

1 **EXTREMELY LOW ACIDITY ULTRASTABLE**
2 **Y ZEOLITE CATALYST COMPOSITION AND PROCESS**

3
4 FIELD OF THE INVENTION

5
6 The present invention relates to catalysts and processes using the catalysts
7 for converting hydrocarbonaceous oils to products of an average lower
8 molecular weight and an average lower boiling point.

9
10 BACKGROUND OF THE INVENTION

11
12 Of the many hydroconversion processes known in the art, hydrocracking is
13 becoming increasingly important since it offers product flexibility together with
14 product quality. Because it is also possible to subject rather heavy feedstocks
15 to hydrocracking, it will be clear that much attention has been devoted to the
16 development of hydrocracking catalysts.

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

28
29 An early synthetic zeolite Y was described in U.S. Patent No. 3,130,007
30 issued April 21, 1964, which is incorporated herein by reference. A number of
31 modifications have been reported for this material, one of which is ultrastable
32 Y zeolite as described in U.S. Patent No. 3,536,605 issued October 27, 1970,

1 which is incorporated herein by reference. Zeolite Y has been constantly
2 improved by techniques like ammonium ion exchange and acid extraction,
3 and various forms of calcination in order to improve the performance of the
4 hydrocracking catalysts.

5

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

14

15 U.S. Patent No. 3,897,327 to Ward, which is incorporated herein by reference,
16 describes a hydrocracking process using a Y zeolite wherein the Y zeolite has
17 a preliminary ammonium ion exchange to replace most of the sodium ion with
18 ammonium ions. This product is then calcined in the presence of at least
19 0.2 psi of water vapor for a sufficient time to reduce the cell size to a range
20 between 24.40-24.64 Å. The patent teaches that the catalyst has increased
21 hydrothermal stability by maintaining crystallinity and surface area after
22 calcination, exposure to water vapor or water vapor at high temperatures.

23

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

1 U.S. Patent No. 3,853,747 to Young, which is incorporated herein by
2 reference, teaches that hydrocracking activity of the catalyst is greater when
3 the hydrogenating component is incorporated in the zeolite in such a manner
4 as to avoid impregnation into the inner adsorption area of the zeolite
5 crystallites or particles. For example, the mixing may consist of stirring,
6 mulling, grinding, or any conventional procedure for obtaining an intimate
7 mixture of solid material. The dispersion of the Group VIB metal
8 hydrogenation component is achieved by adding it to the zeolite in a finely
9 divided but essentially undissolved form. The patent teaches that in some
10 cases the soluble molybdenum or tungsten compounds added to the zeolite
11 by impregnation tends to destroy the zeolite crystal structure and acidity
12 during the subsequent drying and calcination steps. Young teaches, however,
13 that the particle size should range from 0.5 microns to 5 microns.

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

22
23 U.S. Patent No. 4,419,271 to Ward, which is incorporated herein by reference,
24 discloses a composition matter useful as a catalyst base for supporting active
25 hydrogenation metal components or for catalyzing acid catalyzed hydrocarbon
26 conversion reactions comprising in intimate heterogeneous mixture
27 (1) a modified hydrogen crystalline aluminosilicate Y zeolite having activity for
28 catalytically cracking hydrocarbons and having a unit cell size between
29 24.25-24.35 Å and a water absorption capacity, at 4.6 mm water vapor partial
30 pressure and 25 °C, less than 8% by weight of zeolite and (2) a dispersion of
31 silica-alumina in a gamma alumina matrix.

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

4

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

8

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

13

14 GB-A-2,014,970 discloses an ultrahydrophobic zeolite Y which has been
15 given a unit cell size dimension of 24.20-24.45 Å by two ammonium exchange
16 steps with an intermediate calcinations step at 550°-800 °C in steam.

17 EP-B-0,028,938 discloses the use of such a modified zeolite for selective
18 conversion of hydrocarbons boiling above 371 °C into midbarrel fuel products
19 having a distillation range of 149°-371 °C. Improved manufacturing process
20 for producing 24.25-24.35 Å unit cell size Zeolite Y was disclosed in

21 U.S. Patent No. 5,059,567 to Linsten et al.

22

23

SUMMARY OF THE INVENTION

24

25 In a first aspect, there is provided a process for converting hydrocarbonaceous
26 oils into products of lower average molecular weight and lower average boiling
27 point comprising contacting said hydrocarbonaceous oils under hydrocracking
28 conditions with a catalyst comprising a low acidity, highly dealuminated
29 ultrastable Y zeolite having an Alpha value of less than about 5 and Brønsted
30 acidity of from about 1 to about 20 micromole/g measured by FT-IR, an
31 amorphous cracking component and a catalytic amount of hydrogenation
32 component selected from the group consisting of a Group VI metal, a Group

VIII metal, and mixtures thereof.

