A ZSM-5 molecular sieve, its preparation method, and a lightening method

Technical Field

The present invention belongs to the fields of molecular sieve and petrochemical technology. Specifically, the present invention relates to a ZSM-5 molecular sieve and its preparation method, particularly use thereof in a lightening method of light hydrocarbons and naphtha to obtain cracking feedstock. The present invention also relates to a lightening method of light hydrocarbons and naphtha, specifically, a lightening method of light hydrocarbon and naphtha to obtain cracking feedstock.

Background Technology

With the trend towards large-scale, integrated, and base-oriented development of oil refineries and the advancement of processing technologies, light hydrocarbons are no longer cheap byproducts of refineries but are gradually becoming high-value, low-carbon resources that can be utilized. Besides converting light hydrocarbon resources into high-quality oil components, their utilization pathways are becoming increasingly molecularly refined and diversified. Furthermore, with the rapid development of clean energy, the energy consumption structure has undergone profound changes, and the contradiction of overcapacity in oil refining is intensifying. "Crude-to-chemicals" has become one of the main directions for the transformation and development of the refining industry. How to increase the production of high-quality chemical raw materials and reduce the production costs of olefins and aromatics has become a challenge faced by the refining industry on its "crude-to-chemicals" path, both now and in the future.

Ethylene is the leading product in the petrochemical industry, and its production capacity is a crucial indicator of a country's petrochemical industry development level. Steam cracking is the main process for ethylene production, typically using ethane, propane, light hydrocarbons, light naphtha, naphtha, light diesel oil, and hydrotreated tail oil, etc., as cracking feedstocks. The product distribution and yield vary significantly among different types of cracking feedstocks. For example, the yield of naphtha cracking to produce diolefins (ethylene and propylene) is approximately 40%-50%, while the yield of ethylene from ethane cracking can reach 78%, and the yield of diolefines from propane cracking can reach 60%. Studies have showed that higher n-alkane content, lower aromatic

hydrocarbon content, and a higher degree of lightening in the cracking feedstock will be more conducive to increasing the yield of high-value, low-carbon olefins and reducing the production of low-value tar.

For steam cracking units using naphtha as feedstock, the feedstock accounts for up to 80% of the total cost, making feedstock quality a key factor affecting costs. Since naphtha is the primary feedstock for most cracking units in China, improving the overall utilization rate of cracking feedstock and the yield of high-value products through naphtha upgrading is receiving increasing attention from the petrochemical industry.

Currently, many technical solutions have been proposed for naphtha upgrading, including catalytic cracking reactions, hydrogenation reactions (desulfurization), hydroisomerization, as well as aromatization of naphtha either alone or together with C4 liquefied petroleum gas under hydrogenating or non-hydrogenating conditions to produce propane, among others. Among these, the aromatization upgrading technology offers strong feedstock adaptability, operates under a non-hydrogenating system at low pressure, requires low capital investment and energy consumption, and can effectively convert refinery naphtha and light hydrocarbons. However, the liquid product yield and octane number obtained from this process remain relatively low.

Generally, naphtha upgrading catalysts comprisses a dual-functional catalyst comprising a support (such as ZSM-5 molecular sieve, mordenite, SAPO-34 molecular sieve, etc.) and a supported metal oxide. Among them, ZSM-5 molecular sieve is the most widely used in this field due to its unique ten-membered ring intersecting channel system. The pore size of ZSM-5 molecular sieve can meet the generation and diffusion of monocyclic aromatic hydrocarbons, while restricting the condensation, ring condensation, and coking of aromatic hydrocarbons; its three-dimensional intersecting channel system is conducive to the diffusion of reactants and products, improving the catalytic efficiency of the active center of the catalyst, and reducing the probability of pore blockage of zeolite by coke deposition.

CN113385215A discloses a preparation method and application of a catalyst for hydro-upgrading to produce propane. The method employs a modified core-shell structured SAPO-34/ZSM-5 composite molecular sieve catalyst to achieve catalytic cracking of light hydrocarbons for propane production under hydrogenation conditions. However, when used for naphtha hydro-upgrading, the propane yield is below 40%, which still requires

further improvement.

CN112209794A provides a method for the production of propylene through combination oflight hydrocarbon upgrading and propane dehydrogenation. The method combines light hydrocarbon upgrading to produce propane with propane catalytic dehydrogenation to produce propylene, comprising a light hydrocarbon upgrading reaction zone and a propane dehydrogenation reaction zone. The products from the light hydrocarbon upgrading and the products from the propane dehydrogenation are introduced into a common product recovery and separation system, wherein the separated and recovered light hydrocarbons are recycled as feedstock for the light hydrocarbon upgrading, and the propane is recycled as feedstock for the propane dehydrogenation.

CN110947417A discloses a catalyst for producing propane and gasoline from alkanes. The catalyst comprises a composite support and rare earth oxides in a content of 0.1-2.0% by mass based on the support. The composite support comprises 5-85% by mass ZSM-5 zeolite, 5-85% by mass MCM-41 zeolite, and 5-40% by mass alumina. This catalyst is used for the upgrading of straight-run naphtha to produce propane and gasoline under non-hydrogenation conditions, wherein the propane yield is below 40%.

CN101747933A discloses a method for aromatization and upgrading of naphtha and light hydrocarbons. This method involves aromatization and upgrading of naphtha and C_3-C_5 light hydrocarbons under hydrogenation conditions, converting low-octane-value naphtha and low-carbon hydrocarbons into high-octane-calue gasoline components and high-quality liquefied petroleum gas.

CN101367048A discloses a preparation method and application of a catalyst for condensate oil aromatization. The catalyst employs a nano-molecular sieve loaded with metal active components, and a moving-bed reactor is used to produce BTX aromatic products, while simultaneously producing 18–28 wt% of high-quality liquefied petroleum gas as a by-product. The catalyst exhibits strong resistance to coke deposition and achieves a high yield of aromatic products.

US4190519A discloses a combined process for naphtha upgrading. The process includes: fractionating naphtha to obtain light naphtha containing C6 alkanes and a heavier fraction containing methylcyclopentane; the lighter fraction recovered after reforming from the heavier fraction is mixed with the light naphtha and subjected to aromatization upgrading under non-hydrogenation conditions using a ZSM-5 type catalyst to obtain a

high-octane-value gasoline component.

US6190534B1 discloses a combined process for selectively upgrading naphtha to obtain a high-octane-value product rich in aromatics. The process includes: first, reacting naphtha feedstock with a platinum-containing catalyst in a dehydrogenation section to obtain an olefin-containing intermediate; then, reacting the olefin-containing intermediate with a solid acid aromatization catalyst in an aromatization section to obtain a product rich in aromatics.

To improve reaction efficiency, nano-ZSM-5 molecular sieves are often used as molecular sieve for naphtha lightening. This is because the diffusion capacity of reactants on molecular sieves is inversely proportional to the size of the molecular sieve; the smaller size of nano-ZSM-5 molecular sieves facilitates the proximity of reactants to active centers, promoting product diffusion. However, the synthesis of nano-sized molecular sieves involves extremely high energy and water consumption, increasing the cost of industrial production. Furthermore, existing literature reports that propane is often produced as a byproduct during the aromatization of light hydrocarbons, resulting in low propane yields, large plant circulation volumes, increased investment, and lower economic efficiency.

In summary, most of the processes reported in the prior art involve the production of a certain amount of propane as a by-product during the aromatization of light hydrocarbons (or naphtha), and generally suffer from the problem of low propane yield, which results in a large plant circulation volume, increased plant scale, and increased investment. In addition, with regard to existing propane production technologies, for example, CN 113307717 A discloses a method for producing propane by hydro-conversion of light hydrocarbons, which is primarily directed to the conversion of C4-C6 alkane mixtures to propane, and its catalyst is only mentioned to employ an acidic HZSM-5 zeolite, with no disclosure as to how naphtha feedstocks can be converted to cracking feedstocks such as propane with high selectivity. Furthermore, the reaction products obtained by this method require multi-stage separation units including an absorber tower, a stripper tower, a stabilizer tower, and a light hydrocarbon removal tower, etc., to obtain propane and mixed aromatic products, and the unreacted light hydrocarbons need to be recycled, resulting in a long production process, high distillation energy consumption, and relatively low economic efficiency.

Content of the Invention

To overcome the drawbacks of the prior art, the present invention provides a ZSM-5 molecular sieve, a preparation method thereof, and the use thereof. When a catalyst prepared using the ZSM-5 molecular sieve of the present invention is used for naphtha lightening, it can highly selectively convert naphtha (mainly hydrocarbons equal or below C_{12}) into high-quality cracking feedstock containing C_2-C_3 alkanes.

The first aspect of the present invention provides a ZSM-5 molecular sieve, wherein the total specific surface area of the ZSM-5 molecular sieve is 300-500 m^2/g, wherein the external specific surface area accounts for 33%-45% of the total specific surface area, and in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the peak area of the peak at a chemical shift of 53 ppm is ≥50% relative to the peak area of tetra-coordinated Al.

A second aspect of the present invention provides a preparation method of the ZSM-5 molecular sieve described above, comprising:

S1. mixing a first silicon source, a first template, a first alkali source, and water to obtain a seed gel; wherein the first silicon source is a solid silicon source, the molar ratio of the first alkali source to the first silicon source is 0.05-0.10, the molar ratio of the first template to the first silicon source is 0.05-0.10, and the first silicon source is calculated as SiO_2, and the first alkali source is calculated as oxide;

S2. mixing a second silicon source, an aluminum source, a second template, a second alkali source, water, and the seed gel to obtain a synthesis solution;

S3. subjecting the synthesis solution to crystallization treatment to obtain the ZSM-5 molecular sieve.

A third aspect of the present invention provides a catalyst for a lightening reaction, comprising the molecular sieve according to the first aspect or prepared by the method according to the second aspect; a binder, and a modifying metal. The binder is, for example, alumina. Herein the modifying metal is at least one of molybdenum, zinc, copper, gallium, and lanthanum. Preferably, based on the catalyst, the mass content of the molecular sieve is ≥ 70%, more preferably ≥ 75%, and even more preferably ≥ 80%. Preferably, based on the catalyst, the mass content of the modifying metal is 1%-10%, wherein the modifying metal is calculated as an oxide. Preferably, based on the catalyst, the mass content of the binder is ≤ 20%, more preferably 12%-20%.

A fourth aspect of the present invention provides a lightening method, comprising the following steps:

A1. mixing light hydrocarbons and/or naphtha with a hydrogen-rich gas to obtain a mixture;

A2. bringing the mixture obtained in step A1 into contact with an upgrading catalyst based on the ZSM-5 molecular sieve according to the first aspect of the present invention or the ZSM-5 molecular sieve prepared by the method of the second aspect of the present invention, or the catalyst of the third apsect for upgrading treatment to obtain an upgraded product;

A3. optionally, separating the upgraded product obtained in step A2 to obtain a cracking feedstock rich in C2-C3 hydrocarbons and a liquid phase, respectively; preferably, wherein the liquid phase is separated to obtain a recycled material rich in C4-C6 hydrocarbons and a mixed aromatic product, wherein the recycled material is recycled back to step A2.

The fifth aspect of the present invention provides use of the ZSM-5 molecular sieve of the first aspect of the present invention and the upgrading catalyst of the third aspect of the present invention in the lightening of naphtha.

Compared with the prior art, the present invention has the following beneficial effects:

(1) Particularly, the ZSM-5 molecular sieve of the present invention has a specific external surface area proportion, is suitable as a component of a naphtha lightening catalyst, and can significantly increase the yield of cracking feedstocks under a low hydrogen-to-oil volume ratio.

(2) The ZSM-5 molecular sieve of the present invention has an appropriate aluminum (53) content proportion, which is conducive to the adsorption and diffusion of small molecules. Its confinement effect is well suited for the catalytic production of ethane and propane.

(3) The ZSM-5 molecular sieve of the present invention is prepared by using solid silica gel as a silicon source to produce a gel seed, and then subjecting a synthesis solution containing said gel seed to crystallization under suitable conditions. By providing the gel seed, a large number of small crystal nuclei that can be utilized for crystal growth are supplied in the synthesis solution, thereby growing fine-particle molecular sieves with a large specific surface area. Moreover, the proportion of external surface area of the molecular sieve is relatively high, facilitating accessibility for reactants. In contrast, without the use of a gel seed, the molecular sieve directly grown from the synthesis solution exhibits a lower specific surface area and a relatively lower proportion of external surface

area, which is unfavorable for reactant utilization. The resulting ZSM-5 molecular sieve is particularly suitable as a catalyst component for naphtha lightening. When the prepared naphtha lightening catalyst is used in the hydro-upgrading process of naphtha, it can significantly increase the yield of cracking feedstocks under a low hydrogen-to-oil volume ratio.

(4) Surprisingly, the gel seed prepared with solid silica gel as the silicon source resulted in a significant increase in the Al(53) ratio, which indicates that the key channel intersection is rich in active catalytic sites.

(5) In the lightening method of the present invention, the naphtha feedstock is lightened and converted into high-quality cracking feedstock mainly composed of ethane and propane, which can upgrade the naphtha feedstock of the cracking unit, realize the efficient utilization of naphtha, and help improve the diolefine yield of the unit and reduce the amount of cracking tar generated.

(6) The present invention lightens naphtha feedstock under hydrogenation conditions, which can delay coking of catalyst to a certain extent and extend the single-pass operation cycle of catalyst.

(7) Using the catalyst of the present invention in the process of naphtha hydro-lightening, the yield of cracking feedstocks can be significantly increased under a low hydrogen-to-oil volume ratio (0.2–3.0).

(8) The catalyst of the present invention is preferably a metal-modified ZSM-5 zeolite catalyst. The inventors have found through research that when the ZSM-5 zeolite has an external surface area proportion of 33% to 45% and is modified with a specific metal, the resulting catalyst, when used in the process of naphtha hydro-lightening, can significantly increase the yield of cracking feedstocks under a low hydrogen-to-oil volume ratio.

