NOBLE METAL CONTAINING LOW ACIDIC HYDROCRACKING CATALYSTS

The present invention relates to novel hydrocracking catalysts. More particularly, the invention relates to noble metal containing low acidic hydrocracking catalysts.

Hydrocracking utilizing a zeolite catalyst is widely used in petroleum refining for converting various petroleum fractions to lighter and more valuable products, especially gasoline and distillates such as jet fuels, diesel fuels and heating oils.

Known hydrocracking catalysts comprise an acid cracking component and a hydrogenation component. The acid component can be an amorphous material such as an acidic clay or amorphous silica-alumina or, alternatively, a zeolite. Large pore zeolites such as zeolites X and Y possessing relatively low silica:alumina ratios, e.g., less than 40:1, have been conventionally used for this purpose because the principal components of the feedstocks (gas oils, coker bottoms, reduced crudes, recycle oils, FCC bottoms) are higher molecular weight hydrocarbons which will not enter the internal pore structure of the smaller pore zeolites and therefore will not undergo conversion. The hydrogenation component may be a noble metal such as platinum or palladium or a non-noble metal such as nickel, molybdenum or tungsten or a combination of these metals.

A measurement of acidity provides an indication of the amount of framework aluminum in a zeolite. The reduction of acidity indicates that a portion of framework alumina is being lost. Thus, a higher silica to alumina ratio will correspond to a lower acidity. Although the silica to alumina ratio is most often used to refer to the cracking activity of a catalyst, alpha acidity is a more accurate measurement of such activity.

Distillate selective hydrocracking catalysts which rely upon the acidic components of the zeolite for hydrocracking activity cause a significant amount of unwanted secondary cracking of paraffins along with the desired cracking of aromatic and naphthenic components. This secondary cracking results in distillate yield loss.

There is, therefore, a need for a distillate selective hydrocracking catalyst with very low acidity, i.e., a hydrocracking catalyst which does not rely upon acidity of the zeolite for its hydrocracking activity. It has been found that such a catalyst is useful in various

hydrocracking processes, such as a process for increasing diesel fuel cetane levels described in co-pending U.S. application Serial No. 09/222,977, filed concurrently herewith.

The present invention is a hydrocracking catalyst composition that includes a large pore crystalline molecular sieve material component having a faujasite structure and an alpha acidity of less than 1, and a Group VIII noble metal component. Preferred crystalline sieve materials are zeolite Y and zeolite USY. In the preferred embodiment, the crystalline sieve material has an alpha acidity of 0.3 or less. The Group VIII noble metal component can be platinum, palladium, iridium, rhodium, or a combination of one or more of these noble metals. Platinum is preferred. The content of the Group VIII noble metal component can vary between 0.01 and 5 wt.% of the catalyst.

The Group VIII noble metal component is located within the catalyst in dispersed clusters. In the preferred embodiment, the particle size of the Group VIII metal on the catalyst is less than 10Å. Dispersion of the metal can also be measured by hydrogen chemisorption technique in terms of the H/metal ratio. In the preferred embodiment, when platinum is used as the noble metal component, the H/Pt ratio between 1.1 and 1.5.

In a preferred embodiment, the catalyst is prepared by a method which includes: (a) replacing hydrogen on hydroxyl nest groups located within the crystalline molecular sieve material component with the Group VIII noble metal component by impregnation or cation exchange in a basic solution; (b) drying the catalyst to remove the basic solution; and (c) calcining the catalyst. Preferably, the basic solution has a pH of from 7.5 to 10.0.

The catalysts of the present invention have a low acidity that provides selective hydrocracking of the aromatics and naphthenes in a feedstock, while limiting the cracking of paraffins. The catalysts produce improved yields of distillate products, such as diesel fuel, at high conversion rates.

The catalysts of the present invention include a large pore crystalline molecular sieve material component with a faujasite structure having an alpha acidity of less than 1 and, preferably, 0.3 or less. The catalysts also contain a Group VIII noble metal component.

