

Hydrocracking Catalyst, Preparation Method and Use Thereof, and Method for Hydrocracking Catalytic Diesel Oil

Cross Reference to Related Application

- 5 This application claims priority to Chinese Application No.201510761618.4 filed on Nov. 11, 2015, entitled “Catalytic Diesel Oil Hydrocracking Catalyst and Method for Preparing the same”, which is specifically and entirely incorporated by reference.

FIELD OF THE INVENTION

- 10 The present invention relates to the catalytic diesel oil hydrocracking field, in particular to a hydrocracking catalyst, a method for preparing the hydrocracking catalyst and a use of the hydrocracking catalyst, and a method for hydrocracking catalytic diesel oil.

BACKGROUND OF THE INVENTION

- 15 In recent years, as the crude oil processed in China is heavier increasingly, the raw materials processed by catalytic cracking are heavier and poorer; in addition, many enterprises have renovated their catalytic cracking plants or increased the operating severity of their catalytic cracking plants in order to attain a purpose of improving gasoline quality or increasing the yield, resulting in poorer quality of products obtained
- 20 by catalytic cracking, especially catalytic diesel oil.

New hydrocracking processes and techniques for producing naphtha components and low-sulfur clean diesel fuel with a high added value by means of hydro-conversion of diesel oil with high aromatic content have good application prospects, in order to improve the utilization of petroleum resources, improve the overall level of quality of gasoline and diesel fuels, attain an objective of optimized product bending and maximized product value, and meet the increasing demand for clean fuels in China. Domestic and foreign researchers have also made extensive researches. There are reports on conversion of catalytically cracked light cycle oils into blended extra-low-sulfur diesel and high-octane gasoline components with hydrocracking techniques in foreign countries. For example, on the NPRA Annual Seminar 1995, David A. Pappal et al. introduced a single-stage hydrocracking process developed by Mobil, Akzo Nobel/Nippon Ketjen, and M. W. Kellogg. On the NPRA Annual Seminar 2005, Vasant P. Thakkar et al. introduced the LCO Unicracking™ technique developed by UOP. It is reported that both techniques can be used to convert low-value catalytic cycle oils into blended high-octane gasoline component and high-quality diesel component.

A key point in the catalytic diesel oil hydro-conversion process and technique is to accomplish ring-opening and cracking of di-aromatic hydrocarbons and tri-aromatic hydrocarbons in the catalytic diesel fraction while keeping the mono-aromatic hydrocarbons in the gasoline fraction and reducing ring-opening reaction of the aromatic hydrocarbons in the gasoline fraction and the gas produced through further cracking as far as possible, and thereby improve the yield and octane number of the gasoline product.

In addition, as that technique is applied in industrial application, the catalytic diesel oil conversion technique exhibits some drawbacks in industrial application: Firstly, compared with other hydrocracking techniques and processes, the catalytic diesel oil hydro-conversion technique (FD2G) and process results severe deviation in product
5 distribution and product quality from the design objectives in the initial stage of operation, i.e., the octane number of the gasoline product and the gasoline yield are obviously lower than the desired targets; as the production time extends, the product distribution and the quality of gasoline product are gradually improved, till they reach a good and relatively stable level; however, that process is very long (usually longer than
10 1 month).

Secondly, compared with conventional hydrocracking techniques, in the catalytic diesel oil hydro-conversion technique, reaction raw materials have poor quality and high contents of di-aromatic hydrocarbons and tri-aromatic hydrocarbons; moreover, the reaction conditions are demanding. Consequently, the catalyst deactivation rate in the
15 catalytic diesel oil hydro-conversion process is much higher than that in conventional hydrocracking processes, resulting in a shortened operation cycle, and bringing difficulties to production scheduling in the plant.

CN105642335A has disclosed a method for preparing a hydrocracking catalyst, comprising: (1) selecting a hydrocracking catalyst supporter material, which contains at
20 least one acidic cracking material, adding an acidic peptizing agent into the supporter material, and preparing a hydrocracking catalyst supporter through molding, drying, and roasting; (2) preparing a saline solution with 10~30g/100ml active metal content, impregnating the hydrocracking catalyst supporter prepared in the step (1) in the saline

solution in a saturated state, and then drying and roasting the hydrocracking catalyst supporter; (3) impregnating the roasted catalyst obtained in the step (2) in a liquid olefin in a saturated state, and heating the impregnated catalyst at 50~400°C for 1~70h in air, so that a carbon deposition reaction happens on the catalyst and thereby a carbonized catalyst is obtained; (4) loading the carbonized catalyst supporter prepared in the step (3) directly into a muffle furnace preheated to 400~600°C, and roasting for 5~200 minutes, to burnt off the carbon deposit on the surface layer of the catalyst supporter, so that the carbon amount in the supporter accounts for 10~90% of the total carbon amount before the catalyst supporter is roasted; (5) preparing a saline solution with 40~80g/100ml active metal content, impregnating the roasted catalyst supporter obtained in the step (4) in the saline solution in a saturated state, and then drying and roasting, to obtain a finished product of hydrocracking catalyst. In that method, the active metal is impregnated in two steps, to form gradient distribution of active metal on the catalyst, wherein, the active metal content in the surface layer of the catalyst is higher than the active metal content in the core part of the catalyst; thus, the catalyst can be used to process wax oil raw material to produce chemical raw materials such as tail oil and heavy naphtha, etc., increase the hydrogenation saturation rate of the macromolecular tail oil and decrease the saturation rate of the generated naphtha fraction, and thereby improve the reaction selectivity. However, the catalyst is not applicable to catalytic diesel oil hydrocracking.

It can be seen that there are drawbacks in the prior art, including: poor reaction effect of fresh catalyst in the initial stage of operation, and poor catalyst stability.

SUMMARY OF THE INVENTION

To overcome the above-mentioned drawbacks in the catalytic diesel oil hydrocracking process in the prior art, the present invention provides a hydrocracking catalyst, a preparation method and an application of the hydrocracking catalyst, and a catalytic
5 diesel oil hydrocracking method.

To attain the objects described above, the present invention provides a hydrocracking catalyst, wherein the hydrocracking catalyst comprises a supporter, an active metal component, and carbon, wherein, based on the total weight of the hydrocracking catalyst, the content of the supporter is 60~90wt%, the content of the active metal
10 component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~5wt%; measured with an infrared acidimetric estimation method, the acid properties of the hydrocracking catalyst are: the total infrared acid amount is 0.4~0.8mmol/g, wherein, the infrared acid amount of strong acid with desorption temperature greater than 350°C is 0.08mmol/g or lower, and the ratio of the
15 total infrared acid amount to the infrared acid amount of strong acid with desorption temperature greater than 350°C is 5~50.

The present invention further provides a method for preparing a hydrocracking catalyst, comprising the following steps: (1) controlling a supporter to contact with a carbon source and have carbon deposition reaction, to obtain a carbonized supporter; (2)
20 roasting the carbonized supporter in an oxygen-containing gas, to obtain a decarbonized supporter, in which the carbon content is 20~80% of the carbon content in the carbonized supporter, wherein, the oxygen content in the oxygen-containing gas is 0.5~8vol%, the roasting temperature is 250°C~390°C, and the roasting time is 3.5~20h;

(3) introducing a precursor of active metal component into the decarbonized supporter, and drying the decarbonized supporter; (4) treating the product obtained in the step (3) through a heat treatment process, in which the precursor of active metal component is converted into active metal oxides, and the carbon in the decarbonized supporter is kept;
5 wherein, the hydrocracking catalyst contain 1~5wt% carbon calculated in C element, and the supporter and the precursor of active metal component are dosed in a way that the hydrocracking catalyst contains 60~90wt% supporter and 15~40wt% active metal component calculated in metal oxides.

The present invention further provides a hydrocracking catalyst prepared with the
10 method according to the present invention.

The present invention further provides a use of the hydrocracking catalyst according to the present invention in diesel oil hydrocracking reaction.

The present invention further provides a method for hydrocracking catalytic diesel oil, comprising: (a) pre-treating catalytic diesel oil by hydrocracking; and (b) treating the
15 product obtained in the step (a) by hydrocracking in the presence of the hydrocracking catalyst according to the present invention and hydrogen.

