Claims

1. A hydrogenation catalyst, comprising a carrier and a hydrogenation active metal component supported on the carrier, wherein the hydrogenation active metal component comprises at least one Group VIB metal component and at least one Group VIII metal component, the carrier being composed of phosphorus-containing alumina, wherein the hydrogenation catalyst comprises 30-99 wt% of the carrier, 0.5-50 wt% of the Group VIB metal component, calculated as oxides, and 0.5-20 wt% of the Group VIII metal component, calculated as oxides, based on the total amount of the hydrogenation catalyst, and the carrier comprises 94-99 wt% of Al_2O_3; and 1-6 wt% of P_2O_5, calculated as oxides and based on the total amount of the carrier;

when the hydrogenation catalyst is measured using a hydrogen temperature programmed reduction method (H_2-TPR), the ratio of the peak height of the low-temperature reduction peak, $P_{low\text{-}temp\ peak}$, at a temperature of 300-500 ºC to the peak height of the high-temperature reduction peak, $P_{hi\text{-}temp\ peak}$, at a temperature of 650-850 ºC, i.e. $S = P_{low\text{-}temp\ peak}/P_{hi\text{-}temp\ peak}$, is 0.5-2.0; preferably 0.7-1.9, and more preferably 0.8-1.8.

2. The hydrogenation catalyst according to claim 1, wherein:

the Group VIB metal component has a distribution factor $\sigma_{VIB}(R)$ of 0.5-3.5, preferably 0.8-3; and

the Group VIII metal component has a distribution factor $\sigma_{VIII}(R)$ of 0.5-3.5, preferably 0.8-3.

3. The hydrogenation catalyst according to claim 1 or 2, wherein the phosphorus-containing alumina shows an IR spectrum in which $(I_{3670}+I_{3580})/(I_{3770}+I_{3720})$ is 1.9-2.8, preferably 2-2.7; wherein I_{3670} represents the height of the peak at 3670 cm^{-1}, I_{3580} represents the height of the peak at 3580 cm^{-1}, I_{3770} represents the height of the peak at 3770 cm^{-1}, and I_{3720} represents the height of the peak at 3720 cm^{-1}.

4. The hydrogenation catalyst according to any one of claims 1-3, wherein:

the Group VIB metal component is Mo and/or W, and the Group VIII metal component is Co and/or Ni;

the hydrogenation catalyst comprises 40-94 wt% of the carrier, 5-45 wt% of the Group VIB metal component, calculated as oxides, and 1-15 wt% of the Group VIII metal

component, calculated as oxides, based on the total amount of the hydrogenation catalyst.

5. The hydrogenation catalyst according to any one of claims 1-4, wherein the carrier comprises 95-98 wt% of Al_2O_3; and 2-5 wt%, of P_2O_5, calculated as oxides and based on the total amount of the carrier.

6. The hydrogenation catalyst according to claim 3, wherein the phosphorus-containing alumina is obtained by calcining a phosphorus-containing pseudo-boehmite, wherein the phosphorus-containing pseudo-boehmite has an h value satisfying $1.7 \leq h \leq 3$, wherein h = D(031)/D(020), the D(031) represents a grain size of the crystal face represented by a (031) peak in the XRD pattern of the grain of the pseudo-boehmite, the D(020) represents a grain size of the crystal face represented by a (020) peak in the XRD pattern of the grain of the pseudo-boehmite, the (031) peak refers to a peak at a 2θ of 34-43 ° in the XRD pattern, and the (020) peak refers to a peak at a 2θ of 10-15 ° in the XRD pattern, $D = K\lambda/(B\cos\theta)$, wherein K is the Scherrer constant, λ is the diffraction wavelength of the target material, B is the half-peak width of the diffraction peak, and 2θ is the position of the diffraction peak; more preferably, the pseudo-boehmite has an h value satisfying $1.9 \leq h \leq 3$, preferably satisfying $2.2 \leq h \leq 2.8$.

