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(54) Title: HYDROCRACKING WITH A MIDDLE DISTILLATE CATALYST

(57) Abstract

The selectivity of a midbarrel hydrocracking process for middle distillates is significantly increased by using a catalyst containing an amorphous silica-magnesia component in combination with a Y zeolite having a unit cell size below 24.45 angstroms and/or a water vapor sorptive capacity less than 10 weight percent at 25 °C and a p/p_o value of 0.1. LZ-10 zeolite is a preferred zeolite for use in the catalyst.

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HYDROCRACKING WITH A MIDDLE DISTILLATE CATALYST

BACKGROUND OF THE INVENTION

This invention relates to a catalytic hydrocracking process and a catalyst for use therein. The invention is particularly concerned with an improved process for producing middle distillate products using a catalyst highly selective for such products.

Petroleum refiners often produce desirable products such as turbine fuel, diesel fuel, and other hydrocarbon liquids known as middle distillates as well as lower boiling liquids, such as naphtha and gasoline, by hydrocracking a hydrocarbon feedstock derived from crude oil. Feedstocks most often subjected to hydrocracking are gas oils and heavy gas oils recovered from crude oil by distillation. A typical gas oil comprises a substantial proportion of hydrocarbon components boiling above about 700° F., usually at least about 80 percent by weight boiling above 700° F. A typical heavy gas oil has a boiling point range between about 600° F. and 1050° F.

Hydrocracking is generally accomplished by contacting, in an appropriate reaction vessel, the gas oil or other feedstock to be treated with a suitable hydrocracking catalyst under conditions of elevated temperature and pressure in the presence of hydrogen so as to yield a lower overall average boiling point product containing a distribution of hydrocarbon products desired by the refiner. Although the operating conditions within a hydrocracking reactor have some influence on the yield of the products, the hydrocracking catalyst is the prime factor in determining such yields. At the present time, middle distillates are not in high demand relative to gasoline in the United States; however, marketing surveys indicate that there will be an increased demand for middle distillates as the year 2000 approaches. For this reason, refiners have recently been focusing on midbarrel hydrocracking catalysts which selectively produce middle

distillate fractions, such as turbine fuel and diesel fuel, that boil in the 300° F. to 700° F. range.

The three main catalytic properties by which the performance of a midbarrel hydrocracking catalyst is evaluated are activity, selectivity, and stability. Activity may be determined by comparing the temperature at which various catalysts must be utilized under otherwise constant hydrocracking conditions with the same feedstock so as to produce a given percentage, normally about 60 percent, of products boiling below 700° F. The lower the activity temperature for a given catalyst, the more active such a catalyst is in relation to a catalyst of higher activity temperature. Selectivity of midbarrel or middle distillate hydrocracking catalysts may be determined during the foregoing described activity test and is measured as the percentage fraction of the 700° F.- product boiling in the desired midbarrel product range, e.g., 300° F. to 700° F. for diesel fuel and 300° F. to 550° F. for turbine fuel. Stability is a measure of how well a catalyst maintains its activity over an extended time period when treating a given hydrocarbon feedstock under the conditions of the activity test. Stability is generally measured in terms of the change in temperature required per day to maintain a 60 volume percent or other given conversion.

U.S. Patents 4,062,809 and 4,419,271, the disclosures of which are hereby incorporated by reference in their entireties, disclose two different types of very effective middle distillate hydrocracking catalysts. The catalyst of U.S. Patent 4,062,809 contains molybdenum and/or tungsten plus nickel and/or cobalt on a support of silica-alumina dispersed in gamma alumina. U.S. Patent 4,419,271 teaches that the catalyst of U.S. Patent 4,062,809 can be improved by adding an aluminosilicate zeolite to the support, thereby producing a catalyst containing molybdenum and/or tungsten and nickel and/or cobalt supported on a mixture of an aluminosilicate zeolite, preferably an ultrahydrophobic zeolite such as LZ-10 zeolite, and a dispersion of silica-alumina in a gamma alumina matrix. The presence of the zeolite in this

catalyst increases the activity of the catalyst without significantly affecting the selectivity.

Although the catalysts of the above-discussed patents are highly effective middle distillate hydrocracking catalysts and have proven themselves in commercial environments, there is always a demand for new hydrocracking catalysts with superior overall activity, selectivity, and stability for middle distillate hydrocracking.

SUMMARY OF THE INVENTION

In accordance with the invention, it has now been surprisingly found that the activity and selectivity of middle distillate hydrocracking catalysts comprising one or more hydrogenation components and a Y zeolite having either a unit cell size below about 24.45 angstroms or a water vapor sorptive capacity less than about 10 weight percent at 25° C. and p/p_o value of 0.10 can be substantially improved by incorporating an amorphous silica-magnesia component into the catalyst. Under typical hydrocracking conditions, including elevated temperature and pressure and the presence of hydrogen, such catalysts are highly effective for converting gas oils and other hydrocarbon feedstocks to a product of lower average boiling point and lower average molecular weight, which product contains a relatively large proportion of components boiling in the midbarrel range of 300° F. to 700° F. The hydrocracking catalyst normally contains one or more hydrogenation components, such as one or more Group VIB or Group VIII metal components, in combination with the Y zeolite, the amorphous silica-magnesia component, and a porous, inorganic refractory oxide binder, such as alumina. As used herein "p/p_o" represents the water vapor partial pressure to which the Y zeolite is exposed divided by the water vapor partial pressure at 25° C.

Preliminary tests indicate that the catalyst of the invention, when used in hydrocracking to produce middle distillate products such as diesel fuel and turbine fuel, has a surprisingly greater selectivity than other middle distillate catalysts now commercially available for use in

midbarrel hydrocracking processes. These tests surprisingly indicate that, at 60 percent conversion, greater than about 86 volume percent of the 700° F.- product, typically greater than about 88 volume percent, boils in the range between 300° F. and 700° F. while greater than about 75 volume percent, frequently greater than about 77 volume percent, boils in the range between 300° F. and 550° F.

