

HYDROGENATION CATALYST, PREPARATION METHOD THEREFOR, AND APPLICATION THEREOF

TECHNICAL FIELD

5 [0001] The present invention relates to a hydrogenation catalyst, and a preparation method therefor and the use thereof. The hydrogenation catalyst is suitable for hydrogenating unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons, particularly suitable for hydrogenating olefins, alkynes, aromatics, etc., in industrial C4-C9 fractions into corresponding alkanes.

10 BACKGROUND ART

 [0002] With the transformation and upgrading of oil refining and chemical engineering and high-quality development of the petrochemical industry, especially the construction and commissioning of large ethylene units, there is an acute shortage of ethylene feedstocks. How to rationally and efficiently utilize the advantages of integrated oil refining and chemical
15 engineering resources to expand the sources of ethylene raw materials is particularly important. Low-value light hydrocarbons (C4-C9), by-products of refineries are considered as high-quality feedstock, and the effective use thereof to improve economic benefits has become one of the ways for various enterprises to improve quality and efficiency, for example, using reforming raffinate oil to produce high-added-value solvent oils (such as No. 6 and No. 120
20 solvent oils), and using C4 liquefied petroleum gas to produce an ethylene cracking raw material. However, since light hydrocarbons (C4-C9) contain unsaturated components such as olefins and aromatic hydrocarbons, they cannot meet the requirements for ethylene cracking raw materials and high-added-value products, so hydrogenation thereof to remove olefins and aromatic hydrocarbons is required. Currently, single metals having hydrogenation activity to
25 remove olefins and aromatic hydrocarbons mainly comprise Pt, Ni, Ru, W, Fe, Pd, Rh and Co. Among them, Ni, Pt and Pd catalysts are widely recognized and used. The hydrogenation performance k_{Pd} of Pd (the reaction rate of palladium) is 1/7 that of Ni metal, the activity k_{Pt} of Pt (the reaction rate of platinum) is 2.5 times that of Ni, but the price of palladium and platinum is hundreds of times higher than that of nickel. Overall considering the economy and
30 reactivity, nickel, as an active component of a benzene hydrogenation catalyst, has been generally recognized and widely used.

 [0003] In order to achieve good catalytic activity during benzene hydrogenation, the metal content of a nickel-based catalyst is generally as high as 40% or more, which is different from the relatively low load of noble metals. An impregnation method is easy to operate, has a low
35 cost, and has a very good effect on the preparation of low-content catalysts. However, a metal

content exceeding 20% leads to difficult dissolution of a precursor; and even if a relatively high content is achieved by means of impregnation many times, there are also the problems of a cumbersome preparation process, reduced dispersity and utilization rate of a metal active component, i.e. nickel grains, due to the active component being large and being likely to agglomerate on the surface of a catalyst, etc. As a common preparation method for high-content and multi-component catalysts, a co-precipitation method can enable highly dispersed and uniform catalyst components, which is conducive to improving the catalytic activity and stability. During the manufacturing of multi-component catalysts, suitable precipitation conditions are very important to ensure the homogeneity of product composition and to manufacture high-quality catalysts. Therefore, during the process of catalyst preparation, it is necessary to strictly control and select conditions during the process of a precipitation reaction according to the actual application of catalysts in order to achieve ideal catalytic activity.

[0004] In addition, since at a high temperature, a nickel-based catalyst has poor thermal stability and the NiO particles thereof are prone to aggregation and agglomeration, even if a metal component is fully dispersed by means of a co-precipitation method, part of nickel will easily form, together with a carrier, an "Ni-O-Al" bond having strong interaction and is thus dispersed on the surface of the carrier in the form of nickel-aluminum spinel, resulting in problems such as a reduced utilization efficiency of NiO, such that the activity and stability of the catalyst are reduced, and the service life of the catalyst is affected.

[0005] A cocatalyst, a substance with a low content added to a catalyst, is present as an auxiliary component of the catalyst, and has no or very low activity in terms of a catalytic reaction during the occurrence of the catalytic reaction. However, the addition of a cocatalyst has a very important impact on the chemical composition, chemical structure, ionic valence, acid-base property, lattice structure, surface structure, pore structure and dispersion state of a catalyst.

SUMMARY OF THE INVENTION

[0006] In view of the technical defects and technical disadvantages in the prior art, the present invention provides a hydrogenation catalyst and a preparation method therefor to overcome or at least partially solve the above problems.

[0007] In one aspect, the present invention provides a hydrogenation catalyst, which hydrogenation catalyst is composed of a main active component, an auxiliary agent, and a carrier, wherein

the main active component contains nickel and has a weight percentage content of 40-70% in the hydrogenation catalyst in terms of an oxide, and the metal dispersity of nickel is greater than 10%;

the auxiliary agent is one or a combination of more of a group II alkaline earth metal (group IIA), a group IB transition metal, a group IIB transition metal, a group VIB transition metal, a group VIII transition metal, and a rare earth metal; the weight percentage content of the auxiliary agent in the hydrogenation catalyst is 1-10% in terms of an oxide;

5 the carrier is aluminum oxide, or a mixture of aluminum oxide and at least one of silicon oxide (silicon dioxide), titanium oxide (titanium dioxide) and cerium oxide (cerium dioxide); and the weight percentage content of the carrier in the hydrogenation catalyst is 20%-59% in terms of an oxide.

