

Catalytic cracking catalyst, preparation method therefor, and application thereof

Technical Field

The present invention relates to a catalytic cracking catalyst and a preparation method therefor and application thereof.

Background Technology

With the increasing shortage of petroleum resources and the rising crude oil price, major refineries reduce costs through deep processing of heavy oil and using inferior oil to maximize benefits. At present, catalytic cracking is an important means of heavy oil processing.

However, the content of heavy metals (such as vanadium and nickel) in low-quality crude oil is generally high. Especially in recent years, due to the increasingly heavier and worse quality of feedstock oil and the processing of opportunity crude oil, metal poisoning of catalytic cracking catalysts has become increasingly common. Numerous research results have shown that once metals such as iron and nickel are deposited on the surface, they are difficult to migrate, and they will interact with elements such as silicon, aluminium, vanadium, and sodium to form a low-melting eutectic, sintering the surface of the catalyst and further forming a 2-3 μ m thick dense layer on the surface, blocking the channels through which the reactant enters the catalyst and the product diffuses, and deteriorating the product distribution. Severe metal contamination will lead to outstanding problems such as poor catalyst fluidization performance, reduced accessibility of active centers, poor catalyst selectivity, and increased dry gas and coke yields. Some apparatuses even face the risk of the shutdown.

In order to reduce the impact of metals in oils on catalytic cracking, the prior art uses the addition of metal-capturing components to eliminate or weaken its impact, however, since a majority of metal-capturing components will also affect the activity of the catalyst, so most of them are introduced into the catalyst system in the form of separate additives. When directly introduced into the catalyst, it may cause some adverse effects on the performance of the catalyst, and the addition is strictly limited.

CN101939095A discloses a molecular sieve catalyst and a preparation method thereof to prepare light olefins by catalytically cracking naphtha in a harsh environment of high temperature and high humidity. Specifically, the catalyst is prepared by spray-drying and calcining a mixed slurry, wherein in the mixed slurry, 0.01-5.0wt% of MnO₂ and 1-15wt% of P₂O₅ are simultaneously embedded into a catalyst composed of a zeolite, a clay, and an inorganic composite. According to that invention, the method of simultaneously embedding manganese and phosphate into the zeolite and the inorganic composite can be used to improve the thermal stability of the obtained spherical catalyst and increase the olefin yield after the cracking of hydrocarbons (such as naphtha) by protecting the acidic sites of the zeolite. The mixing ratio and sequence of Mn, P, zeolite, and inorganic composite are important to synthesize the desired catalysts. Mixing

manganese and phosphorus in the catalyst slurry in a dissolved form has very limited improvement effect on the catalyst. Said catalyst is mainly used for the conversion of naphtha, and how to improve its heavy oil conversion performance is not involved.

5 Summary of the Invention

The technical problem to be solved by the present invention is to provide a new catalytic cracking catalyst with better heavy oil conversion ability and metal contamination resistance ability. Another technical problem to be solved by the present invention is to provide the preparation method of the catalytic cracking catalyst and the application of the catalytic cracking catalyst in heavy oil catalytic cracking.

The present invention provides a catalytic cracking catalyst, wherein the catalytic cracking catalyst contains a cracking active component, a high specific heat capacity matrix material, a clay and a binder; the high specific heat capacity matrix material contains at least 5 wt% of manganese oxide as MnO_2 , the high specific heat capacity matrix material has a specific heat capacity of 1.3-2.0 J/(g•K) at the temperature of 1000K, the cracking active component comprises a Y zeolite.

Preferably, the high specific heat capacity matrix material contains 5-95wt% of alumina as Al_2O_3 , 5-95 wt% of manganese oxide as MnO_2 and 0-40wt% of a boron compound on the dry basis.

Preferably, in the high specific heat capacity matrix material, the boron compound is boron nitride and/or boron oxide.

Preferably, the high specific heat capacity matrix material has a specific surface area of 150-500 m^2/g .

Preferably, the high specific heat capacity matrix material has a pore volume of 0.3-1.5 cm^3/g .

Preferably, the high specific heat capacity matrix material has an average pore diameter of 3-20 nm.

Preferably, in the XRD spectrum of the high specific heat capacity matrix material, the ratio of the intensity of the peak at 2θ angle of $18\pm 0.5^\circ$ to the intensity of the peak at 2θ angle of $37\pm 0.5^\circ$ is 1:(3-10).

The high specific heat capacity matrix material can be prepared and obtained according to the preparation method comprising the steps:

(1) mixing an aluminium source and an alkali to form a colloid to obtain an aluminium-containing colloid, the pH value of the obtained aluminium-containing colloid is 7-11;

(2) mixing a manganese salt solution with a pH value of 3-7 and urea to obtain a manganese source solution;

(3) forming a mixture of the aluminium-containing colloid, the manganese source solution, and optionally the boron compound; and optionally

(4) washing and/or drying and/or calcining.

In the preparation step (1) of the high specific heat capacity matrix material, the mixing of

the aluminium source and the alkali to form a colloid includes: mixing a solution of the aluminium source and a solution of the alkali to form a colloid with a temperature ranging from room temperature to 85°C and a pH value of 7-11.

The concentration of alumina in the solution of the aluminium source is 150-350g
5 $\text{Al}_2\text{O}_3/\text{L}$, the concentration of the alkali in the solution of the alkali is 0.1-1 mol/L. The aluminium source is one or more of aluminium nitrate, aluminium sulfate, aluminium phosphate, aluminium chloride and the like; the alkali is one or more of a water-soluble carbonate, a water-soluble bicarbonate, and a water-soluble hydroxide.

The solution of the alkali is an alkaline aqueous solution containing one or more of CO_3^{2-} ,
10 HCO_3^- and OH^- ; in the solution of the alkali, the concentration of CO_3^{2-} is 0-0.6 mol/L, the concentration of OH^- is 0-0.5 mol/L, and the concentration of HCO_3^- is 0-1 mol/L, provided that the sum of the concentration of CO_3^{2-} , the concentration of OH^- , and the concentration of HCO_3^- is not zero. Herein, the concentration of CO_3^{2-} , the concentration of OH^- , and the concentration of HCO_3^- are obtained by dividing the molar amount (mol)
15 of the anionic group in the alkali used to form the alkaline aqueous solution by the volume (L) of the alkaline aqueous solution.

In the preparation step (2) of the high specific heat capacity matrix material, the molar ratio of urea to manganese ions is 1-5, for example 2-4, and the concentration of the manganese salt as MnO_2 in the manganese salt solution can be 50-500 g/L.

20 Preferably, in step (2), urea is added to the manganese salt solution, and then the resulting mixture is stirred at room temperature for 30-60 minutes to obtain a manganese source solution.

The boron compound is, for example, boron nitride and/or boron oxide and/or a boron oxide precursor. The boron nitride can be one or more of hexagonal boron nitride, cubic
25 boron nitride, rhombohedral boron nitride and wurtzite boron nitride; the boron oxide precursor can be one or more of ammonium borate, ammonium baborate and boric acid.

In step (3), after mixing the aluminium-containing colloid and the manganese source solution, an aging process is further included. The aging temperature is from room temperature to 120°C, the aging time is 4-72 hours, and the aging is carried out under
30 stirring or under standing alone; preferably, the aging is carried out under stirring, the aging temperature is 60-100°C, and the aging time is 12-36 hours.

In an embodiment, in step (4), the calcining temperature is 500°C-900°C, and the calcining time is 4-8 hours.

The present invention also provides a method for preparing the catalytic cracking catalyst,
35 which comprises a cracking active component, a high specific heat capacity matrix material and/or a precursor thereof, a clay and a binder are vigorously mixed and stirred with water, and the mixture is spray-dried, washed, filtered and dried. The precursor of high specific heat capacity matrix material refers to a high specific heat capacity matrix material obtained without the calcining in step (4). Therefore in the present invention, the
40 "high specific heat capacity matrix material" can refer to a collective name for a high specific heat capacity matrix material obtained with the calcining in step (4) and a high

specific heat capacity matrix material obtained without the calcining in step (4), or just refers to a high specific heat capacity matrix material obtained with the calcining in step (4).

5 The present invention also provides the application of the catalytic cracking catalyst in the heavy oil catalytic cracking.

The catalytic cracking catalyst provided by the present invention can increase the specific heat capacity of the catalytic cracking catalyst by using a specific high specific heat capacity material together with a cracking active component, a clay and a binder, which is beneficial to the atomization and the cracking of the heavy oil macromolecules in the reactor. The catalyst provided by the present invention has a good resistance to abrasion. When the catalytic cracking catalyst provided by the present invention is used for heavy oil catalytic cracking, it can give a high heavy oil conversion rate, a high light oil yield and a high liquid yield. The catalyst provided by the present invention has multi-metal contamination resistance ability. In the case of contamination with iron, vanadium, and nickel, it can give a high total liquid yield, a high light oil yield, and a high gasoline yield. Other features and advantages of the present invention will be described in detail in the following detailed description.

Brief description of the drawings

20 The accompanying drawing is intended to provide a further understanding of the present invention and constitutes a part of the description and together with the following detailed description, serves to explain the present invention, but does not constitute a limitation of the present invention.

Figure 1 is the X-ray diffraction spectrum of the high specific heat capacity matrix material of Example 1. In the spectrum, there are diffraction peaks at 2θ angles of $18\pm 0.5^\circ$, $37\pm 0.5^\circ$, $48\pm 0.5^\circ$, $59\pm 0.5^\circ$, and $66\pm 0.5^\circ$.

Detailed description

Specific embodiments of the present invention will be described in detail below. It should be understood that the specific embodiments described herein are only used to illustrate and explain the present invention and are not intended to limit the present invention.

In the present invention, the high specific heat capacity matrix material refers to a material whose specific heat capacity at 1000K is not less than $1.3 \text{ J}/(\text{g}\cdot\text{K})$.

In the present invention, when referring to the contents of the components of the catalyst, the sum of the contents of the components of the catalyst is 100% by weight; when referring to the content of the components of the high specific heat capacity matrix material, the sum of the contents of the components of the high specific heat capacity matrix material is 100% by weight; when referring to the anhydrous chemical formula of the high specific heat capacity matrix material, the coefficients of the components in the anhydrous chemical formula are based on the weight, and the sum of the coefficients of the components is 100.

A catalytic cracking catalyst is provided by the present invention, wherein based on the total weight of the catalytic cracking catalyst, on the dry basis, the catalytic cracking catalyst contains 1-60 wt% of the cracking active component, 1-50 wt% of the high specific heat capacity matrix material, 1-70 wt% of the clay and 1-70 wt% of the binder;
5 the high specific heat capacity matrix material contains at least 5 wt% of manganese oxide, the high specific heat capacity matrix material has a specific heat capacity at a temperature of 1000K of 1.3-2.0 J/(g•K).

The dry basis refers to the solid product obtained after a material is calcined at 800°C for 1 hour.

10 The room temperature according to the present invention is 15-40°C, for example, 15°C.
According to the catalytic cracking catalyst provided by the present invention, preferably, based on the total weight of the catalytic cracking catalyst, the catalytic cracking catalyst contains 10-50 wt% of a cracking active component on the dry basis, 5-40 wt% of a high specific heat capacity matrix material on the dry basis, 10-60 wt% of a clay on the dry
15 basis and 10-60 wt% of a binder on the dry basis. Controlling the contents of the above-mentioned components within the preferred range can make the obtained catalytic cracking catalyst have better physical and chemical properties and reaction performance.

According to the catalytic cracking catalyst provided by the present invention, when the catalyst exists in the form of particles (individual particles or discrete particles), the
20 cracking active component and the high specific heat capacity matrix material are in the same particle, that is, the cracking active component, the high specific heat capacity matrix material, the clay and the binder are contained in the same particle of the catalytic cracking catalyst.

