

**COMPOSITION FOR CATALYTIC CRACKING CATALYST, CATALYTIC
CRACKING CATALYST, AND PREPARATION METHOD THEREFOR AND USE
THEREOF**

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The application claims the benefit of China patent application No. “202310812512.7”, filed on July 4, 2023, the content of which is specifically and entirely incorporated herein by reference.

TECHNICAL FIELD

[0002] The present disclosure relates to the technical field of catalysts, in particular to a composition for catalytic cracking catalyst, a catalytic cracking catalyst, and a preparation method therefor and use thereof.

BACKGROUND

[0003] As the main means of reducing the weight of heavy oil to light oil, catalytic cracking occupies an important position in China, with a processing capacity of more than 200 million tons. In order to improve the economic benefits of the catalytic cracking unit and make “full use” of crude oil resources, it is often necessary to increase the proportion of residual oil blended in the catalytic cracking unit. However, residual oil usually has a high content of heavy metal V and the like, which may easily form vanadic acid during the catalytic cracking process, resulting in permanent destruction of the molecular sieve structure of the catalyst active component, causing a decrease in the heavy oil conversion capacity and the formation of polluted coke. At the same time, as the largest source of carbon emissions in refineries, catalytic cracking units have directly or indirectly emitted a large amount of greenhouse gases, thus the carbon emission control of catalytic cracking units has become a key research topic in the petrochemical industry. Therefore, it is urgent to develop the catalytic cracking catalysts of heavy oil with resistance to heavy metals and a low production of coke to reduce carbon emissions from the catalytic cracking units.

[0004] The existing technology of heavy metal resistant catalysts generally involves with adding heavy metal resistant matrix during the molding process, designing a metal coating on the carrier, or preparing heavy metal resistant auxiliary agents. CN202010203656.9 discloses a catalytic cracking catalyst capable of resisting heavy metal pollution and a preparation method therefor and

an use thereof, it relates to a catalytic cracking catalyst capable of resisting heavy metal pollution, the catalytic cracking catalyst has a core-shell structure, the core-shell structure comprises a core containing catalytic cracking catalyst finished particles and a shell containing rare earth metal oxide. The catalytic cracking catalyst of this invention has a good heavy metal vanadium pollution resistance effect, and when the catalytic cracking catalyst is used in the catalytic cracking process of high-vanadium raw oil, the conversion rate of the raw oil is high, and the selectivity of dry gas and coke is low. CN1073614C discloses a preparation method of hydrocarbon cracking catalyst containing rare earth for preventing vanadium poisoning, the method comprises: precipitating a mixed rare earth solution with a precipitating agent selected from ammonia water, ammonium hydrogen phosphate or ammonium phosphate, ammonium carbonate or a mixture thereof, then mixing it with a carrier slurry and a molecular sieve slurry, and subsequently spraying and drying to mold the catalyst. The method has a simple process, and the prepared catalyst exhibits desirable vanadium poisoning resistance. CN1223403C discloses a heavy-metal resistant new matrix-type FCC catalyst and its preparation method. The catalyst comprises 20-80m% of clay, 5-40m% of a binder, 1-25m% of a metal capture component (e.g., rare earth oxalate), 0-30m% of other oxides (e.g., activated alumina), 5-40m% of compounds with a lattice constant of 2.432-2.472nm selected from the faujasite, ZSM-5 zeolite, β zeolite or a mixture thereof. The catalyst has excellent heavy metal resistance and is suitable as a catalyst for cracking heavy oil with a high content of Ni, V, and other heavy metals. CN201210420981.6 discloses a metal chelating agent and a preparation method therefor and an use thereof, wherein the metal chelating agent contains magnesium oxide, alumina and a phosphorus-aluminum assistant, and at least part of the magnesium oxide and at least part of the alumina form a magnesium aluminate spinel structure, wherein the bulk density of the metal chelating agent is 0.85-1.2g/cm³. CN201110100491.3 discloses a silicon-carrier lanthanum carbonate catalytic cracking microspherical vanadium-resistant auxiliary agent for use in the heavy oil catalytic cracking process and a preparation method thereof. When the auxiliary agent is used in the heavy oil catalytic cracking process in the form of an additive, it can reduce the poisoning effect of vanadium in the feedstock oil on a catalyst in the system, improve the conversion efficiency and the yield of light hydrocarbons and have a low coke yield.

[0005] Existing technologies have a certain effect on capturing heavy metal V and inhibiting its destruction of the active components in the molecular sieves. However, there are also problems

such as complicated preparation process, dilution of the cracking activity of the main catalyst, and reduced yield of high-value products such as gasoline and liquefied gas in the product. Y-type molecular sieve is still a main active component of FCC catalyst due to its unique three-dimensional pore-channel structure, suitable acidity and desirable stability. Its performance determines the activity, stability, heavy oil conversion performance, heavy metal resistance and product selectivity of the catalyst. The NaY molecular sieve itself is not acidic and usually needs to be exchanged and modified to remove its Na^+ ions and adjust its acidity and pore-channel structure. The commonly used modification method at present is to use ammonium salts and/or rare earths for performing an exchange, and the modified REHY or REUSY molecular sieves with different acidity and pore structures are prepared through heating or hydrothermal calcination. At present, the preparation methods of REHY or REUSY type molecular sieves can be roughly divided into two categories: one category involves exchanging NaY molecular sieves with a small amount of rare earth ions and/or ammonium ions first, followed by calcination, and then performing rare earth ion exchange and/or ammonium ion exchange or dealumination treatment to obtain REUSY molecular sieve; the other category involves initially converting NaY molecular sieve into USY molecular sieve, and then performing rare earth ion exchange to prepare REUSY type molecular sieve.

[0006] CN200610087535.2 discloses a preparation process of REY molecular sieve. Contacting NaY molecular sieve with a rare earth ion-containing aqueous solution or contacting with a rare earth ion-containing aqueous solution and a solution or colloid containing aluminum ion, then contacting with additional precipitating agent makes some rare earth precipitate on the molecular sieve, carrying on water heat-treatment, and finally contacting with an aqueous ammonium salt solution, so that the prepared molecular sieve has a strong vanadium resistance.

[0007] CN200710121664.3 provides a catalytic cracking catalyst, comprising 10-50wt% of REY molecular sieve on a dry basis, 10-40wt% of inorganic oxide adhesive on an oxide basis, and 10-70wt% of clay on a dry basis; wherein the REY molecular sieve is prepared by the method as follows: contacting the NaY molecular sieve with an aqueous solution containing rare earth ions or an aqueous solution containing rare earth ions and a solution or colloid containing aluminum ions, then contacting with an additional precipitating agent to deposit a part of the rare earth on the molecular sieve, subsequently performing a water heat treatment, and finally contacting with an

ammonium salt aqueous solution, wherein the precipitating agent is an alkaline aqueous solution. The catalyst of this invention has a strong heavy oil cracking capability, a high gasoline yield, and a strong resistance to vanadium pollution.

[0008] CN201511020519.7 provides a preparation method of modified Y-type molecular sieve, the preparation method comprises: exchanging a NaY molecular sieve with ammonium salt, filtering, mixing compounds containing IIIB element in a periodic table, and directly performing spray drying and hydrothermal calcination without washing; using the ammonium salt to exchange again, adding a precipitator alone or in combination with a filter aid, filtering, and performing or not performing hydrothermal calcining. In the preparation process of the Y-type molecular sieve of this invention, the IIIB element is basically not lost, the exchange slurry is easy to filter, and the yield of molecular sieve is high, and the prepared Y-type molecular sieve has excellent activity, hydrothermal stability and resistance to heavy metal pollution.

[0009] CN201280056377.8 discloses a process for ion exchange on zeolites. This invention relates to an improved process for exchanging sodium ions with ammonium ions in zeolites comprising sodium ions and rare earth metal ions. For this exchange, aqueous solutions of ammonium salts, for example ammonium sulfate, ammonium nitrate or ammonium chloride, are currently used. The resulting “ammonium zeolites” are calcined to convert them into the H-form zeolites suitable as a catalyst, with a release of ammonia. It is proposed in accordance with this invention to use ammonium carbonate instead of the ammonium compounds mentioned above. Since excess ammonium carbonate, in contrast to the nitrates, sulfates or chlorides, can be recycled in the form of carbon dioxide and ammonia, the amount of salt which has to be discharged can be reduced significantly. The use of ammonium carbonate also minimizes the amount of rare earth metal ions which are leached out of the zeolites comprising rare earth metal ions.

[0010] The literature (“Pre-exchange Processes on the Composition and Nature of NaY Zeolite”, *Biological Chemical Engineering*, 2019, 5(1): 87-90, Wu Chuan-bo) proposed a new process for the exchange and washing of Y-type molecular sieves, and analyzed and discussed the composition and properties of the molecular sieves before and after the new process. The results showed that after the pre-exchange process, the content of Na^+ and SO_4^{2-} in the Y-type molecular sieve was significantly reduced, and the utilization rate of rare earths, the crystallinity after the first calcination, and the pore volume and specific surface area of the finished molecular sieve were

significantly increased.