DETAILED DESCRIPTION OF THE INVENTION

The hydrocracking process of the invention is directed to the production of high yields of middle distillates such as diesel fuel, which, as defined herein, boils in the 300° F. to 700° F. range, and turbine fuel, which, as defined herein, boils in the 300° F. to 550° F. range. These high yields are obtained utilizing a catalyst containing one or more hydrogenation components in combination with an amorphous silica-magnesia component and a Y zeolite having a unit cell size below about 24.45 angstroms and/or a water vapor sorptive capacity less than about 10 weight percent at 25° C. and p/p_o value of 0.10. The Y zeolite preferably has an overall silica-to-alumina mole ratio less than 6.0, usually between about 4.5 and 5.6. Preferably, the catalyst also comprises a porous, inorganic refractory oxide binder.

The Y zeolite which comprises the midbarrel hydrocracking catalyst of the invention has either (1) a unit cell size less than about 24.45 angstroms or (2) a sorptive capacity for water vapor at 25° C. and a p/p_o value of 0.10 of less than 10 weight percent, preferably less than 5 weight percent. Preferred Y zeolites meet both of the foregoing requirements. The term "Y zeolite" as employed herein is meant to encompass all crystalline zeolites having either the essential X-ray powder diffraction pattern set forth in U.S. Patent 3,130,007 or a modified Y zeolite having an X-ray powder diffraction pattern similar to that of U.S. Patent 3,130,007 but with the d-spacings shifted somewhat due, as those skilled in the art will realize, to cation exchanges, calcinations,

etc., which are generally necessary to convert the zeolite into a catalytically active and stable form. The present invention requires a Y zeolite having either or both of the two properties mentioned above, such Y zeolites being modified Y zeolites in comparison to the Y zeolite taught in U.S. Patent 3,130,007.

The Y zeolites used in the catalyst of the invention are large pore zeolites having an effective pore size greater than 7.0 angstroms. Since some of the pores of the Y zeolites are relatively large, the zeolites allow molecules relatively free access to their internal structure. Thus, the Y zeolites useful in the composition of the invention generally have a low Constraint Index, typically below 1.0, preferably below 0.75, and usually below about 0.5.

The preferred Y zeolite for use in the hydrocracking catalyst of the invention is a UHP-Y zeolite, an ultrahydrophobic Y zeolite. The composition and properties of UHP-Y zeolites are disclosed in U.S. Patent 4,401,556 herein incorporated by reference in its entirety. See also Great Britain Patent 2 014 970 B which is also herein incorporated by reference in its entirety. UHP-Y zeolites and similar zeolites are, in essence, produced by a four step procedure in which a Y zeolite in the alkali metal form (usually sodium) and typically having a unit cell size of about 24.65 angstroms is cation exchanged with ammonium ions, calcined in the presence of water vapor (preferably in the presence of at least 0.2 psia water vapor, even more preferably at least 1.0 psia water vapor, and more preferably still, at least 10 psia water vapor, and most preferably of all, an atmosphere consisting essentially of or consisting of steam) so as to produce a unit cell size in the range of 24.40 to 24.64 angstroms, preferably 24.42 to 24.62 angstroms, then ammonium exchanged once again, and then calcined again in the presence of sufficient water vapor (preferably in an atmosphere consisting essentially of steam, and most preferably consisting of steam) so as to yield a unit cell size below 24.40, and most preferably no more than 24.35

angstroms. The first ammonium exchange step typically reduces the sodium content of the starting sodium Y zeolite from a value usually greater than about 8.0 weight percent, usually between 10 and 13 weight percent, calculated as Na_2O, to a value in the range between about 0.6 and 5 weight percent, while the second ammonium exchange further reduces the sodium content to less than about 0.5 weight percent, usually less than 0.3 weight percent. It will be seen from the above-discussed manufacturing procedure that UHP-Y zeolites differ from the Y zeolite taught in U.S. Patent 3,929,672 by the addition of the final steam calcination step, some of the zeolites of said patent being known under the designations Y-82 or LZY-82 and Y-84 or LZY-84.

"UHP-Y" zeolites are defined herein as zeolite aluminosilicates having an overall silica-to-alumina mole ratio greater than 4.5, the essential X-ray powder diffraction pattern of zeolite Y, a unit cell size or dimension a_o of less than 24.45 angstroms, a surface area of at least 300 m^2/g (BET), a sorptive capacity for water vapor of less than 10 weight percent at 25° C. and a p/p_o value of 0.10, and a Residual Butanol Test value of not more than 0.40 weight percent. Preferred UHP-Y zeolites have one or more of the following properties: an overall silica-to-alumina mole ratio from 4.5 to 35; a surface area of at least 350 m^2/g; and a sorptive capacity for water vapor of less than 5 weight percent at 25° C. and a p/p_o value of 0.10. Especially preferred are UHP-Y zeolites having an overall silica-to-alumina mole ratio of 4.5 to 9 and/or a sorptive capacity for water vapor at 25° C. and a p/p_o value of 0.10 of less than 4 weight percent. Although UHP-Y zeolites having silica-to-alumina mole ratios below 6.0 may be most preferred, UHP-Y zeolites that have been treated with a mineral acid to remove aluminum to increase their overall silica-to-alumina mole ratio may also be used. Such acid treated UHP-Y zeolites are discussed in detail in U.S. Patent No. 5,047,139, the disclosure of which is herein incorporated by reference in its entirety.

The more preferred UHP-Y zeolites for use in the present invention have a unit cell size or dimension less than about 24.40 angstroms, and even more preferably no more than 24.35 angstroms. LZ-10 zeolite is the most preferred UHP-Y zeolite, LZ-10 zeolite being available from UOP. LZ-10 zeolite usually has a unit cell size or dimension at or above 24.20 angstroms, preferably between 24.20 and 24.40, and most preferably between about 24.25 and 24.35 angstroms, and has a water vapor sorptive capacity at 4.6 mm water vapor partial pressure and 25° C. less than 8.0 percent by weight of the zeolite. See U.S. Patent 4,419,271 which previously has been incorporated by reference in its entirety.