7. A phosphorus-containing pseudo-boehmite for preparing the hydrogenation catalyst according to any one of claims 1 to 6, comprising 94-99 wt%, preferably 95-98 wt%, of Al_2O_3, and 1-6 wt%, preferably 2-5 wt%, of P_2O_5, calculated as oxides and based on the dry weight of the phosphorus-containing pseudo-boehmite,

wherein the phosphorus-containing pseudo-boehmite has an h value satisfying $1.7 \leq h \leq 3$, wherein h = D(031)/D(020), the D(031) represents a grain size of the crystal face represented by a (031) peak in the XRD pattern of the grain of the pseudo-boehmite, the D(020) represents a grain size of the crystal face represented by a (020) peak in the XRD pattern of the grain of the pseudo-boehmite, the (031) peak refers to a peak at a 2θ of 34-43 ° in the XRD pattern, and the (020) peak refers to a peak at a 2θ of 10-15 ° in the XRD pattern, $D = K\lambda/(B\cos\theta)$, wherein K is the Scherrer constant, λ is the diffraction wavelength of the target material, B is the half-peak width of the diffraction peak, and 2θ is the position of the diffraction peak; more preferably, the pseudo-boehmite has an h value satisfying $1.9 \leq h \leq 3$, preferably satisfying $2.2 \leq h \leq 2.8$.

8. A method for preparing a phosphorus-containing pseudo-boehmite for preparing the

hydrogenation catalyst according to any one of claims 1 to 6, comprising the steps of:

1) contacting a solution of an inorganic aluminum-containing compound with an acid or alkali for precipitation reaction, or contacting an organic aluminum-containing compound with water for hydrolysis reaction, in the presence of a grain growth regulator and a phosphorus-containing compound, at a pH of 4-7, preferably 4-6.5, to obtain a phosphorus-containing hydrated alumina; and

2) subjecting the phosphorus-containing hydrated alumina obtained to aging at a pH of 7-10.5, preferably 8-10, to obtain the phosphorus-containing pseudo-boehmite.

9. The method according to claim 8, wherein the precipitation reaction and hydrolysis reaction of step 1) are each independently carried out at a temperature of 30-90 ºC;

preferably, the conditions of the precipitation reaction include: a reaction temperature of 40-90 ºC, preferably 45-80 ºC, and a reaction time of 10-60 minutes, preferably 10-30 minutes; the conditions of the hydrolysis reaction include: a reaction temperature of 40-90 ºC, preferably 45-80 ºC, and a reaction time of 2-30 hr, preferably 2-20 hr.

10. The method according to claim 8 or 9, wherein the grain growth regulator is a substance capable of regulating the growth rate of the pseudo-boehmite grains on the (020) crystal face and the (031) crystal face;

preferably, the grain growth regulator is at least one selected from the group consisting of polyhydric sugar alcohols, salts of corresponding carboxylic acids thereof, and sulfates; further preferably, the grain growth regulator is at least one selected from the group consisting of sorbitol, glucose, gluconic acid, gluconate, ribitol, ribonic acid, salt of ribonic acid, and sulfate;

preferably, in the precipitation reaction, the grain growth regulator is used in an amount of 1-10 wt%, preferably 1.5-8.5 wt%, and more preferably 2-6 wt%, based on the weight of the inorganic aluminum-containing compound (calculated as alumina);

preferably, in the hydrolysis reaction, the grain growth regulator is used in an amount of 1-10 wt%, preferably 1.5-8.5 wt%, and more preferably 2-6 wt%, based on the weight of the organic aluminum-containing compound (calculated as alumina).

11. The method according to any one of claims 8-10, wherein:

the phosphorus-containing compound is selected from phosphoric acid, ammonium phosphate, ammonium hydrogen phosphate, diammonium hydrogen phosphate, sodium

phosphate, potassium phosphate or any combination thereof; preferably, the phosphorus-containing compound is used in an amount such that P_2O_5 is present in the resulting pseudo-boehmite in an amount of 1-6 wt%, preferably 2-5 wt%, calculated as oxide and based on the dry weight of the phosphorus-containing pseudo-boehmite,

the inorganic aluminum-containing compound is selected from aluminum salts, aluminates, or combinations thereof;

the organic aluminum-containing compound is selected from aluminum alkoxides that can undergo a hydrolysis reaction with water to produce a precipitate of hydrated alumina;

the acid is selected from sulfuric acid, hydrochloric acid, nitric acid, carbonic acid, phosphoric acid, formic acid, acetic acid, citric acid, oxalic acid, or combinations thereof; and/or

the alkali is selected from sodium metaaluminate, potassium metaaluminate, sodium hydroxide, potassium hydroxide, ammonia water or combinations thereof.