[0011] The thesis (“Study on the Preparation of LaY Molecular Sieves via Liquid-Solid Combined Exchange Method”, Zhou Xue-yan et al.) has disclosed a process of preparing the LaY molecular sieve by using magnesium hydroxide to precipitate rare earth for 5 hours and using a solid phase exchange method via high-temperature calcination, thereby improving the exchange degree.

[0012] In the conventional technology, when the rare earth ions and ammonium salt are exchanged at the same time, the exchange efficiency is low due to the existence of competitive exchange; when the ammonium salt exchange is carried out before the rare earth exchange, the use of ammonium chloride and ammonium nitrate will cause problems such as high cost and equipment corrosion; when the low-cost recyclable ammonium sulfate is used, it requires a large amount of water washing to remove sulfate ions to avoid the formation of sulfate precipitation, which will increase water consumption. After the rare earth modified molecular sieve is hydrothermally calcined, it is inevitable that some rare earths cannot be positioned in the sodalite cage, so that ammonium sulfate exchange is used in the subsequent process, resulting in the formation of rare earth sulfate precipitation, an increase in molecular sieve sulfate ions and a decrease in crystallinity. Although pre-exchange can reduce the sodium oxide and sulfate ions of the modified molecular sieve, it has the defects of long process, high water consumption and high costs. The REY molecular sieves prepared without use of ammonium salts suffer from the problems such as high yield of coke.

[0013] In short, the conventional technology inevitably presents problems such as high sulfate radical content, low crystallinity, equipment corrosion, long production processes and high costs. Therefore, it is urgent to develop a new method for preparing a metal ion molecular sieve with a low content of sulfate radical to improve the activity, stability and heavy oil conversion capacity of catalytic cracking catalysts, and avoid the equipment corrosion resulting from the conversion of sulfate radical into sulfide in use.

SUMMARY

[0014] The present disclosure aims to overcome the problems existing in the conventional technology, such as the complicated catalyst preparation process, dilution of the cracking activity of the main catalyst, and reduced yield of high-value products such as gasoline and liquefied gas,

and provides a composition for a catalytic cracking catalyst, a catalytic cracking catalyst, and a preparation method therefor and use thereof. The catalytic cracking catalyst prepared with the composition has excellent heavy metal pollution resistance and low coke selectivity.

[0015] The first aspect of the present disclosure provides a composition for a catalytic cracking catalyst including: a rare-earth-modified Y-type molecular sieve, a binder, a matrix material, a rare earth element source, and optionally an REUSY molecular sieve, wherein a content of SO_4^{2-} in the rare-earth-modified Y-type molecular sieve is not greater than 1wt%.

[0016] The second aspect of the present disclosure provides a method of preparing a catalytic cracking catalyst including:

[0017] (1) homogenizing a slurry containing the composition for a catalytic cracking catalyst according to the present disclosure, followed by molding and a third calcination to obtain a catalyst precursor;

[0018] (2) performing sodium reduction and modification on the catalyst precursor to obtain the catalytic cracking catalyst.

[0019] The third aspect of the present disclosure provides a catalytic cracking catalyst prepared by the method according to the second aspect of the present disclosure.

[0020] The fourth aspect of the present disclosure provides a use of the catalytic cracking catalyst according to the present disclosure in the catalytic cracking of heavy oil.

[0021] Through the above technical scheme, the present disclosure has at least the following beneficial effects.

[0022] (1) The interaction of all components in the composition of the present disclosure significantly improves the activity, stability and heavy oil conversion capacity of the composition; on the other hand, since the independent phase rare earth material on the outer surface of the rare-earth-modified Y-type molecular sieve can preferentially react with heavy metals (e.g., V) to generate heavy metal acid rare earth, thereby effectively protecting the molecular sieve crystal structure and inhibiting the formation of contaminated coke;

[0023] (2) A catalytic cracking catalyst prepared by using the composition exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield during use.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0024] The terminals and any value of the ranges disclosed herein are not limited to the precise ranges or values, such ranges or values shall be comprehended as including the values adjacent to the ranges or values. As for numerical ranges, the endpoint values of the various ranges, the endpoint values and the individual point values of the various ranges, and the individual point values may be combined with one another to produce one or more new numerical ranges, which should be deemed to have been specifically disclosed herein.

[0025] The expression “optionally” used in the present disclosure means that the subsequent material is present or absent, or the subsequent operation occurs or does not occur.

[0026] Unless otherwise specified in the present disclosure, the expressions “first”, “second” and “third” do not indicate a sequence or impose limitations on the materials or steps, but merely serve to distinguish that they are not the same steps or materials. For example, “first” and “second” in the terms “first calcination” and “second calcination” only serve to indicate that they are not the same calcination process.

[0027] The “drying” involved in the present disclosure is a conventional operation means in the art, and can be dried under normal pressure or vacuum conditions, and generally means dried under normal pressure and a temperature of 80-120°C for 8-36 hours.

[0028] The room temperature involved in the present disclosure is “15-25°C”.

The first aspect of the present disclosure provides a composition for a catalytic cracking catalyst including: a rare-earth-modified Y-type molecular sieve, a binder, a matrix material, a rare earth element source, and optionally an REUSY molecular sieve, wherein a content of SO_4^{2-} in the rare-earth-modified Y-type molecular sieve is not greater than 1wt%.

[0029] The rare earth element source in the present disclosure refers to a raw material that can provide rare earth elements.

[0030] The inventors of the present disclosure have discovered through research that the rare earth material in the catalyst prepared with the composition of the present disclosure can preferentially interact with heavy metals, such as V, to form rare earth-heavy metal acids, thereby effectively protecting the molecular sieve crystal structure and inhibiting the formation of contaminated coke. The catalyst exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield during use.

[0031] According to a preferred embodiment of the present disclosure, the rare earth element source is calculated based on the weight of rare earth oxide, and the composition comprises 15-35wt% of the rare-earth-modified Y-type molecular sieve, 0-20wt% of the REUSY molecular sieve, 6-30wt% of the binder, 30-55wt% of the matrix material, and 0.5-4wt% of the rare earth element source. The catalyst prepared with the composition in the aforementioned embodiment exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield during use.

[0032] According to a particularly preferred embodiment of the present disclosure, the rare earth element source is calculated based on the weight of rare earth oxide, and the composition comprises 18-27wt% of the rare-earth-modified Y-type molecular sieve, 8-15wt% of the REUSY molecular sieve, 8-25wt% of the binder, 35-45wt% of the matrix material, and 0.5-3wt% of the rare earth element source. The catalyst prepared with the composition in the aforementioned embodiment exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield during use.

[0033] According to a preferred embodiment of the present disclosure, the content of SO_4^{2-} in the rare-earth-modified Y-type molecular sieve is not greater than 0.5wt%, such as 0.01wt%, 0.1wt%, 0.2wt%, 0.27wt%, 0.3wt%, 0.32wt%, 0.41wt%, 0.45wt%, 0.5wt%, or a random value within the range consisting of any two numerical values mentioned above, and more preferably 0.01-0.45wt%. The catalyst prepared with the composition under the aforementioned embodiment has better stability and metal utilization rate, and when the catalyst is used for catalytic cracking, it has excellent effects of heavy metal resistance and low coke yield.

[0034] According to a preferred embodiment of the present disclosure, a content of sodium in the rare-earth-modified Y-type molecular sieve calculated in terms of Na_2O is not greater than 1.5wt%, such as 0.2wt%, 0.5wt%, 0.62wt%, 0.82wt%, 0.92wt%, 0.98wt%, 1.1wt%, 1.2wt%, 1.5wt%, or a random value within the range consisting of any two numerical values mentioned above, and more preferably 0.5wt%-1.2wt%. The catalyst prepared with the composition under the aforementioned embodiment has better stability and metal utilization rate, and when the catalyst is used for catalytic cracking, it has excellent effects of heavy metal resistance and low coke yield.

[0035] According to a preferred embodiment of the present disclosure, a content of rare earth

calculated in the rare-earth-modified Y-type molecular sieve in terms of rare earth oxide is 5wt%-20wt%, such as 5wt%, 6wt%, 9wt%, 10wt%, 10.4wt%, 12.4wt%, 14.3wt%, 15.6wt%, 16.1wt%, 16.2wt%, 19.8wt%, 20wt%, or a random value within the range consisting of any two numerical values mentioned above, and more preferably 10wt%-20wt%. The catalyst prepared with the composition under the aforementioned embodiment has better stability and metal utilization rate, can effectively protect the crystal structure of the catalyst, and inhibit the generation of polluted coke.

[0036] According to a preferred embodiment of the present disclosure, a crystallinity C/C_0 of said rare-earth-modified Y-type molecular sieve is 50-80%, such as 50%, 55%, 58%, 60%, 62%, 63%, 65%, 70%, 80%, or a random value within the range consisting of any two numerical values mentioned above, and more preferably 58-65%. The catalyst prepared with the composition under the aforementioned embodiment has better stability and metal utilization rate, and when the catalyst is used for catalytic cracking, it has excellent effects of heavy metal resistance and low coke yield.