As discussed above, the Y zeolites used in the catalyst of the invention are typically made by a process which involves two ammonium exchange steps to reduce the sodium or other alkali metal content of the starting Y zeolite to a value less than 0.5 weight percent sodium, usually less than about 0.3 weight percent, calculated as Na_2O. These zeolites of reduced sodium content possess catalytic cracking activity and can be used as components of hydrocracking catalysts. In some cases the selectivity of catalysts containing these Y zeolites for middle distillate production can be substantially increased by ion exchanging the Y zeolites of reduced sodium content with rare earth-containing cations.

If such an ion exchange is desirable, any rare earth metal or combination of rare earth metals having atomic numbers according to the Periodic Table of Elements between 57 and 71 can be introduced into the zeolite. The rare earth metals suitable for ion exchange include lanthanum, cerium, praseodymium, neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. Usually, a mixture of rare earth cations is introduced into the zeolite, with the mixture often containing rare earth metals in a distribution similar to that of the rare earth ore (e.g., bastnasite, monazite, xenotime, and the like) from which the metals were derived.

There are many known methods by which one can exchange rare earth cations for sodium and other cations, particularly hydrogen ions, in a crystalline aluminosilicate Y zeolite. The most usual way is to contact the zeolite with an aqueous solution containing multivalent cations of the rare earth element or elements to be exchanged into the zeolite. Most often, the solution contains more than about 20 grams per liter of rare earth metal cations (calculated as RE_2O_3 where RE is the sum of all rare earth metals under consideration, regardless of whether any one or more of such metals actually forms a trioxide of equivalent formula), and the contacting is usually accomplished by immersing the zeolite into the ion-exchange solution and stirring at ambient temperature or above but usually at no more than about 100° C. If desired, the solution may also contain ammonium ions, and the solution may further contain any of a number of anions that will not interfere with the cation exchange, e.g. chloride, nitrate, sulfate, etc.

For best results, the ion exchange is performed in a manner such that the rare earth-exchanged zeolite contains at least about 1 percent, preferably at least 2 percent, and usually between about 4 and 6 percent, by weight of rare earth metals, calculated as RE_2O_3. Although a small proportion of the rare earth metals exchanged into the zeolite will replace some of the residual sodium ions at exchange sites in the zeolite, the largest proportion will exchange with hydrogen ions and/or ammonium ions because of their relatively high concentration versus the low concentration, usually below 0.3 weight percent, calculated as Na_2O, of sodium cations present. Sometimes, only a single immersion of the zeolite into the ion exchange solution will be sufficient for the necessary exchange. However, in some cases it may be necessary to carry out the ion exchange by several immersions into a solution containing rare earth metal cations, or by immersion serially into several solutions of differing rare earth element content, or by other known methods for introducing rare earth metal cations into a zeolite.

The Y zeolite to be used in the catalyst of the invention, whether or not it has been exchanged with rare earth cations, is combined with a binder material to form support particles which serve to carry one or more hydrogenation components. In the preferred method, this is accomplished by combining the Y zeolite with (1) a material such as an alumina hydrogel or peptized alumina, which, upon calcination, will yield a porous, inorganic refractory oxide binder or (2) a material which itself is a porous, inorganic refractory oxide binder, for example, alumina, silica-alumina, a clay, such as kaolin, as well as physical and chemical combinations of such materials. A sufficient amount of the Y zeolite is normally used such that the support comprises between about 2 and 35 weight percent, preferably between about 3 and 20 weight percent, more preferably between about 5 and 10 weight percent, of the Y zeolite. The most convenient method for physically integrating the zeolite and the binder is to comull the porous, inorganic refractory oxide binder or precursor material with the zeolite, and subsequently extrude the comulled material through a die having small openings therein of desired cross-sectional size and shape, e.g., circle, trilobal clover-leaf, quadralobal clover leafs, etc., breaking or cutting the extruded matter into appropriate lengths, e.g., 1/16 to 3/4 inch, drying the extrudates, and then calcining at a temperature between 800° F. and 1200° F. to produce a material suitable for use in high temperature hydrocracking reactions. At present it is preferred that the support be produced in cylindrical form; however, as stated above, other cross-sectional shapes are possible, such as cloverleafs of polylobal design, for example, trilobal or quadralobal shapes, as shown, for example, in Figures 8 and 10, respectively, in U.S. Patent 4,028,227 herein incorporated by reference in its entirety.

It will be understood in the foregoing description that the porous, inorganic refractory oxide is used as a binder material to hold the Y zeolite particles together in the support. Other materials are normally also

incorporated into the comulled mixture, including for example, amorphous, inorganic refractory oxide diluents, which may or may not possess some type of catalytic activity. In accordance with this invention, it has now been found that the selectivity of catalysts containing the Y zeolites described above can be dramatically improved by incorporating an amorphous silica-magnesia component into the catalysts. Tests indicate that the use of such an amorphous component gives much better selectivities to turbine and diesel fuel than other amorphous components such as alumina, silica-alumina, and dispersions of silica-alumina in gamma alumina.

The silica-magnesia component used in the catalyst of the invention may be prepared by methods generally well known in the art. One such method involves first forming a silica hydrogel by precipitating silica from an aqueous solution of a silicate salt, such as an alkali or alkaline earth metal silicate, or silicic acid by reducing the solution pH, usually by the addition of inorganic acids such as hydrochloric, nitric, and sulfuric. Next, the resultant silica hydrogel is washed and then soaked in a solution of a magnesium salt in proportions sufficient to provide the desired relative amounts of magnesia and silica in the final silica-magnesia composition. Examples of water-soluble magnesium salts which can be used to make the magnesium solutions include magnesium chloride, magnesium nitrate, magnesium sulfate, magnesium acetate, magnesium bromide, magnesium iodide and the like. After the silica hydrogel has been combined with the magnesium salt solution, magnesia is precipitated in situ by adding a base, such as ammonia, ammonium hydroxide and sodium hydroxide, to increase the solution pH. The resultant hydrogel is then water washed to remove soluble salts, dried, and thermally activated by calcining at a temperature above about 600° F. to form the active silica-magnesia component.

In some cases, the silica-magnesia component can be created by mulling magnesium oxide with a dried silica hydrogel. When mulling is used, more effective interaction

of the silica and magnesia is obtained if water is present in sufficient quantities to form a coherent paste. The paste is then dried and calcined to form the silica-magnesia component.

