

CATALYTIC CRACKING COMPOSITE CATALYST, PREPARATION METHOD THEREFOR, AND USE THEREOF

CROSS REFERENCE TO RELATED APPLICATIONS

This application claims priority to Chinese Application No.202311489064.8, filed on November 9, 2023, which is specifically and entirely incorporated by reference.

TECHNICAL FIELD

The present disclosure relates to the field of cracking catalyst preparation, in particular relates to a catalytic cracking composite catalyst, a preparation method therefor and a use thereof.

BACKGROUND

Owing to China's national strategic demand for carbon peaking and carbon neutrality, as well as the impact of new energy vehicles on the traditional fuel vehicle market, China's refined oil market is becoming saturated. Diesel consumption has passed its peak, gasoline consumption is approaching its peak, and aviation kerosene still has a certain room for growth.

Against the background of rising global demand for chemical products, especially for chemical feedstocks such as ethylene and propylene, the development of catalytic cracking technology for chemical production can effectively upgrade conventional fluid catalytic cracking (FCC) technology focused on fuel oil production. By adjusting reaction conditions or replacing catalysts, product distribution can be controlled with relatively low retrofit cost. Therefore, catalytic cracking technology is the core for the transformation from oil refining to petrochemicals at the present stage. However, conventional catalytic cracking catalysts suffer from low yield of low-carbon olefins, which can hardly meet market demand. In addition, the yield of heavy oil fractions in catalytic cracking products is also one of the key indicators for evaluating the performance of catalytic cracking catalysts in refinery applications. Therefore, it is highly necessary to develop a catalytic cracking catalyst capable of processing heavy feedstock oil and producing more low-carbon olefins.

CN111718231A discloses a process for the direct catalytic conversion of crude oil to ethylene and propylene, in which different catalysts are used for light oil and heavy oil respectively. Light oil is catalyzed over a catalyst mainly containing Y-type and ZSM-5 molecular sieves as active components, while heavy oil is catalyzed over a catalyst mainly containing a mixture of multiple molecular sieves as active components. This process is complicated and cannot catalyze the cracking of light oil and heavy oil simultaneously.

CN112642472B discloses an alumina sol-bound catalyst for the conversion of hydrocarbon oils

to low-carbon olefins and BTX, as well as a preparation method and a use thereof. The catalyst employs Type-FAU and Type-IMF molecular sieves as main active components; yet when used as a main catalyst, it is difficult to further increase the yield of low-carbon olefins during catalytic cracking. Furthermore, at present, most heavy oil catalytic cracking catalysts for low-carbon olefin production mainly consist of a conventional FCC main catalyst mixed with a small amount of cocatalyst for boosting low-carbon olefin yield, so as to suppress secondary reactions such as hydrogen transfer of low-carbon olefin products. However, the mixed catalyst formed by adding propylene-enhancing cocatalysts to conventional FCC catalysts often leads to deteriorated conversion capability of heavy oil and diesel, resulting in a low heavy oil conversion rate and a high diesel yield.

Therefore, there is an urgent need to develop a novel catalytic cracking catalyst that can increase propylene yield without reducing the conversion performance of heavy oil and diesel. In other words, this catalyst has the advantage that, when used for the catalytic cracking of heavy feedstock oil, it can increase propylene yield without increasing the yields of heavy oil products and diesel.

SUMMARY

The present disclosure aims to solve the problems in the conventional technology that the catalytic cracking catalysts exhibit low conversion capability of heavy oil products and diesel while increasing the yield of low-carbon olefins, and provides a catalytic cracking composite catalyst, a preparation method therefor and a use thereof. The composite catalyst has excellent wear resistance and high propylene selectivity, and can increase the yield of low-carbon olefins without basically increasing the yields of heavy oil products and diesel.

In order to achieve the objects above, a first aspect of the present disclosure provides a catalytic cracking composite catalyst, including a catalyst A and a catalyst B;

wherein a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87 g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95; wherein a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.

A second aspect of the present disclosure provides a method for preparing a catalytic cracking composite catalyst, including:

(1) slurring Y-type molecular sieve, modified ZSM-5, a portion of a first binder with water to obtain a pre-bonded molecular sieve slurry;

(2) thoroughly mixing clay, a second binder, an inorganic acid, and water to form a matrix slurry, followed by aging;

(3) thoroughly mixing the pre-bonded molecular sieve slurry with the aged matrix slurry, then

adding the remainder of the first binder and mixing uniformly to obtain a catalyst slurry;

(4) subjecting the catalyst slurry to homogenization, spray drying and calcination to obtain a catalyst A or a catalyst B;

(5) mixing the catalyst A and the catalyst B to obtain a composite catalyst;

wherein a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87 g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95;

wherein a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.

A third aspect of the present disclosure provides a use of the catalytic cracking composite catalyst according to the first aspect, or the catalytic cracking composite catalyst prepared by the method according to the second aspect in heavy oil catalytic cracking.

Due to the technical scheme, the beneficial technical effects achieved by the present disclosure are as follows.

(1) By reducing the content of Y-type molecular sieve in the catalyst A and reducing the bulk density difference between the catalyst A and the catalyst B, the catalytic cracking composite catalyst of the present disclosure is conducive to facilitating the conversion of heavy oil and diesel over the surface of the catalyst B while avoiding the problem of increased yields of heavy oil and diesel caused by adding components with a high bulk density ratio in conventional methods, enabling more efficient conversion into gasoline that diffuses to the active sites of the molecular sieves and improving the yield of low-carbon olefins.