Unlike catalysts known in the art, the catalysts of the present invention do not rely on acidity to drive the hydrocracking reactions. Hydrocracking is driven by the Group VIII noble metal component, which acts as a hydrogenation and hydrocracking component. The crystalline molecular sieve material acts as a host for the Group VIII noble metal component.

The low acidity permits the hydrocracking of the aromatics and naphthenic species, but minimizes secondary cracking of paraffins. Also, the faujasitic crystalline molecular sieve material provides reactant selectivity for adsorbing aromatic and naphthenic hydrocarbon structures, as opposed to paraffins. The preference of the catalyst for ringed structures allows the paraffins to pass through with minimal hydrocracking or hydroisomerization, thereby retaining a high distillate yield.

Constraint Index (CI) is a convenient measure of the extent to which a crystalline sieve material allows molecules of varying sizes access to its internal structure. Materials which provide highly restricted access to their internal structures have a high CI value and small pore size, e.g. less than 5 angstroms. On the other hand, materials which provide relatively free access to their internal porous crystalline sieve structure have a low CI value, and usually pores of large size, e.g. greater than 7 angstroms. The method by which CI is determined is described fully in U.S. Pat. No. 4,016,218.

Large pore crystalline sieve materials are typically defined as having a CI of 2 or less. Crystalline sieve materials having a CI of 2-12 are generally regarded to be medium pore materials.

The CI is calculated as follows:

$$\text{Constraint Index} = \frac{\log_{10}(\text{fraction of n-hexane remaining})}{\log_{10}(\text{fraction of 3-methylpentane remaining})} \qquad (1)$$

The CI approximates the ratio of the cracking rate constants for the two hydrocarbons.

TABLE 1

Constraint Index (CI) values for some typical materials

Material	CONSTRAINT INDEX (CI)	Test Temperature
ZSM-4	0.5	316°C
ZSM-5	6 - 8.3	371°C - 316°C
ZSM-11	5 - 8.7	371°C - 316°C
ZSM-12	2.3	316°C
ZSM-20	0.5	371°C
ZSM-22	7.3	427°C
ZSM-23	9.1	427°C
ZSM-34	50	371°C
ZSM-35	4.5	454°C
ZSM-38	2	510°C
ZSM-48	3.5	538°C
ZSM-50	2.1	427°C
TMA Offretite	3.7	316°C
TEA Mordenite	0.4	316°C
Clinoptilolite	3.4	510°C
Mordenite	0.5	316°C
REY	0.4	316°C
Amorphous Silica-alumina	0.6	538°C
Dealuminized Y (Deal Y)	0.5	510°C
Erionite	38	316°C
Zeolite Beta	0.6 - 2.0	316°C - 399°C

The catalysts of the invention contain a large pore crystalline sieve material component with a CI of less than 2. The materials have a pore size sufficiently large to admit most of the components normally found in a feedstock and generally have a pore size greater than 7 Angstroms. These materials can include zeolites, such as Zeolite beta, Zeolite Y, Ultrastable Y (USY), Dealuminized Y (DEALY), Mordenite, ZSM-3, ZSM-4, ZSM-18 and ZSM-20.

The large pore crystalline sieve materials useful for the catalysts of the invention are of the faujasite family. Within the ranges specified above, preferred crystalline sieve materials

useful for the catalysts of the invention are zeolite Y and zeolite USY. Zeolite USY is most preferred.

