

A Bifunctional reduced-state non-noble metal catalyst and a preparation method and application thereof

TECHNICAL FIELD

[0001] The present invention relates to the technical field of biofuel production and zeolite catalyst preparation. Specifically, it relates to a bifunctional reduced-state non-noble metal catalyst, its preparation method and application.

BACKGROUND ART

[0002] In order to address climate change and reduce greenhouse gas emissions, since the 1970s, some countries have started research on the development and application of biofuels. In 1983, American scientist Graham Quick successfully used methyl linoleate prepared by transesterification in an engine for the first time, and defined fatty acid monoesters obtained from the transesterification of renewable oils and fats as biodiesel. Subsequently, many studies have been carried out on the synthesis methods of fatty acid monoesters, and a first-generation biofuel products represented by fatty acid methyl esters have gradually been generated. In recent years, some researchers at home and abroad have proposed a biodiesel synthesis technology route based on the catalytic hydrogenation process, forming a hydrocarbon-based biodiesel preparation technology.

[0003] According to existing literature (Renew. Sustain. Energy Rev. 101(2019)568-589; Catal. Sci. Technol. 3(2013)70-80; Catalysts 9(2019)293; J. Catal. 282(2011)155-164.), hydrocarbon-based biodiesel is a product obtained by the hydrodeoxygenation of bio-oils and fats and their derivatives (fatty acid methyl esters, fatty acids), and the product mainly consists of C₁₅-C₁₈ n-alkanes. Due to the poor cold-flow properties of n-alkanes, an isomerization dewaxing process is required to improve the cold-flow properties of the product. Generally, in the presence of an isomerization catalyst, long-chain alkanes will undergo both isomerization

and cracking reactions. If there are too many cracking reactions, the yield of the product fuel oil will be reduced; if the isomerization is insufficient, the cold-flow property requirements of biofuels cannot be met. Therefore, to obtain as many valuable biofuel products (bio-jet fuel and low-freezing-point biodiesel) as possible, the hydroisomerization reaction process of bio-based long-chain alkanes should be strictly controlled and finely regulated. The selectivities of isomerization and cracking are closely related to the performance of the catalyst. Alkane isomerization catalysts usually contain two types of active centers, metal centers and acid centers, which are used for the activation of C-H bonds and C-C bonds, respectively, which are usually categorized as bifunctional catalysts. Since the acidic centers on the catalyst surface can catalyze the occurrence of both isomerization and cracking reactions of alkanes, appropriate acid strength and acid amount are the key to balancing isomerization and cracking reactions.

[0004] Patent CN200910188170.6 discloses a hydrodewaxing catalyst, its preparation method and application. The catalyst uses a zeolite support modified by metal additives and silicone oil. By depositing additives and silicone oil successively, the acidity of the inner and outer surfaces of the zeolite support and the shape of the pore openings are adjusted, thereby improving the isomerization rate of the raw material. However, the preparation process of this catalyst is complicated, including multiple impregnation and high-temperature calcination processes, and long preparation cycle. In addition, due to the addition of additives and silicone oil, the loading of the active metal is low (1 to 15 wt%), the reaction activity is low; the examples show that the isomerization reaction temperature is as high as 365 °C, leading to high energy consumption and easy coking formation of the catalyst.

[0005] Patent CN201810935163.7 discloses a hydrocracking catalyst, its preparation method and application. The catalyst is prepared by the impregnation method and contains different types of phosphorus-containing zeolites and non-noble metal components. It exhibits

excellent cracking performance in the hydrocracking reaction of Saudi vacuum residue. However, this catalyst cannot achieve the co-production of bio-jet fuel and low-freezing-point biodiesel, and is not suitable for the isomerization reaction of C₁₅-C₁₈ bio-based long-chain alkanes. In addition, this catalyst needs sulfuration during use, and is not suitable for processing bio-based raw materials with almost no sulfur.

[0006] Patent CN201610412721.2 discloses an isomerization dewaxing method for producing bio-jet fuel and a catalyst used for this method. The catalyst comprises one or more medium-pore zeolites such as ZSM-22, ZSM-23, ZSM-12, and SAPO-11 modified with a silicon surface, and the active metal component is selected from precious metals Pt and/or Pd with a loading of 0.1 to 5 wt%. Similarly, patent CN202010497292.X discloses a hydroisomerization catalyst, its preparation method and application. The catalyst uses a ZSM-48 zeolite with a hollow spherical structure as a support, and the active metal component is selected from at least one of the Group VIII precious metal components, which is loaded by the impregnation method. Patents US11603501B2 and US20240034945A1 disclose catalyst preparation methods and their applications in the production of bio-jet fuel. The catalysts used in these patents cannot balance isomerization and cracking, and precious metals are used as active components. Although precious metals have high low-temperature activity, the catalysts show disadvantages of high cost and high sensitivity to impurities, which is extremely prone to poisoning.

[0007] Patent CN202111280384.3 discloses a method for hydrodewaxing of diesel. The hydrodewaxing catalysts used include a non-noble metal catalyst supported on a steam-treated ZSM-5 zeolite and catalysts supported on other zeolite carriers, which are used in a staged loading manner. The invention shows that the complicated preparation process of the ZSM-5 zeolite carrier is prone to generating acidic and alkaline waste liquids, accompanying with high energy consumption.

