Heavy Oil Catalytic Cracking Catalyst and Preparation Method Therefor

Field of Technology

The present invention relates to a heavy oil catalytic cracking catalyst having a high heavy-oil-conversion capacity and the preparation method thereof, and more particularly, to a catalytic cracking catalyst suitable for residual oil blending and the preparation method thereof.

Background Art

Catalytic cracking apparatuses are crucial means for crude oil refining, and the economic benefits of refineries depend on the overall product distribution of these apparatuses. Recently, because of the growing trend towards crude oils having higher density and poorer quality, a higher heavy oil conversion capacity and higher selectivity for high-value products are demanded for FCC catalysts. The type Y molecular sieve has been a major provider of the cracking activity of heavy oil catalytic cracking catalysts, and its activity stability and cracking activity are key factors in determining the heavy oil conversion capacity of FCC catalysts.

Accordingly, extensive investigations have been carried out in domestic and abroad research institutions in order to improve the cracking activity and activity stability of type Y molecular sieves. Currently, it is largely agreed that the framework structural stability and the activity stability of molecular sieves can be improved by localizing as many rare earth ions as possible in sodalite cages in the process of rare earth modification of molecular sieves so as to suppress dealumination of the molecular sieve framework during steam aging. Patent ZL200410058089.3 describes a method for preparing rare earth-modified type Y molecular sieves, comprising steps of adjusting the pH of the system to 8-11 using an alkali solution after completion of a rare earth exchange reaction, and then carrying out conventional subsequent treatment processes. In the molecular sieves prepared by this method, rare earth ions are completely located in small cages (sodalite cages). Patent ZL200410058090.6 describes the reaction performance of the molecular sieves of ZL200410058089.3, wherein the catalyst reaction results show that localization of rare earth metals in sodalite cages improves the structural stability and the activity stability of

the molecular sieves, manifested in that the heavy oil conversion capacity of the catalyst is greatly improved, although this catalyst has poor coke selectivity.

Chinese patent ZL97122039.5 describes a preparation method for ultra-stable Y zeolites, comprising steps of putting a Y zeolite into contact with an acid solution and an ammonium-containing solution, and subjecting them to a high-temperature steam treatment, wherein the amount of the acid used is 1.5 to 6 moles of hydrogen ions per mole of framework aluminum, the concentration of the acid solution is 0.1 to 5 N, the Y zeolite is kept in contact with the acid solution at a temperature of 5 to 100°C for a duration of 0.5 to 72 h, and the weight ratio between the Y zeolite and the ammonium ion is 2 to 20. The modification method in accordance with this patent requires addition of an ammonium-containing solution for the purpose of lowering the sodium oxide content in the molecular sieve or reducing the damage to the molecular sieve structure caused by acidic gases during calcination. The FCC catalyst prepared using such molecular sieves is characteristic in its high capacity of heavy oil conversion and a high light-oil yield. However, this modification technique for molecular sieves have the following technical disadvantages: 1) since a large number of ammonium ions are added in the preparation process, ammonium-containing ions eventually enter the atmosphere or waste water, increasing ammonia nitrogen pollution and the cost for pollution control; 2) the method of this patent is unable to solve the issue of particle agglomeration in molecular sieves, which issue reduces specific surface area and pore volume of the molecular sieve and increases the obstruction in the pore channel during exchange in the molecular sieve, making it difficult to accurately and quantitatively localize the modifying element in the cages of the molecular sieve; 3) moreover, in this patent it is further mentioned that rare earth ions may also be introduced by ion exchange, during or after the contact between the Y zeolite and the ammonium-containing solution, and that during the ion exchange, ammonium ions compete with rare earth ions and preferentially take up the positions intended for rare earth ions, thereby hindering rare earth ions from entering the cages of the molecular sieve by exchange, and also lowering the utilization of rare earth ions.

Chinese patent ZL02103909.7 describes a method for preparing rare earth-containing ultra-stable Y molecular sieves by subjecting a NaY molecular sieve to one exchange process and one calcination process, characterized in that the NaY molecular sieve is placed in an ammonium solution and subjected to chemical dealumination at 25 to 100°C for 0.5 to 5 h, wherein the chemical dealumination chelating agent contains oxalic acid

and/or oxalate salts, a rare earth solution is then introduced under stirring to produce a rare earth precipitate that contains rare earth oxalate, and the precipitate is filtered and washed to give a filter cake, followed by a hydrothermal treatment to afford the molecular sieve product. Although the molecular sieve prepared by this method has certain resistance to vanadium contamination, it has relatively low activity stability and cracking activity, and is insufficient to meet the requirement set out by the growing trend towards crude oils having higher density and poorer quality. This issue is mainly attributed to the distribution of rare earth ions in the super-cages and sodalite cages of the molecular sieve during modification. This method demonstrates that rare earth ions are present in the molecular sieve system in two forms, i.e., a part of the rare earth enters sodalite cages in an ionic form while the other part is scattered over the surface of the molecular sieve as an independent phase of rare earth oxide (the precursor of which is rare earth oxalate and is converted into rare earth oxide after subsequent calcination). Such distribution reduces the stabilizing and supporting effect of rare earth ions on the molecular sieve structure. Furthermore, this method also poses a remarkable problem of ammonium nitrogen pollution, and the oxalic acid or oxalate salts added are also toxic and detrimental to the environment and human.