According to the first embodiment of the catalytic cracking catalyst provided by the
25 present invention, the high specific heat capacity matrix material does not contain any boron compound. Based on the weight of the high specific heat capacity matrix material, the high specific heat capacity matrix material contains 5-95 wt% of alumina as Al_2O_3 and 5-95 wt% of manganese oxide as MnO_2 , for example the high specific heat capacity matrix material is mostly composed of 15-70 wt% or 20-65 wt% or 30-61 wt% of
30 manganese oxide and 30-85 wt% or 35-80 wt% or 39-70 wt% of alumina. The high specific heat capacity matrix material can have a specific surface area of 180-300 m^2/g , for example 200-250 m^2/g or 220-245 m^2/g ; the high specific heat capacity matrix material has a pore volume of 0.35-0.75, for example 0.4-0.65 cm^3/g ; the high specific heat capacity matrix material has an average pore diameter of 5-13 nm, for example 6-11
35 nm.

According to the catalytic cracking catalyst provided by the present invention, the high specific heat capacity matrix material can optionally contain a boron compound. Preferably, the high specific heat capacity matrix material provided by the present invention (abbreviated as the matrix material) contains a boron compound, which can
40 have a better metal contamination resistance performance than the high specific heat capacity matrix material containing no boron compound.

According to the second embodiment of the catalytic cracking catalyst provided by the present invention, in the high specific heat capacity matrix material, the boron compound is boron nitride, and its specific heat capacity is 1.3-2.0 J/(g•K), for example, 1.35-1.95 J/(g•K) or 1.51-1.95 J/(g•K). The anhydrous chemical formula of the high specific heat capacity matrix material can be expressed as (5-94.5)Al₂O₃•(5-94.5)MnO₂•(0.5-40)BN, for example, (20-80)Al₂O₃•(15-75)MnO₂•(5-30)BN, in terms of the weight ratio. Preferably, based on the weight of the high specific heat capacity matrix material, the high specific heat capacity matrix material contains 5-94.5 wt% of alumina, 5-94.5 wt% of manganese oxide as MnO₂ and on the dry basis, greater than 0 and not more than 40 wt%, for example 0.5-35 wt% of boron nitride; more preferably, the high specific heat capacity matrix material contains 15-80 wt% of alumina, 15-70 wt% of manganese oxide and 5-30 wt% of boron nitride; still more preferably, the high specific heat capacity matrix material contains 19-74 wt% of alumina, 14-66 wt% of manganese oxide and 8-26 wt% of boron nitride. The high specific heat capacity matrix material contains boron nitride, which can improve the abrasion resistance of the catalyst.

In the second embodiment of the catalytic cracking catalyst of the present invention, the high specific heat capacity matrix material has a specific surface area of 150-350 m²/g, for example 180-300 m²/g or 200-250 m²/g or 220-245 m²/g, the high specific heat capacity matrix material has a pore volume of 0.35-0.75, for example 0.4-0.65 cm³/g or 0.45-0.75 or 0.5-0.7 cm³/g, the high specific heat capacity matrix material has an average pore diameter of 3-20 nm for example 4-18 nm or 5-15 nm or 6-13 nm or 6-8.5 nm, preferably 5-13 nm or 6-11 nm.

According to the second embodiment of the catalytic cracking catalyst of the present invention, the preparation method of the matrix material comprises the steps:

(1) an aluminium source solution and an alkali solution are mixed at room temperature to 85°C to form a colloid, and the pH of the colloid at which a colloid is formed is controlled to be 7-11;

(2) a manganese salt solution with a pH value of 3-7 is formulated, and the manganese salt solution and urea are mixed and stirred, wherein the molar ratio of urea to manganese ions is 1-5; there is no special requirement for the temperature at which the manganese salt solution and urea are mixed, and the mixing can be carried out at room temperature, and the stirring time is, for example, 30-60 minutes;

(3) the product obtained in step (1), the product obtained in step (2) and boron nitride are mixed, and aged at room temperature to 120°C for 4-72 hours; and optionally,

(4) the product obtained in step (3) is washed with water (preferably, the washing makes the washing solution after the washing become neutral (neutral means that the pH value is 6.5-7.5), for example, the product is flushed with deionized water until the deionized water after the washing is neutral), dried, and calcined to obtain a high specific heat capacity matrix material.

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, the

selection range of the alkali solution in step (1) is relatively wide, preferably, in step (1), the alkali solution is an alkaline aqueous solution containing at least one of CO_3^{2-} , HCO_3^- and OH^- , more preferably the alkaline aqueous solution is an aqueous solution comprising one or more of ammonium bicarbonate, ammonium carbonate, sodium hydroxide, and potassium hydroxide, or is a mixed solution of one or more of ammonium carbonate, sodium hydroxide and potassium hydroxide together with ammonia water. Preferably, the total concentration of the alkali in the alkali solution is 0.1-1 mol/L. In one embodiment, in the alkaline solution, the concentration of CO_3^{2-} is 0-0.6 mol/L, for example 0.3-0.5 mol/L; the concentration of OH^- is 0-0.5 mol/L, for example 0.2-0.35 mol/L, the concentration of HCO_3^- is 0-1.0 mol/L, for example, 0.4-1.0 mol/L. The pH value at which a colloid is formed in step (1) is preferably 8-11, for example 8.5-11 or 9-10. When ammonia water is used, it is assumed that ammonia water is totally ionized, and the required addition amount of ammonia water is calculated according to the calculation amount of hydroxyl groups.

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, the selection range of the type of the aluminium source is relatively wide, and any water-soluble aluminium source that can be dissolved in water can be used in the present invention, for example, the aluminium source may be one or more of aluminium nitrate, aluminium sulfate and aluminium chloride.

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, in step (2), the manganese salt solution having a specific pH value is mixed with urea to form a mixture, and the pH value of the manganese salt solution is 3-7, preferably 5-7.

The selection range of the condition for mixing urea with the manganese salt solution is relatively wide, according to an embodiment of the present invention, the method of the mixing mentioned in step (2) comprises: urea is added to the manganese salt solution, the resulting mixture is stirred at room temperature for 40-60 minutes, wherein the molar ratio of urea to manganese ions is preferably 2-4. The manganese salt solution in step (2) may be an aqueous solution of a water-soluble manganese salt, and/or a salt solution formed after contacting a water-soluble manganese salt, manganese oxide, and/or manganese hydroxide with an acid. The selection range of the kind of the manganese salt is relatively wide, and any water-soluble manganese salt that can be dissolved in water can be used in the present invention, and the manganese salt is for example one or more of manganese nitrate, manganese sulfate, manganese chloride and the like. The manganese salt solution can also be prepared by contacting manganese oxide and/or manganese hydroxide and/or water-soluble manganese salt with an acid, wherein the manganese oxide is for example one or more of manganese monoxide, trimanganese tetraoxide, dimanganese trioxide, and manganese dioxide, and the acid is for example one or more of hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid, preferably one or more of hydrochloric acid, sulfuric acid, and nitric acid.

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, in step (3) the weight ratio of the product obtained in step (1) as Al_2O_3 : the product obtained in step (2) as MnO_2 : boron nitride on the dry basis is
5 (5-95) Al_2O_3 :(5-95) MnO_2 :(0.5-40)BN, for example (20-80) Al_2O_3 :(15-75) MnO_2 :(5-30)BN. Preferably, in step (3), the product obtained in step (1), the product obtained in step (2) and boron nitride are used in such amounts that the prepared/obtained matrix material contains 5-94.5 wt%, for example 15-80 wt% or 19-74 wt% or 20-80 wt% or 19-60 wt% of alumina, 5-94.5 wt%, for example 15-75 wt% or 10-70 wt% or 14-66 wt% or 19-66
10 wt% of manganese oxide as MnO_2 and on the dry basis greater than 0 and not more than 40 wt%, for example 0.5-35 wt% or 5-30 wt% or 8-26 wt% of boron nitride.

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, in step (3), the selection range of the aging condition is relatively wide (for example, the
15 aging temperature is from room temperature to 120°C, the aging time is 4-72 hours), preferably in step (3), the aging condition includes: the aging temperature is 60-100°C, the aging time is 12-36 hours, and the aging is carried out under stirring. There is no special requirement for the stirring manner, for example, the stirring speed may be 50-300 rpm.

20 According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, the boron nitride can be one or more of hexagonal boron nitride (h-BN), cubic boron nitride (c-BN), rhombohedral boron nitride (r-BN) and wurtzite boron nitride (w-BN).

According to the second embodiment of the catalytic cracking catalyst of the present invention, in the preparation method of the high specific heat capacity matrix material, in
25 step (4) the selection ranges of the drying condition and the calcining condition are relatively wide. The methods of drying and calcining can be carried out with reference to the prior art, and the present invention has no special requirements for these. For example, the drying conditions in step (4) include: drying at 100-150°C for 6-24 hours; the
30 calcining conditions in step (4) include: calcining at 550-800°C, for example 550-750°C for 4-8 hours.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the high specific heat capacity matrix material, the boron compound is boron oxide having a specific heat capacity of 1.3-2.0 J/(g•K), for example 1.35-1.95
35 J/(g•K) or 1.51-1.95 J/(g•K). The anhydrous chemical composition formula of the high specific heat capacity mesoporous matrix material provided by the present invention can be expressed as (5-94.5) Al_2O_3 •(5-94.5) MnO_2 •(0.5-10) B_2O_3 , for example, (20-80) Al_2O_3 •(15-75) MnO_2 •(0.5-10) B_2O_3 , or (20-80) Al_2O_3 •(15-75) MnO_2 •(1-8) B_2O_3 in terms of the oxide weight ratio. Preferably, based on the weight of the high specific heat
40 capacity matrix material, the high specific heat capacity matrix material contains 5-94.5 wt% of alumina, 5-94.5 wt% of manganese oxide as MnO_2 and 0.5-10 wt% of boron oxide

as B₂O₃; more preferably, the high specific heat capacity matrix material contains 15-80 wt% of alumina, 15-80 wt% of manganese oxide as MnO₂ and 0.8-8 wt% of boron oxide as B₂O₃ or the high specific heat capacity matrix material contains 20-62 wt% of alumina, 34-72 wt% of manganese oxide as MnO₂ and 2-8 wt% of boron oxide as B₂O₃. Preferably,

5 the high specific heat capacity matrix material has a specific surface area of 300-500 m²/g, for example 310-370 m²/g or 330-370 m²/g, and has a pore volume of 0.5-1.5 cm³/g, for example 0.7-1.4 cm³/g or 0.6-1.3 cm³/g or 0.7-1.2 cm³/g. Preferably, the matrix material is a mesopore matrix material with an average pore diameter of 3-20 nm, for example 5-18 nm or 8-18 nm or 7-15 nm or 8-14 nm or 10-15 nm or 10-13 nm.

10 According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the high specific heat capacity matrix material, the boron compound is boron oxide, and a higher pore volume and a higher specific surface area can be achieved. The introduction of boron oxide modifies/adjusts the acidity of the matrix and improves the pre-cracking ability of the matrix. The matrix material used as the catalytic

15 cracking catalyst or auxiliary in the heavy oil catalytic cracking can reduce the particle temperature when the catalytic cracking catalyst is regenerated, slow down the collapse of the molecular sieve, improve the activity of the catalyst, the metal contamination resistance ability and the heavy oil conversion ability, reduce the coke selectivity of the catalyst, and make the catalyst have a good fluidization performance.