Description of the Accompanying Drawings

Figure 1 is a schematic diagram of the process flow of one embodiment of the method according to the present invention.

Figure 2 is a schematic diagram of the process flow of one embodiment of the method according to the present invention;

Figure 3 is a schematic diagram of the process flow of one embodiment of the method according to the present invention;

Figure 4 is a schematic diagram of the process flow of one embodiment of the method according to the present invention;

Figure 5 is a schematic diagram of the process flow of one embodiment of the method according to the present invention;

Figure 6 is a schematic diagram of the process flow of one embodiment of the method according to the present invention;

The labels in Figures 1–6 are as follows: A. Adsorption denitrification tower, B. Feedstock–reaction product heat exchanger, C. Heater, D. Upgrading reactor, E. Stabilizer tower, F. Propane removal tower, G. Light hydrocarbon removal tower; 1. Feedstock, 2. Hydrogen-rich gas, 3. Light gas (C_1+C_2 with a small amount of H_2), 4. Cracking feedstock (C_3 with a small amount of C_2), 5. Recycled material (C_4–C_6), 6. C_{7+} stream; D1. First lightening reactor, D2. Second lightening reactor, H. Gas–liquid separator, L. Reactor, M. Cooler, N. Gas–liquid separation tank, 21. Supplemental hydrogen-rich gas, 31. Gas phase (mainly hydrogen with a small amount of methane), 51. Gas phase light hydrocarbons, 61. Mixed aromatics; S. Aromatization reactor, K. Cooler, P. Extraction unit, Q. Cooler, R. Gas–liquid separation tank, 32. C1–C3, 41. Gaseous light hydrocarbons, 7. C1+H2 purge gas, 8. C2–C3, 9. Raffinate oil.

Figure 7 is the XRD pattern of the ZSM-5 molecular sieve obtained in Example 1;

Figure 8 is the SEM image of the ZSM-5 molecular sieve obtained in Example 1;

Figure 9 is the aluminum NMR spectrum of the ZSM-5 molecular sieve obtained in Example 1;

Figure 10 is the XRD pattern of the ZSM-5 molecular sieve obtained in Example 2;

Figure 11 is the SEM image of the ZSM-5 molecular sieve obtained in Example 2;

Figure 12 is the SEM image of the ZSM-5 molecular sieve obtained in Example 4;

Figure 13 is the SEM image of the ZSM-5 molecular sieve obtained in Example 5;

Figure 14 is the XRD pattern of the ZSM-5 molecular sieve obtained in Comparative Example 1;

Figure 15 is the SEM image of the ZSM-5 molecular sieve obtained in Comparative Example 1;

Figure 16 is the XRD pattern of the ZSM-5 molecular sieve obtained in Comparative Example 2;

Figure 17 is the SEM image of the ZSM-5 molecular sieve obtained in Comparative Example 2;

Figure 18 is the XRD pattern of the ZSM-5 molecular sieve obtained in Comparative Example 3;

Figure 19 is the SEM image of the ZSM-5 molecular sieve obtained in Comparative Example 3;

Figure 20 is the XRD pattern of the ZSM-5 molecular sieve obtained in Comparative Example 4;

Figure 21 is the SEM image of the ZSM-5 molecular sieve obtained in Comparative Example 4;

Figure 22 is the aluminum NMR spectrum of the ZSM-5 molecular sieve catalyst B obtained in Preparation Example 1.

Across different figures, the same or similar components or equipments are denoted by the same or similar reference numerals.

Specific Embodiments

The present application will be described in further detail with reference to the accompanying drawings and examples hereafter. Through these descriptions, the features and advantages of the present application will become clearer and more apparent.

The term “exemplary” as used herein means “serving as an example, embodiment, or illustration". Any example illustrated herein as “exemplary” is not necessarily to be construed as superior to or better than other examples. Although various aspects of examples are shown in the accompanying drawings, the drawings are not necessarily drawn to scale unless specifically indicated otherwise.

Any specific numerical values disclosed herein (including the endpoints of numerical ranges) are not limited to their exact values, but should be understood to also include values close to the exact values, such as all possible values within ±5% of the exact values. Furthermore, with respect to the disclosed numerical ranges, one or more new numerical

ranges can be obtained by arbitrarily combinations between the endpoint values of the ranges, between the endpoint values and specific point values within the range, and between the specific point values; these new numerical ranges should also be considered as specifically disclosed herein.

Furthermore, the technical features involved in the different embodiments of the present application described below can be combined with each other as long as they do not conflict with each other.

Although the terms first, second, third, etc., may be used herein to describe various steps, elements, components, regions, layers, and/or sections, these steps, elements, components, regions, layers, and/or sections should not be limited by these terms unless otherwise specified. These terms may be used only to distinguish one step, element, component, region, layer, or section from another. Unless clearly indicated by the context, terms such as "first," "second," and other numerical terms used herein do not imply order or sequence. Therefore, the first step, element, component, region, layer, or section discussed below may be referred to as the second step, element, component, region, layer, or section without departing from the teachings of the exemplary embodiments.

The terminology used herein is for the purpose of describing particular exemplary embodiments only and is not intended to be limiting. Unless the context clearly indicates otherwise, the singular forms "a", "an", and "the" as used herein are intended to include the plural forms as well. The terms "comprising", "including", "containing", and "having" are inclusive and thus describe the presence of the stated features, elements, compositions, steps, integers, operations, and/or components, but do not exclude the presence or inclusion of one or more other features, integers, steps, operations, elements, components, and/or sets thereof. Although the open-ended term "comprising" should be understood as a non-limiting term used to describe and claim the various embodiments described herein, in some respects it may instead be understood as a more restrictive and limiting term, such as "consisting of" or "essentially consisting of". Thus, for any given embodiment describing a composition, material, component, element, feature, integer, operation, and/or process step, the present disclosure also particularly includes embodiments consisting of or substantially consisting of such compositions, materials, components, elements, features, integers, operations, and/or process steps. In the case of "consisting of", the alternative embodiments exclude any additional compositions, materials, components, elements,

features, integers, operations, and/or process steps. In the case of "essentially consisting of", any additional compositions, materials, components, elements, features, integers, operations, and/or process steps that substantially affect the essential and novel characteristics are excluded from such embodiments. However, any compositions, materials, components, elements, features, integers, operations, and/or process steps that do not substantially affect the essential and novel characteristics may be included in the embodiments.

Any method steps, processes, and operations described herein shall not be construed as necessarily requiring that they be performed in the specific order discussed or illustrated, unless expressly identified as a certain order of implementation. It is also to be understood that additional or alternative steps may be employed, unless otherwise stated.

The description of the embodiments is provided for illustration and description purposes. It is not intended to be exhaustive or limiting of the present disclosure. Individual elements or features of a particular embodiment are generally not limited to that particular embodiment, but are interchangeable and applicable to the selected embodiment where applicable, even if not explicitly shown or described. It can also be changed in many ways. Such changes should not be considered as departing from the present disclosure, and all such modifications are intended to be included within the scope of the present disclosure.

In the present application, except where expressly stated, any matters or issues not mentioned herein shall be directly applicable to those known in the art without any modification. Furthermore, any embodiments described herein may be freely combined with one or more other embodiments described herein, and the resulting technical solutions or concepts shall be considered part of the original disclosure or original record of the present application, and should not be regarded as new content not disclosed or anticipated herein, unless those skilled in the art consider the combination to be clearly unreasonable.

Unless otherwise stated, the terms used herein have the same meaning as commonly understood by those skilled in the art, and if a term is defined herein and its definition differs from the common understanding in the art, the definition herein shall prevail.

The method of the present invention is described in detail below with reference to Figure 1. The method for lightening naphtha provided by the present invention comprises: naphtha feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich

gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters upgrading reactor D, where it is brought into contact with upgrading catalyst for upgrading treatment to obtain upgraded product. The upgraded product is heat-exchanged in feedstock-reaction product heat exchanger B and then enters stabilizer tower E. Light gas 3 (C_1+C_2 with a small amount of H_2) is obtained at the top of the tower. The bottom material enters propane removal tower F, where cracking feedstock 4 (propane and a small amount of ethane) is obtained at the top of the tower. The bottom material enters light hydrocarbon removal tower G, where recycled material 5 (C_4–C_6) is obtained at the top of the tower. C_{7+} stream 6 (mixed aromatic products) is obtained at the bottom of the tower. The recycled material is mixed with the pretreated feedstock and used as feedstock for upgrading reactor D.

The method of the present invention is described in detail below with reference to Figure 2. The method for lightening naphtha provided by the present invention comprises: naphtha feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters the first reaction zone, that is, it passes through first lightening reactor D1 and second lightening reactor D2 in sequence, where it is brought into contact with naphtha lightening catalyst, that is, the first molecular sieve catalyst, to undergo reaction. The second lightening reactor D2 can be supplemented with hydrogen-rich gas 21. The resulting product enters the second reaction zone, that is, reactor L, and is brought into contact with the second molecular sieve catalyst to undergo ungrading treatment. The upgraded product is heat-exchanged in feedstock-reaction product heat exchanger B, then passes through cooler M and, after the gas phase 31 (mainly hydrogen and a small amount of methane) is discharged, it enters gas-liquid separator N to obtain gas phase product 51 (cracking feedstock) and liquid phase product 61 (mixed aromatics).

The method of the present invention is described in detail below with reference to Figure 3. The method for lightening naphtha provided by the present invention comprises: naphtha feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters the first reaction zone, i.e., reactor D. It passes through reaction

section A1 and reaction section A2 in sequence, where it is brought into contact with naphtha lightening catalyst, that is, the first molecular sieve catalyst to undergo reaction. The reactor D can be supplemented with hydrogen-rich gas 21. The resulting product enters the second reaction zone, that is, reactor L, and is brought into contact with the second molecular sieve catalyst to undergo ungrading treatment. The upgraded product is heat-exchanged in feedstock-reaction product heat exchanger B, then passes through cooler M and, after the gas phase 31 (mainly hydrogen and a small amount of methane) is discharged, it enters gas-liquid separator N to obtain gas phase product 51 (cracking feedstock) and liquid phase product 61 (mixed aromatics).

The method of the present invention is described in detail below with reference to Figure 4. The method for lightening light hydrocarbons and naphtha provided by the present invention includes: light hydrocarbon and/or naphtha feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters upgrading reaction zone, i.e., upgrading reactor D. The obtained product is heat-exchanged in feedstock-reaction product heat exchanger B and then enters stabilizer tower E. The gas phase product at the top of the tower enters propane removal tower F. The top product 32 (C1-C3) of the propane removal tower is used as cracking feedstock. The bottom product of the propane removal tower is mixed with the bottom product of the stabilizer tower E and enters aromatization reactor S. The obtained product is cooled by cooler Q and enters gas-liquid separator R to obtain gas phase product 41 (mainly a small amount of unreacted C4-C6, which can be used as recycled material). The liquid product enters extraction unit P to obtain mixed aromatics 61. The raffinate oil 9 is recycled as feedstock for aromatization reactor.

The method of the present invention is described in detail below with reference to Figure 5. The method for lightening light hydrocarbons and naphtha provided by the present invention includes: light hydrocarbon and/or naphtha feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters upgrading reaction zone, i.e., upgrading reactor D1 and upgrading reactor D2. The

upgrading reactor D2 can be supplemented with hydrogen-rich gas 2. The obtained product is heat-exchanged in feedstock-reaction product heat exchanger B and then enters stabilizer tower E. The gas phase product at the top of the tower enters propane removal tower F. The top product 32 (C1-C3) of the propane removal tower is used as cracking feedstock. The bottom product of the propane removal tower is mixed with the bottom product of the stabilizer tower E and enters aromatization reactor S. The obtained product is cooled by cooler Q and enters gas-liquid separator R to obtain gas phase product 41 (mainly a small amount of unreacted C4-C6, which can be used as recycled material). The liquid product enters extraction unit P to obtain mixed aromatics 61. The raffinate oil 9 is recycled as feedstock for upgrading reactor.

The method of the present invention is described in detail below with reference to Figure 6. The method for reforming light hydrocarbons and naphtha provided by the present invention includes: light hydrocarbon feedstock 1 is first subjected to adsorptive denitrogenation pretreatment in adsorptive denitrogenation tower A. The pretreated feedstock is mixed with hydrogen-rich gas 2 and then heat-exchanged in feedstock-reaction product heat exchanger B. After being heated by heater C, it enters the upgrading reaction zone, i.e., upgrading reactor D. After the obtained product is heat-exchanged in feedstock-reaction product heat exchanger B, and after a small amount of methane and hydrogen purge 7 is discharged, it enters cooler K. Then it enters gas-liquid separation tank H. The gas phase 8 is C2-C3 as cracking feedstock, and the liquid phase enters aromatization reactor S. The obtained product is cooled by cooler Q and enters gas-liquid separator R to obtain gas phase product 41 (mainly a small amount of unreacted C4-C6, which can be used as recycled material). The liquid phase product enters extraction unit P to obtain mixed aromatics 61. The raffinate oil 9 is recycled as feedstock for aromatization reactor.

The first aspect of the present invention provides a ZSM-5 molecular sieve, wherein the total specific surface area of the ZSM-5 molecular sieve is 300-500 m^2/g, wherein the external specific surface area accounts for 33%-45% of the total specific surface area, and in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the peak area of the peak at a chemical shift of 53 ppm is ≥50% relative to the peak area of tetra-coordinated Al.

