silica:alumina ratio.

4
5 WO 00/40675, which is incorporated herein by reference, discloses a
6 low pressure hydrocracking process using a catalyst comprising zeolite USY
7 with a framework silica to alumina molar ratio of at least 200:1 preferably
8 greater than 2000:1, and a hydrogenation component.

9
10 GB-A-2,014,970 discloses an ultra hydrophobic zeolite Y which has been
11 given a unit cell size dimension of 24.20-24.45 Å by two ammonium exchange
12 steps with an intermediate calcinations step at 550°-800° C. in steam.
13 EP-B-0,028,938 discloses the use of such a modified zeolite for selective
14 conversion of hydrocarbons boiling above 371 °C into midbarrel fuel products
15 having a distillation range of 149°-371 °C. Improved manufacturing process
16 for producing 24.25-24.35 Å unit cell size Zeolite Y was disclosed in
17 U.S. Patent No. 5,059,567 to Linsten et al.

18
19 Silica-alumina compounds are well known as catalysts used in hydrocarbon
20 conversion processes. Silica-alumina catalysts such as in the present
21 invention can be used "as is", particularly in reactions that require acidic
22 catalysts, or can optionally be combined with zeolites, clays or other binders,
23 and inorganic oxides for the cracking of liquid hydrocarbons in cracking
24 reactors such as fluid catalytic crackers and hydrocrackers. Silica-alumina
25 composites have been used commercially for a variety of hydrocarbon
26 processing applications, such as cracking, desulphurization, demetalation,
27 and denitrification.

28
29 Amorphous silica-alumina has been prepared previously by a modified cogel
30 process wherein no hydrogenation metals were added during the gellation
31 step. Spray dried, amorphous silica-alumina catalysts were made by the
32 method as described in U.S. Patent No. 4,988,659, Pecoraro to produce
33 catalysts used in hydrocarbon conversion processes.

1 The method of preparation of silica-alumina catalysts affects the chemical and
2 physical properties of the catalysts such as activity (such as cracking or
3 isomerization activity), and physical properties (such as pore structure and
4 volume, surface area, density and catalyst strength). Silica-alumina catalysts
5 such as in the present invention can be used "as is", particularly in reactions
6 that require acidic catalysts, or can optionally be combined with zeolites, clays
7 or other binders, and inorganic oxides for the cracking of liquid hydrocarbons
8 in cracking reactors such as fluid catalytic crackers.

9
10 Numerous silica-alumina catalyst compositions and processes for their
11 preparation are described in the patent literature. The patent literature
12 teaches a number of ways to prepare these compositions.

13
14 U.S. Patent No. 4,499,197, Seese et al., for example, describes the
15 preparation of inorganic oxide hydrogels, and more particularly, catalytically
16 active amorphous silica-alumina and silica-alumina rare earth cogels. The
17 active cogels are prepared by reacting aluminate and silicate solutions to
18 obtain a silica-alumina pregel, and then reacting the pregel with an acidic rare
19 earth and an aluminum salt solution with complete mixing.

20 U.S. Patent No. 4,239,651, Alfandi et al. discloses a process for preparing
21 exchanged ammonium cogels.

22
23 U.S. Patent No. 4,289,653, Jaffe teaches preparing an extruded catalyst by
24 mixing aluminum sulfate and sulfuric acid with sodium silicate to form a silica
25 sol in an alumina salt solution at pH of 1-3, adding NH_4OH under substantially
26 constant pH of at least 4 to 6; adding more NH_4OH to form a cogelled mass to
27 pH 7.5-8.5; washing cogelled mass; mulling the mass with peptizing agent, a
28 Group VI-B metal compound and a Group VIII metal compound to form
29 extrudable dough; extruding; and drying and calcining.

30
31 U.S. Patent No. 4,988,659, Pecoraro teaches a cogelled, silica-alumina matrix
32 prepared by the method which comprises mixing a silicate solution with an
33 aqueous solution of an acid aluminum salt and an acid, to form an acidified

silica sol in said aluminum salt solution, and adjusting said silica sol/aluminum salt solution mixture to a pH in the range of about 1 to 4; slowly adding sufficient base with vigorous stirring, to said acidified silica sol/aluminum salt solution mixture to form a cogel slurry of silica and alumina, and to adjust said slurry to a pH in the range of about 5 to 9; aging said cogel slurry at a temperature of ambient to 95°C. ; adjusting the pH of said cogel slurry to about 5 to 9; recovering acoagulated mass from said slurry ; washing said coagulated mass; adjusting the pH of said coagulated mass to between about 4 and 7, and controlling conditions to induce syneresis; and forming said combination into particles.

SUMMARY OF THE INVENTION

An aspect provides a process for converting hydrocarbonaceous oils into products of lower average molecular weight and lower average boiling point comprising contacting said hydrocarbonaceous oils under hydrocracking conditions with a catalyst comprising (1) a minor amount of a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5, preferable less than about 3, and Broensted acidity of from about 1 to about 20, preferably about 1-10 micromole/g measured by FT-IR, (2) a homogeneous, amorphous silica-alumina cracking component having a Surface to BulkSi/Al ratio (SB ratio) of from about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an amount of no greater than about 10%, preferably no greater than 5% and (3) a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

Another aspect provides a process for producing high quality distillate with increased yield of heavy distillate from heavy gas oils comprising contacting a heavy gas oil under hydrocracking conditions with a catalyst comprising (1) a minor amount of a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5, preferable less than about 3, and Broensted acidity of from about 1 to about 20,

preferably from about 1-10micromole/g measured by FT-IR, (2) a homogeneous, amorphous silica-alumina cracking component having an SB ratio of from about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an amount of no greater than about 10%, preferably no greater than 5% and (3) a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

Another aspect provides a hydrocracking catalyst composition comprising (1) a minor amount of a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5, preferable less than about 3, and having Broensted acidity of from about 1 to about 20, preferably about 1-10 micromole/g measured by FT-IR, (2) a homogeneous, amorphous silica-alumina cracking component having an SB ratio of from about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an amount of no greater than about 10%, preferably no greater than 5% and (3) a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

Another aspect provides a process for producing a lubricating oil base stock which comprises: (a) contacting a feedstock under hydrocracking conditions with a catalyst comprising a minor amount of a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5 and Broensted acidity of from about 1 to about 10 micromole/g, a homogeneous, amorphous silica-alumina cracking component having an SB ratio of from about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an amount of no greater than about 10% and a catalytic amount of hydrogenation component selected from the selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof; and (b) processing the hydrocracked product to provide a lubricating oil base stock.

The presence of a minor amount of a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5 and Broensted acidity of from about 1 to

about 20 micromole/g as measured by FT-IR, together with a homogeneous, amorphous silica-alumina cracking component having an SB ratio of from about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an amount of no greater than about 10% and a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof can produce unexpected benefits. Such benefits may include: (1) the catalyst activity is improved significantly; (2) the total distillate yield is maintained over a broad range of USY concentrations, (3) the respective yields of light-distillate vs. heavy-distillate can be adjusted by varying the USY concentration; and

1 (4) the catalyst became much more stable and showed significantly lower
2 fouling rates.