CN200410029875.0 discloses a preparation method for rare earth ultra-stable type Y zeolite, characterized by a step of treating zeolite with a mixed solution comprising a rare earth salt and citric acid or with a mixed solution comprising an inorganic ammonium salt, a rare earth salt and citric acid. This method simplifies the process, and the zeolite prepared thereby, when serving as an active component of a cracking catalyst, is advantageous in lowering the olefin content in gasoline products obtained from the catalytic cracking, and substantially increasing the yield of light oil products obtained from the catalytic cracking. However, this method does not specify the location of rare earth ions in the molecular sieve.

Summary of the Invention

An objective of the present invention is to provide a new catalytic cracking catalyst with high heavy-oil-conversion efficiency, and preparation methods thereof. The catalyst is characterized by a high heavy-oil-conversion capacity, moderate coke selectivity, and a high yield of the target product(s).

The present invention provides a new catalytic cracking catalyst with high heavy oil

conversion efficiency, characterized in that, in the catalyst composition, there are 2 to 50% by weight of an ultra-stable rare earth type Y molecular sieve, 0.5 to 30% by weight of one or more other molecular sieves, 0.5 to 70% by weight of clay, 1.0 to 65% by weight of high temperature resistant inorganic oxides, and 0.01 to 12.5% by weight of rare earth oxide; wherein the ultra-stable rare earth type Y molecular sieve means an ultra-stable rare earth type Y molecular sieve having 0.5 to 25% by weight of rare earth oxide, not more than 1.2% by weight of sodium oxide, a crystallinity of 40 to 75%, and a lattice parameter of 2.449 nm to 2.472 nm. The preparation process for the ultra-stable rare earth type Y molecular sieve includes a rare-earth exchange and a dispersing pre-exchange, wherein the order of the rare earth exchange and the dispersing pre-exchange is not limited, and the rare earth exchange and the dispersing pre-exchange are consecutively conducted without a calcination process therebetween. The dispersing pre-exchange refers to a process of adjusting the molecular sieve slurry's concentration to a solid content of 80 to 400 g/L and adding 0.2 to 7% by weight of a dispersing agent to carry out dispersing pre-exchange at an exchange temperature of 0 to 100°C for 0.1 to 1.5 h. The dispersing agent in the dispersing pre-exchange process is selected from one or more of sesbania gum powder, boric acid, urea, ethanol, polyacrylamide, acetic acid, oxalic acid, adipic acid, formic acid, hydrochloric acid, nitric acid, citric acid, salicylic acid, tartaric acid, benzoic acid, and starch. No ammonium salt is used in the rare earth exchange or the dispersing pre-exchange.

The present invention further provides a preparation method for the heavy oil catalytic cracking catalyst, comprising:

(1) preparation of an ultra-stable rare earth type Y molecular sieve, wherein the raw material, NaY molecular sieve (preferably with a silica-to-alumina ratio of more than 4.0, and a crystallinity of higher than 70%), is subjected to a rare earth exchange and a dispersing pre-exchange, then the molecular sieve slurry is filtered, washed, and subjected to a first calcination to afford a "one-exchange one-calcination" rare earth sodium Y molecular sieve, wherein the order of the rare earth exchange and the dispersing pre-exchange is not limited; and the "one-exchange one-calcination" rare earth sodium Y molecular sieve is then subjected to ammonium exchange for sodium reduction and a second calcination so as to obtain an ultra-stable rare earth type Y molecular sieve;

(2) preparation of the heavy oil catalyst, wherein the above ultra-stable rare earth type Y molecular sieve component, clay, and a precursor of a high temperature resistant inorganic oxide are mixed, homogenized, shaped by spraying, calcinated and washed, to obtain the

catalyst product.

In step (1) of the preparation process of the heavy oil catalytic cracking catalyst according to the present invention, i.e., in the process to obtain the ultra-stable rare earth type Y molecular sieve, between the rare earth exchange and the dispersing pre-exchange of the NaY molecular sieve, the molecular sieve slurry may or may not be washed and filtered. During the rare earth exchange, the RE_2O_3/Y zeolite (by mass) is preferably 0.005 to 0.25, most preferably 0.01 to 0.20; the exchange temperature is 0 to 100°C, preferably 60 to 95°C; the exchange pH is 2.5 to 6.0, preferably 3.5 to 5.5; and the exchange time is 0.1 to 2 h, preferably 0.3 to 1.5 h. During the dispersing pre-exchange, the amount of the dispersing agent added is 0.2 to 7% by weight, preferably 0.2 to 5% by weight; the exchange temperature is 0 to 100°C, preferably 60 to 95°C; the exchange time is 0.1 to 1.5 h. The molecular sieve slurry after modification is filtered and washed to give a filter cake, which is then dried by flash evaporation to make the water content thereof between 30% and 50%, and eventually calcinated to afford the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve, wherein general conditions may be used for the calcination, for example, calcination at 350 to 700°C under 0 to 100% water vapor for 0.3 to 3.5 h, preferably at 450 to 650°C under 15 to 100% water vapor for 0.5 to 2.5 h. The "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve is then subjected to a second exchange and a second calcination to afford the ultra-stable rare earth type Y molecular sieve according to the present invention, wherein the second exchange and the second calcination are the ammonium exchange for sodium reduction and the ultra-stabilization process well known in the industry of the field, and are not limited in the present invention.