In the present invention, first, a supporter that contacts with a carbon source is controlled to have carbon deposition reaction in an oxygen-containing atmosphere, so that the carbon source covers the acid sites on the supporter; then, the carbonized
20 supporter is roasted slowly at a low temperature in an oxygen-containing gas that has low oxygen content, to selectively burnt off the carbon deposit on non-strong acid, so that the obtained decarbonized supporter has an appropriate infrared acid distribution structure; next, the supporter is impregnated with active metal to obtain a hydrocracking

catalyst; finally, the hydrocracking catalyst is roasted at a high temperature in an inert atmosphere for a long time or roasted at a low temperature in an oxygen-containing atmosphere for a long time, to obtain a hydrocracking catalyst with certain carbon content kept in it ultimately.

5 With the above-mentioned technical scheme, the hydrocracking catalyst provided in the present invention has rational infrared acid intensity distribution and appropriate dispersion of active metal component, and can remarkably improve the reaction effect of the hydrocracking catalyst in the initial stage of operation while obviously improve the yield of gasoline product, total liquid yield, and octane number of gasoline product,
10 when the hydrocracking catalyst is used in catalytic diesel oil hydrocracking reaction. In addition, the catalyst maintains good catalytic stability during the operation.

Other features and advantages of the present invention will be further detailed in the embodiments hereunder.

15 **DETAILED DESCRIPTION**

Hereunder some embodiments of the present invention will be detailed. It should be appreciated that the embodiments described here are only provided to describe and explain the present invention, but shall not be deemed as constituting any limitation to the present invention.

20 The ends points and any value in the ranges disclosed in the present invention are not limited to the exact ranges or values. Instead, those ranges or values shall be comprehended as encompassing values that are close to those ranges or values. For numeric ranges, the end points of the ranges, the end points of the ranges and the

discrete point values, and the discrete point values can be combined to obtain one or more new numeric ranges, which shall be deemed as having been disclosed specifically in this document.

The present inventor has found in the research: in the process of producing high-octane gasoline by hydro-conversion of catalytic diesel oil, the catalyst deactivation rate may be increased easily and causes secondary cracking and hydrogenation saturation of the generated gasoline fraction and decreased octane number and yield of gasoline, if the acidity distribution of the hydrocracking catalyst is irrational, e.g., the infrared acid amount is high, especially the content ratio of strong acid with desorption temperature greater than 350°C is too high, because the catalytic diesel oil raw material has rich content of substances that have a trend of coke formation (e.g., aromatic hydrocarbons and nitrides, etc.) and the hydrocracking reaction conditions are more demanding (low pressure, high temperature). If the acid amount in the catalyst is too low, the aromatic hydrocarbon conversion capability will be compromised, and thereby the product quality will be degraded. In addition, if the acid amount is too low, the catalyst reactivity will be decreased; consequently, the reaction temperature has to be improved in the operation in order to reach the same reaction depth, resulting in increased thermal cracking and decreased yield of C₅⁺ liquid. Based on the above-mentioned research finding, the inventor puts forward the present invention.

The present invention provides a hydrocracking catalyst, wherein the hydrocracking catalyst comprises a supporter, an active metal component, and carbon, wherein, based on the total weight of the hydrocracking catalyst, the content of the supporter is 60~90wt%, the content of the active metal component calculated in metal oxides is

15~40wt%, and the content of carbon calculated in C element is 1~5wt%; measured with an infrared acidimetric estimation method, the acid properties of the hydrocracking catalyst are: the total infrared acid amount is 0.4~0.8mmol/g, wherein, the infrared acid amount of strong acid with desorption temperature greater than 350°C is 0.08mmol/g or
5 lower, and the ratio of the total infrared acid amount to the infrared acid amount of strong acid with desorption temperature greater than 350°C is 5~50.

In the present invention, the sum of the contents of the components in the catalyst is 100%.

In a preferred embodiment of the present invention, based on the total weight of the hydrocracking catalyst, the content of the supporter is 60~90wt%, the content of the
10 active metal component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~3wt%.

In another preferred embodiment of the present invention, based on the total weight of the hydrocracking catalyst, the content of the supporter is 60~85wt%, the content of the
15 active metal component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~3wt%.

In the present invention, preferably, measured with an infrared acidimetric estimation method, the acid property of the hydrocracking catalyst is: the total infrared acid amount is 0.4~0.6mmol/g; the ratio of the total infrared acid amount to the infrared acid amount
20 of strong acid with desorption temperature greater than 350°C is 8~30, preferably is 10~25, more preferably is 20~25.

In the present invention, the infrared acidimetric estimation method employs pyridine adsorption infrared spectrometry, and the measurement is made with a Nicolet 6700 FTIR spectrometer from NICOLET (a US company); the process is as follows:

20mg ground sample (in particle size smaller than 200mpi) is pressed into a thin flake in
5 20mm diameter, and loaded onto a sample holder of an absorption cell, 200mg sample
(in flake shape) is loaded into a cup hung to the lower end of a quartz spring (the spring
length x_1 (mm) is logged before the sample is loaded), the absorption cell is connected
to an adsorption tube, vacuumed to 4×10^{-2} Pa vacuum level, heated up to 500°C and
kept at the temperature for 1h, to remove the adsorbed substance on the surface of the
10 sample (the spring length x_2 (mm) after the sample is purified is logged); then, the
sample is cooled down to room temperature, absorbs pyridine to saturated state, and
heated up to 160°C and held at the temperature for 1h, to desorb the pyridine absorbed
physically (the spring length x_3 (mm) after the sample absorbs pyridine is logged); the
total acid amount is calculated with a pyridine gravimetric adsorption method; in the
15 same way, the sample is heated up to 350°C and held for 1h, to desorb the pyridine
absorbed physically (the spring length x_4 (mm) after the sample absorbs pyridine is
logged); the amount of strong acid with Desorption temperature greater than 350°C is
calculated with a pyridine gravimetric adsorption method.

Wherein, the total acid amount is calculated with a pyridine gravimetric adsorption
20 method as follows:

According to Hooke's law (the relation between spring elongation and stress): $f = k\Delta x$

When the spring is placed vertically: $m = k\Delta x$

Where, m is the mass of the sample, g; Δx is the elongation of the spring, mm; k is the stiffness coefficient of the spring.

$$\frac{\text{Mass of Absorbed Pyridine} / 79.1}{\text{Total Acid}} = \frac{\text{Mass of Sample}}{1g}$$

Total acid amount C (unit: mmol/g):

$$C = \frac{k(x_3 - x_2)}{k(x_2 - x_1) \times 79.1} \text{ mol/g} = \frac{x_3 - x_2}{x_2 - x_1} \times \frac{1}{79.1} \text{ mol/g} = 12.64 \times \frac{x_3 - x_2}{x_2 - x_1} \text{ mmol/g}$$

Note: 79.1 is the mole mass of pyridine, in unit of g/mol.

According to the present invention, preferably, the supporter is a silica-alumina supporter that contains a modified Y-type molecular sieve, and, based on the total weight of the supporter, the supporter contains 20~85wt% modified Y-type molecular sieve and 15~80wt% amorphous silica-alumina and/or alumina. Preferably, the supporter contains 30~70wt% modified Y-type molecular sieve and 30~70wt% amorphous silica-alumina and/or alumina.

According to the present invention, there is no particular restriction on the modified Y-type molecular sieve. Preferably, the modified Y-type molecular sieve is selected from a Y-type molecular sieve obtained through dealumination and silicon reinsertion and/or hydrothermal treatment of ammonium fluosilicate, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the modified Y-type molecular sieve is (5~15):1.

In the present invention, the hydrocracking catalyst is a bi-functional catalyst, and the supporter provides acidity, i.e., provides acidic catalytic sites. In the hydrocracking catalyst provided in the present invention, the supporter surface is at least partially covered by carbon; thus, the acidity distribution on the surface of the supporter can be

adjusted. When the hydrocracking catalyst provided in the present invention is applied in hydrocracking reaction of diesel oil (especially catalytic diesel oil), it can achieve better catalytic activity and reaction stability, and can improve the yield of gasoline product, total liquid yield, and octane number of gasoline product.

- 5 According to the present invention, the active metal component is used as an active component in the hydrocracking catalyst. Preferably, the metal in the active metal component is selected from VIII metal elements and/or VIB metal elements.

