Claims

1. A hydrofining catalyst comprising:

an inorganic refractory component comprising a first hydrodesulfurization catalytically active component in a mixture with at least one oxide selected from the group consisting of alumina, silica, magnesia, calcium oxide, zirconia and titania;

a second hydrodesulfurization catalytically active component supported on the inorganic refractory component; and

an organic component supported on the inorganic refractory component and comprising a carboxylic acid and optionally an alcohol,

wherein the hydrofining catalyst has pores with pore sizes in the ranges of 2-40 nm and 100-300 nm, respectively, wherein the volume of pores having a pore size in the range of 2-40 nm is 60-95%, preferably 75-90%, of the total pore volume, and the volume of pores having a pore size in the range of 100-300 nm is 0.5-30%, preferably 5-15%, of the total pore volume, as determined after being calcined at 400 ºC for 3 h,

wherein said first hydrodesulfurization catalytically active component comprises at least one metal element selected from the group consisting of Group VIIIB metal elements and Group VIB metal elements, and said second hydrodesulfurization catalytically active component comprises at least one Group VIIIB metal element and at least one Group VIB metal element; and

wherein, in the hydrofining catalyst, the total content of the Group VIIIB metal element is 15-35 wt%, preferably 20-30 wt%, and the total content of the Group VIB metal element is 35-75 wt%, preferably 40-65 wt%, based on the weight on a dry basis of the catalyst and calculated as oxides.

2. The hydrofining catalyst according to claim 1, wherein the first hydrodesulfurization catalytically active component comprises at least one Group VIIIB metal element in an amount of 60-90% of the total amount of the Group VIIIB metal element in the hydrofining catalyst;

preferably, the Group VIIIB metal element is at least one selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium and palladium, and/or the Group VIB metal element is at least one selected from the group consisting of chromium, molybdenum

and tungsten;

preferably, the total content of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 5-40 wt%, preferably 10-30 wt%, based on the weight on a dry basis of the catalyst.

3. The hydrofining catalyst according to any one of the preceding claims, wherein the hydrofining catalyst has a specific surface area of 70-200 m^2/g, a total pore volume of 0.15-0.6 mL/g, and an average pore size of 5-25 nm;

preferably, in the hydrofining catalyst, the volume of pores having a pore size in the range of 2-4 nm is no more than 10% of the total pore volume;

preferably, the XRD patterns of the inorganic refractory component and the hydrofining catalyst have characteristic peaks corresponding to XRD characteristic peaks of at least one oxide selected from the group consisting of alumina, silica, magnesia, calcium oxide, zirconia and titania, and characteristic peaks corresponding to XRD characteristic peaks of an oxide of the metal element acting as the first hydrodesulfurization catalytically active component.

4. The hydrofining catalyst according to any one of the preceding claims, wherein:

when the organic component comprises only a carboxylic acid, the ratio of the amount by weight of the carboxylic acid to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.1-0.8 : 1, preferably 0.2-0.6 : 1; or

when the organic component comprises both a carboxylic acid and an alcohol, the ratio of the amount by weight of the carboxylic acid to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.002-0.1 : 1, preferably 0.02-0.06 : 1; the ratio of the molar amount of the alcohol to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.005-0.03 : 1, preferably 0.01-0.02 : 1;

preferably, the carboxylic acid is selected from the group consisting of C_{1-18} monobasic saturated carboxylic acids, C_{7-10} phenyl acids, citric acid, adipic acid, malonic acid, succinic acid, maleic acid, tartaric acid, and combinations thereof;

preferably, the alcohol is selected from the group consisting of C_{1-18} monohydric

saturated alcohols, ethylene glycol, polyethylene glycol, glycerol, polyglycerol, erythritol, pentaerythritol, xylitol, sorbitol, trimethylolethane, and combinations thereof;

preferably, the hydrofining catalyst further comprises phosphorus in an amount of 0.8-10 wt%, preferably 1-8 wt%, based on the weight on a dry basis of the catalyst and calculated as P_2O_5.