[0008] It is well known that there are large differences in the composition of petrochemical diesel and biodiesel. The former contains a certain amount of naphthenes and aromatics, and has a wide carbon number distribution; while the latter contains almost all straight-chain alkanes, and the carbon number is concentrated in 15-18. In addition, the existing post-treatment catalysts for petrochemical diesel tend to demonstrate the function of isomerization to ensure a higher diesel yield, so they cannot balance isomerization and cracking reactions. The most common method is to use two reactors, loaded with cracking catalysts and isomerization catalysts, respectively, but this will increase equipment investment. Therefore, conventional diesel isomerization dewaxing catalysts are not suitable for processing biodiesel, especially for the process of producing bio-jet fuel and simultaneously producing low-freezing-point biodiesel. In view of this, it is necessary to develop a non-noble metal bifunctional isomerization catalyst for the simultaneous production of bio-jet fuel and low-freezing-point biodiesel.

SUMMARY OF THE INVENTION

[0009] In order to solve the above problems, the present invention provides a bifunctional reduced-state non-noble metal catalyst, in which non-noble active nickel metal nanoparticles are in-situ embedded into the Y zeolite through a co-crystallization process of the Y zeolite seeds. The nickel metal atoms are used to induce the growth of the Y zeolite seeds and modify the surface of the zeolite particles, eliminating some acidic centers and forming a metal-Y zeolite catalyst with mild cracking performance. Then, the metal-Y zeolite catalyst is mixed and molded with a ZSM-22 zeolite with isomerization performance to prepare a bifunctional catalyst, which is used to produce oil-based bio-jet fuel and low-freezing-point biodiesel.

[0010] In one aspect, the present invention provides a bifunctional reduced-state non-noble metal catalyst. By mass percentage, the bifunctional reduced-state non-noble metal

catalyst comprises 20-40 wt% Y zeolite, 10-20 wt% ZSM-22 zeolite, 30-45 wt% metallic nickel and γ -Al₂O₃, wherein the total mass percentage of the raw materials of Y zeolite, ZSM-22 zeolite, metallic nickel and γ -Al₂O₃ is 100 wt%.

[0011] The preparation method of the bifunctional reduced-state non-noble metal catalyst comprises the following steps:

[0012] S1: Y zeolite seeds are prepared;

[0013] S2: Nickel metal nanoparticles are in-situ embedded into the Y zeolite seeds obtained in step S1 to obtain a metal-Y zeolite composite;

[0014] S3: the metal-Y zeolite composite prepared in step S2 is treated with an inorganic acid, and then filtration, washing with water, drying and calcination are performed in sequence to obtain a metal-Y zeolite catalyst;

[0015] S4: ZSM-22 zeolite, aluminum hydroxide dry gel powder, dilute nitric acid solution and sesbania powder are added to the metal-Y zeolite catalyst obtained in step S3, and then kneading, molding, drying, calcination and reduction are performed in sequence to obtain the reduced-state non-noble metal bifunctional catalyst.

[0016] Optionally, in step S4, the mass ratio of the metal-Y zeolite catalyst, ZSM-22 zeolite, aluminum hydroxide dry gel powder, dilute nitric acid solution and sesbania powder is (30 to 70):(5 to 20):(5 to 30):(2 to 4):(2 to 4). Optionally, in step S4, the mass ratio of the metal-Y zeolite catalyst, ZSM-22 zeolite, aluminum hydroxide dry gel powder, dilute nitric acid solution and sesbania powder is (30 to 50):(5 to 10):(10 to 20):(2 to 4):(2 to 4).

[0017] Optionally, the preparation method of the Y zeolite seeds in step S1 comprises the following steps:

[0018] A silicon source, an aluminum source and sodium hydroxide are dissolved in deionized water to obtain a viscous liquid mixture, and the mixture is hydrothermally treated at 30 to 80 °C to obtain Y zeolite seeds.

[0019] Wherein, calculated by the mass of oxides, the chemical composition of the viscous liquid mixture is $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = (20 \text{ to } 40):(0.5 \text{ to } 2):(20 \text{ to } 40):(600 \text{ to } 1000)$. Optionally, the chemical composition of the viscous liquid mixture is $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = (20 \text{ to } 30):(0.5 \text{ to } 1.5):(20 \text{ to } 30):(600 \text{ to } 800)$.

[0020] Further, in step S1, obtaining Y zeolite seeds with a specific structure promotes the formation of the subsequent Y zeolite structure and lays a foundation for the subsequent embedding of active metals.

[0021] Optionally, the preparation method of the metal-Y zeolite composite in step S2 comprises the following steps:

[0022] The Y zeolite seeds are dispersed in deionized water, and a template agent is added for dissolution, followed by adding a silicon source, an aluminum source, a nickel salt and sodium hydroxide for reaction at 80 to 120 °C, and then filtration, washing and drying are performed in sequence to obtain the metal-Y zeolite composite with in-situ embedded nickel metal nanoparticles.