The CI provides a means for identifying the crystalline molecular sieve materials which are particularly useful in the present invention. However, the CI is the cumulative result of several variables that are used in the determination and calculation thereof. Thus, other variables, such as the cracking temperature, the conversion rate, the crystal size of the zeolite, the presence of possibly occluded contaminants and binders intimately combined with the zeolite may affect the CI. Therefore, it is possible to select test conditions (e.g., temperature) that establish more than one value for the CI of a particular crystalline sieve material. This explains the range of Constraint Indices for some materials. Accordingly, it is understood to those skilled in the art that the CI, as utilized herein, while affording a highly useful means for characterizing the zeolites of interest, is an approximation. However, in all instances, at a temperature within the above-specified range of 290° to 538°C, the CI will have a value for any given crystalline molecular sieve material of particular interest herein of 2 or less.

It is possible to judge from a known crystalline structure whether a sufficient pore size exists. Pore windows are formed by rings of silicon and aluminum atoms. 12-membered rings are preferred in the catalyst of the invention in order to be sufficiently large to admit the components normally found in a feedstock. Such a pore size is also sufficiently large to allow paraffinic materials to pass through.

The crystalline sieve materials that can be utilized in the hydrocracking catalyst have a hydrocarbon sorption capacity for n-hexane of at least 5%. The hydrocarbon sorption capacity of a zeolite is determined by measuring its sorption at 25°C and at 40 mm Hg (5333 Pa) hydrocarbon pressure in an inert carrier such as helium. The sorption test is conveniently carried out in a thermogravimetric analysis (TGA) with helium as a carrier gas flowing over the zeolite at 25°C. The hydrocarbon of interest, e.g., n-hexane, is introduced into the gas stream adjusted to 40 mm Hg hydrocarbon pressure and the hydrocarbon uptake, measured as an increase in zeolite weight, is recorded. The sorption capacity may then be calculated as a percentage in accordance with the relationship:

$$\text{Hydrocarbon Sorption Capacity (\%)} = \frac{\text{Wt. of Hydrocarbon Sorbed}}{\text{Wt. of zeolite}} \times 100 \qquad (2)$$

The catalysts of the invention contain a Group VIII noble metal component. This metal component acts to catalyze both hydrogenation and hydrocracking of the aromatic and naphthenic species within the feedstock. Suitable noble metal components include platinum, palladium, iridium and rhodium, or a combination thereof. Platinum is preferred. The hydrocracking process is driven by the affinity of the aromatic and naphthenic hydrocarbon molecules to the noble metal supported within the highly siliceous faujasite crystalline molecular sieve material.

The amount of the Group VIII noble metal component can range from 0.01 to 5% by weight and is normally from 0.1 to 3% by weight, preferably .3 to 2 wt.%. The precise amount will, of course, vary with the nature of the component. Less of the highly active noble metals, particularly platinum, is required than of less active metals. Because the hydrocracking activity of the catalyst is metal catalyzed, it is preferred that a larger volume of the metal be incorporated into the catalyst.

Applicants have discovered that highly dispersed Group VIII noble metal particles acting as the hydrogenation/hydrocracking component reside on severely dealuminated crystalline sieve material. The dispersion of the noble metal, such as Pt (platinum), can be measured by the cluster size of the noble metal component. The cluster of noble metal particles within the catalyst should be less than 10Å. For platinum, a cluster size of 10Å would be 30 to 40 atoms. This smaller particle size and greater dispersion provides a greater surface area for the hydrocarbon to contact the hydrogenating/hydrocracking Group VIII noble metal component.

The dispersion of the noble metal can also be measured by the hydrogen chemisorption technique. This technique is well known in the art and is described in J. R. Anderson, Structure of Metallic Catalysts, Academic Press, London, pp. 289-394 (1975). In the hydrogen chemisorption technique, the amount of dispersion of the noble metal, such as Pt (platinum), is expressed in terms of the H/Pt ratio.