[0008] In another aspect, the present invention provides a method for preparing the above
 10 hydrogenation catalyst, which method comprises the following steps:

adding a carrier to deionized water and stirring same, so as to obtain a slurry I;

adding a dispersant and a pore-expanding agent to the slurry I, so as to obtain a slurry I';

mixing a soluble nickel salt solution and a soluble auxiliary agent precursor salt solution until uniform, so as to obtain a solution II;

15 preparing a solution III from a precipitant;

adding the slurry I' to a reaction kettle, stirring same, and heating same to a predetermined reaction temperature;

adding the solution III to the reaction kettle to make the slurry I' reach a predetermined alkaline pH value, so as to pre-adjust the pH value;

20 under stirring conditions, dropwise adding the solution II and the solution III in a parallel flow manner at a predetermined addition speed, so as to control the alkaline pH value at a constant value;

ageing same by stirring same or leaving same to stand at a predetermined aging temperature for a predetermined period of aging time;

25 filtering and washing the obtained material until the filtrate is neutral, followed by drying, roasting and grinding, so as to obtain a precursor of the hydrogenation catalyst; and

reducing the precursor of the hydrogenation catalyst with H_2 , so as to obtain the hydrogenation catalyst.

[0009] In a further aspect, the present invention provides the use of the above hydrogenation
 30 catalyst in the hydrogenation of unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons.

[0010] In still a further aspect, the present invention provides a method for hydrogenating unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons, in which method the above hydrogenation catalyst is used.

[0011] Other features and advantages of the present invention will be described in the following description, and some will become obvious from the description, or understood by implementing the present invention. The purpose and other advantages of the present invention can be realized and obtained by means of the structures specified in the description, the claims and the accompanying drawings.

[0012] The technical solution of the present invention is further described in detail by referring to drawings and embodiments below.

BRIEF DESCRIPTION OF THE DRAWINGS

[0013] The drawings are used to provide a further understanding of the present invention and constitute a part of the specification. Together with the embodiments of the present invention, the drawings are used to explain the present invention and do not constitute a limitation on the present invention. In the drawings:

Fig. 1 shows the H₂-temperature-programmed reduction (H₂-TPR) diagram of example 1 and comparative examples 1, 2 and 3.

Fig. 2 is a diagram showing the benzene removal rates and stability of the catalyst of example 1 and the catalysts of comparative examples 1, 2 and 3.

Fig. 3 is an example of a schematic diagram of an adsorption curve obtained by a static chemisorption instrument.

DETAILED DESCRIPTION OF EMBODIMENTS

[0014] Exemplary embodiments of the present disclosure will be described in more detail below with reference to the accompanying drawings. Although the exemplary embodiments of the present disclosure are shown in the accompanying drawings, it should be understood that the present disclosure can be realized in various forms and should not be limited to the embodiments illustrated herein. In contrast, these embodiments are provided for more thorough understanding of the present disclosure, and for fully conveying the scope of the present disclosure to those skilled in the art.

[0015] Exemplary embodiments are described in detail herein, with examples shown in the accompanying drawings. Unless otherwise indicated, the same numbers in different accompanying drawings represent the same or similar elements when the following description refers to the accompanying drawings. Implementations described in the following exemplary embodiments do not represent all implementations consistent with the present

invention. Instead, the implementations are merely examples of apparatuses and methods consistent with some aspects of the present disclosure as detailed in the appended claims.

[0016] First, technical terms in each embodiment of the present invention are briefly described as follows:

5 [0017] Specific surface area: the total area per unit mass of a material, with a unit thereof being m^2/g , which usually refers to the specific surface area of a solid material, e.g. powdery, fibrous, granular, flaky and blocky materials.

[0018] Pore volume: the total volume of fine pores per unit mass of a porous solid, which is one of the characteristic values of an adsorbent or catalyst having a porous structure.

10 [0019] Metal dispersity: the ratio of the number of active metal atoms on the surface of a catalyst to the number of total metal atoms on the catalyst, which is actually often related to the specific surface area of a metal or the size of metal particles. Since a catalytic reaction is carried out on atoms on a surface, a catalyst with good dispersity generally has a better catalytic effect.

15 [0020] Raffinate oil: generally referring to a remaining material obtained by a solvent extraction method in the industry.

[0021] By research, it is found by the inventor that: the existing precipitation preparation methods involve numerous reaction conditions, and factors such as reactant types, the addition sequence, the pH and the temperature will have a great impact on a precipitation reaction, such
20 that the species of products prepared vary greatly. In the prior art, an unstable pH value and a changing reaction environment will cause problems such as different sizes and agglomeration of precipitated grains, accumulation of active components, excessively weak or strong binding force between active components and carriers, etc., thereby reducing the dispersity and utilization rate of metal active components. Therefore, a problem that needs to be addressed is
25 how to evenly disperse high-content active species during the preparation process of hydrogenation catalysts so as to enable the catalysts of higher activity and stability.

[0022] In view of this, in order to overcome problems regarding the dispersity and utilization rate of active components during the preparation of high-content nickel-based catalysts, the embodiments of the present invention provide a hydrogenation catalyst, which is composed of
30 a main active component, an auxiliary agent and a carrier.

[0023] The main active component of the hydrogenation catalyst contains nickel, and the weight percentage content of the main active component in the hydrogenation catalyst is 40-70%, preferably 50-60%.

35 [0024] The auxiliary agent is one or a combination of more of a group II alkaline earth metal, a group IB transition metal, a group IIB transition metal, a group VIB transition metal, a group VIII transition metal, and a rare earth metal. Preferably, the auxiliary agent is one or a combination of more of Mg, Cu, Zn, Mo, W, Co, La and Ce. The weight percentage content of

the auxiliary agent in the hydrogenation catalyst is 1-10% in terms of an oxide, preferably 3-6%.