[0037] According to a preferred embodiment of the present disclosure, the rare-earth-modified Y-type molecular sieve is obtained by subjecting a Na-type Y molecular sieve to a modification treatment, and the modification treatment preferably includes an ammonium sulfate exchange treatment step.

[0038] According to a particularly preferred embodiment of the present disclosure, a method of the modification treatment includes the following steps:

[0039] (a) subjecting a Na-type Y molecular sieve to a rare earth ion exchange to obtain a rare earth ion slurry;

[0040] (b) adding a first precipitating agent into the rare earth ion slurry to cause a first precipitation on a part of rare earth ions in said rare earth ion slurry to obtain a first precipitation slurry;

[0041] (c) subjecting solid matter in the first precipitation slurry to a first ammonium sulfate exchange, a first water washing and a first calcination to obtain an once-exchanged and once-calcined molecular sieve dry powder;

[0042] (d) mixing a slurry containing the once-exchanged and once-calcined molecular sieve dry powder with a second precipitating agent to cause a second precipitation of a part of rare earth ions

in the once-exchanged and once-calcined molecular sieve dry powder, and then sequentially performing a second ammonium sulfate exchange, a second water washing and an optional heat treatment to obtain the rare-earth-modified Y-type molecular sieve.

[0043] In the present disclosure, through the above-mentioned modification treatment, the formation of precipitation from free metal ions and sulfate radicals in the exchange system solution, on a surface of the molecular sieve or in the supercages during the subsequent ammonium sulfate exchange and sodium reduction process is avoided. On one hand, this achieves the purpose of reducing sulfate, and improving the crystallinity and stability of the molecular sieve. On the other hand, it improves the utilization rate of the modified metals, which can significantly improve the activity, stability and heavy oil conversion capacity of the catalyst prepared with the composition of the present disclosure. At the same time, the independent phase rare earth material on the surface of said catalyst can preferentially generate rare earth vanadate with heavy metal V, thereby effectively protecting the crystal structure of the molecular sieve, and inhibiting the generation of contaminated coke, such that the catalyst exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield.

[0044] According to a preferred embodiment of the present disclosure, in step (a), a process of the rare earth ion exchange includes: carrying out the rare earth ion exchange between Na-type Y molecular sieve and a rare earth source in the presence of water; specifically, after mixing the Na-type Y molecular sieve and water, adding a rare earth source solution containing the rare earth source to carry out the rare earth ion exchange; wherein, the weight ratio of water to the Na-type Y molecular sieve is preferably (1.5-30) : 1, and more preferably (2-5) : 1. The solvent in the rare earth source solution is not particularly limited, it may be any solvent that is capable of dissolving the rare earth source, and in the present disclosure, the solvent is water, the concentration of the rare earth source solution is generally 200-400g/L.

[0045] According to a preferred embodiment of the present disclosure, during the rare earth ion exchange, the rare earth source is selected from chlorate and/or nitrate containing at least one of rare earth elements, and preferably, the rare earth element includes at least one of lanthanum, cerium and yttrium.

[0046] According to a preferred embodiment of the present disclosure, during the rare earth ion exchange, the Na-type Y molecular sieve is calculated on a dry basis, the rare earth source is

calculated in terms of rare earth oxide, and a content of the rare earth source in the Na-type Y molecular sieve is 1-20wt%; more preferably 10-16wt%.

[0047] According to a preferred embodiment of the present disclosure, during the rare earth ion exchange, the rare earth ion exchange conditions include: a temperature between room temperature and 180°C, and more preferably 50-80°C.

[0048] According to a preferred embodiment of the present disclosure, during the rare earth ion exchange, the rare earth ion exchange conditions include: an exchange time 0.3-3.5h, and more preferably 0.5-1.5h.

[0049] According to a preferred embodiment of the present disclosure, during the rare earth ion exchange, the rare earth ion exchange conditions include: a pH of 2.8-6.5, and more preferably a pH of 3.5-4.5

[0050] According to the present disclosure, those skilled in the art can understand that the rare earth sources are generally acidic when dissolved in water. If the pH value is relatively high, an acidic substance such as dilute hydrochloric acid may be used to adjust the pH to a desired pH.

[0051] The addition amount of the first precipitating agent in the present disclosure is determined according to the amount of rare earth ions in the rare earth ion exchange slurry. Preferably, in step (b), a amount of the first precipitating agent is based on a molar ratio for the precipitation of 1-4 wt% of the rare earth ions present in the Na-type Y molecular sieve; preferably, the amount of the first precipitating agent is based on a molar ratio for the precipitation of 1.5-2.5 wt% of the rare earth ions present in the Na-type Y molecular sieve. By adopting the aforementioned embodiments, the formation of precipitates from free RE ions and sulfate radicals in the solution of the exchange system, on the surface of the molecular sieve, or in the supercages during the subsequent sodium reduction process via ammonium sulfate exchange is avoided. This achieves the purpose of reducing sulfate radicals, improves the crystallinity and stability of the molecular sieve, and at the same time increases the utilization rate of rare earths. Additionally, it forms a heavy metal-resistant independent phase rare earth component on the surface of the molecular sieve, thereby enhancing the heavy metal contamination resistance of the catalyst.

[0052] According to the present disclosure, the conditions for the first precipitation in step (b) are not particularly limited as long as the purpose of the present disclosure can be achieved. Preferably, the conditions of the first precipitation in step (b) include: a temperature of 25-180°C,

and preferably 50-80°C; and/or a time of 0.1-5h, and preferably 0.1-2h.

[0053] According to the present disclosure, it can be understood that the first precipitation slurry contains solid matter and a solvent (e.g., water), and the method for obtaining the solid matter in the first precipitation slurry is not particularly limited, for example, the solid matter can be obtained by filtering, drying and the like.

[0054] According to the present disclosure, it can be understood that in step (c), the first ammonium sulfate exchange refers to a first ammonium sulfate exchange using ammonium sulfate. Preferably, in step (c), an amount of ammonium sulfate in the first ammonium sulfate exchange is 5-50wt% of the Na-type Y molecular sieve, and more preferably 10-25wt% of the Na-type Y molecular sieve.

[0055] According to the present disclosure, the conditions for the first ammonium sulfate exchange in step (c) are not particularly limited as long as the purpose of the present disclosure can be achieved. Preferably, the conditions of the first ammonium sulfate exchange in step (c) include: a temperature of 20-85°C, and more preferably 50-80°C; and/or a time of 0.1-5h, and more preferably 0.1-2h.

[0056] According to a preferred embodiment of the present disclosure, the first ammonium sulfate exchange process includes: subjecting the solid matter in the first precipitation slurry to a first ammonium sulfate exchange with an aqueous ammonium sulfate solution; more preferably, a concentration of the aqueous ammonium sulfate solution is 20-400g/L, and further preferably, the concentration of the aqueous ammonium sulfate solution is 120-250g/L.

[0057] The first water washing in step (c) of the present disclosure refers to washing the solid matter obtained from the first ammonium sulfate exchange with water. The method of the water washing is not particularly limited. For example, the solid matter obtained from the first ammonium sulfate exchange is rinsed with water in an amount of 1-8 times, preferably 2-5 times, the weight of the Na-type Y molecular sieve.

[0058] According to a preferred embodiment of the present disclosure, the conditions of the first calcination in step (c) include: 100% water vapor atmosphere. The catalyst prepared with the composition under the aforementioned embodiment exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield during use.

[0059] According to a preferred embodiment of the present disclosure, the conditions of the first calcination in step (c) include: a temperature of 400-700°C, and more preferably 500-650°C.

[0060] According to a preferred embodiment of the present disclosure, the conditions of the first calcination in step (c) include: a time of 0.1-5h, and more preferably a time of 0.5-3h.

[0061] In the present disclosure, the slurry containing the once-exchanged and once-calcined molecular sieve dry powder refers to a slurry obtained by mixing and pupling water with the once-exchanged and once-calcined molecular sieve dry powder. Preferably, in step (d), a weight ratio of water to the once-exchanged and once-calcined molecular sieve dry powder in the slurry containing the once-exchanged and once-calcined molecular sieve dry powder is (1.5-30) : 1, and more preferably (2-5) : 1.

[0062] According to a preferred embodiment of the present disclosure, an amount of the second precipitating agent is based on a molar ratio for the second precipitation of 0.5-3wt% of the rare earth ions present in the once-exchanged and once-calcined molecular sieve dry powder; preferably, the amount of the second precipitating agent is based on the molar ratio for the second precipitation of 1-2wt% of the rare earth ions present in the once-exchanged and once-calcined molecular sieve dry powder. By adopting the above embodiment, the crystallinity and stability of the molecular sieve are improved; meanwhile, the utilization rate of the rare earth is improved; and a heavy metal-resistant independent phase rare earth component is formed on the surface of the molecular sieve, thereby improving the heavy metal pollution resistance of the catalyst.

[0063] According to the present disclosure, the conditions for the second precipitation in step (d) are not particularly limited as long as the purpose of the present disclosure can be achieved. Preferably, the conditions of the second precipitation in step (d) include: a temperature of 15-40°C, and more preferably 20-30°C; and/or a time of 0.1-5h, more preferably 0.1-2h.