5. A method for preparing a hydrofining catalyst comprising the steps of:

(1) mixing a precursor of a first hydrodesulfurization catalytically active component with a precursor of at least one oxide selected from the group consisting of alumina, silica, magnesia, calcium oxide, zirconia and titania, and calcining to obtain an inorganic refractory component;

(2) mixing a precursor of a second hydrodesulfurization catalytically active component with an organic component and optionally a phosphorus-containing compound to obtain an impregnation solution, wherein the organic component comprises a carboxylic acid and optionally an alcohol;

(3) mixing the inorganic refractory component with the impregnation solution, and shaping and drying the resulting mixture to obtain the hydrofining catalyst,

wherein the precursor of the first hydrodesulfurization catalytically active component comprises a precursor of at least one metal element selected from the group consisting of Group VIIIB metal elements and Group VIB metal elements, and the precursor of the second hydrodesulfurization catalytically active component comprises a precursor of at least one Group VIIIB metal element and a precursor of at least one Group VIB metal element; and

wherein the precursors of the first and second hydrodesulfurization catalytically active components are used in such amounts that, in the hydrofining catalyst, the total content of the Group VIIIB metal element is 15-35 wt%, preferably 20-30 wt%, and the total content of the Group VIB metal element is 35-75 wt%, preferably 40-65 wt%, based on the weight on a dry basis of the catalyst and calculated as oxides.

6. The method according to claim 5, wherein the precursor of the first hydrodesulfurization catalytically active component comprises a precursor of at least one Group VIIIB metal element in an amount of 60-90% of the total amount of the precursor of the Group VIIIB metal element;

preferably, the Group VIIIB metal element is at least one selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium and palladium, and/or the Group VIB metal element is at least one selected from the group consisting of chromium, molybdenum and tungsten;

preferably, the inorganic refractory component is used in such an amount that the total content of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 5-40 wt%, preferably 10-30 wt%, based on the weight on a dry basis of the hydrofining catalyst.

7. The method according to claim 5 or 6, wherein:

when the organic component comprises only a carboxylic acid, the ratio of the weight of the carboxylic acid used in step (2) to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.1-0.8 : 1, preferably 0.2-0.6 : 1; or

when the organic component comprises both a carboxylic acid and an alcohol, the ratio of the weight of the carboxylic acid used in step (2) to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.002-0.1 : 1, preferably 0.02-0.06 : 1, and the ratio of the molar amount of the alcohol used to the weight on a dry basis of those constituents, other than the first hydrodesulfurization catalytically active component, of the inorganic refractory component is 0.005-0.03 : 1, preferably 0.01-0.02 : 1;

preferably, the carboxylic acid is selected from the group consisting of C_{1-18} monobasic saturated carboxylic acids, C_{7-10} phenyl acids, citric acid, adipic acid, malonic acid, succinic acid, maleic acid, tartaric acid, and combinations thereof;

preferably, the alcohol is selected from the group consisting of C_{1-18} monohydric saturated alcohols, ethylene glycol, polyethylene glycol, glycerol, polyglycerol, erythritol, pentaerythritol, xylitol, sorbitol, trimethylolethane, and combinations thereof;

preferably, the phosphorus-containing compound is used in step (2) in such an amount that the phosphorus element is present in an amount of 0.8-10 wt%, preferably 1-8 wt%, based on the weight on a dry basis of the hydrofining catalyst and calculated as P_2O_5;

preferably, the phosphorus-containing compound is selected from the group consisting of phosphoric acid, hypophosphorous acid, ammonium phosphate, ammonium dihydrogen

phosphate, and combinations thereof.

8. The method according to any one of claims 5-7, wherein:

in step (1), the calcining conditions include: a calcining temperature of 300-900 ºC, preferably 400-800 ºC; and a calcining time of 1-15 hours, preferably 3-8 hours; and/or

in step (3), the drying conditions include: a drying temperature of 50-250 °C, preferably 100-200 °C; a drying time of 2-10h, preferably 3-8 h;

preferably, the XRD patterns of the resulting inorganic refractory component and the hydrofining catalyst have characteristic peaks corresponding to XRD characteristic peaks of at least one oxide selected from the group consisting of alumina, silica, magnesia, calcium oxide, zirconia and titania, and characteristic peaks corresponding to XRD characteristic peaks of an oxide of the metal element acting as the first hydrodesulfurization catalytically active component.