3

4

5 DESCRIPTION OF THE PREFERRED EMBODIMENTS

6

7 In accordance with the one embodiment of the present invention, the catalyst
8 comprises (1) a minor amount of a low acidity, highly dealuminated ultrastable
9 Y zeolite having an Alpha value of less than about 5, preferable less than
10 about 3, and Broensted acidity of from about 1 to about 20, preferably about
11 1-10 micromole/g, (2) a homogeneous, amorphous silica-alumina cracking
12 component having an SB ratio of from about 0.7 to about 1.3, wherein a
13 crystalline alumina phase is present in an amount of no greater than about
14 10%, preferably no greater than 5% and (3) a catalytic amount of
15 hydrogenation component selected from the group consisting of a Group VI
16 metal, a Group VIII metal, and mixtures thereof.

17

18 The amount of highly dealuminated USY zeolite in the catalyst compositions
19 in accordance with the present invention on a finished catalyst basis including
20 metals ranges from about 0.5-70% by weight, preferably, from about
21 0.5-50% and most preferably from about 1-20%.

22

23 Highly dealuminated USY zeolites having a silica to alumina molar ratio
24 greater than 50 are useful as the zeolite component of the catalyst
25 compositions according to the present invention. Preference is given to
26 USY zeolites having a silica: alumina molar ratio greater 60, and most
27 preferably having silica: alumina molar ratio greater than 80.

28

29 Due to the extremely low acidity of the USY, the hydrocracking catalysts of
30 the present invention require the addition of a secondary amorphous cracking
31 component. Consequently, the catalysts of the present invention also include
32 an amorphous cracking component which comprises a homogeneous,
33 amorphous silica-alumina cracking component having an SB ratio of from

1 about 0.7 to about 1.3, wherein a crystalline alumina phase is present in an
2 amount of no greater than about 10%, preferably no greater than 5%.

3

4 The amount of amorphous cracking component in the catalyst compositions in
5 accordance with the present invention on a finished catalyst basis including
6 metals, ranges from about 10%-80% by weight, preferably from about
7 30%-70% by weight and most preferably from about 40%-60%. The amount
8 of silica in the silica-alumina ranges from about 10%-70% by weight.
9 Preferably, the amount of silica in the silica-alumina ranges from about
10 20%-60% by weight, and most preferably the amount of silica in the silica-
11 alumina ranges from about 25%-50% by weight.

12

13 The binder(s) present in the catalyst compositions suitably comprise inorganic
14 oxides. Both amorphous and crystalline binders can be applied. Examples of
15 suitable binders comprise silica, alumina, clays and zirconia. Preference is
16 given to the use of alumina as binder. The amount of binder in the catalyst
17 compositions in accordance with the present invention on a finished catalyst
18 basis including metals ranges 10%-30% by weight, and is preferably from
19 about 15%-25% by weight.

20

21 The catalysts of the present invention also comprise a hydrogenation
22 component. As used herein the hydrogenation component mainly means
23 metals of Group VI and VIII in the Periodic Table, for example, chromium,
24 molybdenum, tungsten, iron, cobalt, nickel, platinum, palladium, and the like
25 metals and oxides and sulfides of these metals. These metals may be used in
26 combination of two or more members. For example, combination of metals
27 such as nickel-tungsten, nickel-molybdenum cobalt-molybdenum, platinum-
28 palladium, and the like.

29

30 The amount(s) of hydrogenation component(s) in the catalyst compositions
31 suitably range from about 0.2% to about 10% by weight of Group VIII metal
32 component(s) and from about 5% to about 30% by weight of Group VI metal
33 component(s), calculated as metal(s) per 100 parts by weight of total catalyst.

1 The hydrogenation components in the catalyst compositions may be in the
2 oxidic and/or the sulphidic form. If a combination of at least a Group VI and a
3 Group VIII metal component is present as (mixed) oxides, it will be subjected
4 to a sulphiding treatment prior to proper use in hydrocracking.

5
6 The catalyst compositions in accordance with the present invention comprise
7 about 1%-10% by weight of nickel and about 5%-40% by weight tungsten.
8 Preferably, the catalyst compositions in accordance with the present invention
9 comprise about 2%-8% by weight of nickel and about 8%-30% by weight
10 tungsten, calculated as metals per 100 parts by weight of total catalyst.

11
12 When noble metal is used, the catalyst compositions in accordance with the
13 present invention comprise about 0.1%-5% by weight of platinum, or
14 palladium, or a combination of Pt and Pd. Preferably, the catalyst
15 compositions in accordance with the present invention comprise about 0.2%-
16 2% by weight of platinum, or palladium, or a combination of Pt and Pd,
17 calculated as metals per 100 parts by weight of total catalyst.

18
19 It has been found that excellent and unexpected results in terms of
20 performance and activity are obtained using catalysts according to the present
21 invention. Some of these results include: the catalysts of the invention are
22 particularly good for producing more heavy-distillate with 550°-700 °F boiling
23 point range (over 70 Cetane); catalysts of the invention show comparable or
24 lower gas-make than a reference catalyst; and catalysts of the invention
25 produce less naphtha during the hydrocracking process by suppressing
26 undesirable overcracking reactions.

27
28 In addition, the present invention provides for a process for converting
29 hydrocarbonaceous oils into products of lower average molecular weight and
30 lower average boiling point comprising contacting said hydrocarbonaceous
31 oils under hydrocracking conditions with a catalyst comprising a low acidity,
32 highly dealuminated ultrastable Y zeolite having an Alpha value of less than
33 about 5 and Broensted acidity of from about 1 to about 20 micromole/g, a

1 homogeneous, amorphous silica-alumina cracking component having an SB
2 ratio of from about 0.7 to about 1.3, wherein a crystalline alumina phase is
3 present in an amount of no greater than about 5% and a catalytic amount of
4 hydrogenation component selected from the group consisting of a Group VI
5 metal, a Group VIII metal, and mixtures thereof.

6

7 The present invention is also directed to a process for producing high quality
8 distillate and lubricating oil base stock in increased yields from heavy gas oils
9 comprising contacting a heavy gas oil under hydrocracking conditions with a
10 catalyst a minor amount of a low acidity, highly dealuminated ultrastable
11 Y zeolite having an Alpha value of less than about 5, preferable less than
12 about 3 and Broensted acidity of from about 1 to about 20, preferably about
13 1-10 micromole/g as measured by FT-IR, a homogeneous, amorphous silica-
14 alumina cracking component having an SB ratio of from about 0.7 to about
15 1.3, wherein a crystalline alumina phase is present in an amount of no greater
16 than about 10%, preferably no greater than 5%, and a catalytic amount of
17 hydrogenation component selected from the group consisting of a Group VI
18 metal, a Group VIII metal, and mixtures thereof.

19

20 A catalyst according to the present invention is particularly good for increasing
21 the yield of a heavy-distillate fraction with 550°-700 °F boiling point range. The
22 hydrocracked heavy-distillate fraction from vacuum gas oil typically exhibits
23 very high Cetane Numbers of 60-80, while a light-distillate fraction with 250°-
24 550 °F boiling point range exhibits Cetane Numbers of 40-55. In order to
25 achieve high a Cetane Number for the combined diesel fuel, it is desirable to
26 increase the heavy-distillate yield in the combined distillate pool.