An increase in the amount of hydrogen absorbed by a catalyst will correspond to an increase in the H/Pt ratio. A higher H/Pt ratio corresponds to a higher platinum dispersion. Typically, an H/Pt value of greater than 1 indicates the average platinum particle size of a given catalyst is less than 1 nm. For example, an H/Pt value of 1.1 indicates the platinum particles within the catalyst form cluster sizes of less than 10Å. In the process of the

invention, the H/Pt ratio can be greater than 0.8, preferably between 1.1 and 1.5. The H/noble metal ratio will vary based upon the hydrogen chemisorption stoichiometry of the metal. For example, if rhodium is used as the Group VIII noble metal component, the H/Rh ratio will be almost twice as high as the H/Pt ratio, i.e., greater than 1.6 and, preferably between 2.2 and 3.0. Regardless of which Group VIII noble metal is used, the noble metal cluster particle size should be less than 10Å.

The acidity of the catalyst can be measured by its Alpha Value, also called alpha acidity. The catalyst of the invention has an alpha acidity of less than 1, preferably 0.3 or less. The Alpha Value is an approximate indication of the catalytic cracking activity of the catalyst compared to a standard catalyst and it gives the relative rate constant (rate of normal hexane conversion per volume of catalyst per unit time). It is based on the activity of the highly active silica-alumina cracking catalyst which has an Alpha of 1 (Rate Constant = 0.016 sec^{-1}). The test for alpha acidity is described in U.S. Pat. No. 3,354,078; in the Journal of Catalysis, 4, 527 (1965); 6, 278 (1966); 61, 395 (1980). The experimental conditions of the test used therein include a constant temperature of 538°C and a variable flow rate as described in the Journal of Catalysis, 61, 395 (1980).

Alpha acidity provides a measure of framework alumina. The reduction of alpha indicates that a portion of the framework aluminum is being lost. It should be understood that the silica to alumina ratio referred to in this specification is the structural or framework ratio, that is, the ratio of the SiO_4 to the Al_2O_4 tetrahedra which, together, constitute the structure of the crystalline sieve material. This ratio can vary according to the analytical procedure used for its determination. For example, a gross chemical analysis may include aluminum which is present in the form of cations associated with the acidic sites on the zeolite thereby giving a low silica:alumina ratio. Similarly, if the ratio is determined by thermogravimetric analysis (TGA) of ammonia desorption, a low ammonia titration may be obtained if cationic aluminum prevents exchange of the ammonium ions onto the acidic sites. These disparities are particularly troublesome when certain dealuminization treatments are employed which result in the presence of ionic aluminum free of the zeolite structure. Therefore, the alpha acidity should be determined in hydrogen form.

A number of different methods are known for increasing the structural silica:alumina ratios of various zeolites. Many of these methods rely upon the removal of aluminum from the

structural framework of the zeolite employing suitable chemical agents. Specific methods for preparing dealuminized zeolites are described in the following to which reference may be made for specific details: "Catalysis by Zeolites" (International Symposium on Zeolites, Lyon, Sep. 9-11, 1980), Elsevier Scientific Publishing Co., Amsterdam, 1980 (dealuminization of zeolite Y with silicon tetrachloride); U.S. Pat. No. 3,442,795 and U.K. Pat. No. 1,058,188 (hydrolysis and removal of aluminum by chelation); U.K. Pat. No. 1,061,847 (acid extraction of aluminum); U.S. Pat. No 3,493,519 (aluminum removal by steaming and chelation); U.S. Pat. No. 3,591,488 (aluminum removal by steaming); U.S. Pat. No. 4,273,753 (dealuminization by silicon halide and oxyhalides); U.S. Pat. No. 3,691,099 (aluminum extraction with acid); U.S. Pat. No. 4,093,560 (dealuminization by treatment with salts); U.S. Pat. No. 3,937,791 (aluminum removal with Cr(III) solutions); U.S. Pat. No. 3,506,400 (steaming followed by chelation); U.S. Pat. No. 3,640,681 (extraction of aluminum with acetylacetonate followed by dehydroxylation); U.S. Pat. No. 3,836,561 (removal of aluminum with acid); German Offenleg. No. 2,510,740 (treatment of zeolite with chlorine or chlorine-containing gases at high temperatures), Dutch Pat. No. 7,604,264 (acid extraction), Japanese Pat. No. 53/101,003 (treatment with EDTA or other materials to remove aluminum) and J. Catalysis, 54, 295 (1978) (hydrothermal treatment followed by acid extraction).