The amount of silica and magnesia in the silica-magnesia component can vary considerably, but usually at least 5 weight percent magnesia based on the combined weight of silica and magnesia is present. Preferably, the silica-magnesia component contains between about 65 and 75 weight percent silica and between about 25 and 35 weight percent magnesia.

It will be understood that producing the catalyst support in extrudate form, while certainly the most highly preferred method, is still but one option available to those skilled in the art. The catalyst support may also be produced in tablet, granules, spheres, and pellets as desired, by any known method for combining zeolites with porous, inorganic refractory oxide components. Regardless of how the support particles are produced, they typically contain between about 5 and 40, preferably from about 10 to 25, weight percent binder and between about 25 and 90, usually between about 40 and 80, weight percent amorphous silica-magnesia.

After the catalyst support particles are produced, they are converted to catalyst particles by compounding, as by impregnation of the particles, with one or more precursors of at least one catalytically active hydrogenation metal component. The impregnation may be accomplished by any method known in the art, including spray impregnation wherein a solution containing the hydrogenation metal precursors in dissolved form is sprayed onto the support particles. Another method involves soaking the support particles in a large volume of the impregnation solution. Yet another method is the pore volume or pore saturation technique wherein the support particles are introduced into an impregnation solution of volume just sufficient to fill the pores of the support. On occasion, the pore saturation technique may be modified so as to utilize an impregnation solution having a volume

between 10 percent less and 10 percent more than that which would just fill the pores. If the active metal precursors are incorporated by impregnation, a subsequent or second calcination, as for example at temperatures between 700° F. and 1200° F., will convert the metals to their respective oxide forms. In some cases, calcinations may follow each impregnation of individual active metals.

Alternative methods of introducing the active metal components into the catalyst support include (1) mixing an appropriate solid or liquid containing the metal components with the materials to be extruded through the die and (2) impregnating the materials to be extruded with the desired metal components prior to carrying out the extrusion. Such methods may prove less expensive and more convenient than the impregnation methods discussed above and will also result in the active hydrogenation components being intimately mixed with the components of the support.

Hydrogenation components suitable for incorporation into the extruded catalyst support particles comprise metals selected from Group VIII and/or Group VIB of the Periodic Table of Elements. As used herein "Periodic Table of Elements" refers to the version found in the inside front cover of the Handbook of Chemistry and Physics, 65th Edition, published in 1984 by the Chemical Rubber Company, Cleveland, Ohio. Preferred hydrogenation components comprise metals selected from the group consisting of platinum, palladium, cobalt, nickel, tungsten, chromium, and molybdenum. Preferably, the catalyst contains at least one Group VIII metal component and at least one Group VIB metal component, with cobalt or nickel and molybdenum or tungsten being preferred combinations of active components and nickel and tungsten being most preferred. The catalyst typically contains up to about 15, usually between about 1 and 10 weight percent, preferably between 2 and 8 weight percent, of a non-noble Group VIII metal, calculated as the monoxide, and up to 30, usually from about 2 to 28 weight percent, and preferably between about 10 and 25 weight percent, of the Group VIB metal, calculated as the trioxide. If the hydrogenation

component comprises a noble metal such as platinum or palladium, it is generally desired that the catalyst contain between about 0.2 and about 10 weight percent, preferably between about 0.30 and 2.0 weight percent, calculated as the metal.

By the foregoing procedures or their equivalents, catalysts with the hydrogenation metals present in the oxide form are prepared as particulates. The finished hydrocracking catalysts typically have a BET surface area ranging between about 100 and 350 m^2/g. When used to selectively produce middle distillates, these catalysts usually comprise (1) between about 2 and 25 weight percent, preferably between about 3 and 15 weight percent, and more preferably between about 4 and 8 weight percent, Y zeolite having a unit cell size below about 24.45 angstroms and/or a water vapor sorptive capacity less than about 10 weight percent at 25° C. and p/p_o value of 0.10, (2) between about 4 and 35 weight percent porous, inorganic refractory oxide binder, preferably between about 7 and 18 weight percent, (3) between about 15 and about 65 weight percent amorphous silica-magnesia, preferably between about 30 and 70 weight percent, and more preferably between about 50 and 65 weight percent, (4) between about 2 and 28 weight percent Group VIB metal hydrogenation component, preferably between about 10 and 25 weight percent, and (5) between about 0.2 and 15 weight percent Group VIII hydrogenation metal component, preferably between 2 and 8 weight percent.

Catalysts prepared in the oxide form as described above are generally converted to the sulfide form for hydrocracking purposes when non-noble metals are used as hydrogenation components. This can be accomplished by presulfiding the catalyst prior to use at an elevated temperature, e.g., 300° to 700° F., with, for example, a mixture consisting of 10 volume percent H_2S and 90 volume percent H_2. The catalyst can be presulfided ex situ by various sulfiding processes; as an illustration, see "Sulficat^R: Off-Site Presulfiding of Hydroprocessing Catalysts from Eurecat" by J.H. Wilson and G. Berrebi, Catalysis 87, Studies in Surface Science and Catalysts,

Vol. 38, Elsevier Science Publishers B. V., 1988, pages 393-398. Alternatively, the sulfiding is accomplished in situ, i.e., by using the catalyst in the oxide form to hydrocrack a hydrocarbon feedstock containing sulfur compounds under hydrocracking conditions, including elevated temperature and pressure and the presence of hydrogen.

The catalysts described above are useful in the conversion of a wide variety of hydrocarbon feedstocks via hydrocracking to more valuable hydrocarbon products of lower average boiling point and lower average molecular weight, which products typically boil in the range between about 300° F. and about 700° F. The feedstocks that may be subjected to hydrocracking by the process of the invention include mineral oils and synthetic oils such as shale oil, oil derived from tar sands, coal liquids, and the like. Examples of appropriate feedstocks for hydrocracking include atmospheric gas oils, vacuum gas oils, and catalytic cracker cycle oils. Preferred hydrocracking feedstocks include gas oils and other hydrocarbon fractions having at least 50 and usually more than 70 weight percent of their components boiling above 700° F. Normally, heavy hydrocarbon oils such as a heavy crude oil, a reduced crude oil, vacuum distillation residues and similar heavy materials are not suitable feedstocks for the process of the invention.