27

28 The present invention also provides a process for production of a feedstock
29 for lubricating oil base stock comprising contacting the catalyst of the
30 invention with a hydrocarbon oil feedstock boiling above about 650 °F under
31 hydrogenation and conditions to produce a feedstock for lubricating oil base
32 stock. The unconverted 700 °F+ fraction from our invention exhibits high

1 viscosity index indicating high quality lubricating oil base stock can be
2 produced.

3

4 Hydroconversion process configurations in accordance with the present
5 invention are those wherein a substantial reduction in average molecular
6 weight and boiling point can be accomplished by contacting the feed with a
7 catalyst composition comprising a low acidity, highly dealuminated ultrastable
8 Y zeolite having an Alpha value of less than about 5 and Broensted acidity of
9 from about 1 to about 20 micromole/g, a homogeneous, amorphous silica-
10 alumina cracking component having an SB ratio of from about 0.7 to about
11 1.3, wherein a crystalline alumina phase is present in an amount of no greater
12 than about 10%, and a catalytic amount of hydrogenation component selected
13 from the group consisting of a Group VI metal, a Group VIII metal, and
14 mixtures thereof.

15

16 Examples of such hydrocarbon conversion processes in which the catalysts of
17 the present invention may be used are well known in the art and include, but
18 are not limited to, single-stage hydrocracking, two-stage hydrocracking,
19 series-flow hydrocracking, mild hydrocracking, lube hydrocracking,
20 hydrotreating, lube hydrofinishing, hydrodesulphurization, hydrodenitrification,
21 catalytic dewaxing and catalytic cracking.

22

23 Feedstocks which can be suitably applied in the process according to the
24 present invention comprise gas oils, vacuum gas oils, deasphalted oils, long
25 residues, catalytically cracked cycle oils, coker gas oils and other thermally
26 cracked gas oils and syncrudes, optionally originating from tar sands, shale
27 oils, waxy hydrocarbons from Fischer-Tropsch hydrocarbon synthesis
28 process, residue upgrading processes or biomass. Combinations of various
29 feedstocks can also be applied.

30

31 It may be desirable to subject part or all of the feedstock to one or more
32 (hydro) treatment steps prior to its use in the hydrocarbon conversion process
33 according to the present invention. It is often found convenient to subject the

1 feedstock to a (partial) hydrotreatment. When rather heavy feedstocks are to
2 be processed it will be advantageous to subject such feedstocks to a (hydro)
3 demetallization treatment.
4
5 Suitable hydrocracking conditions to be applied comprise temperatures
6 ranging from about 250 °C to about 500 °C, pressures up to about 300 bar
7 and space velocities from about 0.1 to about 10 kg feed per liter of
8 catalyst per hour (kg/l/h). Hydrogen gas to feed ratios range from about 100 to
9 about 5000 NI/kg feed (normal liters at standard temperature and pressure
10 per kilogram) can suitably be used.
11
12 Preferably, hydrocracking conditions to be applied comprise
13 temperatures ranging from about 300 °C to about 450 °C, pressures from
14 about 25 bar to about 200 bar and space velocities from about 0.2 to about
15 10 kg feed per liter of catalyst per hour (kg/l/h). Hydrogen gas to feed ratios
16 preferably range from about 250 to about 2000 NI/kg are applied.
17
18 Use of powder X-ray diffraction (XRD) for characterization of USY is well
19 known per ASTM method D 3942-80. The unit cell size of the USY is inversely
20 correlated with the Al content in the USY. As USY become more
21 dealuminated, the unit cell size of USY is changing from 24.70 Å to 24.54 Å or
22 below. However, for severely dealuminated and ultrastabilized USY with bulk
23 SiO₂/Al₂O₃ ratio of over 50, the cracking activity of USY could not be
24 differentiated with the XRD unit cell size. Instead, FT-IR, and Alpha test (a
25 model compound test for activity measurement) were used to analyze the
26 activity of the USY samples. Standard analysis tests such as bulk composition
27 analysis by ICP and surface area measurements were used to ensure the
28 quality of USY samples.
29
30 Transmission IR spectroscopy was used to compare the acidity of
31 USY samples per published methods elsewhere (T.R. Hughes,
32 H.M. White, J. Phys. Chem., 71, 2192, 1967; M.A. Makarova,
33 A. Garforth, V.L. Zholobenko, J. Dwyer, G.J. Earl, D. Rawlence,

1 Studies in Surface Science and Catalysis, 84, 365, 1994). Two methods
2 were employed: (1) measurement of the acidic OH stretching bands in the
3 3600 cm^{-1} region of the spectrum; and (2) adsorption of pyridine to determine
4 the Brønsted to Lewis acid site concentrations. Self-supporting
5 wafers weighing about 10 mg were dehydrated *in-situ* by heating in flowing He
6 at 5 °C/min to 400 °C and left at this temperature for 1 hour. The wafers were
7 then cooled to 150 °C and the IR spectrum was recorded. This spectrum was
8 fitted to obtain the intensities of the OH bands for the different acidic sites.
9 Pyridine was also used to measure acidity. Once the samples were
10 dehydrated according to the above method, the IR cell was isolated and then
11 4 μL (microliter) of pyridine was injected. The pyridine was allowed to adsorb
12 for 1 hour and then the cell was reopened to flowing He to allow desorption of
13 the physically adsorbed pyridine. Typically, desorption was allowed for
14 12-17 hours, then FT-IR spectra were obtained for the USY sample containing
15 residual chemisorbed pyridine. These spectra were then fitted in the pyridine
16 ring vibration and OH stretching regions to obtain the peak areas as a function
17 of desorption time. The final peak areas were obtained by extrapolating to
18 infinite desorption time.

19

20 It is plausible, other Brønsted acidity measurement techniques such as
21 solid-state NMR and temperature programmed desorption with a base (e.g.,
22 NH_3 TPAD) could also be used to select the optimum range.

23

24 The cracking activity of USY was determined by the Alpha test which was
25 adapted from the published descriptions of the Mobil Alpha test (P.B. Weisz
26 and J.N. Miale, *J. Catal.*, **4**, 527-529, 1965; J.N. Miale, N.Y. Chen, and
27 P.B. Weisz, *J. Catal.*, **6**, 278-87, 1966). The "Alpha Value" is calculated as the
28 cracking rate of the sample in question divided by the cracking rate of a
29 standard silica alumina sample. The resulting "Alpha" is a measure of acid
30 cracking activity which generally correlates with number of acid sites. Other
31 model compound testing with paraffinic hydrocarbons could also be used to
32 select the optimum range of USY acidity.