In a second aspect, there is provided 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 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, an amorphous cracking component and a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

In a third aspect, there is provided a hydrocracking catalyst composition comprising a low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5 and from about 1 to about 20 micromole/g of Broensted acidity measured by FT-IR, an amorphous cracking component and a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

In a fourth aspect, there is provided a process for producing a lubricating oil base stock which comprises: (a) contacting a feedstock under hydrocracking conditions with a catalyst comprising 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, an amorphous cracking component and a catalytic amount of hydrogenation component selected from the group consisting of a Group VI metal, a Group VIII metal, and mixtures thereof; (b) and processing the hydrocracked product to provide a lubricating oil base stock.

An embodiment 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 low acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less than about 5, preferably less than about 3, and having Broensted acidity measured by FT-IR of from about 1 to about 20, preferably about 1-10 micromole/g, (2) an amorphous cracking component and (3) a catalytic

1 amount of hydrogenation component selected from the group consisting of a
2 Group VI metal, a Group VIII metal, and mixtures thereof.

3

4 Another embodiment provides a process for producing high
5 quality distillate with increased yield of heavy distillate from heavy gas oils
6 comprising contacting a heavy gas oil under hydrocracking conditions with a
7 catalyst comprising a low acidity, highly dealuminated ultrastable Y zeolite
8 having an Alpha value of less than about 5 and Broensted acidity of from
9 about 1 to about 20, preferably about 1-10 micromole/g, an amorphous
10 cracking component and a catalytic amount of hydrogenation component
11 selected from the group consisting of a Group VI metal, a Group VIII metal,
12 and mixtures thereof.

13

14 Disclosed herein is a process for producing high quality
15 lubricating oil base stock from heavy gas oils comprising contacting a
16 feedstock under hydrocracking conditions with a catalyst comprising a low
17 acidity, highly dealuminated ultrastable Y zeolite having an Alpha value of less
18 than about 5 and Broensted acidity of from about 1 to about 20 micromole/g,
19 an amorphous cracking component and a catalytic amount of hydrogenation
20 component selected from the group consisting of a Group VI metal, a
21 Group VIII metal, and mixtures thereof and processing the hydrocracked
22 product to provide a lubricating oil base stock.

23

24 Another embodiment provides a hydrocracking catalyst
25 composition comprising a low acidity, highly dealuminated ultrastable
26 Y zeolite having an Alpha value of less than about 5 and Broensted acidity of
27 from about 1 to about 20, preferably about 1-10 micromole/g, an amorphous
28 cracking component and a catalytic amount of hydrogenation component
29 selected from the group consisting of a Group VI metal, a Group VIII metal,
30 and mixtures thereof.

31

1 It has now been found, among other things, that the presence of a low acidity,
2 highly dealuminated ultrastable Y zeolite having an Alpha value of less than
3 about 5 and Broensted acidity of from about 1 to about 20, preferably from
4 about 1-10 micromole/g, together with an amorphous cracking component
5 and a catalytic amount of hydrogenation component selected from the group
6 consisting of a Group VI metal, a Group VIII metal, and mixtures thereof when
7 used in hydrocracking a heavy gas oil can result in an unexpected high selectivity
8 to heavy distillate.

1 DESCRIPTION OF THE PREFERRED EMBODIMENTS

2

3 In accordance with the one embodiment of the present invention, the catalyst
4 comprises a low acidity, highly dealuminated ultrastable Y zeolite having an
5 Alpha value of less than about 5 and Broensted acidity of from about 1 to
6 about 20, preferably about 1-10 micromole/g, an amorphous cracking
7 component and a catalytic amount of hydrogenation component selected from
8 the group consisting of a Group VI metal, a Group VIII metal, and mixtures
9 thereof.

10

11 The amount of highly dealuminated USY zeolite in the catalyst compositions
12 in accordance with the present invention on a finished catalyst basis including
13 metals ranges from about 1-70% by weight, preferably, from about 1.5-50%
14 and most preferably from about 2-20%.

15

16 Highly dealuminated USY zeolites having a silica-to-alumina molar ratio in the
17 bulk composition greater than 50 are useful as the zeolite component of the
18 catalyst compositions according to the present invention. Preference is given
19 to USY zeolites having a silica: alumina molar ratio greater 60, and most
20 preferably having silica: alumina molar ratio greater than 80.