[0023] Wherein, calculated by the mass of oxides, the feeding ratio of Y zeolite seeds, silicon source, aluminum source, nickel salt, sodium hydroxide and water is $(0.5 \text{ to } 1.5):(1.5 \text{ to } 2.5):(0.3 \text{ to } 0.8):(4 \text{ to } 6):(3.5 \text{ to } 5):(300 \text{ to } 400)$. Optionally, calculated by the mass of oxides, the feeding ratio of Y zeolite seeds, silicon source, aluminum source, nickel salt, sodium hydroxide and water is $(0.5 \text{ to } 1.5):(2 \text{ to } 2.5):(0.5 \text{ to } 0.8):(5 \text{ to } 6):(4 \text{ to } 5):(300 \text{ to } 350)$.

[0024] Further, in step S2, through the co-hydrothermal process of the nickel salt and the Y zeolite seeds, the nickel metal nanoparticles are in-situ embedded in the zeolite. On the one hand, the particle size of the zeolite is regulated, and on the other hand, the surface of the zeolite particles is modified to moderately reduce the number and strength of acidic centers, obtaining a zeolite material with moderate cracking performance.

[0025] Optionally, the nickel salt is one or more nickel sources selected from nitrate,

sulfate, chloride, basic carbonate and acetate.

[0026] Optionally, the template agent is one or more template agents selected from pyrrolidine, ethylenediamine, n-butylamine, di-n-propylamine, tetrapropylammonium bromide, tetrapropylammonium hydroxide, cetyltrimethylammonium bromide (CTAB).

[0027] Optionally, the preparation method of the metal-Y zeolite catalyst in step S3 comprises the following steps:

[0028] The metal-Y zeolite composite is treated with an inorganic acid solution at a temperature of 40 to 60 °C, and then filtration, washing with water, drying and calcination at 450 to 600 °C are performed in sequence on the treated material to obtain the metal-Y zeolite catalyst.

[0029] Further, in step S3, removing the template agent through high-temperature treatment can improve the thermal stability and chemical stability of the zeolite.

[0030] Optionally, the metal-Y zeolite catalyst has a BET specific surface area of 250 to 350 m²/g, a total pore volume of 0.3 to 0.45 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 5 to 10.

[0031] Optionally, the ZSM-22 zeolite has a BET specific surface area of 180 to 220 m²/g, a total pore volume of 0.15 to 0.25 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 60 to 100.

[0032] Optionally, the inorganic acid is one or more selected from hydrochloric acid, phosphoric acid, acetic acid and nitric acid; the concentration of the inorganic acid solution is 0.1 to 0.5 mol/L; preferably, the inorganic acid solution is a mixed acid solution of hydrochloric acid and phosphoric acid, in which the mass ratio of hydrochloric acid to phosphoric acid is 1:1.

[0033] Optionally, the silicon source is one or more silicon sources selected from silica sol, sodium silicate and kaolin.

[0034] Optionally, the aluminum source is one or more aluminum sources selected from aluminum sulfate, aluminum nitrate, aluminum chloride and sodium meta-aluminate.

[0035] In another aspect, the present invention provides the use of a bifunctional reduced-state non-noble metal catalyst in the hydroisomerization/cracking reaction of bio-based long-chain alkanes. The bio-based long-chain alkanes are produced from the hydrodeoxygenation process of bio-derived oils and fats, and are a mixture of straight-chain alkanes with a composition of C₁₅-C₁₈ and a sulfur content of lower than 3 ppmw.

[0036] Further, for hydrocarbon-based biodiesel composed of C₁₅-C₁₈ n-alkanes, the existing catalysts have relatively simple structures, and the acid strength and acid amount distribution of the catalysts are non-uniform, resulting in their inability to balance isomerization and cracking capabilities during hydroisomerization or cracking. In the preparation process of the present invention, nickel metal atoms are used to induce the growth of Y zeolite seeds and modify the surface of the zeolite particles, eliminating some acidic centers and forming a metal-Y zeolite catalyst with mild cracking performance. Then, it is mixed and molded with a ZSM-22 zeolite of isomerization performance to prepare a bifunctional catalyst. When applied to hydrocarbon-based biodiesel composed of C₁₅-C₁₈ n-alkanes, under mild conditions (for example, 260 °C), the cracking rate is not lower than 40%, and the isomerization rate is not lower than 30%, which can balance isomerization and cracking capabilities. Preferably, when the reaction is carried out at an elevated temperature (for example, 300 °C), the cracking rate is not lower than 70%, and the isomerization rate is not lower than 40%.

[0037] Optionally, the hydroisomerization reaction conditions are: reaction temperature of 200 to 300 °C, reaction pressure of 3 to 8 MPa, liquid hourly space velocity of 0.2 to 3.0 h⁻¹, and hydrogen-to-oil volume ratio of 400 to 800.

[0038] Optionally, the bio-oils and fats are selected from waste oils and fats such as waste cooking oil, swill oil, palm acid oil, soybean oil, rapeseed oil, palm oil, cottonseed oil, jatropha oil, peanut oil, beef tallow or lard, and/or natural oils and fats.

