MODIFIED MOLECULAR SIEVE, PREPARATION METHOD THEREFOR, AND USE THEREOF

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] The present disclosure claims the benefit of the China patent application No. "202211148910.5", filed on September 20, 2022, the content of which is specifically and entirely incorporated herein by reference.

FIELD

[0002] The present disclosure relates to the technical field of molecular sieve, in particular to a method for preparing a modified molecular sieve, a modified molecular sieve prepared by the method, and use thereof.

BACKGROUND

[0003] The catalytic cracking reaction is a typical acid-catalyzed gas-solid heterogeneous reaction follows the carbonium ion mechanism, however, the NaY molecular sieve per se does not exhibit acidity, it generally needs exchange and modification, in order to remove Na ions and modulate its acidity and pore-channel structure. Because the cations H^+ in acids have strong acidity, they are prone to disrupt the Y-type

molecular sieve skeleton structure, resulting in the decreased crystallinity and selectivity, the REY-type molecular sieve has excessively strong acidity and high acid density, it is apt to coke and deactivate during the catalytic cracking reaction process. Therefore, the commonly used modification methods at present relate to an exchange with ammonium salt or/and rare earth, thereby preparing the REHY-type or REUSY-type modified molecular sieve with different acidities and pore-channel structures through the thermal or hydrothermal calcination.

[0004] Ammonium chloride is prone to decompose at high temperature and crystallize at low temperature, thus it may easily block catalyst flue and bag dust collector, the continuous production cannot be implemented. Ammonium nitrate will explode at high-temperature and high-pressure and in the presence of materials that can be oxidized (i.e., reducing agents) and electric spark, it is a key material in the production of explosives and requires a high price, thus it is not used in the production of molecular sieves. Ammonium sulfate has the advantages of stable performance and cheap price, it is commonly used for exchange and modification of the industrial molecular sieves. However, it easily reacts with a rare earth to generate the precipitate of rare earth sulfate, on the one hand, the precipitate causes that the rare earth ions cannot migrate into the molecular sieve cage to effectively stabilize the molecular sieve skeleton structure, on the other hand, it is prone to cause excessive sulfate radicals

and destroy the molecular sieve skeleton structure, and the sulfate radicals will transform into sulfide in the oil refining process after producing the catalyst, thereby causing corrosion of the equipment.

[0005] In the prior art, the methods for precipitating rare earth are generally adopted for increasing the utilization ratio of rare earth, and generating the rare earth with independent phase to improve resistance of the molecular sieve to vanadium pollution; when the rare earth and the ammonium salt are subjected to exchange at the same time, the exchange efficiency is low due to the existence of competitive exchange; when the exchange of ammonium salt is performed before the exchange of rare earth, the ammonium chloride and ammonium nitrate in use will result in the problems such as high costs and corrosion of equipment; when the low-cost and recyclable ammonium sulfate is used for exchange, it requires a large amount of water washing operations for removing sulfate radicals to avoid the generation of sulfate precipitate, the water consumption will increase accordingly. After hydrothermal roasting of rare earth modified molecular sieve, it is unavoidable that a portion of the rare earth cannot be positioned in the sodalite cage, the rare earth sulfate precipitate is generated during the subsequent exchange of ammonium sulfate, the precipitate will increase the content of sulfate radicals in the molecular sieve and reduce the crystallinity. Although the pre-exchanging can reduce the sodium oxide and sulfate radicals present in the modified

molecular sieve, it has the disadvantages of long flow path, large water consumption and high costs. The REY molecular sieve produced without the use of an ammonium salt exhibits the defect of high coke.

[0006] CN 200610087535.2 discloses a preparation method of REY molecular sieve, the method comprises the following steps: after contacting NaY molecular sieve with an aqueous solution containing rare earth ions, or contacting with an aqueous solution containing rare earth ions and a solution or colloid containing aluminum ion, contacting with additional precipitating agent makes some rare earth precipitate on the molecular sieve, then carrying out a hydrothermal treatment, finally contacting with an ammonium salt aqueous solution, the prepared molecular sieve has strong resistance to vanadium. The one-exchange one-roasting rare earth modified Y-type molecular sieve is prepared through the rare earth exchange, precipitation, filtering, and roasting, the ammonium salt exchange is subsequently performed directly, the REY molecular sieve is prepared. Although the rare earth loss is prevented by precipitation during the one-exchange process, rare earth is inevitably present on the outer surface or super cage space of the one-exchange one-roasting rare earth modified Y-type molecular sieve, if ammonium sulfate is subsequently used as an exchanger, the portion of rare earth is prone to react with sulfate to generate a precipitate of rare earth sulfate, resulting in high content of sulfate radical, low crystallinity, and poor

stability of the molecular sieve.