In the "one-exchange one-calcination" process for the ultra-stable rare earth type Y molecular sieve according to the present invention, tank-type exchange, belt-type exchange and/or filter cake exchange may be employed in the exchange process of the rare earth exchange and the dispersing pre-exchange. The rare earth exchange may be carried out in which the rare earth compound solution may be divided into several portions, provided that the total amount of rare earth is not changed, to undergo tank-type exchange, belt-type exchange and/or filter cake exchange, i.e., multiple exchanges. Similarly, in the dispersing pre-exchange, the dispersing agent may be divided into several portions, provided that the total amount of the dispersing agent is not changed, to undergo tank-type exchange, belt-type exchange and/or filter cake exchange. When the rare earth exchange and the

dispersing pre-exchange are multiple exchanges, these two types of exchange may be carried out alternately.

The rare earth compound according to the present invention is rare earth chloride, rare earth nitrate or rare earth sulfate, and preferably rare earth chloride or rare earth nitrate.

The rare earth according to the present invention may be lanthanum-rich or cerium-rich rare earth, or may be pure lanthanum or pure cerium.

The dispersing agent in the dispersing pre-exchange process according to the present invention is selected from one or more of, preferably two or more of sesbania gum powder, boric acid, urea, ethanol, polyacrylamide, acetic acid, oxalic acid, adipic acid, formic acid, hydrochloric acid, nitric acid, citric acid, salicylic acid, tartaric acid, benzoic acid, and starch.

The other molecular sieves in the composition of the catalyst according to the present invention are one or more selected from type Y zeolite, L zeolite, ZSM-5 zeolite, β zeolite, aluminum phosphate zeolite, Ω zeolite, preferably type Y zeolite, ZSM-5 zeolite and β zeolite, or these zeolite having undergone a conventional physical or chemical modification, including HY, USY, REY, REHY, REUSY, H-ZSM-5, and Hβ.

The clay according to the present invention is one or more selected from kaolin, halloysite, montmorillonite, sepiolite, perlite and the like. The high-temperature-resistant inorganic oxide is one or more selected from Al_2O_3, SiO_2, SiO_2-Al_2O_3, and $AlPO_4$, and the precursor thereof includes silica-alumina gel, silica sol, alumina sol, silica-alumina composite sol, and pseudoboehmite.

The spraying condition according to the present invention is the conventional operation condition for preparation of cracking catalysts and is not limited in the present invention. The post treatment process is the same as that in the prior art, including catalyst calcination, washing, drying, etc., wherein the calcination is preferably calcination of a sprayed microsphere sample at 200 to 700°C, preferably 300 to 650°C, for 0.05 to 4 h, preferably 0.1 to 3.5 h, and the washing condition is preferably a water/catalyst weight ratio of 0.5 to 35, a washing temperature of 20 to 100°C, and a period of time of 0.1 to 0.3 h.

Detailed Description of Preferred Embodiment

Specification of Raw Materials Used in Examples

1. NaY molecular sieves: NaY-1 (the silica/alumina ratio: 4.8, crystallinity: 92%), NaY-2 (the silica/alumina ratio: 4.1, crystallinity: 83%), manufactured by Lanzhou Petrochemical Corporation, Catalyst Division.

2. Ultra-stable "one-exchange one-calcination" molecular sieve samples: crystallinity being 60%, sodium oxide being 4.3m%, manufactured by Lanzhou Petrochemical Corporation, Catalyst Division.

3. Rare earth solutions: rare earth chloride (rare earth oxide: 277.5 g/L), rare earth nitrate (rare earth oxide: 252 g/L), both of which are industrial grade and purchased from Lanzhou Petrochemical Corporation, Catalyst Division.

4. Sesbania gum powder, boric acid, urea, ethanol, polyacrylamide, oxalic acid, adipic acid, acetic acid, formic acid, hydrochloric acid, nitric acid, citric acid, salicylic acid, tartaric acid, and starch, all of which are chemically pure; ammonium chloride, ammonium nitrate, ammonium sulfate, and ammonium oxalate, all of which are industrial grade.

5. Pseudoboehmite (Loss on Ignition: 36.2%), kaolin (Loss on Ignition: 16.4%), halloysite (Loss on Ignition: 21.4%), montmorillonite (Loss on Ignition: 15.8%), perlite (Loss on Ignition: 17.6%) (all of which are solid); alumina sol with an alumina content of 23.0 weight%; silica sol with a silica content of 24.5 weight%, all of which are industrial grade.

6. REY, REHY, USY, REUSY molecular sieves, all of which are industrial grade, manufactured by Lanzhou Petrochemical Corporation, Catalyst Division; β zeolite, industrial grade, manufacture by Fushun Petrochemical Corporation; H-ZSM-5, industrial grade, manufactured by Shanghai Fudan University.