33

1 The silica-alumina composition of the present invention is amorphous and
2 homogeneous. A "Surface to Bulk Si/Al Ratio" (SB Ratio) has been selected
3 as the measure used to define the homogeneity characteristic of the
4 silica-alumina of the present invention and to compare it with other
5 silica-alumina compositions.

$$\text{SB Ratio} = \frac{(\text{Si/Al atomic ratio of the } \textit{surface} \text{ measured by XPS})}{(\text{Si/Al atomic ratio of the } \textit{bulk} \text{ measured by elemental analysis})}$$

11 To determine the SB ratio, the Si/Al atomic ratio of the silica-alumina surface
12 is measured using x-ray photoelectron spectroscopy (XPS). XPS is also
13 known as electron spectroscopy for chemical analysis (ESCA). Since the
14 penetration depth of XPS is less than 50 Å, the Si/Al atomic ratio measured by
15 XPS is for the surface chemical composition. Use of XPS for silica-alumina
16 characterization was published by W. Daneiell et al. in Applied Catalysis A,
17 **196**, 2000, pp 247-260. The XPS technique is, therefore, effective in
18 measuring the chemical composition of the outer layer of catalytic particle
19 surface. Other surface measurement techniques, such as Auger electron
20 spectroscopy (AES) and Secondary ion mass spectroscopy (SIMS), could
21 also be used for measurement of the surface composition.

23 Separately, the bulk Si/Al ratio of the composition is determined from ICP
24 elemental analysis. Then, by comparing the surface Si/Al ratio to the bulk
25 Si/Al ratio, the SB ratio and the homogeneity of silica-alumina are determined.

27 How the SB ratio defines the homogeneity of a particle is explained as
28 follows. An SB ratio of 1.0 means the material is completely homogeneous
29 throughout the particles. An SB ratio of less than 1.0 means the particle
30 surface is enriched with aluminum (or depleted with silicon), and aluminum is
31 predominantly located on the external surface of the particles. The SB ratio of
32 more than 1.0 means the particle surface is enriched with silicon (or depleted

1 with aluminum), and aluminum is predominantly located on the internal area
2 of the particles.

3

4 A silica-alumina composition is homogeneous and is in accordance with the
5 present invention when its Surface to Bulk ratio (SB ratio), i.e., the ratio of the
6 Si/Al atomic ratio of the composition measured by XPS at the surface and the
7 Si/Al atomic ratio of the bulk measured by elemental analysis is from about
8 0.7 to about 1.3.

9

10 The SB ratio of reference silica-alumina samples from two commercial
11 sources (Siral-40 from SasolCondea and MS-25 from W.R. Grace) was
12 measured and the following values were obtained:

13

14 SB ratio of Siral-40 silica-alumina = 2.1 – 2.8

15 SB ratio of MS-25 silica-alumina = 0.2 – 0.6

16

17 The above results indicate that Siral type of silica-alumina is enriched with
18 silicon on the surface of the particles (i.e., depleted with Al) as published
19 earlier by W. Daneiell et al. in Applied Catalysis A, **196**, 2000, pp 247-260. On
20 the other hand, MS-25 silica-alumina is enriched with aluminum on the
21 surface of the particles. The silica-alumina in accordance with the present
22 invention has an SB ratio of from about 0.7 to about 1.3, preferably from about
23 0.9 to about 1.1 and is homogeneous and highly homogeneous, respectively,
24 in that the aluminum is distributed essentially uniformly throughout the
25 particles. To maximize the activity of the silica-alumina, it is most preferable to
26 have a highly homogeneous silica-alumina having an SB ratio of about 1.0.

27

28 In addition to being homogeneous or highly homogeneous, the silica-alumina
29 compositions of the present invention are amorphous, wherein a crystalline
30 alumina phase, such as pseudoboehmite phase, is present in an amount no
31 greater than about 10%, preferably no greater than about 5%.

32

1 Silica-alumina according to the present invention may be prepared by a
2 variety of methods employing batch and continuous processes in different
3 combinations.

4
5 The two most important steps in the preparation of a silica-alumina cogel are
6 (1) preparation of the clear sol containing silica and alumina and
7 (2) gellation of the sol using a base solution. See U.S. Patent No. 4,289,653,
8 Jaffe and U.S. Patent No. 4,988,659, Pecoraro, both of which are
9 incorporated by reference herein. See also commonly assigned
10 U.S. Patent Application titled "Method for Preparing a Highly Homogenous
11 Amorphous Silica-Aluminum Composition", filed concurrently herewith and
12 incorporated by reference herein.

13
14 The starting materials for the sol preparation step include aluminum salt, acid,
15 and a silica source. The aluminum salt source that can be used for the
16 synthesis includes aluminum sulfate, aluminum nitrate, aluminum chloride,
17 aluminum bromide, aluminum iodide, aluminum acetate and aluminum metal
18 or alumina dissolved in acid. Feasible acid sources include acetic acid, formic
19 acid, sulfuric acid, hydrochloric acid, and nitric acid. The silicate sources
20 include, but are not limited to, sodium silicate, precipitated silica dissolved in a
21 base, and colloidal silica.

22
23 The sol preparation can be done either via a batch process or a continuous
24 process. It is critical to maintain the pH less than 3.0, preferably less than 2.5,
25 and to ensure vigorous and complete mixing of the aluminum salt and silicate
26 solutions to minimize any unwanted gel or particle formation.

27
28 A basic precipitant such as ammonium hydroxide is then added to the
29 acidified sol solution. The addition of the precipitant raises the pH of the sol
30 above 3, resulting in cogelling the silica and alumina species. Dilute ammonia
31 solution is the preferred base for the gellation. In addition to dilute ammonia,
32 other bases such as NaOH, NaAlO₂, KOH can also be used for the gellation.

33

1 The gellation step can be done either via batch process or continuous
2 process. The desirable final gellation pH is in the range of 5-9, preferably 6-8.
3 It is critical to have complete, vigorous mixing of the Si-Al solution with the
4 basic precipitant, and to maintain uniform pH throughout the mixture during
5 the precipitant addition step in order to minimize formation of isolated silica
6 domains and alumina domains.

7

8 The precipitated cogel needs to be washed to remove any unreacted silicate
9 and aluminum salt, and then it is ammonium exchanged to remove sodium.
10 The cogel should be aged for approximately 2-5 hours at room temperature or
11 at an elevated temperature of up to about 90 °C and the aged cogel may be
12 spray-dried for convenience in handling and storage, or may be further
13 processed to the final catalyst from the moist state. If the extrudate
14 composition is in the dry form, such as spray-dried powders, sufficient water
15 should be added with the acetic acid to produce a moisture content of
16 approximately 60% by weight. After mulling for approximately 1 hour,
17 optionally in the presence of peptizing acid or base, the material will attain a
18 plastic or doughy state which is suitable for extrusion in commercial extrusion
19 apparatus.

20

21 If desired, the material may be extruded, dried and calcined to produce a
22 silica-alumina catalyst or catalyst support. The preferred method of drying and
23 calcining includes an initial drying step in an air-purged oven at 65°-175 °C
24 and a final calcination at 480 - 650 °C for 0.5-5 hours in a furnace or kiln.
25 These and other methods of finishing the material are set forth in
26 U.S. Patent No. 4,289,653, Jaffe, incorporated by reference herein.

27

28 The following Examples are illustrative of the present invention, but are not
29 intended to limit the invention in any way beyond what is contained in the
30 claims which follow.

