

(12) UK Patent Application (19) GB (11) 2546614 (13) A

(43) Date of A Publication

26.07.2017

(21) Application No: 1621466.0

(22) Date of Filing: 27.11.2015

Date Lodged: 16.12.2016

(30) Priority Data:

(31) 201410711228 (32) 01.12.2014 (33) CN
(31) 201410711208 (32) 01.12.2014 (33) CN
(31) 201410711239 (32) 01.12.2014 (33) CN

(62) Divided from Application No
1520976.0 under section 15(9) of the Patents Act 1977

(51) INT CL:
C01B 39/24 (2006.01) B01J 29/08 (2006.01)
C01B 39/20 (2006.01)

(56) Documents Cited:
CN 105709845 A CN 104828839 A
CN 104591214 A CN 104591212 B
CN 104588122 A US 4857169 A

(58) Field of Search:
INT CL B01J, C01B
Other: EPODOC, WPI

(71) Applicant(s):
China Petroleum & Chemical Corporation
No.22 Chaoyangmen North Street, Chaoyang District,
Beijing, 100728, China

Fushun Research Institute of Petroleum and
Petrochemicals, Sinopec Corp
No. 31 Dandong East Road, Wanghua District,
Fushun 113001, Liaoning, China

(72) Inventor(s):
Chang Liu
Fenglai Wang
Hong Zhao
Minghua Guan
Yanze Du
Wei Huang

(74) Agent and/or Address for Service:
Kilburn & Strode LLP
20 Red Lion Street, LONDON, WC1R 4PJ,
United Kingdom

(54) Title of the Invention: **H-Y Molecular sieve, and preparation methods thereof, hydrocracking catalyst, and hydrocracking method**
Abstract Title: **H-Y molecular sieve and preparation thereof**

(57) The present invention discloses an H-Y molecular sieve and a method for preparing the H-Y molecular sieve from a Na-Y molecular sieve, a hydrocracking catalyst, and a hydrocracking method. The method for preparing the molecular sieve comprises (A) treating a Na-Y molecular sieve by ammonium exchange to prepare a NH₄-Na-Y molecular sieve, (B) treating the NH₄-Na-Y molecular sieve by hydrothermal treatment, and (C) reacting the material obtained in (B) with (NH₄)₂SiF₆ solution. The average grain diameter of the Na-Y molecular sieve is 2~5µm, and the sum of pore volumes of pores in 1-10nm diameter accounts for 70~90% of the total pore volume of the Na-Y molecular sieve. The H-Y molecular sieve obtained from the large-grain Na-Y molecular sieve can be used as an acidic component in the hydrocracking catalyst. When the hydrocracking catalyst containing the H-Y molecular sieve is applied in the hydrocracking reaction of heavy oils that contain macromolecules, it can provide better cracking activity and product selectivity in the hydrocracking reaction.

GB 2546614 A

1/2

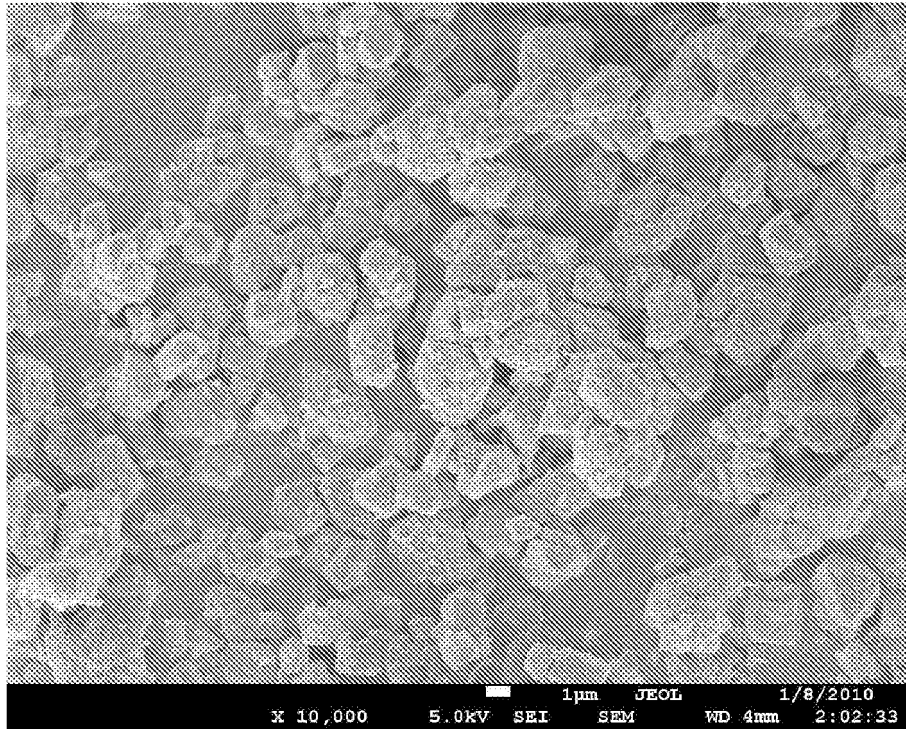


Fig. 1

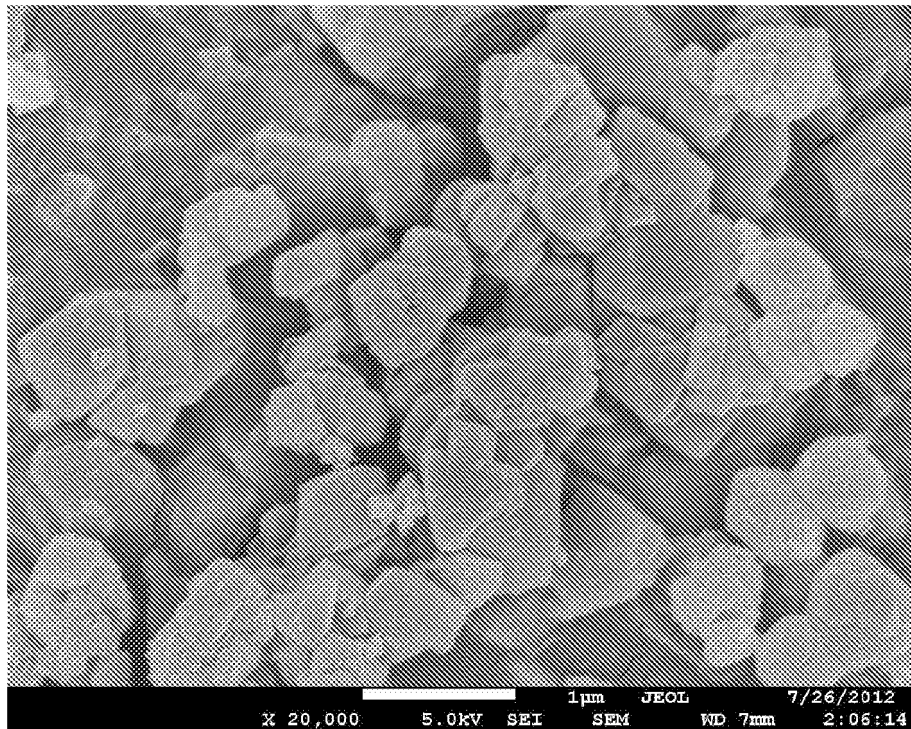


Fig. 2

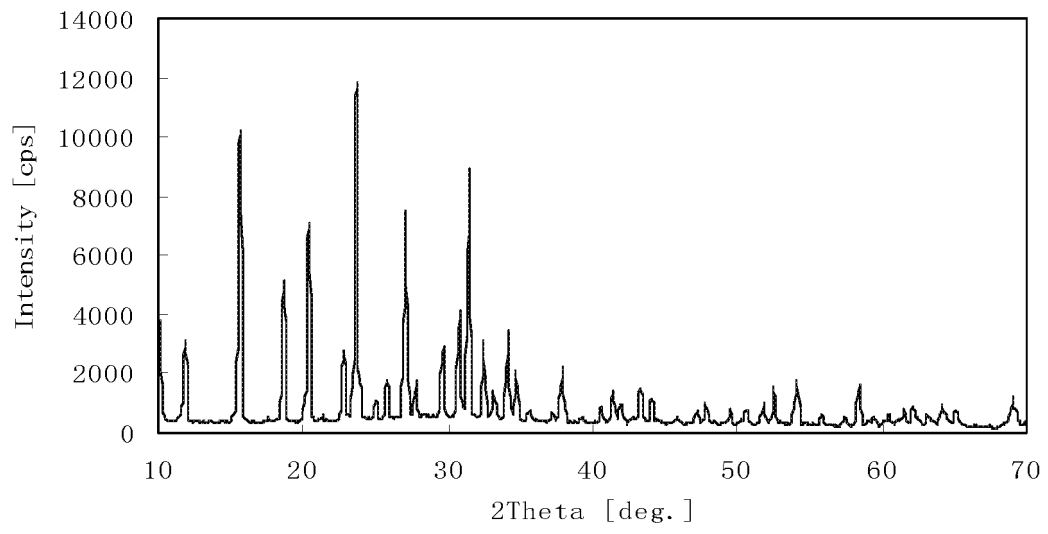


Fig. 3

H-Y Molecular Sieve, and Preparation Methods Thereof, Hydrocracking Catalyst, and Hydrocracking Method

Cross Reference to Related Application

5 This application claims priority to Chinese Application No. 201410711228.1 filed on December 1, 2014, entitled “A NaY Molecular Sieve and Method for Preparing the same”, Chinese Application No. 201410711208.4 filed on December 1, 2014, entitled “A Y Molecular Sieve and Method for Preparing the same”, and Chinese Application No. 201410711239.x filed on December 1, 2014,
10 entitled “Modified Y Molecular Sieve and Method for Preparing the same”, which are specifically and entirely incorporated by reference.