Example 1

To a reaction kettle equipped with a heating mantle, 3000 g NaY-1 molecular sieve (dry basis) and a certain amount of deionized water were consecutively added and blended into a slurry having a solid content of 220 g/L, and 82 g boric acid and 105 g sesbania gum powder were added thereto. The temperature was raised to 85°C, an exchange reaction was carried out for 0.5 h under stirring, followed by filtration and washing, the resultant filter cake was placed in the reaction kettle, and then 1.67 L rare earth chloride was added. The system pH was adjusted to 4.0, the temperature was elevated to 80°C, and an exchange reaction was carried out for 0.3 h. The resultant filter cake was dried by flash evaporation such that the moisture content thereof was 30% to 50%, and was finally calcinated under

70% water vapor at 670°C for 1.0 h to produce a "one-exchange one-calcination" rare earth sodium Y. To a reaction kettle equipped with a heating mantle, 500 g of the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve (dry basis) and a certain amount of deionized water were added to prepare a slurry having a solid content of 120 g/L, to which 120 g ammonium sulfate was added. The system pH was adjusted to 4.2, the temperature was raised to 90°C, and an exchange reaction was carried out for 0.8 h, followed by filtration and washing. The filter cake was calcinated under 80% water vapor at 560°C for 2.5 h to produce the active component of a rare earth ultra-stable Y molecular sieve according to the present invention, designated as Modified Molecular Sieve A-1.

To a reaction kettle with water bath heating, 4.381 L water, 1062 g kaolin, 986 g alumina and 63.5 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 448 g Modified Molecular Sieve A-1, 63 g H-ZSM-5, and 755 g REUSY which were then thoroughly mixed. 1500 g alumina sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 400°C for 0.5 hours. 2 kg calcinated microspheres were weighed, to which 15 kg deionized water was added, followed by washing at 60°C for 15 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as A.

Example 2

In a reaction kettle equipped with a heating mantle, 3000 g NaY-1 molecular sieve (dry basis) and a certain amount of deionized water were consecutively added and blended into a slurry having a solid content of 360 g/L, followed by addition of 0.82 L rare earth nitrate thereto. The system pH was adjusted to 3.3, the temperature was raised to 80°C, and an exchange reaction was carried out for 1.5 h, followed by filtration and washing. The resultant filter cake was placed in the reaction kettle, to which 202 g polyacrylamide and 30 g salicylic acid were then added. The temperature was then elevated to 78°C for dispersing exchange, and the exchange reaction was carried out for 0.5 h under stirring. The resultant filter cake was dried by flash evaporation such that the moisture content thereof was 30% to 50%, and was finally calcinated under 30% water vapor at 630°C for 1.8 h to produce a "one-exchange one-calcination" rare earth sodium Y. To a reaction kettle equipped with a heating mantle, 500 g of the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve (dry basis) and a certain amount of deionized water were added to prepare a slurry having a solid content of 370 g/L, to which 200 g ammonium sulfate was added. The system pH was adjusted to 3.6, the temperature was raised to 90°C, and an

exchange reaction was carried out for 1.2 h, followed by filtration and washing. The filter cake was calcinated under 20% water vapor at 600°C for 0.5 h to produce the active component of a rare earth ultra-stable Y molecular sieve according to the present invention, designated as Modified Molecular Sieve B-1.

In a reaction kettle with water bath heating, 4.620 L water, 1024 g kaolin, 971 g pseudoboehmite and 90.8 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 338 g Modified Molecular Sieve B-1, 129 g β zeolite, 806 g REHY which were then thoroughly mixed. 1304 g alumina sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 400°C for 1.0 h. 2 kg calcinated microspheres were weighed, to which 20 kg deionized water was added and stirred till uniform, followed by washing at 35°C for 40 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as B.

Example 3

To a reaction kettle equipped with a heating mantle, 3000 g NaY-1 molecular sieve (dry basis) and a certain amount of deionized water were consecutively added and blended into a slurry having a solid content of 150 g/L, followed by addition of 43 g HCl thereto. A reaction was carried out at 85°C for 1 h, followed by addition of 1.68 L rare earth chloride. The system pH was adjusted to 3.7, the temperature was raised to 90°C, and an exchange reaction was carried out for 1 h. The molecular sieve slurry was then filtered and subjected to a belt-type exchange using a dispersant under the following belt-type exchange conditions: preparing a pH=3.4 solution with 35 g oxalic acid, raising the temperature to 85°C, and the belt-type filter having a degree of vacuum of 0.04. The resultant filter cake was then dried by flash evaporation such that the moisture content thereof was 30% to 50%, and was finally calcinated under 10% water vapor at 510°C for 2.0 h to produce a "one-exchange one-calcination" rare earth sodium Y. To a reaction kettle equipped with a heating mantle, 500 g of the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve (dry basis) and deionized water were added to prepare a slurry having a solid content of 145 g/L, to which 80 g ammonium sulfate was added. The system pH was adjusted to 3.5, the temperature was raised to 90°C, and an exchange reaction was carried out for 1.2 h, followed by filtration and washing. The filter cake was calcinated under 50% water vapor at 650°C for 2 h to produce the active component of a rare earth ultra-stable Y molecular sieve according to the present invention, designated as Modified Molecular

Sieve C-1.