[0025] The addition of different auxiliary agents to the above hydrogenation catalyst is beneficial for increasing the proportions of dispersed and immobilized NiO active centers, and helps to improve the activity, stability and sulfur resistance of the nickel-based catalyst. For example, the addition of an auxiliary agent containing an alkaline earth metal (such as Mg) can improve the thermal stability and sulfur resistance of an Ni/Al₂O₃ catalyst, prolong the service life of the catalyst, improve the dispersity of Ni, and increase the specific surface area of active nickel. Specifically, an alkaline earth metal has strong electronegativity, which increases the electron cloud density of Ni and causes a negative chemical shift in the electron binding energy of NiO, thereby improving the activity and sulfur resistance of the Ni catalyst. Ni, when used alone, has relatively weak hydrodearomatization activity; and after the addition of a transition metal (such as Mo) thereto, the interaction force between Ni and a carrier is weakened, and Mo and Ni can mutually promote reduction because Mo can increase H₂ retention active sites in the Ni catalyst, such that the hydrogenation performance of the catalyst can be significantly improved. The addition of an auxiliary agent containing a rare earth metal (such as La, Sm and Ce) can increase the randomness and dispersity of the main active component Ni, thereby increasing the number of active centers on the surface of the catalyst, reducing the activation energy of a reaction, increasing the electron cloud density on Ni metal, and improving the hydrodearomatization activity of the catalyst.

[0026] The carrier of the hydrogenation catalyst is aluminum oxide, or a mixture of aluminum oxide and one or more of oxides such as silicon oxide, titanium oxide and cerium oxide. The weight percentage content of the carrier in the hydrogenation catalyst is 20%-59% in terms of an oxide.

[0027] Aluminum oxide mentioned above is added in the form of pseudo-boehmite, which is preferably macroporous aluminum oxide having a specific surface area of $\geq 300 \text{ m}^2/\text{g}$ and a pore volume $\geq 0.7 \text{ cm}^3/\text{g}$. Different from aluminum nitrate and aluminum oxide, the pseudo-boehmite has a moderate binding force with active species, facilitating the catalytic activity of active species. Macroporous pseudo-boehmite has a relatively larger specific surface area and pore volume, which is conducive to the dispersion of the active component.

[0028] In the hydrogenation catalyst provided in the present examples, the metal dispersity of nickel is greater than 10%. For a characterization method for metal dispersity, a static chemisorption instrument is preferably used as a characterization instrument, and H₂ is preferably used as an adsorbed gas. Specifically, a sample is degassed at 130°C and then reduced with H₂ at 400°C; cooled by 35°C and then subjected to first saturation adsorption; and same is vacuumized and then subjected to second saturation adsorption. A difference

value between the two saturation adsorption operations is the volume of chemisorbed hydrogen.

[0029] The metal dispersity is obtained by means of the static chemisorption instrument; an exemplary adsorption curve is shown in Figure 3; and a computational formula is:

$$5 \quad \text{Metal dispersity} = \frac{\text{Number of Ni atoms on catalyst surface}}{\text{Total number of Ni atoms in catalyst}} = \frac{V_{H_2} / 22.414}{W \times P / M_{Ni}}$$

In the formula, V_{H_2} is the volume of chemisorbed hydrogen; W is the total mass of the catalyst; P is the percentage content of nickel (Ni); and M_{Ni} is the molecular mass of Ni.

In Figure 3, $V_{H_2}(\text{First}) = V_{\text{Chemisorption}} + V_{\text{Physisorption}}$

$$V_{H_2}(\text{Second}) = V_{\text{Physisorption}}$$

$$10 \quad \Delta V_{H_2} = V_{(\text{First})} - V_{(\text{Second})}$$

$$H_2 \sim Ni = 1 : 1$$

The grain size is calculated using the Scherrer equation:

$$D = \frac{0.89\lambda}{\beta \cos(\theta)}$$

15 In the formula, D is the grain diameter along a direction perpendicular to a crystal plane, λ is the X-ray wavelength, β is the half-peak width of the diffraction peak of the calculated crystal plane, and θ is the corresponding diffraction angle of the calculated crystal plane. The hydrogenation catalyst provided in the present embodiments has a high dispersity and a high metal content, and overcomes problems regarding the dispersity and utilization rate of the active component during the preparation of the high nickel-based catalyst. In the present
20 invention, the uniform precipitation of the active component is promoted, the nickel active component of the obtained catalyst is highly dispersed and has a more uniform and consistent particle size, and the catalyst has relatively excellent catalytic activity and stability to adapt to the saturation hydrogenation of unsaturated hydrocarbon feedstocks. For example, the hydrogenation catalyst can be used for hydrogenating unsaturated hydrocarbon feedstocks into
25 corresponding saturated hydrocarbons, specifically for hydrogenating olefins, alkynes, aromatics, etc., in industrial C4-C9 fractions into corresponding alkanes.