20 According to the third embodiment of the catalytic cracking catalyst provided by the present invention, the preparation method of the high specific heat capacity matrix material comprises the steps:

(1) an aluminium source solution and an alkali solution are mixed at room temperature to 85°C to form a colloid, and the pH of the colloid at which a colloid is formed is controlled

25 to be 7-11;

(2) a manganese salt solution with a pH value of 3-7 is formulated, and the manganese salt solution and urea are mixed and stirred, for example stirred at room temperature for 30-60 minutes; wherein the molar ratio of urea to manganese ions is 1-5;

(3) the product obtained in step (1) and the product obtained in step (2) are mixed and

30 aged; the aging is for example carried out at room temperature to 120°C for 4-72 hours; the aged solid product is mixed with a boron oxide source or the aged solid product is washed and then mixed with a boron oxide source, optionally the mixture is reacted; wherein the weight ratio of the fed boron oxide source as B₂O₃ to the high specific heat capacity matrix material on the dry basis is (0.005-0.1):1;

35 (4) the solid precipitate (or the solid product) obtained in step (3) is directly dried, calcined or the solid precipitate obtained in step (3) is washed, dried, and calcined; for the washing, the solid product obtained in step (3) can be washed with water, for example, can be flushed with water until the water after washing is neutral.

According to the third embodiment of the catalytic cracking catalyst provided by the

40 present invention, the matrix material prepared and obtained with the preparation method of the high specific heat capacity matrix material, compared with the high specific heat

capacity matrix material within the scope of the present invention obtained by other methods, not only has a higher specific heat capacity, but also can have a higher average pore diameter, a higher specific surface area, and a higher pore volume. When it is used for the catalytic cracking of heavy oils with high metal content, especially high iron content, a higher liquid product yield and lower dry gas and coke yields can be achieved. Compared with the catalyst using the high specific heat capacity matrix material without boron oxide, a higher heavy oil conversion activity and a higher gasoline yield can be achieved.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, the selection range of the alkali solution in step (1) is relatively wide, preferably, in step (1), the alkali solution is an alkaline aqueous solution containing at least one of HCO_3^- , CO_3^{2-} and OH^- , the alkaline aqueous solution is preferably an aqueous solution comprising one or more of ammonium bicarbonate, ammonium carbonate, sodium hydroxide, and potassium hydroxide, or is a mixed solution comprising ammonia water and one or more of ammonium bicarbonate, ammonium carbonate, sodium hydroxide and potassium hydroxide. Preferably, the total concentration of the alkali in the alkali solution is 0.1-1 mol/L. Preferably, in the alkali solution, the concentration of CO_3^{2-} is 0-0.6 mol/L, for example 0.3-0.5 mol/L; the concentration of OH^- is preferably 0-0.5 mol/L, for example 0.2-0.35 mol/L, the concentration of HCO_3^- is 0-1.0 mol/L, for example, 0.4-1.0 mol/L. When ammonia water is used, it is assumed that ammonia water is totally ionized, and the required addition amount of ammonia water is calculated according to the calculation amount of hydroxyl groups. The pH value of the colloid at which a colloid is formed is preferably 9-11 or 10-11.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, the selection range of the type of the aluminium source is relatively wide, and any water-soluble aluminium source that can be dissolved in water can be used in the present invention, for example, the soluble aluminium salt may be one or more of aluminium nitrate, aluminium sulfate, aluminium phosphate, aluminium chloride and the like, preferably one or more of aluminium nitrate, aluminium sulfate, aluminium chloride and the like.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, the manganese salt solution in step (2) may be an aqueous solution of a water-soluble manganese salt, and/or a salt solution formed after contacting a water-soluble manganese salt, manganese oxide, and/or manganese hydroxide with an acid; the pH value of the manganese salt solution is 3-7, preferably 5-7. Preferably, in step (2), the manganese salt solution and urea are mixed, and then the resulting mixture is stirred at room temperature for 40-60 minutes, wherein the molar ratio of urea to manganese ions is 2-4. The manganese salt solution in step (2) may be an aqueous

solution of a water-soluble manganese salt, and/or a salt solution formed after contacting manganese oxide, manganese hydroxide, and/or a water-soluble manganese salt with an acid. The selection range of the kind of the manganese salt is relatively wide, and any water-soluble manganese salt that can be dissolved in water can be used in the present invention, and the water-soluble manganese salt is for example one or more of manganese nitrate, manganese sulfate, manganese phosphate, manganese chloride and the like. The manganese salt solution can also be prepared by contacting water-soluble manganese salt and/or manganese oxide and/or manganese hydroxide with an acid, wherein the manganese oxide is for example one or more of manganese monoxide, trimanganese tetraoxide, dimanganese trioxide, and manganese dioxide, and the acid is for example one or more of hydrochloric acid, sulfuric acid, phosphoric acid, and nitric acid, preferably one or more of hydrochloric acid, sulfuric acid, and nitric acid.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, in step (3), the selection range of the aging condition is relatively wide (for example, the aging temperature is from room temperature to 120°C, the aging time is 4-72 hours), preferably in step (3), the aging condition includes: the aging temperature is 60-100°C, the aging is carried out under stirring, and the aging time is 12-36 hours. The stirring method is an existing method, for example, the stirring rate is 50-300 rpm. The aged product is filtered or filtered and then washed to obtain an aged solid product. In an embodiment, for the washing, according to the weight ratio of the aged solid product (dry basis):H₂O=1:(5-30), the aged solid product (also called precipitate) obtained by aging is contacted with water at room temperature for 1-3 times, and each contact is carried out for 0.5-1 hour, until the washing solution obtained after washing is neutral, usually the pH is 6.5-7.5.

According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, the aged solid product is contacted with a boron source, and there are several contact methods. A filter cake obtained by filtering the aged product, namely an aged solid product can be directly mixed with the boron source or an aged solid product obtained after washing a filter cake obtained by filtering is mixed with the boron source; preferably, the formed mixture is further reacted for a period of time, for example, stirred or stood alone at room temperature to 90°C for 0.2-5 hours. In an embodiment, the aged solid product is vigorously mixed and stirred with water to form a slurry, wherein the weight ratio of the aged solid product (on the dry basis):H₂O is 1:(5-20), and then the boron source is added to the above-mentioned slurry, the mixture is stood or stirred at room temperature to 90°C for 0.2-5 hours, preferably 0.5-3 hours, and filtered to obtain a solid precipitate. It is also possible to mix the aged solid product or the washed aged solid product with the boron source in proportion and grind the resulting mixture uniformly to obtain a solid precipitate.

According to the third embodiment of the catalytic cracking catalyst provided by the

present invention, in the preparation method of the high specific heat capacity matrix material, the boron oxide source is preferably a substance that can produce boron oxide after calcining, for example, one or more of ammonium borate, ammonium baborate, and boric acid.

- 5 According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, in step (3) the weight ratio of the product obtained in step (1) as Al_2O_3 : the product obtained in step (2) as MnO_2 : the boron source as B_2O_3 is (5-94.5) Al_2O_3 :(5-94.5) MnO_2 :(0.5-10) B_2O_3 , for example
- 10 (20-80) Al_2O_3 :(15-75) MnO_2 :(1-8) B_2O_3 . Preferably, in the resulting high specific heat capacity matrix material, the high specific heat capacity matrix material contains 5-94.5 wt%, for example 15-80 wt% or 20-75 wt% or 20-62 wt% of alumina, 5-94.5 wt%, for example 15-80 wt% or 22-72 wt% or 30-72 wt% of manganese oxide as MnO_2 and 0.5-10 wt% or 0.8-8 wt% or 2-8 wt% of boron oxide as B_2O_3 .
- 15 According to the third embodiment of the catalytic cracking catalyst provided by the present invention, in the preparation method of the high specific heat capacity matrix material, in step (4), the solid precipitate obtained in step (3) is directly dried and calcined, or washed and then dried and calcined. For said washing, the solid precipitate can be washed with water, for example, it can be mixed with water and then washed, or it is
- 20 flushed with water, usually, the solid precipitate after washing is neutral, that is, the pH value of the water after contacting with water is 6.5-7.5. The methods of drying and calcining can be carried out with reference to the prior art, the selection ranges of drying and calcining are relatively wide, and the present invention has no special requirements for these. For example, the drying can be done at 100-150°C for 12-24 hours; the
- 25 calcining can be done at 550-800°C, for example 550-750°C for 4-8 hours.
- According to the catalytic cracking catalyst provided by the present invention, the cracking active component contains a Y zeolite. For the variety of the Y zeolite, various Y zeolites obtained by the ion modification or the ultra-stablization modification of NaY can be included. The ion modification includes the modification with rare earth ions,
- 30 alkaline earth metal ions, transition metal ions, phosphorus and the like. The ultra-stablization modification includes the hydrothermal ultra-stablization, the gas-phase ultra-stablization, the chemical ultra-stablization and the like. For example, it can be one or more of a rare earth-containing Y zeolite, e.g. REHY zeolite, a phosphorus and rare earth containing Y zeolite, e.g. DOSY zeolite, an ultra-stablized Y zeolite, e.g. DAS
- 35 Y zeolite, a phosphorus and rare earth containing ultra-stablized Y zeolite, and the like. In addition, in addition to the Y zeolite, optionally, the cracking active component further contains a second molecular sieve, and the second molecular sieve is for example one or more of other faujasites, beta zeolite, MFI-structured molecular sieve (e.g. ZRP-1 molecular sieve) and mordenite. Based on the total weight of the cracking active
- 40 component, the content of the Y zeolite can be 75 wt% or more, preferably 90 wt% or more, more preferably 95wt% or more; the content of the second molecular sieve (the

total content of other faujasites, beta zeolite, MFI-structured molecular sieve and mordenite) may be 25wt% or less, preferably 10wt% or less, more preferably 5wt% or less.

According to the catalytic cracking catalyst provided by the present invention, the clay
5 can be various existing clays that can be used in catalytic cracking catalysts, and for example can be one or more of kaolin, giagerite, montmorillonite, diatomite, halloysite, saponite, rectorite, sepiolite, attapulgite, hydrotalcite and bentonite.

According to the catalytic cracking catalyst provided by the present invention, the binder
10 can be various existing binders that can be used in catalytic cracking catalysts, and for example can be one or more of silica sol, aluminium sol and pseudo-boehmite.

In addition, the catalytic cracking catalyst may also contain additional rare earths. The additional rare earth may be formed by additionally adding rare earth chloride during the preparation of the catalytic cracking catalyst. In the catalytic cracking catalyst, the additional rare earth usually exists in the form of rare earth oxide (RE_2O_3). Based on the
15 dry basis weight of the catalytic cracking catalyst, the content of the additional rare earth as rare earth oxide may be 0-3 wt%, preferably 0.5-2 wt%. The rare earth elements in the additional rare earth refer to various conventional rare earth elements involved in the field of catalytic cracking catalysts, such as lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, and the like.

The method for preparing the catalytic cracking catalyst provided by the present invention
20 comprises a cracking active component, a high specific heat capacity matrix material, a clay and a binder are vigorously mixed and stirred with water, and then the resulting mixture is successively spray-dried, washed, filtered and dried. In addition, when the catalytic cracking catalyst also contains an additional rare earth, the preparation method
25 of the catalytic cracking catalyst provided by the present invention also comprises a cracking active component, a high specific heat capacity matrix material, a clay and a binder, together with the rare earth chloride, are vigorously mixed and stirred with water, and then the resulting mixture is successively spray-dried, washed, filtered and dried.

According to the method for preparing the catalytic cracking catalyst provided by the
30 present invention, the implementation methods of the operations, such as the cracking active component, the high specific heat capacity matrix material, the clay and the binder, and the optional rare earth chloride being vigorously mixed and stirred with water, and the subsequent spray-drying, washing and filtering and drying, can be implemented by conventional methods, and their specific implementation methods are described in detail
35 in CN1916166A, CN1098130A, CN1362472A, CN1727442A, CN1132898C and CN1727445A, all of which are incorporated herein by reference. In addition, generally, after the spray-drying and before washing, the preparation method of the catalytic cracking catalyst usually further includes a step of calcining the spray-dried product. The calcining conditions generally include that the calcining temperature can be 500-700°C,
40 and the calcining time can be 1-4 hours.