[0039] Compared with the prior art, the present invention achieves at least one of the

following beneficial effects:

[0040] (1) The bifunctional reduced-state non-noble metal catalyst of the present invention exhibits both isomerization and cracking capabilities, and the selectivity of both reactions can be adjusted by changing the content of the zeolite, thereby improving the flexibility of the entire production process. The proportion of bio-jet fuel and biodiesel can be flexibly adjusted according to market demand.

[0041] (2) The catalyst of the present invention is a reduced-state catalyst. It does not need sulfuration before use, and there is no need to add sulfur during the use process. It will neither affect the sulfur content of the product nor generate sulfur-containing waste gas, avoiding environmental pollution. The catalyst prepared by the present invention does not contain precious metals, has a much lower production cost than precious-metal catalysts, and has a stronger tolerance to raw materials.

[0042] (3) The catalyst prepared by the method of the present invention is a non-supported type. The loading of the active metal is 2 to 3 times that of conventional supported catalysts, showing higher catalytic activity, and the reaction can be carried out at a lower temperature.

BRIEF DESCRIPTION OF THE DRAWINGS

[0043] The accompanying drawings are provided to further illustrate this invention and form part of the invention. Exemplary embodiments of the invention and their descriptions are provided to explain the principles of the invention and should not be construed as imposing undue limitations on the scope of the invention. In the drawings:

[0044] FIG.1 shows the transmission electron micrograph (TEM) image of the metal-Y zeolite catalyst in Example 1 of the present invention;

[0045] FIG.2 shows the TEM image of the Y zeolite in Comparative Example 1 of the present invention;

[0046] FIG.3 shows the gas chromatography (GC) chromatogram of the liquid product obtained when the metal-Y zeolite catalyst in Example 4 of the present invention is applied to the hydroisomerization of hydrocarbon-based biodiesel.

Detailed Description

[0047] To more clearly elucidate the overall concept of the present invention, a detailed description will be given below by way of examples with reference to the accompanying drawings.

[0048] Although numerous specific details are set forth in the following description to facilitate a full understanding of the invention, the invention may be practiced in other ways different from those described herein. Accordingly, the scope of protection of the present invention should not be construed as being limited by the specific embodiments disclosed below.

[0049] Example 1

[0050] The reduced-state non-noble metal bifunctional catalyst comprises, by mass percentage, 40 wt% Y zeolite, 20 wt% ZSM-22 zeolite, 30 wt% metallic nickel, and 10 wt% γ - Al_2O_3 .

[0051] The preparation method of the bifunctional reduced-state non-noble metal catalyst comprises the following steps:

[0052] S1: Sodium silicate, sodium meta-aluminate and sodium hydroxide are dissolved in deionized water to obtain a viscous liquid mixture with a molar feed ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = 30:1.5:30:800$. The mixture is then subjected to hydrothermal treatment at 60 °C for 48 h to obtain Y-type zeolite seeds.

[0053] S2: The Y zeolite seeds obtained in step S1 are dispersed in deionized water, and

2 wt% CTAB is added for dissolution, followed by adding sodium silicate, sodium meta-aluminate, nickel nitrate and sodium hydroxide. The mixture is crystallized at 100 °C for 36 h. The product is filtered, washed with deionized water to neutrality and dried in sequence to obtain a metal-Y zeolite composite. Based on the mass of oxides, the feed ratio of Y-type zeolite seeds, sodium silicate, sodium meta-aluminate, nickel nitrate, sodium hydroxide, and water is 0.5:2.5:0.8:4:3.5:300.

[0054] S3: The metal-Y zeolite composite obtained in step S2 is then added in a 0.15 mol/L mixed acid solution of hydrochloric acid and phosphoric acid (mass ratio 1:1), followed by treating at 60 °C for 6 h. After washing to neutrality, drying, and calcination at 450 °C for 4 h, a metal-Y zeolite catalyst is obtained. The resulting catalyst has a BET surface area of 250 m²/g, a total pore volume of 0.3 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 5.

[0055] S4: Subsequently, 30 g of the metal-Y zeolite catalyst obtained in step S3, 6 g of ZSM-22 zeolite, 4 g of aluminum hydroxide dry gel powder, 2 g of 20 wt% nitric acid solution, and 2 g of sesbania powder are taken, and then kneading, molding, drying, calcination at 500 °C for 4 h and reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with a nickel loading of 30 wt%. The ZSM-22 zeolite has a BET surface area of 180 m²/g, a total pore volume of 0.25 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 60.

[0056] Example 2

[0057] The bifunctional reduced-state non-noble metal catalyst comprises, by mass percentage, 30 wt% Y zeolite, 20 wt% ZSM-22 zeolite, 45 wt% metallic nickel and 5 wt% γ -Al₂O₃.

[0058] The preparation method of the bifunctional reduced-state non-noble metal catalyst comprises the following steps:

[0059] S1: Sodium silicate, aluminum nitrate and sodium hydroxide are dissolved in

deionized water to obtain a viscous liquid mixture with a feeding ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = 30:1.5:30:800$; then hydrothermal treatment is performed at 30 °C for 2 d to obtain Y zeolite seeds.