(2) By adding the first binder and the second binder in separate steps to obtain a composite catalyst with high shape-selective (ZSM-5) content, the catalytic cracking composite catalyst of the present disclosure reduces the amount of the binder; the Y-type molecular sieve employed with a relatively low silica-alumina ratio is more conducive to combining with the binder. The prepared catalyst has good strength, low wear index with small deviation, and strong wear resistance.

(3) During the process of the catalytic cracking of heavy oil, the catalytic cracking composite catalyst of the present disclosure can increase the yield of low-carbon olefins while keeping the yields of heavy oil products and diesel unchanged on the premise of reducing the content of Y-type molecular sieve, and can provide a high yield of liquefied petroleum gas (LPG) and a high propylene concentration in LPG, leading to a significant improvement in overall economic benefit.

DETAILED DESCRIPTION OF THE EMBODIMENTS

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 comprising 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.

A first aspect of the present disclosure provides a catalytic cracking composite catalyst, including a catalyst A and a catalyst B, a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87 g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95, and a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.

In the present disclosure, a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95, for example, 0.88, 0.89, 0.9, 0.91, 0.92, 0.93, 0.94, 0.95, and any value within the range formed by any two of these values. A dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1, for example, 2:1, 2.5:1, 3:1, 3.5:1, 4:1, and any value within the range formed by any two of these values. Controlling the bulk density of the catalyst A, the bulk density of the catalyst B, and the bulk density ratio of the catalyst A to the catalyst B, and the dry-basis weight ratio of the Y-type molecular sieve contained in the catalyst A to the Y-type molecular sieve contained in the catalyst B within the above ranges is conducive to improving the strength of the catalytic cracking composite catalyst and its catalytic activity in the catalytic cracking of heavy feedstock oil. Such control can increase the yield of low-carbon olefins and the propylene selectivity in low-carbon olefins, while keeping the yields of heavy oil products and diesel unchanged on the premise of reduced Y-type molecular sieve content, achieving excellent catalytic effects. The yield of heavy oil products is correlated with the processing capacity of heavy feedstock oil. In the present disclosure, the processing capacity of heavy feedstock oil can be enhanced by controlling the yield of heavy oil products.

Conventional catalytic cracking catalysts have a high content of Y-type molecular sieve, thus demonstrating distinct advantages in the conversion of heavy oil products and diesel. Taking Comparative Example 1, Comparative Example 4 and Example 1 as examples, a neat catalyst with 15wt% of Y-type molecular sieve content was used for conversion in Comparative Example 1, making the yield of heavy oil products 11.19% and the yield of diesel 19.08%. In Comparative Example 4, the content of Y-type molecular sieve was reduced, making the yield of heavy oil products 12.67% and the yield of diesel 19.84%, indicating that both were significantly increased. In Example 1, with a reduced content of Y-type molecular sieve, the yield of heavy oil was 11.28%, and the yield of diesel was 19.10%, which were basically unchanged, while the yield of propylene was increased by 1.19%. Therefore, the use of the catalytic cracking composite catalyst can solve the problem of increased

yields of heavy oil products and diesel caused by the reduction in the content of Y-type molecular sieve.

In some embodiments of the present disclosure, preferably, a weight ratio of catalyst A to catalyst B is 1-9:1, more preferably 7-26:3. In the present disclosure, controlling the weight ratio of the catalyst A to the catalyst B within the above range is conducive to improving the yield of low-carbon olefins and propylene selectivity of the catalytic cracking composite catalyst, while keeping the yields of heavy oil products and diesel from increasing. Within the preferred ranges, the catalytic cracking composite catalyst tends to have better catalytic effects. When the weight ratio of the catalyst A to the catalyst B is less than 1:1, the catalytic cracking composite catalyst shows a lower propylene yield and increased yields of heavy oil products and diesel.

In some embodiments of the present disclosure, preferably, a pore volume of the catalyst A is 0.31-0.37 cm³/g, and a pore volume of the catalyst B is 0.29-0.31 cm³/g. In the present disclosure, controlling the pore volume of the catalyst A and the catalyst B within the above ranges is conducive to the catalytic cracking composite catalyst exhibiting favorable catalytic performance.

In some embodiments of the present disclosure, preferably, the catalyst A contains a Y-type molecular sieve, modified ZSM-5, a binder and clay; wherein, based on a dry basis weight of the catalyst A, the catalyst A contains, on a dry basis: 10-25 wt% of a Y-type molecular sieve, 15-35 wt% of modified ZSM-5, 15-27 wt% of a binder, and 30-50 wt% of clay. Or, based on a total mass of the catalyst A, the catalyst A contains: 10-25 wt% of a Y-type molecular sieve, 15-35 wt% of modified ZSM-5, 15-27 wt% of a binder and 30-50 wt% of clay.

In some embodiments of the present disclosure, preferably, the catalyst B contains a Y-type molecular sieve, modified ZSM-5, a binder and clay; wherein, based on a dry basis weight of the catalyst B, the catalyst B contains, on a dry basis: 3-8 wt% of a Y-type molecular sieve, 25-40 wt% of modified ZSM-5, 15-27 wt% of a binder, and 30-50 wt% of clay. Or, based on a total mass of the catalyst B, the catalyst B contains: 3-8 wt% of a Y-type molecular sieve, 25-40 wt% of modified ZSM-5, 15-27 wt% of a binder, and 30-50 wt% of clay.