In addition, the present invention also provides the application of the above catalytic

cracking catalyst in the heavy oil catalytic cracking.

The application method of the catalytic cracking catalyst in the heavy oil catalytic cracking provided by the present invention comprises a step of contacting the catalytic cracking catalyst with heavy oil to react, and the heavy oil is for example one or more of vacuum residue, vacuum gas oil, atmospheric residue, atmospheric gas oil, and deasphalted oil. The reaction conditions of the reaction by contacting include: the reaction temperature is 480-530°C, the catalyst-oil ratio (the weight ratio) is 3-10, and the reaction time is 0.1-5 seconds.

In an embodiment of the present invention, the heavy oil satisfies one or more or all of the following conditions: (a) specific gravity (20°C) of 0.82-0.95, preferably greater than 0.91 and not greater than 0.95; (b) carbon content of 85wt%-89wt%; (c) hydrogen content of 10wt%-13wt%; (d) sulfur content of 0.1%-4wt%; (e) solidification temperature from -10 to 40°C.

Specifically, the present invention provides the following technical solutions:

1. A high specific heat capacity matrix material, containing at least 5 wt% of manganese oxide, the high specific heat capacity matrix material has a specific heat capacity of 1.3-2.0 J/(g•K) at the temperature of 1000K.
2. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein the high specific heat capacity matrix material contains 5-95 wt%, for example 19.6-74.8 wt% of alumina as Al_2O_3 , 5-95 wt%, for example 15.3-71.8 wt% of manganese oxide as MnO_2 , and on the dry basis 0-40 wt%, 0-25.2 wt% of a boron compound; for example the high specific heat capacity matrix material contains 19.6-74.8 wt% of alumina as Al_2O_3 , 15.3-71.8 wt% of manganese oxide as MnO_2 , and on the dry basis 0-25.2 wt% of a boron compound.
3. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein in the high specific heat capacity matrix material, the boron compound is boron nitride and/or boron oxide.
4. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein the high specific heat capacity matrix material has a specific surface area of 150-500 m^2/g , for example 200-400 m^2/g , e.g. 221-365 m^2/g .
5. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein the high specific heat capacity matrix material has a pore volume of 0.3-1.5 cm^3/g , for example 0.35-1.2 cm^3/g , e.g. 0.38-1.17 cm^3/g .
6. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein the high specific heat capacity matrix material has an average pore diameter of 3-20 nm, for example 5-15 nm, e.g. 6.4-13.6 nm.
7. The high specific heat capacity matrix material according to any of precedent technical solutions, wherein in the XRD spectrum of the high specific heat capacity matrix material, the ratio of the intensity of the peak at 2θ angle of $18\pm 0.5^\circ$ to the intensity of the peak at 2θ angle of $37\pm 0.5^\circ$ is 1:(3-10).
8. The preparation method of the high specific heat capacity matrix material according to

any of the precedent technical solutions 1-7, comprises the steps:

- (1) mixing an aluminium source and an alkali to form a colloid to obtain an aluminium-containing colloid, the pH value of the obtained aluminium-containing colloid is 7-11;
- 5 (2) mixing a manganese salt solution with a pH value of 3-7 and urea to obtain a manganese source solution;
- 3) forming a mixture of the aluminium-containing colloid, the manganese source solution, and optionally the boron compound; and optionally
- (4) washing and/or drying and/or calcining.
- 10 9. The preparation method according to technical solution 8, wherein the mixing of the aluminium source and the alkali to form a colloid includes: mixing a solution of the aluminium source and a solution of the alkali to form a colloid with a temperature ranging from room temperature to 85°C and a pH value of 7-11.
10. The preparation method according to any of technical solution 8 to the previous
- 15 technical solution, wherein the concentration of alumina in the solution of the aluminium source is 150-350g Al₂O₃/L, the concentration of the alkali in the solution of the alkali is 0.1-1 mol/L.
11. The preparation method according to any of technical solution 8 to the previous technical solution, wherein the aluminium source is selected from aluminium nitrate,
- 20 aluminium sulfate, aluminium phosphate, aluminium chloride and a mixture thereof; the alkali is selected from a water-soluble carbonate, a water-soluble bicarbonate, a water-soluble hydroxide, and a mixture thereof.
12. The preparation method according to any of technical solution 8 to the previous technical solution, wherein the solution of the alkali is an alkaline aqueous solution
- 25 containing one or more of CO₃²⁻, HCO₃⁻ and OH⁻, in the solution of the alkali, the concentration of CO₃²⁻ is 0-0.6 mol/L, the concentration of OH⁻ is 0-0.5 mol/L, the concentration of HCO₃⁻ is 0-1 mol/L, provided that the sum of the concentration of CO₃²⁻, the concentration of OH⁻, and the concentration of HCO₃⁻ is not zero, wherein the concentration of CO₃²⁻, the concentration of OH⁻, and the concentration of HCO₃⁻ are
- 30 obtained by dividing the molar amount (mol) of the anionic group in the alkali used to form the alkaline aqueous solution by the volume (L) of the alkaline aqueous solution.
13. The preparation method according to any of technical solution 8 to the previous technical solution, wherein in step (2), the molar ratio of urea to manganese ions is 1-5, for example 2-4, the concentration of the manganese salt as MnO₂ in the manganese salt
- 35 solution can be 50-500 g/L.
14. The preparation method according to any of technical solution 8 to the previous technical solution, wherein in step (2), urea is added to the manganese salt solution, and then the resulting mixture is stirred at room temperature for 30-60 minutes to obtain a manganese source solution.
- 40 15. The preparation method according to any of technical solution 8 to the previous technical solution, wherein the boron compound is boron nitride and/or boron oxide

and/or a boron oxide precursor.

16. The preparation method according to technical solution 15, wherein the boron nitride is one or more of hexagonal boron nitride, cubic boron nitride, rhombohedral boron nitride and wurtzite boron nitride; the boron oxide precursor is one or more of ammonium borate, ammonium diborate and boric acid.
17. The preparation method according to any of technical solution 8 to the previous technical solution, wherein in step (3), after mixing the aluminium-containing colloid and the manganese source solution, an aging process is also included; the aging temperature is from room temperature to 120°C, the aging time is 4-72 hours, and the aging is carried out under stirring or under standing alone; preferably, the aging is carried out under stirring, the aging temperature is 60-100°C, and the aging time is 12-36 hours.
18. The preparation method according to any of technical solution 8 to the previous technical solution, wherein the boron compound is boron nitride; the process of forming a mixture of the aluminium-containing colloid, the manganese source solution, and the boron compound in step (3) is as follows: mixing the aluminium-containing colloid, the manganese source solution, and the boron compound, and aging.
19. The preparation method according to any of technical solution 8 to the previous technical solution, wherein the boron compound is boron oxide and/or a precursor of boron oxide; the process of forming a mixture of the aluminium-containing colloid, the manganese source solution, and the boron compound in step (3) is as follows: mixing the aluminium-containing colloid and the manganese source solution, aging, optionally washing, and then mixing with the boron compound.
20. The preparation method according to any of technical solution 8 to the previous technical solution, wherein in step (4), the calcining temperature is 500°C-900°C, and the calcining time is 4-8 hours.
21. A catalytic cracking catalyst, wherein the catalytic cracking catalyst contains a cracking active component comprising a Y zeolite, a high specific heat capacity matrix material according to any of the aforementioned technical solutions 1-7 or a high specific heat capacity matrix material obtained through the preparation method according to any of the aforementioned technical solutions 8-20, a clay and a binder.
22. The catalytic cracking catalyst according to the aforementioned technical solution 21, wherein based on the total weight of the catalytic cracking catalyst, the catalytic cracking catalyst contains 1-60 wt% of the cracking active component, 1-50 wt% of the high specific heat capacity matrix material, 1-70 wt% of the clay and 1-70 wt% of the binder, or, based on the total weight of the catalytic cracking catalyst, the catalytic cracking catalyst contains 10-50 wt% of the cracking active component, 5-40 wt% of the high specific heat capacity matrix material, 10-60 wt% of the clay and 10-60 wt% of the binder, wherein the weight of the catalytic cracking catalyst is 100 wt%.
23. The catalytic cracking catalyst according to any of technical solution 21 to the previous technical solution, wherein the cracking active component contains a Y zeolite.
24. The catalytic cracking catalyst according to any of technical solution 21 to the

previous technical solution, wherein the cracking active component further contains a second molecular sieve, and the second molecular sieve is one or more of faujasite, beta zeolite, MFI-structured molecular sieve and mordenite.

25. The catalytic cracking catalyst according to any of technical solution 21 to the previous technical solution, wherein based on the total weight of the cracking active components, the content of the Y zeolite is 75 wt% or more, and the content of the second molecular sieve is 25 wt% or less.

26. A method for preparing the catalytic cracking catalyst according to any of technical solutions 1-25, wherein the method comprises a cracking active component, a high specific heat capacity matrix material, a clay and a binder are mixed and stirred with water, and then the resulting mixture is successively spray-dried, calcined, washed, filtered and dried.

27. Use of the catalytic cracking catalyst according to any of technical solutions 21-25 in the heavy oil catalytic cracking.

15 The present invention will be described in detail below through examples.

The raw materials used in the following preparation examples, comparative preparation examples, examples and comparative examples are as follows:

Hydrochloric acid was produced by Beijing Chemical Plant, chemically pure, and its concentration was 36 wt%;

20 Sodium water glass (sodium silicate) was commercially available with a SiO₂ concentration of 26.0 wt% and a modulus of 3.2;

Kaolin was a product of Suzhou Kaolin Company, and its solid content was 74.0 wt%;

Pseudo-boehmite was an industrial product of Shandong Aluminium Factory, with a solid content of 62.0 wt%;

25 The aluminium sol was a product of Sinopec Catalyst Qilu Branch, and the Al₂O₃ content was 21.5 wt%;

DASY zeolite (the solid content was 92.0 wt%, the RE₂O₃ content was 1.8 wt%, the Na₂O content was 1.0 wt%, the crystallinity was 60%), ZRP -1 zeolite (the solid content was 97.8 wt%, the Na₂O content was 1.1 wt%, the crystallinity was 70%), REHY zeolite (the solid content was 88.0 wt%, the RE₂O₃ content was 5.0 wt%, the Na₂O content was 0.9 wt%, the crystallinity was 65%), beta molecular sieve (the solid content was 95.2 wt%, the Na₂O content was 1.2 wt%, the crystallinity was 60%), DOSY zeolite (the solid content was 93.5 wt%, the RE₂O₃ content was 8.0 wt%, the Na₂O content was 0.8 wt%, the crystallinity was 80%), HSY zeolite (the solid content was 91.5 wt%, the RE₂O₃ content was 10.5 wt%, the Na₂O content was 0.9 wt%, the crystallinity was 85%) were all produced by Sinopec Catalyst Qilu Branch;

Rare earth chloride was purchased from Baotou Steel Rare Earth High Technology Co., Ltd., and the rare earth elements were La and Ce.

40 The present invention will be further described below in conjunction with specific examples, but the present invention is not limited thereby.

In the present invention, the catalyst-oil ratio refers to the mass ratio of the catalyst to the

feedstock oil.

In the present invention, unless otherwise specified, ppm is the ppm by weight.

The used BN is the hexagonal boron nitride.