[0064] According to the present disclosure, it can be understood that in step (d), the second ammonium sulfate exchange refers to the use of ammonium sulfate for the second ammonium sulfate exchange. Preferably, in step (d), an amount of ammonium sulfate in the second ammonium sulfate exchange is 5-50wt%, and more preferably 10-25wt% of a weight of said once-exchanged and once-calcined molecular sieve dry powder.

[0065] According to the present disclosure, the conditions for the first ammonium sulfate exchange in step (d) are not particularly limited as long as the purpose of the present disclosure

can be achieved. Preferably, the conditions for the second ammonium sulfate exchange in step (d) include: a temperature of 20-85°C, and more preferably 50-80°C; and/or a time of 0.1-5h, and more preferably 0.1-2h.

[0066] According to a preferred embodiment of the present disclosure, the process of the second ammonium sulfate exchange is as follows: performing a second ammonium sulfate exchange on a product of the second precipitation with a second aqueous ammonium sulfate solution, wherein a concentration of the second ammonium sulfate aqueous solution is 20-400g/L, and more preferably 120-250g/L.

[0067] The exchange process of the first ammonium sulfate exchange and the second ammonium sulfate exchange in the present disclosure can adopt a tank exchange, a belt exchange, or a tank exchange and a belt exchange carried out simultaneously. The present disclosure has no special limitation on the mode and the content will not be elaborated in detail herein.

[0068] The second water washing in step (d) of the present disclosure refers to washing the solid matter obtained from the second ammonium sulfate exchange with water. The method of the water washing is not particularly limited. For example, the solid matter obtained from the second ammonium sulfate exchange is washed with water in an amount of 1-8 times, preferably 2-5 times, the weight of the once-exchanged and once-calcined molecular sieve dry powder.

[0069] According to a preferred embodiment of the present disclosure, the heat treatment includes drying and a second calcination.

[0070] According to a preferred embodiment of the present disclosure, the conditions of the second calcination include: in an oxygen-containing atmosphere. By adopting the aforementioned embodiment, the crystallinity and stability of the molecular sieve are improved, and the utilization rate of the rare earth is improved; in addition, a heavy metal-resistant independent phase rare earth component is formed on the surface of the molecular sieve, thereby improving the heavy metal pollution resistance of the catalyst.

[0071] The oxygen-containing atmosphere in the present disclosure includes oxygen or air, and air is preferred in the present disclosure.

[0072] According to a preferred embodiment of the present disclosure, the conditions for the second calcination include: a temperature 400-700°C, more preferably 450-650°C.

[0073] According to a preferred embodiment of the present disclosure, the conditions for the

second calcination include: a time 0.1-10h, more preferably of 0.5-5h.

[0074] According to a preferred embodiment of the present disclosure, the Na-type Y molecular sieve includes at least one of NaY molecular sieve, NaHY molecular sieve, NaUSY molecular sieve, NaREHY molecular sieve and NaREUSY molecular sieve; more preferably NaY molecular sieve.

[0075] According to the present disclosure, the specific types of the first precipitating agent and the second precipitating agent are not particularly limited as long as the purpose of the present disclosure can be achieved. Preferably, the first precipitating agent and the second precipitating agent are each independently selected from ammonium compounds that can provide rare earth ions to generate anions of oxide precipitation precursors; more preferably, selected from one or more of ammonium oxalate, ammonium carbonate, ammonium bicarbonate and aqueous ammonia.

[0076] According to the present disclosure, the type of the matrix material is not particularly limited as long as the purpose of the present disclosure can be achieved. Preferably, the matrix material contains clay, wherein the clay includes at least one of kaolin, halloysite, porous stone, diatomite and sepiolite.

[0077] According to the present disclosure the rare earth element source is selected from at least one of rare earth chloride, rare earth nitrate, rare earth oxide, rare earth carbonate, rare earth oxalate and rare earth acetate, preferably rare earth acetate and/or rare earth oxide; wherein the rare earth metal elements in the rare earth element source are not particularly limited, such as lanthanum element and/or cerium element.

[0078] According to a preferred embodiment of the present disclosure, the REUSY molecular sieve includes at least one of a LaUSY molecular sieve, a CeUSY molecular sieve, and a mixed rare earth USY molecular sieve; the mixed rare earth USY molecular sieve refers to a molecular sieve containing at least two different types of rare earth elements, such as the mixed rare earth USY molecular sieve of La and Ce. The catalyst prepared with the aforementioned composition has good resistance to heavy metal pollution, especially resistance to vanadium pollution. When the catalyst is used in the catalytic cracking process of high-vanadium heavy oil, the conversion rate of heavy oil is high, and the selectivity of dry gas and coke is low.

[0079] The advantages of the present disclosure is exemplified and illustrated by using the REUSY molecular sieve containing RE_2O_3 in an amount of 1.8wt%, specifically containing La_2O_3

in an amount of 1.44wt% and Ce_2O_3 in an amount of 0.36wt%, but the present disclosure is not limited thereto.

[0080] The second aspect of the present disclosure provides a method of preparing the catalytic cracking catalyst including:

[0081] (1) homogenizing a slurry containing the composition for a catalytic cracking catalyst according to the disclosure, followed by molding and a third calcination to obtain a catalyst precursor;

[0082] (2) performing sodium reduction and modification on the catalyst precursor to obtain the catalytic cracking catalyst.

[0083] The catalyst prepared in the present disclosure exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield.

[0084] The slurry containing the composition for a catalytic cracking catalyst according to the present disclosure refers to a slurry obtained by mixing the composition for a catalytic cracking catalyst in the present disclosure with a solvent. The mixing conditions are not particularly limited, and the mixing is preferably carried out at room temperature; preferably, the solid content of the slurry containing the composition for a catalytic cracking catalyst is 25-45wt%, and more preferably 35-45wt%.

[0085] The molding method in step (1) of the present disclosure is not particularly limited, and preferably spray molding, which is a conventional technical means in the art and will not be further described herein.

[0086] According to a preferred embodiment of the present disclosure, conditions of the third calcination include: a temperature of 400-550°C, and more preferably 450-500°C; and/or a time of 0.1-5h, and more preferably 0.1-2h.

[0087] According to a preferred embodiment of the present disclosure, the method for sodium reduction and modification includes: mixing a slurry containing the catalyst precursor with an ammonium salt to obtain a mixed solution, and then separating the solid matter in the mixed solution for drying.

[0088] The catalyst precursor-containing slurry in the present disclosure refers to a slurry obtained by mixing a catalyst precursor with water, and the solid content of the catalyst precursor-containing slurry is preferably 0.5wt%-35wt%, more preferably 20wt%-25wt%.

[0089] According to a preferred embodiment of the present disclosure, the ammonium salt includes at least one of ammonium chloride, ammonium phosphate, diammonium hydrogen phosphate and diammonium dihydrogen phosphate, more preferably ammonium chloride.

[0090] According to a preferred embodiment of the present disclosure, a weight ratio of the ammonium salt to the catalyst precursor is (2-10) :100, more preferably (3-6) :100.

[0091] The third aspect of the present disclosure provides a catalytic cracking catalyst prepared by the preparation method according to the second aspect of the present disclosure.

[0092] The catalyst in the present disclosure exhibits high activity, excellent stability, strong heavy oil conversion capability, superior heavy metal resistance and low coke yield.

[0093] According to a preferred embodiment of the present disclosure, the content of sodium ions Na^+ calculated in terms of Na_2O in the catalytic cracking catalyst is not greater than 0.2wt%, and more preferably 0.1-0.18wt%.

[0094] The fourth aspect of the present disclosure provides a use of the catalytic cracking catalyst according to the present disclosure in the catalytic cracking of heavy oil.

[0095] The catalyst of the present disclosure has the advantages of high activity, excellent stability and strong heavy oil conversion capacity when used in catalytic cracking of heavy oil.

[0096] According to a preferred embodiment of the present disclosure, the catalytic cracking catalyst according to the present disclosure is used in the catalytic cracking of heavy oil with a high content of heavy metals, more preferably, the heavy metals include V and optionally Ni.

[0097] The catalyst of the present disclosure has good resistance to heavy metal pollution, especially resistance to vanadium pollution, when the catalyst is used in the catalytic cracking process of high-vanadium heavy oil, it has the characteristics of high conversion rate, excellent heavy metal resistance and low coke yield.

[0098] The present disclosure will be described in detail below with reference to examples. In the following examples, the analysis and evaluation methods were used as follows.

[0099] 1. Unit cell constant (a_0): X-ray diffraction method.

[00100] 2. Crystallinity (C/C_0): X-ray diffraction method.

[00101] 3. Silicon-aluminum ratio: X-ray diffraction method.

[00102] Na_2O content: XRF fluorescence method.

[00103] RE_2O_3 content: XRF fluorescence method.

[00104] 6. Sulfate content: XRF fluorescence method.

[00105] 7. Micro-reaction activity: the samples were pre-treated at 800°C and 100% water vapor atmosphere condition for different time. The reaction feedstock was Dagang light diesel oil in Tianjin, China, the reaction temperature was 460°C, the reaction time was 70 seconds, the catalyst loading amount was 5.0 grams, the catalyst-oil weight ratio was 3.2, and the total conversion rate was taken as the micro-reaction activity.