Furthermore, the total specific surface area of the ZSM-5 molecular sieve is 350-500 m^2/g. For example, the total specific surface area of the ZSM-5 molecular sieve is 300 m^2/g, 310 m^2/g, 320 m^2/g, 330 m^2/g, 340 m^2/g, 350 m^2/g, 360 m^2/g, 370 m^2/g, 380 m^2/g, 390 m^2/g,

400 m^2/g, 410 m^2/g, 420 m^2/g, 430 m^2/g, 440 m^2/g, 450 m^2/g, 460 m^2/g, 470 m^2/g, 480 m^2/g, 490 m^2/g, 500 m^2/g and ranges formed by any two of these values. More preferably, the total specific surface area of the ZSM-5 molecular sieve is 350-500 m^2/g, more preferably 380-500 m^2/g, and even more preferably 400-500 m^2/g.

Furthermore, in the ZSM-5 molecular sieve, the external specific surface area accounts for 33%-45% of the total specific surface area, preferably 34%-45%, for example 33%, 34%, 35%, 36%, 37%, 38%, 39%, 40%, 41%, 42%, 43%, 44%, 45%, etc., and any value within the range formed by any two of these values.

Further, the ZSM-5 molecular sieve has an external specific surface area of 99-225 m^2/g. For example, the external specific surface area of the ZSM-5 molecular sieve is 100 m^2/g, 110 m^2/g, 120 m^2/g, 130 m^2/g, 140 m^2/g, 150 m^2/g, 160 m^2/g, 170 m^2/g, 180 m^2/g, 190 m^2/g, 200 m^2/g, 210 m^2/g, 220 m^2/g, 225 m^2/g, and any value within the range formed by any two of these values. More preferably, the external specific surface area of the ZSM-5 molecular sieve is 125-225 m^2/g, more preferably 132-225 m^2/g. In the context of the present invention, both specific surface area and external specific surface area refer to BET specific surface area. Specific surface area is typically determined using the BET nitrogen adsorption method, with the total surface area calculated based on multilayer adsorption theory. The microporous surface area is separated from the total surface area using the t-plot method or α-s plot method; the remaining portion is the external specific surface area.

Further, in the ZSM-5 molecular sieve, the SiO_2/Al_2O_3 molar ratio is 50-250. For example, the SiO_2/Al_2O_3 molar ratio is 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 210, 210, 220, 230, 240, or 250. Preferably, the SiO_2/Al_2O_3 molar ratio is 60-220, more preferably 70-210.

Further, in the ZSM-5 molecular sieve, the surface silica-to-alumina ratio is 30%-90% of the bulk silica-to-alumina ratio, for example, 30%, 35%, 40%, 45%, 50%, 55%, 60%, 65%, 70%, 75%, 80%, 85%, and 90%. Preferably, the surface silica-to-alumina ratio is 30%-85% of the bulk silica-to-alumina ratio, more preferably 30%-65%.

In the context of the present invention, the silica-to-alumina ratio refers to the molar ratio of SiO_2 to Al_2O_3. The surface silica-to-alumina ratio of the molecular sieve is the silica-to-alumina ratio over a thickness range of approximately 5 nm from the surface of the molecular sieve to the direction of the spherical center of the molecular sieve. The surface silica-to-alumina ratio is determined by X-ray photoelectron spectroscopy (XPS).

The bulk silica-to-alumina ratio of the molecular sieve is the overall silica-to-alumina ratio of the molecular sieve. Unless otherwise specified, the silica-to-alumina ratio refers to the bulk silica-to-alumina ratio.

In a preferred embodiment, in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the ratio of the peak area of the peak at a chemical shift of 53 ppm to the peak area of tetra-coordinated Al in the ZSM-5 molecular sieve is 50-70%, for example, 50-65%, or 50-60%. For example, in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the ratio of the peak area of the peak at a chemical shift of 53 ppm to the peak area of tetra-coordinated Al in the ZSM-5 molecular sieve is ≥50%, ≥51%, ≥52%, ≥53%, ≥54%, ≥55%, ≥56%, ≥57%, ≥58%, ≥59%, ≥60%, ≥61%, ≥62%, ≥63%, ≥64%, or ≥65%. For example, in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the ratio of the peak area of the peak at a chemical shift of 53 ppm to the peak area of tetra-coordinated Al in the ZSM-5 molecular sieve is ≤70%, ≤69%, ≤68%, ≤67%, and ≤66%.

In this context, the peak area of tetra-coordinated Al in a molecular sieve refers to the sum of the peak areas of all tetra-coordinated Al. According to some embodiments of the present invention, the tetra-coordinated Al in the molecular sieve ZSM-5 accounts for ≥90% of the total aluminum content of the molecular sieve, for example 90%, 91%, 92%, 93%, 94%, 95%, 96%, 97%, 98%, 99%, or even 100%.

In the ^{27}Al NMR spectrum of molecular sieve, the peak assignment of framework aluminum is mainly based on its coordination state, local chemical environment and dynamic evolution characteristics. In ZSM-5 molecular sieve, the chemical shift range of 50-70 ppm is usually regarded as the framework aluminum of the molecular sieve. According to the structural characteristics of the molecular sieve, it is further subdivided into different aluminum species, usually at the following chemical shifts: 49 ppm, 53 ppm, 56 ppm, 59 ppm, which are denoted here as Al (49), Al (53), Al (56), and Al (59).

Without being bound by any particular theory, the inventors of the present invention believe that the chemical shift at 53 ppm (corresponding to the channel intersection point) in the ^{27}Al NMR spectrum is the most critical, which is more suitable for the adsorption and diffusion of small molecules. Its confinement effect is suitable for the catalytic production of ethane and propane, and the aluminum (53) content is more suitable between 50-65%.

Furthermore, the ZSM-5 molecular sieve is a nanosheet aggregate, wherein the

nanosheets have a particle size of 20–300 nm and a thickness of 10–100 nm. For example, the particle size of the nanosheets is 20 nm, 40 nm, 60 nm, 80 nm, 100 nm, 120 nm, 150 nm, 180 nm, 200 nm, 220 nm, 240 nm, 260 nm, 280 nm, or 300 nm, or a range obtained by any combination of the foregoing values. For example, the thickness of the nanosheets is 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, or 100 nm, or a range obtained by any combination of the foregoing values.

In the context of the present invention, the average particle size of molecular sieve nanosheets refers to the average size of the nanosheets in the largest dimension, such as the transverse direction, and the average thickness refers to the average size of the nanosheets in the direction perpendicular to the transverse direction. The average particle size of molecular sieve aggregates refers to the average size of the molecular sieve aggregates in the largest dimension.

Furthermore, the particle size of the nanosheet aggregates of the ZSM-5 molecular sieve is 0.3-10 μm. The particle size of the aggregates can be, for example, 0.3 μm, 0.5 μm, 0.7 μm, 1 μm, 1.5 μm, 2 μm, 2.5 μm, 3 μm, 3.5 μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, 10 μm, or a range obtained by any combination of the foregoing values.

In the preferred embodiment, ZSM-5 molecular sieve is aggregates composed of nanosheets that are clustered and stacked. This not only retains the large specific surface area of the nano molecular sieve, but also effectively reduces the separation difficulty of the mother liquor and molecular sieve due to the larger size of the aggregates. This reduces the energy and water consumption in the separation process of nanoscale molecular sieves and significantly reduces industrial production costs.

Furthermore, the ZSM-5 molecular sieve has a pore volume of 0.24-0.35 cm^3/g. For example, the ZSM-5 molecular sieve has a pore volume of 0.24 cm^3/g, 0.25 cm^3/g, 0.26 cm^3/g, 0.27 cm^3/g, 0.28 cm^3/g, 0.29 cm^3/g, 0.30 cm^3/g, 0.31 cm^3/g, 0.32 cm^3/g, 0.33 cm^3/g, 0.34 cm^3/g, 0.35 cm^3/g, or a range obtained by any combination of the foregoing values.

In the context of the present invention, pore volume, also referred to as void volume, means the total volume occupied by pores within a porous material.

Furthermore, the ZSM-5 molecular sieve has a micropore volume of 0.10-0.22 cm^3/g. For example, the ZSM-5 molecular sieve has a micropore volume of 0.10 cm^3/g, 0.11 cm^3/g, 0.12 cm^3/g, 0.13 cm^3/g, 0.14 cm^3/g, 0.15 cm^3/g, 0.16 cm^3/g, 0.17 cm^3/g, 0.18 cm^3/g, 0.19 cm^3/g, 0.20 cm^3/g, 0.21 cm^3/g, 0.22 cm^3/g, or a range obtained by any combination of the

foregoing values.

In the context of the present invention, micropore volume refers to the volume occupied by micropores with a pore size of less than 2 nanometers in a porous material, such as a molecular sieve.

Furthermore, the ZSM-5 molecular sieve has an average pore size of 2.1-3.5 nm. For example, the ZSM-5 molecular sieve has an average pore size of 2.1 nm, 2.2 nm, 2.3 nm, 2.4 nm, 2.5 nm, 2.6 nm, 2.7 nm, 2.8 nm, 2.9 nm, 3.0 nm, 3.1 nm, 3.2 nm, 3.3 nm, 3.4 nm, 3.5 nm, or a range obtained by any combination of the foregoing values.

In the context of the present invention, average pore size refers to the average diameter of the internal pores of a molecular sieve.

In the context of the present invention, agglomerates are aggregates formed by interconnected nanosheets. Agglomerates not only retain the large specific surface area of molecular sieve nanosheets, but also effectively reduce the difficulty of separating the mother liquor from the molecular sieve due to their larger size, thereby reducing industrial production costs.

The second aspect of the present invention provides a preparation method of the ZSM-5 molecular sieve described above, comprising:

S1. mixing a first silicon source, a first template, a first alkali source, and water to obtain a seed gel; wherein the first silicon source is a solid silicon source, the molar ratio of the first alkali source to the first silicon source is 0.05-0.10, the molar ratio of the first template to the first silicon source is 0.05-0.10, and the first silicon source is calculated as SiO_2, and the first alkali source is calculated as oxide;

S2. mixing a second silicon source, an aluminum source, a second template, a second alkali source, water, and the seed gel to obtain a synthesis solution;

S3. subjecting the synthesis solution to crystallization treatment to obtain the ZSM-5 molecular sieve.

Without being bound by any particular theory, the slower dissolution rate of the solid silicon source results in more uniform release of silicon species (such as silicate ions), which is beneficial for forming a highly ordered microporous structure. By contrast, silica sol, being nanoscale silica, exhibits higher activity in gel solutions, potentially leading to localized gel inhomogeneity and a greater likelihood of untransformed silica during synthesis. Furthermore, from a manufacturing perspective, silica gel powder is easier to

transport and store, and its purity is controllable, making it suitable for industrial production. In actual catalyst development, silica gel powder has proven more effective in preparing gel precursors. It is speculated that during gel precrystallization, the slower dissolution and release of the silicon source compared to the particle activity of silica sol allows for the growth of numerous small crystal nuclei during precrystallization, which are then available for secondary crystallization to produce nano-aggregates.

In the context of the present invention, the alkali source is calculated as oxide. For example, when sodium hydroxide is used, it is calculated as Na_2O. When potassium hydroxide is used, it is considered as K_2O. In the case of ammonia, it is considered as two moles of ammonia.

Furthermore, in the preparation process of the seed gel described in step S1, conditions of the mixing are stirring at 40-120 °C for 6-30 hours.

Further, in the preparation process of the seed gel decribed in step S1, the solid silicon source is silica gel powder with a particle size of 60-800 mesh, preferably 100-300 mesh. For example, the particle size of the silica gel powder can be 60 mesh, 80 mesh, 100 mesh, 120 mesh, 140 mesh, 160 mesh, 180 mesh, 200 mesh, 220 mesh, 240 mesh, 260 mesh, 280 mesh, 300 mesh, 350 mesh, 400 mesh, 450 mesh, 500 mesh, 550 mesh, 600 mesh, 650 mesh, 700 mesh, 750 mesh, or 800 mesh. Smaller particle sizes of silica gel powder are also feasible.

Further, in step S1, the first template is at least one of n-butylamine, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium bromide, tetraethylammonium bromide, ethylenediamine, or hexamethylenediamine.

Further, in step S1, the first alkali source is at least one of sodium hydroxide, potassium hydroxide, and ammonia water.

Furthermore, the molar ratio of water to the first silicon source is 5-30; wherein the first silicon source is calculated as SiO_2.

Furthermore, the second template is an organic amine, preferably at least one of n-butylamine, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium bromide, tetraethylammonium bromide, ethylenediamine, triethylamine, or hexamethylenediamine.

Further, the second silicon source is at least one selected from silica sol, water glass, fumed silica, and silica gel, preferably silica gel, more preferably silica gel powder, with a

particle size of 60-800 mesh, preferably 100-300 mesh. For example, the particle size of the silica gel powder can be 60 mesh, 80 mesh, 100 mesh, 120 mesh, 140 mesh, 160 mesh, 180 mesh, 200 mesh, 220 mesh, 240 mesh, 260 mesh, 280 mesh, 300 mesh, 350 mesh, 400 mesh, 450 mesh, 500 mesh, 550 mesh, 600 mesh, 650 mesh, 700 mesh, 750 mesh, or 800 mesh. Smaller particle sizes of silica gel powder are also feasible.

Furthermore, the aluminum source is at least one of sodium aluminate, aluminum sulfate, and aluminum isopropoxide.

Furthermore, the second alkali source is at least one of sodium hydroxide, potassium hydroxide, and ammonia water.

According to a preferred aspect, the molar ratio of the second silicon source to the aluminum source is 30-100; wherein the second silicon source is calculated as SiO_2 and the aluminum source is calculated as Al_2O_3.

According to a preferred aspect, the molar ratio of the second template to the second silicon source is 0.02-0.10, wherein the second silicon source is calculated as SiO_2.

According to a preferred aspect, the molar ratio of the second alkali source to the second silicon source is 0.07-0.12, wherein the second silicon source is calculated as SiO_2 and the second alkali source is calculated as oxide.