Usually, the feedstocks described above are hydrotreated before being subjected to the hydrocracking process of the invention. The hydrotreating is performed in conjunction with hydrocracking, usually by a method referred to as "integral operation." In this process, the hydrocarbon feedstock is introduced into a catalytic hydrotreating zone wherein, in the presence of a suitable catalyst and under suitable conditions, including an elevated temperature (e.g., 400° to 1000° F.) and an elevated pressure (e.g., 100 to 5000 p.s.i.g.) and with hydrogen as a reactant, the organonitrogen components and the organosulfur components contained in the feedstock are converted to ammonia and hydrogen sulfide, respectively.

Suitable hydrotreating catalysts include zeolite- or molecular sieve-free, particulate catalysts comprising a Group VIII metal component and a Group VIB metal component on a porous, inorganic, refractory oxide support most often composed of alumina. The entire effluent removed from the hydrotreating zone is subsequently treated in the hydrocracking zone maintained under suitable conditions of elevated temperature, pressure, and hydrogen partial pressure, and containing the hydrocracking catalyst of the invention. Usually, the hydrotreating and hydrocracking zones in integral operation are maintained in separate reactor vessels, but, on occasion, it may be advantageous to employ a single, downflow reactor vessel containing one or more upper beds of the hydrotreating catalyst particles and one or more lower beds of the hydrocracking catalyst particles. Examples of integral operation may be found in U.S. Patents 3,159,564, 3,655,551, 4,040,944, and 4,584,287, all of which are herein incorporated by reference in their entireties. In some cases, the effluent from the hydrocracking zone is subjected to hydrotreating in a manner similar to that described above in order to remove trace mercaptans from the product.

The catalyst of the invention is usually employed as a fixed bed of catalytic extrudates in a hydrocracking reactor into which hydrogen and the feedstock are introduced and passed in a downwardly direction. The reactor vessel is maintained at conditions so as to convert the feedstock into the desired product, which is normally a hydrocarbon product containing a substantial portion of turbine fuel and diesel fuel components boiling in the range between 300° F. and 700° F. In general, the temperature of the reaction vessel is maintained between about 450° F. and about 850° F., preferably between about 500° F. and 800° F. The pressure normally ranges between about 750 p.s.i.g. and about 3500 p.s.i.g., preferably between about 1000 and about 3000 p.s.i.g. The liquid hourly space velocity (LHSV) is typically between about 0.3 and 5.0, preferably between about 0.5 and 3.0, reciprocal hours. The ratio of hydrogen gas to feedstock utilized

usually ranges between about 1,000 and 10,000 standard cubic feet per barrel, preferably between about 2,000 and 8,000 standard cubic feet per barrel, as measured at 60° C. and 1 atmosphere.

The typical gas oil feedstock contains no more than about 35 volume percent, usually less than 15 volume percent, constituents boiling in the 300° F. to 700° F. range. When middle distillates are desired, the hydrocracking operation conditions are chosen so that at least about 80 volume percent, preferably at least about 86 volume percent, and more preferably yet at least about 87 volume percent, of the 700° F.- product boils in the range between 300° F. and 700° F. Usually, the 700° F.- product contains greater than about 76 volume percent, preferably at least about 78 volume percent, and more preferably greater than about 79 volume percent, hydrocarbons boiling in the range between 300° F. and 550° F.

Based on presently available data, the catalyst of the present invention as compared to a highly successful commercial middle distillate hydrocracking catalyst containing a dispersion of silica-alumina particles in a gamma alumina matrix in lieu of an amorphous silica-magnesia component provides for enhanced results when used to selectively produce turbine and diesel fuel. In particular, the catalyst of the invention provides for significant increases in the yield of hydrocarbon distillates boiling in the 300° F. to 550° F. range and the 300° F. to 700° F. range. These achievements, and others, are proven in the following example which is provided for illustrative purposes and not to limit the invention as defined by the claims.

EXAMPLE

Catalyst 1

Catalyst 1, a catalyst of the invention, was prepared by mixing 5 weight percent LZ-10 zeolite, 75 weight percent amorphous silica-magnesia (SM-30 silica-magnesia obtained from the Davison Chemical Division of W.

R. Grace and Company), which contained about 70 weight percent silica and about 30 weight percent magnesia, and 20 weight percent peptized Catapal alumina binder. The LZ-10 zeolite, which was obtained from UOP, had a unit cell size of about 24.30 angstroms, an effective pore size above about 7.0 angstroms and an overall silica-to-alumina mole ratio of about 5.2. The wetted mixture was mulled and then extruded through a 1/16-inch cylindrical die to form cylindrical extrudates that were cut into 1/8 to 1/2 inch lengths. The extrudates were dried at 100° C. and then calcined at 900° F. The dried and calcined extrudates were then impregnated by the pore saturation method with an aqueous solution containing nickel nitrate and ammonium metatungstate in sufficient quantities such that, after the impregnated extrudates were dried at 100° C. and calcined at 900° F., the resultant catalyst particles contained about 5 weight percent nickel, calculated as NiO, and about 22 weight percent tungsten, calculated as WO_3, on a support consisting of 5 weight percent LZ-10 zeolite, 75 weight percent silica-magnesia, and 20 weight percent alumina binder.

Catalyst 2

Catalyst 2, a comparative catalyst, was prepared similarly to Catalyst 1 except that amorphous gamma alumina was used in lieu of the amorphous silica-magnesia. The finished catalyst contained the nickel and tungsten in the proportions above specified for Catalyst 1 on a support consisting of 5 weight percent LZ-10 zeolite, 75 weight percent amorphous gamma alumina, and 20 weight percent alumina binder.

Catalyst 3

Catalyst 3, another comparative catalyst, was prepared similarly to Catalyst 1 except that an amorphous silica-alumina containing about 75 weight percent silica and about 25 weight percent alumina was used instead of the amorphous silica-magnesia. The finished catalyst contained the nickel and tungsten in the proportions specified for

Catalyst 1 on a support consisting of 5 weight percent LZ-10 zeolite, 75 weight percent amorphous silica-alumina and 20 weight percent alumina binder.