To a reaction kettle with water bath heating, 4.854 L water, 1125 g halloysite, 825 g pseudoboehmite and 51.4 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 406 g Modified Molecular Sieve C-1 and 903 g USY which were then thoroughly mixed. 1224 g silica sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 600°C for 0.3 h. 2 kg calcinated microspheres were weighted, to which 15 kg deionized water was added, followed by washing at 80°C for 30 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as C.

Example 4

To a reaction kettle equipped with a heating mantle, 3000 g NaY-1 molecular sieve (dry basis) and a certain amount of deionized water were consecutively added and blended into a slurry having a solid content of 320 g/L, followed by addition of 30 g nitric acid thereto. The temperature was raised to 85°C, and an exchange reaction was carried out for 0.8 h under strirring, followed by addition of 0.95 L rare earth nitrate. The system pH was adjusted to 3.3, the temperature was raised to 80°C, and an exchange reaction was carried out for 1.8 h. Finally 62 g starch was added, and the reaction was continued at 80°C for 0.5 h, followed by filtration and washing. The resultant filter cake was dried by flash evaporation such that the moisture content thereof was 30% to 50%, and was finally calcinated under 60% water vapor at 560°C for 2 h to produce a "one-exchange one-calcination" rare earth sodium Y. To a reaction kettle equipped with a heating mantle, 500 g of the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve (dry basis) and deionized water were added to prepare a slurry having a solid content of 280 g/L, to which 130 g ammonium sulfate was added. The system pH was adjusted to 4.0, the temperature was raised to 90°C, and an exchange reaction was carried out for 0.5 h, followed by filtration and washing. The filter cake was calcinated under 60% water vapor at 680°C for 1 h to produce the active component of a rare earth ultra-stable Y molecular sieve according to the present invention, designated as Modified Molecular Sieve D-1.

To a reaction kettle with water bath heating, 4.577 L water, 1055 g kaolin, 983 g alumina and 63.5 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 892 g Modified Molecular Sieve D-1, 63 g ZSM-5 zeolite, 118 g USY and 188 g REY which were then thoroughly mixed. 1500 g alumina sol was slowly

added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 400°C for 0.5 hours. 2 kg calcinated microspheres were weighed, to which 10 kg deionized water was added, followed by washing at 40°C for 20 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as D.

Example 5

To a reaction kettle equipped with a heating mantle, 3000 g NaY-1 molecular sieve (dry basis) and a certain amount of deionized water were consecutively added and blended into a slurry having a solid content of 350 g/L. 42 g citric acid and 28 g sesbania gum powder were then added thereto. The temperature was raised to 82°C, and an exchange reaction was carried out for 1.3 h under stirring. When the reaction was completed, 0.56 L rare earth nitrate was added, and an exchange reaction was carried out at 85°C for 0.8 h. Subsequently, the molecular sieve slurry was filtered and subjected to a belt-type exchange under the following belt-type exchange conditions: raising the temperature of the rare earth nitrate solution to 88°C, the pH for exchange being 4.7, the rare earth nitrate being added at RE_2O_3/Y zeolite of 0.04, and the belt-type filter having a degree of vacuum of 0.03. The resultant filter cake was then dried by flash evaporation such that the moisture content thereof was 30% to 50%, and was finally calcinated under 80% water vapor at 530°C for 1.5 h to produce a "one-exchange one-calcination" rare earth sodium Y. To a reactor equipped with a heating mantle, 500 g of the "one-exchange one-calcination" ultra-stable rare earth sodium Y molecular sieve (dry basis) and deionized water were added to prepare a slurry having a solid content of 150 g/L, to which 100 g ammonium sulfate was added. The system pH was adjusted to 4.0, the temperature was raised to 90°C, and an exchange reaction was carried out for 1 h, followed by filtration and washing. The filter cake was calcinated under 60% water vapor at 620°C for 2 h to produce the active component of a rare earth ultra-stable Y molecular sieve according to the present invention, designated as Modified Molecular Sieve E-1.

To a reaction kettle with water bath heating, 6.5 L water, 995 g kaolin, 676 g alumina and 130 ml HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 558 g Modified Molecular Sieve E-1, 19 g H-ZSM-5, and 830 g REUSY which were then thoroughly mixed. 1359 g alumina sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 500°C for 0.6 h. 2 kg calcinated microspheres were weighed, to which 19 kg deionized water was added, followed by washing at 80°C for 10 min, and were filtered and dried to

produce a cracking catalyst prepared by the present invention, designated as E.

Comparative Example 1

A REUSY molecular sieve was prepared by the same method as that shown in Example 3, except that HCl and oxalic acid were not added. The resultant ultra-stable rare earth type Y molecular sieve is designated as F-1, and the resultant catalyst is designated as F.

Comparative Example 2

In this comparative example, the molecular sieve preparation method described in CN200510114495.1 was used in order to examine the reaction performance of this molecular sieve. The preparation process for the catalyst was the same as that in Example 5.