FIELD OF THE INVENTION

The present invention relates to a Na-Y molecular sieve and a method for
15 preparing the Na-Y molecular sieve, an H-Y molecular sieve obtained from the molecular sieve and a method for preparing the H-Y molecular sieve, a hydrocracking catalyst containing the H-Y molecular sieve, and a hydrocracking method utilizing the hydrocracking catalyst.

BACKGROUND OF THE INVENTION

20 At present, in the heavy oil cracking field, molecular sieves that can be used as cracking active components include Y molecular sieve, β molecular sieve, and ZSM molecular sieve, etc., wherein Y molecular sieve is used most widely. Existing methods for producing Y molecular sieve products in industrial
25 production are essentially based on the method of using a crystallization directing agent (CDA) disclosed by GRACE Company (a US company) in the US patents US3639099 and US4166099, and the ordinary Y molecular sieve products produced with such methods have crystal grains usually in about 1 μ m grain size, with about 300~400 crystal cells in each dimension. In Y molecular sieve

powder in ordinary grain size synthesized conventionally, the distribution percentage of pores in diameter smaller than 1nm is 15~20%, the distribution percentage of pores in diameter within 1~10nm range is 45~50%, and the distribution percentage of pores in diameter greater than 10nm is 30~40%. For a
5 macromolecular cracking reaction, the ideal pore diameter range suitable for raw material reaction and product diffusion is 1~10nm. Though Y molecular sieve can be modified appropriately to an ideal pore diameter distribution range by post-modification, the final distribution of pore diameter range in the post-modified molecular sieve directly depends on the original pore diameter
10 distribution in the molecular sieve; moreover, pore expansion has impacts on the skeleton structure of the molecular sieve, and thereby has impacts on the activity and stability of the molecular sieve.

In the prior art, the direct synthesis process refers to a process in which a Y molecular sieve (usually Na-Y molecular sieve) to be prepared is synthesized
15 directly in one operation without post-treatment. At present, a CDA method is used conventionally. With that method, the chemical silica-alumina ratio ($\text{SiO}_2/\text{Al}_2\text{O}_3$) in the synthesized Y molecular sieve is 3.5~5.5. To obtain a Y molecular sieve with a higher chemical silica-alumina ratio, expensive and highly toxic organic materials such as crown ether have to be added. In addition, in the
20 preparation process of a Y molecular sieve, the lower the silica-alumina ratio is, the easier the preparation is; in contrast, the higher the silica-alumina ratio is, the harsher the conditions are, and the more difficult the preparation is. There are many influencing factors in preparation of a molecular sieve with a high silica-alumina ratio, such as the composition of the reaction mixture, the
25 preparation method, the source of the reactants, the preparation of the directing agent, the acidity/alkalinity of the gel, and the conditions of crystallization, etc.

In CN103449468A, a Na-Y molecular sieve synthesis method is disclosed, comprising: mixing sodium silicate, sodium metaaluminate, and deionized water,

and aging at 15~70° C for 0.5~48.0h to obtain a crystallization directing agent; mixing the crystallization directing agent, sodium silicate, an acidic aluminum salt, and sodium aluminate solution to a homogeneous state to prepare a silica-alumina gel; crystallizing the silica-alumina gel at 80~140° C for 5 0.1~80.0h; adding peroxide into the crystallized silica-alumina gel at a mole ratio of peroxide to Al₂O₃ in the gel equal to 0.05~20, and then continuing the crystallization for 5~20h. With that method, no organic or inorganic template agent is added, no post-treatment or modification is required, and a Y molecular sieve with a high silica-alumina ratio can be prepared directly in a short time, and 10 crystallinity of the obtained molecular sieve is equal to or higher than 80%, silica-alumina ratio not lower than 5.8, and average grain diameter within 200~300nm range. Though that method can be used to synthesize a Y molecular sieve with high silica-alumina ratio, the preparation process is complex, the grain diameter of the obtained molecular sieve is too small, and a specific amount of 15 peroxide has to be added into the gel. Hence, the conditions of molecular sieve synthesis are demanding.

In US3671191 and US3639099, a CDA method is used to synthesize a Y molecular sieve, wherein a directing agent is prepared first; then, a silica-alumina gel is prepared; next, the aged directing agent is added, and crystallization is 20 carried out at a high temperature. In the method described above, an inorganic acid and an aluminum salt are used to decrease the alkalinity of the reaction system, and thereby improve the silica-alumina ratio of the resultant molecular sieve. However, only an ordinary Y molecular sieve can be prepared with that method, and a directing agent has to be synthesized first in the preparation 25 process. In addition, the preparation process involves over many steps and high cost.

In CN101481120A, a method for preparation of a Y molecular sieve through a rapid crystallization process is disclosed. In that method, first, a silica-alumina

gel is prepared from a silica source, an alumina source, and an alkali source; then, a W/O emulsion system is prepared from the silica-alumina gel, oil, surfactant, and co-surfactant; next, the W/O emulsion system is transferred into a reactor for rapid crystallization. The method employs an expansive surfactant to prepare
5 the Y molecular sieve, and the preparation process is complex; consequently, the preparation cost is severely increased.

In CN1209358A, a Y zeolite rich in secondary pores is disclosed. Specifically, a method for preparation of a zeolite is disclosed, wherein Na-Y zeolite is used as the initial powder, and ammonium exchange is carried out first,
10 to release Na⁺; then, hydrothermal treatment and acid extraction are carried out twice, wherein the second round of hydrothermal treatment and second round of acid extraction are carried out after the first round of hydrothermal treatment and first round of acid extraction. In the obtained Y zeolite, the pore volume of pores in diameter greater than 2nm accounts for 40~66% of the total pore volume.
15 In hydrocracking process, the transformation of macromolecular aromatics in the raw material is affected adversely, and the distribution and quality of the prepared catalyst product should be further improved.

Viewed from the aspect of application of molecular sieve products with a cracking function in industrial catalytic processes, the performance of molecular
20 sieve products mainly depend on the two aspects: selective absorptivity and reactivity. The molecules of the reactants can diffuse into the pore canals of the molecular sieve and have specific catalyzed reactions only if the molecular size of the reactant is smaller than the pore size of the molecular sieve and the molecules can overcome the surface energy barrier of the crystals in the molecular sieve;
25 here, the diffusivity of the absorbed molecules through the pores and cages of the crystals in the molecular sieve plays a decisive role. Hence, it is desirable to overcome the drawback of existing Y molecular sieve products in ideal pore diameter distribution and provide a Y molecular sieve with pore diameter

distribution suitable for macromolecular cracking reactions.

SUMMARY OF THE INVENTION

To overcome the drawbacks in the prior art, the present invention provides a Na-Y molecular sieve, a H-Y molecular sieve and a method for preparing the Na-Y molecular sieve, a H-Y molecular sieve and a method for preparing the H-Y molecular sieve, a hydrocracking catalyst, and a hydrocracking method.

To attain the objects described above, the present invention provides a Na-Y molecular sieve, wherein the average grain diameter of the Na-Y molecular sieve is 2~5 μ m, and the sum of pore volumes of pores in 1-10nm diameter accounts for 70~90% of the total pore volume of the Na-Y molecular sieve.

The present invention further provides a method for preparing the Na-Y molecular sieve provided in the present invention, comprising: (1) mixing sodium silicate, high alkaline sodium metaaluminate solution, aluminum sulfate solution, and low alkaline sodium metaaluminate solution at a mole ratio of Na₂O : Al₂O₃ : SiO₂ : H₂O equal to (10~15) : 1 : (10~20) : (500~600), and aging the obtained mixture to obtain a gel; and (2) treating the gel obtained in step (1) by hydrothermal crystallization, and then filtering, washing, and drying the gel after hydrothermal crystallization.

The present invention further provides an H-Y molecular sieve, wherein the crystal cell parameter of the H-Y molecular sieve is 2.425~2.450nm; the mole ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 10~120:1; the sum of pore volumes of pores in 2~7nm diameter in the H-Y molecular sieve is 60~95% of the total pore volume, preferably is 70~90%; the specific surface area of the H-Y molecular sieve is 750~980m²/g; and, the total acid amount measured by near infrared spectroscopy in the H-Y molecular sieve is 0.1~1.0mmol/g.

The present invention further provides a method for preparing a H-Y molecular sieve, comprising: (A) treating the Na-Y molecular sieve provided in the present invention by ammonium exchange to prepare a NH₄-Na-Y molecular

sieve; (B) treating the $\text{NH}_4\text{-Na-Y}$ molecular sieve obtained in step (A) by hydrothermal treatment; and (C) controlling the material obtained in step (B) to have a contact reaction with $(\text{NH}_4)_2\text{SiF}_6$ solution.

The present invention further provides an H-Y molecular sieve prepared
5 with the method provided in the present invention.