In each of examples and comparative examples, the contents of Al_2O_3 , MnO_2 , B, N, and Fe in the sample are determined by X-ray fluorescence method (see "Petrochemical Analysis Method (RIPP Experimental Method)", edited by Yang Cuiding, etc., Science Press, published in 1990). The sample phase was determined by the X-ray diffraction method. The specific surface area, the pore volume and the average pore diameter of the sample were measured by the low-temperature nitrogen adsorption-desorption method, and the pore diameter distribution was obtained by the calculation with the BJH method.

Preparation Example 1

The preparation method of the high specific heat capacity matrix material provided by the present invention was illustrated in this preparation example.

An $\text{Al}_2(\text{SO}_4)_3$ solution with a concentration of 300g $\text{Al}_2\text{O}_3/\text{L}$ and an ammonium carbonate solution with a CO_3^{2-} concentration of 0.10 mol/L were mixed at 20°C to form a colloid. The resulting colloid had a pH value of 7.5, and slurry A was obtained. Hydrochloric acid was added to a MnCl_2 solution with a concentration of 450g MnO_2/L , the pH value was controlled to 3.5, then urea was added to the resulting solution, the molar ratio of urea to manganese ions was 2, and the mixture was stirred at room temperature for 30 minutes to obtain solution B. Solution B was added to slurry A. The mixture was stirred and aged at 80°C for 4 hours. When the temperature of the system was dropped to room temperature, the mixture was flushed with deionized water until the water after washing was neutral. The mixture was dried at 120°C for 12 hours to obtain a matrix material precursor. Then the precursor was calcined at 550°C for 6 hours, and cooled to room temperature in the furnace to obtain a high specific heat capacity matrix material provided by the present invention, which was denoted as AM-1. The proportioning ratio, the preparation condition parameters, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of AM-1 are listed in Table 1.

The X-ray diffraction spectrum of AM-1 was shown in Figure 1, where there were characteristic peaks at 2θ angle of $18\pm 0.5^\circ$ and 2θ angle of $37\pm 0.5^\circ$, and the intensity ratio of the two (I_1/I_2) was 1:5.2. Its elemental analysis chemical composition formula (by weight) was $60.5\text{MnO}_2\cdot 39.5\text{Al}_2\text{O}_3$; the specific heat capacity was 1.36 J/(g•K), the specific surface area was 238 m^2/g , the pore volume was 0.38 cm^3/g , and the average pore diameter was 6.4 nm.

Preparation Examples 2-4

The preparation method of the high specific heat capacity matrix material provided by the present invention was illustrated in Preparation Examples 2-4.

The high specific heat capacity matrix materials AM-2 to AM-4 were prepared according to the method of Preparation Example 1, except for the raw material proportioning ratios, the preparation condition parameters, and the elemental composition, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of the

products listed in Table 1, wherein solution B was added to slurry A, and then boron nitride was added, and then the aging was carried out.

Preparation Example 5

The preparation method of the high specific heat capacity matrix material provided by the present invention was illustrated in Preparation Example 5.

An $\text{Al}(\text{NO}_3)_3$ solution with a concentration of 350g $\text{Al}_2\text{O}_3/\text{L}$ and a solution with a CO_3^{2-} concentration of 0.1mol/L (ammonium carbonate) and an OH^- concentration of 0.1mol/L (ammonia water) were mixed at 25°C to form a colloid. The pH value was controlled to 10.5, and slurry A was obtained. Mn_3O_4 , hydrochloric acid and water were mixed to obtain a manganese chloride solution with a concentration of 116.5g MnO_2/L , the pH value was controlled to 6, then urea was added to the solution, wherein the molar ratio of urea to manganese ions was 3, the mixture was stirred at room temperature for 40 minutes to obtain solution B. Solution B and 145.6g BN (having a solid content of 80 wt%) was added to slurry A. The mixture was stirred and aged at 60°C for 24 hours. When the temperature of the system was dropped to room temperature, the mixture was flushed with deionized water until the water after washing was neutral. The mixture was dried at 120°C for 12 hours to obtain a matrix material precursor. Then the precursor was calcined at 650°C for 4 hours, and cooled to room temperature in the furnace to obtain a high specific heat capacity matrix material provided by the present invention, which was denoted as AM-5. The proportioning ratio, the preparation condition parameters, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of AM-5 are listed in Table 1.

The X-ray diffraction spectrum of AM-5 was identical to that in Figure 1, where there were characteristic peaks at 2θ angle of $18 \pm 0.5^\circ$ and 2θ angle of $37 \pm 0.5^\circ$, and the intensity ratio of the two was 1:6.6. The chemical composition formula (by weight) of AM-5 was $20.6\text{MnO}_2 \cdot 59.4\text{Al}_2\text{O}_3 \cdot 19.4\text{BN}$; the specific heat capacity was 1.48 J/(g·K), the specific surface area was 243m²/g, the pore volume was 0.46cm³/g, and the average pore diameter was 7.6nm.

Preparation Example 6

The preparation method of the high specific heat capacity matrix material provided by the present invention was illustrated in Preparation Example 6.

The matrix material AM-6 was prepared according to the method for Preparation Example 5, except for the raw material proportioning ratios, the preparation condition parameters, and the elemental composition, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of the product listed in Table 1, wherein in the alkali solution for forming the colloid, the CO_3^{2-} concentration was 0.2mol/L, and the OH^- concentration was 0.15mol/L.

The X-ray diffraction spectra of AM-2 to AM-6 were similar to that shown in Figure 1, and there were peaks at 2θ angle of $18 \pm 0.5^\circ$ and at 2θ angle of $37 \pm 0.5^\circ$.

Comparative Preparation Example 1

An $\text{Al}(\text{NO}_3)_3$ solution with a concentration of 350g $\text{Al}_2\text{O}_3/\text{L}$ and a manganese nitrate

solution with a concentration of 525g MnO₂/L were respectively formulated with deionized water, and mixed uniformly to obtain solution A. Ammonium bicarbonate solution was formulated, and the pH was controlled to 10.0. It was denoted as solution B. Solution A and solution B were mixed under continuous stirring to obtain a mother liquor C, and the pH of the mother liquor C was controlled to 8-9 by controlling the addition amount of solution B during the mixing process. After the completion of mixing, the mixture was aged at 180°C for 20 hours. When the temperature of the system was dropped to room temperature, the mixture was flushed with deionized water until neutral. The mixture was dried at 120°C for 12 hours to obtain a Mn-Al matrix precursor. Then the precursor was calcined at 1000°C for 4 hours, and cooled to room temperature in the furnace to obtain a comparative matrix material, which was denoted as DAM-1. According to the X-ray diffraction spectrum of DAM-1, there were characteristic peaks at 2θ angle of 18±0.5° and at 2θ angle of 37±0.5°, and the intensity ratio of the two was 1:1.9. The elemental analysis chemical composition formula (by weight) of DAM-1 was 60.6MnO₂•39.4Al₂O₃; the specific heat capacity was 0.62 J/(g•K), the specific surface area was 224 m²/g, the pore volume was 0.31 cm³/g, and the average pore diameter was 5.5 nm.

Comparative Preparation Example 2

An Al₂(SO₄)₃ solution with the concentration of 350g Al₂O₃/L was mixed with ammonium carbonate to form a colloid, and the pH was controlled to 10.0 to obtain slurry A. A MnSO₄ solution with the concentration of 209.7g MnO₂/L was added to slurry A and stirred at room temperature for 30 minutes to obtain slurry B. 95.4g of boron nitride (solid content: 80 wt%) was added into slurry B. The mixture was aged at 80°C for 24 hours. When the temperature of the system was dropped to room temperature, the mixture was flushed with deionized water until neutral. The mixture was dried at 120°C for 12 hours to obtain a Mn-Al matrix precursor. Then the precursor was calcined at 990°C for 6 hours, and cooled to room temperature in the furnace to obtain a sample of comparative matrix material, which was denoted as DAM-2.

The elemental analysis chemical composition formula (by weight) of DAM-2 was 33.3MnO₂•54.7Al₂O₃•11.7BN; the specific heat capacity was 0.85 J/(g•K), the specific surface area was 19m²/g, the pore volume was 0.25cm³/g, and the average pore diameter was 4.6nm.

Table 1

	Preparation Example 1	Preparation Example 2	Preparation Example 3	Preparation Example 4	Preparation Example 5	Preparation Example 6
Slurry A						
Aluminium source type	Aluminium sulfate	Aluminium sulfate	Aluminium nitrate	Aluminium nitrate	Aluminium nitrate	Aluminium sulfate
Concentration of aluminium source solution (as Al_2O_3)/ $\text{g}\cdot\text{L}^{-1}$	300	350	350	150	350	350
Alkali type	Ammonium carbonate	Ammonium carbonate	Ammonium bicarbonate	Ammonium bicarbonate	Ammonium carbonate+ Ammonia water	Ammonium carbonate+ Ammonia water
Concentration of alkali solution (as anion)/ $\text{mol}\cdot\text{L}^{-1}$	0.10	0.50	0.40	0.95	0.20	0.35
pH value at which colloid formed	7.5	11	8.5	10.5	10.5	11
Temperature at which colloid formed/ $^{\circ}\text{C}$	20	25	65	40	75	30
Solution B						
Manganese source type	Manganese chloride	Manganese sulfate	Manganous nitrate	Manganese chloride	Mn_3O_4	MnO_2
Concentration of manganese salt solution(as MnO_2)/ $\text{g}\cdot\text{L}^{-1}$	450	400	455	487.5	116.5	70
Acid type	Hydrochloric acid				Hydrochloric acid	Sulphuric acid

	Preparation Example 1	Preparation Example 2	Preparation Example 3	Preparation Example 4	Preparation Example 5	Preparation Example 6
pH of manganese salt solution	3.5	7	7	7	6	5
Urea:Mn (molar ratio)	2	3	2.5	4	3	3.5
BN (dry basis)/g	0	250	70	112.5	116.5	46.7
Aging conditions	80°C/4 hrs	80°C/24 hrs	60°C/30 hrs	60°C/60 hrs	60°C/24 hrs	80°C/24 hrs
Calcining conditions	550°C/6 hrs	600°C/6 hrs	750°C/4 hrs	700°C/4 hrs	650°C/4 hrs	600°C/6 hrs
High specific heat capacity matrix material						
MnO ₂ /wt%	60.5	39.5	52.9	65.4	20.6	15.3
Al ₂ O ₃ /wt%	39.5	35.3	39.1	19.6	59.4	73.9
BN/wt%	0	25.2	8.0	14.6	19.4	10.8
I ₁ /I ₂	1:5.2	1:10	1:8.5	1:3.5	1:6.6	1:7.2
Specific heat capacity/J•g ⁻¹ •K ⁻¹	1.36	1.95	1.62	1.39	1.48	1.44
Specific surface/ m ² /g	238	250	235	221	243	239
Pore volume/cm ³ /g	0.38	0.42	0.63	0.54	0.46	0.52
Average pore diameter/nm	6.4	6.7	10.7	9.8	7.6	8.7

Note: In Table 1 and Table 4, I₁/I₂ is the ratio of the intensity of the peak at 2θ angle of 18±0.5° to the intensity of the peak at 2θ angle of 37±0.5°.

Example 1

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

20 parts by weight (on the dry basis) of pseudo-boehmite and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 15 wt%). Hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio (the weight ratio of 36 wt% hydrochloric acid to pseudo-boehmite as alumina) was 0.20:1. Then the system was warmed up to 65°C and acidified for 1 hour. Then a slurry (the solid content was 25 wt%) of 28 parts by weight (on the dry basis) of kaolin, 13 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 18 wt%) of 10 parts by weight (on the dry basis) of high specific heat capacity matrix material AM-1 prepared in Preparation Example 1 were added respectively. The mixture was stirred for 20 minutes, then further added thereto a slurry (the solid content was 35 wt%) of 29 parts by weight (on the dry basis) of the DASY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C1, wherein based on the total weight of the catalytic cracking catalyst C1, the catalytic cracking catalyst C1 contained 10 wt% of the high specific heat capacity matrix material, 29 wt% of DASY zeolite, 28 wt% of kaolin, 33 wt% of Al₂O₃ binder.