31

32

Example 1: USY Zeolite

2

3 Properties of the desirable USY zeolites are summarized as follows:

4

5

6

7

Table 1
Physical Properties of Highly Dealuminated USY

	<i>Desirable USY #1</i>	<i>Desirable USY #2</i>
SiO ₂ /Al ₂ O ₃ molar ratio	88	126
Na ₂ O, wt%	<0.05	0.1
Surface area, m ² /g	686	690
Micropore pore volume, cc/g	0.25	0.27
Total pore volume, cc/g	0.51	0.54
Unit cell size, Å	24.24	24.25
% Crystallinity	-	99
Alpha	1.1	1.4
Broensted acidity by FT-IR, μmole/g	9	15

8

9 Desirable USY zeolites are highly dealuminated and stabilized with the bulk
10 SiO₂/Al₂O₃ ratio of over 80. The unit cell size measured by powder X-ray
11 diffraction shows the unit cell size of 24.25 Å or less. In addition, we found
12 that USY with very low Broensted acidity is critical for performance of finished
13 hydrocracking catalysts. We found that Broensted acidity measurement by
14 FT-IR and a model compound cracking testing using n-hexane can distinguish
15 desirable USY samples. Desirable USY for heavy-distillate selective
16 hydrocracking shows Alpha values of less than 5, and Broensted acidity of 1-
17 20 micromole/g measured by FT-IR. Hydrocracking catalysts comprising this
18 type of USY show significantly superior distillate selectivity over a catalyst
19 made with USY with greater than 5 alpha and greater than 40 micromole/g of
20 Broensted acidity.

21

22 Due to extremely low acidity of these preferred USY, the hydrocracking
23 catalysts require to have a secondary homogeneous cracking component.
24 The most desirable homogeneous cracking component is silica-alumina with
25 isomerization and cracking activity. By combining the homogeneous cracking

1 component and low acidity zeolite we were able to produce unique catalysts
2 with desirable product selectivity, activity, and stability.

3
4 **Example 2: Homogeneous Cogel Silica-Alumina**

5 The following three homogeneous cogel silica-alumina samples were used for
6 catalyst preparations. The silica-alumina has approximately 1.0 Si/Al atomic
7 ratio in bulk. The composition is uniform in that the surface Si/Al ratios
8 measured by XPS matches that of the bulk composition, and a separate phase
9 of crystalline alumina detected by XRD is less than 10 wt%. Properties of the
10 homogeneous cogel silica-alumina are summarized as follows:

11
12 **Table 2**
13 **Physical Properties of Homogeneous Cogel Silica-Alumina**

	Desirable Silica-Alumina #1	Desirable Silica-Alumina #2	Desirable Silica-Alumina #3
Surface area, m ² /g (a)	362	401	418
Total pore volume, cc/g (b)	0.51	0.58	0.55
<u>Pore size distribution by N₂ Adsorption (b)</u>			
30 Å-, %	8.6	6.7	11.4
30 - 60 Å, %	55.5	63.4	54.7
60 - 100 Å, %	32.9	28.5	25.2
100 - 200 Å, %	1.4	0.9	6.3
200 - 300 Å+, %	0.4	0.2	1.0
300 Å+, %	1.2	0.3	1.4
Mean Pore Diameter, Å	69	62	71
Na, wt%	<0.05	<0.05	<0.05
Surface Si/Al atomic ratio, by XPS	0.98	0.72	1.07
Bulk Si/Al atomic ratio, by elemental anal.	1.03	0.98	1.03
Surface to Bulk Si/Al Ratio	0.95	0.73	1.04
% crystalline alumina phase, by XRD	0 %	9%	0 %
<u>nC₈ + iC₈ Model Compound Testing (b)</u>			
Total conversion, wt%	8.2	9.1	11.3
nC ₈ conversion, wt%	1.0	0.9	1.3
iC ₈ conversion, wt%	15.4	17.3	21.3

14 (a): BET measurements after activation at 1000 °F for 1 hr.

15 (b): determined after activation at 1000 °F for 1 hr.

1 **Example 3:** Preparation of NiW Hydrocracking Catalyst with Homogeneous
2 Cogel Silica-Alumina (Catalyst A – base-case)

3

4 A base-case hydrocracking catalyst containing homogeneous silica-alumina
5 sample #1 from Table 2 was prepared per following procedure.

6 75 parts silica-alumina powder #1 (synthesized per patent application XXXX)

7 and 25 parts crystalline alumina powder (obtained from Vista) were mixed

8 well. To the mix, diluted HNO₃ acid and sufficient amount of deionized water

9 were added to form an extrudable paste (3 wt% HNO₃ to the total powders).

10 These weights are on 100% solids basis. The paste was extruded in

11 1/16" cylinder, and dried at 250 °F overnight. The dried extrudates were

12 calcined at 1100 °F for 1 hour with purging excess dry air, and cooled down to

13 room temperature.

14

15 Impregnation of Ni and W was done using a solution containing ammonium

16 metatungstate and nickel nitrate to the target metal loadings of 4 wt% NiO and

17 28 wt% WO₃ in the finished catalyst. The total volume of the solution matched

18 the 100% water pore volume of the base extrudate sample (incipient wetness

19 method). The metal solution was added to the base extrudates gradually while

20 tumbling the extrudates. When the solution addition was complete, the soaked

21 extrudates were aged for 2 hours. Then the extrudates were dried at 250 °F

22 overnight. The dried extrudates were calcined at 935 °F for 1 hour with

23 purging excess dry air, and cooled down to room temperature. This catalyst is

24 named Catalyst A and its physical properties are summarized in Table 4.

25

26 **Example 4:** Preparation of NiW USY Hydrocracking Catalysts (Catalyst B)

27

28 Catalyst B, a NiW USY catalyst useful for this invention containing USY #1

29 from Table 1 and silica-alumina #2 from Table 2 was prepared per following

30 procedure. 10 parts USY, 65 parts silica-alumina powder and 25 parts

31 pseudoboehmite alumina powder were mixed well. To the mix, diluted HNO₃

32 acid and sufficient amount of deionized water were added to form an

33 extrudable paste (3 wt% HNO₃ to the total powders). These weights are on

1 100% solids basis. The paste was extruded in 1/16" cylinder, and dried at 250
2 °F overnight. The dried extrudates were calcined at 1100 °F for 1 hour with
3 purging excess dry air, and cooled down to room temperature.

4
5 Impregnation of Ni and W was done using a solution containing ammonium
6 metatungstate and nickel nitrate to the target metal loadings of 4 wt% NiO and
7 28 wt% WO₃ in the finished catalyst. The total volume of the solution matched
8 the 100% water pore volume of the base extrudate sample (incipient wetness
9 method). The metal solution was added to the base extrudates gradually while
10 tumbling the extrudates. When the solution addition was complete, the soaked
11 extrudates were aged for 2 hours. Then the extrudates were dried at 250 °F
12 overnight. The dried extrudates were calcined at 935 °F for 1 hour with
13 purging excess dry air, and cooled down to room temperature. This catalyst is
14 named Catalyst B and its physical properties are summarized in Table 4.