[0007] CN 201511020519.7 discloses a preparation method of modified Y-type molecular sieve, the preparation method comprises the following steps: initially using ammonium salt to exchange a NaY molecular sieve, filtering, mixing with the compounds containing a group IIIB element in a periodic table of elements, and directly performing spray drying and hydrothermal calcining without washing; using the ammonium salt to exchange again, adding a precipitator or the precipitator and a filter aid, filtering, and performing or not performing hydrothermal calcining. Although the method relates to mixing the ammonium salt exchanged molecular sieve filter cake with the compound containing the group IIIB element, and calcining the mixture, and adding a precipitant after the second exchange with an ammonium salt, avoiding loss of the compound containing the group IIIB element, the method also involve with exchanging with ammonium salt directly after one-exchange and one-roasting, if ammonium sulfate is used as an exchanger, this part of group IIIB element is prone to generate a rare earth sulfate precipitate with the sulfate radical, resulting in high content of sulfate radical, low crystallinity, and poor stability of the molecular sieve.

[0008] As a result, it is urgently needed to develop a novel method for preparing the modified molecular sieve.

SUMMARY

[0009] The present disclosure aims to overcome the defects of high content of sulfate radical, low crystallinity, corrosion of equipment, long production process, and high costs in the preparation method of the modified molecular sieve in the prior art, and provides a method for preparing a modified molecular sieve, a modified molecular sieve prepared by the method, and a use thereof. The modified molecular sieve prepared by the method has the characteristics of low content of sulfate radical, high crystallinity, and desirable stability, and the method simplifies the process flow and facilitates the industrial production.

[0010] In order to achieve the above object, the first aspect of the present disclosure provides a method for preparing a modified molecular sieve comprising the following steps:

[0011] (1) subjecting a Na-type molecular sieve to metal ion exchange to obtain a metal ion exchange slurry;

[0012] (2) adding a first precipitant to allow part of metal ions in the metal ion exchange slurry to be subjected to first precipitation to obtain a first precipitation slurry;

[0013] (3) subjecting the first precipitation slurry to filtering, first ammonium sulfate exchange, first water washing, and first roasting sequentially to obtain a one-exchange one-roasting molecular sieve dry powder;

[0014] (4) adding a second precipitant to allow part of metal ions in the one-exchange one-roasting molecular sieve dry powder to be subjected to second precipitation, and then carrying out second ammonium sulfate exchange, second water washing, and optional second roasting sequentially to obtain the modified molecular sieve.

[0015] The second aspect of the present disclosure provides a modified molecular sieve prepared by the method according to the first aspect.

[0016] The third aspect of the present disclosure provides a use of the modified molecular sieves according to the second aspect in the heavy oil conversion and the resistance to heavy metal vanadium pollution.

[0017] The present disclosure has the following advantages over the prior art:

[0018] (1) The method for preparing modified molecular sieve provided by the present disclosure comprises the steps of adding precipitants (i.e., a first precipitant and a second precipitant) into the Na-type molecular sieve after the metal ion exchange and before the ammonium sulfate exchange, and generating a precipitate precursor of metal oxides with the metal ions, the method prevents the generation of a precipitate of sulfate radicals with the free metal ions in the exchange system solution, molecular sieve surface or super cages during the subsequent process of ammonium sulfate exchange and sodium reduction, thereby fulfilling the purpose of decreasing content of sulfate radicals.

[0019] (2) The method provided by the present disclosure also improves the crystallinity and stability of the modified molecular sieve, and increases the metal utilization ratio, generates the polyvalent metal oxide with a separate phase, enhances the heavy oil transformative capacity and resistance to heavy metal vanadium pollution; in addition, the method has a simple operation and simplified process flow, can facilitate the industrial production.

DESCRIPTION OF THE PREFERRED EMBODIMENT

[0020] The terminals and any value of the ranges disclosed herein are not limited to the precise ranges or values, such ranges or values shall be comprehended as comprising the values adjacent to the ranges or values. As for numerical ranges, the endpoint values of the various ranges, the endpoint values and the individual point values of the various ranges, and the individual point values may be combined with one another to produce one or more new numerical ranges, which should be deemed to have been specifically disclosed herein.

[0021] Unless otherwise specified in the present disclosure, the expressions “first” and “second” neither indicate a sequence, nor impose the limitations on the materials or steps, the expressions merely serve to distinguish the steps or materials. For instance, the expressions “first” and “second” in the terms “first ammonium sulfate exchange” and “second

ammonium sulfate exchange" merely serve to indicate that the operations are not the same ammonium sulfate exchange.

[0022] The first aspect of the present disclosure provides a method for preparing a modified molecular sieve comprising the following steps:

[0023] (1) subjecting a Na-type molecular sieve to metal ion exchange to obtain a metal ion exchange slurry;

[0024] (2) adding a first precipitant to allow part of metal ions in the metal ion exchange slurry to be subjected to first precipitation to obtain a first precipitation slurry;

[0025] (3) subjecting the first precipitation slurry to filtering, first ammonium sulfate exchange, first water washing, and first roasting sequentially to obtain a one-exchange one-roasting molecular sieve dry powder;

[0026] (4) adding a second precipitant to allow part of metal ions in the one-exchange one-roasting molecular sieve dry powder to be subjected to second precipitation, and then carrying out second ammonium sulfate exchange, second water washing, and optional second roasting sequentially to obtain the modified molecular sieve.