In the present disclosure, the catalyst A and the catalyst B contain the same type of molecular sieve raw material, and the main difference lies in the different contents of Y-type molecular sieve and modified ZSM-5 molecular sieve. Controlling the contents of the Y-type molecular sieve, modified ZSM-5, the binder and clay in the catalyst A and the catalyst B within the above ranges is conducive to obtaining the catalyst A and the catalyst B with satisfactory bulk density and bulk density ratio, so that the catalytic cracking composite catalyst can solve the problem of increased yields of heavy oil products and diesel, and improve the yield of low-carbon olefins and propylene selectivity. In the present disclosure, the contents of the Y-type molecular sieve, modified ZSM-5, the binder and clay

in the catalyst A and the catalyst B are the theoretical calculated values of the raw materials added during catalyst preparation.

In some embodiments of the present disclosure, preferably, the Y-type molecular sieve has a silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 3.1-5.

In some embodiments of the present disclosure, preferably, the Y-type molecular sieve is selected from ReUSY-type and/or USY-type molecular sieves.

In some embodiments of the present disclosure, preferably, a Re_2O_3 content in the ReUSY-type molecular sieve is $\leq 3\text{wt}\%$.

In some embodiments of the present disclosure, preferably, the modified ZSM-5 includes modified element oxides and ZSM-5; wherein modified elements contained in the modified ZSM-5 are selected from at least one of phosphorus, alkaline earth metal element and transition metal element, preferably at least two thereof.

In some embodiments of the present disclosure, preferably, the alkaline earth metal element is Mg.

In some embodiments of the present disclosure, preferably, the transition metal element is selected from at least one of Fe, Co, Ni, Zn and Cu.

In some embodiments of the present disclosure, preferably, a content of the modified elements in the modified ZSM-5 is 1.5-5wt% in terms of oxide.

In some embodiments of the present disclosure, preferably, the modified ZSM-5 is P_2O_5 -ZnO-modified ZSM-5; wherein a mass content of P_2O_5 is 2-3%, and a mass content of ZnO is 0.1-1%.

In some embodiments of the present disclosure, preferably, the binder is selected from alumina and/or silica, preferably alumina.

In some embodiments of the present disclosure, preferably, the clay is selected from at least one of kaolin, halloysite, and bentonite, preferably kaolin.

A second aspect of the present disclosure provides a method for preparing a catalytic cracking composite catalyst, including:

(1) slurring Y-type molecular sieve, modified ZSM-5, a portion of a first binder with water to obtain a pre-bonded molecular sieve slurry;

(2) thoroughly mixing clay, a second binder, an inorganic acid, and water to form a matrix slurry, followed by aging;

(3) thoroughly mixing the pre-bonded molecular sieve slurry with the aged matrix slurry, then adding the remainder of the first binder and mixing uniformly to obtain the catalyst slurry;

(4) subjecting the catalyst slurry to homogenization, spray drying and calcination to obtain a catalyst A or a catalyst B;

(5) mixing the catalyst A and the catalyst B to obtain a composite catalyst;

wherein a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87 g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95;

wherein a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.

In the present disclosure, the catalyst A and the catalyst B prepared by the above method exhibit good compatibility, and the difference in wear strength between the catalyst A and the catalyst B is small, so that the wear loss between the two catalysts is low.

In step (1)

In some embodiments of the present disclosure, preferably, in the method for preparing catalyst A, based on a dry basis weight of the pre-bonded molecular sieve slurry, a dry-basis weight ratio of the Y-type molecular sieve to the modified ZSM-5 in the pre-bonded molecular sieve slurry is 10-25:15-35.

In some embodiments of the present disclosure, preferably, in the method for preparing the catalyst B, based on a dry basis weight of the pre-bonded molecular sieve slurry, a dry-basis weight ratio of the Y-type molecular sieve to the modified ZSM-5 in the pre-bonded molecular sieve slurry is 3-8:25-40.

In some embodiments of the present disclosure, preferably, the Y-type molecular sieve has a silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 3.1-5. In the present disclosure, the relatively low silica-alumina ratio of the Y-type molecular sieve is conducive to combining with the binder, thereby improving the wear resistance of the catalytic cracking composite catalyst.

In some embodiments of the present disclosure, preferably, the Y-type molecular sieve is selected from ReUSY-type and/or USY-type molecular sieves.

In some embodiments of the present disclosure, preferably, a Re_2O_3 content in the ReUSY-type molecular sieve is $\leq 3\text{wt}\%$. In the present disclosure, controlling the Re_2O_3 content in the ReUSY-type molecular sieve within the above range is conducive to ensuring the hydrothermal stability of the catalyst, reducing the hydrogen transfer activity of the catalyst, and increasing the yield of low-carbon olefin products.

In some embodiments of the present disclosure, preferably, modified elements in the modified ZSM-5 are selected from at least one of phosphorus, alkaline earth metal element and transition metal element, preferably at least two thereof.

In some embodiments of the present disclosure, preferably, the alkaline earth metal element is Mg.

In some embodiments of the present disclosure, preferably, the transition metal element is selected from at least one of Fe, Co, Ni, Zn, and Cu.

In some embodiments of the present disclosure, preferably, a content of the modified elements in the modified ZSM-5 is 1.5-5wt% in terms of oxide. In the present disclosure, the method for preparing the modified ZSM-5 can be methods known in the art, which are not repeated here in detail.