[0060] S2: The Y zeolite seeds obtained in step S1 are dispersed in deionized water, and 2 wt% CTAB was added for dissolution, followed by adding sodium silicate, sodium meta-aluminate, nickel sulfate and sodium hydroxide. The mixture is crystallized at 80 °C for 36 h. The product is filtered, washed with deionized water to neutrality and dried in sequence to obtain a metal-Y zeolite composite. Calculated by the mass of oxides, the feeding ratio of Y zeolite seeds, sodium silicate, sodium meta-aluminate, nickel sulfate, sodium hydroxide and water is 0.5:2.5:0.8:5:3.5:300.

[0061] S3: The metal-Y zeolite composite obtained in step S2 is added to a 0.15 mol/L mixed solution of hydrochloric acid and phosphoric acid with a mass ratio of hydrochloric acid to phosphoric acid of 1:1, followed by treating at 40 °C for 6 h. The acid-treated composite is washed to neutrality, and then dried and calcined at 500 °C for 4 h to obtain a metal-Y zeolite catalyst. The metal-Y zeolite catalyst has a BET specific surface area of 270 m²/g, a total pore volume of 0.4 cm³/g, and a $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of 5.

[0062] S4: Subsequently, 30 g of the metal-Y zeolite catalyst obtained in step S3, 15 g of ZSM-22 zeolite, 5 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken and then kneading, molding, drying, calcination at 500 °C for 4 h and reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with a nickel loading of 45 wt%. Wherein, the ZSM-22 zeolite has a BET specific surface area of 180 m²/g, a total pore volume of 0.25 cm³/g, and a $\text{SiO}_2:\text{Al}_2\text{O}_3$ molar ratio of 60.

[0063] Example 3

[0064] The bifunctional reduced-state non-noble metal catalyst comprises, by mass

percentage, 20 wt% Y zeolite, 20 wt% ZSM-22 zeolite, 30 wt% metallic nickel and 30 wt% γ - Al_2O_3 .

[0065] The preparation method of the bifunctional reduced-state non-noble metal catalyst comprises the following steps:

[0066] S1: Sodium silicate, aluminum nitrate and sodium hydroxide are dissolved in deionized water to obtain a viscous liquid mixture with a feeding ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{Na}_2\text{O}:\text{H}_2\text{O} = 30:1.5:30:800$; then hydrothermal treatment is performed at 80 °C for 2 d to obtain Y zeolite seeds.

[0067] S2: the Y zeolite seeds obtained in step S1 are dispersed in deionized water, and 2 wt% CTAB is added into the above mixture for dissolution, followed by adding sodium silicate, sodium meta-aluminate, nickel acetate and sodium hydroxide. The mixture is crystallized at 120 °C for 36 h. The product is filtered, washed with deionized water to neutrality and dried in sequence to obtain a metal-Y zeolite composite. Calculated by the mass of oxides, the feeding ratio of Y zeolite seeds, sodium silicate, sodium meta-aluminate, nickel acetate, sodium hydroxide and water is 0.5:2.5:0.8:4.6:3.5:300.

[0068] S3: The metal-Y zeolite composite obtained in step S2 is added to a 0.15 mol/L mixed solution of hydrochloric acid and phosphoric acid with a mass ratio of hydrochloric acid:phosphoric acid=1:1, followed by treating at 40 °C for 6 h. The acid-treated composite is washed to neutrality, and then dried and calcined at 600 °C for 4 h to obtain a metal-Y zeolite catalyst. The metal-Y zeolite catalyst has a BET specific surface area of 300 m^2/g , a total pore volume of 0.35 cm^3/g , and a molar ratio of $\text{SiO}_2:\text{Al}_2\text{O}_3$ of 5.

[0069] S4: Subsequently, 30 g of the metal-Y zeolite catalyst obtained in step S3, 6 g of ZSM-22 zeolite, 12 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken and then kneading, molding, drying, calcination at 500 °C for 4 h and reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with

a nickel loading of 30 wt%. Wherein, the ZSM-22 zeolite has a BET specific surface area of 180 m²/g, a total pore volume of 0.25 cm³/g, and a molar ratio of SiO₂:Al₂O₃ of 100.

[0070] Example 4

[0071] Based on Example 1, the main differences from Example 1 are as follows: In step S2, the feeding ratio of Y zeolite seeds, sodium silicate, sodium meta-aluminate, nickel nitrate, sodium hydroxide and water is 0.5:2:0.5:5:4.2:350;

[0072] In step S3, the metal-Y zeolite catalyst has a BET specific surface area of 210 m²/g, a total pore volume of 0.26 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 4;

[0073] In step S4, 30 g of the metal-Y zeolite catalyst, 6 g of ZSM-22 zeolite, 2 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken and then kneading, molding, drying, calcination at 500 °C for 4 h and reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with a nickel loading of 40 wt%. Wherein, the ZSM-22 zeolite has a BET specific surface area of 200 m²/g, a total pore volume of 0.2 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 80.