[0030] The present embodiments provide a method for preparing the above hydrogenation catalyst by using a co-precipitation method. The specific preparation method may comprise the following steps:

30 step 1) adding a carrier to deionized water and stirring same, so as to obtain a slurry I,

wherein specifically, the carrier may be added to deionized water at a mass ratio of 1 : 3-1 : 6;

step 2) adding a dispersant and a pore-expanding agent to the slurry I, so as to obtain a slurry I',

wherein the dispersant may be at least one of isopropanol, sec-butyl alcohol, levulinate and

polyethylene glycol, and the mass ratio of the dispersant to the carrier is 1 : 100-1 : 10; and the

pore-expanding agent may be at least one of polyvinyl alcohol, polyacrylic acid, sodium

polyacrylate and polyacrylate, and the mass ratio of the pore-expanding agent to the carrier is

1 : 100-1 : 10;

step 3) mixing a soluble main active component nickel salt solution and a soluble auxiliary agent precursor salt solution until uniform, so as to obtain a solution II,

wherein the soluble nickel salt and the soluble auxiliary agent precursor salt are selected from one or a combination of two or more of a nitrate, an oxalate, a sulfate and an acetate; and the concentration of the solution II may be 0.5-2.5 mol/L;

step 4) preparing a solution III from a precipitant,

wherein the precipitant may be one or a combination of two or more of potassium carbonate,

sodium carbonate, potassium hydroxide, sodium hydroxide, ammonium carbonate, ammonium bicarbonate, potassium bicarbonate, sodium bicarbonate, ammonia water and urea; and the concentration of the solution III may be 0.5-2.5 mol/L, and further 1-2.5 mol/L;

step 5) adding the slurry I' from step 1) to a reaction kettle, starting, and heating same to a reaction temperature,

wherein the reaction temperature may be, e.g., 40-90°C;

step 6) pre-adjusting the pH value, and adding a given amount of the precipitant solution III to the reaction kettle to make the slurry I' reach an alkaline pH value,

wherein the volume ratio of the precipitant solution, which is added to pre-adjust the pH, to water is 1 : 10 to 1 : 80; the pH value is pre-adjusted to 8-11, which is the key to ensure a consistent precipitation environment, the uniform dispersion of active component particles and the uniform size of precipitate particles;

step 7) under stirring conditions, dropwise adding the solution II obtained from step 2) and the solution III obtained from step 3) in a parallel flow manner at a given addition speed, so as to control the alkaline pH value at a constant value,

wherein the solution II is dropwise added at a speed of 20-100 ml/min, the solution III is dropwise added at a speed of 10-300 ml/min, and the constant alkaline pH value is consistent with the alkaline pH value after the pre-adjustment in step 5), both being 8-11;

step 8) after the addition of the solutions is completed, aging same at a given aging temperature for a given period of aging time under stirring or in a state of standing,

wherein the ageing temperature may be 40-90°C, and the ageing time may be 1-5 h;

step 9) filtering and washing the material obtained in step 8) until a filtrate is neutral, and grinding, drying and roasting the resulting cake, so as to obtain a precursor of a hydrogenation catalyst; and

step 10) reducing the precursor of the hydrogenation catalyst obtained from step 9) with H₂, so as to obtain a high-dispersity high-metal-content hydrogenation catalyst,

[0031] wherein the specific reduction conditions may involve reducing the nickel-based hydrogenation catalyst precursor at 250-500°C for 1-15 h in a high-purity hydrogen or hydrogen-containing atmosphere.

[0032] The high-dispersity high-metal-content hydrogenation catalyst is prepared by the preparation method of the present embodiments, and the high-content nickel active component can be highly dispersed on an aluminum oxide carrier, the dispersity of Ni metal reaching 10% or more.

[0033] By using pseudo-boehmite as a precursor of the carrier, in-situ growth of nickel particles on the pseudo-boehmite is achieved, which can make full use of the large specific surface area of the carrier to disperse the high-content nickel active component; and the active component and the carrier of the resulting catalyst have a moderate binding force.

[0034] The pH in the reaction vessel before a precipitation reaction, during the reaction process and during the aging process is always consistent by pre-adjusting the pH, which promotes the uniform precipitation of the active component, such that the high-content nickel active component can be highly dispersed on the carrier aluminum oxide and the size of particles is more uniform; therefore, the catalyst has an increased active specific surface area and good catalytic activity and stability.

[0035] Hereinafter, the technical effect of the present invention will be further illustrated by means of comparison of implementation data.

Example 1 (Mg)

[0036] Catalyst preparation: 11.50 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 46 ml of deionized water was added thereto, same was stirred until uniform, 0.12 g of a dispersant, i.e. polyethylene glycol, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 12.82 g of magnesium nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a

volume of 50 ml to prepare a 1 mol/L a magnesium nitrate solution. 207.3 g of anhydrous potassium carbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1 mol/L nickel nitrate solution and 28.5 ml of the 1 mol/L magnesium nitrate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 665.3 ml of the 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 100 ml/min and 300 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was stirred and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 1.

[0037] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Mg, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 5% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 35% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 4; the dispersant was polyethylene glycol, and the mass ratio of the dispersant to the carrier was 1 : 100; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Example 2 (Ce)

[0038] Catalyst preparation: 3.29 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) and 2.30 g of silicon oxide were weighed, 34 ml of deionized water was added thereto, 0.56 g of a dispersant, i.e. isopropanol, was added thereto, and same was stirred to prepare a uniform slurry. 72.70 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 100 ml to prepare a 2.5 mol/L nickel nitrate solution. 21.71 g of cerium nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to

prepare a 2.5 mol/L cerium nitrate solution. 20.00 g of sodium hydroxide was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 2.5 mol/L sodium hydroxide solution. 86.2 ml of the 2.5 mol/L nickel nitrate solution and 5.4 ml of the 2.5 mol/L cerium nitrate solution were measured out and then
 5 mixed until uniform, so as to form a metal mixed solution for subsequent use. 155.0 ml of the 2.5 mol/L sodium hydroxide solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 90°C. The pH was pre-adjusted by adding 1.0 ml of the precipitant solution to the reaction kettle to make the slurry reach an
 10 alkaline pH value of 11. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 60 ml/min, respectively, and the pH value was controlled to be constant at 11. After the addition of the solutions was completed, same was stirred and aged at 90°C for 5 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an
 15 oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 2.