Preferably, the VIII metal elements are Ni and/or Co, and the VIB metal elements are W and/or Mo.

- 10 More preferably, the content of the VIII metal elements calculated in metal oxides is 2~15wt%, and the content of the VIB metal elements calculated in metal oxides is 10~30wt%.

According to the present invention, the active metal component is carried on at least a part of the surface of the supporter. The degree of dispersion of the active metal

- 15 component on the surface of the hydrocracking catalyst may be expressed by the atomic ratio of the active metal component to the Al element on the surface of the hydrocracking catalyst. In a preferred embodiment, on the surface of the catalyst, the atomic ratio of the VIII metal elements to Al element is (0.2~0.5):1, preferably is (0.2~0.4):1.

- 20 In another preferred embodiment, on the surface of the catalyst, the atomic ratio of the VIB metal elements to Al element is (0.4~0.8):1, preferably is (0.4~0.6):1.

In the present invention, the degree of dispersion may be measured by measuring the atomic ratio of Ni (Co)/Al or atomic ratio of Mo (W)/Al on the surface of the hydrocracking catalyst by X-ray photoelectron spectroscopy.

According to the present invention, preferably, the specific surface area of the hydrocracking catalyst is 200~400m²/g, and the pore volume is 0.25~0.38ml/g.

The hydrocracking catalyst provided in the present invention has appropriate acid intensity distribution and appropriate dispersion of active metal component, and can remarkably improve the operating process of diesel oil hydro-conversion system and the reaction effect of the hydrocracking catalyst in the initial stage of operation, while obviously improve the yield of gasoline product, total liquid yield, and octane number of gasoline product.

The present invention further provides a method for preparing a hydrocracking catalyst, comprising the following steps: (1) controlling a supporter to contact with a carbon source and have carbon deposition reaction, to obtain a carbonized supporter; (2) roasting the carbonized supporter in an oxygen-containing gas, to obtain a decarbonized supporter, wherein, the carbon content in the decarbonized supporter is 20~80% of the carbon content in the carbonized supporter; the oxygen content in the oxygen-containing gas is 0.5~8vol%, the roasting temperature is 250°C~390°C, and the roasting time is 3.5~20h; (3) introducing a precursor of active metal component into the decarbonized supporter, and drying the decarbonized supporter; and (4) treating the product obtained in the step (3) through a heat treatment process, in which the precursor of active metal component is converted into active metal oxides, and the carbon in the decarbonized supporter is kept; wherein, the hydrocracking catalyst contain 1~5wt%

carbon calculated in C element, and the supporter and the precursor of active metal component are dosed in a way that the hydrocracking catalyst contains 60~90wt% supporter and 15~40wt% active metal component calculated in metal oxides.

Preferably, the carbon content in the decarbonized supporter is 30~70% of the carbon
5 content in the carbonized supporter.

In a preferred embodiment of the present invention, based on the total weight of the hydrocracking catalyst, the content of the supporter is 60~90wt%, the content of the active metal component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~3wt%.

10 In another preferred embodiment of the present invention, based on the total weight of the catalyst, the content of the supporter is 60~85wt%, the content of the active metal component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~3wt%.

In the present invention, the sum of the contents of the components in the catalyst is
15 100%.

According to the present invention, preferably, the supporter is a silica-alumina supporter that contains a modified Y-type molecular sieve, and, based on the total weight of the supporter, the supporter contains 20~85wt% modified Y-type molecular sieve and 15~80wt% amorphous silica-alumina and/or alumina. Preferably, the
20 supporter contains 30~70wt% modified Y-type molecular sieve and 30~70wt% amorphous silica-alumina and/or alumina.

According to the present invention, there is no particular restriction on the modified Y-type molecular sieve. Preferably, the modified Y-type molecular sieve is selected

from a Y-type molecular sieve obtained through dealumination and silicon reinsertion and/or hydrothermal treatment of ammonium fluosilicate, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the modified Y-type molecular sieve is (5~15):1. The modified Y-type molecular sieve may be a commercial product or prepared with a conventional method.

5 In the present invention, the method for preparing the modified Y-type molecular sieve by dealumination and silicon reinsertion of ammonium fluosilicate usually includes the following steps:

- (I) 1,000g NaY molecular sieve powder (the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is (3~6):1, the Na content calculated in Na_2O is 8~15wt%) is mixed with 0.4~0.8mol/L
10 ammonium nitrate at liquid-solid mass ratio of (1~5):1 and exchanges for 3~5h at $80^\circ\text{C}\sim 100^\circ\text{C}$; the process is repeated for 3 times, so that the Na content calculated in Na_2O in the Y-type molecular sieve after the exchange is 2.0~3.0wt%;
- (II) The Y-type molecular sieve obtained in the step (I) is mixed with distilled water at liquid-solid mass ratio of (5~8):1, 300ml 0.8~1.2mol/L ammonium fluosilicate
15 solution is added into the mixture, and then the mixture is treated for 2~4h at $80^\circ\text{C}\sim 100^\circ\text{C}$;
- (III) The molecular sieve obtained in the step (II) is loaded into a hydrothermal treatment furnace, and treated by hydrothermal treatment for 1~3h at water vapor pressure of 0.1~1MPa and temperature of $520\sim 560^\circ\text{C}$; thus, a modified Y-type
20 molecular sieve is obtained.

In the present invention, the hydrothermal treatment method for preparing the modified Y-type molecular sieve usually includes the following steps:

- (i) 1,000g NaY molecular sieve powder (the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is (3~6):1, the Na content calculated in Na_2O is 8~15wt%) is mixed with 0.4~0.8mol/L ammonium nitrate at liquid-solid mass ratio of (1~5):1 and exchanges for 3~5h at $80^\circ\text{C}\sim 100^\circ\text{C}$; the process is repeated for 3 times, so that the Na content calculated in Na_2O in the Y-type molecular sieve after the exchange is 2.0~3.0wt%;
- (ii) The Y-type molecular sieve obtained in the step (i) is loaded into a hydrothermal treatment furnace, and treated by hydrothermal treatment for 1~3h at water vapor pressure of 0.2~1MPa and temperature of $600\sim 640^\circ\text{C}$; thus, a modified Y-type molecular sieve is obtained.

10 In the present invention, the amorphous silica-alumina and alumina may be commercial products or prepared with a conventional method.

According to the present invention, preferably, in the step (1), the supporter is obtained by mixing the modified Y-type molecular sieve with amorphous silica-alumina and/or alumina homogeneously, extruding the mixture into strips, and then drying and roasting the strips.

In the present invention, the strip extrusion process may be a matured forming process well known to those skilled in the art, and conventional auxiliary agents for forming, such as peptizing agent and extrusion aiding agent, can be added. The peptizing agent may be one or more of hydrochloric acid, nitric acid, sulfuric acid, acetic acid and oxalic acid. The extrusion-aiding agent refers to a substance helpful for extrusion forming, such as one or more of sesbania powder, soot carbon, graphite powder, and citric acid. In the extrusion forming process, based on the total amount of the modified Y-type molecular sieve and the amorphous silica-alumina and/or alumina, the amount of

the extrusion aiding agent accounts for 1~10wt% (calculated on dry basis). Furthermore, the drying conditions are: drying for 1~5h at 80°C~120°C; the roasting conditions are: roasting for 1~5h at 400°C~700°C.

According to the present invention, in the step (1), the surface of the supporter is
5 covered by the carbon source, and then carbon is coated on the surface of the supporter through the carbon deposition reaction. Preferably, the carbon source is selected from a gaseous or liquid carbonaceous material, which may be a liquid or gaseous unsaturated olefins, such as C₂~C₁₀ normal olefins or isomeric olefins, and dienes. To improve the carbon deposition efficiency, the carbon source may be selected from at
10 least one of petroleum ether, benzene, methyl benzene, dimethyl benzene, catalytic gasoline, coker gasoline, butadiene, pentylene, hexadiene, butylene, pentene, heptylene, and nonylene.