[0027] In some embodiments of the present disclosure, preferably, the conditions of metal ion exchange in step (1) comprises: a temperature of 25°C-180°C, preferably of 50°C -80°C; a pH of 2.8-6.5, preferably of 3.4-4.5; a time of 0.3h -3.5h, preferably of 0.5h -1.5h.

[0028] In some embodiments of the present disclosure, preferably, the metal ion exchange process comprises the following steps: mixing the Na-type molecular sieve with water, and then adding a soluble metal salt to perform the metal ion exchange.

[0029] In some embodiments of the present disclosure, preferably, the weight ratio of said Na-type molecular sieve to water is 1: (1.5-30), such as 1:1.5, 1:2, 1:3, 1:4, 1:5, 1:10, 1:20, 1:30, and a random value within the range consisting of any two numerical values, further preferably is 1: (2-5).

[0030] In some embodiments of the present disclosure, preferably, the content of said soluble metal salt calculated in terms of oxide in the Na-type molecular sieve on a dry basis is 1-20 wt%, such as 1wt%, 4wt%, 6wt%, 8wt%, 10wt%, 12wt%, 14wt%, 16wt%, 20wt%, and a random value within the range consisting of any two numerical values, further preferably is 6-16 wt%. The use of the preferred conditions is more conducive to reducing the content of sulfate radicals in the modified molecular sieve, thereby eliminating the effect of sulfate radicals on the properties of said modified molecular sieve, and improving the crystallinity and catalytic performance of the modified molecular sieve.

[0031] In the present disclosure, during the metal ion exchange process, the metal ions in the soluble metal salt are completely attached to the surface and internal pore-channel of the Na-type molecular sieve.

Therefore, the weight ratio of the Na-type molecular sieve on a dry basis to the soluble metal salt calculated in terms of oxide is 100: (1-20), preferably is 100: (6-16).

[0032] Unless otherwise specified in the present disclosure, solubility refers to that the substance is soluble in water, or is soluble in water under the effect of an auxiliary agent.

[0033] In some embodiments of the present disclosure, preferably, the soluble metal salt is chlorate and/or nitrate containing at least one element selected from a rare earth element, an alkaline earth metal element, and a transition metal element, further preferably is the chlorates and/or nitrates containing the rare earth element, further preferably selected from lanthanum chloride and/or lanthanum nitrate. In the present disclosure, the alkaline earth metal element is selected from calcium and/or barium; and the transition metal element is selected from silver and/or lead.

[0034] In the present disclosure, the species of Na-type molecular sieve has a wider selected range. Preferably, the Na-type molecular sieve has a silica/alumina ratio of 2-100, preferably of 2-50. Further preferably, the Na-type molecular sieve is at least one selected from the group consisting of NaY molecular sieve, NaHY molecular sieve, NaUSY molecular sieve, NaREHY molecular sieve, NaREUSY molecular sieve, Naβ molecular sieve, NaHβ molecular sieve, NaREHβ molecular sieve, NaX molecular sieve, NaREX molecular sieve, and NaHX molecular sieve, preferably

selected from NaY molecular sieve and/or NaHY molecular sieve, more preferably is NaY molecular sieve.

[0035] In some embodiments of the present disclosure, preferably, in step (2), the first precipitant is used in an amount satisfying the molar ratio of 1-4wt% of metal ions in the Na-type molecular sieve subjecting to the first precipitation; further preferably, the first precipitant is used in an amount satisfying the molar ratio of 1.5-2.5 wt% of metal ions in the Na-type molecular sieve subjecting to the first precipitation. The use of the preferred conditions is more conducive to reducing the content of sulfate radicals in the modified molecular sieve, thereby improving the crystallinity and catalytic performance of the modified molecular sieve.

[0036] The present disclosure has a wider selection range for the species of the first precipitant, as long as the metal ions produce a metal oxide. Preferably, the first precipitant is at least one selected from the group consisting of ammonium oxalate, ammonium carbonate, ammonium bicarbonate, aqueous ammonia, urea, and ammonium acetate; preferably at least one selected from the group consisting of ammonium oxalate, ammonium carbonate, ammonium bicarbonate, and aqueous ammonia.

[0037] In some embodiments of the present disclosure, preferably, the first precipitation conditions comprise: a temperature of 25°C -180°C, preferably of 50°C -80 °C; and a time of 0.1h -5h, preferably of 0.1h -2 h.

[0038] In the present disclosure, the first ammonium sulfate exchange

serves to further exchange Na^+ in the Na-type molecular sieve. Preferably, the first ammonium sulfate exchange process in step (3) comprises: exchanging the filtering product with a first ammonium sulfate aqueous solution.

[0039] In some embodiments of the present disclosure, preferably, the weight ratio of the first ammonium sulfate aqueous solution calculated in terms of ammonium sulfate to the Na-type molecular sieve is preferably (5-50): 100, such as 5:100, 10:100, 15:100, 20:100, 25:100, 30:100, 40:100, 50:100, and a random value within the range consisting of any two numerical values, further preferably is (10-25): 100.