21

22 Due to extremely low acidity of these USY, the hydrocracking catalysts of the
23 present invention require the addition of a secondary amorphous cracking
24 component. Consequently, the catalysts of the present invention also include
25 an amorphous cracking component. Preferably, silica-alumina based
26 amorphous cracking components are used. However, other amorphous
27 cracking components that are well known in the art can be used. These
28 include, but are not limited to, magnesia, zirconia, titania, silica, and alumina.
29 Silica-alumina is the preferred amorphous cracking component. The most
30 preferred amorphous cracking component is a silica-alumina composition
31 described in commonly assigned U.S. Patent Application No. XX/XXX,XXX,
32 titled "Highly Homogenous Amorphous Silica-Alumina Catalyst Composition",

1 filed concurrently herewith and incorporated by reference herein. By
2 combining an amorphous cracking component and a low acidity, highly
3 dealuminated ultrastable Y zeolite having an Alpha value of less than about
4 5 and Broensted acidity of from about 1 to about 20 micromole/g, we were
5 able to produce unique catalysts with desirable product selectivity, activity,
6 and stability.

7

8 The amount of amorphous cracking component in the catalyst compositions in
9 accordance with the present invention on a finished catalyst basis including
10 metals, ranges from about 10%-80% by weight, preferably from about
11 30%-70% by weight and most preferably from about 40%-60%. The amount
12 of silica in the silica-alumina ranges from about 10%-70% by weight.
13 Preferably, the amount of silica in the silica-alumina ranges from about
14 20%-60% by weight, and most preferably the amount of silica in the silica-
15 alumina ranges from about 25%-50% by weight.

16

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

24

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

1 The amount(s) of hydrogenation component(s) in the catalyst compositions
2 suitably range from about 0.2% to about 10% by weight of Group VIII metal
3 component(s) and from about 5% to about 30% by weight of Group VI metal
4 component(s), calculated as metal(s) per 100 parts by weight of total catalyst.
5 The hydrogenation components in the catalyst compositions may be in the
6 oxidic and/or the sulphidic form. If a combination of at least a Group VI and a
7 Group VIII metal component is present as (mixed) oxides, it will be subjected
8 to a sulphiding treatment prior to proper use in hydrocracking.

9
10 Preferred catalyst compositions in accordance with the present invention
11 comprise from about 1%-10% by weight of nickel and from about 5%-40% by
12 weight tungsten. Preferably, the catalyst compositions in accordance with the
13 present invention comprise from about 2%-8% by weight of nickel and from
14 about 8%-30% by weight tungsten, calculated as metals per 100 parts by
15 weight of total catalyst.

16
17 It has been found that excellent and unexpected results in terms of
18 performance and activity are obtained using catalysts according to the present
19 invention. Some of these results include: the catalysts of the invention are
20 particularly good for producing more heavy-distillate with 550°-700 °F boiling
21 point range (over 70 cetane); catalysts of the invention show comparable or
22 lower gas-make than a reference catalyst; and catalysts of the invention
23 produce less naphtha during the hydrocracking process by suppressing
24 undesirable overcracking reactions.

25
26 In addition, the present invention provides for a process for converting
27 hydrocarbonaceous oils into products of lower average molecular weight and
28 lower average boiling point comprising contacting said hydrocarbonaceous
29 oils under hydrocracking conditions with a catalyst comprising a low acidity,
30 highly dealuminated ultrastable Y zeolite having an Alpha value of less than
31 about 5 and Broensted acidity measured by FT-IR of from about 1 to about 20
32 micromole/g, an amorphous cracking component and a catalytic amount of

1 hydrogenation component selected from the group consisting of a Group VI
2 metal, a Group VIII metal, and mixtures thereof.

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, an amorphous cracking component
10 and a catalytic amount of hydrogenation component selected from the group
11 consisting of a Group VI metal, a Group VIII metal, and mixtures thereof.

12

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

19

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

27

28 It may be desirable to subject part or all of the feedstock to one or more
29 (hydro) treatment steps prior to its use in the hydrocarbon conversion process
30 according to the present invention. It is often found convenient to subject the
31 feedstock to a (partial) hydrotreatment. When rather heavy feedstocks are to

1 be processed it will be advantageous to subject such feedstocks to a (hydro)
2 demetallization treatment.

3

4 Suitable hydrocracking conditions to be applied comprise temperatures
5 ranging from about 250 °C to about 500 °C, pressures up to about 300 bar
6 and space velocities from about 0.1 to about 10 kg feed per liter of
7 catalyst per hour (kg/l/h). Hydrogen gas to feed ratios range from about 100 to
8 about 5000 NI/kg feed (normal liters at standard temperature and
9 pressure per kilogram) can suitably be used.