The present invention further provides a hydrocracking catalyst, wherein the support in the catalyst contains the H-Y molecular sieve provided in the present invention.

The present invention further provides a hydrocracking method, comprising:
10 (a) hydro-pretreating a raw oil, with hydrogen and a pretreating agent in presence; and (b) hydrocracking the pretreated product obtained in step (a), with hydrogen and a hydrocracking catalyst in presence; wherein the hydrocracking catalyst is the hydrocracking catalyst provided in the present invention.

The large-grain Na-Y molecular sieve provided in the present invention has
15 $2\sim 5\mu\text{m}$ crystal granularity, high silica-alumina ratio, more concentrated effective pore diameter distribution, high thermostability, and high hydrothermal stability. In the method for preparing the molecular sieve, no additive such as directing agent, template agent or surfactant is added; the product is synthesized by hydrothermal crystallization in one operation, by selecting appropriate raw
20 materials and optimizing the preparation process; in addition, the utilization efficiency of silica source and alumina source is high, the process is brief, and the cost is low.

Moreover, the H-Y molecular sieve obtained from the large-grain Na-Y molecular sieve can be used as an acidic component in the hydrocracking
25 catalyst. Since the large-grain molecular sieve synthesized in the present invention has large crystal grains, with $1,000\sim 2,000$ crystal cells in each dimension, it is ideal for using in macromolecular cracking. In addition, the molecular sieve has a better pore diameter distribution range, so that the cracking

degree of the reactants can be effectively controlled and it is helpful for diffusion of the product through the pores and channels. Therefore, when a catalyst containing the molecular sieve is applied in a hydrocracking reaction of a heavy oil that contains macromolecules, the molecular sieve can provide more active sites so that the macromolecules in the heavy oil are cracked to an appropriate degree; hence, the catalyst containing the molecular sieve can improve heavy oil cracking capability, decrease coke yield, and provide better cracking activity and product selectivity in the hydrocracking reaction.

Other aspects and advantages of the present invention will be further detailed in the embodiments hereunder.

BRIEF DESCRIPTION OF THE DRAWINGS

The accompanying drawings are provided here to facilitate further understanding on the present invention, and constitute a part of this document. They are used in conjunction with the following embodiments to explain the present invention, but shall not be comprehended as constituting any limitation to the present invention. Among the figures:

Fig. 1 is a SEM photo of LY-1 obtained in example 1;

Fig. 2 is a SEM photo of DLY-1 obtained in comparative example 1;

Fig. 3 is a XRD diagram of LY-1 obtained in example 1.

DETAILED DESCRIPTION

Hereunder some embodiments of the present invention will be detailed. It should be appreciated that the embodiments described here are only provided to describe and explain the present invention, but shall not be deemed as constituting any limitation to the present invention.

The present invention provides a Na-Y molecular sieve, wherein the average grain diameter of the Na-Y molecular sieve is 2~5 μ m, and the sum of pore volumes of pores in 1-10nm diameter accounts for 70~90% of the total pore volume of the Na-Y molecular sieve.

The present invention provides a large-grain Na-Y molecular sieve, which, compared with conventional molecular sieves, has larger internal surface area, is more suitable for use as pore and channel structures in macromolecular reactions, provides a chance for secondary cracking and transformation of more macromolecules in the molecular sieve, is more suitable for use in treatment of oil products that contain big molecules or raw materials that contain heavy fractions, and has superior performance in improvement of the transformation probability of macromolecules, etc..

In the present invention, preferably, the average grain diameter is 2~4.5 μm , more preferably is 3~4.5 μm .

In the present invention, preferably, the sum of pore volumes of pores in 1-10nm diameter accounts for 70~85% of the total pore volume in the Na-Y molecular sieve. In contrast, in Na-Y molecular sieves in the prior art, especially in large-grain Na-Y molecular sieves, the sum of pore volumes of pores in 1-10nm diameter usually accounts for a percentage lower than 50% of the total pore volume in the Na-Y molecular sieves.

In addition, the large-grain Na-Y molecular sieve provided in the present invention has high silicon content, more concentrated effective pore diameter distribution, and better thermostability and hydrothermal stability.

According to the present invention, the mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the Na-Y molecular sieve is 3.5~6.5:1, preferably is 4~6:1.

According to the present invention, the specific surface area of the Na-Y molecular sieve is 800~1,000 m^2/g , the total pore volume of the Na-Y molecular sieve is 0.3~0.4 mL/g , and the external specific surface area of the Na-Y molecular sieve is 60~100 m^2/g .

According to the present invention, the relative crystallinity of the Na-Y molecular sieve is 110~150%, and the crystal cell parameter of the Na-Y molecular sieve is 2.46~2.465nm.

The present invention further provides a method for preparing the Na-Y molecular sieve, comprising: (1) mixing sodium silicate, high alkaline sodium metaaluminate solution, aluminum sulfate solution, and low alkaline sodium metaaluminate solution at a mole ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ equal to 5 (10~15) : 1 : (10~20) : (500~600), and aging the obtained mixture to obtain a gel; and (2) treating the gel obtained in step (1) by hydrothermal crystallization, and then filtering, washing, and drying the gel after hydrothermal crystallization.

In the method for preparing the Na-Y molecular sieve provided in the present invention, no additive such as directing agent, template agent, or 10 surfactant is added in the step (1); the gel to be used to synthesize the molecular sieve is directly prepared from silica source and alumina source materials selected appropriately, and then the large-grain Na-Y molecular sieve is synthesized by hydrothermal crystallization in one operation in the step (2). The Na-Y molecular sieve prepared with that method has 2.0~5.0 μm crystal granularity, 15 high silica-alumina ratio, and more concentrated effective pore diameter distribution; specifically, the distribution percentage of pores in 1nm~10nm pore diameter, which are helpful for transformation of macromolecules, is as high as 70%~90%, much higher than that in conventional Y molecular sieves synthesized with the aid of a directing agent.

In the prior art, in the process of preparing a Y molecular sieve with the aid 20 of a directing agent, a directing agent has to be prepared first, and the directing agent has to be aged for days. In the crystallization procedure, the directing agent provides crystal nuclei in the Y molecular sieve, and then the silica source and alumina source in the gel are deposited and crystallized on the crystal nuclei, 25 so that a conventional Y molecular sieve is obtained. In such a conventional Y molecular sieve, the grain diameter is about 1 μm , and the distribution percentage of pores in 1nm~10nm diameter is 45%~50%.

In the present invention, in step (1), the sodium silicate, high alkaline

sodium metaaluminate solution, aluminum sulfate solution, and low alkaline sodium metaaluminate solution are mixed in the following way: mixing the sodium silicate with the high alkaline sodium metaaluminate solution while stirring, and then mixing the obtained mixture with the aluminum sulfate solution and low alkaline sodium metaaluminate solution. Wherein, water can be added separately or added together with the water solution of alumina source and/or silica source, the silica source is sodium silicate, and the alumina source is aluminum sulfate, high alkaline sodium metalluminate, and low alkaline sodium metaaluminate.

10 According to the present invention, the aluminum sulfate, high alkaline sodium metaaluminate, and low alkaline sodium metaaluminate control the amount of alumina provided; preferably, in step (1), calculated in Al_2O_3 , the weight ratio of dosage of aluminum sulfate : high alkaline sodium metaaluminate : low alkaline sodium metaaluminate is 1 : (0.5~0.7) : (0.6~0.8).

15 According to the present invention, preferably, in the high alkaline sodium metaaluminate solution, the content of Na_2O is 260~320g/L, and the content of Al_2O_3 is 30~50g/L.

According to the present invention, in the low alkaline sodium metaaluminate solution, the content of Na_2O is 100~130g/L, and the content of Al_2O_3 is 60~90g/L.

20 According to the present invention, in the aluminum sulfate solution, the content of Al_2O_3 is 80~100g/L.

According to the present invention, in the sodium silicate, the content of SiO_2 is 200~300g/L, and the modulus of the sodium silicate is 2.8~3.5.

25 According to the present invention, preferably, in step (1), the mixing temperature is 20~40°C, preferably is 25~35°C.

According to the present invention, in step (2), the gel is heated to the temperature for hydrothermal crystallization at 2~4°C/min., and then is treated by

hydrothermal crystallization.

According to the present invention, in step (2), the hydrothermal crystallization is carried out at 80~120°C temperature for 12~24h.

The present invention further provides an H-Y molecular sieve, wherein the
5 crystal cell parameter of the H-Y molecular sieve is 2.425~2.450nm; the mole
ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 10~120:1; the sum of pore
volumes of pores in 2~7nm diameter in the H-Y molecular sieve is 60~95% of the
total pore volume, preferably is 70~90%; the specific surface area of the H-Y
molecular sieve is 750~980m²/g; and, the total acid amount measured by near
10 infrared spectroscopy in the H-Y molecular sieve is 0.1~1.0mmol/g.

According to the present invention, in a preferred embodiment of the present
invention, specifically, the average grain diameter of the H-Y molecular sieve is
2~5μm, preferably is 2~4.5μm, more preferably is 3~4.5μm.

The relative crystallinity of the H-Y molecular sieve is 110~150%.

15 The crystal cell parameter of the H-Y molecular sieve is 2.436~2.450nm.

The mole ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 10~50:1.