In some embodiments of the present disclosure, preferably, the modified ZSM-5 is P_2O_5 -ZnO-modified ZSM-5; wherein a mass content of P_2O_5 is 2-3%, and a mass content of ZnO is 0.1-1%.

In some embodiments of the present disclosure, preferably, the first binder is at least divided into a portion of the first binder and a remainder of the first binder, wherein the portion of the first binder is used in step (1), and the remainder of the first binder is used in step (3).

In some embodiments of the present disclosure, preferably, the first binder is selected from at least one of silica sol, alumina sol and pseudo-boehmite, more preferably silica sol and/or alumina sol. In the present disclosure, the portion of the first binder acts as a forming aid. When the resulting catalytic cracking composite catalyst is used for heavy oil catalytic cracking, the cooperation of the portion of the first binder with the Y-type molecular sieve and the modified ZSM-5 can improve the cracking of macromolecular hydrocarbons in the matrix, endow the catalyst with favorable catalytic cracking performance, and increase the yield of low-carbon olefins while keeping the yields of heavy oil and diesel unchanged.

In some embodiments of the present disclosure, preferably, when preparing the pre-bonded molecular sieve slurry by mixing the Y-type molecular sieve, the modified ZSM-5, a portion of the first binder and water, the amount of water used is not particularly limited in the present disclosure, as long as the Y-type molecular sieve, the modified ZSM-5 and a portion of the first binder can be thoroughly mixed to obtain the pre-bonded molecular sieve slurry. For example, based on a total amount of the pre-bonded molecular sieve slurry, an amount of water is 35-40 wt%; the water is not particularly limited and is preferably deionized water.

In step (2)

In some embodiments of the present disclosure, preferably, the second binder is selected from at least one of silica sol, alumina sol and pseudo-boehmite, preferably pseudo-boehmite.

In some embodiments of the present disclosure, preferably, on a dry basis, a dry-basis weight ratio of the first binder to the second binder is 7-12: 8-15.

In some embodiments of the present disclosure, preferably, the clay is selected from at least one of kaolin, halloysite and bentonite, preferably kaolin.

In some embodiments of the present disclosure, preferably, on a dry basis, a dry-basis weight ratio of the clay to the second binder is 30-50:8-15.

In some embodiments of the present disclosure, preferably, the inorganic acid is selected from at least one of hydrochloric acid, nitric acid and sulfuric acid.

In some embodiments of the present disclosure, preferably, a molar ratio of the inorganic acid (calculated as H^+) to the second binder (on a dry basis) is 0.1-0.5:1. In the present disclosure, adding an inorganic acid to the second binder for moderate peptization is conducive to improving the fluidity of the resulting matrix slurry.

In some embodiments of the present disclosure, the clay, the second binder, inorganic acid and water are mixed to form a matrix slurry. The mixing manner in step (2) is not particularly limited in the present disclosure. Preferably, the mixing is carried out under stirring, and the stirring conditions is not particularly limited. For example, the stirring may be conducted at 100-150 r/min. In the process of forming the matrix slurry, the amount of water is not particularly limited, as long as the clay, the second binder, and inorganic acid can be thoroughly mixed to obtain the matrix slurry. For example, based on a total amount of the matrix slurry, an amount of water is 35-40 wt%; the water is not particularly limited and is preferably deionized water.

In some embodiments of the present disclosure, preferably, an aging conditions include: an aging temperature of 70-80°C, and an aging time of 0.5-1.5 h.

In step (3)

In some embodiments of the present disclosure, preferably, on a dry basis, a dry-basis weight ratio of the portion of the first binder to the remainder of the first binder is 1:1-9. That is, in the present disclosure, a mass of the portion of the first binder accounts for 10-50% of the total mass of the first binder, and a mass of the remainder of the first binder accounts for 50-90% of the total mass of the first binder.

In the present disclosure, the stepwise addition of the portion of the first binder, the remainder of the first binder and the second binder is conducive to enhancing the wear resistance of the catalytic cracking composite catalyst.

In step (4)

In some embodiments of the present disclosure, preferably, homogenization refers to high-speed dispersion of the catalyst slurry using devices known in the art with dispersing function, such as a high-speed disperser, a colloid mill, etc., so as to achieve the effects of reducing particle size and achieving uniformity.

In some embodiments of the present disclosure, preferably, a temperature for spray drying is 370-450°C, a temperature for calcination is 400-550°C, and a calcination time is 0.5-2 h.

In the present disclosure, controlling the temperature for spray drying, and the temperature and the time for calcination within the above ranges is conducive to forming a catalyst with favorable mechanical strength. The catalyst can increase the yield of low-carbon olefins while keeping the yields of heavy oil products and diesel basically unchanged in the process of heavy oil catalytic cracking.

In some embodiments of the present disclosure, more preferably, the spray drying is performed at 370-450 °C for 0.05-10 min; the calcination is performed at 400-550 °C for 0.5-2 h. In the present disclosure, a heating rate from room temperature to the set calcination temperature is 5-15°C/min, and the calcination is performed in an air atmosphere. In the present disclosure, controlling the temperature and time for spray drying and the calcination of the catalyst slurry within the aforementioned ranges is conducive to preparing a catalyst with favorable mechanical strength. The catalyst can increase the yield of low-carbon olefins while keeping the yields of heavy oil and diesel basically unchanged in the process of heavy oil catalytic cracking. Preferably, the mixing is carried out under stirring; the stirring condition is not particularly limited, and for example, the stirring may be performed at a stirring rate of 50-70 r/min.