10

11 Preferably, hydrocracking conditions to be applied comprise temperatures
12 ranging from about 300 °C to about 450 °C, pressures from about 25 bar to
13 about 200 bar and space velocities from about 0.2 to about 10 kg feed
14 per liter of catalyst per hour (kg/l/h). Hydrogen gas to feed ratios preferably
15 range from about 250 to about 2000 NI/kg are applied.

16

17 The present invention is also directed to a process for producing high quality
18 distillate and a feedstock for a lubricating oil base stock in increased yields
19 from heavy gas oils. The process includes a hydrocracking step employing a
20 catalyst composition comprising a severely dealuminated and stabilized Y
21 zeolite component according to the invention, a silica-alumina amorphous
22 cracking component, and a hydrogenation component.

23

24 A catalyst according to the present invention is particularly good for increasing
25 the yield of a heavy-distillate fraction with 550°-700 °F boiling point range. The
26 hydrocracked heavy-distillate fraction from vacuum gas oil typically exhibits
27 very high Cetane Numbers of 60-80, while a light-distillate fraction with 250°-
28 550 °F boiling point range exhibits Cetane Numbers of 40-55. In order to
29 achieve high a Cetane Number for the combined diesel fuel, it is desirable to
30 increase the heavy-distillate yield in the combined distillate pool. The
31 unconverted 700 °F fraction from our invention exhibits high viscosity index
32 indicating high quality lubricating oil base stock can be produced.

1
2 Use of powder X-ray diffraction (XRD) for characterization of USY is well
3 known per ASTM method D 3942-80. The unit cell size of the USY is inversely
4 correlated with the Al content in the USY. As USY become more
5 dealuminated, the unit cell size of USY is changing from 24.70 Å to 24.54 Å or
6 below. However, for severely dealuminated and ultrastabilized USY with bulk
7 $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio of over 50, the cracking activity of USY could not be
8 differentiated with the XRD unit cell size. Instead, FT-IR, and Alpha test
9 (a model compound test for activity measurement) were used to analyze the
10 activity of USY samples. Standard analysis tests such as bulk composition
11 analysis by ICP and surface area measurements were used to ensure the
12 quality of USY samples.
13
14 Transmission IR spectroscopy was used to compare the acidity
15 of USY samples per published methods elsewhere (T.R. Hughes,
16 H.M. White, J. Phys. Chem., 71, 2192, 1967; M.A. Makarova,
17 A. Garforth, V.L. Zholobenko, J. Dwyer, G.J. Earl, D. Rawlence,
18 Studies in Surface Science and Catalysis, 84, 365, 1994). Two methods
19 were employed: (1) measurement of the acidic OH stretching bands in the
20 3600 cm^{-1} region of the spectrum; and (2) adsorption of pyridine to determine
21 the Broensted to Lewis acid site concentrations. Self-supporting wafers
22 weighing about 10 mg were dehydrated in-situ by heating in flowing heat 5
23 °C/min to 400 °C and left at this temperature for 1 hour. The wafers were then
24 cooled to 150 °C and the IR spectrum was recorded. This spectrum was fitted
25 to obtain the intensities of the OH bands for the different acidic sites. Pyridine
26 was also used to measure acidity. Once the samples were dehydrated
27 according to the above method, the IR cell was isolated and then 4 μL
28 (microliter) of pyridine was injected. The pyridine was allowed to adsorb for
29 1 hour and then the cell was reopened to flowing He to allow desorption of the
30 physically adsorbed pyridine. Typically, desorption was allowed for
31 12-17 hours, then FT-IR spectra were obtained for the USY sample containing
32 residual chemisorbed pyridine. These spectra were then fitted in the pyridine

1 ring vibration and OH stretching regions to obtain the peak areas as a function
2 of desorption time. The final peak areas were obtained by extrapolating to
3 infinite desorption time.

4

5 It is plausible, other Broensted acidity measurement techniques such as
6 solid-state NMR and temperature programmed desorption with a base (e.g.,
7 NH_3 TPAD) could also be used, instead of FT-IR, to select the optimum range.

8

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

18

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

EXAMPLES

Examples 1 through 4: Comparison of USY Zeolite

Four USY zeolites were used for catalyst preparations. Properties of the USY zeolites are summarized as follows:

Table 1
USY Properties

	USY #1 Example 1 Non-invention	USY #2 Example 2 Invention	USY #3 Example 3 Invention	USY #4 Example 4 Invention
SiO ₂ /Al ₂ O ₃ molar ratio (bulk)	94	92	92	88
Na ₂ O, wt%	<0.05	<0.05	0.14	<0.05
Surface area, m ² /g	772	652	712	686
Micropore pore volume, cc/g	0.21	0.20	0.20	0.25
Total pore volume, cc/g	0.51	0.50	0.54	0.51
Unit cell size, Å	24.23	24.23	24.25	24.24
% Crystallinity	-	80	106	-
Alpha	9.1	1.0	2.4	1.1
Broensted acidity by FT-IR, (μmole/g)	80	3	8	9

All four USY zeolites are highly dealuminated and the bulk SiO₂/Al₂O₃ ratio of over 80. The unit cell size measured by powder X-ray diffraction cannot differentiate these USY samples, all show the unit cell size of 24.25 Å or less.