[0040] In some embodiments of the present disclosure, preferably, the concentration of ammonium sulfate in the first ammonium sulfate aqueous solution is within the range of 20 g/L -400 g/L, such as 20 g/L, 50 g/L, 80 g/L, 120 g/L, 150 g/L, 200 g/L, 250 g/L, 300 g/L, 400g/L, and a random value within the range consisting of any two numerical values, further preferably within the range of 120 g/L -250 g/L.

[0041] In some embodiments of the present disclosure, preferably, the conditions of the first ammonium sulfate exchange comprise: a temperature of 15°C -150°C, preferably 50°C -80°C; and a time of 0.1h -5 h, preferably of 0.5h -2 h.

[0042] In some embodiments of the present disclosure, preferably, the dosage of water in the first water washing is 1-8 times of the weight of

said Na-type molecular sieve, for example, 1time, 2time, 3time, 4time, 5time, 8time, and a random value within the range consisting of any two numerical values, preferably is 2-5 times.

[0043] In some embodiments of the present disclosure, preferably, the conditions of the first roasting comprise: an atmosphere of 100% water vapor, a temperature of 400°C -700°C, preferably of 500°C -650°C, and a time of 0.1h -5h, preferably 0.5h -3h.

[0044] In some embodiments of the present disclosure, preferably, the second precipitant is used in an amount satisfying the molar ratio of 0.5-3wt% of the metal ions in the one-exchange one-roasting molecular sieve dry powder subjecting to the second precipitation; further preferably, the second precipitation is used in an amount satisfying the molar ratio of 1-2 wt% of the metal ions in the one-exchange one-roasting molecular sieve dry powder subjecting to the second precipitation. The use of the preferred conditions is more conducive to reducing the content of sulfate radicals in the modified molecular sieve, thereby improving the crystallinity and catalytic performance of the modified molecular sieve.

[0045] In some embodiments of the present disclosure, preferably, the second precipitant is at least one selected from the group consisting of ammonium oxalate, ammonium carbonate, ammonium bicarbonate, aqueous ammonia, urea, and ammonium acetate; further preferably at least one selected from the group consisting of ammonium oxalate,

ammonium carbonate, ammonium bicarbonate, and aqueous ammonia.

[0046] In some embodiments of the present disclosure, preferably, the second prediction conditions preferably comprises: a temperature of 15°C -40°C, preferably of 20°C -30°C, and a time of 0.1h-5 h, preferably of 0.1h-2 h.

[0047] In some embodiments of the present disclosure, preferably,the second ammonium sulfate exchange process in step (4) comprises: exchanging the second precipitation product with the second ammonium sulfate aqueous solution.

[0048] In some embodiments of the present disclosure, preferably, the weight ratio of the second ammonium sulfate aqueous solution calculated in terms of ammonium sulfate to the one-exchange one-roasting molecular sieve dry powder is (5-50): 100, such as 5:100, 10:100, 15:100, 20:100, 25:100, 30:100, 40:100, 50:100, and a random value within the range consisting of any two numerical values, further preferably is (10-25): 100.

[0049] In some embodiments of the present disclosure, preferably, the concentration of ammonium sulfate in the second ammonium sulfate aqueous solution is within the range of 20 g/L -400 g/L, such as 20 g/L, 50 g/L, 80 g/L, 120 g/L, 150 g/L, 200 g/L, 250 g/L, 300 g/L, 400g/L, and a random value within the range consisting of any two numerical values, further preferably within the range of 120 g/L -250 g/L.

[0050] In some embodiments of the present disclosure, preferably, the conditions of the second ammonium sulfate exchange comprise: a temperature of 20°C-85°C, preferably of 50°C-80°C; and a time of 0.1h-5 h, preferably of 0.1h-2h.

[0051] In some embodiments of the present disclosure, preferably, the dosage of water in the second water washing is 1-8 times of the weight of the one-exchange one-roasting molecular sieve dry powder, for example, 1time, 2time, 3time, 4time, 5time, 8time, and a random value within the range consisting of any two numerical values, further preferably is 2-5 times.

[0052] In some embodiments of the present disclosure, preferably, the conditions of the second roasting comprise: an atmosphere of 20-100 v % water vapor(If not specified, the atmosphere consists of water vapor and optional air); a temperature of 400°C -700°C, preferably of 450°C -650°C; and a time of 0.1h-10 h, further preferably of 0.5h-5 h.

[0053] In some embodiments of the present disclosure, preferably, the one-exchange one-roasting molecular sieve dry powder is mixed with water before the second precipitation.

[0054] In some embodiments of the present disclosure, preferably, the weight ratio of the one-exchange one-roasting molecular sieve dry powder in step (4) to water is 1: (1.5-30), such as 1:1.5, 1:2, 1:3, 1:4, 1:5, 1:10, 1:20, 1:30, and a random value within the range consisting of any

two numerical values, further preferably is 1: (2-5).