In step (5)

In some embodiments of the present disclosure, preferably, a weight ratio of the catalyst A to the catalyst B is 1-9:1, preferably 7-26:3.

In some embodiments of the present disclosure, preferably, the mixing process of the catalyst A and the catalyst B includes, but is not limited to, one or more of mixing modes such as grinding mixing, sieving mixing, stirring mixing and the like. Preferably, the mixing is carried out under stirring; the stirring condition is not particularly limited, and for example, the stirring may be conducted at 50-70 r/min.

A third aspect of the present disclosure provides a use of the catalytic cracking composite catalyst according to the first aspect or the catalytic cracking composite catalyst prepared by the method according to the second aspect, in heavy oil catalytic cracking.

In the present disclosure, unless otherwise specified, the amount of all materials is calculated on a dry basis.

The present disclosure will be described in detail below with reference to examples.

Main analytical methods used in the present disclosure are listed as follows.

Pore volume was measured in accordance with the standard method NB/SH/T 0955.

Bulk density was measured in accordance with the standard method NB/SH/T 0954.

Wear index was measured in accordance with the standard method NB/SH/T 0964.

Micro-reactivity was measured in accordance with the standard method NB/SH/T 0952.

Performance evaluation: The reaction performance was evaluated using an ACE unit, with ACE standard feedstock as the feed oil (properties are shown in Table 1). Prior to evaluation, the catalyst was subjected to hydrothermal aging treatment at 800°C with 100 vol% water vapor for 17 h; the catalytic reaction temperature was 530°C, and the catalyst-to-oil ratio was 6.

Heavy feedstock oil conversion (wt%)=100(wt%)-heavy oil product yield (wt%)-diesel product yield (wt%)

In the present disclosure, heavy feedstock oil is converted into coke, dry gas, liquefied petroleum gas (LPG), gasoline, diesel and heavy oil products under the action of the catalytic cracking composite catalyst. The liquefied petroleum gas (LPG) contains C₂-C₄ olefins.

C₂-C₄ olefins yield (wt%)=ethylene yield (wt%)+propylene yield (wt%)+butene yield (wt%)

Propylene selectivity (wt%)=[propylene yield (wt%)×100 (wt%)]/liquefied petroleum gas (LPG) yield (wt%)

The main raw materials and their sources used in the present disclosure are listed as follows.

ReUSY-1 molecular sieve (industrial grade) was purchased from Lanzhou Petrochemical Catalyst Factory with a rare earth content (calculated as Re₂O₃) of 2.5 wt% and a silica-alumina ratio (molar ratio of SiO₂/Al₂O₃) of 3.3.

ReUSY-2 molecular sieve (industrial grade) was purchased from Lanzhou Petrochemical Catalyst Factory with a rare earth content (calculated as Re₂O₃) of 3 wt% and a silica-alumina ratio (molar ratio of SiO₂/Al₂O₃) of 3.2.

USY molecular sieve (industrial grade) was purchased from Lanzhou Petrochemical Catalyst Factory with a silica-alumina ratio (molar ratio of SiO₂/Al₂O₃) of 3.2.

Modified ZSM-5 was purchased from Lanzhou Petrochemical Catalyst Factory with a phosphorus content (calculated as P₂O₅) of 2.5 wt% and a zinc content (calculated as ZnO) of 0.5 wt%.

Silica sol was purchased from Lanzhou Petrochemical Catalyst Factory with a solid content of 30 wt%.

Alumina sol was purchased from Lanzhou Petrochemical Catalyst Factory with a solid content of 20 wt%.

Pseudo-boehmite (industrial grade) was purchased from Lanzhou Petrochemical Catalyst Factory.

Kaolin (industrial grade) was purchased from Lanzhou Petrochemical Catalyst Factory.

Hydrochloric acid (analytical grade) was purchased from Sinopharm Group with a concentration of 36 wt%.

Example 1

Preparation of a catalyst A.

(1) Subjecting ReUSY-1 molecular sieve, P₂O₅-ZnO modified ZSM-5, a portion of alumina sol and deionized water to uniformly mixing and then slurring for 60 min to obtain a pre-bonded molecular sieve slurry. On a dry basis, the amount of the portion of alumina sol accounted for 40% of the total amount of alumina sol (the sum of the mass of the portion of alumina sol and the mass of the remainder of alumina sol).

(2) Uniformly mixing kaolin, pseudo-boehmite and hydrochloric acid and deionized water under stirring, and aging the mixture at 60°C for 1 h to obtain an aged matrix slurry. The molar ratio of the hydrochloric acid (calculated as H^+) to the pseudo-boehmite (calculated as Al_2O_3) was 0.14.

(3) Mixing the aforementioned pre-bonded molecular sieve slurry with the above aged matrix slurry, then adding the remainder of the alumina sol, and continuing to mix uniformly for 30 min to obtain a catalyst slurry.

(4) Subjecting the catalyst slurry to homogenization, and spray drying at 400°C followed by calcination at 500°C for 1 h to obtain a catalyst A.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation of the catalyst A, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve, and the amount of the portion of alumina sol accounted for 20% of the total amount of the alumina sol on a dry basis;

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 17:3 to obtain a catalytic cracking composite catalyst.