According to the present invention, preferably, in the step (1), the conditions under which the supporter contacts with the carbon source include: pressure of 0.1~1MPa and
15 time of 0.1~6h. The pressure is 0.1~1MPa, and the time is 0.1~2h if the carbon source is in gas state; the pressure is 0.1~1MPa, and the time is 0.5~6h if the carbon source is in liquid state. In the step (1), the supporter contacts with the carbon source fully, usually at normal temperature, i.e., 25°C~40°C.

According to the present invention, through the carbon deposition reaction, the carbon
20 source is converted to carbon on the surface of the supporter. Preferably, the carbon deposition reaction happens in an oxygen-containing atmosphere, and the temperature of the carbon deposition reaction is 100°C~500°C, preferably is 180°C~300°C; the time of the carbon deposition reaction is 20~200h, preferably is 50~100h.

According to the present invention, in the carbon deposition reaction, preferably the oxygen content in the oxygen-containing atmosphere is 10~100vol%, and the oxygen-containing atmosphere is selected from a mixture of air or oxygen and an inert gas, and preferably is air. The inert gas may be a mixture of one or more of CO₂, N₂,
5 He, Ne, and Ar.

In the present invention, the carbon content in the carbonized supporter obtained in the step (1) may be measured with an elemental analysis method, for example.

According to the present invention, the step (2) is used to decarbonize the carbonized supporter appropriately, so that the carbonized supporter can have rational acidity
10 distribution. In the roasting process in the step (2), preferably the oxygen content in the oxygen-containing gas is 2~5vol%; the oxygen-containing gas is a mixture of oxygen and at least one of CO₂, N₂, He, Ne and Ar.

In the step (2) of the method for preparing a hydrocracking catalyst provided in the present invention, preferably the roasting temperature is 300°C~390°C; the roasting
15 time is 4~20h.

According to the present invention, in the step (2), the carbonized supporter decarbonized preferably through the following roasting process: in the step (2), the carbonized supporter is loaded into a roasting furnace, heated up from room temperature at 20~40□/h heating rate to the roasting temperature, and kept at the roasting
20 temperature till the roasting time is reached; the volume ratio of the oxygen-containing gas to the carbonized supporter is (500~5,000):1.

In the present invention, the roasting atmosphere, heating rate, final heating temperature, and roasting time are controlled to achieve appropriate decarburization; specifically, the

carbonized supporter is placed in an atmosphere with low oxygen content in a roasting furnace, heated up from room temperature at a specific heating rate to a roasting temperature that is lower than the ordinary high temperature roasting temperature, and is held for a long roasting time, i.e., the carbonized supporter is roasted slowly at a low roasting temperature for a long time. In the present invention, the room temperature is 25°C~40°C.

In contrast, in the prior art, decarburization is usually carried out by roasting at a high temperature for a short time in an atmosphere with high oxygen content (e.g., air), the roasting temperature (usually 500°C~600°C) is much higher than the roasting temperature in the present invention, and the roasting time is 1h or shorter. In the prior art, to accomplish rapid roasting for decarburization, usually the carbonized supporter is directly loaded into a roasting furnace pre-heated to the roasting temperature, i.e., there is no operation of loading the carbonized supporter into the roasting furnace and heating up the carbonized supporter from room temperature at a specific heating rate to the roasting temperature as described in the step (2) in the present invention.

In the present invention, the carbon content in the obtained decarbonized supporter may be measured with an elemental analysis method, for example. The quantitative relation between the carbon content in the decarbonized supporter and the carbon content in the carbonized supporter can be ascertained further, and the rate of decarburization through the roasting process in the step (2) can be calculated with the following formula:

Rate of decarburization = $[1 - (\text{carbon content in decarbonized supporter} / \text{carbon content in carbonized supporter})] \times 100\%$.

According to the present invention, the step (3) is used to load the active metal component to the decarbonized supporter. A deposition or impregnation approach may be used. Preferably, saturated impregnation may be used, with a water solution of a precursor of active metal component, for example. Preferably, in the step (3), the method for introducing the precursor of active metal component is to impregnate the decarbonized supporter in an impregnation liquid that contains the precursor of active metal component.

In the present invention, preferably the precursor of active metal component is a compound that contains metal elements selected from VIII metal elements and/or VIB metal elements, wherein, the VIII metal element preferably is Ni and/or Co; the VIB metal element preferably is W and/or Mo. The precursor of active metal component is preferably selected from nitrates, basic carbonates, citrates, or oxides of Ni and/or Co; and oxides of W and/or Mo or W-containing compounds or Mo-containing compounds; more preferably, the precursor of active metal component is selected from at least one of nickel nitrate, basic nickel carbonate, nickel citrate, cobalt citrate, cobalt nitrate, molybdenum oxide, ammonium molybdate, and ammonium metatungstate.

Preferably, the liquid-solid mass ratio of the impregnation liquid to the decarbonized supporter is (1.5~3):1.

Preferably, in the impregnation liquid, the content of the precursor of active metal component selected from VIB metal elements is 20~60g/100ml calculated in metal oxides, and the content of the precursor of active metal component selected from VIII metal elements is 3~20g/100ml calculated in metal oxides.

In the present invention, the content of the precursor of active metal component in the impregnation liquid may be adjusted appropriately according to the requirement for the product.

According to the present invention, in the step (3), preferably the drying is carried out
5 for 2~8h at 90°C~150°C.

According to the present invention, the step (4) may be accomplished a variety of ways, as long as the purpose of converting the precursor of active metal component into active metal oxides while keeping the carbon in the decarbonized supporter. In a preferred embodiment, the heat treatment comprises: roasting the product obtained in the step (3)
10 in an inert gas for 2~10h at 400°C~700°C, to obtain a hydrocracking catalyst.

Specifically, the process may be: the roasting is carried out in a roasting furnace by: first, introducing an inert gas into the roasting furnace for displacement, wherein, the volume ratio of gas/agent for controlling the introduction speed of the inert gas (inert gas : impregnated and dried decarbonized supporter) is (500~5,000):1; then, heating up the
15 roasting furnace at 20°C/h~40°C/h heating rate to the roasting temperature when the oxygen purity in the atmosphere in the roasting furnace is lower than 0.1vol% after the inert gas is displaced into the atmosphere in the roasting furnace; and accomplishing the roasting within the roasting time at the roasting temperature. The inert gas used in the roasting process may be a mixture of one or more of CO₂, N₂, He, Ne, and Ar.

20 In another preferred embodiment, the product obtained in the step (3) is activated at 150°C~300°C in an oxygen-containing atmosphere for 1~5h, to obtain the hydrocracking catalyst.

The present invention further provides a hydrocracking catalyst prepared with the method according to the present invention.

The present invention further provides a use of the hydrocracking catalyst according to the present invention in diesel oil hydrocracking reaction.

- 5 The present invention further provides a method for hydrocracking catalytic diesel oil, comprising: (a) pre-treating catalytic diesel oil by hydrocracking; and (b) treating the product obtained in the step (a) by hydrocracking in the presence of the hydrocracking catalyst according to the present invention and hydrogen.

According to the present invention, in the step (a), the catalytic diesel oil may contact
10 with a hydro-pretreating agent. The conditions of the hydrocracking pretreatment may include: reaction pressure of 6~20MPa, reaction temperature of 330°C~400°C, volumetric space velocity of material feeding of 0.1~2h⁻¹, and volume ratio of hydrogen to oil of (500~2,000):1. Preferably, the hydrocracking pretreatment in the step (a) is made under conditions that ensure the nitrogen content in the obtained product is
15 1~100ppm, wherein, the nitrogen content is in unit of ppm (weight).

According to the present invention, in the step (b), the oil product obtained in the step (a) may be hydrocracked. Preferably, the conditions of the hydrocracking in the step (b) include: reaction pressure of 6~20MPa, reaction temperature of 350°C~420°C, volumetric space velocity of material feeding of 0.1~2h⁻¹, and volume ratio of hydrogen
20 to oil of (500~2,000):1, wherein, the volume ratio of hydrogen to oil is the volume ratio of hydrogen to the oil product obtained in the step (a), which may be the volume ratio at 25°C.

In the present inventions, all pressure values are gauge pressure values.

Hereunder the present invention will be detailed in embodiments. However, the present invention is not limited to those embodiments.

In the following examples and comparative examples, the infrared acid amount in the catalyst is measured by pyridine adsorption infrared spectrometry with a Nicolet 6700 FTIR spectrometer from NICOLET (a US company).