[0055] The second aspect of the present disclosure provides a modified molecular sieve prepared by the method according to the first aspect.

[0056] The modified molecular sieve prepared by the method provided in the present disclosure has a low content of sulfate radical, high crystallinity, and desirable stability, it exhibits high activity during its use in the heavy oil conversion and the resistance to heavy metal vanadium pollution.

[0057] In some embodiments of the present disclosure, preferably, the content of SO_4^{2-} in the modified molecular sieve is less than or equal to 0.5 wt%, further preferably within the range of 0.01-0.45 wt%.

[0058] In some embodiments of the present disclosure, preferably, the modified molecular sieve has a Na_2O content less than or equal to 1wt% and a RE_2O_3 content larger than or equal to 5wt%, more preferably, the modified molecular sieve has a Na_2O content within the range of 0.5-1wt% and a RE_2O_3 content within the range of 10-20 wt%.

[0059] In some embodiments of the present disclosure, preferably, the modified molecular sieve has a crystallinity C/C_0 larger than or equal to 50%, further preferably within the range of 55-75%.

[0060] Unless otherwise specified in the present disclosure, the parameter SO_4^{2-} content is measured by using the X-Ray Fluorescence (XRF) method; the parameter crystallinity is determined by means of the X-ray

diffraction method; the parameter micro-activity is measured with the following process: the samples are pretreated at the conditions of a temperature of 800°C and 100% water vapor for different time; the reaction feedstock is light diesel derived from the Dagang Oilfield in China, the reaction temperature is 460°C, the reaction time is 70s, the loading amount of said catalyst is 5g, the catalyst-oil weight ratio is 3.2, and total conversion rate is regarded as the micro-activity.

[0061] The third aspect of the present disclosure provides a use of the modified molecular sieves according to the second aspect in the heavy oil conversion and the resistance to heavy metal vanadium pollution.

[0062] According to a particularly preferred embodiment of the present disclosure, a method for preparing a modified molecular sieve, the method comprises the following steps:

[0063] (1) subjecting a Na-type molecular sieve to metal ion exchange to obtain a metal ion exchange slurry;

[0064] (2) adding a first precipitant to allow part of metal ions in the metal ion exchange slurry to be subjected to first precipitation to obtain a first precipitation slurry;

[0065] (3) subjecting the first precipitation slurry to filtering, first ammonium sulfate exchange, first water washing, and first roasting sequentially to obtain a one-exchange one-roasting molecular sieve dry powder;

[0066] (4) adding a second precipitant to allow part of metal ions in the one-exchange one-roasting molecular sieve dry powder to be subjected to second precipitation, and then carrying out second ammonium sulfate exchange, second water washing, and optional second roasting sequentially to obtain the modified molecular sieve;

[0067] wherein the first precipitant in step (2) is used in an amount satisfying the molar ratio of 1.5-2.5 wt% of metal ions in the Na-type molecular sieve subjecting to the first precipitation;

[0068] wherein the conditions of the first roasting in step (3) comprise: an atmosphere of 100% water vapor, a temperature of 500-650°C, and a time of 0.5-3 h;

[0069] wherein the second precipitant in step (4) is used in an amount satisfying the molar ratio of 1-2 wt% of the metal ions in the one-exchange one-roasting molecular sieve dry powder subjecting to the second precipitation; the conditions of the second roasting comprise: an atmosphere of 20-100 v % water vapor, a temperature of 450°C -650°C, and a time of 0.5h-5 h.

[0070] The present disclosure will be described in detail below with reference to examples.

[0071] The NaY molecular sieve was commercially available from Lanzhou Catalyst Plant.

[0072] The parameter SO_4^{2-} content was measured by using the X-Ray

Fluorescence (XRF) method;

[0073] The parameter crystallinity was determined by means of the X-ray diffraction method;

[0074] The parameter micro-activity was measured with the following process: the samples were pretreated at the conditions of a temperature of 800°C and 100% water vapor for different time; the reaction feedstock was light diesel derived from the Dagang Oilfield in China, the reaction temperature was 460°C, the reaction time was 70s, the loading amount of said catalyst was 5g, the catalyst-oil weight ratio was 3.2, and total conversion rate was regarded as the micro-activity.

[0075] The physical properties of modified molecular sieves (Z1-Z7 and DZ1-DZ4) prepared in Examples 1-7 and Comparative Examples 1-4 were illustrated in Table 1.