Comparative Example 1

This comparative example was used to illustrate the comparative catalytic cracking catalyst and its preparation method.

The catalytic cracking catalyst was prepared according to the method of Example 1, except that the high specific heat capacity matrix material AM-1 prepared in Preparation Example 1 was replaced by the matrix material DAM-1 prepared in Comparative Preparation Example 1 in the same weight part to produce a comparative catalytic cracking catalyst CB1, wherein based on the total weight of the comparative catalytic cracking catalyst CB1, the comparative catalytic cracking catalyst CB1 contained 10 wt% of the comparative matrix material, 29 wt% of DASY zeolite, 28 wt% of kaolin, 33 wt% of Al₂O₃ binder.

Comparative Example 2

This comparative example was used to illustrate the comparative catalytic cracking catalyst and its preparation method.

The catalytic cracking catalyst was prepared according to the method of Example 1, except that the high specific heat capacity matrix material AM-1 prepared in Preparation Example 1 was replaced by the matrix material DAM-2 prepared in Comparative Preparation Example 2 in the same weight part to produce a comparative catalytic cracking catalyst CB2, wherein based on the total weight of the comparative catalytic

cracking catalyst CB2, the comparative catalytic cracking catalyst CB2 contained 10 wt% of the comparative matrix material, 29 wt% of DASY zeolite, 28 wt% of kaolin, 33 wt% of Al₂O₃ binder.

Comparative Example 3 This comparative example was used to illustrate the comparative catalytic cracking catalyst and its preparation method.

The catalytic cracking catalyst was prepared according to the method of Example 1, except that no high specific heat capacity matrix material was added, but the high specific heat capacity matrix material AM-1 was replaced by kaolin in the same weight (dry basis) to produce a comparative catalytic cracking catalyst CB3, wherein based on the total weight of the comparative catalytic cracking catalyst CB3, the comparative catalytic cracking catalyst CB3 contained 29 wt% of DASY zeolite, 38 wt% of kaolin, 33 wt% of Al₂O₃ binder.

Example 2

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

20 parts by weight (on the dry basis) of kaolin and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 40 wt%), and then 20 parts by weight (on the dry basis) of pseudo-boehmite was added, and hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio (by weight) was 0.20:1. Then the system was warmed up to 65°C and acidified for 1 hour. Then 5 parts by weight (on the dry basis) of an aluminium sol, and a slurry of (the solid content was 20 wt%) 30 parts by weight (on the dry basis) of the high specific heat capacity matrix material AM-2 prepared in Preparation Example 2 were added respectively. The mixture was stirred for 20 minutes, then further added thereto a mixed slurry (the solid content was 35 wt%) of 20 parts by weight (on the dry basis) of DASY zeolite and 5 parts by weight (on the dry basis) of ZRP-1 zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C2, wherein based on the total weight of the catalytic cracking catalyst C2, the catalytic cracking catalyst C2 contained 30 wt% of high specific heat capacity matrix material, 20 wt% of DASY zeolite, 5 wt% of ZRP -1 zeolite, 20 wt% of kaolin, 25 wt% of Al₂O₃ binder.

Example 3

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

28 parts by weight (on the dry basis) kaolin and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 40 wt%), and then 25 parts by weight (on the dry basis) of pseudo-boehmite was added, and hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio

(weight ratio) was 0.20 : 1. Then the system was warmed up to 65°C and acidified for 1 hour. Then a slurry (the solid content was 25 wt%) of 20 parts by weight (on the dry basis) of the high specific heat capacity matrix material AM-3 prepared in Preparation Example 3 and 5 parts by weight (on the dry basis) of an aluminium sol were added respectively.

- 5 The mixture was stirred for 20 minutes, then further added thereto a mixed slurry (the solid content was 35 wt%) of 15 parts by weight (on the dry basis) of the REHY zeolite and 5 parts by weight (on the dry basis) of the beta molecular sieve, and 2 parts by weight (as rare earth oxide) of a rare earth chloride solution. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was
- 10 calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C3, wherein based on the total weight of the catalytic cracking catalyst C3, the catalytic cracking catalyst C3 contained 20 wt% of the high
- 15 specific heat capacity matrix material, 15 wt% of REHY zeolite, 5 wt% of beta zeolite, 28 wt% of kaolin, 30 wt% of Al₂O₃ binder, 2 wt% of rare earth oxide.

Example 4

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

- 20 40 parts by weight (on the dry basis) of kaolin and 15 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 20 wt%) of 15 parts by weight (on the dry basis) of the high specific heat capacity matrix material AM- 4 prepared in Preparation Example 4 were vigorously mixed and stirred with water. The mixture was stirred for 120 minute, then further added thereto a slurry (the solid content was 35 wt%)
- 25 of 30 parts by weight (on the dry basis) of the DOSY zeolite. The system was continuously stirred, spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and
- 30 filtered, then dried at 110°C to produce a catalytic cracking catalyst C4, wherein based on the total weight of the catalytic cracking catalyst C4, the catalytic cracking catalyst C4 contained 15 wt% of high specific heat capacity matrix material, 30 wt% of DOSY zeolite, 40 wt% of kaolin, 15 wt% of Al₂O₃ binder.

Example 5

- 35 This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

(1) Preparation of silica sol:

- 1.7L of hydrochloric acid was diluted with 8.0 kg of decationized water, 7.7kg of sodium water glass was diluted with 8.0kg of decationized water, and the diluted sodium water
- 40 glass was slowly added into the diluted hydrochloric acid solution under stirring to obtain a silica sol having a SiO₂ concentration of 7.8 wt% and a pH value of 2.8.

(2) Preparation of catalytic cracking catalyst:

10 parts by weight (on the dry basis) of kaolin was added to 20 parts by weight (on the dry basis) of the above silica sol. The mixture was stirred for 1 hour and then added a slurry (the solid content was 18 wt%) of 40 parts by weight (on the dry basis) of high specific heat capacity matrix material AM-5 prepared in Preparation Example 5. The resulting mixture was vigorously mixed and stirred with water, and then further added thereto a slurry (the solid content was 30 wt%) of 30 parts by weight (on the dry basis) of the DASY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C5, wherein based on the total weight of the catalytic cracking catalyst C5, the catalytic cracking catalyst C5 contained 40 wt% of high specific heat capacity matrix material, 30 wt% of DASY zeolite, 10 wt% of kaolin, 20 wt% of SiO₂ binder.

Example 6

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

40 parts by weight (on the dry basis) of kaolin and 15 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 20 wt%) of 15 parts by weight (on the dry basis) of high specific heat capacity matrix material AM- 6 prepared in Preparation Example 6 were vigorously mixed and stirred with water. The mixture was stirred for 120 minute, then further added thereto a slurry (the solid content was 35 wt%) of 30 parts by weight (on the dry basis) of the HSY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C6, wherein based on the total weight of the catalytic cracking catalyst C6, the catalytic cracking catalyst C6 contained 15 wt% of high specific heat capacity matrix material, 30 wt% of HSY zeolite, 40 wt% of kaolin, 15 wt% of Al₂O₃ binder.

Examples 7-12

Examples 7-12 were used to illustrate the performance test of the catalytic cracking catalyst provided by the present invention.

The catalytic cracking catalysts C1-C6 prepared above were respectively contaminated by the impregnation with 5000ppm of iron, 5000ppm of nickel and 5000ppm of vanadium by the Mitchell method, that is, vanadium naphthenate as vanadium source, nickel naphthenate as nickel source, and iron naphthenate as iron source, and toluene as solvent were used to prepare a metal-containing solution, the catalyst was impregnated in the metal-containing solution, then dried, and then calcined at about 600°C to remove organic

matter. The catalytic cracking catalysts were aged at 780°C under 100% steam for 6 hours. The cracking performance evaluation was conducted on a small fixed fluidized bed. The evaluation process for each sample was conducted through five reaction regeneration cycles, that is, five consecutive processes of feedstock oil reaction and regeneration were conducted without unloading the same catalyst. The results of the last reaction were taken as the evaluation result of the catalyst cracking performance. The evaluation conditions for the heavy oil microreaction were as follows: the catalyst-oil ratio was 5 (weight ratio), the sample loading capacity was 9g, the reaction temperature was 520°C, the WHSV is 8/hour, the oil feeding time was 70 seconds, the regeneration temperature was 720°C, and the feedstock oil was a vacuum gas oil. The properties of the feedstock oil were shown in Table 2. The evaluation results were listed in Table 3.

Comparative Examples 4-6

The comparative catalytic cracking catalysts CB1-CB3 prepared above were subjected to performance tests according to the same method as in Examples 7-12, and the evaluation results are listed in Table 3.

Table 2

Feedstock oil properties	
Density (20°C), g/cm ³	0.9154
Refraction (70°C)	1.4717
Freezing point, °C	37
Carbon residue, m%	4.3
SARA, m%	
<u>S</u> aturates	63.1
<u>A</u> romatics	21.2
<u>R</u> esin	14.9
<u>A</u> sphaltene	0.8
Elementary composition, m%	
C	85.95
H	12.78
S	0.62
N	0.65
Metal elements, (ppm)	
Ca	21.4
Fe	30.6
Mg	0.6
Na	1.5
Ni	7.4
V	11.8
Pb	2.1

Table 3

Example No.	7	Comp. Ex 4	Comp. Ex 5	Comp. Ex 6	8	9	10	11	12
Catalyst	C1	CB1	CB2	CB3	C2	C3	C4	C5	C6
Conversion/w%	65.19	61.87	62.03	62.47	65.83	64.71	66.78	66.23	64.66
Product yield									
Dry gas/w%	1.29	2.28	1.71	1.48	1.31	1.22	1.43	1.30	1.20
Liquefied gas/w%	12.12	9.86	10.03	10.23	12.55	12.45	12.61	12.58	12.17
Gasoline/w%	46.52	44.35	44.86	45.21	46.79	46.03	47.28	46.94	46.24
Diesel/w%	19.49	20.16	19.92	19.73	18.64	19.71	18.99	19.07	19.85
slurry oil/w%	15.32	17.97	18.05	17.80	15.53	15.58	14.23	14.70	15.49
Coke/w%	5.26	5.38	5.43	5.55	5.18	5.01	5.46	5.41	5.05
Total liquid yield/w%	78.13	74.37	74.81	75.17	77.98	78.19	78.88	78.59	78.26
Dry gas selectivity	1.98	3.69	2.76	2.36	1.99	1.89	2.14	1.96	1.86
Coke selectivity	8.07	8.70	8.75	8.88	7.87	7.74	8.18	8.17	7.81
H ₂ /CH ₄	0.11	0.2	0.17	0.16	0.13	0.11	0.14	0.12	0.1

In Table 3 and Table 5, w% is weight %, and H₂/CH₄ is based on the weight ratio.

In the present invention, conversion rate=gasoline yield+liquefied gas yield+dry gas yield+coke yield, total liquid yield (also known as total liquid product yield) = gasoline yield +diesel oil yield +liquefied gas yield, coke selectivity = coke yield / conversion rate, dry gas selectivity = dry gas yield / conversion rate.

Preparation Example B1

The preparation method of the high specific heat capacity mesoporous matrix material provided by the present invention was illustrated in this example.

An Al₂(SO₄)₃ solution with a concentration of 350g Al₂O₃/L and an ammonium carbonate solution with a CO₃²⁻ concentration of 0.10 mol/L were mixed at 30°C to form a colloid.