We found that Broensted acidity measurement by FT-IR and a model compound cracking testing using n-hexane can differentiate the USY samples. Desirable USY for distillate selective hydrocracking shows Alpha values of less than 5, and Broensted acidity of 1-20 micromole/g measured by FT-IR. Hydrocracking catalysts comprising this type of USY show significantly superior distillate selectivity over a catalyst made with USY with greater than 5 Alpha and greater than 40 micromole/g of Broensted acidity.

1 Example 5: Preparation of NiW USY Hydrocracking Catalyst

2 (Catalyst A – base-case)

3

4 A base-case hydrocracking catalyst containing the USY #1 from Table 1 was
5 prepared per following procedure. 10 parts USY, 70 parts silica-alumina
6 powder (Siral-40, obtained from SasolCondea) and 20 parts pseudoboehmite
7 alumina powder were mixed well. To the mix, diluted HNO_3 acid and sufficient
8 amount of deionized water were added to form an extrudable paste
9 (3 wt% HNO_3 to the total powders). These weights are on 100% solids basis.
10 The paste was extruded in 1/16" cylinder, and dried at 250 °F overnight. The
11 dried extrudates were calcined at 1100 °F for 1 hour with purging excess dry
12 air, and cooled down to room temperature.

13

14 Impregnation of Ni and W was done using a solution containing ammonium
15 metatungstate and nickel nitrate to the target metal loadings of 4 wt% NiO and
16 28 wt% WO_3 in the finished catalyst. The total volume of the solution matched
17 the 100% water pore volume of the base extrudate sample (incipient wetness
18 method). The metal solution was added to the base extrudates gradually while
19 tumbling the extrudates. When the solution addition was complete, the soaked
20 extrudates were aged for 2 hours. Then the extrudates were dried at 250 °F
21 overnight. The dried extrudates were calcined at 935 °F for 1 hour with
22 purging excess dry air, and cooled down to room temperature. This catalyst is
23 named Catalyst A and its physical properties are summarized in Table 3.

1 Example 6: Preparation of NiW Hydrocracking Catalysts with Various
2 USY samples (Catalysts B, C, E and F).

3

4 Catalyst B, a NiW catalyst useful for this invention containing USY #2, was
5 prepared using a procedure similar to Catalyst A. For Catalyst B, 10 parts
6 USY #2 from Table 1, 65 parts silica-alumina powder and 25 parts
7 pseudoboehmite alumina powder were used to prepare the base extrudates.
8 Other than the USY source, other ingredients were identical to the Catalyst A.
9 Then Ni and W were loaded via impregnation as described in the Example 5.
10 The target metal loadings were 4 wt% NiO and 28 wt% WO₃. Physical
11 properties of Catalyst B are summarized in Table 3.

12

13 Catalyst C, a NiW catalyst useful for this invention containing USY #3, was
14 prepared using a procedure nearly identical to Catalyst B. For Catalyst C,
15 USY #3 was used to prepare the base extrudates. Physical properties of
16 Catalyst B and C are summarized in Table 3. Physical properties of
17 Catalyst C are summarized in Table 3.

18

19 Catalyst E, a NiW catalyst useful for this invention containing USY #4, was
20 prepared using a procedure similar to Catalyst A. For Catalyst E, 20 parts
21 USY #4, 60 parts silica-alumina powder and 20 parts pseudoboehmite
22 alumina powder were used to prepare the base extrudates. Other than the
23 USY source, other ingredients were identical to the Catalyst A. Then Ni and W
24 were loaded via impregnation as described in the Example 5. Physical
25 properties of Catalyst E are summarized in Table 4.

26

27 Catalyst F, a NiW catalyst useful for this invention containing USY #4, was
28 prepared using a similar procedure. For Catalyst F, 6 parts USY #4, 69 parts
29 silica-alumina powder and 25 parts pseudoboehmite alumina powder were
30 used to prepare the base extrudates. Compared to Catalyst A-C, Catalyst F
31 was made with different silica-alumina which contains 25 wt% Al₂O₃. Then Ni

1 and W were loaded via impregnation as described in the Example 5. Physical
2 properties of Catalyst F are summarized in Table 4.