In the H-Y molecular sieve, the sum of pore volumes of pores in 2-6nm
diameter accounts for 60~90% of the total pore volume, preferably accounts for
70~85%.

20 The total pore volume of the H-Y molecular sieve is 0.35~0.50cm³/g.

The specific surface area of the H-Y molecular sieve is 750~950m²/g.

In the H-Y molecular sieve, the amount of non-skeleton aluminum accounts
for 0.1~1% of the total amount of aluminum, preferably accounts for 0.1~0.5%.

The total acid amount measured by near infrared spectroscopy (NIS) in the
25 H-Y molecular sieve is 0.5~1.0mmol/g.

The content of Na₂O in the H-Y molecular sieve is 0.15 wt% or lower.

According to the present invention, in another preferred embodiment of the
present invention, specifically, the average grain diameter of the H-Y molecular

sieve is 2~5 μm , preferably is 2~4.5 μm , more preferably is 3~4.5 μm .

The relative crystallinity of the H-Y molecular sieve is 110~150%.

The crystal cell parameter of the H-Y molecular sieve is 2.425~2.435nm, preferably is 2.427~2.434nm.

5 The mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the H-Y molecular sieve is 60~120:1.

In the H-Y molecular sieve, the sum of pore volumes of pores in 3~7nm diameter in the H-Y molecular sieve is 70~95% of the total pore volume, preferably is 75~90%.

The total pore volume of the H-Y molecular sieve is 0.35~0.50 cm^3/g .

10 The specific surface area of the H-Y molecular sieve is 800~980 m^2/g .

In the H-Y molecular sieve, the amount of non-skeleton aluminum accounts for 0.1~1.0% of the total amount of aluminum, preferably accounts for 0.1~0.5%.

The total acid amount measured by NIS in the H-Y molecular sieve is 0.1~0.5 mmol/g .

15 The present invention further provides a method for preparing a H-Y molecular sieve, comprising: (A) treating the Na-Y molecular sieve provided in the present invention by ammonium exchange to prepare a $\text{NH}_4\text{-Na-Y}$ molecular sieve; (B) treating the $\text{NH}_4\text{-Na-Y}$ molecular sieve obtained in step (A) by hydrothermal treatment, under the following conditions: 0.05~0.25MPa gage
20 pressure, 400~550 $^\circ\text{C}$ temperature, and 0.5~5h treatment time; and (C) controlling the material obtained in step (B) to have a contact reaction with $(\text{NH}_4)_2\text{SiF}_6$ solution.

According to the present invention, the ammonium exchange can be repeated for several times, as long as the content of Na_2O in the $\text{NH}_4\text{-Na-Y}$
25 molecular sieve after the ammonium exchange is acceptable. Preferably, the content of Na_2O in the $\text{NH}_4\text{-Na-Y}$ molecular sieve obtained in step (A) is 2.5~5 wt%.

In the present invention, the ammonium salt can be one or more of

ammonium chloride, ammonium nitrate, ammonium sulfate, ammonium acetate, and ammonium oxalate, and the concentration of the water solution of ammonium salt can be 0.3~6mol/L.

5 In a preferred embodiment of the present invention, in step (B), the conditions of hydrothermal treatment include: gage pressure: 0.05~0.25MPa, preferably 0.1~0.2MPa; temperature: 400~550°C, preferably 450~550°C; time: 0.5~5h, preferably 1~3h.

10 In step (C), the material obtained in step (B) is mixed with $(\text{NH}_4)_2\text{SiF}_6$ solution at weight ratio of liquid : solid equal to 3:1~8:1 at 70-90°C, and then the obtained mixture is held at 80-120°C for 0.5-5h for reaction, wherein in relation to 100pbw $\text{NH}_4\text{-Na-Y}$ molecular sieve, the dosage of the $(\text{NH}_4)_2\text{SiF}_6$ is 10~35pbw; more preferably, in each hour, in relation to 100pbw $\text{NH}_4\text{-Na-Y}$ molecular sieve, the dosage of the $(\text{NH}_4)_2\text{SiF}_6$ is 3~30pbw.

15 According to the preferred embodiment, the present invention further provides an H-Y molecular sieve prepared with the method provided in the present invention.

Specifically, the average grain diameter of the H-Y molecular sieve is 2~5 μm , preferably is 2~4.5 μm , more preferably is 3~4.5 μm .

20 The relative crystallinity of the H-Y molecular sieve is 110~150%, and the crystal cell parameter of the H-Y molecular sieve is 2.436~2.450nm.

The mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the H-Y molecular sieve is 10~50:1.

In the H-Y molecular sieve, the sum of pore volumes of pores in 2-6nm diameter accounts for 60~90% of the total pore volume, preferably accounts for 70~85%.

25 The total pore volume of the H-Y molecular sieve is 0.35~0.50 cm^3/g , and the specific surface area of the H-Y molecular sieve is 750~950 m^2/g .

In the H-Y molecular sieve, the amount of non-skeleton aluminum accounts for 0.1~1% of the total amount of aluminum, preferably accounts for 0.1~0.5%.

The total acid amount measured by NIS in the H-Y molecular sieve is 0.5~1.0mmol/g.

The content of Na₂O in the H-Y molecular sieve is 0.15 wt% or lower.

In another preferred embodiment of the present invention, in step (B), the conditions of hydrothermal treatment include: gage pressure: 0.28~0.5MPa, preferably 0.3~0.5MPa; temperature: 450~700°C, preferably 600~700°C; time: 0.5~5h, preferably 1~3h.

In step (C), the material obtained in step (B) is mixed with (NH₄)₂SiF₆ solution at weight ratio of liquid : solid equal to 8:1~15:1 at 95-130°C, and then the obtained mixture is held at 80-120°C for 0.5-5h for reaction, wherein in relation to 100pbw NH₄-Na-Y molecular sieve, the dosage of the (NH₄)₂SiF₆ is 35~80pbw; more preferably, in each hour, in relation to 100pbw NH₄-Na-Y molecular sieve, the dosage of the (NH₄)₂SiF₆ is 3~30pbw.

According to the above preferred embodiment, the present invention further provides an H-Y molecular sieve prepared with the method provided in the present invention.

Specifically, the average grain diameter of the H-Y molecular sieve is 2~5μm, preferably is 2~4.5μm, more preferably is 3~4.5μm.

The relative crystallinity of the H-Y molecular sieve is 110~150%, and the crystal cell parameter of the H-Y molecular sieve is 2.425~2.435nm, preferably is 2.427~2.434nm.

The mole ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 60~120:1.

In the H-Y molecular sieve, the sum of pore volumes of pores in 3-7nm diameter accounts for 70~95% of the total pore volume, preferably accounts for 75~90%.

The total pore volume of the H-Y molecular sieve is 0.35~0.50cm³/g, and the specific surface area of the H-Y molecular sieve is 800~980m²/g.

In the H-Y molecular sieve, the amount of non-skeleton aluminum accounts

for 0.1~1.0% of the total amount of aluminum, preferably accounts for 0.1~0.5%.

The total acid amount measured by NIS in the H-Y molecular sieve is 0.1~0.5mmol/g.

The content of Na₂O in the H-Y molecular sieve is 0.15 wt% or lower.

5 The present invention further provides a hydrocracking catalyst, wherein the support in the catalyst contains the H-Y molecular sieve provided in the present invention.

According to the present invention, preferably, the content of the H-Y molecular sieve in the support is 15~90 wt%. The support can further contain
10 amorphous silica-alumina and/or alumina.

According to the present invention, preferably, the specific surface area of the catalyst is 200~400m²/g, and the pore volume of the catalyst is 0.2~0.5ml/g.

The catalyst can further comprise hydrogenation active components.

According to the present invention, preferably, the hydrogenation active
15 components are a metal element in VIB Family and a metal element in VIII Family; preferably, the metal element in VIB Family is Mo and/or W, and the metal element in VIII Family is Co and/or Ni.

According to the present invention, preferably, based on the total weight of the catalyst and calculated in metal oxide, the content of the metal element in VIB
20 Family is 10~40 wt%, and the content of the metal element in VIII Family is 3~15 wt%; the content of the support is 45~87 wt%.

The present invention further provides a hydrocracking method, comprising:
(a) hydro-pretreating a raw oil in presence of hydrogen and a pretreating agent;
and (b) hydrocracking the pretreated product obtained in step (a), in presence of
25 hydrogen and a hydrocracking catalyst, wherein the hydrocracking catalyst is the hydrocracking catalyst provided in the present invention.

According to the present invention, preferably, the conditions of hydro-pretreatment in step (a) include: 6~20MPa reaction pressure, 350~420°C

reaction temperature, $0.1\sim 2\text{h}^{-1}$ volumetric space velocity of input of the raw oil, and 500:1~2,000:1 volume ratio of hydrogen to the raw oil.

According to the present invention, preferably, the conditions of hydrocracking in step (b) include: 6~20MPa reaction pressure, 350~420°C reaction temperature, $0.1\sim 2\text{h}^{-1}$ volumetric space velocity of input of the pretreatment product, and 500:1~2,000:1 volume ratio of hydrogen gas to the pretreatment product.

Hereunder the present invention will be further detailed in some embodiments.