9. The method according to any one of claims 5-8, wherein the precursor of the alumina is selected from the group consisting of pseudo-boehmite, aluminum hydroxide powder, aluminum nitrate, aluminum carbonate, aluminum citrate, and combinations thereof; the precursor of the silica is selected from the group consisting of silica sol, white carbon black, silica and combinations thereof; the precursor of the magnesia is selected from the group consisting of magnesium hydroxide, magnesium nitrate, magnesium carbonate, magnesium acetate, magnesium oxide and combinations thereof; the precursor of the calcium oxide is selected from calcium hydroxide, calcium carbonate, calcium oxalate, calcium nitrate, calcium acetate, calcium oxide and combinations thereof; the precursor of the zirconia is selected from the group consisting of zirconium hydroxide, zirconium carbonate, zirconium nitrate, zirconium acetate, zirconium oxide and combinations thereof; the precursor of the titania is selected from the group consisting of titanium hydroxide, titanium nitrate, titanium acetate, titanium oxide and combinations thereof;

preferably, the precursors of alumina, silica, magnesia, calcium oxide, zirconia and titania have an average pore size of no less than 10 nm, in which the volume of pores having a pore size in the range of 2-6 nm is no more than 15% of the total pore volume, and the volume of pores having a pore size in the range of 6-40 nm is no less than 75% of the total pore volume.

10. A hydrofining catalyst system comprising a first catalyst and a second catalyst, wherein:

the first catalyst is a hydrofining catalyst according to any one of claims 1-4 or 10;

the second catalyst comprises a second inorganic refractory component comprising alumina, a third hydrodesulfurization catalytically active component supported on the second inorganic refractory component, and an organic component supported on the second inorganic refractory component, wherein the organic component is selected from the group consisting of carboxylic acids and alcohols, and the pore size of the second catalyst is concentrated in the range of 2-100 nm;

wherein the volume ratio of the first catalyst to the second catalyst is from 1:1 to 1:8, preferably from 1:2 to 1: 6.

11. The hydrofining catalyst system according to claim 10, wherein:

in the second catalyst, the third hydrodesulfurization catalytically active component comprises at least one Group VIIIB metal element and at least one Group VIB metal element;

preferably, in the second catalyst, the total content of the Group VIIIB metal element is 1-8 wt%, preferably 2-6 wt%, and the total content of the Group VIB metal element is 10-35 wt%, preferably 15-30 wt%, based on the weight on a dry basis of the second catalyst and calculated as oxides;

preferably, the Group VIIIB metal element is at least one selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium and palladium, and/or the Group VIB metal element is at least one selected from the group consisting of chromium, molybdenum and tungsten;

preferably, the second inorganic refractory component is present in the second catalyst in an amount of 60-85 wt%, preferably 70-80 wt%, based on the weight on a dry basis of the second catalyst.

12. The hydrofining catalyst system of claim 10 or 11, wherein:

the second catalyst has a specific surface area of 130-300 m^2/g, a total pore volume of 0.2-0.7 mL/g, and an average pore size of 6-20 nm;

preferably, in the second catalyst, the molar ratio of the organic component to the Group VIIIB metal element contained in the second catalyst is 0.5-8, preferably 1-5;

preferably, the carboxylic acid in the second catalyst is selected from the group consisting of C_{1-18} monobasic saturated carboxylic acids, C_{7-10} phenyl acids, citric acid, adipic acid, malonic acid, succinic acid, maleic acid, tartaric acid, and combinations thereof;

preferably, the alcohol in the second catalyst is selected from the group consisting of C_{1-18} monohydric saturated alcohols, ethylene glycol, polyethylene glycol, glycerol, polyglycerol, erythritol, pentaerythritol, xylitol, sorbitol, trimethylolethane, and combinations thereof;

preferably, the second catalyst further comprises phosphorus in an amount of 0.8-10 wt%, preferably 1-8 wt%, based on the weight on a dry basis of the second catalyst and calculated as P_2O_5.