12. The method according to any one of claims 8 to 11, wherein the aging conditions of step 2) include: an aging temperature of 50-95 ºC, preferably 55-90 ºC; an aging time of 0.5-8 hours, preferably 2-6 hours.

13. A method for preparing a hydrogenation catalyst, comprising the steps of:

i) providing a phosphorus-containing pseudo-boehmite, preferably the phosphorus-containing pseudo-boehmite is the phosphorus-containing pseudo-boehmite according to claim 7 or the phosphorus-containing pseudo-boehmite obtained by the method according to any one of claims 8-12;

ii) loading a hydrogenation active metal component on the phosphorus-containing pseudo-boehmite to obtain a hydrogenation catalyst precursor, wherein the hydrogenation active metal component comprises at least one Group VIB metal component and at least one Group VIII metal component; and

iii) calcining the hydrogenation catalyst precursor to obtain the hydrogenation catalyst, wherein the calcining conditions include: a calcining temperature of 560-800 ºC, preferably 610-780 ºC, more preferably 630-750ºC, and most preferably 650-730 ºC, and a calcining time of 1-10 hours, preferably 3-6 hours.

14. The method according to claim 13, wherein the step ii) further comprises:

A) shaping and drying the phosphorus-containing pseudo-boehmite to obtain a shaped

product, wherein no calcining is carried out after the drying; and

B) loading a hydrogenation active metal component on the shaped product obtained in the step A), and optionally drying, to obtain the hydrogenation catalyst precursor;

preferably, the step B) further comprises impregnating the shaped product with an impregnating solution comprising at least one Group VIB metal compound and at least one Group VIII metal compound, followed by drying, to obtain a hydrogenation catalyst precursor;

preferably, the drying conditions of step B) include: a drying temperature of 50-350 ºC, preferably 80-250 ºC; a drying time of 1-12 hours, preferably 2-8 hours.

15. The method according to claim 13, wherein the step ii) further comprises: mixing, shaping and drying the phosphorus-containing pseudo-boehmite and a precursor of the hydrogenation active metal component to obtain the hydrogenation catalyst precursor;

preferably, said mixing the phosphorus-containing pseudo-boehmite with a precursor of the hydrogenation active metal component comprising kneading at least one Group VIB metal compound and at least one Group VIII metal compound with said phosphorus-containing pseudo-boehmite;

preferably, the drying conditions include: a drying temperature of 50-350 ºC, preferably 80-250 ºC; a drying time of 1-12 hours, preferably 2-8 hours.

16. The method according to claim 15, wherein the precursor of the hydrogenation active metal component is at least one selected from the group consisting of salts, oxides, and hydroxides of the hydrogenation active metal component;

preferably, the precursor of the Group VIB metal component is at least one selected from the group consisting of molybdenum oxide, molybdate, paramolybdate, phosphomolybdate, tungsten oxide, and tungstate, more preferably at least one selected from the group consisting of molybdenum oxide, ammonium molybdate, ammonium paramolybdate, phosphomolybdic acid, ammonium metatungstate, phosphotungstic acid, and ammonium paratungstate.

preferably, the precursor of the Group VIII metal component is at least one selected from the group consisting of cobalt nitrate, cobalt acetate, basic cobalt carbonate, cobalt chloride, and nitrate, chloride, formate, acetate, phosphate, citrate, oxalate, carbonate, basic carbonate, hydroxide, phosphide, sulfide, aluminate, and oxide of nickel.

17. The method according to any one of claims 13-16, wherein the heating rate of the calcining of step iii) is 50-600 ºC/hour, preferably 100-550 ºC/hour.

18. The method according to any one of claims 13-17, wherein the Group VIB metal component is Mo and/or W, the Group VIII metal component is Co and/or Ni;

preferably, the hydrogenation active metal component is used in such an amount that, in the hydrogenation catalyst, the carrier is present in an amount of 30-99 wt%, preferably 40-94 wt%; the Group VIB metal component is present in an amount of 0.5-50 wt%, preferably 5-45 wt%, calculated as oxides; and the Group VIII metal component is present in an amount of 0.5-20 wt%, preferably 1-15 wt%, calculated as oxides, based on the total amount of the hydrogenation catalyst.

19. Use of the hydrogenation catalyst according to any one of claims 1 to 6 or the hydrogenation catalyst obtained by the method according to any one of claims 13 to 18 in the hydrogenation of hydrocarbon oils.