In the following examples and comparative examples, the specific surface area, pore volume, external specific surface area, and pore distribution are measured with an ASAP2420 cryogenic nitrogen adsorption analyzer from Micromeritics, with the cryogenic nitrogen physical adsorption method defined in GB/T 19587-2004;

The relative crystallinity and crystal cell parameter are measured with a Dmax-2500 X-ray diffractometer from Rigaku, with an X-ray diffraction method;

The silica-alumina mole ratio is measured with a ZSX100e XRF analyzer from Rigaku, with chemical analysis method.

The grain size of the molecular sieve is measured with a JEM-7500L SEM from JEOL.

Example 1

(1) Preparation of gel: add 165mL sodium silicate (the SiO_2 content is 235g/L, the modulus is 2.9) into 63mL high alkaline sodium metaaluminate solution (the Na_2O content is 280g/L, the Al_2O_3 content is 35g/L) slowly at 25°C while stirring; after the mixture is mixed to a homogeneous state, add 42.5mL aluminum sulfate solution (the Al_2O_3 content is 85g/L) and 35.6mL low alkaline

sodium metaaluminate solution (the Na_2O content is 110g/L, and the Al_2O_3 content is 68g/L) sequentially, and stir for 0.5h at the temperature; then, hold the obtained synthetic liquid at the temperature for 1h for aging; thus, a gel is obtained;

5 (2) Crystallization: heat up the gel in the synthesis reactor at $2.5^\circ\text{C}/\text{min}$ heating rate to 100°C while stirring, and then stir for 16h at the temperature for crystallization; next, cool down with cold water quickly, and take out the synthesized molecular sieve from the synthesis reactor, filter, wash, and dry the molecular sieve; thus, a large-grain Na-Y molecular sieve product LY-1 is
10 obtained. The properties of the product are shown in Table 1.

Observe LY-1 on a SEM and carry out XRD analysis. The SEM photo is shown in Fig. 1. It can be seen that the grain size of the molecular sieve obtained in the present invention is $3.5\mu\text{m}$, which is very large, and the crystal grains are uniform.

15 The XRD diagram is shown in Fig. 3. It can be seen that the large-grain Y molecular sieve obtained in the present invention has obvious characteristic peaks, indicating that the molecular sieve prepared with the method disclosed in the present invention has integral crystal morphology and relative high crystallinity.

20

Example 2

(1) Preparation of gel: add 170mL sodium silicate (the SiO_2 content is 235g/L, the modulus is 2.9) into 56mL high alkaline sodium metaaluminate solution (the Na_2O content is 275g/L, the Al_2O_3 content is 40g/L) slowly at 30°C
25 while stirring; after the mixture is mixed to a homogeneous state, add 45.6mL aluminum sulfate solution (the Al_2O_3 content is 90g/L) and 39.8mL low alkaline sodium metaaluminate solution (the Na_2O content is 120g/L, and the Al_2O_3 content is 77g/L) sequentially, and stir for 0.5h at a constant stirring rate at the

temperature; then, hold the obtained synthetic liquid at the temperature for 1h for aging; thus, a gel is obtained;

(2) Crystallization: heat up the gel in the synthesis reactor at 3°C/min. heating rate to 120°C while stirring, and then stir for 20h at the temperature for crystallization; next, cool down with cold water quickly, and take out the synthesized molecular sieve from the synthesis reactor, filter, wash, and dry the molecular sieve; thus, a large-grain Na-Y molecular sieve product LY-2 is obtained. The properties of the product are shown in Table 1.

Observe LY-2 on a SEM and carry out XRD analysis. The results obtained are similar to those shown in Fig. 1 and Fig. 3, and are not shown here.

Example 3

(1) Preparation of gel: add 156mL sodium silicate (the SiO₂ content is 260g/L, the modulus is 3.0) into 48mL high alkaline sodium metaaluminate solution (the Na₂O content is 300g/L, the Al₂O₃ content is 45g/L) slowly at 35°C while stirring; after the mixture is mixed to a homogeneous state, add 39.6mL aluminum sulfate solution (the Al₂O₃ content is 90g/L) and 28.5mL low alkaline sodium metaaluminate solution (the Na₂O content is 120g/L, and the Al₂O₃ content is 82g/L) sequentially, and stir for 1h at a constant stirring rate at the temperature; then, hold the obtained synthetic liquid at the temperature for 2h for aging; thus, a gel is obtained;

(2) Crystallization: heat up the gel in the synthesis reactor at 3°C/min. heating rate to 110°C while stirring, and then stir for 24h at the temperature for crystallization; next, cool down with cold water quickly, and take out the synthesized molecular sieve from the synthesis reactor, filter, wash, and dry the molecular sieve; thus, a large-grain Na-Y molecular sieve product LY-3 is obtained. The properties of the product are shown in Table 1.

Observe LY-3 on a SEM and carry out XRD analysis. The results obtained

are similar to those shown in Fig. 1 and Fig. 3, and are not shown here.

Example 4

(1) Preparation of gel: add 156mL sodium silicate (the SiO₂ content is 280g/L, the modulus is 3.0) into 52.5mL high alkaline sodium metaaluminate solution (the Na₂O content is 280g/L, the Al₂O₃ content is 35g/L) slowly at 35°C while stirring; after the mixture is mixed to a homogeneous state, add 47.9mL aluminum sulfate solution (the Al₂O₃ content is 85g/L) and 42.3mL low alkaline sodium metaaluminate solution (the Na₂O content is 120g/L, and the Al₂O₃ content is 70g/L) sequentially, and stir for 1h at a constant stirring rate at the temperature; then, hold the obtained synthetic liquid at the temperature for 2h for aging; thus, a gel is obtained;

(2) Crystallization: heat up the gel in the synthesis reactor at 3°C/min. heating rate to 120°C while stirring, and then stir for 24h at the temperature for crystallization; next, cool down with cold water quickly, and take out the synthesized molecular sieve from the synthesis reactor, filter, wash, and dry the molecular sieve; thus, a large-grain Na-Y molecular sieve product LY-4 is obtained. The properties of the product are shown in Table 1.

Observe LY-4 on a SEM and carry out XRD analysis. The results obtained are similar to those shown in Fig. 1 and Fig. 3, and are not shown here.

Comparative example 1

Prepare a molecular sieve with the CDA method disclosed in USP 3639099. The Preparation process is as follows: preparation of a directing agent: dissolve 26g aluminum hydroxide in 153g sodium hydroxide and 279mL water to form a raw material A; add 525g sodium silicate (the SiO₂ content is 150g/L, and the modulus is 3.3) into the raw material A, stir the gel quickly and then hold for 24h at room temperature for aging;

Add 601g aluminum sulfate solution (content of the aluminum sulfate is calculated in Al_2O_3 , = 16.9 wt%) into 2223g sodium silicate at 37.8°C , and then add 392g directing agent into the solution and stir to a homogeneous state; next, add 191g sodium aluminate solution (containing 126g aluminum hydroxide and 5 96.5g sodium hydroxide), stir the solution quickly, and then treat the solution by hydrothermal crystallization for 10h at 98.8°C ; thus, a Na-Y molecular sieve DLY-1 is obtained; the physical and chemical properties of DLY-1 are shown in Table 1.

Observe DLY-1 on a SEM and carry out XRD analysis. The SEM photo is 10 shown in Fig. 2. It can be seen that the molecular sieve prepared with the method described in the comparative example 1 has $1.0\mu\text{m}$ grain size, which indicates that the Y molecular sieve prepared with the method described in the comparative example 1 is a conventional molecular sieve.

15 Comparative example 2

Prepare a molecular sieve with the method disclosed in CN101481120A. Mix and stir 0.699g silicasol (40 wt%), 0.156g sodium hydroxide, 0.212g sodium aluminate, and 2.94mL deionized water at room temperature to a homogeneous state to obtain white gel; then, add 2.4g OP10, 1.6g n-butyl alcohol, and 1.8mL 20 cyclohexane, stir to a homogeneous state, and treat by hydrothermal crystallization for 24h at 100°C ; thus, a product DLY-2 is obtained; the product properties are shown in Table 1.

Comparative example 3

25 Preparation of a directing agent: dissolve 153g solid sodium hydroxide in 279mL deionized water, cool down the solution to room temperature, add 22.5g sodium metaaluminate to prepare high alkaline sodium metaaluminate solution (the Na_2O content is 140g/L, and the Al_2O_3 content is 25g/L). Next, add the

high alkaline sodium metaaluminate solution into 525g sodium silicate (the SiO_2 content is 230g/L, and the modulus is 2.9), and hold the mixture for 24h at room temperature for aging after the mixture is mixed to a homogeneous state.

5 Add 720g deionized water, 222.5g low alkaline sodium metaaluminate solution (the Na_2O content is 80g/L, and the Al_2O_3 content is 45g/L) and 242g directing agent sequentially, mix the mixture to a homogeneous state and then load it into a stainless steel reactor; hold for 24h at 100°C for crystallization, and then filter, wash, and dry; thus, a product DLY-3 is obtained; the product properties are shown in Table 1.

10

Comparative example 4

Prepare a Na-Y molecular sieve with the method disclosed in CN104773741A.