According to a preferred aspect, the molar ratio of water to the second silicon source is 15-30, wherein the second silicon source is calculated as SiO_2.

According to a preferred aspect, the mass ratio of the seed gel to the second silicon source is 1%-20%, preferably 3%-10%, wherein the second silicon source is calculated as SiO_2 and the seed gel is calculated as SiO_2.

Conventional methods for crystallization are well known to those skilled in the art. According to a preferred aspect, conditions of the crystallization in step S3 include: crystallization temperature of 125-180 °C and crystallization time of 16-96 h, for example, 16-60 h, under sealed conditions. According to a preferred aspect, the crystallization in step S3 can be carried out at a relatively low temperature, for example, 130 °C, for 24-48 h, and then further crystallized at a relatively high temperature, for example, 170 °C, for another 24-48 h. According to a preferred aspect, the crystallization in step S3 is carried out in an autoclave.

In the above technical solution, after the crystallization step is completed, the molecular sieve can be separated from the obtained product mixture as a product by any

conventionally known separation method, thereby obtaining the ZSM-5 molecular sieve of the present invention. Examples of such separation methods include filtering, washing, and drying the obtained product mixture, and optionally, a calcination step. Here, the filtering, washing, and drying can be performed in any manner conventionally known in the art. The filtering can be performed using a vacuum filtration method. The washing can be performed using deionized water. The drying temperature of the drying step is 40~150°C, preferably 50~120°C, and the drying time is 1~30 hours, preferably 3~20 hours. The purpose of the calcination is to remove organic templates and any present moisture, thereby obtaining the calcined molecular sieve. The calcination can be performed in any manner conventionally known in the art, wherein the calcination temperature is 300~750°C, preferably 400~650°C, the calcination time is 1~12 hours, preferably 2~10 hours, and the calcination atmosphere is air or nitrogen atmosphere.

Furthermore, the molecular sieve according to the present invention can be processed for use as an upgrading catalyst. In the upgrading catalyst, the mass content of the molecular sieve is ≥ 70%, preferably ≥ 75%, and more preferably ≥ 80%.

Further, preferably, the upgrading catalyst is a metal-modified ZSM-5 molecular sieve catalyst. In which, the modifying metal is at least one selected from molybdenum, zinc, copper, gallium, and lanthanum, preferably at least one selected from molybdenum and gallium.

Further, preferably, based on the mass of the metal-modified ZSM-5 molecular sieve catalyst, the content of the modifying metal is 1%-10%, for example, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, etc., and any value within a range formed by any two of these values.

Furthermore, the upgrading catalyst may also contain a binder, which may be alumina. The binder accounts for less than 20% of the mass of the upgrading catalyst, preferably 12%-20%.

The third aspect of the present invention provides a lightening method, comprising the following steps:

A1. mixing light hydrocarbons and/or naphtha with a hydrogen-rich gas to obtain a mixture;

A2. bringing the mixture obtained in step A1 into contact with an upgrading catalyst based on the ZSM-5 molecular sieve according to the first aspect of the present invention

or the ZSM-5 molecular sieve prepared by the method of the second aspect of the present invention for upgrading treatment to obtain an upgraded product.

The lightening method of the present invention may optionally include the following step:

A3. separating the upgraded product obtained in step A2 to obtain a cracking feedstock rich in C2-C3 hydrocarbons and a liquid phase, respectively; preferably, wherein the liquid phase is separated to obtain a recycled material rich in C4-C6 hydrocarbons and a mixed aromatic product, wherein the recycled material is recycled back to step A2.

Further, the naphtha feedstock in step A1 is selected from at least one of straight-run gasoline, hydrocracked gasoline, catalytic cracked gasoline, hydrocoked gasoline, reforming topping oil, reforming raffinate oil, condensate oil, cracked gasoline, and cracked gasoline raffinate oil.

Furthermore, the naphtha feedstock in step A1 has an initial boiling point of 30-120 °C and a final boiling point of 120-220 °C.

Further, in step A1, the light hydrocarbon and/or naphtha feedstock has a nitrogen content of 0.1–10 ppm by mass. Preferably, when the light hydrocarbon and/or naphtha feedstock has a nitrogen content of ≥3 ppm by mass, denitrification treatment is performed first, followed by step A1. The denitrification treatment method is preferably adsorptive denitrogenation. The adsorptive denitrogenation can use conventional adsorption denitrifying agents, such as one or more of acid-treated X-type molecular sieves, Y-type molecular sieves, L-type molecular sieves, and ZSM-5 type molecular sieves. The acid-treatment can use inorganic acid, such as at least one of phosphoric acid, nitric acid, sulfuric acid, etc. For example, the denitrification adsorbent described in CN 201010543689.4.

Furthermore, conditions for the adsorptive denitrogenation include: a temperature of 20-150 °C, a pressure of 0.5-15 MPa, and a volume hourly space velocity of 0.5-5 h^{-1}.

Furthermore, the upgrading treatment in step A2 can employ a fixed bed, a moving bed, a fluidized bed, or a combination thereof.

Further, conditions of the upgrading treatment in step A2 include: a mass hourly space velocity of naphtha feedstock of 0.3-2 h^{-1}, a reaction temperature of 280-450°C, preferably 320-380°C, a reaction pressure of 0.5-3.0 MPa, preferably 1.0-2.0 MPa, and a hydrogen-oil volume ratio of 0.2-3.0: 1 for the hydrogen-rich gas to the naphtha feedstock.

Further, the hydrogen-rich gas mentioned in step A1 is at least one of hydrogen, a

mixture of hydrogen and methane, and hydrogen-rich dry gas. The hydrogen volume content of the hydrogen-rich gas is ≥50%.

Furthermore, the ZSM-5 molecular sieve is preferably a hydrogen-form ZSM-5 molecular sieve.

Furthermore, the preparation method of the metal-modified ZSM-5 molecular sieve catalyst includes: preparing a ZSM-5 molecular sieve catalyst, and then loading a metal component to obtain the metal-modified ZSM-5 molecular sieve catalyst.

Further, preferably, the preparation method of the ZSM-5 molecular sieve catalyst includes: mixing the ZSM-5 molecular sieve and optional molding aids, such as binders, pectizing acids, etc., molding, drying and calcining to obtain a ZSM-5 molecular sieve catalyst intermediate, and then subjecting it to ammonium exchange, drying and calcining to obtain the ZSM-5 molecular sieve catalyst.

Furthermore, in the preparation method of the ZSM-5 molecular sieve catalyst, the ammonium exchange adopts the conventional ammonium exchange method, with the purpose of converting the ZSM-5 molecular sieve into a hydrogen-form ZSM-5 molecular sieve.

Furthermore, the drying and calcination after molding, as well as the drying and calcination after ammonium exchange, can be carried out using conventional manners and conditions. Generally, conditions of drying are as follows: a drying temperature of 80-150°C, a drying time of 6-18h; conditions of calcination are as follows: a calcination temperature of 500-600°C, a calcination time of 2-6h.

Furthermore, the method for loading the metal component can be an impregnation method, such as saturated impregnation or supersaturated impregnation. After impregnation, the catalyst is dried and calcined to obtain the metal-modified ZSM-5 molecular sieve catalyst. Generally, drying and calcination can be carried out using conventional manners and conditions. For example, conditions of the drying are as follows: drying temperature of 80-150°C and drying time of 6-18h; conditions of the calcination are as follows: calcination temperature of 500-600°C and calcination time of 2-6h.

Furthermore, the separation described in step A3 can be achieved through distillation, such as by setting up a stabilizer tower, a propane removal tower and a light hydrocarbon removal tower to obtain a cracking feedstock, a recycled material, and mixed aromatics. The cracking feedstock is mainly C_2-C_3 products (the gas phase product from the top of the

propane removal tower), with propane accounting for ≥95v%. The recycled material is mainly C_4-C_6 products (the gas phase product from the tope of the light hydrocarbon removal tower), and the mixed aromatics are C_{7+} products (liquid phase product from the bottom of the light hydrocarbon removal tower). Optionally, a butane removal tower can be installed between the propane removal tower and the light hydrocarbon removal tower to separate C_4 from the bottom product of the propane removal tower. The top product of the butane removal tower is mainly C_4, which is then separated to obtain n-C_4 (n-butane) and i-C_4 (isobutane). The n-C_4 can be used as cracking feedstock. The bottom product of the butane removal tower enters the light hydrocarbon removal tower. The gas phase product from the top of the light hydrocarbon removal tower is mainly C_5-C_6, which, together with i-C_4, is used as recycled material.

Furthermore, after the light hydrocarbons and/or naphtha feedstock is mixed with the hydrogen-rich gas and the recycled material, it is preferably first heat-exchanged with the upgraded product obtained in step A2, then heated to the upgrading reaction temperature, and then contacted with the upgrading catalyst. The heating can be performed using a separate heating device.

Furthermore, the upgraded product obtained in step A2 is cooled before separation.

According to some embodiments of the lightening method of the third aspect of the present invention, the upgrading treatment is carried out through a first reaction zone and a second reaction zone; wherein, the first reaction zone is used to lighten light hydrocarbons and/or naphtha to produce cracking feedstock, and the second reaction zone is used to cause chain scission reaction in long-chain hydrocarbons. This method can selectively convert naphtha (mainly hydrocarbons equal or below C12) into high-quality cracking feedstock with C2-C3 alkanes as the main component, and produce mixed aromatics as byproducts. It also eliminates the need for complex separation and recovery systems, saves energy, and effectively improves economic efficiency.

According to a preferred aspect of the present invention, the first reaction zone employs a fixed bed, or one or more reactors, or one or more catalyst beds within a single fixed-bed reactor.

According to a preferred aspect of the present invention, the second reaction zone employs a fixed bed, a moving bed, a fluidized bed, or a combination thereof.

According to a preferred aspect of the present invention, the first reaction zone is

packed with a first molecular sieve catalyst. Preferably, the molecular sieve content in the first molecular sieve catalyst is greater than or equal to 70% by mass.

According to a preferred aspect of the present invention, the reaction conditions in the first reaction zone are as follows: a mass hourly space velocity of 0.3-2 h^{-1}, a reaction temperature of 280-400 °C, a reaction pressure of 0.5-2.0 MPa, and a volume ratio of the hydrogen-rich gas to naphtha of 0.3-5: 1.

According to a preferred aspect of the present invention, the first reaction zone comprises at least two reaction sections. Preferably, the reaction temperature of the upstream reaction section is at least 10-120°C lower than that of the adjacent downstream reaction section, and more preferably at least 20-80°C lower. In the present invention, in the first reaction zone, it is preferable that the downstream reaction section employs more severe reaction conditions than the upstream section, such that the feedstocks which are more difficult to convert are allowed to continue reacting in the downstream section, thereby further increasing the yield of the cracking feedstock.

According to a preferred aspect of the present invention, the second reaction zone is packed with a second molecular sieve catalyst. Preferably, the SiO_2/Al_2O_3 molar ratio of the molecular sieve is 150-300.

According to a preferred aspect of the present invention, the reaction conditions in the second reaction zone are as follows: a reaction temperature of 420-550°C, a reaction pressure of 1.0-4.0 MPa, and a mass hourly space velocity of 0.1-1.5 h^{-1}.

According to a preferred aspect of the present invention, the reaction products leaving the second reaction zone are first heat-exchanged with a mixture of naphtha and hydrogen-rich gas before being separated.

Preferably, the first molecular sieve catalyst is a metal-modified ZSM-5 molecular sieve catalyst. In which, the modifying metal is at least one selected from molybdenum, zinc, copper, gallium, and lanthanum, preferably at least one selected from molybdenum, gallium, and zinc, and more preferably zinc and gallium. Preferably, the mass ratio of Zn to Ga (calculated as oxide) is 4-10:1, for example, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, etc., and any value within a range formed by any two of these values.

Further, preferably, based on the mass of the metal-modified ZSM-5 molecular sieve catalyst, the content of the modifying metal is 1%-10%, for example, 1%, 2%, 3%, 4%, 5%, 6%, 7%, 8%, 9%, 10%, etc., and any value within a range formed by any two of these

values.

Furthermore, the first molecular sieve catalyst may further contain a binder, which may be alumina. The binder accounts for equal to or less than 20% of the mass of the upgrading catalyst, preferably 12%-20%.

Furthermore, the preparation method of the metal-modified ZSM-5 molecular sieve catalyst includes: preparing a ZSM-5 molecular sieve catalyst, and then loading a metal component to obtain a metal-modified ZSM-5 molecular sieve catalyst.

Furthermore, the mixed reaction products leaving the second reaction zone is first heat-exchanged with the mixture of the naphtha feedstock and hydrogen-rich gas and then cooled to release light gases (hydrogen and a small amount of methane). Then, it undergoes gas-liquid separation. The resulting gas phase products are mainly C1-C5, with ethane and propane as the main components, which can be used as cracking feedstock. The liquid phase products are mainly mixed aromatics, which can be used as blending feedstock for finished gasoline.

By providing two reaction zones and subjecting the reaction products directly to gas-liquid separation, the naphtha can be converted into a high-quality cracking feedstock predominantly comprising ethane and propane. This greatly reduces the process flow, saves energy, and can effectively enhance economic benefits.

According to some embodiments of the lightening method of the third aspect of the present invention, the liquid phase of step A3 is introduced into the aromatization reaction zone to undergo a catalytic reaction, and the resulting reaction product is extracted to obtain a mixed aromatic product.

This method enables the conversion of light hydrocarbons and naphtha, which are by-products of refinery, into a high-quality cracking feedstock with C2-C3 alkanes as the main components, while also producing mixed aromatics as a co-product. In addition, it also eliminates the need for a separation and recovery system, thus saving energy.

According to some embodiments of the lightening method of the third aspect of the present invention, the mixed reaction product of step A3 is separated, and the resulting gas phase product is used as cracking feedstock.