3

4 Feedstock for Catalyst Performance Evaluation

5

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

8

9

10

Table 2
Feedstock Properties

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

11

12

13 Example 7: Comparison of Catalyst Performance (Catalyst A vs. B and C)

14

15 Catalysts of the present invention (Catalysts B and C) were compared in a
16 single-pass micro unit with a reference catalyst, Catalyst A. Catalyst A was
17 prepared with a USY outside of our invention (USY #1). Catalysts B and C
18 were prepared with highly dealuminated USY #2 and #3, respectively.

19

20 Micro unit evaluation of catalysts was done in a once-through, down-flow
21 micro unit with 6 cc of 24/40 (US) meshed catalyst. Process conditions were
22 approximately 2000 psig reactor pressure, a feed rate of 1.5 hour⁻¹ LHSV and
23 once-through H₂ flow rate corresponding 5000 SCF of H₂/ bbl of oil. The
24 catalyst bed temperature was varied to cover 60-80 wt% of conversion of the
25 700 °F⁺ feed to 700 °F⁻ product. The yields of C₄⁻ gas, naphtha, light and
26 heavy-distillate components were calculated using D2887 Simdis analysis

1 results. The overall yields and reactor temperature data were interpolated to
 2 70 wt% conversion and summarized in Table 3.

3
 4 Table 3

5 Physical Properties and Performance of Catalysts

	Catalyst A Non-Invention	Catalyst B Invention	Catalyst C Invention
<u>Composition (before metals addition)</u>			
USY	10% USY #1	10% USY #2	10% USY #3
Silica-Alumina	70%	65%	65%
Al ₂ O ₃ Binder	20%	25%	25%
<u>Properties after Metals Addition</u>			
Ni, wt%	3.2	3.1	3.1
W, wt%	21.0	20.2	20.6
Surface area, m ² /g	-	256	260
<u>Catalyst Performance in Single-Pass Micro Unit</u>			
Activity, °F for 70% Conv. of 700 °F+	661	716	690
<u>No-Loss Yields @ 70% Conv., wt%</u>			
C4 ⁺ Gas	3.1	3.1	2.7
Naphtha (C5 – 250 °F)	16.0	13.1	13.4
Light-distillate (250 – 550 °F)	40.4	39.2	40.7
Heavy-distillate (550 – 700 °F)	14.5	18.8	17.3
Total Distillate (250 – 700 °F)	55.0	58.0	58.0
Sum of converted product, wt%	74.0	74.1	74.1

6
 7 Catalysts of the present invention (Catalysts B and C) required higher reactor
 8 temperatures to obtain the target conversion of 70 wt% due to the lower
 9 activity of the USY zeolite samples used to make the catalysts. Even though
 10 the reactor temperatures were higher, the catalysts of the invention have
 11 significant advantage in distillate production which is quite unexpected.
 12 Compared to Catalyst A (the base case), the catalysts of the invention
 13 produce less naphtha during the hydrocracking process by suppressing
 14 undesirable overcracking reactions. Catalysts of the invention show
 15 comparable or lower gas-make than the base case catalyst. Relative to the
 16 base case, Catalysts B and C exhibited 3 wt% higher distillate yield, and
 17 approximately 3 wt% less naphtha yield.

1 The catalysts of the invention are particularly good for producing more
2 heavy-distillate with 550°-700 °F boiling point range (over 70 cetane). The
3 catalyst of the invention shows 3-4% advantage in the heavy-distillate yield.
4 Since the cetane number of this fraction is much higher than that of the
5 light-distillate with 250°-550 °F boiling point range (around 50 cetane), the
6 combined distillate fraction will have much higher blending cetane.

7
8 Example 8: Comparison of Catalyst Performance for Distillate Production
9 (Cogel Catalyst vs. Catalysts E and F)

10
11 Catalysts of the invention (Catalysts E and F) were compared with Catalyst D,
12 which is the state-of-the-art cogel catalyst for a hydrocracking process in a
13 recycle pilot unit.

14
15 Recycling pilot unit evaluations were done with 130 cc of extrudate catalyst by
16 recycling unconverted 700 °F+ bottoms and H₂ gas. Fresh feed was added to
17 the recycled feed and the feed rate was adjusted to maintain 60 vol%
18 pre-pass conversions. Fresh make-up H₂ gas was added to the recycled H₂
19 gas stream to maintain 5000 SCF/bbl of recycled gas flow. Process conditions
20 were:

21
22 Pressure: 2300 psig total reactor pressure
23 LHSV: 1.0 hour⁻¹
24 Recycle H₂: 5000 SCF/ bbl
25

26 The yields of C₄- gas, naphtha, light- and heavy-distillate components were
27 calculated using D2887 Simdis analysis results. The overall yields and reactor
28 temperature data were summarized in Table 4.