Catalyst 4

Catalyst 4, another comparative catalyst, was prepared similarly to Catalyst 1 except that a dispersion of silica-alumina particles in a gamma alumina matrix (Aero 5545 obtained from Criterion Catalyst Company L.P.) was substituted for the amorphous silica-magnesia. The dispersion was amorphous and contained about 55 weight percent alumina and about 45 weight percent silica. The finished catalyst contained nickel and tungsten in the proportions specified for Catalyst 1 on a support consisting of 5 weight percent LZ-10 zeolite, 75 weight percent amorphous dispersion of silica-alumina in gamma alumina, and 20 weight percent alumina binder.

Catalyst 5

Catalyst 5 is a sample of a commercial middle distillate hydrocracking catalyst obtained from UOP. It was prepared similarly to Catalyst 4 except it contained about 7 weight percent nickel, calculated as NiO, 10 weight percent LZ-10 zeolite, and 70 weight percent of the amorphous dispersion of silica-alumina particles in a gamma alumina matrix used in Catalyst 4. Thus, the catalyst contained about 7 weight percent nickel, calculated as NiO, and about 22 weight percent tungsten, calculated as WO_3, on a support consisting of 10 weight percent LZ-10 zeolite, 70 weight percent dispersion of silica-alumina particles in a gamma alumina matrix, and 20 weight percent alumina binder.

Catalyst 6

Catalyst 6 was prepared similarly to Catalyst 1, except 10 weight percent LZ-10 zeolite and 70 weight percent of the same silica-magnesia were used. Thus, the finished catalyst contained about 5 weight percent nickel, calculated as NiO, and about 22 weight percent tungsten, calculated as WO_3, on a support consisting of 10 weight

percent LZ-10 zeolite, 70 weight percent silica-magnesia, and 20 weight percent alumina binder.

Each of the above-described six catalysts was presulfided by passing a gas stream consisting of 10 volume percent hydrogen sulfide and the balance hydrogen through a bed of the catalyst at a temperature initially of about 300° F. and slowly increased to 700° F. and held at that temperature for about one hour.

The six catalysts were then tested for activity and selectivity in middle distillate hydrocracking using a hydrotreated light Arabian vacuum gas oil having an API gravity of 37°, an initial boiling point of 436° F., a final boiling point of 1073° F. and a 50 percent boiling point of 813° F., with about 20 volume percent boiling below about 698° F. and 5 volume percent boiling below 588° F., as determined by a modified ASTM D1160 distillation. The vacuum gas oil was passed on a once-through basis through an isothermal reactor containing about 140 ml of the catalyst mixed with 95 ml of six to eight mesh quartz. The reactor was operated at a liquid hourly space velocity (LHSV) of 1.0 reciprocal hour, a total pressure of 2,000 psig and a once-through hydrogen flow rate of 10,000 standard cubic feet per barrel. The temperature of the reactor was adjusted to provide a 60 volume percent conversion to materials boiling below 700° F. In addition, tertiary butyl amine and thiophene were added to the reactor in amounts commensurate with the amounts of ammonia and hydrogen sulfide, respectively, that would be present from hydrotreating the gas oil from which the feedstock was derived. Thus, the conditions under which the catalysts were tested simulated those one would expect to pertain in a hydrocracking vessel employed in an integral hydrotreating-hydrocracking operation wherein the entire effluent from the hydrotreater, plus added hydrogen, is passed to the hydrocracker for further refinement, in this case, conversion primarily to a middle distillate product. The results of these tests are set forth in Table I below:

TABLE I

Catalyst Designation	Composition of Support (Wt.%)	Activity (° F.) Reactor Temp. to Provide 60% Conversion to 700° F.-	Selectivity (Vol.% of 700°F.- Product) Turbine 300-550° F.	Diesel 300-700° F.
1	75% amorphous silica-magnesia 20% binder 5% LZ-10 zeolite	729	79.4	89.8
2	75% amorphous alumina 20% binder 5% LZ-10 zeolite	729	72.2	83.8
3	75% amorphous silica-alumina 20% binder 5% LZ-10 zeolite	732	74.2	85.0

TABLE I (Continued)

Catalyst Designation	Composition of Support (Wt.%)	Activity (° F.) Reactor Temp. to Provide 60% Conversion to 700° F.-	Selectivity (Vol.% of 700°F.- Product) Turbine 300-550° F.	Diesel 300-700° F.
4	75% amorphous silica-alumina in alumina 20% binder 5% LZ-10 zeolite	732	71.1	83.0
5	70% amorphous silica-alumina in alumina 20% binder 10% LZ-10 zeolite	719	71.3	83.4
6	70% amorphous silica-magnesia 20% binder 10% LZ-10 zeolite	719	70.3	82.1

As can be seen from the data in Table I, Catalysts 1 through 4, which differ only in the amorphous component of their supports, all have about the same activity, i.e., 729° F. to 732° F. However, Catalyst 1, the catalyst of the invention, has much superior and unexpected selectivities to turbine and diesel fuel. The differences in selectivities to turbine fuel range from a high of 8.3 volume percent (79.4 - 71.1) between Catalysts 1 and 4 to a low of 5.2 volume percent (79.4 - 74.2) between Catalysts 1 and 3. The differences in selectivities to diesel fuel range from a high of 6.8 volume percent (89.8 - 83.0) between Catalysts 1 and 4 to a low of 4.8 volume percent (89.8 - 85.0) between Catalysts 1 and 3. The fact that the presence of the silica-magnesia amorphous component in Catalyst 1 would result in such significant increases in selectivity to both turbine and diesel fuel as compared to similar catalysts in which the amorphous component was alumina, silica-alumina, or a dispersion of silica-alumina in gamma alumina is surprising and unexpected. Such increases in selectively are extremely important in view of the fact a 4.0 percent increase is considered commercially to be very significant because substantially more of the feed is converted to the desired product and less to lower valued products. For example, in a once-through hydrocracking process which yields 14,000 barrels per day of diesel fuel, a 4.8 percent increase in selectivity associated with Catalyst 1 as compared to Catalyst 4 will yield 672 more barrels per day and approximately 210,000 more barrels per year of the desired product. Assuming diesel fuel is priced at $40 per barrel, this increase in selectively is worth almost 8.5 million dollars per year to the refiner--a significant amount of money.