Furthermore, the light hydrocarbon feedstock and/or naphtha feedstock in step A1 means that light hydrocarbons can be used alone as feedstock, naphtha feedstock can be used alone as feedstock, or light hydrocarbons and naphtha can be used together as

feedstock.

Further, the light hydrocarbon feedstock in step A1 is at least one of the alkanes with four to eight carbon atoms, such as at least one of n-butane, isobutane, n-pentane, isopentane, and n-hexane, etc., preferably at least one of the alkanes with four to six carbon atoms. The light hydrocarbon feedstock can be a mixture of alkanes with the same number of carbon atoms, such as mixed C4 alkanes, mixed C5 alkanes, or mixed C6 alkanes, or a mixture of alkanes with several different carbon atom numbers, such as a C4-C6 alkanes mixture. The light hydrocarbons can come from a refinery's catalytic cracking unit, heavy oil and wax oil processing unit, etc. The naphtha feedstock is selected from at least one of coal-based naphtha, straight-run naphtha, straight-run gasoline, hydrocracked gasoline, catalytic cracked gasoline, hydrocoked gasoline, reforming topping oil, reforming raffinate oil, condensate oil, cracked gasoline, and cracked gasoline raffinate oil.

Furthermore, the hydrogenation upgrading reaction zone in step A1 employs a fixed bed, or one or more reactors, or one or more catalyst beds within a single fixed-bed reactor.

Further, preferably, the first molecular sieve catalyst is a metal-modified catalyst based on the ZSM-5 molecular sieve according to the present invention. The modifying metal is at least one selected from molybdenum, zinc, copper, gallium, and lanthanum, preferably at least one selected from molybdenum, gallium, and zinc.

Furthermore, the method for loading the metal component can be an impregnation method, such as saturated impregnation or supersaturated impregnation. After impregnation, the catalyst is dried and calcined to obtain the metal-modified ZSM-5 molecular sieve catalyst. Generally, drying and calcination can be carried out using conventional manners and conditions. For example, conditions of drying are as follows: a drying temperature of 80-150°C and a drying time of 6-18h; conditions of calcination are as follows: a calcination temperature of 500-600°C and a calcination time of 2-6h.

Further, reaction conditions in the hydrogenation upgrading reaction zone in step A1 are as follows: a mass hourly space velocity of the feedstock of 0.3-3 h^{-1}; a reaction temperature of 280-400°C, preferably 300-380°C; a reaction pressure of 0.5-3.0 MPa, preferably 1.0-2.0 MPa; and a hydrogen-to-oil volume ratio of hydrogen-rich gas to naphtha feedstock of 0.3-5:1.

Furthermore, the aromatization reaction zone in step A3 employs a fixed bed, a moving bed, or a fluidized bed. The aromatization reaction zone is packed with an

aromatization catalyst.

Furthermore, the aromatization catalyst comprises a support and a metal oxide, based on the total mass of the catalyst and expressed in mass percentage: 1%-10% zinc oxide, 1%-5% copper oxide, 0.1%-3% lanthanum oxide, 1%-8% phosphorus, 50%-70% molecular sieve, and 20%-40% binder (preferably alumina as the binder).

Furthermore, in the aromatization catalyst, the molecular sieve is at least one selected from ZSM-5 molecular sieve, Y-type molecular sieve, β-molecular sieve, mordenite, and SAPO-34 molecular sieve. The SiO_2/Al_2O_3 molar ratio of the molecular sieve is 40-200.

Furthermore, the aromatization catalyst can be prepared using conventional methods in the art, such as impregnation or kneading.

Furthermore, the reaction conditions for the aromatization reaction in step A3 are as follows: a reaction temperature of 420-600°C, a reaction pressure of 0.1-2MPa, and a mass hourly space velocity of 0.2-2 h^{-1}.

Further, in step A3, the separation is carried out in a stabilizer tower or a gas-liquid separator. The gas phase products are mainly C1-C3, which serve as cracking feedstock. The liquid phase products are mainly aromatics, non-aromatics, and water. The purpose of step (2) extraction is to separate the mixed aromatics in the liquid phase products. Conventional extraction methods can be used, for example, extraction solvents can be at least one of sulfolane, N-methylpyrrolidone, dimethyl sulfoxide, etc., where the mixed aromatics refer to benzene, toluene, xylene, etc.

Preferably, the mixed reaction product from step A2 is first heat-exchanged with the mixture of naphtha feedstock and hydrogen-rich gas, and then the material after separating C2-C3 (as cracking feedstock) is fed into the aromatization reactor.

The present invention eliminates the need for complex separation and recovery systems. The reaction products are directly separated by gas-liquid separation, with the gas phase serving as the cracking feedstock and the liquid phase undergoing aromatization and then extraction to obtain a mixed aromatic hydrocarbon product, which saves energy and effectively improves economic benefits.

The fourth aspect of the invention provides a lightening catalyst comprising the molecular sieve of the first aspect or the molecular sieve prepared by the method according to the second aspect.

The catalyst comprises the molecular sieve according to the first aspect or prepared

by the method according to the second aspect, a binder, and a modifying metal. The binder is, for example, alumina. The modifying metal is, for example, at least one selected from molybdenum, zinc, copper, gallium, and lanthanum. Preferably, based on the catalyst, the mass content of the molecular sieve is ≥ 70%, more preferably ≥ 75%, and even more preferably ≥ 80%. Preferably, based on the catalyst, the mass content of the modifying metal is 1%-10%, wherein the modifying metal is calculated as oxide. Preferably, based on the catalyst, the mass content of the binder is ≤20%, more preferably 12%-20%.

According to some preferred embodiments, the catalyst further contains phosphorus, and the mass content of phosphorus, based on the catalyst and calculated as elemental phosphorus, is 1%-10%, preferably 3-7%.

The preparation method of the catalyst includes:

B1. molding the ZSM-5 molecular sieve according to the first aspect, subjecting it to ammonium exchange, and calcining;

B2. optionally, contacting and impregnating the solid product from step B1 with a phosphorus-containing solution, and calcining the impregnated solid;

B3. optionally, impregnating the solid product from step B2 with a metal active component source solution, and calcining the impregnated solid.

Preferably, the phosphorus source in the phosphorus-containing solution is selected from at least one of phosphoric acid, metaphosphoric acid, pyrophosphoric acid, ammonium phosphate, ammonium hydrogen phosphate, and ammonium dihydrogen phosphate, and more preferably at least one of ammonium hydrogen phosphate and ammonium dihydrogen phosphate. Preferably, the phosphorus content in the phosphorus-containing solution is 1-10 wt%. Preferably, the manner of contacting and impregnating the solid product from step B1 with the phosphorus-containing solution in step B2 includes: adding the phosphorus-containing solution dropwise to the solid product from step B1 at 20-30°C, and performing heat treatment at 80-110°C after the addition is completed. Preferably, the dropping rate is 0.1-2 ml/g·min. Preferably, the heat treatment time is 2-4 h.

In the present invention, the ZSM-5 molecular sieve has an aluminum-rich surface, and in the catalyst obtained after phosphorus treatment, the surface aluminum content is increased by 10%.

The fifth aspect of the invention provides use of the ZSM-5 molecular sieve according

to the first aspct or the lightening catalyst according to the fourth aspect in a lightening method of light hydrocarbons and/or naphtha.

Furthermore, the use is as follows: light hydrocarbon and/or naphtha feedstocks are contacted with an upgrading catalyst based on ZSM-5 molecular sieve according to the first aspect or a lightening catalyst according to the third aspect to rection, and separating the products to obtain a cracking feedstock mainly comprising propane.

Further, the light hydrocarbon feedstock is at least one of the alkanes with four to eight carbon atoms, such as at least one of n-butane, isobutane, n-pentane, isopentane, and n-hexane, etc., preferably at least one of the alkanes with four to six carbon atoms. The light hydrocarbon feedstock can be a mixture of alkanes with the same number of carbon atoms, such as mixed C4 alkanes, mixed C5 alkanes, or mixed C6 alkanes, or a mixture of alkanes with several different carbon atom numbers, such as a C4-C6 alkanes mixture. The light hydrocarbons can come from a refinery's catalytic cracking unit, heavy oil and wax oil processing unit, etc. The naphtha feedstock is selected from at least one of straight-run gasoline, hydrocracked gasoline, catalytic cracked gasoline, hydrocoked gasoline, reforming topping oil, reforming raffinate oil, condensate oil, cracked gasoline, and cracked gasoline raffinate oil.

Furthermore, the naphtha feedstock has an initial boiling point of 30-120 °C and a final boiling point of 120-220 °C.

Furthermore, the lightening method of naphtha can be carried out using a fixed bed or a fluidized bed.

Further, the reaction conditions include: a mass hourly space velocity of 0.3-2 h^{-1} for the light hydrocarbon and/or naphtha feedstock, a reaction temperature of 280-450°C, preferably 320-380°C, a reaction pressure of 0.5-3.0 MPa, preferably 1.0-2.0 MPa, and a hydrogen-to-oil volume ratio of the hydrogen-rich gas and the light hydrocarbon and/or naphtha feedstock of 0.2-3.0:1.

Furthermore, the hydrogen-rich gas is at least one of hydrogen, a mixture of hydrogen and methane, and hydrogen-rich dry gas. The hydrogen volume content in the hydrogen-rich gas is ≥50%.

Furthermore, the upgrading catalyst includes a ZSM-5 molecular sieve and a modifying metal, wherein the mass content of molecular sieve is ≥ 70%, preferably ≥ 75%, and more preferably ≥ 80%.

Furthermore, the upgrading catalyst may further contain a binder, which may be alumina. The binder accounts for equal to or less than 20% of the mass of the upgrading catalyst, preferably 12%-20%.

Furthermore, in the upgrading catalyst, the modifying metals are preferably Zn and Ga, and more preferably, the mass ratio of Zn to Ga (based on oxides) is 4-10:1, for example, 4:1, 5:1, 6:1, 7:1, 8:1, 9:1, 10:1, etc., and any value within a range formed by any two of these values.

Further, the preparation method of the upgrading catalyst preferably includes: mixing the above-mentioned ZSM-5 molecular sieve with a binder, molding, drying and calcining, undergoing ammonium exchange, and then drying and calcining again. The drying and calcining after molding and the drying and calcining after ammonium exchange can be carried out using conventional methods and conditions. The ammonium exchange uses a conventional ammonium exchange method, the purpose of which is to convert the ZSM-5 molecular sieve into a hydrogen-form ZSM-5 molecular sieve. The method for loading the modifying metal can be an impregnation method, such as a saturated impregnation method or a supersaturated impregnation method. After impregnation, the upgrading catalyst is obtained by drying and calcining. Generally, drying and calcining can be carried out using conventional methods and conditions, for example, the drying conditions are as follows: a drying temperature of 80-150°C and a drying time of 6-18h; the calcination conditions are as follows: a calcination temperature of 500-600°C and a calcination time of 2-6h.

Furthermore, the cracking feedstock is mainly propane, and also contains a small amount of ethane, wherein the volume content of propane accounts for ≥95%.

Examples

To better understand the present invention, the present invention is further described with referring to Examples. However, the scope of protection claimed by the present invention is not limited to the scope described by the Examples.

In the following examples, unless otherwise specified, all experimental instruments and raw materials involved are commercially available products.

In the present invention, XRD was performed using a Rigaku D/max-2004 X-ray powder diffractometer for phase analysis, using Cu Kα radiation, tube voltage 40 kV, tube current 100 mA, scanning range 2θ 5-50°, and scanning step 0.02°.

In the present invention, SEM was performed using a NOVA Nano SEM450 ultra-high resolution field emission scanning electron microscope from FEI Corporation, USA.

In the present invention, the silica-to-alumina ratio of the molecular sieve was determined by inductively coupled plasma atomic emission spectrometry (ICP-AES). The experiment was conducted on a Plasma-Spec-I inductively coupled plasma atomic emission spectrometer from Item Labs, USA.

In the present invention, the specific surface area, external specific surface area, pore volume, micropore volume, and average pore size were obtained by specific surface area measurement (BET). Specific surface area was typically determined using the BET nitrogen adsorption method, with the total surface area calculated based on multilayer adsorption theory. External specific surface area was obtained by separating the micropore surface area from the total surface area using the t-plot method or α-s plot method; the remaining portion is the external specific surface area. The tests were performed on a Micromeritics ASAP-2020 specific surface area and pore size analyzer. The samples were first activated at 300°C and evacuated to 5 mHg, then the tests were conducted at liquid nitrogen temperature.

Example 1

Silica gel powder (300 mesh) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O) = 1:0.05:0.08:15$, to obtain a seed gel.

A mixture of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3) = 80$ and $n(SiO_2):n(template):n(Na_2O):n(H_2O) = 1:0.06:0.10:29$. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 5% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175 °C for 48 h. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S1). A

portion of the molecular sieve raw powder S1 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S1 molecular sieve showed a total specific surface area of 425.1 m^2/g, an external specific surface area/total specific surface area ratio of 34.4%, and a pore volume of 0.301 cm^3/g, a micropore volume of 0.165 cm^3/g, an average pore size of 2.533 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S1 molecular sieve was 78.

The XRD pattern of the calcined S1 molecular sieve was shown in Figure 7. As can be seen from the XRD pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined S1 molecular sieve was shown in Figure 8. Figure 8 showed that the ZSM-5 molecular sieve was a nanosheet aggregate with a nanosheet particle size of 100-200 nm and a thickness of 20-50 nm, and an aggregate particle size of 1-5 μm. The chemical analysis results (XPS) of its surface atoms were shown in Table 2. The NMR results of Example 1 were shown below, and the NMR spectrum was shown in Figure 9.