[0074] Example 5

[0075] Based on Example 1, the main differences from Example 1 are as follows: In step S2, calculated by the mass of oxides, the feeding ratio of Y zeolite seeds, sodium silicate, sodium meta-aluminate, nickel nitrate, sodium hydroxide and water is 0.5:2.5:0.8:6:5:350;

[0076] In step S3, the metal-Y zeolite catalyst has a BET specific surface area of 180 m²/g, a total pore volume of 0.25 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 5;

[0077] In step S4, 30 g of the metal-Y zeolite catalyst, 6 g of ZSM-22 zeolite, 2 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken and then kneading, molding, drying, calcination at 500 °C for 4 h and

reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with a nickel loading of 45 wt%. Wherein, the ZSM-22 zeolite has a BET specific surface area of 220 m²/g, a total pore volume of 0.15 cm³/g, and a SiO₂:Al₂O₃ molar ratio of 60.

[0078] Comparative Example 1

[0079] The preparation method of the catalyst comprises the following steps:

[0080] S1: Sodium silicate, sodium meta-aluminate and sodium hydroxide are dissolved in deionized water to obtain a viscous liquid mixture with a feeding ratio of SiO₂:Al₂O₃:Na₂O:H₂O = 30:1.5:30:800, and then a hydrothermal treatment is performed at 60 °C for 2 d to obtain Y zeolite seeds.

[0081] S2: The Y zeolite seeds obtained in step S1 are dispersed in deionized water, and then 2 wt% of CTAB is added into the above mixture for dissolution, followed by adding sodium silicate, sodium meta-aluminate and sodium hydroxide. Calculated by the mass of corresponding oxides, the feeding ratio is Y zeolite seeds: SiO₂:Al₂O₃:Na₂O:H₂O = 0.5:2.5:0.8:3.5:300. The mixture is then crystallized at 100 °C for 36 h. The products are filtered, washed with deionized water to neutrality, and then dried to obtain Y zeolite.

[0082] S3: The Y zeolite obtained in step S2 is treated in a 0.15 mol/L mixed solution of hydrochloric acid and phosphoric acid at 60 °C for 6 h. The acid-treated composite is washed with deionized water to neutrality, and then dried and calcined at 450 °C for 4 h to obtain Y zeolite powder.

[0083] S4: Subsequently, 30 g of Y zeolite powder obtained in step S3, 15 g of ZSM-22 zeolite, 10 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken, and then kneading, molding, drying, and calcination at 500 °C for 4 h are performed to obtain a composite zeolite support.

[0084] S5: An aqueous solution of nickel nitrate is prepared and loaded on the composite

zeolite support obtained in step S4 by using the incipient-wetness impregnation method. After drying, calcination at 400 °C for 4 h and reduction at 400 °C for 4 h, an isomerization catalyst with a nickel loading of 30 wt% is obtained.

[0085] Comparative Example 2

[0086] Based on Example 1, the main difference from Comparative Example 1 is as follows: In step S4, 30 g of the metal-Y zeolite catalyst, 10.8 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken, and then kneading, molding, drying, calcination at 500 °C for 4 h and reduction at 500 °C for 4 h are performed to obtain an isomerization catalyst with a nickel loading of 30 wt%.

[0087] Comparative Example 3

[0088] Based on Comparative Example 1, the main differences from Comparative Example 1 are as follows: In step S4, 30 g of Y zeolite powder, 10.8 g of aluminum hydroxide dry gel powder, 2 g of dilute nitric acid solution and 2 g of sesbania powder are taken, and then kneading, molding, drying, and calcination at 500 °C for 4 h are performed to obtain a composite zeolite support.

[0089] In step S5, an aqueous solution of chloroplatinic acid is prepared, which is loaded on the support by an incipient-wetness impregnation method. After drying, calcination at 400°C for 4 h and reduction at 400 °C for 4 h, an isomerization catalyst with a Pt loading of 0.5 wt% is obtained.

[0090] Experimental Example 1

[0091] The catalysts prepared in the examples and comparative examples are loaded onto a high-pressure fixed-bed reactor, respectively, and then treated at 200 °C under an

atmospheric-pressure hydrogen for 4 h to remove adsorbed water and other gas impurities in the catalysts. Then, the hydrogen pressure in the reactor is raised to 4 MPa. After the tail-gas flow rate behind the back-pressure valve is stable, the reactor temperature is elevated to 260 °C in a programmed manner. Then the raw materials are fed into the reactor for the isomerization reaction. The volume space velocity is 1.5 h⁻¹, and the hydrogen-to-oil volume ratio is 800:1. The raw material used in the reaction is a mixture of straight-chain alkanes of C₁₅-C₁₈ obtained by the hydrodeoxygenation of waste cooking oil, with a freezing point of 17 °C and a sulfur content of 2 ppmw. The catalytic performance is tested, as shown in Table 1.