13. A method for preparing a hydrofining catalyst system comprising a first catalyst and a second catalyst, said method comprising:

(1) preparing the first catalyst by the method according to any one of claims 5-9;

(2) preparing the second catalyst by the steps of:

(2a) mixing an alumina precursor with an extrusion aid and a peptizing agent, and subjecting the resulting mixture to shaping, drying and calcining sequentially to obtain a second inorganic refractory component;

(2b) mixing a precursor of a third hydrodesulfurization catalytically active component with an organic component selected from the group consisting of carboxylic acids and alcohols and optionally a phosphorus-containing compound to obtain a second impregnation solution;

(2c) mixing the second impregnation solution with the second inorganic refractory component and then drying to obtain the second catalyst; and

(3) loading the first catalyst and the second catalyst into a first catalyst bed and a second catalyst bed, respectively, in a volume ratio of 1:1 to 1:8, preferably 1:2 to 1:6, to obtain the hydrofining catalyst system;

preferably, in step (2), the precursor of the third hydrodesulfurization catalytically active component comprises a precursor of at least one Group VIIIB metal element and a precursor of at least one Group VIB metal element;

preferably, the precursor of the third hydrodesulfurization catalytically active

component is used in such an amount that, in the second catalyst, the total content of the Group VIIIB metal element is 1-8 wt%, preferably 2-6 wt%; the content of the Group VIB metal element is 10-35 wt%, preferably 15-30 wt%, based on the weight on a dry basis of the second catalyst and calculated as oxides;

preferably, in step (2), the second inorganic refractory component is used in such an amount that the second inorganic refractory component is present in the second catalyst in an amount of 60-85 wt%, preferably 70-80 wt%, based on the weight on a dry basis of the second catalyst;

preferably, the Group VIIIB metal element is at least one selected from the group consisting of iron, cobalt, nickel, ruthenium, rhodium and palladium, and/or the Group VIB metal element is at least one selected from the group consisting of chromium, molybdenum and tungsten.

14. The method according to claim 13, wherein:

in step (2b), the molar ratio of the organic component to the Group VIIIB metal element used in the preparation of the second catalyst is 0.5-8, preferably 1-5;

preferably, the carboxylic acid used in step (2b) is selected from the group consisting of C_{1-18} monohydric saturated carboxylic acids, C_{7-10} phenyl acids, citric acid, adipic acid, malonic acid, succinic acid, maleic acid, tartaric acid, and combinations thereof;

preferably, the alcohol used in step (2b) is selected from the group consisting of C_{1-18} monohydric saturated alcohols, ethylene glycol, polyethylene glycol, glycerol, polyglycerol, erythritol, pentaerythritol, xylitol, sorbitol, trimethylolethane and combinations thereof;

preferably, in step (2b), the phosphorus-containing compound is used in such an amount that the phosphorus element is present in an amount of 0.8-10 wt%, preferably 1-8 wt%, based on the weight on a dry basis of the second catalyst and calculated as P_2O_5;

preferably, the phosphorus-containing compound used in step (2b) is selected from the group consisting of phosphoric acid, hypophosphorous acid, ammonium phosphate, ammonium dihydrogen phosphate and combinations thereof.

15. The method according to claim 13 or 14, wherein:

in step (2a), the calcining conditions include: a calcining temperature of 400-1000 ºC, preferably 500-800 ºC; and a calcining time of 1-15 hours, preferably 3-8 hours; and/or

in step (2c), the drying conditions include: a drying temperature of 50-250 °C, preferably 100-200 °C; a drying time of 2-10h, preferably 3-8 h;

preferably, step (2a) is performed under such conditions that, in the resulting second inorganic refractory component, the volume of pores having a pore size in the range of 2-4 nm is 0-2% of the total pore volume, the volume of pores having a pore size in the range of 4-6 nm is 2-15% of the total pore volume, the volume of pores having a pore size in the range of 6-40 nm is 85-95% of the total pore volume, the remaining pores have a pore size in the range of 40-100 nm, and there are no pores having a pore size greater than 100 nm.

16. Use of a hydrofining catalyst according to any one of claims 1-4 or a hydrofining catalyst system according to claim 10 in the hydrofining of distillate oils.

17. A process for the hydrofining of distillate oils, comprises the following steps:

subjecting a hydrofining catalyst according to any one of claims 1-4 or a hydrofining catalyst system according to claim 10 to sulfurization; and

contacting a distillate oil to be hydrodesulfurized with the sulfurized hydrofining catalyst or hydrofining catalyst system under hydrodesulfurization conditions.