3000 g (dry basis) ultra-stable one-exchange one-calcination molecular sieve sample (Na_2O content: 1.4 weight%, RE_2O_3 content: 8.6 weight%, lattice parameter: 2.468 nm, relative crystallinity: 62%) produced hydrothermally by the Catalyst Division of Lanzhou Petrochemical Corporation was added into a 3 L aquaeous solution of 2N oxalic acid, and was stirred until thoroughly mixed. The temperature was raised to 90 to 100°C, and a reaction was carried out for 1 hour, followed by filtration and washing. The resultant filter cake was placed into 6 L deionized water, to which a 1.46 L solution of rare earth nitrate was added. The temperature was raised to 90 to 95°C, at which a reaction was carried out for 1 hour, followed by filtration and washing. The filter cake was oven dried at 120°C to afford the molecular sieve sample of this comparative example, designated as H-1.

To a reaction kettle with water bath heating, 6.5 L water, 995 g kaolin, 676 g alumina and 130 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 558 g Modified Molecular Sieve H-1, 19 g H-ZSM-5, and 830 g REUSY which were then thoroughly mixed. 1359 g alumina sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 500°C for 0.6 h. 2 kg calcinated microspheres were weighed, to which 19 kg deionized water was added, followed by washing at 80°C for 10 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as H.

Comparative Example 3

In this comparative example, the molecular sieve preparation method described in

CN97122039.5 was used, and the preparation process for the catalyst was the same as that in Example 3.

To a reaction kettle equipped with a heating mantle, deionized water and 3000 g (dry basis) NaY-1 molecular sieve were added and blended into a slurry having a solid content of 90 g/L. The temperature was raised to 80°C under stirring, 50g HCl was added, the temperature was maintained for 8 hours, and then a 1.65 L solution of rare earth chloride and 1200 g solid ammonium chloride were added and stirred for 1 hour. Filtration and washing were performed until no chloride anion was detectable. The resultant wet filter cake (with a water content of 47%) was calcinated at 600°C for 2 hours to afford the molecular sieve sample of this comparative example, designated as G-1.

To a reaction kettle with water bath heating, 4.854 L water, 1125 g halloysite, 825 g pseudoboehmite and 51.4 mL HCl were added and thoroughly mixed, and were stirred for 1 hour, followed by consecutive addition of 406 g Modified Molecular Sieve G-1 and 903 g USY which were then thoroughly mixed. 1224 g silica sol was slowly added for gelation, and was then shaped by spraying. The resultant microspheres were calcinated at 600°C for 0.3 h. 2 kg calcinated microspheres were weighted, to which 15 kg deionized water was added, followed by washing at 80°C for 30 min, and were filtered and dried to produce a cracking catalyst prepared by the present invention, designated as G.

Industrial Applicability

Method for Analysis and Evaluation Used in the Examples

1. Lattice parameter (a_0): X-ray diffraction.
2. Crystallinity (C/C_0): X-ray diffraction.
3. Silica-to-alumina ratio: X-ray diffraction.
4. Na_2O content: flame photometry.
5. RE_2O_3 content: colorimetry.
6. Microreactor activity: samples were pretreated at 800°C under 100% water vapor for 4 hours. The raw material for the reaction was Dagang light diesel, the reaction temperature was 460°C, the reaction time was 70 seconds, the catalyst load was 5.0 g, the catalyst/oil weight ratio was 3.2, and the overall conversion percentage was taken as the microreactor activity.
7. ACE heavy oil microreactor: the reaction temperature was 530°C, the catalyst/oil ratio was 5, and the raw oil was Xinjiang oil blended with 30% vacuum residual oil.

The physical and chemical properties of the ultra-stable rare earth type Y molecular sieves prepared in the Examples and Comparative Examples in connection with the present invention are listed in Table 1. The analysis results show that the new molecular sieves are characterized by good structural stability and a small grain size as compared to those of the Comparative Examples.

Table 1. Analysis of physical and chemical properties of molecular sieves

Item	Molecular Sieve No.	Rare Earth Oxide m%	Sodium Oxide m%	Lattice Parameter nm	Relative Crystallinity %	Retaining of Relative Crystallinity %	Collapse Temperature °C	Particle size Distribution μm	
								D(v,0.5)	D(v,0.9)
Examples	A-1	15.45	1.1	2.468	51	68.2	1019	2.86	14.59
	B-1	6.89	0.94	2.462	59	72.1	1022	2.75	13.67
	C-1	15.54	0.92	2.469	51	70.2	1018	2.92	17.26
	D-1	7.98	1.05	2.461	57	70.3	1025	2.92	15.92
	E-1	8.70	0.86	2.461	55	68.8	1017	2.65	13.67
Comparative Examples	F-1	6.78	1.1	2.464	52	51.2	998	4.23	33.58
	H-1	8.27	1.60	24.67	54	54.5	1002	4.83	37.42
	G-1	12.86	1.82	24.68	49	56.3	1000	4.85	41.48

The results of evaluation of the reaction performance of the catalysts prepared in Examples 1 to 5 and the Comparative Examples are listed in Table 2.