The preferred dealuminization method for preparing the catalyst of the invention is steaming dealuminization, due to its convenience and low cost. More specifically, the preferred method of obtaining the low acidic crystalline molecular sieve material utilized in the catalyst of the invention is through steaming an already low acidic USY zeolite (e.g., alpha acidity of 10 or less) to the level required, i.e., an alpha acidity of less than 1.

The steaming dealuminization method includes contacting the USY zeolite with steam at an elevated temperature of from 550° to 815°C for a period of time, e.g., 0.5 to 24 hours, sufficient for structural alumina to be displaced, thereby lowering the alpha acidity to the desired level of less than 1, preferably less than 0.3. In contrast, the alkaline cation exchange method of dealuminization is less useful because it tends introduce residual protons upon H_2 reduction during hydroprocessing, which may contribute unwanted acidity to the catalyst and also reduce the noble metal catalyzed hydrocracking activity.

The Group VIII noble metal component can be incorporated by any means known in the art. However, it should be noted that a hydrogenation/hydrocracking component, such as

noble metal, would not be incorporated into such a dealuminated crystalline molecular sieve material under conventional exchange conditions because very few exchange sites exist for the noble metal cationic precursors.

The preferred methods of incorporating the Group VIII noble metal component onto the interior sites of the crystalline molecular sieve material are either impregnation or cation exchange. The metal can be incorporated in the form of a cationic or neutral complex. $Pt(NH_3)_4^{2+}$ and cationic complexes of this type are convenient for exchanging metals onto the crystalline molecular sieve component. Anionic complexes are not preferred.

The steaming dealuminzation process described above creates defect sites, also called hydroxyl nests, where the structural alumina has been removed. The formation of hydroxyl nests is described in Gao, Z. et al., "Effect of Dealumination Defects on the Properties of Zeolite Y", J. Applied Catalysis, 56:1 pp. 83-94 (1989); Thakur, D., et al., "Existence of Hydroxyl Nests in Acid-Extracted Mordenites," J. Catal., 24:1 pp. 543-6 (1972). Hydroxyl nests can also be created by other dealumination processes listed above, such as acid leaching (*see*, Thakur et. al.), or can be created during synthesis of the crystalline molecular sieve material component.

In the preferred method of preparing the catalyst of the invention, the Group VIII noble metal component is introduced onto the interior sites of the crystalline molecular sieve material component via impregnation or cation exchange with the hydroxyl nest sites in a basic solution, preferably pH of from 7.5 to 10, more preferably pH 8-9. The solution can be inorganic, such a H_2O, or organic such as alcohol. In this basic solution, the hydrogen on the hydroxyl nest sites can be replaced with the Group VIII noble metal containing cations, such as at $Pt(NH_3)_4^{2+}$.

After the Group VIII noble metal component is incorporated onto the interior sites of the crystalline molecular sieve material, the basic solution is removed by drying at 130° to 140°C for several hours. The catalyst is then dry air calcined for several hours, preferably 3 to 4 hours, at a temperature of 350°C.

To be useful in a reactor, the catalyst will need to be formed either into an extrudate, beads, pellets, or the like. To form the catalyst, an inert support can be used that will not induce acidity in the catalyst, such as self- and/or silica binding of the catalyst. A binder that is not inert, such as alumina, should not be used since aluminum could migrate from the binder

and become re-inserted into the crystalline molecular sieve material. This re-insertion can lead to creation of the undesirable acidity sites during the post steaming treatment.

The preferred low acidic hydrocracking catalyst is a dealuminated Pt/USY catalyst.