Table 4
Physical Properties and Performance of Catalysts for Distillate Production

	Catalyst D State-of-the Art Cogel Catalyst Non-Invention	Catalyst E Invention	Catalyst F Invention
<u>Composition (before metals addition)</u>			
USY	No USY	20% USY #4	6% USY #4
Silica-Alumina	-	60%	69%
Al ₂ O ₃ Binder	-	20%	25%
<u>Properties after Metals Addition</u>			
Ni, wt%	7.7	3.1	3.1
W, wt%	18.2	21.0	20.8
Surface area, m ² /g	289	284	240
<u>Catalyst Performance in Recycle Pilot Unit</u>			
Activity, °F, Catalyst Average Temp.	681	682	689
<u>No-Loss Yields</u>			
C ₄ Gas, wt%	4.8	3.2	3.8
Naphtha (C ₅ – 250 °F), vol%	20.9	21.9	21.4
Light-Distillate (250 – 550 °F), vol%	50.4	58.8	54.0
Heavy-Distillate (550 – 700 °F), vol%	35.8	28.8	33.0
Total Distillate (250 – 700 °F), vol%	86.5	87.6	87.0
<u>Product Properties of Light-Distillate</u>			
Smoke Point, mm	40	45	40
Freeze Point, °C	-61	-59	-60
Cetane Number	51.5	-	53
<u>Product Properties of Heavy-Distillate</u>			
Cetane Number	71	77	73
<u>Catalyst Deactivation via Accelerated Fouling Test (Activity loss in °F/ 1000 hour)</u>			
	36	-	9

Catalysts of the invention (Catalysts E and F) show performance exceeding that of the state-of-the-art cogel catalyst (Catalyst D). Catalysts of the invention show an advantage in that Catalysts E and F make substantially less, undesirable light gas and produce more distillate fraction. The light and heavy-distillate yields can be adjusted by adjusting the USY content in the catalyst. With Catalyst F, we were able to produce the heavy-distillate yield comparable to that of Catalyst D, the state-of-the-art cogel catalyst reference.

1 The overall product properties with the catalysts of the invention are
2 comparable or better than those of the cogel catalyst. The catalyst of the
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 stabilities of the catalysts were compared in a single-pass micro unit at
8 accelerated fouling conditions (50% increase of oil flow rate and
9 25% reduction in reactor pressure). The stability data were calculated using
10 the reactor temperature change required to maintain a 70% conversion
11 per 1000 hours of stream time. The catalyst of our invention shows superior
12 aging characteristics in that it deactivated only at $\frac{1}{4}$ the rate of the cogel
13 catalyst.
14

15 To summarize, catalysts according the invention produced improved quality
16 distillate products in high yields while having advantages of zeolite containing
17 hydrocracking catalysts.
18

19 Example 9: Comparison of Catalyst Performance for Unconverted Oil
20 (Bottoms) Properties for Lubricating Oil Production (Cogel Catalyst vs. and
21 Catalyst F)
22

23 The per-pass conversion of the recycle pilot unit evaluation in Example 8 was
24 changed to 40 vol%, and 40 vol% of the unconverted oil (700 °F⁺ fraction) was
25 drained. Then product properties were evaluated to examine the potential of
26 this process for lubricating oil production.
27

Table 5

Performance of Catalysts for Lube Production

	Catalyst D State-of-the Art Cogel Catalyst Non-Invention	Catalyst F Invention
<u>Unconverted Oil (700 °F⁺), As-Produced</u>		
API Gravity at 60/60	37.4	36.8
Viscosity Index	136	142
<u>Solvent Dewaxed Oil</u>		
Viscosity Index	131	134

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 used 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.

There are numerous variations on the present invention which are possible in light of the teachings and supporting examples described herein. It is therefore understood that within the scope of the following claims, the invention may be practiced otherwise than as specifically described or exemplified herein.

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 a low acidity, highly dealuminated
7 ultrastable Y zeolite having an Alpha value of less than about 5 and
8 Broensted acidity of from about 1 to about 20 micromole/g measured
9 by FT-IR, an amorphous cracking component and a catalytic amount of
10 hydrogenation component selected from the group consisting of a
11 Group VI metal, a Group VIII metal, and mixtures thereof.
- 12
- 13 2. A process according to claim 1, wherein the ultrastable Y zeolite has a
14 unit cell size less than or equal to 24.26 Å.
- 15
- 16 3. A process according to claim 1, wherein the ultrastable Y zeolite has a
17 bulk silica to alumina ratio of greater than 50.
- 18
- 19 4. A process according to claim 1, wherein the catalyst comprises from
20 about 1% to 70% by weight of ultrastable Y zeolite, from about 10% to
21 80% by weight of amorphous cracking component, and from about
22 10% to 30% by weight of a binder.
- 23
- 24 5. A process according to claim 4, wherein the amorphous cracking
25 component is silica-alumina.
- 26
- 27 6. A process according to claim 4, wherein the binder comprises an
28 inorganic oxide.