[0076] Example 1

[0077] (1) 1,000g of NaY molecular sieve (on a dry basis by weight) was pulped with 5L of deionized water, 0.537L of a $LaCl_3$ solution (0.98 mole of La^{3+}) having a concentration of 298g/L (calculated in terms of La_2O_3) was added to perform the metal ion exchange (at a temperature of 80°C for 0.5h), a metal ion exchange slurry was obtained, wherein the content of $LaCl_3$ calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 16wt%;

[0078] (2) (32g, 0.225mol) of ammonium oxalate monohydrate was

added such that 2.4wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 80°C for 0.5h), a first precipitation slurry was obtained;

[0079] (3) the first precipitation slurry was subjected to filtering and unwatering, 0.833L of an aqueous ammonium sulfate solution with a concentration of 180g/L was added, subjected to exchanging at 60°C for 1h, and then unwatering, 3L of water was added for rinsing, subsequently subjected to roasting at 500°C in 100% water vapor atmosphere for 2h, a one-exchange one-roasting molecular sieve dry powder was obtained;

[0080] (4) 1,000g (on a dry basis by weight) of the one-exchange one-roasting molecular sieve dry powder was pulped with 5L of deionized water, (25.6g, 0.18mol) of ammonium oxalate monohydrate was then added, such that 2wt% of La^{3+} in the one-exchange one-roasting molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for 0.5h), 0.6L of an aqueous ammonium sulfate solution with a concentration of 250g/L was added, subjected to exchanging at 80°C for 1.5h, filtering and unwatering, 5L of water was added for rinsing, subsequently subjected to roasting at 450°C in 100% water vapor atmosphere for 2h, a modified molecular sieve Z1 was prepared.

[0081] Example 2

[0082] (1) 1,000g of NaY molecular sieve (on a dry basis by weight) was

pulped with 5L of deionized water, 0.358L of a $La(NO_3)_3$ solution (0.615 mole of La^{3+}) having a concentration of 280g/L (calculated in terms of La_2O_3) was added to perform a metal ion exchange (at a temperature of 50°C for 1.5h), a metal ion exchange slurry was obtained, wherein the content of $La(NO_3)_3$ calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 10wt%;

[0083] (2) (25.6g, 0.18mol) of ammonium oxalate monohydrate was added such that 2wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 50°C for 0.5h), a first precipitation slurry was obtained;

[0084] (3) the first precipitation slurry was subjected to filtering and unwatering, 1.111L of an aqueous ammonium sulfate solution with a concentration of 180g/L was added, subjected to exchanging at 80°C for 1h, and then unwatering, 3L of water was added for rinsing, subsequently subjected to roasting at 600°C in a 100% water vapor atmosphere for 2h, a one-exchange one-roasting molecular sieve dry powder was obtained;

[0085] (4) 1,000g (on a dry basis by weight) of the one-exchange one-roasting molecular sieve dry powder was pulped with 5L of deionized water, (13g, 0.135mol) of ammonium carbonate was then added, such that 1.5wt% of La^{3+} in the one-exchange one-roasting molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for 0.5h), 1.666L of an aqueous ammonium sulfate

solution with a concentration of 120g/L was added, subjected to exchanging at 50°C for 1h, filtering and unwatering, 2L of water was added for rinsing, subsequently subjected to roasting at 500°C in 80% water vapor atmosphere for 2.5h, a modified molecular sieve Z2 was prepared.

[0086] Example 3

[0087] (1) 1,000g of NaY molecular sieve (on a dry basis by weight) was pulped with 5L of deionized water, 0.336L of a $LaCl_3$ solution (0.615 mole of La^{3+}) having a concentration of 298g/L (calculated in terms of La_2O_3) was added to perform the metal ion exchange (at a temperature of 50°C for 1h), a metal ion exchange slurry was obtained, wherein the content of $LaCl_3$ calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 10wt%;

[0088] (2) 16mL of industrial aqueous ammonia with a concentration of 28wt% was added such that 1.5wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 50°C for 0.5h), a first precipitation slurry was obtained;

[0089] (3) the first precipitation slurry was subjected to filtering and unwatering, 1.389L of an aqueous ammonium sulfate solution with a concentration of 180g/L was added, subjected to exchanging at 50°C for 1.5h, and then unwatering, 3L of water was added for rinsing, subsequently subjected to roasting at 650°C in 100% water vapor

atmosphere for 2h, a one-exchange one-roasting molecular sieve dry powder was obtained;

[0090] (4) 1,000g (on a dry basis by weight) of the one-exchange one-roasting molecular sieve dry powder was pulped with 5L of deionized water, (12.8g, 0.09mol) of ammonium oxalate monohydrate was then added, such that 1wt% of La^{3+} in the one-exchange one-roasting molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for 0.5h), 1.389L of an aqueous ammonium sulfate solution with a concentration of 180g/L was added, subjected to exchanging at 50°C for 1h, filtering and unwatering, 3L of water was added for rinsing, subsequently subjected to roasting at 650°C in 60v% water vapor atmosphere for 2h, a modified molecular sieve Z3 was prepared.