[0039] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 70% in terms of an oxide; the auxiliary agent was Ce, and
 20 the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 10% in terms of an oxide; the carrier was Al₂O₃ and SiO₂, and the weight percentage content of the carrier in the hydrogenation catalyst was 20% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 6; the dispersant was isopropanol, and the mass ratio of the dispersant to the carrier was 1 : 10; the soluble nickel salt and the soluble auxiliary agent
 25 precursor salt were both nitrates; the concentration of the solution II was 2.5 mol/L, and the concentration of the solution III was 2.5 mol/L; the precipitant was NaOH; the reaction temperature was 90°C; the pH value was 11; the aging temperature was 90°C; and the aging time was 5 h.

Example 3 (La)

[0040] Catalyst preparation: 16.10 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) and 2.30 g of silicon oxide were weighed, 55 ml of deionized water was added thereto, 1.84 g of a pore-expanding agent, i.e. polyvinyl alcohol, was added thereto, and same was stirred to prepare a uniform slurry. 72.70 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a
 35 volume of 500 ml to prepare a 0.5 mol/L nickel nitrate solution. 4.33 g of lanthanum nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to prepare a 0.5 mol/L lanthanum nitrate solution. 15.81 g of

ammonium bicarbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L ammonium bicarbonate solution. 246.3 ml of the 0.5 mol/L nickel nitrate solution and 2.8 ml of the 0.5 mol/L lanthanum nitrate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 191.1 ml of the 1 mol/L ammonium bicarbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 80°C. The pH was pre-adjusted by adding 1.2 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 8. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 20 ml/min and 15 ml/min, respectively, and the pH value was controlled to be constant at 8. After the addition of the solutions was completed, same was stirred and aged at 80°C for 3 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 3.

[0041] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 40% in terms of an oxide; the auxiliary agent was La, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 1% in terms of an oxide; the carrier was Al₂O₃ and SiO₂, and the weight percentage content of the carrier in the hydrogenation catalyst was 59% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3; the pore-expanding agent was polyvinyl alcohol, and the mass ratio of the pore-expanding agent to the carrier was 1 : 10; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 0.5 mol/L, and the concentration of the solution III was 1 mol/L; the precipitant was NH₄HCO₃; the reaction temperature was 80°C; the pH value was 8; the aging temperature was 80°C; and the aging time was 3 h.

Example 4 (Cu)

[0042] Catalyst preparation: 11.50 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 40 ml of deionized water was added thereto, 0.12 g of a pore-expanding agent, i.e. polyvinyl alcohol, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 4.83 g of copper nitrate trihydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to prepare a 1 mol/L copper nitrate solution. 207.32 g of anhydrous potassium carbonate was weighed and

dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1 mol/L nickel nitrate solution and 14.5 ml of the 1 mol/L copper nitrate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 621.4 ml of the 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 100 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 109 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was left to stand and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The catalyst precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 4.

[0043] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Cu, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 5% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 35% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3.5; the pore-expanding agent was polyvinyl alcohol, and the mass ratio of the pore-expanding agent to the carrier was 1 : 100; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Example 5 (Zn)

[0044] Catalyst preparation: 11.50 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 40 ml of deionized water was added thereto, 0.68 g of a dispersant, i.e. sec-butyl alcohol, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 5.95 g of zinc nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to prepare a 1 mol/L zinc nitrate solution. 207.32 g of anhydrous potassium carbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to

prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1 mol/L nickel nitrate solution and 14.1 ml of the 1 mol/L zinc nitrate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 620.4 ml of the 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 109 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was left to stand and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The catalyst precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 5.

[0045] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Zn, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 5% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 35% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3.5; the dispersant was sec-butyl alcohol, and the mass ratio of the dispersant to the carrier was 1 : 17; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Example 6 (Mo)

[0046] Catalyst preparation: 9.86 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 35 ml of deionized water was added thereto, 0.66 g of a dispersant, i.e. a levulinate, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 24.7 g of ammonium heptamolybdate tetrahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to prepare a 1 mol/L ammonium molybdate solution. 207.32 g of anhydrous potassium carbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1

mol/L nickel nitrate solution and 2.3 ml of the 1 mol/L ammonium molybdate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 465.3 ml of the 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 300 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 87 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was left to stand and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The catalyst precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 6.

[0047] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Mo, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 10% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 30% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3.5; the dispersant was levulinate, and the mass ratio of the dispersant to the carrier was 1 : 15; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Example 7 (Co)

[0048] Catalyst preparation: 12.81 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 45 ml of deionized water was added thereto, 0.67 g of a dispersant, i.e. polyvinyl alcohol, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 5.82 g of cobalt nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to volume of 20 ml to prepare a 1 mol/L cobalt nitrate solution. 207.32 g of anhydrous potassium carbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1 mol/L nickel nitrate solution and 3.1 ml of the 1 mol/L cobalt nitrate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 585.9 ml of the 1.5

mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 400 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 109 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was left to stand and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The catalyst precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 7.