The formulations of the catalyst A and the catalyst B (parts by weight of the raw materials used in the preparation process on a dry-weight basis) are shown in Table 2, and the performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Example 2

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst A is shown in Table 2, and the amount of the portion of alumina sol accounted for 20% of the total amount of the alumina sol on a dry basis.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve, the formulation of the catalyst B is shown in Table 2, and the amount of the portion of alumina sol accounted for 20% of the total amount of alumina sol on a dry basis.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 1:1 to obtain a catalytic cracking composite catalyst.

The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Example 3

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), ReUSY-2 molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst A is shown in Table 2, and the amount of the portion of alumina sol accounted for 50% of the total amount of alumina sol on a dry basis.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that: In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst B is shown in Table 2, and the amount of the portion of alumina sol accounted for 20% of the total amount of alumina sol on a dry basis.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 17:3 to obtain a catalytic cracking composite catalyst. The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Example 4

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), the formulation of the catalyst A is shown in Table 2.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst B is shown in Table 2, and the amount of the portion of alumina sol accounted for 20% of the total amount of the alumina sol on a dry basis.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 9:1 to obtain a catalytic cracking composite catalyst.

The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Example 5

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), the formulation of the catalyst A is shown in Table 2, and the amount of the portion of the alumina sol accounted for 50% of the total amount of the alumina sol on a dry basis.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst B is shown in Table 2.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 9:1 to obtain a catalytic cracking composite catalyst. The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Example 6

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 10:1 to obtain a catalytic cracking composite catalyst. The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Comparative Example 1

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that the preparation of the catalyst B and step (5) were omitted.

The formulation of the catalyst A is shown in Table 2, and the performance parameters of the catalyst A as well as the composite catalyst (catalyst A) are shown in Table 3.

Comparative Example 2

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst A is shown in Table 2, and the amount of the portion of alumina sol accounted for 10% of the total amount of alumina sol on a dry basis.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), USY molecular sieve was used instead of ReUSY-1 molecular sieve. The formulation of the catalyst B is shown in Table 2, and the amount of the portion of alumina sol accounted for 20% of the total amount of alumina sol on a dry basis.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 1:1 to obtain a catalytic cracking composite catalyst. The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Comparative Example 3

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that:

In step (1), the formulation of the catalyst B is shown in Table 2, and the amount of the portion of alumina sol accounted for 5% of the total amount of alumina sol on a dry basis.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 17:3 to obtain a catalytic cracking composite catalyst. The performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Comparative Example 4

Preparation of a catalyst A.

The preparation of the catalyst A was carried out according to the preparation method of the catalyst A in Example 1.

Preparation of a catalyst B.

The preparation of the catalyst B was carried out according to the preparation method of the catalyst A in Example 1, except that: In step (1), no Y-type molecular sieve was added, alumina sol was replaced with silica sol, and the amount of the portion of silica sol accounted for 100% of the total amount of silica sol on a dry basis; In step (3), no remainder of silica sol was added, and 75 vol% phosphoric acid was added to adjust the pH value of the catalyst slurry to 3.

(5) Mixing the catalyst A and the catalyst B at a mass ratio of 17:3 to obtain a catalytic cracking composite catalyst. The formulations of the catalyst A and the catalyst B are shown in Table 2, and the

performance parameters of the catalyst A and the catalyst B as well as the effects of the composite catalyst are shown in Table 3.

Comparative Example 5

Only the catalyst A was included, and the preparation method of the catalyst A was the same as that of the catalyst A in Comparative Example 2.

Table 1 Properties of heavy feedstock oil

Item	ACE Standard Feedstock for Evaluation
Density (20°C)/(kg/cm ³)	0.90
Carbon residue (m%)	0.47
Saturates/S (m%)	56.51
Aromatics/Ar (m%)	33.51
Resins/R (m%)	5.55
Asphaltenes (m%)	4.61
Carbon content (m%)	86.88
Hydrogen content (m%)	12.66

Table 2 Formulation of the catalyst A and the catalyst B

No.		Y-type molecular sieve	Modified ZSM-5	Alumina sol	Silica sol	Pseudo-boehmite	Kaolin
Example 1	Catalyst A	R-1/15	25	10	0	10	40
	Catalyst B	U/5	30	10	0	15	40
Example 2	Catalyst A	U/25	20	10	0	15	30
	Catalyst B	U/7	32	8	0	14	38
Example 3	Catalyst A	R-2/12	28	12	0	15	35
	Catalyst B	U/3	34	10	0	8	45
Example 4	Catalyst A	R-1/20	30	7	0	11	32
	Catalyst B	U/8	40	10	0	12	30
Example 5	Catalyst A	R-1/15	35	10	0	10	30
	Catalyst B	U/5	27	4	4	10	50
Example 6	Catalyst A	R-1/15	25	10	0	10	40
	Catalyst B	U/5	30	10	0	15	40
Comparative Example 1	Catalyst A	R-1/15	25	10	0	10	40
	Catalyst B	0	0	0	0	0	0

Comparative	Catalyst A	U/25	20	10	0	15	30
Example 2	Catalyst B	U/15	23	8	0	14	40
Comparative	Catalyst A	R-1/15	25	10	0	10	40
Example 3	Catalyst B	U/2	33	10	0	15	40
Comparative	Catalyst A	R-1/15	25	10	0	10	40
Example 4	Catalyst B	0	38	0	8	15	39
Comparative	Catalyst A	U/25	20	10	0	15	30
Example 5	Catalyst B	0	0	0	0	0	0

The content of each component in Table 2 is the weight percentage content on a dry basis. R-1 stands for ReUSY-1 molecular sieve, R-2 stands for ReUSY-2 molecular sieve, and U stands for USY molecular sieve. The content of each component in the catalyst A and the catalyst B is the theoretically calculated value based on the feed amount.