[0092] Table 1

	Conversion / %	Liquid Yield / wt%	Freezing Point / °C	Cracking Rate / %	Isomerization Rate / %
Example 1	48.9	98.6	-23	44.0	44.9
Example 2	46.4	96.9	-27	47.2	39.2
Example 3	52.7	97.4	-24	44.9	34.8
Example 4	72.2	98.4	-44	65.2	56.7
Example 5	66.7	98.2	-40	62.2	52.5
Comparative Example 1	37.5	97.4	-18	38.8	22.7
Comparative Example 2	42.9	94.6	-20	40.6	24.9
Comparative Example 3	64.6	91.8	-38	67.2	36.7

[0095] As shown in Table 1, when the bifunctional catalyst of the present invention is applied to the hydroisomerization of hydrocarbon-based biodiesel, an ideal effect can be achieved at a relatively low reaction temperature, wherein the liquid yield is not lower than 95 wt%, the freezing point is not higher than -20°C, the cracking rate is not lower than 40%, and the isomerization rate is not lower than 30%. The metal loading and addition method can significantly affect the performance of the catalysts. With the increase of the nickel loading,

the activity of the catalyst increases significantly, but too high nickel loading will affect the structure and ratio of the zeolite, thereby reducing the cracking rate and isomerization rate of the raw materials.

[0096] Compared with the catalyst prepared by in situ embedding method in Example 1, the catalyst prepared by the conventional impregnation method in Comparative Example 1 demonstrates lower metal dispersion and too high metal covering of on a large number of acidic centers on the surface of the zeolite support, resulting in a decrease in the activity, cracking and isomerization performance of the catalyst.

[0097] Compared with Example 1, using a single zeolite support in Comparative Example 2 will affect the isomerization rate of straight-chain alkanes in the raw materials.

[0098] Compared with Example 1, the non-noble metal catalyst prepared by the present invention in Comparative Example 3 shows a relatively higher raw-material conversion. Although the cracking performance is relatively low, the product yield is higher. The non-noble metal bifunctional catalyst prepared by the present invention demonstrates catalytic capability comparable to that of the precious-metal catalyst.

[0099] Experimental Example 2

[0100] The catalysts prepared in the examples and comparative examples are loaded onto a high-pressure fixed-bed reactor, respectively, and then treated at 200 °C under an atmospheric-pressure hydrogen atmosphere for 4 h to remove adsorbed water and other gas impurities in the catalysts. Then, the hydrogen pressure in the reactor is elevated to 4 MPa. After the tail-gas flow rate behind the back-pressure valve is stable, the reactor temperature is raised to 300 °C in a programmed manner. Then the raw materials are fed into the reactor for the isomerization reaction. The volume space velocity is 1.5 h⁻¹, and the hydrogen-to-oil volume ratio is 800:1. The raw material used in the reaction is a mixture of straight-chain

alkanes of C₁₅-C₁₈ obtained by the hydrodeoxygenation of swill oil, with a freezing point of 15 °C and a sulfur content of 2 ppmw. The catalytic performance is tested, as shown in Table 2.

[0101] Table 2

	Conversion / %	Liquid Yield / wt%	Freezing Point / °C	Cracking Rate / %	Isomerization Rate / %
Example 1	72.7	92.2	-36	66.1	57.2
Example 2	70.6	90.7	-36	68.3	46.5
Example 3	74.3	91.4	-39	72.4	42.2
Example 4	96.2	88.8	-44	79.5	67.8
Example 5	92.7	87.4	-44	72.7	67.4
Comparative Example 1	62.4	85.8	-21	54.1	32.2
Comparative Example 2	64.4	84.5	-35	65.6	33.7
Comparative Example 3	94.4	76.2	-43	71.4	32.8

[0104] As can be seen from Table 2, when the bifunctional catalyst of the present invention is applied to the hydroisomerization of hydrocarbon-based biodiesel at a relatively high reaction temperature, the liquid yield is not lower than 95 wt%, the freezing point is not higher than -20 °C, the cracking rate is not lower than 70%, and the isomerization rate is not lower than 40%. Increasing the reaction temperature can improve the reaction activity of the catalyst and the cracking rate and isomerization rate of n-alkanes, but high temperature will significantly reduce the product yield and generate more gases. Therefore, for the same catalyst, more target products can be achieved at an appropriate reaction temperature. The straight-chain alkane raw materials from different sources have little impact on the reaction processes and results.

[0105] FIG. 1 shows the TEM image of the metal-Y zeolite catalyst in Example 1 of the present invention. It can be seen that in the composite catalyst prepared by the in-situ

embedding method, the small metal nanoparticles are uniformly dispersed inside the zeolite, which provides more metal active centers and thereby benefits the activation of C-H bonds in the raw-material molecules.

[0106] FIG. 2 shows the TEM image of the Y zeolite in Comparative Example 1 of the present invention. The zeolite is composed of particles. Since it does not contain metal particles, its particle size is significantly larger than that of the metal-Y composite catalyst, limiting the exposure of metal active centers on the particle surface.

[0107] FIG. 3 shows the GC chromatogram of the liquid products obtained by using the metal-Y zeolite catalyst in Example 4 of the present invention. The products consist of normal and isomeric alkanes with different carbon numbers, and are concentrated in the jet-fuel components of C₈-C₁₆. Combining with the freezing point of the products in Table 2, it can be known that the bifunctional catalyst prepared by the present invention shows excellent cracking and isomerization capabilities and is very suitable for the production of bio-jet-fuels.