[0091] Example 4

[0092] (1) 1,000g of NaY molecular sieve (on a dry basis by weight) was pulped with 5L of deionized water, 0.43L of a mixed $RECl_3$ solution (the weight ratio of Ce_2O_3 and La_2O_3 was 6: 4, 0.9287 mole of RE^{3+}) having a concentration of 326g/L (calculated in terms of RE_2O_3) was added to perform the metal ion exchange (at a temperature of 60°C for 1h), a metal ion exchange slurry was obtained, wherein the content of $RECl_3$ calculated in terms of RE_2O_3 in the NaY molecular sieve on a dry basis was 14wt%;

[0093] (2) (25.6g, 0.18mol) of ammonium oxalate monohydrate was added, 5mL of industrial aqueous ammonia with a concentration of 28wt% was further added, such that 2.4% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 60°C for 0.5h), a first precipitation slurry was obtained;

[0094] (3) the first precipitation slurry was subjected to filtering and unwatering, 1.222L of an aqueous ammonium sulfate solution with a concentration of 180g/L was added, subjected to exchanging at 100°C for 0.5h, and then unwatering, 5L of water was added for rinsing, subsequently subjected to roasting at 600°C in 100% water vapor atmosphere for 2h, a one-exchange one-roasting molecular sieve dry powder was obtained;

[0095] (4) 1,000g (on a dry basis by weight) of the one-exchange one-roasting molecular sieve dry powder was pulped with 5L of deionized water, (18g, 0.187mol) of ammonium carbonate was then added, such that 1.8wt% of RE^{3+} in the one-exchange one-roasting molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for 0.5h), 1L of an aqueous ammonium sulfate solution with a concentration of 120g/L was added, subjected to exchanging at 25°C for 1h, filtering and unwatering, 4L of water was added for rinsing, subsequently subjected to roasting at 550°C in 20v% water vapor atmosphere for 2h, a modified molecular sieve Z4 was

prepared.

[0096] Example 5

[0097] The modified molecular sieve was prepared according to the method of Example 1, except that in step (1), 0.537L of a $LaCl_3$ solution having a concentration of 298g/L (calculated in terms of La_2O_3) was replaced with 0.67L of a $LaCl_3$ solution having a concentration of 298g/L (calculated in terms of La_2O_3), the content of $LaCl_3$ calculated in terms of La_2O_3 in the NaY molecular sieve on a dry basis was 20wt%.

[0098] The remaining conditions were the same, a modified molecular sieve Z5 was obtained.

[0099] Example 6

[00100] The modified molecular sieve was prepared according to the method of Example 1, except that in step (2), (32g, 0.225mol) of ammonium oxalate monohydrate was replaced with (12.8g, 0.09mol) of ammonium oxalate monohydrate, such that 1wt% of La^{3+} in the metal ion exchange slurry was subjected to a first precipitation (at a temperature of 80°C for 0.5h).

[00101] The remaining conditions were the same, a modified molecular sieve Z6 was obtained.

[00102] Example 7

[00103] The modified molecular sieve was prepared according to the method of Example 1, except that in step (4), (25.6g, 0.18mol) of

ammonium oxalate monohydrate was replaced with (6.4g, 0.045mol) of ammonium oxalate monohydrate, such that 0.5wt% of La^{3+} in the one-exchange one-roasting molecular sieve dry powder was subjected to a second precipitation (at a temperature of 25°C for 0.5h).

[00104] The remaining conditions were the same, a modified molecular sieve Z7 was obtained.

[00105] Comparative Example 1

[00106] The modified molecular sieve DZ1 was prepared according to the method disclosed in CN101088613A with an application number "200610087535.2", namely

[00107] 1,000g of NaY molecular sieve (on a dry basis by weight) was pulped with 8L of deionized water, 0.385L of a $RECl_3$ solution with a concentration of 312g/L (calculated in terms of La_2O_3) was added, 240g of aluminum sulfate was added to perform the ion exchange at a temperature of 90°C for 1h, 75g of ammonium bicarbonate was further added, and stirred at a constant temperature for 0.25h, subjected to filtering, and rinsing with 5L of water, the filter cake was subsequently subjected to roasting at 600°C in 100% water vapor atmosphere for 2h, a one-exchange one-roasting molecular sieve dry powder was obtained;

[00108] 1,000g (on a dry basis by weight) of the one-exchange one-roasting molecular sieve dry powder was pulped with 6L of deionized water, 300g of ammonium sulfate was added, subjected to

exchanging at 75°C for 1h, filtering, and rinsing with 6L of water, the filter cake was dried, a modified molecular sieve DZ1 was prepared.

[00109] Comparative Example 2

[00110] The modified molecular sieve was prepared according to the method of Example 1, except that in step (2), (32g, 0.225mol) of ammonium oxalate monohydrate was not added, the remaining conditions were the same, a modified molecular sieve DZ2 was obtained.

[00111] Comparative Example 3

[00112] The modified molecular sieve was prepared according to the method of Example 2, except that in step (4), (13g, 0.135mol) of ammonium carbonate was not added, the remaining conditions were the same, a modified molecular sieve DZ3 was obtained.

[00113] Comparative Example 4

[00114] The modified molecular sieve was prepared according to the method of Example 3, except that 16mL of industrial aqueous ammonia with a concentration of 28wt% was not added in step (2), (12.8g, 0.09mol) of ammonium oxalate monohydrate was not added in step (4), the remaining conditions were the same, a modified molecular sieve DZ4 was obtained.