Table 3 Performance parameters of the catalysts and the composite catalyst

No.		Example					
		1	2	3	4	5	6
Pore volume (cm ³ /g)	Catalyst A	0.34	0.37	0.33	0.31	0.32	0.34
	Catalyst B	0.30	0.31	0.29	0.30	0.30	0.30
Bulk density (g/cm ³)	Catalyst A	0.75	0.73	0.79	0.77	0.75	0.75
	Catalyst B	0.84	0.83	0.87	0.81	0.85	0.84
Bulk density ratio (catalyst A/catalyst B)		0.89	0.88	0.91	0.95	0.88	0.89
Wear index (m·h ⁻¹ ·% ⁻¹)	Catalyst A	1.5	1.2	1.6	2.0	1.2	1.5
	Catalyst B	1.4	1.9	2.1	1.7	1.8	1.4
Micro- reactivity (wt%, 800°C×4h)	Catalyst A	57	61	57	58	58	57
	Catalyst B	52	53	50	55	52	52
Heavy feedstock oil conversion (wt%)		69.62	71.31	67.61	71.56	68.84	70.30
Propylene yield (wt%)		13.41	13.72	13.75	15.30	13.32	13.20
C ₂ -C ₄ olefins yield (wt%)		26.58	27.14	27.25	30.29	26.58	26.51
Liquefied petroleum gas (LPG) yield (wt%)		29.68	30.68	29.54	32.83	29.63	30.08

Gasoline yield (wt%)	26.97	27.18	26.50	25.62	26.69	27.26
Diesel yield (wt%)	19.10	18.91	19.73	17.62	19.20	18.48
Heavy oil product yield (wt%)	11.28	9.78	12.67	10.83	11.96	11.22
Propylene selectivity (wt%)	45.18	44.72	46.55	46.53	44.93	43.88

Table 3 (Continued)

No.		Comparative Example				
		1	2	3	4	5
Pore volume (cm ³ /g)	Catalyst A	0.34	0.37	0.34	0.34	0.37
	Catalyst B	-	0.33	0.27	0.28	-
Bulk density (g/cm ³)	Catalyst A	0.75	0.73	0.75	0.75	0.73
	Catalyst B	-	0.76	0.88	0.90	-
Bulk density ratio (catalyst A/catalyst B)		-	0.96	0.85	0.83	-
Wear index (m·h ⁻¹ ·% ⁻¹)	Catalyst A	1.5	1.2	1.5	1.5	1.2
	Catalyst B	-	1.4	2.3	3.0	-
Micro-reactivity (wt%, 800°C×4h)	Catalyst A	57	61	57	57	61
	Catalyst B	-	57	48	43	-
Heavy feedstock oil conversion (wt%)		69.72	72.52	68.49	67.50	72.76
Propylene yield (wt%)		12.22	13.08	12.73	12.57	11.33
C ₂ -C ₄ olefins yield (wt%)		25.06	26.71	25.41	25.09	23.37
Liquefied petroleum gas (LPG) yield (wt%)		28.54	30.59	28.64	28.11	29.08
Gasoline yield (wt%)		28.74	29.65	26.72	26.75	36.27
Diesel yield (wt%)		19.08	17.90	18.81	19.84	17.02
Heavy oil product yield (wt%)		11.19	9.58	12.70	12.67	10.21
Propylene selectivity (wt%)		42.82	42.76	44.45	44.72	38.96

The catalytic cracking composite catalyst provided by the present disclosure has a low wear index. When used in the catalytic cracking of heavy feedstock oil, it exhibits a high yield of low-carbon olefins (the yield of C₂-C₄ olefins is in the range of 26.51-30.29%) and high propylene selectivity (the

propylene yield is in the range of 13.20-15.30%), with a diesel yield in the range of 9.78-12.67% and a heavy oil product yield in the range of 9.78-11.96%. It can be seen that when the catalytic cracking composite catalyst provided by the present disclosure is used to catalyze heavy feedstock oil, on the premise of increasing the yield of low-carbon olefins and propylene yield, the diesel yield is controlled to no more than 12.67% and the heavy oil product yield is controlled to no more than 11.96%, that is, the yields of heavy oil products and diesel are not increased.

From the results of Example 1 to Example 5, it can be seen that by controlling the bulk density of the catalyst A, the bulk density of the catalyst B, the bulk density ratio of the catalyst A to the catalyst B, and the weight ratio of the Y-type molecular sieve contained in the catalyst A and the Y-type molecular sieve contained in the catalyst B within the ranges defined in the present disclosure, the obtained composite catalyst has both a high yield of low-carbon olefins and high propylene selectivity, without increasing the yields of diesel and heavy oil products, thus achieving a better overall catalytic cracking effect.

By comparing the results of Example 1 and Example 6, it can be seen that, since the weight ratio of the catalyst A to the catalyst B defined in the present disclosure is not adopted, the yield of low-carbon olefins and propylene selectivity of the obtained composite catalyst are slightly reduced.