1) Load 200g sodium silicate (the Na_2O content is 6.91 wt%, and the SiO_2 content is 19.87 wt%) into a beaker, and place the beaker in water bath at 34°C ; add 145g high alkaline sodium metaaluminate (the Na_2O content is 21.02 wt%, and the Al_2O_3 content is 3.10 wt%) into the beaker quickly while stirring, and then stir for 1h in sealed state; next, treat the mixture by aging for 16h; thus, a directing agent is obtained, and the mole ratio of material input is $16\text{Na}_2\text{O} : \text{Al}_2\text{O}_3$
15 : $15\text{SiO}_2 : 325\text{H}_2\text{O}$;
20

2) Load 450g sodium silicate into a beaker, and place the beaker in water bath at 50°C ; then, add 100.02g directing agent, 149.30g high alkaline sodium metaaluminate, and 170g water sequentially while stirring; keep stirring for 5h, and then add 281.74g aluminum sulfate (the Al_2O_3 content is 7.09 wt%) slowly,
25 and mix and stir for 1h; thus, a gel mixture is obtained, and the mole ratio of material input is $2.5\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 6.6\text{SiO}_2 : 207\text{H}_2\text{O}$;

3) Load the gel mixture into a reactor, and hold for 40h at 100°C for crystallization; then, filter, wash, and dry; thus, a Na-Y molecular sieve DLY-4 is

obtained; the product properties are shown in Table 1.

Example 5

5 First, carry out ammonium exchange for the large-grain Na-Y molecular sieve LY-1. Prepare 10L 0.5mol/L ammonium nitrate solution. Weigh 2,000g small-grain Na-Y molecular sieve, dissolve it in 10L ammonium nitrate solution prepared above, and stir for 1h at 300rpm stirring rate at 90°C; then, filter the molecular sieve, and take samples to analyze the Na₂O content; repeat above operations, till the Na₂O content in the molecular sieve reaches 3 wt%; thus, a
10 dried sample LYN-1 is obtained.

Weight 200g molecular sieve LYN-1 and load it into a tubular hydrothermal treatment furnace, heat up to 530°C by programmed heating, and treat for 1h at 0.15MPa gage pressure; after the hydrothermal treatment, dissolve the molecular sieve in 1L deionized water, and heat up quickly to 80°C while stirring at 300rpm
15 stirring rate. Add (NH₄)₂SiF₆ solution into the slurry of the molecular sieve at a constant adding rate within 2h, till 28.6.6g (NH₄)₂SiF₆ is added; next, stir for 2h at a constant stirring rate at constant temperature, and the filter and dry; thus, a H-Y molecular sieve product LYNS-1 is obtained. The properties of the product are shown in Table 2.

20

Example 6

First, carry out ammonium exchange for the large-grain Na-Y molecular sieve LY-2. Prepare 10L 0.5mol/L ammonium nitrate solution. Weigh 2,000g small-grain Na-Y molecular sieve, dissolve it in 10L ammonium nitrate solution
25 prepared above, and stir for 1h at 300rpm stirring rate at 90°C; then, filter the molecular sieve, and take samples to analyze the Na₂O content; repeat above operations, till the Na₂O content in the molecular sieve reaches 2.5 wt%; thus, a dried sample LYN-2 is obtained.

Weight 200g molecular sieve LYN-2 and load it into a tubular hydrothermal treatment furnace, heat up to 500°C by programmed heating, and treat for 2h at 0.2MPa gage pressure; after the hydrothermal treatment, dissolve the molecular sieve in 1L deionized water, and heat up quickly to 75°C while stirring at 300rpm stirring rate. Add $(\text{NH}_4)_2\text{SiF}_6$ solution into the slurry of the molecular sieve at a constant adding rate within 2h, till 24.6.6g $(\text{NH}_4)_2\text{SiF}_6$ is added; next, stir for 2h at a constant stirring rate at constant temperature, and the filter and dry; thus, a H-Y molecular sieve product LYNS-2 is obtained. The properties of the product are shown in Table 2.

10

Example 7

First, carry out ammonium exchange for the large-grain Na-Y molecular sieve LY-3. Prepare 10L 0.5mol/L ammonium nitrate solution. Weigh 2,000g small-grain Na-Y molecular sieve, dissolve it in 10L ammonium nitrate solution prepared above, and stir for 1h at 300rpm stirring rate at 90°C; then, filter the molecular sieve, and take samples to analyze the Na_2O content; repeat above operations, till the Na_2O content in the molecular sieve reaches 2.5 wt%; thus, a dried sample LYN-3 is obtained.

Weight 200g molecular sieve LYN-3 and load it into a tubular hydrothermal treatment furnace, heat up to 590°C by programmed heating, and treat for 2h at 0.3MPa gage pressure; after the hydrothermal treatment, dissolve the molecular sieve in 1L deionized water, and heat up quickly to 100°C while stirring at 300rpm stirring rate. Add $(\text{NH}_4)_2\text{SiF}_6$ solution into the slurry of the molecular sieve at a constant adding rate within 2h, till 38.6.6g $(\text{NH}_4)_2\text{SiF}_6$ is added; next, stir for 2h at a constant stirring rate at constant temperature, filter and dry; thus, a H-Y molecular sieve product LYNS-3 is obtained. The properties of the product are shown in Table 2.

Example 8

First, carry out ammonium exchange for the large-grain Na-Y molecular sieve LY-4. Prepare 10L 0.5mol/L ammonium nitrate solution. Weigh 2,000g small-grain Na-Y molecular sieve, dissolve it in 10L ammonium nitrate solution prepared above, and stir for 1h at 300rpm stirring rate at 90°C; then, filter the molecular sieve, and take samples to analyze the Na₂O content; repeat above operations, till the Na₂O content in the molecular sieve reaches 2.5 wt%; thus, a dried sample LYN-4 is obtained.

Weight 200g molecular sieve LYN-4 and load it into a tubular hydrothermal treatment furnace, heat up to 650°C by programmed heating, and treat for 1h at 0.4MPa gage pressure; after the hydrothermal treatment, dissolve the molecular sieve in 1L deionized water, and heat up quickly to 120°C while stirring at 300rpm stirring rate. Add (NH₄)₂SiF₆ solution into the slurry of the molecular sieve at a constant adding rate within 2h, till 67.6g (NH₄)₂SiF₆ is added; next, stir for 2h at a constant stirring rate at constant temperature, and the filter and dry; thus, a H-Y molecular sieve product LYNS-4 is obtained. The properties of the product are shown in Table 2.

Example 9

Load 111.1g molecular sieve LYNS-1 (90 wt% on dry basis), 100g macropore alumina (1.0 mL/g pore volume, 400m²/g specific surface area, and 70 wt% on dry basis), 100g binder (micropore alumina, with 0.40~0.56mL/g pore volume, 30 wt% on dry basis, and mole ratio of nitric acid to micropore alumina equal to 0.4) into a grinder for mixed grinding, add water and grind to a paste state, and extrude into strips; dry the extruded strips for 4h at 110°C, and then calcinating for 4h at 550°C; thus, a support FHS-1 is obtained.

Impregnate the support with an impregnation liquid that contains wolframium and nickel for 2h; then, dry for 4h at 120°C, and heat up to 500°C by

programmed heating and then calcinating for 4h; thus, a catalyst CAT-1 is obtained. The compositions of the support and catalyst are shown in Table 3.

Examples 10-12

5 Use the method described in the example 9, but replace "LYNS-1" with "LYNS-2", "LYNS-3", and "LYNS-4" respectively; thus, supports FHS-2, FHS-3 and FHS-4 and catalysts CAT-2, CAT-3 and CAT-4 are obtained respectively. The compositions are shown in Table 3.

10 Comparative examples 5-8

Use the method described in the example 5, but replace "LY-1" with "DLY-1", "DLY-2", "DLY-3" and "DLY-4" respectively; thus, H-Y molecular sieves DLYNS-1, DLYNS-2, DLYNS-3 and DLYNS-4 are obtained respectively. The product properties are shown in Table 2.

15 Use the method described in the example 9, but replace "LYNS-1" with "DLYNS-1", "DLYNS-2", "DLYNS-3" and "DLYNS-4" respectively; thus, supports DFHS-1, DFHS-2, DFHS-3 and DFHS-4 and catalysts DCAT-1, DCAT-2, DCAT-3 and DCAT-4 are obtained respectively. The compositions of the supports and catalysts are shown in Table 3.

20

Example 13

Treat poor-quality input material HLCO and high dry-point VGO with CAT-1. The properties of the raw oils are listed in Table 4, and the comparative assessment results of the hydrocracking catalysts are listed in Table 5 and Table 6.

25

Examples 14-16

Use the method described in the example 13, but replace "CAT-1" with "CAT-2", "CAT-3" and "CAT-4" respectively. The comparative assessment

results of the hydrocracking catalysts are listed in Table 5 and Table 6.

Comparative examples 9-12

5 Use the method described in the example 13, but replace "CAT-1" with "DCAT-1", "DCAT-2", "DCAT-3" and "DCAT-4" respectively. The comparative assessment of results the hydrocracking catalysts are listed in Table 5 and Table 6.