[00106] 8. ACE heavy oil microreactor: the catalyst sample was pre-contaminated with 5,000ppm V and 3,000ppm Ni, and treated at 800°C and 100% water vapor for 5h, the reaction temperature was 530°C, catalyst-oil ratio was 5, and the feedstock oil was the feedstock oil from 3 million tons heavy oil catalytic unit in the Lanzhou Petrochemical Company.

[00107] In the following examples, the specifications of the raw materials in use were as follows:

[00108] 1. NaY molecular sieve: NaY (silicon-aluminum ratio 5.1, crystallinity 95%), produced by Changting Catalyst Co., Ltd.

[00109] 2. Rare earth solution: rare earth chloride and rare earth nitrate were both industrial products, purchased from the catalyst plant of Lanzhou Petrochemical Company.

[00110] 3. Ammonium sulfate, ammonium oxalate, ammonium carbonate, ammonium bicarbonate, aqueous ammonia, urea, ammonium acetate, ammonium chloride and ammonium nitrate were all analytically pure products.

[00111] 4. Pseudo-boehmite (loss on ignition: 36.7wt%), kaolin (loss on ignition: 18.4wt%), halloysite (loss on ignition: 23.2wt%), porous stone (loss on ignition: 18.2wt%), diatomite (loss on ignition: 23.6wt%), sepiolite (loss on ignition: 25.3wt%), REUSY [loss on ignition: 5.3%, RE content calculated in terms of RE₂O₃: 1.8wt%, specifically 1.44wt% of La₂O₃ and 0.36wt% of Ce₂O₃, Na₂O content: 1.2wt%, unit cell size: 24.56Å) solid; aluminum sol containing 22.6wt% of alumina; silica sol containing 30.5wt% silica, all are industrial qualified products.

[00112] Preparation Examples 1-11

[00113] Preparation Example 1

[00114] Preparation of rare-earth-modified Y-type molecular sieve:

[00115] (a) 1,000g (dry basis weight) of NaY molecular sieve was pulped with 5L of deionized water to form a slurry. Then, 0.537L of LaCl₃ aqueous solution (calculated in terms of La₂O₃) with a concentration of 298g/L (0.98mol of La³⁺) was added for rare earth ion exchange (at a

temperature of 80°C for a time of 0.5h) to obtain a rare earth ion exchange slurry. Among them, the content of LaCl_3 calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 16wt%.

[00116] (b) Ammonium oxalate monohydrate (32g, 0.225mol) was added, such that 2.4wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 80°C for a time of 0.5h) to obtain a first precipitation slurry.

[00117] (c) The first precipitation slurry was filtered and drained. Then, 0.833L of ammonium sulfate aqueous solution with a concentration of 180g/L was added, followed by the exchange at 60°C for 1h. After filtration and draining, 3L of water was added for rinsing, and then calcined in a 100% water vapor atmosphere at 500°C for 2h to obtain an once-exchanged and once-calcined molecular sieve dry powder.

[00118] (d) 1,000g of the once-exchanged and once-calcined molecular sieve dry powder (dry basis weight) was pulped with 5L of deionized water to form a slurry. Ammonium oxalate monohydrate (25.6g, 0.18mol) was then added, such that 2wt% of La^{3+} in the once-exchanged and once-calcined molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for a time of 0.5h). 0.6L of ammonium sulfate aqueous solution with a concentration of 250g/L was subsequently added to exchange at 80°C for 1.5h. The product was filtered, drained, then rinsed with 5L of water, dried, and then calcined in an air atmosphere at 450°C for 2h, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z1.

[00119] Preparation Example 2

[00120] (a) 1,000g (dry basis weight) of NaY molecular sieve was pulped with 5L of deionized water to form a slurry. Then, 0.358L of $\text{La}(\text{NO}_3)_3$ aqueous solution (calculated in terms of La_2O_3) with a concentration of 280g/L (0.615mol of La^{3+}) was added for rare earth ion exchange (at a temperature of 50°C for a time of 1.5h) to obtain a rare earth ion exchange slurry. Among them the content of $\text{La}(\text{NO}_3)_3$ calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 10wt%.

[00121] (b) Ammonium oxalate monohydrate (25.6g, 0.18mol) was added, such that 2wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 50°C for a time of 0.5h) to obtain a first precipitation slurry.

[00122] (c) The first precipitation slurry was filtered and drained. Then, 1.111L of ammonium

sulfate aqueous solution with a concentration of 180g/L was added, followed by the exchange at 80°C for 1h. After filtration and draining, 3L of water was added for rinsing, and then calcined in a 100% water vapor atmosphere at 600°C for 2h to obtain an once-exchanged and once-calcined molecular sieve dry powder.

[00123] (d) 1,000g of the once-exchanged and once-calcined molecular sieve dry powder (dry basis weight) was pulped with 5L of deionized water to form a slurry. Ammonium carbonate (13g, 0.135mol) was then added, such that 1.5wt% of La^{3+} in the once-exchanged and once-calcined molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for a time of 0.5h). 1.666L of ammonium sulfate aqueous solution with a concentration of 120g/L was subsequently added to exchange at 50°C for 1h. The product was filtered, drained, then rinsed with 2L of water, dried, and then calcined in an air atmosphere at 500°C for 2.5h, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z2.

[00124] Preparation Example 3

[00125] (a) 1,000g (dry basis weight) of NaY molecular sieve was pulped with 5L of deionized water to form a slurry. Then, 0.403L of LaCl_3 aqueous solution (calculated in terms of La_2O_3) with a concentration of 298g/L (0.74mol of La^{3+}) was added for rare earth ion exchange (at a temperature of 60°C for a time of 1h) to obtain a rare earth ion exchange slurry. Among them the content of LaCl_3 calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 12.08wt%.

[00126] (b) Ammonium oxalate monohydrate (28g, 0.197mol) was added, such that 2.1wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 60°C for a time of 0.5h) to obtain a first precipitation slurry.

[00127] (c) The first precipitation slurry was filtered and drained. Then, 1.0L of ammonium sulfate aqueous solution with a concentration of 180g/L was added, followed by the exchange at 60°C for 1.5h. After filtration and draining, 3L of water was added for rinsing, and then calcined in a 100% water vapor atmosphere at 630°C for 2h to obtain an once-exchanged and once-calcined molecular sieve dry powder.

[00128] (d) 1,000g of the once-exchanged and once-calcined molecular sieve dry powder (dry basis weight) was pulped with 5L of deionized water to form a slurry. Ammonium oxalate monohydrate (15.4g, 0.11mol) was then added, such that 1.2wt% of La^{3+} in the once-exchanged

and once-calcined molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for a time of 0.5h), 1.278L of ammonium sulfate aqueous solution with a concentration of 180g/L was subsequently added to exchange at 50°C for 1h. The product was filtered, drained, then rinsed with 3L of water, dried, and calcined in an air atmosphere at 400°C for 2h, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z3.

[00129] Preparation Example 4

[00130] (a) 1,000g (dry basis weight) of NaY molecular sieve was pulped with 5L of deionized water to form a slurry. Then, 0.43L of RECl₃ aqueous solution (calculated in terms of RE₂O₃) with a concentration of 326g/L (the weight ratio of Ce₂O₃ to La₂O₃ was 6: 4; 0.9287mol of RE³⁺) was added for metal ion exchange (at a temperature of 60°C for a time of 1h) to obtain a metal ion exchange slurry. Among them the content of RECl₃ calculated in terms of RE₂O₃ in the NaY molecular sieve on a dry basis was 14wt%.

[00131] (b) Ammonium oxalate monohydrate (25.6g, 0.18mol) was added, and 5mL of industrial ammonia water with a concentration of 28% was further added, such that 2.4wt% of RE³⁺ in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 60°C for a time of 0.5h) to obtain a first precipitation slurry.

[00132] (c) The first precipitation slurry was filtered and drained, 1.222L of ammonium sulfate aqueous solution with a concentration of 180g/L was added, followed by the exchange at 100°C for 0.5h. After filtration and draining, 5L of water was added for rinsing, and then calcined in a 100% water vapor atmosphere at 600°C for 2h to obtain an once-exchanged and once-calcined molecular sieve dry powder.

[00133] (d) 1,000g of the once-exchanged and once-calcined molecular sieve dry powder (dry basis weight) was pulped with 5L of deionized water to form a slurry. Ammonium carbonate (18g, 0.187mol) was then added, such that 1.8wt% of RE³⁺ in the once-exchanged and once-calcined molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for a time of 0.5h), 1L of ammonium sulfate aqueous solution with a concentration of 120g/L was subsequently added to exchange at 25°C for 1h. The product was filtered, drained, then rinsed with 4L of water, dried, and calcined in an air atmosphere at 550°C for 2h, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z4.