[0049] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Co, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 1% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 39% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3.5; the dispersant was polyethylene glycol, and the mass ratio of the dispersant to the carrier was 1 : 19; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Example 8 (W)

[0050] Catalyst preparation: 9.86 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 35 ml of deionized water was added thereto, 0.66 g of a dispersant, i.e. a levulinate, was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 37.75 g of ammonium tungstate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 20 ml to prepare a 1 mol/L ammonium tungstate solution. 42.08 g of potassium hydroxide was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 500 ml to prepare a 1.5 mol/L potassium hydroxide solution. 184.7 ml of the 1 mol/L nickel nitrate solution and 2.3 ml of the 1 mol/L ammonium tungstate solution were measured out and then mixed until uniform, so as to form a metal mixed solution for subsequent use. 308.3 ml of the 1.5 mol/L potassium hydroxide solution was measured out as a precipitant solution for

subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 300 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.3 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 20 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same was left to stand and aged at 60°C for 2 h. The obtained material was filtered and washed until the filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The catalyst precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of example 8.

[0051] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was W, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 10% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 30% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 3.5; the dispersant was levulinate, and the mass ratio of the dispersant to the carrier was 1 : 15; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was KOH; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Comparative example 1

[0052] Catalyst preparation: 13.14 g of a pseudo-boehmite powder (containing Al₂O₃, 70% (mass fraction)) was weighed, 45 ml of deionized water was added thereto, and same was stirred to prepare a uniform slurry. 58.16 g of nickel nitrate hexahydrate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 200 ml to prepare a 1 mol/L nickel nitrate solution. 207.32 g of anhydrous potassium carbonate was weighed and dissolved in deionized water, with the resulting solution being brought to a volume of 1000 ml to prepare a 1.5 mol/L potassium carbonate solution. 184.7 ml of the 1 mol/L nickel nitrate solution was measured out for subsequent use. 576.3 ml of the 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. A slurry was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 60°C. The pH was pre-adjusted by adding 1.5 ml of the precipitant solution to the reaction kettle to make the slurry reach an alkaline pH value of 10. Under stirring conditions, the nickel nitrate solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 109 ml/min, respectively, and the pH value was controlled to be constant at 10. After the addition of the solutions was completed, same

was stirred and aged at 60°C for 2 h. The obtained material was filtered and washed until a filtrate was neutral. The resulting filter cake was dried in an oven at 120°C for 4 h and ground, and same was then roasted in a muffle furnace at 500°C for 5 h and ground to obtain a catalyst precursor. The precursor was reduced by high purity H₂ at 400°C for 10 h, so as to obtain the catalyst of comparative example 1.

[0053] In the present example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; no auxiliary agent was used, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 0% in terms of an oxide; the carrier was Al₂O₃, and the weight percentage content of the carrier in the hydrogenation catalyst was 40% in terms of an oxide; the mass ratio of the carrier to deionized water was 1 : 4; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; the reaction temperature was 60°C; the pH value was 10; the aging temperature was 60°C; and the aging time was 2 h.

Comparative example 2

[0054] Catalyst preparation: 93.78 g of aluminum nitrate nonahydrate was weighed and brought to a volume of 250 ml to prepare a 1 mol/L aluminum nitrate solution; 184.7 ml of a 1 mol/L nickel nitrate solution, 28.5 ml of a 1 mol/L magnesium nitrate solution and 157.9 ml of the 1 mol/L aluminum nitrate solution are measured out and then mixed until uniform to form a metal mixed solution for subsequent use. 750.2 ml of a 1.5 mol/L potassium carbonate precipitant solution was measured out for subsequent use. 40 ml of purified water was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 50°C. Under stirring conditions, the metal mixed solution and the precipitant solution were added in a parallel flow manner at 35 ml/min and 71 ml/min, respectively, and the pH value was controlled to be constant at 10. The rest were the same as those in example 1, such that the catalyst of comparative example 2 was obtained.

[0055] In the present comparative example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Mg, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 5% in terms of an oxide; the carrier was Al₂O₃, the carrier precursor was aluminum nitrate nonahydrate, and the weight percentage content of the carrier in the hydrogenation catalyst was 35% in terms of an oxide; no dispersant was used; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K₂CO₃; and the reaction temperature was 50°C, and the pH value was 10.

Comparative example 3

[0056] Catalyst preparation: 11.50 g of a pseudo-boehmite powder (containing Al_2O_3 , 70% (mass fraction)), 184.7 ml of a 1 mol/L nickel nitrate solution and 28.5 ml of a 1 mol/L magnesium nitrate solution were weighed and then mixed until uniform, so as to form a metal mixed slurry for subsequent use. 206.1 ml of a 1.5 mol/L potassium carbonate solution was measured out as a precipitant solution for subsequent use. 40 ml of purified water was first added to a reaction kettle, stirring at a speed of 200 rpm was started, and same was heated to a reaction temperature of 80°C. Under stirring conditions, the metal mixed slurry and the precipitant solution were added in a parallel flow manner at 35 ml/min and 26 ml/min, respectively, and the pH value was controlled to be 7.2. After the addition was completed, 203 ml of a precipitant was added thereto to adjust the pH to 10.5, and same was then left to stand for 2 h. The rest were the same as those in example 1, such that the catalyst of comparative example 3 was obtained.

[0057] In the present comparative example, the weight percentage content of the main active component in the hydrogenation catalyst was 60% in terms of an oxide; the auxiliary agent was Mg, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst was 5% in terms of an oxide; the carrier was Al_2O_3 , the carrier precursor was pseudo-boehmite, and the weight percentage content of the carrier in the hydrogenation catalyst was 35% in terms of an oxide; the mixed slurry of the carrier and the metal solution and the precipitant formed parallel flows; the soluble nickel salt and the soluble auxiliary agent precursor salt were both nitrates; the concentration of the solution II was 1 mol/L, and the concentration of the solution III was 1.5 mol/L; the precipitant was K_2CO_3 ; and the reaction temperature was 80°C, the pH value of the reaction was 7.2, and the pH value of the ageing was 10.5.