15
16 **Example 5:** Preparation of Hydrocracking Catalysts with Various USY and
17 Silica-Alumina Samples (Catalysts C, D and E)

18
19 Catalyst C, a NiW catalyst useful for this invention containing USY, was
20 prepared using a procedure similar to Catalyst B. For Catalyst C, 3 parts
21 USY #1 from Table 1, 72 parts silica-alumina #3 from Table 2 and 25 parts
22 pseudoboehmite alumina powder were used to prepare the base extrudates.
23 Then Ni and W were loaded via impregnation as described in the Example 5.
24 The target metal loadings were 4 wt% NiO and 28 wt% WO₃. Physical
25 properties of Catalyst C are summarized in Table 4.

26
27 Catalyst D, a noble metal USY catalyst useful for this invention, was prepared
28 from the same H-form extrudate base as the Catalyst C. Impregnation of
29 Pt and Pd was done using a solution containing platinum tetraammine nitrate
30 and palladium tetraammine nitrate to the target metal loadings of 0.2 wt%
31 Pt and 0.15 wt% Pd in the finished catalyst. The total volume of the solution
32 matched the 100% water pore volume of the base extrudate sample
33 (incipient wetness method). The metal solution was added to the base

extrudates gradually while tumbling the extrudates. When the solution addition was complete, the soaked extrudates were aged for 2 hours. Then the extrudates were dried at 250 °F overnight. The dried extrudates were calcined at 750 °F for 1 hour with purging excess dry air, and cooled down to room temperature.

Catalyst E, a NiW catalyst useful for this invention containing USY #2 and homogeneous silica-alumina with properties described in Table 2, was prepared using a procedure nearly identical to Catalyst C.

Feedstock for Catalyst Performance Evaluation

A petroleum feedstock with the following properties was used to evaluate the catalysts.

Table 3
Feedstock Properties

Properties	
API Gravity	33.7
Sulfur, ppm wt	7
Nitrogen, ppm wt	0.7
D2887 Simdis, °F	
Start Point	645
10 wt%	707
30 wt%	769
50 wt%	826
70 wt%	890
90 wt%	977
End Point	1079

Example 6: Comparison of Catalyst Performance for Distillate Production in a Single-Pass Mode (Catalyst A vs. B, C, and D)

Catalysts of our invention (Catalysts B through D) were compared in a single-pass micro unit with a reference catalyst, Catalyst A. Catalyst A was made with the homogeneous silica-alumina from Table 2 and Al₂O₃ binding material, and no zeolite was added to the base formulation. Catalysts B, C,

1 and D contain 2-7 wt% highly dealuminated USY zeolite in the finished
 2 catalysts. Catalysts A, B, and C contain the Group VI and VIII base metals
 3 (Ni and W), and Catalyst D contains Group VIII noble metals (Pd and Pt).
 4
 5 Micro unit evaluation of catalysts was done in a once-through, down-flow
 6 micro unit with 6 cc of 24/40 (US) meshed catalyst. Process conditions were
 7 approximately 2000 psig reactor pressure, a feed rate of 1.5 hr⁻¹ LHSV and
 8 once-through H₂ flow rate corresponding 5000 SCF of H₂/ bbl of oil. The
 9 catalyst bed temperature was varied to cover 60-80 wt% of conversion of the
 10 700 °F⁺ feed to 700 °F⁻ product. The yields of C₄⁻ gas, naphtha, light and
 11 heavy-distillate components were calculated using D2887 Simdis analysis
 12 results. The overall yields and reactor temperature data were interpolated to
 13 70 wt% conversion and summarized in Table 4.

14
 15 **Table 4**
 16 **Catalyst Properties and Performance**

	<i>Catalyst A Non-Invention</i>	<i>Catalyst B Invention</i>	<i>Catalyst C Invention</i>	<i>Catalyst D Invention</i>
<u>Composition (before metals addition)</u>				
USY	No USY	10% USY	3% USY	3% USY
Silica-Alumina	80% Cogel #1	65% Cogel #2	72% Cogel #3	72% Cogel #3
Al ₂ O ₃ Binder	20%	25%	25%	25%
<u>Properties after Metals Addition</u>				
Metal #1, wt%	3.9% Ni	3.1% Ni	3.0% Ni	0.2% Pt
Metal #2, wt%	18.7% W	20.6% W	19.9% W	0.15% Pd
Surface area, m ² /g	182	217	168	280
<u>Catalyst Performance in Single-Pass Micro Unit</u>				
Activity, F for 70% Conv. of 700 °F ⁺	717	705	712	683
<u>No-Loss Yields @ 70% Conv., wt%</u>				
C ₄ - Gas	2.9	3.0	3.3	2.7
Naphtha (C ₅ - 250 °F)	12.8	13.1	12.4	11.7
Light-Distillate (250 - 550 °F)	37.2	39.1	38.1	39.2
Heavy-Distillate (550 - 700 °F)	21.1	18.9	20.3	20.5
Total Distillate (250 - 700 °F)	58.3	58.0	58.4	59.7
<u>Accelerated Fouling Test</u>				
Fouling rate, °F/ 1000 hrs	43	15	9	-

17

1 Our catalysts of invention (Catalysts B and C) showed improvement of
2 catalyst activity by 5-12 °F relative to the cogel catalyst. Compared to Catalyst
3 A (the base case), our catalysts maintained the total distillate yield while
4 showing improved activity. By adjusting the zeolite content, the fractional
5 yields of light- and heavy-distillate can be varied to the desirable level (for jet
6 production vs. diesel production). A noble metal catalyst of our invention
7 (Catalyst D) showed further improvement in the catalyst activity and the total
8 distillate yield over the reference and corresponding base metal catalysts.

9
10 The stabilities of the catalysts were compared in a sing-pass micro unit at
11 accelerated fouling conditions (50% increase of oil flow rate and 25%
12 reduction in reactor pressure). The stability data were calculated using the
13 reactor temperature change required to maintain a 70% conversion per
14 1000 hours of stream time. The catalyst of our invention shows superior aging
15 characteristics in that it deactivated only at 1/4 - 1/3 the rate of the cogel
16 catalyst.

17
18 To summarize, our catalysts of invention showed that combination of a small
19 amount of highly dealuminated USY zeolite and homogeneous cogel
20 silica-alumina in a hydrocracking catalyst generated unexpected
21 benefits: (1) the catalyst activity is improved significantly, (2) the total distillate
22 yield is maintained with the broad range of USY addition, (3) the respective
23 yields of light-distillate vs. heavy-distillate can be adjusted with the
24 USY content, and (4) the catalyst become much more stable and showed
25 significantly lower fouling rates.

26
27 **Example 7:** Comparison of Catalyst Performance for Max Distillate Production
28 (Cogel Catalyst vs. Catalyst B)

29
30 Catalyst B of our invention was compared with Catalyst F, which is the
31 state-of-the-art cogel catalyst for a hydrocracking process in a recycle pilot
32 unit.