Table 1. NMR data of molecular sieves

Molecular sieve / Proportion	Al(49)	Al(53)	Al(56)	Al(58)
S1	11	54.9	33	1.1
S2	16.4	52.1	30	1.5
S3	11.8	56.3	29.6	2.3
S4	14.7	51	31.2	3.1
S5	9	55.8	33.2	2
D1	13.5	40	45	1.5
D2	8.8	39.8	49.2	2.2
D3	7.8	48.2	43.2	1.3
D4	13.4	45.2	39.3	2.1

In which, the peaks at 49, 53, and 58 ppm are attributable to aluminum atoms situated at the T1-T3, T5-T7, T9, and T12 sites at the channel intersections, whereas the peak at 56 ppm is attributable to aluminum atoms situated at the T4, T10, T8, and T11 sites within the 10-membered-ring (10-MR) straight channels.

In Figure 8, the following labels were used: nanosheet length (L), nanosheet thickness (T), and agglomerate particle size width (W).

Example 2

(1) Synthesis of ZSM-5 molecular sieve raw powder

Silica gel powder (300 mesh) was used as the silicon source, tetrapropylammonium

bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.03:0.10:15, to obtain a seed gel.

A mixture of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 225 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.03:0.12:21. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 5% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 125°C for 24 hours and then at 175°C for 24 hours. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S2). A portion of the molecular sieve raw powder S2 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S2 molecular sieve showed a total specific surface area of 410 m^2/g, an external specific surface area/total specific surface area ratio of 42.3%, and a pore volume of 0.283 cm^3/g, a micropore volume of 0.181 cm^3/g, an average pore size of 2.598 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S2 molecular sieve was 210.

The XRD pattern of the calcined S2 molecular sieve was shown in Figure 10. As can be seen from its XRD pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined S2 molecular sieve was shown in Figure 11. The scanning electron microscope image showed that the ZSM-5 molecular sieve was a nanosheet aggregate with a nanosheet particle size of 100-300 nm and a thickness of 20-50 nm, and an aggregate particle size of 1-5 μm.

Example 3

Silica gel powder (300 mesh) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:15, to obtain a seed gel.

A mixture of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.10:0.10:29. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 5% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175°C for 48 hours. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S3). A portion of the molecular sieve raw powder S3 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S3 molecular sieve showed a total specific surface area of 424.6 m^2/g, an external specific surface area/total specific surface area ratio of 34.0%, and a pore volume of 0.256 cm^3/g, a micropore volume of 0.179 cm^3/g, an average pore size of 2.816 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S3 molecular sieve was 75.

The XRD pattern of the calcined S3 molecular sieve showed that the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined S3 molecular sieve showed that the ZSM-5 molecular sieve was a nanosheet aggregate with a nanosheet particle size of 50-100 nm and a thickness of 50-100 nm, and an aggregate particle size of 0.5-5 μm.

Example 4

Silica gel powder (300 mesh) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:15, to obtain a seed gel.

A mixture of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.06:0.10:29. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 10% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for

crystallization at 175°C for 48 hours. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S4). A portion of the molecular sieve raw powder S4 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S4 molecular sieve showed a total specific surface area of 419.5 m^2/g, an external specific surface area/total specific surface area ratio of 35.2%, and a pore volume of 0.251 cm^3/g, a micropore volume of 0.181 cm^3/g, an average pore size of 2.778 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S4 molecular sieve was 78.

The XRD pattern of the calcined S4 molecular sieve showed that the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined S4 molecular sieve was shown in Figure 12. As can be seen from Figure 12, the ZSM-5 molecular sieve was a nanosheet aggregate with a nanosheet particle size of 20-100 nm and a thickness of 20-50 nm, and an aggregate particle size of 0.3-3 μm.

Example 5

Silica gel powder (300 mesh) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:15, to obtain a seed gel.

A mixture of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.06:0.10:29. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 5% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 130°C for 72 hours. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S5). A portion of the molecular sieve raw powder S5 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S5 molecular sieve showed a total specific surface area of

440.3 m^2/g, an external specific surface area/total specific surface area ratio of 35.5%, and a pore volume of 0.253 cm^3/g, a micropore volume of 0.139 cm^3/g, an average pore size of 2.688 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S5 molecular sieve was 78.

The XRD pattern of the calcined S5 molecular sieve showed that the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined S5 molecular sieve was shown in Figure 13. As can be seen from Figure 13, the ZSM-5 molecular sieve was a nanosheet aggregate with a nanosheet particle size of 50-200 nm and a thickness of 20-100 nm, and an aggregate particle size of 1-10 μm.

Example 6

(1) Synthesis of ZSM-5 molecular sieve raw powder

Silica gel powder (100 mesh) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:15, to obtain a seed gel.

A mixture of silica gel powder (100 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.06:0.10:29. After stirring at room temperature for 30 min, seed gel (calculated as silica) was added at 5% of the mass of the silicon source (calculated as silica) in the mixture, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175°C for 48 hours. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as S6). A portion of the molecular sieve raw powder S6 was calcined in air at 550 °C for 4 hours. The BET results of the calcined S6 molecular sieve showed a total specific surface area of 417.8 m^2/g, an external specific surface area/total specific surface area ratio of 35.0%, and a pore volume of 0.289 cm^3/g, a micropore volume of 0.144 cm^3/g, an average pore size of 3.130 nm. The SiO_2/Al_2O_3 molar ratio of the calcined S6 molecular sieve was 75.

Example 7

S1 molecular sieve was used as support and was impregnated with an equal amount of ammonium dihydrogen phosphate solution (with a phosphorus content of 5%), and then the impregnated sample was calcined. The resulting processed molecular sieve raw powder was denoted as SP, and the chemical analysis results (XPS) of its surface atoms were shown in Table 2.

Table 2. Surface atomic chemical analysis results of molecular sieve raw powder

Sample	Si atomic concentration%	Al atomic concentration%	Silica-to-alumina ratio
S1	22.65	0.70	64.7
SP	25.69	0.88	58.38
S2			81.9
S3			42
S4			49.8
S5			30.2
D1			79.2
D2			85.3
D3			81.2
D4			77.2

Comparative Example 1

A systhesis solution of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.06:0.10:29 and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175 °C for 48 h. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as D1). A portion of the molecular sieve raw powder D1 was calcined in air at 550 °C for 4 hours. The BET results of the calcined D1 molecular sieve showed a total specific surface area of 365 m^2/g, an external specific surface area/total specific surface area ratio of 24.3%, and a pore volume of 0.215 cm^3/g, a micropore volume of 0.151 cm^3/g, an average pore size of 2.012 nm.

The XRD pattern of the calcined D1 molecular sieve was shown in Figure 14. As can be seen from the XRD pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined D1 molecular sieve was shown in Figure 15. The ZSM-5 molecular sieve was a nanosheet aggregate with a

nanosheet particle size of 300-500 nm and a thickness of more than 200 nm, and an aggregate particle size of > 20 μm.

Comparative Example 2

A systhesis solution of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 85 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:29. After stirring at room temperature for 30 min, ZSM-5 molecular sieve (SiO_2/Al_2O_3 molar ratio = 168, purchased from Shanghai Fuxu Molecular Sieve Co., Ltd) was added at 5% of the mass of the silicon source (calculated as silica) in the synthesis solution, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175 °C for 48 h. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as D2).

A portion of the molecular sieve raw powder D2 was calcined in air at 550 °C for 4 hours. The BET results of the calcined D2 molecular sieve showed a total specific surface area of 341 m^2/g, an external specific surface area/total specific surface area ratio of 22.1%, and a pore volume of 0.223 cm^3/g, a micropore volume of 0.181 cm^3/g, an average pore size of 1.851 nm.

The XRD pattern of the calcined D2 molecular sieve was shown in Figure 16. As can be seen from the XRD pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined D2 molecular sieve was shown in Figure 17. The ZSM-5 molecular sieve had a polycrystalline block-like morphology, and the nanosheets had a thickness of approximately 1 μm.

Comparative Example 3

A systhesis solution of silica gel powder (300 mesh), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 85 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:29. After stirring at room temperature for 30 min, D1 powder was added at 5% of the mass of the silicon source (calculated as silica) in the synthesis solution, and stirred

at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175 °C for 48 h. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as D3). A portion of the molecular sieve raw powder D3 was calcined in air at 550 °C for 4 hours. The BET results of the calcined D3 molecular sieve showed a total specific surface area of 398 m^2/g, an external specific surface area/total specific surface area ratio of 27%, and a pore volume of 0.230 cm^3/g, a micropore volume of 0.154 cm^3/g, an average pore size of 1.923 nm.

The XRD pattern of the calcined D3 molecular sieve was shown in Figure 18. As can be seen from the XRD pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined D3 molecular sieve was shown in Figure 19. The ZSM-5 molecular sieve was nanosheet aggregates with a thickness of the nanosheet of about 500 nm and an aggregate particle size >20 μm.

Comparative Example 4

Silica sol (25% by mass of silica) was used as the silicon source, tetrapropylammonium bromide was used as the template, and sodium hydroxide was used as the alkali source. The silicon source, the template, the alkali source, and water were mixed at 80°C for 24 hours with a ratio of $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:15, to obtain a seed gel.

A synthesys solution of silica sol (25% by mass of silica), sodium aluminate, tetrapropylammonium bromide, sodium hydroxide, and water was prepared according to the following ratios: $n(SiO_2):n(Al_2O_3)$ = 80 and $n(SiO_2):n(template):n(Na_2O):n(H_2O)$ = 1:0.05:0.08:29. After stirring at room temperature for 30 min, seed gel was added at 5% of the mass of the silicon source (calculated as silica) in the synthesis solution, and stirred at room temperature for 3 h. The mixture was then transferred to a stainless steel autoclave for crystallization at 175 °C for 48 h. The crystallized solution was then subjected to sedimentation/filtration to recover the mother liquor. The solid was washed with deionized water until neutral and dried to obtain molecular sieve raw powder (denoted as D4). A portion of the molecular sieve raw powder D4 was calcined in air at 550 °C for 4 hours. The BET results of the calcined D4 molecular sieve showed a total specific surface area of

367 m^2/g, an external specific surface area/total specific surface area ratio of 23.0%, and a pore volume of 0.230 cm^3/g, a micropore volume of 0.154 cm^3/g, an average pore size of 1.923 nm.

The XRD pattern of the calcined D4 molecular sieve was shown in Figure 20. As can be seen from the pattern, the molecular sieve had apparent ZSM-5 characteristic peaks.

The scanning electron microscope image of the calcined D4 molecular sieve was shown in Figure 21.

Preparation Example

Preparation Example 1

300 g of the above-mentioned sodium-form ZSM-5 molecular sieve raw powder S1 was taken and mixed with 120 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A.

50 g of catalyst intermediate A was taken and mixed with 8 wt% ammonium acetate solution (liquid-to-solid volume ratio of 10), and exchanged at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst B, the aluminum NMR result of which was shown in Figure 22.

20 g of ZSM-5 molecular sieve catalyst B was taken and impregnated with an ammonium dihydrogen phosphate solution in an equal-volume manner (with a phosphorus content of 5%). The impregnated sample was then calcined, followed by equal-volume impregnation with an impregnating solution containing zinc and gallium, where the metal sources were all nitrates. After impregnation, the sample was dried at 120 °C for 10 hours and calcined at 550 °C for 6 hours to obtain a metal-modified molecular sieve catalyst C-1, which contained 4 wt% zinc and 0.5 wt% gallium.

Preparation Example 2

Compared with Preparation Example 1, the only difference was the change in the loading of zinc and gallium to obtain catalyst C-2, which contained 2 wt% zinc and 0.2 wt% gallium.

Preparation Example 3

300 g of the above-mentioned sodium-form ZSM-5 molecular sieve raw powder S1 was taken and mixed with 120 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A.

50 g of catalyst intermediate A was taken and mixed with 8 wt% ammonium acetate solution (liquid-to-solid volume ratio of 10), and exchanged at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst B.

20 g of ZSM-5 molecular sieve catalyst B was taken and impregnated with an excess of aqueous ammonium molybdate solution. After impregnation, the sample was dried at 120 °C for 10 hours and calcined at 500 °C for 2 hours to obtain 5wt% molybdenum metal modified molecular sieve catalyst C-3.

Preparation Example 4

Catalyst Synthesis

The catalyst preparation steps were the same as in Preparation Example 3, except that molecular sieve S2 was used instead of molecular sieve S1 to obtain catalyst C-4.

Preparation Example 5

The synthesis steps of the ZSM-5 molecular sieve raw powder are the same as in Example 1, resulting in molecular sieve S1.

Catalyst Synthesis:

300 g of the above-mentioned sodium-form ZSM-5 molecular sieve raw powder S1 was taken and mixed with 120 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A.

50 g of catalyst intermediate A was taken and mixed with 8 wt% ammonium acetate solution (liquid-to-solid volume ratio of 10), and exchanged at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst B.

20 g of ZSM-5 molecular sieve catalyst B was taken and impregnated with an

impregnation solution containing gallium in an equal-volume manner. After impregnation, it was dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain a 6wt% gallium metal modified molecular sieve catalyst C-5.

Preparation Example 6

The first molecular sieve catalyst packed in the first reaction zone in Figure 2-3:

300 g of the above-mentioned sodium-form ZSM-5 molecular sieve raw powder S1 was taken and mixed with 140 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A.

50 g of catalyst intermediate A was taken and mixed with 8 wt% ammonium acetate solution (liquid-to-solid volume ratio of 10), and exchanged at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst B.

20 g of ZSM-5 molecular sieve catalyst B was taken and impregnated with an impregnation solution containing zinc and gallium in an equal-volume manner. After impregnation, it was dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain a metal-modified molecular sieve catalyst C-6, which contained 5wt% zinc and 1wt% gallium.

Preparation Example 7

The second molecular sieve catalyst packed in the second reaction zone in Figure 2-3:

Commercial hydrogen-form HZSM-5 molecular sieve, SiO_2/Al_2O_3 molar ratio = 168.

300 g of the above-mentioned hydrogen-form ZSM-5 molecular sieve powder was taken and mixed with 100 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst C-7.