The process is as follows:

20mg ground sample (in particle size smaller than 200 μ m) is pressed into a thin flake in 20mm diameter, and loaded onto a sample holder of an absorption cell, 200mg sample (in flake shape) is loaded into a cup hung to the lower end of a quartz spring (the spring length x_1 (mm) is logged before the sample is loaded), the absorption cell is connected to an adsorption tube, vacuumed to 4×10^{-2} Pa vacuum level, heated up to 500 $^{\circ}$ C and kept at the temperature for 1h, to remove the adsorbed substance on the surface of the sample (the spring length x_2 (mm) after the sample is purified is logged); then, the sample is cooled down to room temperature, absorbs pyridine to saturated state, and heated up to 160 $^{\circ}$ C and held at the temperature for 1h, to desorb the pyridine absorbed physically (the spring length x_3 (mm) after the sample absorbs pyridine is logged); the total acid amount is calculated with a pyridine gravimetric adsorption method; in the same way, the sample is heated up to 350 $^{\circ}$ C and held for 1h, to desorb the pyridine absorbed physically (the spring length x_4 (mm) after the sample absorbs pyridine is logged); the amount of strong acid with Desorption temperature greater than 350 $^{\circ}$ C is calculated with a pyridine gravimetric adsorption method.

Wherein, the total acid amount is calculated with a pyridine gravimetric adsorption method as follows:

According to Hooke's law (the relation between spring elongation and stress): $f = k\Delta x$

When the spring is placed vertically: $m = k\Delta x$

- 5 Where, m is the mass of the sample, g; Δx is the elongation of the spring, mm; k is the stiffness coefficient of the spring.

$$\frac{\text{Mass of Absorbed Pyridine} / 79.1}{\text{Total Acid}} = \frac{\text{Mass of Sample}}{1g}$$

Total acid amount C (unit: mmol/g):

$$C = \frac{k(x_3 - x_2)}{k(x_2 - x_1) \times 79.1} \text{ mol/g} = \frac{x_3 - x_2}{x_2 - x_1} \times \frac{1}{79.1} \text{ mol/g} = 12.64 \times \frac{x_3 - x_2}{x_2 - x_1} \text{ mmol/g}$$

- 10 Note: 79.1 is the mole mass of pyridine, in unit of g/mol.

- The carbon content is measured with an elementary analysis method with a HORIBA EMIA-820V infrared carbon-sulfur analyzer, utilizing a principle of combustion in oxygen flow and infrared absorption measurement. Specifically, the sample is heated in oxygen flow to have an oxidizing reaction, so that the majority of carbon (C) is
- 15 turned into carbon dioxide (CO₂), a small part of carbon is turned into carbon monoxide (CO), and the sulfur (S) is turned into sulfur dioxide (SO₂). In that process, the moisture in the sample is gasified, the hydrogen (H) in the sample is oxidized into water; therefore, there is some moisture in the gas flow. The moisture may be removed by means of magnesium perchlorate Mg(ClO₄)₂. The oxygen flow is adjusted to a
- 20 constant flow rate and then introduced into an infrared detector, to detect the quantities

of CO₂, CO, and SO₂, and then the carbon concentration and sulfur concentration in the sample are calculated.

The specific surface area and pore volume of the catalyst are measured with a low-temperature nitrogen adsorption BET method. The specific surface area, pore
5 volume and pore distribution of the sample are read directly on an ASAP 2400 specific surface area tester from Micromeritics (a US company). All samples are desorbed for 12h at 473K before the test. Nitrogen is used as a adsorption gas, and the adsorption is measured at 77K temperature, the specific surface area is calculated with the Brunauer-Emmett-Teller (BET) equation, the total pore volume is the volume
10 corresponding to the adsorption quantity when the relative pressure is 1, the pore volume and pore distribution are obtained from a BJH adsorption curve or desorption curve, the micro-pore system and pore distribution are obtained by calculation with a Horvath-Kawazon (HK) adsorption curve.

The catalyst composition and content are determined through materials input
15 calculation;

The atomic ratio of the active metal component to Al on the catalyst surface is measured by X-ray photoelectron spectroscopy. Specifically, the test is carried out on a Multilab 2000 X-ray photoelectron spectrometer from ThermoFisher (a US company), the energy scanning range of which is 0~5000eV; the throughput can be adjusted continuously
20 within 1~400eV range, with adjusting step size ≤ 1 eV.

The NaY molecular sieve powder and macro-pore alumina used in the following preparation examples, examples, and comparative examples are from SINOPEC Fushun

Catalyst Branch, and the ammonium nitrate and ammonium fluosilicate are from Tianjin Yongda Chemical Reagent Co., Ltd. and Shanghai Third Reagent Plant respectively.

Preparation example 1

This preparation example is provided here to describe the preparation of the modified
5 molecular sieve.

- (1) 1,000g NaY molecular sieve powder is mixed with 0.6mol/L ammonium nitrate at liquid-solid mass ratio of 3:1, and exchanges for 3h at 80°C; the process is repeated for 3 times, so that the Na content in the Y-type molecular sieve after the exchange is 2.0wt% calculated in Na₂O;
- 10 (2) The Y-type molecular sieve obtained in the step (1) is mixed with distilled water at liquid-solid mass ratio of 5:1, 300ml 1.0mol/L ammonium fluosilicate solution is added into the mixture, and then the mixture is treated for 2h at 80°C;
- (3) the molecular sieve obtained in the step (2) is treated by hydrothermal treatment in a hydrothermal treatment furnace at water vapor pressure of 0.1MPa and 540°C
15 for 2h, so as to obtain a modified Y-type molecular sieve 1, denoted as MY-1, in which the molar ratio of SiO₂/Al₂O₃ is 11.0:1.

Preparation example 2

This preparation example is provided here to describe the preparation of the modified molecular sieve.

- 20 (1) 1,000g NaY molecular sieve powder is mixed with 0.6mol/L ammonium nitrate at liquid-solid mass ratio of 3:1, and exchanges for 3h at 80°C; the process is

repeated for 3 times, so that the Na content in the Y-type molecular sieve after the exchange is 2.0wt% calculated in Na_2O ;

- (2) the molecular sieve obtained in the step (1) is treated by hydrothermal treatment in a hydrothermal treatment furnace at water vapor pressure of 0.2MPa and 620°C for 2h, so as to obtain a modified Y-type molecular sieve 2, denoted as MY-2, in which the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ is 5.4:1.

Example 1

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of 0.3MPa and temperature of 25°C; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;
- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 1vol% oxygen content is charged into the

roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 350°C, and the carbonized supporter is roasted for 4h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.8wt%;

- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 32g/100ml and 10g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and N₂ gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 2,000:1;
- (7) When the oxygen purity reaches 0.08vol% in the N₂ displacement process, the roasting furnace is heated up at 40°C/h to 550°C, and held at the temperature for 6h, so as to obtain a hydrocracking catalyst, which is numbered as C-1.

Example 2

- (1) 60g modified Y-type molecular sieve (MY-1) is mixed with 40g macro-pore alumina, 40ml dilute nitric acid at 6g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and

the strips is dried for 6h at 80°C, and then roasted for 5h at 400°C, to obtain a supporter;

- (2) The supporter obtained in the step (1) is immersed in heptylene at 30°C for 4h, and then the supporter is heated up in an air atmosphere to 180°C and held at the temperature for 150h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 10.2wt%;
- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 3vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 40°C/h heating rate to 360°C, and the carbonized supporter is roasted for 10h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.5wt%;
- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 32g/100ml and 10g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 5:1, and the impregnated product is dried for 3h at 150°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and He gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 1,000:1;

- (7) When the oxygen purity reaches 0.05vol% in the N₂ displacement process, the roasting furnace is heated up at 25°C/h to 600°C, and held at the temperature for 4h, so as to obtain a hydrocracking catalyst, which is numbered as C-2.