33

1 Recycling pilot unit evaluations were done with 130 cc of extrudate catalyst by
2 recycling unconverted 700 °F bottom and H₂ gas. Fresh feed was added to
3 the recycled feed and the feed rate was adjusted to maintain 60 vol%
4 pre-pass conversions. Fresh make-up H₂ gas was added to the recycled
5 H₂ gas stream to maintain 5000 SCF/bbl of recycled gas flow. Process
6 conditions were:

7

8 Pressure: 2300 psig total reactor pressure

9 LHSV: 1.0 hr⁻¹

10 Recycle H₂: 5000 SCF/ bbl

11

12 The yields of C₄⁺ gas, naphtha, light- and heavy-distillate components were
13 calculated using D2887 Simdis analysis results. The overall yields and reactor
14 temperature data were summarized in Table 5.

Table 5
Physical Properties and Performance of Catalysts for Distillate Production

	<i>Catalyst F</i> <i>State-of-the Art</i> <i>Cogel Catalyst</i> <i>Non-Invention</i>	<i>Catalyst B</i> <i>Invention</i>
<u>Composition (before metals addition)</u>		
USY	No USY	10% USY
Silica-Alumina	-	65% Cogel
Al ₂ O ₃ Binder	No binder	25%
<u>Properties after Metals Addition</u>		
Ni, wt%	7.7	3.1
W, wt%	18.2	20.6
Surface area, m ² /g	289	217
<u>Catalyst Performance in Recycle Pilot Unit</u>		
Activity, Catalyst Average Temp °F+	681	677
<u>No-Loss Yields</u>		
C ₄ ⁻ Gas, wt%	4.8	3.0
Naphtha (C ₅ – 250 °F), vol%	20.9	20.2
Light-Distillate (250 – 550 °F), vol%	50.4	55.1
Heavy-Distillate (550 – 700 °F), vol%	35.8	33.8
Total Distillate (250F – 700 °F), vol%	86.5	88.9
<u>Product Properties of Light-Distillate</u>		
Smoke Point, mm	40	43
Freeze Point, °C	-61	-59
Cetane Number	51.5	53
<u>Product Properties of Heavy-Distillate</u>		
Cetane Number	71	74

Our catalyst of invention (Catalyst B) shows performance exceeding that of the state-of-the-art cogel catalyst (Catalyst F). Our catalyst shows advantage in that Catalyst B has comparable or better activity, makes substantially less undesirable light-gas and naphtha, and produces more distillate fraction. Catalyst B exhibited over 2 vol% advantage in the total distillate yield where the improvement is mainly in the light distillate fraction. By lowering the USY zeolite content further, we expect the distillate distribution is shifted toward the heavier fraction.

1 The overall product properties with the catalysts of our invention are
2 comparable or better than those of the cogel catalyst. The catalyst of our
3 invention produces distillate with improved Cetane Numbers. Other properties
4 of the distillate products such as the Smoke Point, Freeze Point, and Cloud
5 Point were comparable.

6
7 The catalyst of our invention is good at maintaining the heavy-distillate with
8 550 - 700 °F boiling point range (over 70 cetane). Since the cetane number of
9 this fraction is much higher than that of the light-distillate with 250 – 550 °F
10 boiling point range (around 50 cetane), it is desirable to maximize the
11 heavy-distillate contribution to the combined distillate pool.

12
13 To summarize, our catalyst produced improved quality distillate products in
14 high yields while having advantages of zeolite containing hydrocracking
15 catalysts.

16
17 While we do not want to be bound by the theory, the performance advantage
18 of our catalyst appears to come from enhancement of isomerization activity of
19 the catalyst by adding a small amount of highly dealuminated USY. Typically
20 addition of USY zeolite to the distillate-selective amorphous hydrocracking
21 catalyst causes unwanted overcracking toward naphtha. In our catalyst
22 system, we were able to suppress the unwanted overcracking by USY and
23 able to obtain synergistic performance advantage of homogeneous cogel
24 silica-alumina and extremely low acidity of USY.

25
26 **Example 8:** Comparison of Catalyst Performance for Unconverted Oil
27 (Bottoms) Properties for Lubricating Oil Production (Cogel Catalyst vs. and
28 Catalyst E)

29
30 The per-pass conversion of the recycle pilot unit evaluation in Example 7 was
31 changed to 40 vol%, and 40 wt% of the unconverted oil (700 °F⁺ fraction) was
32 drained. Then product properties were evaluated to examine the potential of
33 this process for lubricating oil base stock production.

Table 6

Performance of Catalysts for Lube Base Stock Production

	<i>Catalyst F</i> <i>State-of-the Art</i> <i>Cogel Catalyst</i> <i>Non-Invention</i>	<i>Catalyst E</i> <i>Invention</i>
<u>Unconverted Oil (700°F+), As-Produced</u>		
API Gravity at 60/60	37.4	37.2
Viscosity Index	136	145
<u>Solvent Dewaxed Oil</u>		
Viscosity Index	131	133

The Viscosity Index (waxy VI) of the unconverted oil from the catalyst of our invention showed substantially higher value than that from the cogel catalyst. It was completely unexpected that the zeolite containing hydrocracking catalyst produced 700 °F+ bottoms with higher waxy VI than the amorphous catalyst. The fractions were subjected to MEK/toluene dewaxing step to provide the finished lubricating oil base stock products. The improved VI with our catalyst was maintained after the solvent dewaxing.

While this example included the solvent dewaxing step to produce the finished lubricating oil base stock, it is preferable to perform catalytic dewaxing to generate high quality lube base stock.

The following Examples are illustrative of the present invention, but are not intended to limit the invention in any way beyond what is contained in the claims which follow.

1 WHAT IS CLAIMED IS:

2

- 3 1. A process for converting hydrocarbonaceous oils into products of lower
4 average molecular weight and lower average boiling point comprising
5 contacting said hydrocarbonaceous oils under hydrocracking
6 conditions with a catalyst comprising (1) a minor amount of a low
7 acidity, highly dealuminated ultrastable Y zeolite having an Alpha value
8 of less than about 5 and Broensted acidity of from about 1 to about 20
9 micromole/g measured by FT-IR, (2) a homogeneous, amorphous
10 silica-alumina cracking component having an SB ratio of from about 0.7
11 to about 1.3, wherein a crystalline alumina phase is present in an
12 amount of no greater than about 10% and (3) a catalytic amount of
13 hydrogenation component selected from the group consisting of a
14 Group VI metal, a Group VIII metal, and mixtures thereof.
- 15
- 16 2. A process according to claim 1, wherein the catalyst composition
17 comprises from about 0.5 to about 30 wt% of the ultrastable Y zeolite.
- 18
- 19 3. A process according to claim 1, wherein the catalyst composition
20 comprises from about 1 to about 20 wt% of the ultrastable Y zeolite.
- 21
- 22 4. A process according to claim 1, wherein the catalyst further comprises
23 an inorganic oxide binder.
- 24
- 25 5. A process according to claim 1, wherein the homogeneous
26 silica-alumina cracking component is highly homogeneous having an
27 SB silica to alumina ratio of from about 0.9 to about 1.1 and a
28 crystalline alumina phase present in an amount no more than about
29 5%.
- 30
- 31 6. A process according to claim 5, wherein the homogeneous
32 silica-alumina cracking component has an SB ratio of about 1.0.
- 33