Preparation Example 8

The first molecular sieve catalyst used for being packed in the first reaction zone:

The catalyst preparation steps were the same as in Preparation Example 6, except that

molecular sieve S2 was used instead of molecular sieve S1, and the zinc-gallium loading was changed to obtain catalyst C-8, which contained 3 wt% zinc and 0.5 wt% gallium.

Preparation Example 9

Catalyst in the hydrogenation upgrading reaction zone:

300 g of the above-mentioned sodium-form ZSM-5 molecular sieve powder S1 was taken and mixed with 140 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A.

50 g of catalyst intermediate A was taken and mixed with 8 wt% ammonium acetate solution (liquid-to-solid volume ratio of 10), and exchanged at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst B.

20 g of ZSM-5 molecular sieve catalyst B was taken and impregnated with an excess of ammonium molybdate aqueous solution. After impregnation, it was dried at 120 °C for 10 hours and calcined at 500 °C for 4 hours to obtain a 3wt% molybdenum metal modified molecular sieve catalyst C-9-1.

Aromatization reactor catalyst:

300 g of the hydrogen-form ZSM-5 molecular sieve powder (SiO_2/Al_2O_3 molar ratio = 100) was taken and mixed with 120 g of alumina. A 2 wt% dilute nitric acid solution was added dropwise, and the mixture was kneaded and extruded into shape, then dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst intermediate A'.

50 g of catalyst intermediate A' was taken and treated with 1 wt% phosphoric acid solution (liquid-to-solid volume ratio of 5) at 80 °C for 1 hour. The product was washed with water, dried at 120 °C for 10 hours, and calcined at 550 °C for 4 hours to obtain ZSM-5 molecular sieve catalyst intermediate B'.

20 g of ZSM-5 molecular sieve catalyst B' was taken and impregnated with an impregnating solution containing copper, zinc, and lanthanum in an equal-volume manner. After impregnation, it was dried at 120 °C for 10 hours and calcined at 550 °C for 4 hours to obtain catalyst C-9-2. The resulting catalyst contained 2 wt% copper oxide, 2 wt% zinc oxide, 0.2 wt% lanthanum oxide, and 3 wt% phosphorus.

Preparation Example 10

The catalyst preparation steps were the same as in Example 9, except that molecular sieve S2 was used instead of molecular sieve S1, and the modifying metals were replaced with zinc and gallium to obtain catalyst C-10-1, which contained 2 wt% zinc and 0.5 wt% gallium.

Comparative Preparation Examples 1-4

Compared with Preparation Example 1, the only difference was that sodium-form ZSM-5 molecular sieve raw powder S1 was replaced with sodium-form ZSM-5 molecular sieve raw powders D1, D2, D3, and D4 respectively, to obtain catalysts C-D-1, C-D-2, C-D-3, and C-D-4.

Test Example

Unless otherwise specified, the composition of the naphtha used in the following test examples was shown in the table below:

Table 3. Composition of naphtha feedstock used in the test examples

	feedstock wt%
	naphtha
C5	2.23
C6	11.98
C7	25.38
C8	28.81
C9	18.04
C10	8.13
Aromatics	5.43

Note: In the table, C6, C7, C8, C9, and C10 refer to the contents of non-aromatic hydrocarbons.

Test Examples 1-2

Using C-1 and C-2 as catalysts, respectively, and using hydrocracked light naphtha

(with a distillation range of 60-140 °C and a nitrogen content of 2 ppm by mass) as the feedstock, the process shown in Figure 1 was adopted, except that the adsorptive denitrogenation tower A was not installed. A fixed-bed reactor was employed, with a reaction temperature of 335 °C, a reaction pressure of 1.2 MPa, a feedstock mass space velocity of 1.5 h^{-1}, and a hydrogen-to-oil volume ratio of 0.7:1. The yields of the cracking feedstock from the top of the propane removal tower F were shown in Table 9, in which the propane volume content in the cracking feedstock accounted for equal to or more than 95%.

Test Example 3-5

Using C-3, C-4, and C-5 as catalysts, respectively, and using hydrocracked light naphtha (with a distillation range of 60-140 °C and a nitrogen content of 2.5 ppm by mass) as the feedstock, the process shown in Figure 1 was adopted, except that the adsorptive denitrogenation tower A was not installed. The upgrading reactor E was a fixed-bed reactor, with a reaction temperature of 350 °C, a reaction pressure of 1 MPa, a feedstock mass space velocity of 1.5 h^{-1}, and a hydrogen-to-oil volume ratio of 0.5:1. The yields of the cracking feedstock from the top of the propane removal tower F were shown in Table 9, in which the propane volume content in the cracking feedstock accounted for equal to or more than 95%.

Test Example 6

Using C-3 as catalysts, respectively, and using hydrocracked light naphtha (with a distillation range of 60-140 °C and a nitrogen content of 2.5 ppm by mass) as the feedstock, the process shown in Figure 1 was adopted, except that the adsorptive denitrogenation tower A was not installed. The upgrading reactor E was a fixed-bed reactor, with a reaction temperature of 370 °C, a reaction pressure of 1.2 MPa, a feedstock mass space velocity of 1.4 h^{-1}, and a hydrogen-to-oil volume ratio of 0.2:1. The yield of the cracking feedstock from the top of the propane removal tower F was 80.6%, in which the propane volume content in the cracking feedstock accounted for equal to or more than 95%.

Test Example 7

The first molecular sieve catalyst packed in the first reaction zone was C-6, and

the second molecular sieve catalyst packed in the second reaction zone was C-7.

In this example, naphtha was used as the feedstock, and the process shown in Figure 2 was adopted, except that the adsorptive denitrogenation tower A was not installed. In the first reaction zone, a first lightening reactor D1 and a second lightening reactor D2 were employed, and in the second reaction zone, reactor L was employed. All reactors were fixed-bed reactors, and the specific reaction conditions for each reactor were shown in Table 4. The composition of the resulting product was shown in Table 5.

Table 4 Operating conditions of each reactor in Test Example 7

	Reactor D1	Reactor D2	Reactor L
Reaction temperature /°C	300	350	450
Pressure/MPa	1.4	1.4	1.8
Mass hourly space velocity/h^{-1}	1.5	1.5	1.5
Hydrogen-to-oil volume ratio	0.5	0.5	-

Table 5 Composition of the product obtained in Test Example 7

	Product wt%	
	Cracking feedstock	Mixed Aromatics
Methane	4.35	
Ethane	28.61	
Propane	49.30	
C4	3.63	
Aromatics		14.11

Test Example 8

In this test example, the first molecular sieve catalyst and the second molecular sieve catalyst were the same as those in Test Example 7.

In this example, light naphtha was used as the feedstock (with its composition shown in Table 7), and the process shown in Figure 3 was adopted, except that the adsorptive denitrogenation tower A was not installed. Both reactor D1 and reactor L

were fixed-bed reactors, and the specific reaction conditions for each reactor were shown in Table 6. The composition of the resulting product was shown in Table 7.

Table 6. Operating conditions of each reactor in Test Example 8

	First reaction zone A1	First reaction zone A2	Reactor L
Reaction temperature/°C	280	330	450
Pressure/MPa	1.5	1.5	1.8
Mass hourly space velocity/h^{-1}	1.5	1.5	1.5
Hydrogen-to-oil volume ratio	0.5	0.5	-

Table 7. Composition of the naphtha feedstock used and products obtained in Test Example 8

	Feedstock wt%	Product wt%	
	Light naphtha	Cracking feedstock	Mixed Aromatics
Methane		6.21	
Ethane		32.15	
Propane	0.26	43.81	
C4	0.51	8.63	
C5	48.87		
C6	45.3		
C7	5.06		
Aromatics			9.20

Test Example 9

In this example, naphtha was used as the feedstock, and the process shown in Figure 2 was adopted, except that the adsorptive denitrogenation tower A was not installed. In the first reaction zone, a first lightening reactor D1 and a second lightening reactor D2 were employed, and in the second reaction zone, reactor L was employed. All reactors were fixed-bed reactors. The first molecular sieve catalyst packed in the first reaction zone was catalyst C-8. The second molecular sieve catalyst packed in the second reaction zone was

catalyst C-7. The specific reaction conditions for each reactor were shown in Table 4. The composition of the resulting product was shown in Table 8. Among them, the yield of cracking feedstock (C2–C4) was 78.79%, and the yield of mixed aromatics was 14.86%.

Table 8. Composition of the product obtained in Test Example 9

	Product wt%	
	Cracking feedstock	Mixed Aromatics
Methane	6.35	
Ethane	23.20	
Propane	45.26	
C4	10.33	
Aromatics		14.86

Comparative Test Examples 1-4

Using C-D-1, C-D-2, C-D-3, and C-D-4 as catalysts, respectively, the same feedstock and evaluation method as those in Test Examples 1-2 were adopted. The yields of the cracking feedstock from the top of the propane removal tower F were shown in Table 9, in which the propane volume content in the cracking feedstock accounted for equal to or more than 95%.

Table 9 Evaluation results of catalysts in Test Example 1-5 and Comparative Test Example 1-4

Test Example	Catalyst number	Cracking feedstock yield/%
Test Example 1	C-1	86.2
Test Example 2	C-2	83.5
Test Example 3	C-3	84.3
Test Example 4	C-4	82.0
Test Example 5	C-5	83.6
Comparative Test Example 1	C-D-1	60.2
Comparative Test Example 2	C-D-2	61.6
Comparative Test Example 3	C-D-3	62.4
Comparative Test Example 4	C-D-4	61.3

Comparative Test Example 5

The first molecular sieve catalyst packed in the first reaction zone was catalyst C-D-1.

The second molecular sieve catalyst packed in the second reaction zone was catalyst C-7.

In this example, naphtha was used as the feedstock, and the process shown in Figure 2 was adopted, except that the adsorptive denitrogenation tower A was not installed. In the first reaction zone, a first lightening reactor D1 and a second lightening reactor D2 were employed, and in the second reaction zone, reactor L was employed. All reactors were fixed-bed reactors, and the specific reaction conditions for each reactor were shown in Table 4. The composition of the resulting product was shown in Table 10. Among them, the yield of cracking feedstock (C2–C4) was 65.79%, and the yield of mixed aromatics was 11.20%.

Table 10. Composition of the product obtained from Comparative Test Example 5

	Product wt%	
	Cracking feedstock	Mixed Aromatics
Methane	23.01	
Ethane	18.99	
Propane	33.24	
C4	13.56	
Aromatics		11.20

Test Example 10

In this example, cracked C_5 fraction produced as a by-product from a certain refinery was used as the light hydrocarbon feedstock. The cracked C_5 fraction was composed of more than 20 components with similar boiling points that readily formed azeotropes with one another. The components were classified and summarized as follows: the contents of isoprene, piperylene, and cyclopentadiene (dicyclopentadiene) were each about 20%, the contents of branched-chain monoolefins and straight-chain monoolefins were each about 15%–20%, and small amounts of alkanes, olefins, and C_4 and C_6 components were also present. The process shown in Figure 4 was adopted, except that the adsorptive denitrogenation tower A was not installed, in which both

the hydrogenation upgrading reactor D and the aromatization reactor G were fixed-bed reactors. The catalyst used in the hydrogenation upgrading reaction zone was catalyst C-9-1, and the catalyst used in the aromatization reactor was catalyst C-9-2. The reaction conditions employed were shown in Table 11. The yield of product cracking feedstock (C2–C3) was 78.8%, and the yield of mixed aromatics was 21.1%.

Table 11. Operating conditions of each reactor in Test Example 10

	hydrogenation upgrading reactor D	Aromatization reactor G
Reaction temperature/°C	350	530
Pressure/MPa	1.5	0.1
Mass hourly space velocity/h^{-1}	1.5	0.5
Hydrogen-to-oil volume ratio	0.5	-

Test Example 11

In this example, the catalysts packed in the hydrogenation upgrading reactor and the aromatization reactor were the same as those in Test Example 10.

This test example employed light naphtha as the feedstock (with its composition shown in Table 13), and the process shown in Figure 5 was adopted, except that the adsorptive denitrogenation tower A was not installed. In which, the hydrogenation upgrading reactor D1, the hydrogenation upgrading reactor D2, and the aromatization reactor G were all fixed-bed reactors, and the reaction conditions employed were shown in Table 12. The composition of the product was shown in Table 13.

Table 12. Operating conditions of each reactor in Test Example 11

	Hydrogenation upgrading reactor D1	Hydrogenation upgrading reactor D2	Aromatization reactor G
Reaction temperature/°C	330	380	530
Pressure/MPa	1.3	1.5	0.1
Mass hourly space velocity/h^{-1}	1.3	1.3	0.8
Hydrogen-to-oil volume ratio	0.5	0.5	-

Table 13. Composition of naphtha feedstock used and product obtained in Test

Example 11

	Feedstock wt%	Product wt%	
	Naphtha	Cracking feedstock (C1-C3)	Mixed Aromatics
Methane		5.15	
Ethane		26.40	
Propane		51.42	
C4			
C5	2.23		
C6	11.98		
C7	25.38		
C8	28.81		
C9	18.04		
C10	8.13		
Aromatics	5.43		17.03

Note: In the table, C6, C7, C8, C9, and C10 refer to the contents of non-aromatic hydrocarbons.

Test Example 12

In this example, the catalysts packed in the hydrogenation upgrading reactor and the aromatization reactor were the same as those in Test Example 10.

In this example, 65 wt% isobutane and 35 wt% n-butane were used as the feedstock, and the process shown in Figure 6 was adopted, except that the adsorptive denitrogenation tower A was not installed. In which, both the hydrogenation upgrading reactor D and the aromatization reactor G were fixed-bed reactors, and the reaction conditions employed were shown in Table 14. The yield of product cracking feedstock (C2–C3) was 87.0%, and the yield of mixed aromatics was 9.1%.