Table 2. Evaluation results for the microreactor activity of ACE heavy oil

Catalyst No.		A	B	C	D	E	F	H	G
Molecular sieves		A-1	B-1	C-1	D-1	E-1	F-1	H-1	G-1
Mass balance m%	Dry gas	2.67	2.68	2.67	2.67	2.69	2.81	2.90	2.84
	Liquified gas	22.54	22.40	22.36	22.37	22.64	23.26	23.59	23.22
	Gasoline	54.15	54.07	54.17	54.18	53.67	52.92	52.84	53.22
	Diesel	10.46	10.56	10.54	10.50	10.59	9.82	9.69	9.99
	Heavy oil	3.58	3.59	3.61	3.64	3.70	4.31	3.94	4.11
	Coke	6.60	6.71	6.65	6.64	6.71	6.88	7.05	6.61
	Total	100	100	100	100	100	100	100	100
Conversion, m%		85.96	85.86	85.84	85.86	85.71	85.87	86.38	85.90
Total liquid yield, m%		87.15	87.03	87.07	87.05	86.89	86.00	86.11	86.44

Light oil yield, m%	64.61	64.63	64.71	64.68	64.25	62.75	62.52	63.21

From the evaluation results about the microreactor activity of ACE heavy oil, it can be seen that the catalysts prepared by the methods according to the present invention have superior heavy-oil-conversion capacity and coke selectivity as compared to comparative catalysts, and also have a total liquid yield and a light oil yield much higher than those of the comparative catalysts. Table 4 shows the evaluation results of a catalyst B riser. As compared to catalyst G, the total liquid yield of the catalyst of the present invention is increased by 0.97%, and the light oil yield thereof is increased by 0.77%, while the gasoline properties are similar.

Table 4. Evaluation results of a catalyst riser

Catalysts		Comparative catalyst G	Inventive catalyst
Mass balance, ω%	Dry gas (H2-C2)	1.05	1.17
	Liquified gas (C3-C4)	17.95	18.16
	Gasoline (C5-204°C)	50.20	50.44
	Diesel (204°C-350°C)	16.58	17.12
	Heavy oil (>350°C)	6.54	5.55
	Coke	7.36	7.30
	Loss	0.30	0.27
Selectivity ω%	Conversion	76.87	77.33
	Light oil yield	66.79	67.56
	Total liquid yield	84.74	85.71
Gasoline composition ω%	Normal alkanes	4.48	4.34
	Isoalkanes	23.75	24.50
	Gasoline olefins	45.05	44.00
	Cycloalkanes	9.97	10.01
	Aromatic hydrocarbons	16.75	17.15
Gasoline MON		83.40	83.42
Gasoline RON		93.69	93.82

One of the major active components of the novel heavy oil catalyst according to the present invention is a rare earth ultra-stable type Y molecular sieve having high cracking activity stability. In the process of preparing this molecular sieve by rare earth modification, a dispersing agent is used to pre-disperse NaY molecular sieves, thereby lowering the degree of agglomeration of molecular sieve particles, allowing more molecular sieve surface to be in contact with rare earth ions, and reducing the hindrance to rare earth ion exchange. As a result, more rare earth ions are exchanged into molecular sieve cages and then migrate into

sodalite cages in the subsequent water-vapor calcination process, and the structural stability and activity stability of the molecular sieve are improved. As rare earth ions are located in sodalite cages, there are no rare earth ions present in super-cages or on the surface, thereby reducing the acidic intensity and density in these areas, lowering the coking probability in these active sites, and satisfactorily resolving the conflict between the heavy oil conversion capacity and the coke selectivity of the catalyst.

What is claimed is:

1. A heavy oil catalytic cracking catalyst, characterized in that the catalyst comprises 2% to 50% by weight of an ultra-stable rare earth type Y molecular sieve, 0.5% to 30% by weight of one or more other molecular sieves, 0.5% to 70% by weight of clay, 1.0% to 65% by weight of high-temperature resistant inorganic oxides, and 0.01% to 12.5% by weight of rare earth oxide; wherein the ultra-stable rare earth type Y molecular sieve means an ultra-stable rare earth type Y molecular sieve having 0.5% to 25% by weight of rare earth oxide, not more than 1.2% by weight of sodium oxide, a crystallinity of 40% to 75%, and a lattice parameter of 2.449 nm to 2.472 nm; and wherein the preparation process of the ultra-stable rare earth type Y molecular sieve includes a rare earth exchange and a dispersing pre-exchange, where the order of the rare earth exchange and the dispersing pre-exchange is not limited, and the rare earth exchange and the dispersing pre-exchange are consecutively conducted without a calcination process therebetween; the dispersing pre-exchange refers to a process of adjusting the molecular sieve slurry's concentration to a solid content of 80 to 400 g/L and adding 0.2% to 7% by weight of a dispersing agent to carry out dispersing pre-exchange at an exchange temperature of 0 to 100°C for 0.1 to 1.5 h; the dispersing agent in the dispersing pre-exchange process is selected from one or more of sesbania gum powder, boric acid, urea, ethanol, polyacrylamide, acetic acid, oxalic acid, adipic acid, formic acid, hydrochloric acid, nitric acid, citric acid, salicylic acid, tartaric acid, benzoic acid, and starch; no ammonium salt is used in the rare earth exchange or the dispersing pre-exchange.