5 Example 3

- (1) 45g modified Y-type molecular sieve (MY-1) is mixed with 55g macro-pore alumina, 60ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and
10 the strips is dried for 1h at 120°C, and then roasted for 1h at 700°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is immersed in heptylene at 40°C for 4h, and then the supporter is heated up in an air atmosphere to 280°C and held at the temperature for 80h for carbon deposition reaction, so as to obtain a carbonized
15 supporter, in which the measured carbon content is 11.2wt%;
- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 3vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 330°C, and the carbonized supporter is roasted for 15h at the temperature, so as to obtain
20 a decarbonized supporter, in which the measured carbon content is 5.0wt%;

- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO_3 and NiO are 40g/100ml and 12g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 4:1, and the impregnated product is dried for 3h at 150°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and CO_2 gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 3,000:1;
- (7) When the oxygen purity reaches 0.05vol% in the N_2 displacement process, the roasting furnace is heated up at 40°C/h to 650°C, and held at the temperature for 4h, so as to obtain a hydrocracking catalyst, which is numbered as C-3.

Example 4

- (1) 55g modified Y-type molecular sieve (MY-2) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of

0.3MPa and temperature of 25°C; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;

- 5 (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 1vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 350°C, and the carbonized supporter is roasted for 4h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.8wt%;
- 10 (4) 1,000ml W-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in WO₃ and NiO are 32g/100ml and 10g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the W-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at
15 120°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and N₂ gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 2,000:1;
- (7) When the oxygen purity reaches 0.08vol% in the N₂ displacement process, the
20 roasting furnace is heated up at 40°C/h to 550°C, and held at the temperature for 6h, so as to obtain a hydrocracking catalyst, which is numbered as C-4.

Example 5

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of 0.3MPa and temperature of 25°C; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;
- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 1vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 350°C, and the carbonized supporter is roasted for 4h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.8wt%;
- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 32g/100ml and 10g/100ml respectively;

- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and
5 roasted for 3h at 250°C in an air atmosphere for activation, so as to obtain a hydrocracking catalyst, which is numbered as C-5.

Example 6

- (1) 60g modified Y-type molecular sieve (MY-2) is mixed with 40g macro-pore
10 alumina, 40ml dilute nitric acid at 6g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 6h at 80°C, and then roasted for 5h at 400°C, to obtain a supporter;
- 15 (2) The supporter obtained in the step (1) is immersed in heptylene at 30°C for 4h, and then the supporter is heated up in an air atmosphere to 180°C and held at the temperature for 150h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 10.2wt%;
- 20 (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 3vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 40°C/h heating rate to 360°C,

and the carbonized supporter is roasted for 10h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.5wt%;

- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO_3 and NiO are 32g/100ml and 10g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 5:1, and the impregnated product is dried for 3h at 150°C ;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and roasted for 2h at 150°C in an air atmosphere for activation, so as to obtain a hydrocracking catalyst, which is numbered as C-6.

Example 7

- (1) 45g modified Y-type molecular sieve (MY-1) is mixed with 55g macro-pore alumina, 60ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 1h at 120°C , and then roasted for 1h at 700°C , to obtain a supporter;
- (2) The supporter obtained in the step (1) is immersed in heptylene at 40°C for 4h, and then the supporter is heated up in an air atmosphere to 280°C and held at the

temperature for 80h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 11.2wt%;

- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 3vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 330°C, and the carbonized supporter is roasted for 15h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 5.0wt%;
- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 40g/100ml and 12g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 4:1, and the impregnated product is dried for 3h at 150°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and roasted for 1h at 250°C in an air atmosphere for activation, so as to obtain a hydrocracking catalyst, which is numbered as C-7.

Comparative example 1

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and

the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;

- (2) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 24g/100ml and 8g/100ml respectively;

- (3) The supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C; then, the supporter is roasted for 3h at 500°C in an air atmosphere, so as to obtain a hydrocracking catalyst, which is numbered as B-1.

Comparative example 2

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of 0.3MPa and temperature of 25°C; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon

deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;

- 5
- (3) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO_3 and NiO are 42g/100ml and 12g/100ml respectively;
- (4) The carbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C ; then, the supporter is treated for 4h at 550°C in an nitrogen atmosphere, so as to obtain a hydrocracking catalyst, which is numbered as B-2.

10

Comparative example 3

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is
15 suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C , and then roasted for 3h at 550°C , to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of
20 0.3MPa and temperature of 25°C ; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon

deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;

- (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, air is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 500°C, and the carbonized supporter is roasted for 4h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 0.3wt%;
- (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 28g/100ml and 9g/100ml respectively;
- (5) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C;
- (6) The dried sample obtained in the step (5) is loaded into a roasting furnace, and N₂ gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 2,000:1;
- (7) When the oxygen purity reaches 0.08vol% in the N₂ displacement process, the roasting furnace is heated up at 40°C/h to 550°C, and held at the temperature for 6h, so as to obtain a hydrocracking catalyst, which is numbered as B-3.

Comparative example 4

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) 1,000ml Mo-Ni impregnation liquid 1 is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 16g/100ml and 6g/100ml respectively; then, the supporter obtained in the step (1) is impregnated in the Mo-Ni impregnation liquid 1 at liquid-solid mass ratio of 3:1, and then is dried for 4h at 120°C, to obtain an intermediate product;
- (3) The intermediate product obtained in the step (2) is loaded into an enclosed container filled with butadiene gas, and contacts with butadiene fully for 20min. at pressure of 0.3MPa and temperature of 25°C; then, the supporter is heated up to 200°C in an air atmosphere and held at the temperature for 60h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;
- (4) The carbonized supporter prepared in the step (3) is directly loaded into a muffle furnace preheated to 550°C, and roasted for a short time (30min.) in an air atmosphere (with high oxygen content), so as to burn off the carbon deposit on the surface layer of the carbonized supporter and obtain a decarbonized supporter;

- (5) 1,000ml Mo-Ni impregnation liquid 2 is prepared, in which the contents of active metal components calculated in MoO_3 and NiO are 25g/100ml and 8g/100ml respectively;
- (6) The decarbonized supporter is impregnated in the Mo-Ni impregnation liquid 2 at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C, to obtain a dried sample;
- (7) The dried sample obtained in the step (6) is loaded into a roasting furnace, and N_2 gas is charged into the roasting furnace for displacement, while the volume ratio of gas/agent is controlled at 2,000:1;
- (8) When the oxygen purity reaches 0.08vol% in the N_2 displacement process, the roasting furnace is heated up at 40°C/h to 550°C, and held at the temperature for 6h, so as to obtain a hydrocracking catalyst, which is numbered as B-4.

Comparative example 5

- (1) 55g modified Y-type molecular sieve (MY-1) is mixed with 45g macro-pore alumina, 50ml dilute nitric acid at 4g/100ml concentration is added into the mixture, and then the mixture is mixed and pressed in a mixer to a state that is suitable for extrusion; next, the mixture is extruded in an extruder into strips, and the strips is dried for 4h at 100°C, and then roasted for 3h at 550°C, to obtain a supporter;
- (2) The supporter obtained in the step (1) is loaded into an enclosed container filled with butadiene gas, the supporter contacts with butadiene for 20min. at pressure of

0.3MPa and temperature of 25°C; then, the supporter is heated up in an air atmosphere to 200°C temperature and held at the temperature for 60h for carbon deposition reaction, so as to obtain a carbonized supporter, in which the measured carbon content is 7.5wt%;

- 5 (3) The carbonized supporter obtained in the step (2) is loaded into a roasting furnace, an oxygen/nitrogen mixed gas with 1vol% oxygen content is charged into the roasting furnace, the roasting furnace is heated up at 25°C/h heating rate to 350°C, and the carbonized supporter is roasted for 4h at the temperature, so as to obtain a decarbonized supporter, in which the measured carbon content is 2.8wt%;
- 10 (4) 1,000ml Mo-Ni impregnation liquid is prepared, in which the contents of active metal components calculated in MoO₃ and NiO are 32g/100ml and 10g/100ml respectively;
- (5) The supporter is impregnated in the Mo-Ni impregnation liquid at liquid-solid mass ratio of 3:1, and the impregnated product is dried for 4h at 120°C; then, the
- 15 supporter is roasted for 3h at 500°C in an air atmosphere, so as to obtain a hydrocracking catalyst, which is numbered as B-5.

Testing Examples 1-12

To evaluate the hydrocracking performance of the hydrocracking catalysts prepared in

20 the examples and comparative examples, evaluation tests of the catalysts C-1 to C-7, and B-1 to B-5 are carried out on a small tester.