The pH value was controlled to 7.5, and slurry A was obtained. Urea was added to a MnCl₂ solution with a concentration of 145g MnO₂/L, wherein the molar ratio of urea to manganese ions was 2, and the mixture was stirred at room temperature for 30 minutes to obtain solution BB. Solution BB was added to slurry BA. The resulting mixture was

stirred and aged at 80°C for 24 hours. When the temperature of the system was dropped to room temperature, the solid precipitate obtained by filtering was vigorously mixed and stirred with water according to the weight ratio of the solid precipitate (dry basis):H₂O=1:10. Ammonium borate was added according to the weight ratio of B₂O₃:high specific heat capacity matrix material (dry basis)=0.01:1. Then the resulting mixture was stirred at 50°C for 2 hours, and filtered. The solid precipitate was exchanged at room temperature for 3 times according to the weight ratio of the precipitate (dry basis):H₂O=1:8. Each exchange was performed for 0.5 hours. The solid precipitate obtained after washing was neutral, and then dried at 120°C for 12 hours to obtain a matrix material precursor. Then the precursor was calcined at 550°C for 6 hours, and cooled to room temperature in the furnace to obtain a high specific heat capacity matrix material provided by the present invention, which was denoted as BAM-1. The proportioning ratio, the preparation condition parameters, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of BAM-1 are listed in Table 4.

The elemental analysis chemical composition formula (by weight) of BAM-1 was 29.7MnO₂•69.2Al₂O₃•1.1B₂O₃; the specific heat capacity was 1.3 J/(g•K), the specific surface area was 310m²/g, the pore volume was 0.65cm³/g, and the average pore diameter was 8.4nm.

Preparation Examples B2-B4

The preparation method of the high specific heat capacity mesoporous matrix material provided by the present invention was illustrated in Preparation Examples 2-4.

The high specific heat capacity mesoporous matrix materials BAM-2 to BAM-4 were prepared according to the method of Preparation Example B1, except for the raw material proportioning ratios, the preparation condition parameters, and the elemental composition, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of the product listed in Table 4.

Preparation Example B5

The preparation method of the high specific heat capacity mesoporous matrix material provided by the present invention was illustrated in Preparation Example 5.

5 An $\text{Al}(\text{NO}_3)_3$ solution with a concentration of 350g $\text{Al}_2\text{O}_3/\text{L}$ was mixed with an ammonium carbonate solution with a CO_3^{2-} concentration of 0.30 mol/L and an ammonia-water solution with a OH^- concentration of 0.1 mol/L to form a colloid. The pH value was controlled to 10.5, and slurry BA was obtained. Mn_3O_4 was mixed with hydrochloric acid and water to obtain a manganese chloride solution with a concentration of 201.7g MnO_2/L . The pH value was controlled to 6. Then urea was added to the solution, 10 wherein the molar ratio of urea to manganese ions was 3. The mixture was stirred at room temperature for 40 minutes to obtain solution BB. Solution BB was added to slurry BA. The resulting mixture was stirred and aged at 60°C for 24 hours. When the temperature of the system was dropped to room temperature, the solid precipitate obtained by filtering was vigorously mixed and stirred with water according to the weight ratio of the 15 precipitate (dry basis): H_2O =1:10. Ammonium borate was added according to the weight ratio of B_2O_3 :the obtained high specific heat capacity matrix material (dry basis)=0.01:1. Then the resulting mixture was stirred at 50°C for 2 hours, filtered, water-washed (i.e., washed with water), and then dried at 120°C for 12 hours to obtain a matrix material precursor. Then the precursor was calcined at 650°C for 4 hours, and cooled to room 20 temperature in the furnace to obtain a matrix material provided by the present invention, which was denoted as BAM-5. The proportioning ratio, the preparation condition parameters, the specific heat capacity, the specific surface area, the pore volume and the average pore diameter of BAM-5 are listed in Table 4.

The elemental analysis chemical composition formula (by weight) of BAM-5 was 25 $34.8\text{MnO}_2 \cdot 60.4\text{Al}_2\text{O}_3 \cdot 4.8\text{B}_2\text{O}_3$; the specific heat capacity was 1.43 J/(g•K), the specific surface area was 338m²/g, the pore volume was 0.94cm³/g, and the average pore diameter was 11.1nm.

Preparation Example B6

30 The preparation method of the high specific heat capacity mesoporous matrix material provided by the present invention was illustrated in Preparation Example B6.

The matrix material BAM-6 was prepared according to the method of Preparation Example B5, except for the raw material proportioning ratios, the preparation condition parameters, and the elemental composition, the specific surface area, the pore volume and the average pore diameter of the product listed in Table 4.

Table 4

Preparation Example	B1	B2	B3	B4	B5	B6
Slurry BA						
Aluminium source type	Aluminium sulfate	Aluminium sulfate	aluminium nitrate	aluminium nitrate	aluminium nitrate	Aluminium sulfate
Concentration of aluminium source solution (as Al_2O_3)/ $\text{g}\cdot\text{L}^{-1}$	350	350	350	150	350	350
Alkali type	Ammonium carbonate	Ammonium carbonate	Ammonium bicarbonate	Ammonium bicarbonate	Ammonium carbonate+Ammonia water	Ammonium carbonate+Ammonia water
Concentration of alkali solution (as anion)/ $\text{mol}\cdot\text{L}^{-1}$	0.10	0.50	0.40	0.95	0.30	0.35 ($\text{CO}_3^{2-}=0.2$, $\text{OH}^-=0.15$)
pH value at which colloid formed	7.5	11	10	10.5	10.5	11
Solution BB						
Manganese source type	Manganese chloride	Manganese sulfate	Manganous nitrate	Manganese chloride	Mn_3O_4	MnO_2
Concentration of manganese salt solution (as MnO_2)/ $\text{g}\cdot\text{L}^{-1}$	145	267.3	481.25	540	201.7	104.3
Acid type					Hydrochloric acid	Sulphuric acid
pH of manganese salt solution	7	7	7	7	6	5
Urea:Mn (molar ratio)	2	3	2.5	4	3	3.5

Preparation Example	B1	B2	B3	B4	B5	B6
Boron source type	Ammonium borate	Boric acid	Ammonium biborate	Boric acid	Ammonium borate	Boric acid
Concentration of boron source solution (as B ₂ O ₃)/g•L ⁻¹	5	19	43.75	60	27.8	13.6
Aging conditions	80°C/24 hrs	80°C/24 hrs	60°C/30 hrs	60°C/24 hrs	60°C/24 hrs	80°C/24 hrs
Calcining conditions	550°C/6 hrs	600°C/6 hrs	750°C/4 hrs	700°C/4 hrs	650°C/4 hrs	600°C/6 hrs
High specific heat capacity matrix material						
MnO ₂ /wt%	29.7	42.1	54.6	71.8	34.8	22.3
Al ₂ O ₃ /wt%	69.2	55.6	40.3	20.2	60.4	74.8
B ₂ O ₃ /wt%	1.1	2.3	5.1	8	4.8	2.9
Specific heat capacity/J•g ⁻¹ •K ⁻¹	1.3	1.45	1.51	1.92	1.43	1.32
Specific surface/ m ² /g	310	352	365	345	338	331
Pore volume/cm ³ /g	0.65	0.78	1.06	1.17	0.94	0.85
Average pore diameter/nm	8.4	8.9	11.6	13.6	11.1	10.3
I ₁ /I ₂	1:3.8	1:6.5	1:7.2	1:9.4	1:6.1	1:4.2

Example 13

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

13 parts by weight (on the dry basis) of pseudo-boehmite and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 15 wt%), and hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio (weight ratio) was 0.20 : 1. Then the system was warmed up to 65°C and acidified for 1 hour. Then a slurry (the solid content was 25 wt%) of 35 parts by weight (on the dry basis) of kaolin, 5 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 18 wt%) of 15 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-1 prepared in Preparation Example B1 were added respectively. The mixture was stirred for 20 minutes, then further added thereto a slurry (the solid content was 35 wt%) of 32 parts by weight (on the dry basis) of the DASY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C19, wherein based on the total weight of the catalytic cracking catalyst C19, the catalytic cracking catalyst C19 contained 15 wt% of high specific heat capacity matrix material, 32 wt% of DASY zeolite, 35 wt% of kaolin, 18 wt% of Al₂O₃ binder.

Example 14

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

21 parts by weight (on the dry basis) of kaolin and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 40 wt%), then added 20 parts by weight (on the dry basis) of pseudo-boehmite, and hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio (weight ratio) was 0.20 : 1. Then the system was warmed up to 65°C and acidified for 1 hour. Then 4 parts by weight (on the dry basis) of an aluminium sol, and a slurry (the solid content was 20 wt%) of 20 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-2 prepared in Preparation Example B2 were added respectively. The mixture was stirred for 20 minutes, then further added thereto 35 parts by weight (on the dry basis) of the REHY zeolite (the solid content was 35 wt%). The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C20, wherein based on the total weight of the catalytic cracking catalyst C20, the catalytic cracking catalyst C20 contained 20 wt% of high specific heat capacity matrix material, 35 wt% of REHY

zeolite, 21 wt% of kaolin, 24 wt% of Al_2O_3 binder.

Example 15

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

- 5 28 parts by weight (on the dry basis) of kaolin and deionized water were vigorously mixed and stirred (the resulting slurry had a solid content of 40 wt%), then added 20 parts by weight (on the dry basis) of pseudo-boehmite, and hydrochloric acid was added to the obtained slurry to perform the peptization, wherein the acid-alumina ratio (weight ratio) was 0.20 : 1. Then the system was warmed up to 65°C and acidified for 1 hour. Then a
10 slurry (the solid content was 25 wt%) of 25 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-3 prepared in Preparation Example B3 was added. The mixture was stirred for 20 minutes, then further added thereto a slurry (the solid content was 35 wt%) of 27 parts by weight (on the dry basis) of the HSY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst.
15 Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a $(\text{NH}_4)_2\text{SO}_4$ solution (wherein, $(\text{NH}_4)_2\text{SO}_4$: microspherical catalyst : H_2O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C21, wherein based on the total weight of the catalytic cracking catalyst C21, the catalytic cracking
20 catalyst C21 contained 25 wt% of high specific heat capacity matrix material, 27 wt% of HSY zeolite, 28 wt% of kaolin, 20 wt% of Al_2O_3 binder.

Example 16

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

- 25 42 parts by weight (on the dry basis) of kaolin and 20 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 20 wt%) of 10 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-4 prepared in Preparation Example B4 were vigorously mixed and stirred with water. The mixture was stirred for 120 minute, then further added thereto a slurry (the solid content was 35 wt%)
30 of 28 parts by weight (on the dry basis) of the DASY zeolite. The system was continuously stirred for 30 minutes, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was calcined at 500°C for 1 hour, then washed at 60°C with a $(\text{NH}_4)_2\text{SO}_4$ solution (wherein, $(\text{NH}_4)_2\text{SO}_4$: microspherical catalyst : H_2O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water
35 and filtered, then dried at 110°C to produce a catalytic cracking catalyst C22, wherein based on the total weight of the catalytic cracking catalyst C22, the catalytic cracking catalyst C22 contained 10 wt% of high specific heat capacity matrix material, 28 wt% of DASY zeolite, 42 wt% of kaolin, 20 wt% of Al_2O_3 binder.

Example 17

- 40 This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

(1) Preparation of silica sol:

1.7L of hydrochloric acid was diluted with 8.0 kg of decaionized water, 7.7kg of sodium water glass was diluted with 8.0kg of decaionized water, and the diluted sodium water glass was slowly added into the diluted hydrochloric acid solution under stirring to obtain a silica sol having a SiO₂ concentration of 7.8 wt% and a pH value of 2.8.