[00134] Preparation Example 5

[00135] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00136] in step (a), 0.537L of LaCl_3 aqueous solution (calculated in terms of La_2O_3) with a concentration of 298g/L was replaced by 0.67L of LaCl_3 aqueous solution (calculated in terms of La_2O_3) with a concentration of 298g/L, such that the content of LaCl_3 calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 20wt%; the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z5.

[00137] Preparation Example 6

[00138] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00139] in step (b), ammonium oxalate monohydrate (32g, 0.225mol) was replaced with ammonium oxalate monohydrate (12.8g, 0.09mol), such that 1wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 80°C for a time of 0.5h); the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z6.

[00140] Preparation Example 7

[00141] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00142] In step (d), ammonium oxalate monohydrate (25.6g, 0.18mol) was replaced by ammonium oxalate monohydrate (6.4g, 0.045mol), such that 0.5wt% of La^{3+} in the once-exchanged and once-calcined molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for a time of 0.5h), the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as Z7.

[00143] Preparation Example 8

[00144] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00145] The modified molecular sieve DZ1 was prepared according to the method disclosed in CN200610087535.2, that is,

[00146] 1,000g (dry basis weight) of NaY molecular sieve was taken, and pulped with 8L of deionized water to form a slurry. Then, 0.385L of RECl_3 solution (calculated in terms of La_2O_3)

with a concentration of 312g/L was then added, , followed by the addition of 240g of aluminum sulfate. The mixture was subjected to ion exchange at 90°C for 1 h, and then 75 g of ammonium bicarbonate was added.. After constant-temperature stirring for 0.25 h, the mixture was filtered and rinsed with 5 L of water. The filter cake was then calcined at 600°C for 2 h in a 100% vapor atmosphere, yielding the once-exchanged and once-calcined molecular sieve dry powder.

[00147] 1,000g of the once-exchanged and once-calcined molecular sieve dry powder (dry basis weight) was taken, pulped with 6L of deionized water to form a slurry. Then,300g of ammonium sulfate was added. The mixture was exchanged at 75°C for 1h, filtered, and rinsed with 6L of water. The filter cake was dried to obtain a rare-earth-modified Y-type molecular sieve, denoted as DZ1.

[00148] Preparation Example 9

[00149] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00150] in step (d), ammonium oxalate monohydrate (32g, 0.225mol) was not added, and the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as DZ2.

[00151] Preparation Example 10

[00152] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 1, except that:

[00153] in step (b), ammonium oxalate monohydrate (25.6g, 0.18mol) was not added, and the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as DZ3.

[00154] Preparation Example 11

[00155] The rare-earth-modified Y-type molecular sieve was prepared according to the method of the preparation example 4, except that:

[00156] in step (b), ammonium oxalate monohydrate (25.6g, 0.18mol) and 5mL of industrial ammonia water with a concentration of 28% were not added, and in step (d), ammonium carbonate (18g, 0.187mol) was not added, and the other conditions were identical, obtaining a rare-earth-modified Y-type molecular sieve, denoted as DZ4.

[00157] The physical property parameters of rare-earth-modified Y-type molecular sieves (Z1-Z7 and DZ1-DZ4) obtained in Preparation Examples 1-11 were shown in Table 1.

[00158] Table 1

	Rare-earth-modified Y-type molecular sieves	SO ₄ ²⁻ content, wt%	Na ₂ O content, wt%	RE ₂ O ₃ content, wt%	Crystallini ty, C/C ₀ , %
Preparation Example 1	Z1	0.27	0.92	16.2	60
Preparation Example 2	Z2	0.41	0.98	10.4	65
Preparation Example 3	Z3	0.30	0.62	12.4	63
Preparation Example 4	Z4	0.32	0.82	14.3	62
Preparation Example 5	Z5	0.67	0.92	19.8	58
Preparation Example 6	Z6	0.82	1.1	15.6	60
Preparation Example 7	Z7	0.95	1.1	16.1	59
Preparation Example 8	DZ1	2.53	1.8	12.1	55
Preparation Example 9	DZ2	1.55	1.5	14.6	60
Preparation Example 10	DZ3	1.46	1.3	9.6	62
Preparation Example 11	DZ4	2.12	1.3	12.6	58

[00159] Test Example 1

[00160] The rare-earth-modified Y-type molecular sieves obtained in Preparation Examples 1-11 (Z1-Z7 and DZ1-DZ4) were subjected to a hydrothermal stability test.

[00161] The test conditions included: 100g (dry basis) of modified molecular sieves (Z1-Z7 and

DZ1-DZ4) were respectively tableted and crushed into 20-40 mesh particles. These particles were aged for 10 hours at 800°C under 100% water vapor in a fixed bed hydrothermal treatment device, and the micro-activity index (MA) was then measured on an automatic micro-reaction activity evaluator for catalytic cracking. The test results were shown in Table 2.

[00162] Table 2

	Modified molecular sieves	MA, wt%
Preparation Example 1	Z1	71
Preparation Example 2	Z2	65
Preparation Example 3	Z3	69
Preparation Example 4	Z4	68
Preparation Example 5	Z5	69
Preparation Example 6	Z6	67
Preparation Example 7	Z7	65
Preparation Example 8	DZ1	60
Preparation Example 9	DZ2	61
Preparation Example 10	DZ3	59
Preparation Example 11	DZ4	60

[00163] Example 1

[00164] Preparation of catalytic cracking catalyst

[00165] (1) The rare-earth-modified Y-type molecular sieve Z1, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, lanthanum oxalate and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 32wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve Z1, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and lanthanum oxalate (calculated in terms of RE_2O_3) was 20:15:7:18:38.5:1.5.

[00166] (2) The slurry was sequentially subjected to homogenizing, spray molding, and calcination at 450°C for 30min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 5 times of water, and dried at 100°C for 12h to obtain a catalytic cracking catalyst C1.

[00167] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00168] Wherein the content of Na^+ in the catalytic cracking catalyst C1 calculated in terms of Na_2O was 0.16wt%.

[00169] Example 2

[00170] Preparation of catalytic cracking catalyst

[00171] (1) The rare-earth-modified Y-type molecular sieve Z2, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, lanthanum oxalate and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 43wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve Z2, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and lanthanum oxalate (calculated in terms of RE_2O_3) was 30:9:9:8:41.4: 2.6.

[00172] (2) The slurry was sequentially subjected to homogenizing, spray molding, and calcination at 470°C for 20 min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 25wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 8 times of water, and dried at 120°C for 8h to obtain a catalytic cracking catalyst C2.

[00173] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00174] Wherein the content of Na^+ in the catalytic cracking catalyst C2 calculated in terms of Na_2O was 0.11wt%.

[00175] Example 3

[00176] Preparation of catalytic cracking catalyst

[00177] (1) The rare-earth-modified Y-type molecular sieve Z3, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, cerium oxalate and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 35wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve Z3, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and cerium oxalate (calculated in terms of RE_2O_3) was 26:12:8:15:38: 1.

[00178] (2) The slurry was sequentially subjected to homogenizing, spray molding, and

calcination at 460°C for 35 min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 5 times of water, and dried at 110°C for 10h to obtain a catalytic cracking catalyst C3.

[00179] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00180] Wherein the content of Na^+ in the catalytic cracking catalyst C3 calculated in terms of Na_2O was 0.15wt%.

[00181] Example 4

[00182] Preparation of catalytic cracking catalyst

[00183] (1) The rare-earth-modified Y-type molecular sieve Z4, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, cerium oxalate and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 39wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve Z4, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and cerium oxalate (calculated in terms of RE_2O_3) was 24:11:7.5:12:43.7: 1.8.

[00184] (2) The slurry was sequentially subjected to homogenizing, spray molding, and calcination at 450°C for 30min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 6 times of water, and dried at 110°C for 10h to obtain a catalytic cracking catalyst C4.

[00185] Wherein the weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00186] Wherein the content of Na^+ in the catalytic cracking catalyst C4 calculated in terms of Na_2O was 0.12wt%.

[00187] Example 5

[00188] The catalytic cracking catalyst was prepared according to the method in Example 1, except that:

[00189] in step (1), the rare-earth-modified Y-type molecular sieve Z1 was replaced by the rare-earth-modified Y-type molecular sieve Z5, and the other conditions were the same, the catalytic

cracking catalyst C5 was obtained.

[00190] Example 6

[00191] The catalytic cracking catalyst was prepared according to the method in Example 1, except that:

[00192] in step (1), the rare-earth-modified Y-type molecular sieve Z1 was replaced by the rare-earth-modified Y-type molecular sieve Z6, and the other conditions were the same, the catalytic cracking catalyst C6 was obtained.

[00193] Example 7

[00194] The catalytic cracking catalyst was prepared according to the method in Example 1, except that:

[00195] in step (1), the rare-earth-modified Y-type molecular sieve Z1 was replaced by the rare-earth-modified Y-type molecular sieve Z7, and the other conditions were the same, the catalytic cracking catalyst C7 was obtained.

[00196] Comparative Example 1

[00197] (1) The rare-earth-modified Y-type molecular sieve DZ1, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, lanthanum chloride and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 28wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve DZ1, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and lanthanum chloride (calculated in terms of RE_2O_3) was 22:12:7:20:38.2:0.8.