A comparison of Catalyst 1 with Catalyst 5, a commercial catalyst which differs from Catalyst 1 by containing 5 weight percent more LZ-10 zeolite and 70 weight percent dispersion of silica-alumina in alumina

instead of 75 weight percent silica-magnesia, indicates that Catalyst 1 is 10° F. less active (729° F. - 719° F.) than Catalyst 5. This lower activity is expected since Catalyst 1 contains less zeolite than Catalyst 5. However, Catalyst 1 is much more selective. According to the data, Catalyst 1 yields 8.1 volume percent (79.4 - 71.3) more turbine fuel boiling in the range between 300° F. and 550° F. and 6.4 volume percent (89.8 - 83.4) more diesel fuel boiling in the range between 300° F. and 700° F. These selectivity differences are commercially very significant. If an analysis similar to that set forth above for the selectivity difference for diesel fuel between the Catalysts 1 and 3 is followed, the use of Catalyst 1 in lieu of the commercial catalyst, i.e., Catalyst 5, results in an income of about 11.3 million dollars per year more to the refiner.

A comparison of Catalyst 1 with Catalyst 6, which differs from Catalyst 1 in containing 5 weight percent more LZ-10 zeolite and 5 weight percent less silica-magnesia, indicates, as would be expected due to its increased zeolite content, that Catalyst 1 is 10° F. less active (729° F. - 719° F.). A comparison of the selectivity data for both catalysts shows that Catalyst 1 is much more selective with respect to both turbine fuel (79.4 volume percent vs. 70.3 volume percent) and diesel fuel (89.8 volume percent vs. 82.1 volume percent). Since the only differences between these two catalysts are the amounts of zeolite and amorphous silica-magnesia present, these data tend to indicate that it is preferred, in order to maintain high selectivities, to keep the zeolite content of the support below about 10 weight percent and the silica-magnesia content above about 70 weight percent. Thus, it appears that preferred catalysts of the invention will have supports which contain between about 2 and 9 weight percent Y zeolite, preferably between 3 and 8 weight percent, and between 70 and 90 weight percent silica-magnesia, preferably 75 to 85 weight percent.

Although the invention has been primarily described in conjunction with an example and by references to embodiments thereof, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace within the invention all such alternatives, modifications, and variations that fall within the spirit and scope of the appended claims.

CLAIMS

1. A hydrocracking process for selectively producing middle distillate products which comprises contacting a hydrocarbon feedstock with a hydrocracking catalyst under conditions of elevated temperature and pressure in the presence of hydrogen so as to produce a product of lower average boiling point, said catalyst comprising:

(a) one or more hydrogenation components;

(b) a Y zeolite selected from the group consisting of Y zeolites having a unit cell size below about 24.45 angstroms and Y zeolites having a water vapor sorptive capacity less than about 10 weight percent at 25° C. and a p/p_o value of 0.10; and

(c) an amorphous silica-magnesia component.

2. A hydrocracking process as defined by claim 1 wherein said Y zeolite has a unit cell size below about 24.45 angstroms.

3. A hydrocracking process as defined by claim 1 wherein said Y zeolite has a water vapor sorptive capacity less than about 10 weight percent at 25° C. and a p/p_o value of 0.10.

4. A hydrocracking process as defined by claim 1 wherein said Y zeolite has both a unit cell size below about 24.45 angstroms and a water vapor sorptive capacity less than about 10 weight percent at 25° C. and a p/p_o value of 0.10.

5. A hydrocracking process as defined by claim 1 wherein said catalyst further comprises an inorganic refractory oxide binder.

6. A hydrocracking process as defined by claim 5 wherein said inorganic refractory oxide binder comprises alumina.

7. A hydrocracking process as defined by claim 1 wherein said lower average boiling point product contains components boiling below 700° F. and greater than about 86 volume percent of said components boil in the range between 300° F. and 700° F.

8. A hydrocracking process as defined by claim 1 wherein said Y zeolite is a UHP-Y zeolite.

9. A hydrocracking process as defined by claim 1 wherein said Y zeolite has been exchanged with rare earth-containing cations.

10. A hydrocracking process as defined by claim 9 wherein said Y zeolite contains at least about 2 weight percent rare earth metals, calculated as RE_2O_3.

11. A hydrocracking process as defined by claim 1 wherein said lower average boiling point product contains components boiling below 700° F. and greater than about 75 volume percent of said components boil in the range between 300° F. and 550° F.

12. A hydrocracking process as defined by claim 1 wherein said Y zeolite has an overall silica-to-alumina mole ratio less than 6.0.

13. A hydrocracking process as defined by claim 6 wherein said catalyst contains both a nickel hydrogenation component and a tungsten hydrogenation component, said Y zeolite is LZ-10 zeolite, and greater than about 86 volume percent of the hydrocarbons in the 700° F.- boiling fraction of said lower average boiling point product boils in the range between 300° F. and 700° F.

14. A hydrocracking process as defined by claim 1 wherein said Y zeolite is prepared by a process comprising the steps of:

(a) partially ammonium exchanging a sodium Y zeolite;

(b) calcining the resultant zeolite in the presence of water vapor;

(c) ammonium exchanging a second time; and

(d) calcining the zeolite from step (c) in the presence of water vapor.

15. A hydrocracking process as defined by claim 14 wherein said Y zeolite is prepared such that in step (a) the sodium Y zeolite is reduced in sodium content to between about 0.6 and 5 weight percent, calculated as Na_2O, in step (b) a steam atmosphere is employed and the unit cell size of the zeolite is reduced to a value between about 24.40 and 24.64 angstroms, in step (c) the ammonium exchange reduces the sodium content to below about 0.5 weight percent, calculated as Na_2O, and in step (d) the calcination is conducted in the presence of steam and the unit cell size of the zeolite after calcination is less than about 24.40 angstroms.