Table 1

Example No.	LY-1	LY-2	LY-3	LY-4
Specific surface area, m ² /g	897	906	956	918
Pore volume, cm ³ /g	0.35	0.34	0.37	0.33
External specific surface area, m ² /g	80	75	82	79
Crystal cell constant, nm	2.465	2.462	2.463	2.465
Relative crystallinity, %	118	126	128	116
Average grain size, μm	3.0	3.5	2.5	4.5
SiO ₂ /Al ₂ O ₃ mole ratio	5.68	5.84	5.32	5.10
Sum of pore volumes of pores in 1nm ~10nm diameter to total pore volume, %	78	83	87	82
Relative crystallinity after calcination *, %	95	98	92	93
Relative crystallinity after hydrothermal treatment *, %	108	112	115	104
Comparative Example No.	DLY-1	DLY-2	DLY-3	DLY-4
Specific surface area, m ² /g	840	820	738	719
Pore volume, cm ³ /g	0.32	0.32	0.30	0.31
External specific surface area, m ² /g	150	132	121	110
Crystal cell constant, nm	2.468	2.468	2.472	2.743
Relative crystallinity, %	96	146.7	92	102
Average grain size, μm	0.95	1.80	1.10	3.0
SiO ₂ /Al ₂ O ₃ mole ratio	4.21	4.35	5.10	5.17
Sum of pore volumes of pores in 1nm ~10nm diameter to total pore volume, %	51	56	43	29
Relative crystallinity after calcination *, %	69	81	44	79
Relative crystallinity after hydrothermal treatment *, %	70	70	76	58

Note: * The conditions of calcination are: calcination for 3h at 600°C in air;

* The conditions of hydrothermal treatment are: treat for 1h at 650°C in water vapor.

Table 2

Example No.	LYNS-1	LYNS-2	LYNS-3	LYNS-4
Specific surface area, m ² /g	920	899	965	947
Pore volume, cm ³ /g	0.44	0.45	0.46	0.47
Crystal cell constant, nm	2.440	2.442	2.433	2.428
Relative crystallinity, %	133	130	136	143
Average grain size, μm	3.0	3.0	3.0	3.0
SiO ₂ /Al ₂ O ₃ mole ratio	33.5	28.4	69.8	105.6
Sum of pore volumes of pores in 3nm~7nm diameter to total pore volume, %	78	75	83	91
Percentage of amount of non-skeleton aluminum to total aluminum content, %	0.3	0.1	0.2	0.1
Total acid amount measured by NIS, mmol/g	0.67	0.75	0.42	0.28
Na ₂ O, wt%	0.12	0.10	0.10	0.09
Comparative Example No.	DYNS-1	DYNS-2	DYNS-3	DYNS-4
Specific surface area, m ² /g	611	650	569	585
Pore volume, cm ³ /g	0.36	0.35	0.37	0.36
Crystal cell constant, nm	2.443	2.439	2.429	2.431
Relative crystallinity, %	91	81	79	81
Average grain size, μm	0.95	0.95	0.95	0.95
SiO ₂ /Al ₂ O ₃ mole ratio	9.8	15.3	16.9	23.5
Sum of pore volumes of pores in 3nm~7nm diameter to total pore volume, %	29	32	36	33
Percentage of amount of non-skeleton aluminum to total aluminum content, %	1.8	1.5	1.8	2.1
Total acid amount measured by NIS, mmol/g	1.02	0.87	0.29	0.38
Na ₂ O, wt%	0.16	0.18	0.16	0.18

5 Table 3

Examples				
Support	FHS-1	FHS-2	FHS-3	FHS-4

Modified Y molecular sieve, wt%	25.0	25.0	25.0	25.0
Macro-pore alumina, wt%	40.0	40.0	40.0	40.0
Binder, wt%	35	35	35	35
Catalyst	CAT-1	CAT-2	CAT-3	CAT-4
WO ₃ , wt%	22.50	22.51	22.48	22.49
NiO, wt%	6.02	5.97	6.03	6.02
Comparative Examples				
Support	DFHS-1	DFHS-2	DFHS-3	DFHS-4
Modified Y molecular sieve, wt%	25.0	25.0	25.0	25.0
Macro-pore alumina, wt%	40.0	40.0	40.0	40.0
Binder, wt%	35	35	35	35
Catalyst	DCAT-1	DCAT-2	DCAT-3	DCAT-4
WO ₃ , wt%	22.48	22.49	22.51	22.36
NiO, wt%	6.01	6.02	5.99	5.87

Table 4

Raw oil	HLCO	VGO
Density (@ 20°C), g/cm ³	0.9440	0.9096
Distillation range, °C		
IBP/10%	136/227	305/361
30%/50%	252/275	394/417
70%/90%	303/343	443/481
95%/EBP	357/371	509/533
Pour point, °C	-24	33
Cetane number	15	
Cetane index (ASTMD 4737-96a)	23.8	
S, wt%	0.81	1.98
N, µg/g	914	1228
C, wt%	89.70	85.28
H, wt%	9.40	12.46
BMCI value		45.0

Table 5

Raw oil	HLCO	HLCO	HLCO	HLCO
Catalyst	CAT-1	DCAT-1	DCAT-2	DCAT-3
Total reaction pressure, MPa	14.7	14.7	14.7	14.7
Total LHSV, h ⁻¹	1.2	1.2	1.2	1.2
Volume ratio of hydrogen/oil	1200: 1	1200: 1	1200: 1	1200: 1
Reaction temperature, °C	385	390	401	393
Product Distribution and Major Product Properties				
Fraction <65°C				
Yield, wt%	5.97	6.55	7.65	6.89
Octane number (RON)	85.5	85.4	82.11	84.61
Fraction within 65°C~165°C range				
Yield, wt%	50.35	44.70	46.69	45.11
Aromatic potential, wt%	75.5	72.1	68.5	70.3
Fraction > 165°C				
Yield, wt%	35.09	37.78	35.50	36.08
Cetane index (ASTMD 4737-96a)	41.8	38.3	37.5	39.1

Table 6

Raw oil	VGO	VGO	VGO	VGO
Catalyst in the example	CAT-1	CAT-2	CAT-3	CAT-4
LHSV, h ⁻¹	1.0	1.0	1.0	1.0
Volume ratio of hydrogen/oil	1200:1	1200:1	1200:1	1200:1
Total reaction pressure, MPa	14.7	14.7	14.7	14.7
Reaction temperature, °C	390	392	391	393
Product Yield and Properties				
Heavy naphtha				
Yield, %	8.8	9.2	9.1	9.6
Aromatic potential, wt%	62.7	61.5	62.9	61.9
Jet fuel				
Yield, %	23.1	23.8	23.8	24.3
Smoke point, mm	23	24	25	25
Aromatics, v%	10.0	9.8	8.7	8.6
Diesel oil				
Yield, %	35.5	34.6	34.1	34.0
Cetane number	62.0	63.0	65.0	65.0
Tailings				
Yield, %	28.9	28.1	28.0	28.5
BMCi value	9.0	8.5	7.3	7.0

Chemical hydrogen consumption, wt%	2.18	2.19	2.20	2.20
Liquid yield, %	98.4	98.3	98.3	98.2
Catalyst in comparative example	DCAT-1	DCAT-2	DCAT-3	DCAT-4
LHSV, h ⁻¹	1.0	1.0	1.0	1.0
Volume ratio of hydrogen/oil	1200:1	1200:1	1200:1	1200:1
Total reaction pressure, MPa	14.7	14.7	14.7	14.7
Reaction temperature, °C	396	400	398	407
Product Yield and Properties				
Heavy naphtha				
Yield, %	9.9	10.6	10.5	11.2
Aromatic potential, wt%	61.6	59.8	59.9	57.6
Jet fuel				
Yield, %	22.6	23.2	24.0	25.6
Smoke point, mm	22	23	21	22
Aromatics, v%	12.5	11.8	15.6	14.7
Diesel oil				
Yield, %	33.2	31.5	32.3	33.2
Cetane number	60.1	61.2	59.6	57.3
Tailings				
Yield, %	28.0	26.0	25.6	26.8
BMCI value	10.8	10.3	11.3	11.0
Chemical hydrogen consumption, wt%	2.24	2.32	2.30	2.36
Liquid yield, %	97.6	97.1	96.8	96.8

It can be seen from the examples, comparative examples, and data in Tables 5-6: the performance of the catalysts prepared from the large-grain Na-Y molecular sieve provided in the present invention in hydrocracking reactions is superior to that of the catalysts prepared from the comparative molecular sieves.

The present application discloses:

1. A Na-Y molecular sieve, wherein the average grain diameter of the Na-Y molecular sieve is 2~5 μ m, and the sum of pore volumes of pores in 1-10nm diameter accounts for 70~90% of the total pore volume of the Na-Y molecular sieve.
2. The Na-Y molecular sieve according to paragraph 1, wherein the average

grain diameter is 2~4.5 μm , preferably is 3~4.5 μm .

3. The Na-Y molecular sieve according to paragraph 1 or 2, wherein the sum of pore volumes of pores in 1-10nm diameter accounts for 70~85% of the total pore volume of the Na-Y molecular sieve.

5 4. The Na-Y molecular sieve according to any of paragraphs 1-3, wherein the specific surface area of the Na-Y molecular sieve is 800~1,000 m^2/g , the total pore volume of the Na-Y molecular sieve is 0.3~0.4 mL/g , and the external specific surface area of the Na-Y molecular sieve is 60~100 m^2/g .

10 5. The Na-Y molecular sieve according to any of paragraphs 1-4, wherein the relative crystallinity of the Na-Y molecular sieve is 110~150%, and the crystal cell parameter of the Na-Y molecular sieve is 2.46~2.465nm.