[00198] (2) The slurry was subjected to homogenizing, spray molding, and calcination at 450°C for 30min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 4 times of water, and dried at 105°C for 10h to obtain a catalytic cracking catalyst DC1.

[00199] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00200] Wherein the content of Na^+ in the catalytic cracking catalyst DC1 calculated in terms of Na_2O was 0.28wt%.

[00201] Comparative Example 2

[00202] (1) The rare-earth-modified Y-type molecular sieve DZ2, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, cerium nitrate and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 26wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve DZ2, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and cerium nitrate (calculated in terms of RE_2O_3) was 22:10:6.5:22:39:0.5.

[00203] (2) The slurry was sequentially subjected to homogenizing, spray molding, and calcination at 470°C for 30min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 4 times of water, and dried at 120°C for 10h to obtain a catalytic cracking catalyst DC2.

[00204] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00205] Wherein the content of Na^+ in the catalytic cracking catalyst DC2 calculated in terms of Na_2O was 0.23wt%.

[00206] Comparative Example 3

[00207] (1) The rare-earth-modified Y-type molecular sieve DZ3, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin, cerium chloride and water were mixed at room temperature for 1h to obtain a slurry with a solid content of 32wt%; wherein the weight ratio of the rare earth modified Y-type molecular sieve DZ3, REUSY molecular sieve, aluminum sol, acidified pseudo-boehmite, kaolin and cerium chloride (calculated in terms of RE_2O_3) was 22:12:7:20:38.2:0.8.

[00208] (2) The slurry was sequentially subjected to homogenizing, spray molding, and calcination at 430°C for 45min to obtain a catalyst precursor, which was blended with water to form a slurry containing the catalyst precursor with a solid content of 20wt%, and the slurry was then mixed with ammonium chloride, filtered, washed with 6 times of water, and dried at 100°C for 10h to obtain a catalytic cracking catalyst DC3.

[00209] The weight ratio of ammonium chloride to the slurry containing the catalyst precursor calculated in terms of the catalyst precursor was 5:100.

[00210] Wherein the content of Na^+ in the catalytic cracking catalyst DC3 calculated in terms of

Na₂O was 0.25wt%.

[00211] Comparative Example 4

[00212] The catalytic cracking catalyst was prepared according to the method in Example 1, except that:

[00213] the rare-earth-modified Y-type molecular sieve Z1 was replaced by the rare-earth-modified Y-type molecular sieve DZ4, and the other conditions were the same, the catalytic cracking catalyst DC4 was obtained.

[00214] Wherein the content of Na⁺ in the catalytic cracking catalyst DC4 calculated in terms of Na₂O was 0.23wt%.

[00215] Test Example 2

[00216] The catalytic cracking catalysts (C1-C7 and DC1-DC4) prepared in Examples 1-7 and Comparative Examples 1-4 were subjected to a reaction performance test, and the test conditions included: the aforementioned catalytic cracking catalysts (C1-C7 and DC1-DC4) were contaminated with 5,000ppm of V and 3,000ppm of Ni respectively, and treated at 800°C and 100% water vapor atmosphere condition for 5h, and then added into the ACE heavy oil microreactor with the feedstock oil from the 3 million tons heavy oil catalytic unit of Lanzhou Petrochemical Company for catalytic cracking (at a temperature of 530°C; with a catalyst-oil ratio of 5) to obtain the catalytic cracking products. The catalytic cracking products contained dry gas, liquefied gas, gasoline, diesel, heavy oil and coke. The weight ratio of the catalytic cracking catalyst to the feedstock oil from the 3 million tons heavy oil catalytic unit of Lanzhou Petrochemical Company was 5:1. The test results were shown in Table 3 and Table 4.

[00217] Table 3

	Catalytic cracking catalysts	Rare-earth-modified Y-type molecular sieves	Yield, %		
			Dry gas	Liquefied gas	Gasoline
Example 1	C1	Z1	3.94	14.96	47.12
Example 2	C2	Z2	4.02	15.45	48.55
Example 3	C3	Z3	3.86	15.97	45.91
Example 4	C4	Z4	3.92	15.64	47.43
Example 5	C5	Z5	4.31	15.78	46.01

Example 6	C6	Z6	3.79	14.38	46.47
Example 7	C7	Z7	3.88	14.75	46.64
Comparative Example 1	DC1	DZ1	4.15	14.35	43.53
Comparative Example 2	DC2	DZ2	4.08	14.65	42.97
Comparative Example 3	DC3	DZ3	4.17	14.88	43.24
Comparative Example 4	DC4	DZ4	4.23	13.92	45.22

[00218] Table 4

	Yield, %			Conversion rate ¹ , %	Total liquid recovery ² , %	Coke factor ³ , %
	Diesel	Heavy oil	Coke			
Example 1	15.36	9.33	9.29	75.31	77.44	3.046
Example 2	15.21	8.05	8.72	76.74	79.21	2.643
Example 3	15.57	9.57	9.12	74.86	77.45	3.063
Example 4	15.08	9.08	8.85	75.84	78.15	2.819
Example 5	15.00	8.95	9.95	76.05	76.79	3.133
Example 6	15.91	10.02	9.43	74.07	76.76	3.301
Example 7	15.75	9.53	9.45	74.72	77.14	3.197
Comparative Example 1	15.21	12.28	10.48	72.51	73.09	3.973
Comparative Example 2	14.47	12.85	10.98	72.68	72.09	4.127
Comparative Example 3	15.06	11.63	11.02	73.31	73.18	4.012
Comparative Example 4	15.83	10.82	9.98	73.35	74.97	3.626

Note: 1 refers to the conversion rate of feedstock oil from 3 million tons heavy oil catalytic unit in

Lanzhou Petrochemical Company, namely 100 - yield of diesel oil – yield of heavy oil; 2 refers to the total yields of liquefied gas, gasoline and diesel; 3 refers to [yield of coke* (100-conversion rate of coke)]/conversion rate.

[00219] As can be seen from the test results in Table 3 and Table 4, compared with the catalytic cracking catalysts prepared in Comparative Examples 1-4, the catalytic cracking catalysts prepared in Examples 1-7 have excellent heavy metal pollution resistance and coke selectivity, that is, the catalysts have a high conversion rate, total liquid recovery and a low coke yield and coke factor.

[00220] The above content describes in detail the preferred embodiments of the present disclosure, but the present disclosure is not limited thereto. A variety of simple modifications can be made in regard to the technical solutions of the present disclosure within the scope of the technical concept of the present disclosure, including a combination of individual technical features in any other suitable manner, such simple modifications and combinations thereof shall also be regarded as the content disclosed by the present disclosure, each of them falls into the protection scope of the present disclosure.

CLAIMS

1. A composition for a catalytic cracking catalyst comprising: a rare-earth-modified Y-type molecular sieve, a binder, a matrix material, a rare earth element source, and optionally an REUSY molecular sieve,

wherein a content of SO_4^{2-} in the rare-earth-modified Y-type molecular sieve is not greater than 1wt%.

2. The composition according to claim 1, wherein the rare earth element source is calculated based on the weight of rare earth oxide, and the composition comprises 15-35wt% of the rare-earth-modified Y-type molecular sieve, 0-20wt% of the REUSY molecular sieve, 6-30wt% of the binder, 30-55wt% of the matrix material, and 0.5-4wt% of the rare earth element source.

3. The composition according to claim 2, wherein the rare earth element source is calculated based on the weight of rare earth oxide, and the composition comprises 18-27wt% of the rare-earth-modified Y-type molecular sieve, 8-15wt% of the REUSY molecular sieve, 8-25wt% of the binder, 35-45wt% of the matrix material, and 0.5-3wt% of the rare earth element source.

4. The composition according to claim 1, wherein in the rare-earth-modified Y-type molecular sieve,

the content of SO_4^{2-} is not greater than 0.5wt%; and/or

a content of sodium calculated in terms of Na_2O is not greater than 1.5wt%; and/or

a content of rare earth calculated in terms of rare earth oxide is 5wt% -20wt%; and/or

a crystallinity C/C_0 of said rare-earth-modified Y-type molecular sieve is 50-80%.

5. The composition according to claim 4, wherein in the rare-earth-modified Y-type molecular sieve:

the content of sodium calculated in terms of Na_2O is 0.5wt%-1.2wt%; and/or

the content of rare earth calculated in terms of rare earth oxide is 10wt% -20wt%; and/or

the crystallinity C/C_0 of the rare-earth-modified Y-type molecular sieve is 58-65%.

6. The composition according to any one of claims 1-5, wherein the rare-earth-modified Y-type molecular sieve is obtained by subjecting a Na-type Y molecular sieve to a modification treatment, and the modification treatment comprises an ammonium sulfate exchange treatment step.