[0058] Table 1 showed the test results of the metal dispersity and grain size of the catalysts of various examples and comparative examples.

Table 1 Metal dispersity and grain size in various examples and comparative examples

Sample	Metal dispersity (%)	Grain size (nm)
Example 1	15.5	7.6
Example 2	15.8	7.4
Example 3	16.2	7.0
Example 4	14.8	8.8
Example 5	15.0	8.6
Example 6	16.5	6.8
Example 7	14.3	9.0
Example 8	16.7	6.7

Comparative example 1	10.62	12.2
Comparative example 2	3.59	29.3
Comparative example 3	8.85	14.7

[0059] The catalysts prepared above were loaded into 20-ml fixed-bed reactors respectively, and the feedstock was reformed C6 naphtha from a refinery. The feedstock and the properties of products were shown in Table 2.

Table 2 Feedstock and the properties of products obtained from hydrogenation with catalysts

Item	Group composition (PONA)					Bromine index mg Br/100 g	Benzene removal rate, %	Saturation rate of olefins, %
	n-Alkanes	Iso-alkanes	Olefins	Naphthenes	Aromatic hydrocarbons			
Raffinate oil feedstock	22.68	71.01	0.62	2.52	3.15	1790	/	/
Example 1	22.03	70.39	0.00	7.59	0.00	4.88	100	100
Example 2	22.06	70.37	0.00	7.57	0.00	3.53	100	100
Example 3	22.06	70.36	0.00	7.58	0.00	2.78	100	100
Example 4	22.05	70.36	0.00	7.59	0.00	5.01	100	100
Example 5	22.04	70.38	0.00	7.58	0.00	5.26	100	100
Example 6	22.05	70.38	0.00	7.57	0.00	2.08	100	100
Example 7	22.05	70.37	0.00	7.58	0.00	6.15	100	100
Example 8	22.04	70.36	0.00	7.59	0.00	2.01	100	100
Comparative example 1	21.92	70.45	0.00	7.63	0.00	16.42	100	100
Comparative example 2	22.60	70.83	0.00	5.67	0.94	449	70.7	100
Comparative example 3	22.02	70.38	0.00	7.60	0.00	12.32	100	100

[0060] Reduction process: at a pressure of 1 MPa, the amount of fresh hydrogen: 12 L/h; raising the temperature to 120°C from room temperature at 30°C/h; and (2) after maintaining the temperature constant at 120°C for 2 h, raising the temperature to 380°C at 30°C/h, and maintaining the temperature at 380°C for 15 h, then stopping reduction, and cooling to 120°C.

[0061] Hydrogenation reaction conditions: reaction temperature: 120°C, reaction pressure: 1.0 MPa, hydrogen/oil volume ratio: 100 : 1, and volume space velocity: 3.0 h⁻¹.

[0062] In addition, it could be seen from Figure 1 that: in example 1, there was only one reduction peak, indicating that the binding force of nickel metal and the carrier was consistent and proving that the dispersion of the surface active metal on the carrier was more uniform

and consistent, which was beneficial for improving the stability of the catalyst; however, in each of comparative examples 1, 2 and 3, there were a plurality of reduction peaks with different reduction temperatures, proving that the binding forces of these reducible nickel species and the carrier were quite different. Therefore, the dispersity of comparative examples 1, 2 and 3 were poorer than that of example 1.

[0063] The high-dispersity high-metal-content hydrogenation catalyst prepared in example 1 was selected and was subjected to stability evaluation tests in a fixed-bed reaction device together with the catalysts of comparative examples 1, 2 and 3, and the obtained comparison results of the benzene removal rates of the catalysts were shown in Figure 2. It could be seen from Figure 2 that: the catalyst of example 1 had better benzene removal stability, which is far better than those of the catalysts of comparative examples 1, 2 and 3. Compared with comparative example 1, the period when the benzene removal rate was stabilized at 100% in example 1 was extended by 2 times or more, proving that the preparation method of the present invention could improve the catalytic stability of the catalyst. It should be finally noted that the above embodiments are merely used for illustrating rather than limiting the technical solution of the present invention; although the present invention is illustrated in detail with reference to the foregoing embodiments, those of ordinary skill in the art should understand that they can still make modifications to the technical solution recorded in the foregoing embodiments or make equivalent replacements on some of the technical features thereof; and the modifications or replacements do not make the essence of the corresponding technical solutions depart from the spirit and scope of the technical solutions of the embodiments of the present invention.

Claims

1. A hydrogenation catalyst consisting of a main active component, an auxiliary agent, and a carrier, wherein

the main active component contains nickel, the weight percentage content of the main active component in the hydrogenation catalyst is 40-70% in terms of an oxide, and the metal dispersity of nickel is greater than 10%;

the auxiliary agent is one or a combination of two or more of a group II alkaline earth metal, a group IB transition metal, a group IIB transition metal, a group VIB transition metal, a group VIII transition metal, and a rare earth metal, and the weight percentage content of the auxiliary agent in the hydrogenation catalyst is 1-10% in terms of an oxide;

the carrier is aluminum oxide, or a mixture of aluminum oxide and at least one of silicon oxide, titanium oxide and cerium oxide, and the weight percentage content of the carrier in the hydrogenation catalyst is 20-59% in terms of an oxide;

the hydrogenation catalyst is prepared by a method comprising the following steps:

adding the carrier to deionized water and stirring, so as to obtain a slurry I;