The following example is provided to assist in a further understanding of the invention. The particular materials and conditions employed are intended to be further illustrative of the invention and are not limiting upon the reasonable scope thereof.

EXAMPLE 1

This example illustrates the preparation of a hydrocracking catalyst of this invention.

A commercial TOSOH 390 USY (alpha acidity of 5) was steamed at 1025°F for 16 hours. X-ray diffraction showed an excellent crystallinity retention of the steamed sample. n-Hexane, cyclo-hexane, and water sorption capacity measurements revealed a highly hydrophobic nature of the resultant siliceous large pore zeolite. The properties of the severely dealuminated USY are summarized in Table 2.

TABLE 2

Properties of Dealuminated USY

PROPERTY	VALUE
Zeolite Unit Cell Size	24.23A
BET Surface Area	642 m^2/g
Na	115 ppm
n-Hexane Sorption Capacity	19.4%
cyclo-Hexane Sorption Capacity	21.4%
Water Sorption Capacity	3.1%
Zeolite Acidity, α	0.3

0.6 wt.% of Pt was introduced onto the USY zeolite by cation exchange technique, using $Pt(NH_3)_4(OH)_2$ as the precursor. During the exchange in a pH 8.5-9.0 aqueous solution, $Pt(NH_3)_4^{+2}$ cation replaced H^+ associated with the zeolitic silanol groups and hydroxyl nests. Afterwards, excess water rinse was applied to the Pt exchanged zeolite material to demonstrate the extra high $Pt(NH_3)_4^{+2}$ cation exchange capacity of this highly siliceous USY. The water was then removed at 130°C for 4 hours. Upon dry air calcination at 350°C for four hours, the resulting catalyst had an H/Pt ratio of 1.12, determined by standard hydrogen

chemisorption procedure. The chemisorption result indicated that the dealuminated USY zeolite supported highly dispersed Pt particles (i.e., <10Å). The properties of the resulting hydrocracking catalysts are set forth in Table 3.

TABLE 3

Hydrocracking Catalyst Properties

PROPERTY	VALUE
H/Pt Ratio	1.12
Pt Content	0.60%

While there have been described what are presently believed to be the preferred embodiments of the invention, those skilled in the art will realize that changes and modifications may be made thereto without departing from the spirit of the invention, and it is intended to claim all such changes and modifications as fall within the true scope of the invention.

CLAIMS:

1. A hydrocracking catalyst comprising:

a) a large pore crystalline molecular sieve material component having a faujasite structure and an alpha acidity of less than 1, and

b) a Group VIII noble metal component.

2. A catalyst as described in claim 1 wherein the crystalline molecular sieve material is zeolite Y or zeolite USY.

3. A catalyst as described in claim 1 wherein the crystalline molecular sieve material has an alpha acidity of 0.3 or less.

4. A catalyst as described in claim 1 wherein the Group VIII noble metal component is selected from the group consisting of platinum, palladium, iridium, rhodium, or a combination thereof.

5. A catalyst as described in claim 1 wherein the Group VIII metal component is platinum.

6. A catalyst as described in claim 1 wherein the Group VIII noble metal component has a particle size of less than 10Å.

7. A catalyst as described in claim 5 wherein the platinum is dispersed on the crystalline molecular sieve component, the dispersion being characterized by an H/Pt ratio of between 1.1 and 1.5.

8. A catalyst as described in claim 1 wherein the content of the Group VIII noble metal component is between 0.01 and 5 wt.% of the catalyst.

9. A catalyst as described in claim 1 wherein the catalyst is prepared by a method comprising:

a) replacing hydrogen on hydroxyl nest groups located within the crystalline molecular sieve material component with the Group VIII noble metal component by impregnation or cation exchange in a basic solution;

b) drying the catalyst to remove the basic solution; and

c) calcining the catalyst.

10. A catalyst as described in claim 9 wherein the basic solution has a pH of from 7.5 to 10.0.