The evaluation tester employs a single-stage and single-pass process with two reactors connected in series, wherein, the first reactor is charged with a hydrocracking pretreating catalyst FF-36 that is widely used in the art (from SINOPEC Fushun Research Institute of Petroleum and Petrochemicals) for hydrocracking Pretreatment of the raw oil; the second reactor is charged with a catalyst.

In the test cases 1-8, the second reactor is charged with the catalysts C-1, C-2, C-3, C-4, C-5, C-6, C-7, B-1, B-2, B-3, B-4, and B-5, respectively. The properties of the catalysts are shown in Table 1. The raw oil is catalytic diesel oil, of which the basic physical parameters are shown in Table 2. Table 3 shows the hydrocracking conditions. Table 4 shows the hydrocracking results after 300h operation under the conditions shown in Table 3. Table 5 shows the long-time operation results of the hydrocracking catalysts C-1 and B-1.

Table 1

Catalyst	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Content of active metal, wt%							
MoO ₃	13.9	15.2	15.6	-	13.7	15.2	15.4
WO ₃	-	-	-	14.2	-	-	-
NiO	4.6	5.0	5.2	4.4	4.6	5.1	5.0
Carbon content, wt%	2.8	2.5	5.0	2.9	2.8	2.5	5.0
Surface properties							
Pore volume, ml/g	0.30	0.32	0.25	0.29	0.29	0.30	0.25
Specific surface area,	302	320	292	300	300	315	285

m ² /g							
Infrared acid amount, mmol/g							
Total acid amount	0.55	0.58	0.44	0.54	0.54	0.58	0.43
Content of strong acid with desorption temperature >350°C	0.026	0.029	0.018	0.027	0.027	0.028	0.018
Ratio of total acid/strong acid	20.3	20.0	24.4	20.0	20.0	20.7	23.8
Atomic ratio of Mo/Al on surface	0.52	0.55	0.56	-	0.46	0.46	0.47
Atomic ratio of W/Al on surface	-	-	-	0.50	-	-	-
Atomic ratio of Ni/Al on surface	0.33	0.34	0.38	0.33	0.28	0.29	0.29

Table 1 (continued)

Catalyst	B-1	B-2	B-3	B-4	B-5
Content of active metal, wt%					
MoO ₃	14.2	13.4	14.2	14.3	14.0
WO ₃	-	-	-	-	-
NiO	4.7	4.3	4.4	4.3	4.6
Carbon content, wt%	-	7.5	0.3	5.9	0.1

Surface properties					
Pore volume, ml/g	0.35	0.13	0.35	0.22	0.35
Specific surface area, m ² /g	350	100	340	280	345
Infrared acid amount, mmol/g					
Total acid amount	0.66	0.22	0.64	0.24	0.65
Content of strong acid with desorption temperature >350°C	0.15	0.017	0.14	0.020	0.15
Ratio of total acid/strong acid	4.4	12.9	4.57	12.0	4.3
Atomic ratio of Mo/Al on surface	0.49	0.52	0.52	0.51	0.49
Atomic ratio of Ni/Al on surface	0.31	0.32	0.33	0.33	0.30

Table 2

Raw oil	Catalytic diesel oil
Density, g/cm ³	0.9204
Distillation range, °C	180~350
S, wt%	1.2
N, wt%	0.07
Aromatic content, wt%	69
Cetane number	20

Table 3

Catalyst	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Reaction temperature, °C	396	394	398	393	400	397	400
Reaction pressure, MPa	8.0	8.0	8.0	8.0	8.0	8.0	8.0
Volumetric space velocity in	2.0	2.0	2.0	2.0	2.0	2.0	2.0

cracking section, h ⁻¹							
Volume ratio of hydrogen/oil	1200	1200	1200	1200	1200	1200	1200
Operation time, h	300	300	300	300	300	300	300
Nitrogen content in inputted material in cracking section, ppm	30	30	30	30	30	30	30
Single-pass conversion, %	70	70	70	70	70	70	70
Chemical hydrogen consumption, %	3.35	3.38	3.32	3.39	3.37	3.38	3.36

Table 3 (continued)

Catalyst	B-1	B-2	B-3	B-4	B-5
Reaction temperature, °C	390	410	391	403	390
Reaction pressure, MPa	8.0	8.0	8.0	8.0	8.0
Volumetric space velocity in cracking section, h ⁻¹	2.0	2.0	2.0	2.0	2.0
Volume ratio of hydrogen/oil	1200	1200	1200	1200	1200
Operation time, h	300	300	300	300	300
Nitrogen content in inputted material in cracking section, ppm	30	30	30	30	30
Single-pass conversion, %	70	70	70	70	70
Chemical hydrogen consumption, %	3.52	3.44	3.52	3.42	3.52

Table 4

Catalyst	C-1	C-2	C-3	C-4	C-5	C-6	C-7
Product distribution, wt%							
C ₅ ~210°C gasoline fraction	61.2	61.0	61.8	59.2	59.7	60.2	61.0
>210°C diesel fraction	30	30	30	30	30	30	30
Liquid yield of C ₅ ⁺ fraction	91.2	91.0	91.8	89.2	89.7	90.2	91.0
Product properties							
Naphtha (<210°C)							
Octane number	86.9	86.0	88.0	86.4	87.0	85.8	88.0

Table 4 (continued)

Catalyst	B-1	B-2	B-3	B-4	B-5
Product distribution, wt%					
C ₅ ~ 210°C gasoline fraction	55.7	53.0	55.8	52.6	55.8
>210°C diesel fraction	30	30	30	30	30
Liquid yield of C ₅ ⁺ fraction	85.7	83.0	85.8	82.6	85.8
Product properties					
Naphtha (<210°C)					
Octane number	80.7	89.6	80.9	89.8	80.9

Table 5

Catalyst	C-1	B-1
Reaction temperature, °C	402	406
Reaction pressure, MPa	8.0	8.0
Volumetric space velocity in cracking section, h ⁻¹	2.0	2.0
Volume ratio of hydrogen/oil	1200	1200
Operation time, h	2000	2000
Nitrogen content in inputted material in cracking section, ppm	30	30
Single-pass conversion, %	70	70
Chemical hydrogen consumption, %	3.22	3.46
Product distribution, wt%		
C ₅ ~ 210°C gasoline fraction	63.8	61.5
>210°C diesel fraction	30	30
Liquid yield of C ₅ ⁺ fraction	93.8	91.5
Product properties		
Naphtha (<210°C)		
Octane number	93.3	90.5

It can be seen from the above examples, comparative examples, and Tables 1-5: the catalysts obtained in the examples have better acidity distribution, such as a higher ratio of total acid/strong acid, and can achieve higher gasoline yield and total liquid yield than the catalysts obtained in the comparative examples, as indicated by the results of

5 evaluation tests.

In the comparative example 4, the hydrocracking catalyst is prepared with the method in the prior art, wherein, in the decarburization process in the step (4), roasting is carried out for a short time at a high temperature in an atmosphere with high oxygen content; that process can only burn off the carbon deposit on the surface layer of the carbonized supporter, but can't realize appropriate decarburization and adjustment of acidity distribution in the supporter to rational acidity distribution, when compared with the method in the present invention. In the obtained hydrocracking catalyst, the ratio of total acid/strong acid is only 12.0, much lower than that in the hydrocracking catalysts obtained in the examples. Consequently, both the gasoline yield and the total liquid yield are inferior to those achieved by the hydrocracking catalysts obtained in the examples, as indicated by the results of the evaluation tests.

In the comparative example 5, the roasting in the step (5) is roasting at a high temperature in an oxygen-containing atmosphere; as a result, the shielding effect of carbon for the strong acid sites on the catalyst is lost. Consequently, the performance of the catalyst in the reaction is close to that of the catalyst without carbon deposit in the comparative example 1.