adding a dispersant and a pore-expanding agent to the slurry I, so as to obtain a slurry I';

mixing a solution prepared from soluble salts of nickel and a precursor of the auxiliary agent to be uniform, so as to obtain a solution II;

preparing a solution III from a precipitant;

adding the slurry I' to a reaction kettle, stirring, and heating to a predetermined reaction temperature;

adding the solution III to the reaction kettle to make the slurry I' reach a predetermined alkaline pH value, so as to pre-adjust the pH value;

under a stirring condition, adding the solution II and the solution III in a parallel flow manner at a predetermined dropwise addition speed, so as to control the alkaline pH value at a constant value;

ageing by stirring or leaving to stand at a predetermined aging temperature for a predetermined period of aging time;

filtering and washing the obtained material until the filtrate is neutral, followed by drying, roasting and grinding, so as to obtain a precursor of the hydrogenation catalyst; and

reducing the precursor of the hydrogenation catalyst with H₂, so as to obtain the hydrogenation catalyst.

2. The hydrogenation catalyst according to claim 1, wherein the auxiliary agent is one or a combination of two or more of Mg, Cu, Zn, Mo, W, Co, La and Ce.

5 3. The hydrogenation catalyst according to claim 1, wherein the weight percentage content of the auxiliary agent in the hydrogenation catalyst is 3-6% in terms of an oxide.

4. The hydrogenation catalyst according to claim 1, wherein the aluminum oxide is added in the form of pseudo-boehmite.

10 5. The hydrogenation catalyst according to claim 4, wherein the pseudo-boehmite is a precursor of macroporous aluminum oxide, and has a specific surface area of $\geq 300 \text{ m}^2/\text{g}$ and a pore volume of $\geq 0.7 \text{ cm}^3/\text{g}$.

6. A method for preparing the hydrogenation catalyst according to any one of claims 1-5, comprising the following steps:

adding a carrier to deionized water and stirring, so as to obtain a slurry I;

15 adding a dispersant and a pore-expanding agent to the slurry I, so as to obtain a slurry I';

mixing a solution prepared from soluble salts of nickel and a precursor of the auxiliary agent to be uniform, so as to obtain a solution II;

preparing a solution III from a precipitant;

20 adding the slurry I' to a reaction kettle, stirring, and heating to a predetermined reaction temperature;

adding the solution III to the reaction kettle to make the slurry I' reach a predetermined alkaline pH value, so as to pre-adjust the pH value;

25 under a stirring condition, adding the solution II and the solution III in a parallel flow manner at a predetermined dropwise addition speed, so as to control the alkaline pH value at a constant value;

ageing by stirring or leaving to stand at a predetermined aging temperature for a predetermined period of aging time;

filtering and washing the obtained material until the filtrate is neutral, followed by drying, roasting and grinding, so as to obtain a precursor of the hydrogenation catalyst; and

30 reducing the precursor of the hydrogenation catalyst with H₂, so as to obtain the hydrogenation catalyst.

7. The method according to claim 6, wherein the adding a carrier to deionized water comprises adding the carrier to deionized water at a mass ratio of 1 : 3 to 1 : 6.

8. The method according to claim 7, wherein

the dispersant is at least one of isopropanol, sec-butyl alcohol, levulinate and polyethylene glycol, and the mass ratio of the dispersant to the carrier is 1 : 100 to 1 : 10; and

the pore-expanding agent is at least one of polyvinyl alcohol, polyacrylic acid, sodium polyacrylate and polyacrylate, and the mass ratio of the pore-expanding agent to the carrier is 1 : 100 to 1 : 10.

9. The method according to claim 6, wherein the soluble salts of nickel and the precursor of the auxiliary agent are selected from one or a combination of two or more of a nitrate, an oxalate, a sulfate and an acetate.

10. The method according to claim 6, wherein the solution II has a concentration of 0.5-2.5 mol/L.

11. The method according to claim 6, wherein the precipitant is one or a combination of two or more of sodium carbonate, potassium carbonate, sodium hydroxide, potassium hydroxide, ammonium carbonate, ammonium bicarbonate, sodium bicarbonate, potassium bicarbonate, ammonia water and urea.

12. The method according to claim 6, wherein the solution III has a concentration of 0.5-2.5 mol/L.

13. The method according to claim 6, wherein the reaction temperature is 40-90°C.

14. The method according to claim 6, wherein the volume ratio of the solution III to water added during the pre-adjustment of the pH value is 1: 10 to 1: 80, and the alkaline pH value achieved after the pre-adjustment is 8-11.

15. The method according to claim 14, wherein the solution II is dropwise added at a speed of 20-100 ml/min, the solution III is dropwise added at a speed of 10-300 ml/min, and the constant alkaline pH value is consistent with the alkaline pH value after the pre-adjustment.

16. The method according to claim 6, wherein the ageing is carried out a temperature of 40-90°C for a time of 1-5 h.

17. The method according to claim 6, wherein the reducing is carried out under conditions such that the nickel-based hydrogenation catalyst precursor is reduced at 250-500°C for 1-15 h in a high-purity hydrogen or a hydrogen-containing atmosphere.

18. Use of the hydrogenation catalyst according to any of claims 1-5 in the hydrogenation of unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons.

19. The use according to claim 18, wherein the hydrogenation of unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons comprises hydrogenation of olefins, alkynes and aromatic hydrocarbons in industrial C4-C9 fractions into corresponding alkanes.

5 20. A method for hydrogenating unsaturated hydrocarbon feedstocks into corresponding saturated hydrocarbons, using the hydrogenation catalyst according to any one of claims 1-5.