[00115] Table 1

	Na_2O content, wt%	RE_2O_3 content, wt%	SO_4^{2-} content, wt%	C/C_0, %
Example 1	0.92	16.2	0.27	58

Example 2	0.98	10.4	0.41	62
Example 3	0.76	6.5	0.38	67
Example 4	0.82	14.3	0.32	59
Example 5	0.92	19.8	0.67	55
Example 6	1.1	15.6	0.82	57
Example 7	1.1	16.1	0.95	56
Comparative Example 1	1.8	12.1	2.53	55
Comparative Example 2	1.5	14.6	1.55	57
Comparative Example 3	1.3	9.6	1.46	59
Comparative Example 4	1.4	4.8	1.86	63

[00116] As can be seen from the results of Table 1, the modified molecular sieve prepared with the method of the present disclosure has higher rare earth utilization ratio, lower sulfate radical content, and higher crystallinity.

[00117] Comparison with Example 5, Example 1 controls a scheme that the content of soluble metal salt calculated in terms of oxide in the Na-type molecular sieve on a dry basis is within the preferred protection range, the obtained modified molecular sieve has lower sulfate radical content and higher crystallinity.

[00118] Compared with Example 6, Example 1 controls a scheme that the first precipitant is used in such an amount that the content of metal ions in the first precipitant falls into the preferred protection scope, the obtained modified molecular sieve has lower sulfate radical content and higher crystallinity.

[00119] Compared to Example 7, Example 1 controls a scheme that

the second precipitant is used in such an amount that the content of precipitated metal ions falls into the preferred protection scope, the obtained modified molecular sieve has lower sulfate radical content and higher crystallinity.

[00120] Test Example 1

[00121] The modified molecular sieves (Z1-Z7 and DZ1-DZ4) prepared in Examples 1-7 and Comparative Examples 1-4 were subjected to the hydrothermal stability test.

[00122] The test conditions comprised: 100g (dry basis) modified molecular sieves (Z1-Z7 and DZ1-DZ4) were tabletted, pulverized to particles of 20-40 mesh respectively, then subjected to aging on a fixed-bed hydrothermal treatment unit under the conditions of 100% water vapor and a temperature of 800°C for 10 hours, the micro-activity index (MA1) was measured on an catalytic cracking automatic micro-activity evaluator, the test results are shown in Table 2.

[00123] Test Example 2

[00124] The modified molecular sieves (Z1-Z7 and DZ1-DZ4) prepared in Examples 1-7 and Comparative Examples 1-4 were subjected to the performance test for resistance to heavy metal vanadium pollution.

[00125] The test conditions included: the modified molecular sieves (Z1-Z7 and DZ1-DZ4) were subjected to an equivalent-volume impregnation in an ammonium metavanadate solution with a

concentration of 2,000 ppm (by volume) respectively, sufficiently mixed, sealed and subjected to standing still for 12h, then dried in a blast drying oven at 120°C for 16h, tabletted, pulverized to particles of 20-40 mesh, then subjected to aging on a fixed-bed hydrothermal treatment unit under the conditions of 100% water vapor and a temperature of 800°C for 2 hours, the micro-activity index (MA2) was measured on an catalytic cracking automatic micro-activity evaluator, the test results are shown in Table 2.

[00126] Table 2

	MA1, wt%	MA2, wt%
Example 1	72	59
Example 2	65	55
Example 3	62	54
Example 4	70	58
Example 5	71	58
Example 6	68	56
Example 7	66	55
Comparative Example 1	60	51
Comparative Example 2	61	53
Comparative Example 3	58	50
Comparative Example 4	52	46

[00127] As illustrated by the data in Table 2, compared with Comparative Examples 1-4, the modified molecular sieves prepared in Examples 1-7 have obviously higher micro-activity (i.e., higher values of MA1) after subjected to aging under the conditions of 100% water vapor and a temperature of 800°C for 10 hours. Therefore, the modified

molecular sieves provided by the present disclosure have better hydrothermal stability and cracking activity.

[00128] Similarly, as can be seen from the data in Table 2, compared with Comparative Examples 1-4, the modified molecular sieves prepared in Examples 1-7 have obviously higher micro-activity (i.e., higher values of MA2) after polluted with an ammonium metavanadate solution with a concentration of 2,000 ppm, subjected to aging under the conditions of 100% water vapor and a temperature of 800°C for 2 hours. Thus the modified molecular sieves provided by the present disclosure exhibit better resistance to heavy metal vanadium pollution.

[00129] The above content describes in detail the preferred embodiments of the present disclosure, but the present disclosure is not limited thereto. A variety of simple modifications can be made in regard to the technical solutions of the present disclosure within the scope of the technical concept of the present disclosure, including a combination of individual technical features in any other suitable manner, such simple modifications and combinations thereof shall also be regarded as the content disclosed by the present disclosure, each of them falls into the protection scope of the present disclosure.