2. The catalyst according to claim 1, characterized in that the other molecular sieves are selected from one or more of type Y zeolite, L zeolite, ZSM-5 zeolite, β zeolite, aluminum phosphate zeolite, Ω zeolite, or these zeolites that have been modified.

3. The catalyst according to claim 1, characterized in that the other molecular sieves are one or more of HY, USY, REY, REHY, REUSY, H-ZSM-5, and β zeolite.

4. The catalyst according to claim 1, characterized in that the clay is selected from one or more of kaolin, halloysite, montmorillonite, sepiolite, and perlite.

5. The catalyst according to claim 1, characterized in that the high-temperature-resistant inorganic oxide is selected from one or more of Al_2O_3, SiO_2, SiO_2-Al_2O_3, and $AlPO_4$.

6. A preparation method of the catalyst according to claim 1, characterized in that the method comprises:

(1) preparation of an ultra-stable rare earth type Y molecular sieve, wherein the raw material is NaY molecular sieve, and the molecular sieve slurry is subjected to a rare earth exchange and a dispersing pre-exchange, then the molecular sieve slurry is further filtered, washed, and subjected to a first calcination to afford a "one-exchange one-calcination" rare earth sodium Y molecular sieve, wherein the order of the rare earth exchange and the dispersing pre-exchange is not limited; and the "one-exchange one-calcination" rare earth sodium Y molecular sieve is then subjected to an ammonium salt exchange for sodium reduction and a second calcination so as to obtain an ultra-stable rare earth type Y molecular sieve; and

(2) preparation of the heavy oil catalyst, wherein the above ultra-stable rare earth type Y molecular sieve, clay, and a precursor of a high-temperature resistant inorganic oxide are mixed, homogenized, shaped by spraying, calcinated and washed, to obtain the catalyst product.

7. The preparation method of the catalyst according to claim 6, characterized in that during the rare earth exchange, the mass ratio RE_2O_3/Y zeolite is 0.005 to 0.25, the exchange temperature is 0 to 100°C, the exchange pH is 2.5 to 6.0, and the exchange time is 0.1 to 2 h.

8. The preparation method of the catalyst according to claim 6, characterized in that during the dispersing pre-exchange, the amount of the dispersing agent added is 0.2% to 7% by weight, the exchange temperature is 0 to 100°C, and the exchange time is 0.1 to 1.5 h.

9. The preparation method of the catalyst according to claim 6, characterized in that

during the rare earth exchange, the mass ratio RE_2O_3/Y zeolite is 0.01 to 0.20, the exchange temperature is 60 to 95°C, exchange pH is 3.5 to 5.5, and the exchange time is 0.3 to 1.5 h; and

during the dispersing pre-exchange, the amount of the dispersing agent added is 0.2% to 5% by weight, the exchange temperature is 60 to 95°C, and the exchange time is 0.1 to 1.5 h.

10. The preparation method of the catalyst according to claim 6, characterized in that,

between the rare earth exchange and the dispersing pre-exchange, the molecular sieve slurry may or may not be washed and filtered.

11. The preparation method of the catalyst according to claim 6, characterized in that tank-type exchange, belt-type exchange and/or filter cake exchange is employed for the exchange process of the rare earth exchange or the dispersing pre-exchange.

12. The preparation method of the catalyst according to claim 6, characterized in that, in the process of the rare earth exchange, the rare earth compound solution is divided into several portions for tank-type exchange, belt-type exchange and/or filter cake exchange, i.e., multiple exchanges.

13. The preparation method of the catalyst according to claim 6, characterized in that, in the process of the dispersing pre-exchange, the dispersing agent is divided into several portions for tank-type exchange, belt-type exchange and/or filter cake exchange, i.e., multiple exchanges.

14. The preparation method of the catalyst according to claim 6, characterized in that, when the rare earth exchange and the dispersing pre-exchange are multiple exchanges, these two types of exchange are carried out alternately.

15. The preparation method of the catalyst according to claim 6, characterized in that the calcination condition for the first calcination of the molecular sieve is calcination at 350 to 700°C under 0 to 100% water vapor for 0.3 to 3.5 h.

16. The preparation method of the catalyst according to claim 6, characterized in that the precursor of the high-temperature-resistant inorganic oxide is selected from silica-alumina gel, silica sol, alumina sol, silica-alumina composite sol, and pseudoboehmite.

17. The preparation method of the catalyst according to claim 12, characterized in that the rare earth compound is rare earth chloride, rare earth nitrate or rare earth sulfate.

18. The preparation method of the catalyst according to claim 17, wherein the rare earth of the invention is lanthanum-rich rare earth, cerium-rich rare earth, pure lanthanum or pure cerium.

19. The preparation method of the catalyst according to claim 6, characterized in that the calcination condition in step (2) is calcinating the sprayed microspheres at 200 to 700°C for 0.05 to 4 hours.

20. The preparation method of the catalyst according to claim 6, characterized in that the calcination condition in step (2) is calcinating the sprayed microspheres at 300 to 650°C for 0.1 to 3.5 hours.

21. The preparation method of the catalyst according to claim 6, characterized in that the washing condition in step (2) is as follows: the weight ratio water/catalyst is 0.5 to 35, the washing temperature is 20 to 100°C, and the washing duration is 0.1 to 0.3 hours.