(2) Preparation of catalytic cracking catalyst:

35 parts by weight (on the dry basis) of kaolin was added to 30 parts by weight (on the dry basis) of the above silica sol. The mixture was stirred for 1 hour and then added a slurry (the solid content was 18 wt%) of 10 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-5 prepared in Preparation Example 5. The resulting mixture was vigorously mixed and stirred with water, and then further added thereto a slurry (the solid content was 30 wt%) of 25 parts by weight (on the dry basis) of the DASY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst was washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C23, wherein based on the total weight of the catalytic cracking catalyst C23, the catalytic cracking catalyst C23 contained 10 wt% of high specific heat capacity matrix material, 25 wt% of DASY zeolite, 35 wt% of kaolin, 30 wt% of SiO₂ binder.

Example 18

This example was used to illustrate the catalytic cracking catalyst provided by the present invention and its preparation method.

42 parts by weight (on the dry basis) of kaolin and 15 parts by weight (on the dry basis) of an aluminium sol and a slurry (the solid content was 20 wt%) of 40 parts by weight (on the dry basis) of high specific heat capacity matrix material BAM-6 prepared in Preparation Example B6 were vigorously mixed and stirred with water. The mixture was stirred for 120 minutes, then further added thereto a slurry (the solid content was 35 wt%) of 33 parts by weight (on the dry basis) of the REHY zeolite. The system was continuously stirred, and spray-dried to produce microspherical catalyst. Then the microspherical catalyst were calcined at 500°C for 1 hour, then washed at 60°C with a (NH₄)₂SO₄ solution (wherein, (NH₄)₂SO₄ : microspherical catalyst : H₂O = 0.05:1:10) until the Na₂O content of less than 0.25 wt%, then rinsed with deionized water and filtered, then dried at 110°C to produce a catalytic cracking catalyst C24, wherein based on the total weight of the catalytic cracking catalyst C24, the catalytic cracking catalyst C24 contained 40 wt% of high specific heat capacity matrix material, 33 wt% of REHY zeolite, 42 wt% of kaolin, 15 wt% of Al₂O₃ binder.

Examples 19-24

Examples 25-30 were used to illustrate the performance test of the catalytic cracking catalyst provided by the present invention.

The catalytic cracking catalysts C19-C24 prepared above were respectively contaminated

by the impregnation with 5000ppm of iron, 5000ppm of nickel, and 5000ppm of vanadium by the Mitchell method, and aged at 780°C under 100% steam for 6 hours. The cracking performance evaluation was conducted on a small fixed fluidized bed. The evaluation process for each sample was conducted through five reaction regeneration cycles, that is, five consecutive processes of feedstock oil reaction and regeneration were conducted without unloading the same catalyst. The results of the last reaction were taken as the evaluation result of the catalyst cracking performance. The evaluation conditions for the heavy oil microreaction were as follows: the catalyst-oil ratio was 5 (weight ratio), the sample loading capacity was 9g, the reaction temperature was 520°C, the WHSV is 8/hour, the oil feeding time was 70 seconds, the regeneration temperature was 720°C, and the feedstock oil was a vacuum gas oil. The properties of the feedstock oil was shown in Table 2. The evaluation results were listed in Table 5.

Table 5

Example No.	19	20	21	22	23	24
Catalyst No.	C19	C20	C21	C22	C23	C24
Conversion/w%	69.32	69.57	68.81	68.45	68.37	69.18
Dry gas/w%	1.56	1.52	1.52	1.50	1.59	1.54
Liquefied gas/w%	12.86	13.07	12.82	12.71	12.54	12.76
Gasoline/w%	49.26	49.36	48.94	48.88	48.62	49.17
Diesel/w%	16.81	16.87	16.71	16.52	16.36	16.58
slurry oil/w%	13.87	13.56	14.48	15.03	15.27	14.24
Coke/w%	5.64	5.62	5.53	5.36	5.62	5.71
Total liquid yield/w%	78.93	79.30	78.47	78.11	77.52	78.51
Dry gas selectivity	2.25	2.18	2.21	2.19	2.33	2.23
Coke selectivity	8.14	8.08	8.04	7.83	8.22	8.25
H ₂ /CH ₄	0.11	0.1	0.12	0.13	0.12	0.11

From the results of Table 3 and Table 5, it can be seen that compared with the catalyst with the same zeolite content but without high specific heat capacity matrix material, the catalyst provided by the present invention has excellent metal contamination resistance ability, greatly improved heavy oil conversion ability, and significantly improved product distribution, especially the significantly improved selectivity of dry gas and coke, the increased total liquid yield, and the increased light oil yield. Compared to catalysts with the same component contents but different matrix materials than those of the present invention, the catalyst provided by the present invention can provide the reduced yield of dry gas and coke, and the significantly improved selectivity of dry gas and coke. It can be seen that the catalytic cracking catalyst provided by the present invention can exhibit better metal contamination resistance ability, catalytic cracking activity, and better selectivity of dry gas and coke during the process of the heavy oil catalytic cracking. The catalyst provided by the present invention is used for the heavy oil conversion, and can have higher total liquid yield and higher gasoline and liquefied gas yield. When the boron compound is boron oxide, it can have higher gasoline yield and conversion rate.

Claims

1. A catalytic cracking catalyst, wherein the catalytic cracking catalyst contains a cracking active component comprising a Y zeolite, a high specific heat capacity matrix material, a clay and a binder; the high specific heat capacity matrix material contains at least 5 wt% of manganese oxide, the high specific heat capacity matrix material has a specific heat capacity of 1.3-2.0 J/(g•K) at a temperature of 1000K, wherein preferably, based on the total weight of the catalytic cracking catalyst, the catalytic cracking catalyst contains 1-60 wt% of the cracking active component, 1-50 wt% of the high specific heat capacity matrix material, 1-70 wt% of the clay and 1-70 wt% of the binder, or, based on the total weight of the catalytic cracking catalyst, the catalytic cracking catalyst contains 10-50 wt% of the cracking active component, 5-40 wt% of the high specific heat capacity matrix material, 10-60 wt% of the clay and 10-60 wt% of the binder.
2. The catalytic cracking catalyst as claimed in any of the precedent claims, wherein the high specific heat capacity matrix material contains 5-95wt% of alumina as Al_2O_3 , 5-95 wt% of manganese oxide as MnO_2 and 0-40wt% of a boron compound on the dry basis, wherein preferably, the boron compound is boron nitride and/or boron oxide.
3. The catalytic cracking catalyst as claimed in any of the precedent claims, wherein the high specific heat capacity matrix material has a specific surface area of 150-500 m^2/g ; and/or, the high specific heat capacity matrix material has a pore volume of 0.3-1.5 cm^3/g ; and/or, the high specific heat capacity matrix material has an average pore diameter of 3-20 nm.
4. The catalytic cracking catalyst as claimed in any of the precedent claims, wherein in the XRD spectrum of the high specific heat capacity matrix material, the ratio of the intensity of the peak at 2θ angle of $18\pm 0.5^\circ$ to the intensity of the peak at 2θ angle of $37\pm 0.5^\circ$ is 1:(3-10).
5. The catalytic cracking catalyst as claimed in any of the precedent claims, wherein the preparation method of the high specific heat capacity matrix material comprises the steps:
 - (1) mixing an aluminium source and an alkali to form a colloid to obtain an aluminium-containing colloid, the pH value of the obtained aluminium-containing colloid is 7-11;
 - (2) mixing a manganese salt solution with a pH value of 3-7 and urea to obtain a manganese source solution;
 - (3) forming a mixture of the aluminium-containing colloid, the manganese source solution, and optionally the boron compound; and optionally
 - (4) washing and/or drying and/or calcining.
6. The catalytic cracking catalyst as claimed in claim 5, wherein in step (1), mixing the aluminium source and the alkali to form a colloid includes: mixing a solution of the aluminium source and a solution of the alkali to form a colloid with a temperature ranging from room temperature to 85°C and a pH value of 7-11; and/or, the concentration of alumina in the solution of the aluminium source is 150-350g $\text{Al}_2\text{O}_3/\text{L}$,

- the concentration of the alkali in the solution of the alkali is 0.1-1 mol/L; and/or,
the aluminium source is one or more of aluminium nitrate, aluminium sulfate, aluminium phosphate, aluminium chloride and the like; the alkali is one or more of a water-soluble carbonate, a water-soluble bicarbonate, and a water-soluble hydroxide; wherein,
5 preferably, the solution of the alkali is an alkaline aqueous solution containing one or more of CO_3^{2-} , HCO_3^- and OH^- ; in the solution of the alkali, the concentration of CO_3^{2-} is 0-0.6 mol/L, the concentration of OH^- is 0-0.5 mol/L, and the concentration of HCO_3^- is 0-1 mol/L.
7. The catalytic cracking catalyst as claimed in any of claims 5-6, wherein in step (2),
10 the molar ratio of urea to manganese ions is 1-5, for example 2-4, and the concentration of the manganese salt as MnO_2 in the manganese salt solution may be 50-500 g/L.
8. The catalytic cracking catalyst as claimed in any of claims 5-7, wherein in step (2), urea is added to the manganese salt solution, and then the resulting mixture is stirred at room temperature for 30-60 minutes to obtain a manganese source solution.
- 15 9. The catalytic cracking catalyst as claimed in any of claims 5-8, wherein the boron compound is boron nitride and/or boron oxide and/or a boron oxide precursor, wherein, preferably, the boron nitride is one or more of hexagonal boron nitride, cubic boron nitride, rhombohedral boron nitride and wurtzite boron nitride; the boron oxide precursor is one or more of ammonium borate, ammonium baborate and boric acid.
- 20 10. The catalytic cracking catalyst as claimed in any of claims 5-9, wherein in step (3), after mixing the aluminium-containing colloid and the manganese source solution, an aging process is further included; the aging temperature is from room temperature to 120°C, the aging time is 4-72 hours, and the aging is carried out under stirring or under standing alone; preferably, the aging is carried out under stirring, the aging temperature is
25 60-100°C, and the aging time is 12-36 hours.
11. The catalytic cracking catalyst as claimed in any of claims 5-9, wherein the boron compound is boron nitride; the process of forming a mixture of the aluminium-containing colloid, the manganese source solution, and the boron compound in step (3) is as follows: mixing the aluminium-containing colloid, the manganese source solution, and the boron
30 compound, and aging; or the boron compound is boron oxide and/or a precursor of boron oxide; the process of forming a mixture of the aluminium-containing colloid, the manganese source solution, and the boron compound in step (3) is as follows: mixing the aluminium-containing colloid and the manganese source solution, aging, optionally washing, and then mixing
35 with the boron compound.
12. The catalytic cracking catalyst as claimed in any of claims 5-9, wherein in step (4) the calcining temperature is 500°C-900°C, and the calcining time is 4-8 hours.
13. The catalytic cracking catalyst as claimed in any of claims 1-4, wherein the cracking active component contains a Y zeolite, and optionally the cracking active component
40 further contains a second molecular sieve, the second molecular sieve is one or more of faujasite, beta zeolite, MFI-structured molecular sieve and mordenite;

wherein preferably based on the total weight of the cracking active components, the content of the Y zeolite is 75 wt% or more, and the content of the second molecular sieve is 25 wt% or less.

14. A method for preparing the catalytic cracking catalyst as claimed in any of claims 1-13, wherein the method comprises a cracking active component, a high specific heat capacity matrix material, a clay and a binder are mixed and stirred with water, and then the resulting mixture is successively spray-dried, calcined, washed, filtered and dried.
15. Use of the catalytic cracking catalyst as claimed in any of claims 1-13 in the heavy oil catalytic cracking.