[0108] The above-mentioned examples are only the embodiments of the present invention and are not intended to limit the present invention. For those skilled in the art, the present invention can have various modifications and changes. Any modifications, equivalent replacements, improvements, etc. made within the spirit and principles of the present invention shall be included in the scope of the claims of the present invention.

Claims

1. A bifunctional reduced-state non-noble metal catalyst comprising Y zeolite of 20 to 40 wt%, ZSM-22 zeolite of 10 to 20 wt%, metallic nickel of 30 to 45 wt% and γ -Al₂O₃, wherein the total mass percentage of Y zeolite, ZSM-22 zeolite, metallic nickel and γ -Al₂O₃ is 100 wt%;

wherein the preparation method of said bifunctional reduced-state non-noble metal catalyst comprises the following steps:

S1: Y zeolite seeds are prepared;

S2: nickel metal nanoparticles are in situ embedded into the Y zeolite seeds obtained in step S1 to form a metal-Y zeolite composite;

S3: the metal-Y zeolite composite prepared in step S2 is treated with an inorganic acid, and then filtration, washing with water, drying and calcination were performed in sequence to obtain a metal-Y zeolite catalyst;

S4: ZSM-22 zeolite, aluminum hydroxide dry gel powder, dilute nitric acid solution and sesbania powder are added to the metal-Y zeolite catalyst obtained in step S3, and then kneading, molding, drying, calcination and reduction are performed in sequence to obtain the bifunctional reduced-state non-noble metal catalyst.

2. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein the preparation method of the Y zeolite seeds in step S1 comprises the following steps:

a silicon source, an aluminum source and sodium hydroxide are dissolved in deionized water to obtain a viscous liquid mixture, and the mixture is hydrothermally treated at 30 to 80 °C to obtain Y zeolite seeds;

wherein, calculated by the mass of oxides, the chemical composition of the viscous liquid mixture is SiO₂:Al₂O₃:Na₂O:H₂O = (20 to 40):(0.5 to 2):(20 to 40):(600 to 1000).

3. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein the preparation method of the metal-Y zeolite composite in step S2 comprises the following steps:

the Y zeolite seeds are dispersed in deionized water, followed by adding a template agent, and after dissolution, a silicon source, an aluminum source, a nickel salt and sodium hydroxide are added for reaction at 80 to 120 °C, and then filtration, washing and drying are performed in sequence to obtain the metal-Y zeolite composite with in-situ embedded nickel metal nanoparticles;

wherein, calculated by the mass of oxides, the feeding mass ratio of Y zeolite seeds, silicon source, aluminum source, nickel salt, sodium hydroxide and water is (0.5 to 1.5):(1.5 to 2.5):(0.3 to 0.8):(4 to 6):(3.5 to 5):(300 to 400).

4. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein the preparation method of the metal-Y zeolite catalyst in step S3 comprises the following steps:

the metal-Y zeolite composite is treated with an inorganic acid solution at 40 to 60 °C, and then filtration, washing with water, drying and calcination at 450 to 600 °C are performed in sequence on the treated material to obtain the metal-Y zeolite catalyst.

5. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein the metal-Y zeolite catalyst has the following properties: BET specific surface area is 250 to 350 m²/g, total pore volume is 0.3 to 0.45 cm³/g, and the molar ratio of SiO₂:Al₂O₃ = 5 to 10.

6. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein said ZSM-22 zeolite has the following properties: BET specific surface area of 180 to 220 m²/g, total pore volume of 0.15 to 0.25 cm³/g, and the molar ratio of SiO₂:Al₂O₃= 60 to 100.

7. The bifunctional reduced-state non-noble metal catalyst according to claim 1, wherein said inorganic acid is one or more selected from hydrochloric acid, phosphoric acid, acetic acid and nitric acid; the concentration of the inorganic acid solution is 0.1 to 0.5 mol/L; preferably, the inorganic acid solution is a mixed acid solution of hydrochloric acid and phosphoric acid, wherein the mass ratio of hydrochloric acid to phosphoric acid is 1:1.

8. The bifunctional reduced-state non-noble metal catalyst according to claim 3, wherein said nickel salt is one or more selected from nickel nitrate, nickel sulfate, nickel chloride, nickel carbonate hydroxide and nickel acetate.

9. The bifunctional reduced-state non-noble metal catalyst according to claim 2 or 3, wherein said silicon source is one or more selected from silica sol, sodium silicate and kaolin; and/or the aluminum source is one or two aluminum sources selected from aluminum sulfate, aluminum nitrate, aluminum chloride and sodium aluminate.

10. Use of a bifunctional reduced-state non-noble metal catalyst according to any one of claims 1 to 9 in the hydroisomerization/cracking reaction of bio-based long-chain alkanes, wherein the bio-based long-chain alkanes are produced from the hydrodeoxygenation process of bio-derived oils and fats, and are a mixture of straight-chain alkanes with a composition of C₁₅-C₁₈ and a sulfur content of lower than 3 ppmw.