By comparing the results of Example 1 and Comparative Example 1, it can be seen that, since only a single catalyst A is used in Comparative Example 1, the yield of low-carbon olefins and propylene selectivity of the obtained composite catalyst are lower than that of Example 1. By comparing the results of Example 1, Comparative Example 2 and Comparative Example 3, it can be seen that, in Comparative Example 2 and Comparative Example 3, the weight ratio of the Y-type molecular sieve contained in the catalyst A to that contained in the catalyst B are not within the range defined in the present disclosure, resulting in a reduced yield of low-carbon olefins and poor propylene selectivity of the obtained composite catalyst. By comparing Example 1 and Comparative Example 4, it can be seen that, in Comparative Example 4, the catalyst B is not prepared by the preparation method provided in the present disclosure, but by a conventional cocatalyst preparation method; the obtained catalyst B and the catalyst A have a large difference in wear index, resulting in high wear loss between the two catalysts, and thus the obtained composite catalyst has a low yield of low-carbon olefins.

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 which falls into the protection scope of the present disclosure.

Claims

1. A catalytic cracking composite catalyst, comprising a catalyst A and a catalyst B, wherein a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87 g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95; wherein a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.
2. The composite catalyst according to claim 1, wherein a weight ratio of catalyst A to catalyst B is 1-9:1.
3. The composite catalyst according to claim 1 or 2, wherein a pore volume of the catalyst A is 0.31-0.37 cm³/g;
and/or, a pore volume of the catalyst B is 0.29-0.31 cm³/g.
4. The composite catalyst according to claim 1, wherein, based on a dry basis weight of the catalyst A, the catalyst A comprises, on a dry basis: 10-25wt% of Y-type molecular sieve, 15-35wt% of modified ZSM-5, 15-27wt% of binder, and 30-50wt% of clay.
5. The composite catalyst according to claim 1, wherein, based on a dry basis weight of the catalyst B, the catalyst B comprises, on a dry basis: 3-8wt% of Y-type molecular sieve, 25-40wt% of modified ZSM-5, 15-27wt% of binder, and 30-50wt% of clay.
6. A method for preparing a catalytic cracking composite catalyst, comprising:
 - (1) slurring Y-type molecular sieve, modified ZSM-5, a portion of a first binder with water to obtain a pre-bonded molecular sieve slurry;
 - (2) thoroughly mixing clay, a second binder, an inorganic acid, and water to form a matrix slurry, followed by aging;
 - (3) thoroughly mixing the pre-bonded molecular sieve slurry with the aged matrix slurry, then adding the remainder of the first binder and mixing uniformly to obtain a catalyst slurry;
 - (4) subjecting the catalyst slurry to homogenization, spray drying and calcination to obtain a catalyst A or a catalyst B;
 - (5) mixing the catalyst A and the catalyst B to obtain the composite catalyst;wherein a bulk density of the catalyst A is 0.7-0.79 g/cm³, a bulk density of the catalyst B is 0.81-0.87

g/cm³, and a bulk density ratio of the catalyst A to the catalyst B is 0.88-0.95;

wherein a dry-basis weight ratio of a Y-type molecular sieve contained in catalyst A to a Y-type molecular sieve contained in catalyst B is 2-4:1.

7. The method according to claim 6, wherein, in the method for preparing the catalyst A, based on a dry basis weight of the pre-bonded molecular sieve slurry, a dry-basis weight ratio of the Y-type molecular sieve to the modified ZSM-5 in the pre-bonded molecular sieve slurry is 10-25:15-35;

and/or, in the method for preparing the catalyst B, based on a dry basis weight of the pre-bonded molecular sieve slurry, a dry-basis weight ratio of the Y-type molecular sieve to the modified ZSM-5 in the pre-bonded molecular sieve slurry is 3-8:25-40;

and/or, the Y-type molecular sieve is selected from ReUSY-type and/or USY-type molecular sieves;

and/or, the Y-type molecular sieve has a silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) of 3.1-5;

and/or, a Re_2O_3 content in the ReUSY-type molecular sieve is $\leq 3\text{wt}\%$;

and/or, modified elements contained in the modified ZSM-5 are selected from at least one of phosphorus, alkaline earth metal element, and transition metal element, preferably at least two thereof;

and/or, the alkaline earth metal element is Mg;

and/or, the transition metal element is selected from at least one of Fe, Co, Ni, Zn, and Cu;

and/or, a content of the modified elements in the modified ZSM-5 is 1.5-5wt% in terms of oxide.

8. The method according to claim 6 or 7, wherein the first binder is selected from at least one of silica sol, alumina sol, and pseudo-boehmite;

and/or, the second binder is selected from at least one of silica sol, alumina sol, and pseudo-boehmite;

and/or, on a dry basis, a dry-basis weight ratio of the first binder to the second binder is 7-12: 8-15;

and/or, the first binder consists of a portion of the first binder and a remainder of the first binder;

and/or, on a dry basis, a dry-basis weight ratio of the portion of the first binder to the remainder of the first binder is 1:1-9;

and/or, the clay is selected from at least one of kaolin, halloysite, and bentonite, preferably kaolin;

and/or, on a dry basis, a dry-basis weight ratio of the clay to the second binder is 30-50:8-15;

and/or, the inorganic acid is selected from at least one of hydrochloric acid, nitric acid, and sulfuric acid;

and/or, a molar ratio of the inorganic acid (calculated as H^+) to the second binder (on a dry basis) is 0.1-0.5:1.

9. The method according to claim 6, wherein in step (4), a temperature for spray drying is 370-450°C,

a temperature for calcination is 400-550°C, and a calcination time is 0.5-2 h.

10. Use of the catalytic cracking composite catalyst according to any one of claims 1-5, or the catalytic cracking composite catalyst prepared by the method according to any one of claims 6-9 in heavy oil catalytic cracking.