Table 14 Operating conditions of each reactor in Test Example 12

	Hydrogenation upgrading reactor D	Aromatization reactor S
Reaction temperature/°C	330	530
Pressure/MPa	1.75	0.1
Mass hourly space	1.5	0.4

velocity/h^{-1}		
Hydrogen-to-oil volume ratio	0.5	-

Test Example 1 3

The catalyst used in the hydrogenation upgrading reaction zone was catalyst C-10-1, and the catalyst used in the aromatization reactor was catalyst C-9-2.

In this example, light naphtha was used as the feedstock (the same as that in Test Example 12), and the process of Test Example 12 was adopted, with the reaction conditions shown in Table 15. The composition of the product was shown in Table 16.

Table 15. Operating conditions of each reactor in Test Example 13

	Hydrogenation upgrading reactor D1	Hydrogenation upgrading reactor D2	Aromatization reactor S
Reaction temperature/°C	350	380	540
Pressure/MPa	1.5	1.5	0.1
Mass hourly space velocity/h^{-1}	1.5	1.5	1
Hydrogen-to-oil volume ratio	0.5	0.5	-

Table 16. Composition of the product obtained in Test Example 13

	Product wt%	
	Cracking feedstock (C1-C3)	Mixed Aromatics
Methane	5.11	
Ethane	21.93	
Propane	53.76	
Aromatics		19.20

Comparative Test Example 6

The catalyst used in the hydrogenation upgrading reaction zone was catalyst C-D-4, and the catalyst used in the aromatization reactor was catalyst C-9-2.

In this example, light naphtha was used as the feedstock (the same as that in Test

Example 11), and the process of Test Example 11 was adopted, with the reaction conditions shown in Table 17. The yield of the cracking feedstock (C2-C3) was 61.49%, and the yield of mixed aromatics was 24.31%.

Table 17. Composition of the product obtained from Comparative Test Example 6

	Product wt%	
	Cracking feedstock (C1-C3)	Mixed Aromatics
Methane	14.20	
Ethane	26.16	
Propane	35.33	
Aromatics		24.31

The above description is merely specific examples of the present invention and is not intended to limit the present invention in any way. Although the present invention has been disclosed above with specific examples, it is not intended to limit the present invention. Any person skilled in the art can make some modifications or alterations to the above-disclosed technical content to create equivalent exampless without departing from the scope of the present invention. Any simple modifications, equivalent changes and alterations made to the above examples based on the technical essence of the present invention without departing from the scope of the present invention shall still fall within the scope of the present invention.

Claims

1. A ZSM-5 molecular sieve, wherein the total specific surface area of the ZSM-5 molecular sieve is 300-500 m^2/g, wherein the external specific surface area accounts for 33%-45% of the total specific surface area, preferably 34%-45%, and in the ^{27}Al NMR spectrum of the ZSM-5 molecular sieve, the peak area of the peak at a chemical shift of 53 ppm is ≥50% relative to the peak area of tetra-coordinated Al, for example 50-70%.

2. The ZSM-5 molecular sieve according to claim 1 or 2, wherein the ZSM-5 molecular sieve is an agglomerate of nanosheets, the nanosheets have an average particle size of 20-300 nm, and an average thickness of 10-100 nm; preferably, the agglomerate has an average particle size of 0.3-10 μm.

3. The ZSM-5 molecular sieve according to claim 1, wherein the ZSM-5 molecular sieve has a SiO_2/Al_2O_3 molar ratio of 50-250; preferably, the surface silicon-aluminum ratio is 30%-90% of the bulk silicon-aluminum ratio.

4. The ZSM-5 molecular sieve according to any one of claims 1-3, wherein the ZSM-5 molecular sieve has a pore volume of 0.24-0.35 cm^3/g, and/or

the ZSM-5 molecular sieve has an external specific surface area of 99-225 m^2/g, preferably 125-225 m^2/g, and more preferably 132-225 m^2/g.

5. The ZSM-5 molecular sieve according to any one of claims 1-4, wherein the ZSM-5 molecular sieve has a micropore volume of 0.10-0.22 cm^3/g.

6. The ZSM-5 molecular sieve according to any one of claims 1-5, wherein the ZSM-5 molecular sieve has an average pore size of 2.1-3.5 nm.

7. A preparation method of the ZSM-5 molecular sieve according to any one of claims 1-6, comprising:

S1. mixing a first silicon source, a first template, a first alkali source, and water to obtain a seed gel; wherein the first silicon source is a solid silicon source, the molar ratio

of the first alkali source to the first silicon source is 0.05-0.10, the molar ratio of the first template to the first silicon source is 0.05-0.10, and the first silicon source is calculated as SiO_2, and the first alkali source is calculated as oxide;

S2. mixing a second silicon source, an aluminum source, a second template, a second alkali source, water, and the seed gel to obtain a synthesis solution;

S3. subjecting the synthesis solution to crystallization treatment to obtain the ZSM-5 molecular sieve.

8. The preparation method according to claim 7, wherein step S1 satisfies at least one of the following features:

the solid silicon source is silica gel powder with a particle size of 60-800 mesh;

the first template is at least one selected from n-butylamine, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium bromide, tetraethylammonium bromide, ethylenediamine, or hexamethylenediamine;

the first alkali source is at least one selected from sodium hydroxide, potassium hydroxide, and ammonia water; and

the molar ratio of water to the first silicon source is 5-30, wherein the first silicon source is calculated as SiO_2.

9. The preparation method according to claim 7 or 8, wherein step S2 satisfies at least one of the following features:

the second template is an organic amine, preferably at least one selected from n-butylamine, tetrapropylammonium hydroxide, tetraethylammonium hydroxide, tetrapropylammonium bromide, tetraethylammonium bromide, ethylenediamine, triethylamine or hexamethylenediamine;

the second silicon source is at least one of silica sol, water glass, fumed silica and silica gel, preferably silica gel, more preferably silica gel powder with a particle size of 60-800 mesh;

the aluminum source is at least one of sodium aluminate, aluminum sulfate, and aluminum isopropoxide;

the second alkali source is at least one of sodium hydroxide, potassium hydroxide, and ammonia water.

10. The preparation method according to any one of claims 7-9, wherein step S2 satisfies at least one of the following features:

the molar ratio of the second silicon source to the aluminum source is 30-100;

the molar ratio of the second template to the second silicon source is 0.02-0.10;

the molar ratio of the second alkali source to the second silicon source is 0.07-0.12;

the molar ratio of water to the second silicon source is 15-30;

the mass ratio of the seed gel to the second silicon source is 1%-20%, preferably 3%-10%;

wherein the second silicon source is calculated as SiO_2, the aluminum source is calculated as Al_2O_3, the second alkali source is calculated as oxide, and the seed gel is calculated as SiO_2.

11. The preparation method according to any one of claims 7-10, wherein conditions for crystallization treatment in step S3 include: a crystallization temperature of 125-180 °C and a crystallization time of 16-96 h under sealed conditions.

12. A catalyst for a lightening reaction, comprising:

the molecular sieve according to any one of claims 1-6 or prepared by the method according to any one of claims 7-11;

a binder, such as alumina, and

a modifying metal, wherein the modifying metal is at least one of molybdenum, zinc, copper, gallium, and lanthanum;

preferably, based on the catalyst, the mass content of the molecular sieve is ≥ 70%, more preferably ≥ 75%, and even more preferably ≥ 80%;

preferably, based on the catalyst, the mass content of the modifying metal is 1%-10%, wherein the modifying metal is calculated as oxide;

preferably, based on the catalyst, the mass content of the binder is ≤ 20%, more preferably 12%-20%.

13. The catalyst according to claim 12, wherein the catalyst further contains phosphorus;

based on the catalyst, the mass content of phosphorus, calculated as elemental phosphorus, is 1%-10%, preferably 3-7%.

14. A lightening method, comprising the following steps:

A1. mixing light hydrocarbons and/or naphtha with a hydrogen-rich gas to obtain a mixture;

A2. bringing the mixture obtained in step A1 into contact with a catalyst based on the ZSM-5 molecular sieve according to any one of claims 1-6 or the ZSM-5 molecular sieve prepared by the method according to any one of claims 7-11, or the catalyst according to claim 12 or 13 for upgrading treatment to obtain an upgraded product;

A3. optionally, separating the upgraded product obtained in step A2 to obtain a cracking feedstock rich in C2-C3 hydrocarbons and a liquid phase, respectively; preferably, wherein the liquid phase is separated to obtain a recycled material rich in C4-C6 hydrocarbons and a mixed aromatic product, wherein the recycled material is recycled back to step A2.

15. The method according to claim 14, wherein step A1 satisfies at least one of the following features:

the light hydrocarbons or naphtha are selected from at least one of straight-run gasoline, hydrocracked gasoline, catalytic cracked gasoline, hydrocoked gasoline, reforming topping oil, reforming raffinate oil, condensate oil, cracked gasoline, and cracked gasoline raffinate oil;

the light hydrocarbons or naphtha have an initial boiling point of 30–120°C and a final boiling point of 120–220°C;

the light hydrocarbons or naphtha have a nitrogen content of 0.1–10 ppm by mass; preferably, when the nitrogen content in the naphtha feedstock is greater than or equal to 3 ppm by mass, a denitrogenation treatment is first performed, followed by step A1;

the hydrogen-rich gas is one of hydrogen, a mixture of hydrogen and methane, and hydrogen-rich dry gas; preferably, the hydrogen volume content in the hydrogen-rich gas is greater than or equal to 50%.

16. The method according to claim 14, wherein step A2 satisfies at least one of the

following features:

the upgrading treatment employs a fixed bed, a moving bed, or a fluidized bed;

conditions of the upgrading treatment include: a mass hourly space velocity of the light hydrocarbon and/or naphtha feedstock of 0.3-2 h^{-1}, a reaction temperature of 280-450°C, preferably 320-380°C, a reaction pressure of 0.5-3.0 MPa, preferably 1.0-2.0 MPa, and a hydrogen-to-oil volume ratio of the hydrogen-rich gas to the light hydrocarbon and/or naphtha feedstock of 0.2-3.0: 1;

the upgrading catalyst is a catalyst obtained by a metal modification of the ZSM-5 molecular sieve; wherein the modifying metal is at least one of molybdenum, zinc, copper, gallium, and lanthanum, preferably at least one of zinc, molybdenum, and gallium; preferably, the mass content of the modifying metal is 1%-10% based on the mass of the metal-modified ZSM-5 molecular sieve catalyst, wherein the modifying metal is calculated as oxide.

17. The method according to claim 14, wherein in step A3, the proportion of propane in the cracking feedstock is ≥95v% and the recycled material is mainly C4-C6 hydrocarbons.

18. The method according to claim 14, wherein:

the upgrading treatment in step A2 is carried out through a first reaction zone and a second reaction zone;

wherein the first reaction zone is used to lighten light hydrocarbons and/or naphtha to produce cracking feedstock, and the second reaction zone is used to cause chain scission reactions in long-chain hydrocarbons.

19. The method according to claim 18, wherein step A2 satisfies at least one of the following features:

the first reaction zone employs a fixed bed, or one or more reactors, or one or more catalyst beds within a single fixed-bed reactor;

the second reaction zone emoloys a fixed bed or a fluidized bed;

the first reaction zone is filled with a first molecular sieve catalyst; preferably, the molecular sieve content in the first molecular sieve catalyst is greater than or equal to 70%

by mass;

the reaction conditions in the first reaction zone are as follows: a mass hourly space velocity of 0.3-2 h^{-1}; a reaction temperature of 280-400°C; a reaction pressure of 0.5-2.0 MPa; and a volume ratio of the hydrogen-rich gas to light hydrocarbons and/or naphtha of 0.3-5: 1;

the first reaction zone employs at least two reaction sections; preferably, the reaction temperature of the upstream reaction section is at least 10-120°C lower than that of the adjacent downstream reaction section, and more preferably at least 20-80°C lower;

the second reaction zone is filled with a second molecular sieve catalyst; preferably, the SiO_2/Al_2O_3 molar ratio of the molecular sieve is 150-300;

the reaction conditions in the second reaction zone are as follows: a reaction temperature of 420-550°C, a reaction pressure of 1.0-4.0 MPa, and a mass hourly space velocity of 0.1-1.5 h^{-1}.

20. The method according to claim 18, wherein the reaction products leaving the second reaction zone are first heat-exchanged with the mixture of light hydrocarbons and/or naphtha and hydrogen-rich gas before being separated.

21. The method according to claim 14, wherein the liquid phase of step A3 is introduced into an aromatization reaction zone to undergo a catalytic reaction, and the resulting reaction product is extracted to obtain the mixed aromatic product.

22. The method according to claim 21, wherein it has at least one of the following features:

the aromatization reaction zone employs a fixed bed, a moving bed, or a fluidized bed;

the catalyst used in the aromatization reaction zone comprises a support and a metal oxide, and contains, based on the mass of the catalyst, the following components by mass percentage: 1%-10% zinc oxide, 1%-5% copper oxide, 0.1%-3% lanthanum oxide, 1%-8% phosphorus, 50%-70% molecular sieve, and 20%-40% binder; preferably, the molecular sieve is at least one of ZSM-5 molecular sieve, Y-type molecular sieve, β-molecular sieve, mordenite, and SAPO-34 molecular sieve; more preferably, the SiO_2/Al_2O_3 molar ratio of

the molecular sieve is 40-200;

the reaction conditions of the aromatization reaction are as follows: a reaction temperature of 420-600°C, a reaction pressure of 0.1-2MPa, and a mass hourly space velocity of 0.2-2 h^{-1};

the separation of the upgraded products is carried out in a stabilizer tower or a gas-liquid separator.

23. Use of the ZSM-5 molecular sieve according to any one of claims 1-6 or the catalyst according to claim 12 or 13 in lightening of light hydrocarbons and/or naphtha.