In the art, when a fresh catalyst is applied in a catalytic diesel oil hydrocracking reaction, the quality of the gasoline product generated by cracking is poor and the liquid yield of the apparatus is poor in the initial production stage. As the operation time of the apparatus extends, the quality of the gasoline product is improved gradually. Table 4 shows the evaluation results of a catalyst obtained in an example and a catalyst obtained in a comparative example after 300h operation under the conditions shown in Table 3, wherein, the catalyst B-1 (the hydrocracking catalyst obtained in the comparative

example 1) doesn't contain carbon when compared with the catalyst C-1 (the hydrocracking catalyst obtained in the example 1), and there is no acidity distribution adjustment step in the preparation process. As shown in the reaction results, though the reactivity of the catalyst C-1 is slightly lower than that of the catalyst B-1, the
5 octane number of the gasoline product is 85 or higher, and the liquid yield of C_5^+ fraction is 89% or higher, obviously higher than those achieved by the catalyst B-1 (80.7 octane number, and 85.7% liquid yield of C_5^+ fraction).

Table 5 shows the evaluation results of the catalysts C-1 and B-1 after 2,000h operation. It can be seen that the deactivation rate of the catalyst C-1 is obviously decreased, when
10 compared with the deactivation rate of the catalyst B-1. After 2,000h operation, the activity of the catalyst C-1 is apparently higher than that of the catalyst B-1, and the octane number of gasoline product and the liquid yield of C_5^+ fraction are higher. Those results indicate that the catalyst provided in the present invention exhibit better operation stability. Compared with the catalyst B-1, the hydrocracking catalyst
15 provided in the present invention has apparent advantages in terms of reactivity and total liquid yield of C_5^+ product when it is used in catalytic diesel oil hydrocracking for producing gasoline.

Claims

1. A hydrocracking catalyst, comprising a supporter, an active metal component, and carbon, wherein, based on the total weight of the catalyst, the content of the supporter is 60~90wt%, the content of the active metal component calculated in metal oxides is 15~40wt%, and the content of carbon calculated in C element is 1~5wt%; measured with an infrared acidimetric estimation method, the acid properties of the hydrocracking catalyst are: the total infrared acid amount is 0.4~0.8mmol/g, wherein, the infrared acid amount of strong acid with desorption temperature greater than 350°C is 0.08mmol/g or lower, and the ratio of the total infrared acid amount to the infrared acid amount of strong acid with desorption temperature greater than 350°C is 5~50.
2. The catalyst according to claim 1, wherein, the supporter is a silica-alumina supporter that contains a modified Y-type molecular sieve, and, based on the total weight of the supporter, the supporter contains 20~85wt% modified Y-type molecular sieve and 15~80wt% amorphous silica-alumina and/or alumina; the modified Y-type molecular sieve is selected from a Y-type molecular sieve modified by dealumination and silicon reinsertion and/or hydrothermal treatment of ammonium fluosilicate, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the modified Y-type molecular sieve is (5~15):1.
3. The catalyst according to claim 1, wherein, the metal in the active metal component is selected from VIII metal elements and/or VIB metal elements; the content of the VIII metal elements calculated in metal oxides is 2~15wt%, and the content of the VIB metal elements calculated in metal oxides is 10~30wt%.

4. The catalyst according to claim 3, wherein, on the surface of the catalyst, the atomic ratio of the VIII metal elements to Al is (0.2~0.5):1; the atomic ratio of the VIB metal elements to Al is (0.4~0.8):1.
5. The catalyst according to claim 1, wherein, the content of carbon calculated in C element is 1~3wt%; the total infrared acid amount is 0.4~0.6mmol/g; the ratio of the total infrared acid amount to the infrared acid amount of strong acid with desorption temperature greater than 350°C is 8~30.
6. The catalyst according to claim 1, wherein, the specific surface area of the catalyst is 200~400m²/g, and the pore volume of the catalyst is 0.25~0.38ml/g.
- 10 7. A method for preparing a hydrocracking catalyst, comprising the following steps:
- (1) controlling a supporter to contact with a carbon source and have carbon deposition reaction, to obtain a carbonized supporter;
- (2) roasting the carbonized supporter in an oxygen-containing gas, to obtain a decarbonized supporter, in which the carbon content is 20~80% of the carbon content in the carbonized supporter, wherein, the oxygen content in the oxygen-containing gas is 0.5~8vol%, the roasting temperature is 250°C ~390°C, and the roasting time is 3.5~20h;
- 15 (3) introducing a precursor of active metal component into the decarbonized supporter, and drying the decarbonized supporter; and
- 20 (4) treating the product obtained in the step (3) through a heat treatment process, in which the precursor of active metal component is converted into active metal oxides, and the carbon in the decarbonized supporter is kept;

wherein, the hydrocracking catalyst contain 1~5wt% carbon calculated in C element, and the supporter and the precursor of active metal component are dosed in a way that the hydrocracking catalyst contains 60~90wt% supporter and 15~40wt% active metal component calculated in metal oxides.

- 5 8. The method according to claim 7, wherein, the supporter is a silica-alumina supporter that contains a modified Y-type molecular sieve, and, based on the total weight of the supporter, the supporter contains 20~85wt% modified Y-type molecular sieve and 15~80wt% amorphous silica-alumina and/or alumina; the modified Y-type molecular sieve is selected from a Y-type molecular sieve
- 10 modified by dealumination and silicon reinsertion and/or hydrothermal treatment of ammonium fluosilicate, and the molar ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the modified Y-type molecular sieve is (5~15):1.
9. The method according to claim 7 or 8, wherein, in the step (1), the supporter is obtained by mixing the modified Y-type molecular sieve with amorphous
- 15 silica-alumina and/or alumina homogeneously, extruding the mixture into strips, and then drying and roasting the strips.
10. The method according to claim 7, wherein, the carbon source is selected from at least one of petroleum ether, benzene, methyl benzene, dimethyl benzene, catalytic gasoline, coker gasoline, butadiene, pentylene, hexadiene, butylene,
- 20 pentene, heptylene, and nonylene.
11. The method according to claim 7, wherein, in the step (1), the conditions under which the supporter contacts with the carbon source include: pressure of 0.1~1MPa and time of 0.1~6h; the carbon deposition reaction happens in an

oxygen-containing atmosphere, the temperature of the carbon deposition reaction is 100°C~500°C, and the time of the carbon deposition reaction is 20~200h; the oxygen content in the oxygen-containing atmosphere is 10~100vol%, and the oxygen-containing atmosphere is selected from a mixture of air or oxygen and an inert gas.

12. The method according to claim 7, wherein, in the step (2), the oxygen content in the oxygen-containing gas is 2~5vol%; the oxygen-containing gas is a mixture of oxygen and at least one of CO₂, N₂, He, Ne and Ar.
13. The method according to claim 7, wherein, in the step (2), the carbonized supporter is loaded into a roasting furnace, heated up from room temperature at 20~40°C/h heating rate to the roasting temperature, and kept at the roasting temperature till the roasting time is reached; the volume ratio of the oxygen-containing gas to the carbonized supporter is (500~5,000):1.
14. The method according to claim 7, wherein, in the step (3), the method for introducing the precursor of active metal component is to impregnate the decarbonized supporter in an impregnation liquid that contains the precursor of active metal component; the drying is carried out at 90°C~150°C for 2~8h.
15. The method according to claim 7, wherein, the heat treatment process comprises: roasting the product obtained in the step (3) in an inert gas at 400°C~700°C for 2~10h, to obtain the hydrocracking catalyst; or activating the product obtained in the step (3) is an oxygen-containing atmosphere at 150°C~300°C for 1~5h, to obtain the hydrocracking catalyst.

16. A hydrocracking catalyst prepared with the method according to any of claims 7-15.
17. A use of the hydrocracking catalyst according to any of claims 1~6 and 16 in diesel oil hydrocracking reaction.
- 5 18. A method for hydrocracking catalytic diesel oil, comprising:
- (a) pre-treating catalytic diesel oil by hydrocracking; and
 - (b) treating the product obtained in the step (a) by hydrocracking in the presence of the hydrocracking catalyst according to any of claims 1~6 and 16 and hydrogen.
- 10 19. The method according to claim 18, wherein, in the step (a), the hydrocracking pre-treatment is made under conditions that ensure the nitrogen content in the product in 1~100ppm; the conditions of the hydrocracking in the step (b) include: reaction pressure of 6~20MPa, reaction temperature of 350°C~420°C, volumetric space velocity of material feeding of $0.1\sim 2\text{h}^{-1}$, and volume ratio of hydrogen to oil
- 15 of (500~2,000):1.