- 1 7. A process according to claim 4, wherein the catalyst comprises from
2 about 0.5% to 30% by weight of ultrastable Y zeolite, from about 10%
3 to 80% by weight of amorphous cracking component, and from about
4 10% to 30% by weight of a binder.
5
- 6 8. A process according to claim 1, wherein the Group VIII metal
7 hydrogenation component is selected from the group consisting of
8 nickel, cobalt, platinum, palladium and mixtures thereof and wherein
9 the Group VI metal hydrogenation component is selected from the
10 group consisting of molybdenum, tungsten and mixtures thereof.
11
- 12 9. A process according to claim 8, wherein the hydrogenation component
13 comprises from about 2% to about 8% by weight of nickel and from
14 about 8% to about 30% by weight of tungsten, calculated as
15 metals per 100 parts by weight of total catalyst.
16
- 17 10. A process according to claim 8, wherein the hydrogenation component
18 comprises from 0.2% to about 2% by weight of platinum, or from about
19 0.2% to about 2% by weight of palladium, or a combination of from
20 0.2% to about 2% by weight of platinum and palladium, calculated as
21 metals per 100 parts by weight of total catalyst.
22
- 23 11. A process for producing high quality distillate with increased yield of
24 heavy distillate from heavy gas oils comprising contacting a heavy gas
25 oil under hydrocracking conditions with a catalyst comprising (1) a
26 minor amount of a low acidity, highly dealuminated ultrastable Y zeolite
27 having an Alpha value of less than about 5, and Broensted acidity of
28 from about 1 to about 20 micromole/g measured by FT-IR, (2) a
29 homogeneous, amorphous silica-alumina cracking component having
30 an SB ratio of from about 0.7 to about 1.3, wherein a crystalline
31 alumina phase is present in an amount of no greater than about
32 10% and (3) a catalytic amount of hydrogenation component selected

- 1 from the group consisting of a Group VI metal, a Group VIII metal, and
2 mixtures thereof.
3
- 4 12. A process according to claim 11, wherein the catalyst composition
5 comprises from about 0.5 to about 30 wt% of the ultrastable Y zeolite.
6
- 7 13. A process according to claim 11, wherein the catalyst composition
8 comprises from about 1 to about 20 wt% of the ultrastable Y zeolite.
9
- 10 14. A process according to claim 11, wherein the catalyst further comprises
11 an inorganic oxide binder.
12
- 13 15. A process according to claim 11, wherein the homogeneous
14 silica-alumina cracking component is highly homogeneous having an
15 SB silica to alumina ratio of from about 0.9 to about 1.1 and a
16 crystalline alumina phase present in an amount no more than about
17 5%.
18
- 19 16. A process according to claim 15, wherein the homogeneous
20 silica-alumina cracking component has an SB ratio of about 1.0.
21
- 22 17. A process according to claim 14, wherein the catalyst comprises from
23 about 0.5% to 30% by weight of ultrastable Y zeolite, from about 10%
24 to 80% by weight of amorphous cracking component, and from about
25 10% to 30% by weight of a binder.
26
- 27 18. A process according to claim 11, wherein the Group VIII metal
28 hydrogenation component is selected from the group consisting of
29 nickel, cobalt, platinum, palladium and mixtures thereof and wherein
30 the Group VI metal hydrogenation component is selected from the
31 group consisting of molybdenum, tungsten and mixtures thereof.
32

- 1 19. A process according to claim 18, wherein the hydrogenation
2 component comprises from 2% to about 8% by weight of nickel and
3 from about 8% to about 30% by weight of tungsten, calculated as
4 metals per 100 parts by weight of total catalyst.
5
- 6 20. A process according to claim 18, wherein the hydrogenation
7 component comprises from 0.2% to about 2% by weight of platinum, or
8 from about 0.2% to about 2% by weight of palladium, or a combination
9 of from 0.2% to about 2% by weight of platinum and palladium,
10 calculated as metals per 100 parts by weight of total catalyst.
11
- 12 21. A hydrocracking catalyst composition comprising (1) a minor amount of
13 a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha
14 value of less than about 5 and Broensted acidity of from about 1 to
15 about 20 micromole/g, (2) a homogeneous, amorphous silica-alumina
16 cracking component having an SB ratio of from about 0.7 to about 1.3,
17 wherein a crystalline alumina phase is present in an amount of no
18 greater than about 10% and (3) a catalytic amount of hydrogenation
19 component selected from the group consisting of a Group VI metal, a
20 Group VIII metal, and mixtures thereof.
21
- 22 22. A composition according to claim 21, wherein the catalyst comprises
23 from about 0.5 to about 30 wt% of the ultrastable Y zeolite.
24
- 25 23. A composition according to claim 21, wherein the catalyst comprises
26 from about 1 to about 20 wt% of the ultrastable Y zeolite.
27
- 28 24. A composition according to claim 21, wherein the catalyst further
29 comprises an inorganic oxide binder.
30
- 31 25. A composition according to claim 21, wherein the homogeneous
32 silica-alumina cracking component is highly homogeneous having an
33 SB silica to alumina ratio of from about 0.9 to about 1.1 and a

- 1 crystalline crystalline alumina phase present in an amount no more
2 than about 5%.
3
- 4 26. A composition according to claim 25, wherein the homogeneous
5 silica-alumina cracking component has an SB ratio of about 1.0.
6
- 7 27. A composition according to claim 21, wherein the catalyst comprises
8 from about 0.5% to 30% by weight of ultrastable Y zeolite, from about
9 10% to 80% by weight of amorphous cracking component, and from
10 about 10% to 30% by weight of a binder.
11
- 12 28. A composition according to claim 21, wherein the Group VIII metal
13 hydrogenation component is selected from the group consisting of
14 nickel, cobalt, platinum, palladium and mixtures thereof and wherein
15 the Group VI metal hydrogenation component is selected from the
16 group consisting of molybdenum, tungsten and mixtures thereof.
17
- 18 29. A composition according to claim 28, wherein the hydrogenation
19 component comprises from 2% to about 8% by weight of nickel and
20 from about 8% to about 30% by weight of tungsten, calculated as
21 metals per 100 parts by weight of total catalyst.
22
- 23 30. A composition according to claim 28, wherein the hydrogenation
24 component comprises from 0.2% to about 2% by weight of platinum, or
25 from about 0.2% to about 2% by weight of palladium, or a combination
26 of from 0.2% to about 2% by weight of platinum and palladium,
27 calculated as metals per 100 parts by weight of total catalyst.
28
- 29 31. A process for producing a lubricating oil base stock which comprises:
30 (a) contacting a feedstock under hydrocracking conditions with a
31 catalyst comprising a minor amount of a low acidity, highly
32 dealuminated ultrastable Y zeolite having an Alpha value of less
33 than about 5 and Broensted acidity of from about 1 to about 10

- 1 micromole/g, a homogeneous, amorphous silica-alumina
2 cracking component having an SB ratio of from about 0.7 to
3 about 1.3, wherein a crystalline alumina phase is present in an
4 amount of no greater than about 10% and a catalytic amount of
5 hydrogenation component selected from the group consisting of
6 a Group VI metal, a Group VIII metal, and mixtures thereof; and
7
8 (b) processing the hydrocracked product to provide a lubricating oil
9 base stock.