6. The Na-Y molecular sieve according to any of paragraphs 1-5, wherein the mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the Na-Y molecular sieve is 3.5~6.5:1, preferably is 4~6:1.

15 7. A method for preparing a Na-Y molecular sieve, comprising:

(1) mixing sodium silicate, high alkaline sodium metaaluminate solution, aluminum sulfate solution, and low alkaline sodium metaaluminate solution at a mole ratio of $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : \text{SiO}_2 : \text{H}_2\text{O}$ equal to (10~15) : 1 : (10~20) : (500~600), and aging the obtained mixture to obtain a gel; and

20 (2) treating the gel obtained in step (1) by hydrothermal crystallization, and then drying, washing, and drying the gel after hydrothermal crystallization.

8. The method according to paragraph 7, wherein in step (1), calculated in Al_2O_3 , the weight ratio of dosage of aluminum sulfate: high alkaline sodium metaaluminate : low alkaline sodium metaaluminate is 1 : (0.5~0.7) : (0.6~0.8).

25 9. The method according to paragraph 7 or 8, wherein in the high alkaline sodium metaaluminate solution, the content of Na_2O is 260~320 g/L , and the content of Al_2O_3 is 30~50 g/L ; in the low alkaline sodium metaaluminate solution, the content of Na_2O is 100~130 g/L , and the content of Al_2O_3 is 60~90 g/L ; in the

aluminum sulfate solution, the content of Al_2O_3 is 80~100g/L; in the sodium silicate, the content of SiO_2 is 200~300g/L, and the modulus of the sodium silicate is 2.8~3.5.

10. The method according to any of paragraphs 7-9, wherein in step (1), the
5 mixing temperature is 20~40°C, preferably is 25~35°C.

11. The method according to any of paragraphs 7-10, wherein in step (1), the sodium silicate, high alkaline sodium metaaluminate solution, aluminum sulfate solution, and low alkaline sodium metaaluminate solution are mixed in the following way: mixing the sodium silicate with the high alkaline sodium
10 metaaluminate solution while stirring, and then mixing the obtained mixture with the aluminum sulfate solution and low alkaline sodium metaaluminate solution.

12. The method according to any of paragraphs 7-11, wherein in step (2), the gel is heated to the temperature for hydrothermal crystallization at 2~4°C/min., and then is treated by hydrothermal crystallization.

15 13. The method according to any of paragraphs 7-12, wherein in step (2), the hydrothermal crystallization is carried out at 80~120°C temperature for 12~24h.

CLAIMS

1. A method for preparing an H-Y molecular sieve, comprising:
 - (A) treating a Na-Y molecular sieve by ammonium exchange to prepare a
5 NH₄-Na-Y molecular sieve,
 where the Na-Y molecular sieve has an average grain diameter of
 2~5μm, and the sum of pore volumes of pores in 1-10nm diameter
 accounts for 70-90% of the total pore volume,
 - (B) treating the NH₄-Na-Y molecular sieve obtained in step (A) by
10 hydrothermal treatment; and
 - (C) controlling the material obtained in step (B) to have a contact reaction
 with (NH₄)₂SiF₆ solution.
2. The method according to claim 1, wherein in the NH₄-Na-Y molecular sieve
 obtained in step (A), the content of Na₂O is 2.5~5 wt%.
- 15 3. The method according to claim 1, wherein in step (B), the conditions of
 hydrothermal treatment include: gage pressure: 0.05~0.25MPa, preferably
 0.1~0.2MPa; temperature: 400~550°C, preferably 450~550°C; time: 0.5~5h,
 preferably 1~3h.
4. The method according to claim 3, wherein in step (C), the material obtained in
20 step (B) is mixed with (NH₄)₂SiF₆ solution at weight ratio of liquid: solid
 equal to 3:1~8:1 at 70-90°C, and then the obtained mixture is held at
 80-120°C for 0.5-5h for reaction, wherein in relation to 100pbw NH₄-Na-Y
 molecular sieve, the dosage of the (NH₄)₂SiF₆ is 10~35pbw.
5. The method according to claim 1, wherein in step (B), the conditions of
25 hydrothermal treatment include: gage pressure: 0.28~0.5MPa, preferably
 0.3~0.5MPa; temperature: 450~700°C, preferably 600~700°C; time: 0.5~5h,
 preferably 1~3h.
6. The method according to claim 5, wherein in step (C), the material obtained in

step (B) is mixed with $(\text{NH}_4)_2\text{SiF}_6$ solution at weight ratio of liquid: solid equal to 8:1~15:1 at 95-130°C, and then the obtained mixture is held at 80-120°C for 0.5-5h for reaction, wherein in relation to 100pbw $\text{NH}_4\text{-Na-Y}$ molecular sieve, the dosage of the $(\text{NH}_4)_2\text{SiF}_6$ is 35~80pbw.

- 5 7. An H-Y molecular sieve, wherein the crystal cell parameter of the H-Y molecular sieve is 2.425~2.450nm; the mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the H-Y molecular sieve is 10~120:1; the sum of pore volumes of pores in 2~7nm diameter in the H-Y molecular sieve is 60~95% of the total pore volume, preferably is 70~90%; the specific surface area of the H-Y molecular sieve is 750~980 m^2/g ; and, the total acid amount measured by near infrared spectroscopy in the H-Y molecular sieve is 0.1~1.0mmol/g.
- 10 8. The H-Y molecular sieve according to claim 7, wherein the crystal cell parameter of the H-Y molecular sieve is 2.436~2.450nm; the mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the H-Y molecular sieve is 10~50:1; the sum of pore volumes of pores in 2~6nm diameter in the H-Y molecular sieve is 60~90% of the total pore volume, preferably is 70~85%; the specific surface area of the H-Y molecular sieve is 750~950 m^2/g ; and, the total acid amount measured by near infrared spectroscopy in the H-Y molecular sieve is 0.5~1.0mmol/g.
- 15 9. The H-Y molecular sieve according to claim 7, wherein the crystal cell parameter of the H-Y molecular sieve is 2.425~2.435nm, preferably is 2.427~2.434nm; the mole ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$ in the H-Y molecular sieve is 60~120:1; the sum of pore volumes of pores in 3~7nm diameter in the H-Y molecular sieve is 70~95% of the total pore volume, preferably is 75~90%; the specific surface area of the H-Y molecular sieve is 800~980 m^2/g ; and, the total acid amount measured by near infrared spectroscopy in the H-Y molecular sieve is 0.1~0.5mmol/g.
- 20 25 10. An H-Y molecular sieve prepared with the method according to any of claims 1-4, wherein the crystal cell parameter of the H-Y molecular sieve is

2.436~2.450nm; the mole ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 10~50:1; the sum of pore volumes of pores in 2~6nm diameter in the H-Y molecular sieve is 60~90% of the total pore volume, preferably is 70~85%; the specific surface area of the H-Y molecular sieve is 750~950m²/g; and, the total acid amount measured by near infrared spectroscopy (NIS) in the H-Y molecular sieve is 0.5~1.0mmol/g.

11. An H-Y molecular sieve prepared with the method according to any of claims 1, 2, 5, and 6, wherein the crystal cell parameter of the H-Y molecular sieve is 2.425~2.435nm, preferably is 2.427~2.434nm; the mole ratio of SiO₂/Al₂O₃ in the H-Y molecular sieve is 60~120:1; the sum of pore volumes of pores in 3~7nm diameter in the H-Y molecular sieve is 70~95% of the total pore volume, preferably is 75~90%; the specific surface area of the H-Y molecular sieve is 800~980m²/g; and, the total acid amount measured by near infrared spectroscopy in the H-Y molecular sieve is 0.1~0.5mmol/g.

12. A hydrocracking catalyst, wherein the support in the catalyst contains the H-Y molecular sieve according to any of claims 7-11.

13. A hydrocracking method, comprising:

(a) hydro-pretreating a raw oil in the presence of hydrogen gas and a pretreating agent; and

(b) hydrocracking the pretreated product obtained in step (a), in the presence of hydrogen gas and a hydrocracking catalyst;

wherein the hydrocracking catalyst is the hydrocracking catalyst according to claim 12.



Application No: GB1621466.0

Examiner: Mr Martin Price

Claims searched: 1-6, 10-13 (in part)

Date of search: 18 May 2017

Patents Act 1977: Search Report under Section 17

Documents considered to be relevant:

Category	Relevant to claims	Identity of document and passage or figure of particular relevance
A,E	-	CN 105709845 A China Petroleum - see WPI abstract number 2016-44750M
A,E	-	CN 104828839 A China Petroleum - see WPI abstract number 2015-602252
A,E	-	CN 104588122 A China Petroleum - see WPI abstract number 2015-42413U
A,E	-	CN 104591214 A China Petroleum - see WPI abstract number 2015-42387L
A,E	-	CN 104591212 B China Petroleum - see WPI abstract number 2015-42387N
A	-	US 4857169 A Abdo - see e.g. the abstract

Categories:

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.

Field of Search:

Search of GB, EP, WO & US patent documents classified in the following areas of the UKC^X :

Worldwide search of patent documents classified in the following areas of the IPC

B01J; C01B

The following online and other databases have been used in the preparation of this search report

EPODOC, WPI



International Classification:

Subclass	Subgroup	Valid From
None		