- 1 7. A process according to claim 1, wherein the Group VIII metal
2 hydrogenation component is selected from the group consisting of
3 nickel, cobalt, platinum, palladium and mixtures thereof and wherein
4 the Group VI metal hydrogenation component is selected from the
5 group consisting of molybdenum, tungsten and mixtures thereof.
6
- 7 8. A process according to claim 1, wherein the hydrogenation component
8 comprises from about 2% to about 8% by weight of nickel and from
9 about 8% to about 30% by weight of tungsten, calculated as meals
10 per 100 parts by weight of total catalyst.
11
- 12 9. A process for producing high quality distillate with increased yield of
13 heavy distillate from heavy gas oils comprising contacting a heavy gas
14 oil under hydrocracking conditions with a catalyst comprising a low
15 acidity, highly dealuminated ultrastable Y zeolite having an Alpha value
16 of less than about 5 and Broensted acidity of from about 1 to about 20
17 micromole/g, an amorphous cracking component and a catalytic
18 amount of hydrogenation component selected from the group
19 consisting of a Group VI metal, a Group VIII metal, and mixtures
20 thereof.
21
- 22 10. A process according to claim 9, wherein the ultrastable Y zeolite has a
23 unit cell size less than or equal to 24.26 Å.
24
- 25 11. A process according to claim 9, wherein the ultrastable Y zeolite has a
26 bulk silica to alumina ratio of greater than 50.
27
- 28 12. A process according to claim 9, wherein the catalyst comprises from
29 about 1% to 70% by weight of ultrastable Y zeolite, from about 10% to
30 80% by weight of amorphous cracking component, and from about
31 10% to 30% by weight of a binder.
32

- 1 13. A process according to claim 9, wherein the amorphous cracking
2 component is silica-alumina.
3
- 4 14. A process according to claim 12, wherein the binder comprises an
5 inorganic oxide.
6
- 7 15. A process according to claim 9, wherein the Group VIII metal
8 hydrogenation component is selected from the group consisting of
9 nickel, cobalt, platinum, palladium and mixtures thereof and wherein
10 the Group VI metal hydrogenation component is selected from the
11 group consisting of molybdenum, tungsten and mixtures thereof.
12
- 13 16. A process according to claim 15, wherein the hydrogenation
14 component comprises from about 2% to about 8% by weight of nickel
15 and from about 8% to about 30% by weight of tungsten, calculated as
16 metals per 100 parts by weight of total catalyst.
17
- 18 17. A hydrocracking catalyst composition comprising a low acidity, highly
19 dealuminated ultrastable Y zeolite having an Alpha value of less than
20 about 5 and from about 1 to about 20 micromole/g of Brønsted acidity
21 measured by FT-IR, an amorphous cracking component and a catalytic
22 amount of hydrogenation component selected from the group
23 consisting of a Group VI metal, a Group VIII metal, and mixtures
24 thereof.
25
- 26 18. A composition according to claim 17, wherein the ultrastable Y zeolite
27 has a unit cell size less than or equal to 24.26 Å.
28
- 29 19. A composition according to claim 17, wherein the ultrastable Y zeolite
30 has a bulk silica to alumina ratio of greater than 50.
31

- 1 20. A composition according to claim 17, wherein the catalyst comprises
2 from about 1% to 70% by weight of ultrastable Y zeolite, from about
3 10% to 80% by weight of amorphous cracking component, and from
4 about 10% to 30% by weight of a binder.
5
- 6 21. A composition according to claim 20, wherein the amorphous cracking
7 component is silica-alumina.
8
- 9 22. A composition according to claim 20, wherein the binder comprises an
10 inorganic oxide.
11
- 12 23. A composition according to claim 17, 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 24. A process for producing a lubricating oil base stock which comprises:
19
- 20 (a) contacting a feedstock under hydrocracking conditions with a
21 catalyst comprising a low acidity, highly dealuminated ultrastable
22 Y zeolite having an Alpha value of less than about 5 and
23 Broensted acidity of from about 1 to about 20 micromole/g, an
24 amorphous cracking component and a catalytic amount of
25 hydrogenation component selected from the group consisting of
26 a Group VI metal, a Group VIII metal, and mixtures thereof; and
27
- 28 (b) processing the hydrocracked product to provide a lubricating oil
29 base stock.