7. The composition according to claim 6, wherein a method of the modification treatment comprises the following steps:

(a) subjecting a Na-type Y molecular sieve to a rare earth ion exchange to obtain a rare earth ion slurry;

(b) adding a first precipitating agent into the rare earth ion slurry to cause a first precipitation of a part of rare earth ions in said rare earth ion slurry to obtain a first precipitation slurry;

(c) subjecting solid matter in the first precipitation slurry to a first ammonium sulfate exchange, a first water washing and a first calcination to obtain an once-exchanged and once-calcined molecular sieve dry powder;

(d) mixing a slurry containing the once-exchanged and once-calcined molecular sieve dry powder with a second precipitating agent to cause a second precipitation of a part of rare earth ions in the once-exchanged and once-calcined molecular sieve dry powder, and then sequentially performing a second ammonium sulfate exchange, a second water washing and an optional heat treatment to obtain the rare-earth-modified Y-type molecular sieve.

8. The composition according to claim 7, wherein in step (a), a process of the rare earth ion exchange comprises: carrying out the rare earth ion exchange between Na-type Y molecular sieve and a rare earth source in the presence of water; and/or

the rare earth ion exchange conditions comprise: a temperature between room temperature and 180°C; and/or an exchange time of 0.3-3.5h; and/or a pH of 2.8-6.5.

9. The composition according to claim 8, wherein the rare earth source is selected from chlorate and/or nitrate containing at least one of rare earth elements; and/or

the Na-type Y molecular sieve is calculated on a dry basis, the rare earth source is calculated in terms of rare earth oxide, and a content of the rare earth source in the Na-type Y molecular sieve is 1-20wt%; and/or

a weight ratio of water to the Na-type Y molecular sieve is (1.5-30) : 1.

10. The composition according to claim 9, wherein the rare earth element comprises at least one of lanthanum, cerium and yttrium; and/or

the Na-type Y molecular sieve is calculated on a dry basis, the rare earth source is calculated in terms of rare earth oxide, and the content of the rare earth source in the Na-type Y molecular sieve is 10-16wt%; and/or

the weight ratio of water to the Na-type Y molecular sieve is (2-5) : 1; and/or

the rare earth ion exchange conditions comprise: a temperature is of 50-80°C; and/or an exchange

time of 0.5-1.5h; and/or a pH of 3.5-4.5.

11. The composition according to claim 7, wherein in step (b), an amount of the first precipitating agent is based on a molar ratio for the precipitation of 1-4 wt% of the rare earth ions present in the Na-type Y molecular sieve; and/or

the conditions of the first precipitation comprise: a temperature of 25-180°C; and/or a time of 0.1-5h.

12. The composition according to claim 11, wherein in step (b), the amount of the first precipitating agent is based on a molar ratio for the precipitation of 1.5-2.5 wt% of the rare earth ions present in the Na-type Y molecular sieve; and/or

the conditions of the first precipitation comprise: a temperature of 50-80°C; and/or a time of 0.1-2h.

13. The composition according to claim 7, wherein in step (c), an amount of ammonium sulfate in the first ammonium sulfate exchange is 5-50wt% of the Na-type Y molecular sieve; and/or

the conditions of the first ammonium sulfate exchange comprise: a temperature of 20-85°C; and/or a time of 0.1-5h; and/or

the conditions of the first calcination comprise: 100% water vapor atmosphere; and/or a temperature of 400-700°C; and/or a time of 0.1-5h.

14. The composition according to claim 13, wherein in step (c), the amount of ammonium sulfate in the first ammonium sulfate exchange is 10-25wt% of the weight of Na-type Y molecular sieve; and/or

the conditions of the first ammonium sulfate exchange comprise: a temperature of 50-80°C; and/or a time of 0.1-2h; and/or

the conditions of the first calcination comprise: a temperature of 500-650°C; and/or a time of 0.5-3h; and/or

the first ammonium sulfate exchange process comprises: subjecting the solid matter in the first precipitation slurry to a first ammonium sulfate exchange with an aqueous ammonium sulfate solution.

15. The composition according to claim 14, wherein a concentration of the aqueous ammonium sulfate solution is 20-400g/L.

16. The composition according to claim 7, wherein in step (d), a weight ratio of water to the once-

exchanged and once-calcined molecular sieve dry powder in the slurry containing the once-exchanged and once-calcined molecular sieve dry powder is (1.5-30) : 1; and/or
an amount of the second precipitating agent is based on a molar ratio for the second precipitation of 0.5-3wt% of the rare earth ions present in the once-exchanged and once-calcined molecular sieve dry powder; and/or
the conditions of the second precipitation comprise: a temperature of 15-40°C; and/or a time of 0.1-5h; and/or
an amount of ammonium sulfate in the second ammonium sulfate exchange is 5-50wt% of a weight of said once-exchanged and once-calcined molecular sieve dry powder; and/or
the conditions for the second ammonium sulfate exchange comprise: a temperature of 20-85°C; and/or a time of 0.1-5h; and/or
the heat treatment comprises drying and a second calcination, and the conditions of the second calcination comprise: in an oxygen-containing atmosphere; and/or a temperature of 400-700°C; and/or a time of 0.1-10h.

17. The composition according to claim 16, wherein in step (d), the weight ratio of water to the once-exchanged and once-calcined molecular sieve dry powder in the slurry containing the once-exchanged and once-calcined molecular sieve dry powder is (2-5) : 1; and/or
the amount of the second precipitating agent is based on the molar ratio for the second precipitation of 1-2wt% of the rare earth ions present in the once-exchanged and once-calcined molecular sieve dry powder; and/or
the conditions of the second precipitation comprise: a temperature of 20-30°C; and/or a time of 0.1-2h; and/or
the amount of ammonium sulfate in the second ammonium sulfate exchange is 10-25wt% of the weight of said once-exchanged and once-calcined molecular sieve dry powder; and/or
the conditions for the second ammonium sulfate exchange comprise: a temperature of 50-80°C; and/or a time of 0.1-2h; and/or
the conditions of the second calcination comprise: a temperature of 450-650°C; and/or a time of 0.5-5h.

18. The composition according to claim 17, wherein a process of the second ammonium sulfate exchange is as follows: performing a second ammonium sulfate exchange on a product of the

second precipitation with a second aqueous ammonium sulfate solution, wherein a concentration of the second ammonium sulfate aqueous solution is 20-400g/L.

19. The composition according to claim 7, wherein the Na-type Y molecular sieve comprises at least one of NaY molecular sieve, NaHY molecular sieve, NaUSY molecular sieve, NaREHY molecular sieve and NaREUSY molecular sieve; and/or
the first precipitating agent and the second precipitating agent are each independently selected from ammonium compounds that can provide rare earth ions to generate anions of oxide precipitation precursors.

20. The composition according to claim 19, wherein the first precipitating agent and the second precipitating agent are each independently selected from one or more of ammonium oxalate, ammonium carbonate, ammonium bicarbonate and aqueous ammonia.

21. The composition according to any one of claims 1-5, wherein the binder comprises at least one of aluminum sol, acidified pseudo-boehmite, acidic silica sol and phosphate-aluminum sol; and/or
the matrix material contains clay, wherein the clay comprises at least one of kaolin, halloysite, porous stone, diatomite and sepiolite; and/or
the rare earth element source is selected from at least one of rare earth chloride, rare earth nitrate, rare earth oxide, rare earth carbonate, rare earth oxalate and rare earth acetate; and/or
the REUSY molecular sieve comprises at least one of a LaUSY molecular sieve, a CeUSY molecular sieve, and a mixed rare earth USY molecular sieve.

22. A method of preparing a catalytic cracking catalyst comprising:

- (1) homogenizing a slurry containing the composition for a catalytic cracking catalyst according to any one of claims 1-21, followed by molding and a third calcination to obtain a catalyst precursor;
- (2) performing sodium reduction and modification on the catalyst precursor to obtain the catalytic cracking catalyst.

23. The preparation method according to claim 22, wherein the solid content of the slurry containing the composition for a catalytic cracking catalyst is 25-45wt%; and/or
conditions of the third calcination comprise: a temperature of 400-550°C; and/or a time of 0.1-5h; and/or

the method for sodium reduction and modification comprises: mixing a slurry containing the

catalyst precursor with an ammonium salt to obtain a mixed solution, and then separating the solid matter from the mixed solution for drying.

24. The method according to claim 23, wherein the solid content of the slurry containing the composition for a catalytic cracking catalyst is of 35-45wt%; and/or

the conditions of the third calcination comprise: a temperature of 450-500°C; and/or a time of 0.1-2h; and/or

the ammonium salt comprises at least one of ammonium chloride, ammonium phosphate, diammonium hydrogen phosphate and diammonium dihydrogen phosphate; and/or

a weight ratio of the ammonium salt to the catalyst precursor is (2-10) :100; and/or

a solid content of the catalyst precursor-containing slurry is 0.5wt%-35wt%.

25. A catalytic cracking catalyst prepared by the method according to any one of claims 22-24.

26. The catalytic cracking catalyst according to claim 25, wherein a content of Na^+ in the catalytic cracking catalyst calculated in terms of Na_2O is not greater than 0.2wt%.

27. A use of the catalytic cracking catalyst according to claim 25 or 26 in the catalytic cracking of heavy oil.

28. The use according to claim 27, wherein the catalytic cracking catalyst is used in the catalytic cracking of heavy oil with a high content of heavy metals.

29. The use according to claim 28, wherein the heavy metals comprise V, and optionally Ni.