16. A hydrocracking process as defined by claim 15 wherein the zeolite in step (d) has a final unit cell size between about 24.20 and 24.35 angstroms.

17. A hydrocracking process as defined by claim 1 wherein said catalyst contains a Group VIII metal hydrogenation component selected from the group consisting of nickel, cobalt, and the oxides and sulfides thereof and a Group VIB metal hydrogenation component selected from the group consisting of molybdenum, tungsten, and the oxides and sulfides thereof.

18. A hydrocracking process as defined by claim 17 wherein at least about 70 volume percent of the components in said hydrocarbon feedstock boil above about 700° F. and said process is carried out under conditions such that the products produced which boil below 700° F. contain at least about 87 volume percent components boiling in the range between 300° F. and 700° F.

19. A hydrocracking process as defined by claim 18 wherein said lower average boiling point product contains components boiling below 700° F. and greater than about 76 volume percent of said components boil in the range between 300° F. and 550° F.

20. A hydrocracking process as defined by claim 18 wherein said catalyst contains between about 4 and 8 weight percent Y zeolite.

21. A hydrocracking process as defined by claim 20 wherein said catalyst contains between about 50 and 65 weight percent silica-magnesia.

22. A hydrocracking process which comprises contacting a hydrocarbon feedstock with a catalyst under conditions of elevated temperature and pressure in the presence of hydrogen so as to produce a product of lower average boiling point, said catalyst comprising one or more hydrogenation components in combination with a support comprising:

(a) an inorganic refractory oxide binder;

(b) a Y zeolite having an overall silica-to-alumina mole ratio less than 6.0, a unit cell size between about 24.20 and 24.35 angstroms and a water vapor sorptive capacity less than about 10 weight percent at 25° C. and p/p_o value of 0.10; and

(c) an amorphous silica-magnesia component.

23. A hydrocracking process as defined by claim 22 wherein said Y zeolite has a water vapor sorptive capacity less than about 5 weight percent of said zeolite at 25° C. and a p/p_o value of 0.10.

24. A hydrocracking process as defined by claim 23 wherein said hydrogenation components comprise components selected from the group consisting of Group VIB and Group VIII metals and compounds thereof.

25. A hydrocracking process as defined by claim 24 wherein said Group VIB metal hydrogenation component is selected from the group consisting of molybdenum, tungsten, and the oxides and sulfides thereof and said Group VIII metal hydrogenation component is selected from the group consisting of nickel, cobalt, and the oxides and sulfides thereof.

26. A hydrocracking process as defined by claim 22 wherein said lower average boiling point product contains components boiling below 700° F. and greater than about 88 volume percent of said components boil in the range between about 300° F. and 700° F.

27. A hydrocracking process as defined by claim 23 wherein said Y zeolite has been exchanged with rare earth-containing cations.

28. A hydrocracking process as defined by claim 23 wherein said inorganic refractory oxide binder comprises alumina.

29. A hydrocracking process as defined by claim 28 wherein said catalyst comprises a nickel hydrogenation component and a tungsten hydrogenation component.

30. A hydrocracking process as defined by claim 29 wherein said Y zeolite is LZ-10 zeolite.

31. A hydrocracking process as defined by claim 22 wherein said support contains between about 2 and 9 weight percent of said Y zeolite.

32. A hydrocracking process as defined by claim 27 wherein said Y zeolite contains at least about 4 weight percent rare earth metals calculated as RE_2O_3.

33. A hydrocracking process as defined by claim 30 wherein said lower average boiling point product contains components boiling below 700° F. and greater than about 77 volume percent of said components boil in the 300° F. to 550° F. range.

34. A hydrocracking process as defined by claim 22 wherein said hydrocarbon feedstock is hydrotreated prior to being contacted with said catalyst.

35. A hydrocracking process as defined by claim 31 wherein said support comprises between about 75 and 85 weight percent of said amorphous silica-magnesia component.

36. A hydrocracking catalyst comprising;

(a) one or more hydrogenation components;

(b) a Y zeolite selected from the group consisting of Y zeolites having a unit cell size below about 24.45 angstroms and Y zeolites having a water vapor sorptive capacity less than about 10 weight percent at 25° C. and a p/p_o value of 0.10; and

(c) an amorphous silica-magnesia component.

37. A hydrocracking catalyst as defined by claim 35 further comprising an inorganic refractory oxide binder.

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 93/06690

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [6]

According to International Patent Classification (IPC) or to both National Classification and IPC

IPC[5]: C 10 G 47/16,B 01 J 29/08

II. FIELDS SEARCHED

Minimum Documentation Searched [7]

Classification System	Classification Symbols
IPC[5]	C 10 G,B 01 J

Documentation Searched other than Minimum Documentation to the Extent that such Documents are included in the Fields Searched [8]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [9]

Category *	Citation of Document, [11] with indication, where appropriate, of the relevant passages [12]	Relevant to Claim No. [13]
X	US, A, 3 835 027 (WARD) 10 September 1974 (10.09.74), the whole document. --	1-37
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X	US, A, 3 838 040 (WARD) 24 September 1974 (24.09.74), the whole document. --	1,22, 36
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* Special categories of cited documents: [10]

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

IV. CERTIFICATION

Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report
29 October 1993	01. 12. 93
International Searching Authority	**Signature of Authorized Officer**
EUROPEAN PATENT OFFICE	BECK e.h.

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
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ANHANG — ANNEX — ANNEXE

zum internationalen Recherchenbericht über die internationale Patentanmeldung Nr.

to the International Search Report to the International Patent Application No.

au rapport de recherche international relatif á la demande de brevet international n°

PCT/US 93/06690 SAE 77321

In diesem Anhang sind die Mitglieder der Patentfamilien der im obengenannten internationalen Recherchenbericht angeführten Patentdokumente angegeben. Diese Angaben dienen nur zur Unterrichtung und erfolgen ohne Gewähr.

This Annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The Office is in no way liable for these particulars which are given merely for the purpose of information.

La présente annexe indique les membres de la famille de brevets relatifs aux documents de brevets cités dans le rapport de recherche international visée ci-dessus. Les reseignements fournis sont donnés á titre indicatif et n'engagent pas la responsibilité de l'Office.

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