

A Y-ZEOLITE-CONTAINING COMPOSITE MATERIAL AND
A PROCESS FOR PREPARING THE SAME

5 Technical Field

The present invention relates to a Y-zeolite-containing composite material made from raw materials comprising kaolin by in-situ crystallization and a process for preparing the same.

Background Arts

10 Study on the synthesis of zeolite with kaolin as a raw material has been going on since USP 3,119,659 disclosed such a process in 1964. Early work mainly focused on the synthesis of pure zeolite, e.g. US 3,574,538 disclosed a process for synthesizing Y-zeolite from kaolin, which comprised calcining kaolin to form amorphous
15 metakaolin, adding a certain amount of sodium silicate and sodium hydroxide to make the mole ratio of silica/alumina approach that of the zeolite to be synthesized, then adding 0.1-10% by weight of guide agent, and conducting crystallization at 60-110°C to yield highly pure Y-zeolite with a silica/alumina ratio of
20 4.5-5.95 by mole.

EP 0209332A₂ discloses a process for crystallizing kaolin raw material to prepare Y-zeolite under stirring, which comprises calcining kaolin at 550-925°C to yield metakaolin, then adding sodium compound and water, adjusting silica to alumina ratio to
25 2.1-15:1 by mole and water to sodium oxide ratio to 15-70:1 by mole, crystallizing the reactant to form Y-zeolite under stirring, optionally adding a guide agent to the feed. The synthesized Y-zeolite is dispersive powder with an average diameter of 3 μm and a NaY purity of 97%.

30 Y-zeolite is prepared from kaolin (Gao Dawei et al, Petroleum Refining, 1983 (7): 12-16) by calcining kaolin at a relatively low temperature, e.g. 640-660°C, into metakaolin, then adding

sodium hydroxide, a guide agent, and water glass, aging at 50-60°C for 1 hour, and crystallizing at 98-100°C for 2-24 hours. After drying, NaY zeolite with a crystallinity of higher than 80% and a silica/alumina ratio of higher than 4.5 by mole is obtained.

5 This zeolite exhibits high hydrothermal stability after exchanging with rare-earths.

CN 1334142A calcines a part of kaolin raw material at 940-1000°C into spinel-containing kaolin and calcines another part at 700-900°C into metakaolin, and then mixes the two parts
10 of calcined kaolin in a certain ratio, followed by adding sodium silicate, guide agent, sodium hydroxide, and water, crystallizes at 90-95°C for 16-36 hours, yielding a molecular sieve containing 40-90% of NaY after drying. The temperature for calcining kaolin in preparing the molecular sieve in this process exceeds 700°C,
15 the energy consumption is high and the obtained molecular sieve is not a nanometer level product.

Since Y-zeolite is an active component of fluidized bed catalytic cracking catalyst, researchers expected to directly make kaolin into microsphere, and then into Y-zeolite by in-situ
20 crystallization. USP 4,493,902 discloses a microsphere zeolite containing at least 40% of NaY by calcining fine kaolin particle, mixing with kaolin to form a slurry, spray drying to form microsphere, calcining again to convert kaolin to metakaolin, adding the raw material for synthesizing zeolite and the guide
25 agent, and crystallizing under stirring and heating. This zeolite may contain spinel obtained by calcining kaolin at high temperatures and the presence of spinel provide a stable "framework" for the growth of zeolite. Therefore, a zeolite with high activity, selectivity, hydrothermal stability, wear
30 resistance, and high anti-metal ability can be obtained.

CN 1334318A discloses a zeolite having a lower content of NaY, only 25-35%, and having a mole ratio of silica/alumina of 4.0-5.5

obtained by mixing kaolin and a binder, spray drying the mixture to form microspheres having a diameter of 20-111 μm , calcining a part of microspheres at 940-1000°C and calcining another part at 700-900°C into metakaolin, mixing the kaolin calcined at 940-1000°C and metakaolin, adding sodium silicate, guide agent, sodium hydroxide and water, crystallizing at 98-100°C for 16-36 hours.

In recent years, the variation in the structure of petrochemical industry products and price of crude oil requires the development of the petroleum refining industry towards the direction of deep processing, and the technology for catalytic cracking of heavy oils has become an important path to increase the economic benefit. The crystal size of conventional Y-zeolite is generally in a range of 0.8-1.2 μm , which cannot allow large molecules of resid with diameters greater than 1.0 nm to enter the pore of zeolite with diameters of only about 0.8 nm, and these molecules can enter the pore merely after adsorbing on the outer surface of the zeolite and cracking into smaller molecules. Therefore, the magnitude of the outer surface area of the zeolite becomes an important factor affecting the cracking of large molecules of resid, but the increase of the surface area of zeolite means preparing zeolite with small crystal. Therefore, preparing Y-zeolite with small crystal to enhance the diffusion rate within crystal has gradually become a hotpot of research.

Rajagopal (Appl. Catal. 1986, 23:69) uses a microsphere catalyst made from synthesized zeolite with a crystal size of 60 nm to crack crude oil, and the result shows that zeolite with small crystal size produces more gasoline and light diesel oil, and less dry gas and coke deposit. However, smaller zeolite crystal size may result in poorer hydrothermal stability, more difficulty in filtering, higher surface energy and thereby a stronger tendency for the crystal to aggregate. Thus, the shortcoming of the gelling

method in synthesizing NaY with smaller crystal size has become the greatest obstacle to its industrialized application.

Disclosure of the invention

The objective of the present invention is to provide a Y-zeolite-containing composite material and a process for preparing the same. The composite material is made from raw materials comprising kaolin by in-situ crystallization. This composite material possesses the advantages of high hydrothermal stability, strong ability to resist coke deposition, and the composite material obtained in preparing procedure facilitates to filter.

In particular, the present invention provides a Y-zeolite-containing composite material, wherein said composite material comprises nest-like structure.

In a preferred embodiment, said composite material comprises Y-zeolite in the content of 30-85% by weight and matrix formed after in-situ crystallization of the materials comprising kaolin. More preferably the content of Y-zeolite is in the range of 30-70% by weight of composite material.

In another preferred embodiment, the nest-like structure is comprised of at least 70% of rodlike crystal, wherein said rodlike crystal has a diameter of 50-200 nm and a length of 100-600 nm. Said nest-like structure can further comprise flaky crystal and blocky crystal, wherein blocky crystal has an equivalent diameter of about 50-500 nm and flaky crystal has a thickness of about 50-200 nm. Said rodlike crystal, flaky crystal and blocky crystal are comprised of matrix formed after in-situ crystallization of the materials comprising kaolin and Y-zeolite on the surface of said matrix.

The present invention further provides a process for preparing a Y-zeolite-containing composite material, which process comprises calcining raw material powder comprising kaolin at lower temperatures into metakaolin and conducting in-situ

crystallization under stirring. In preparing the composite material, calcination of kaolin at lower temperatures may effectively save energy. The particle of the obtained composite material is mainly rodlike crystal, and Y-zeolite crystal grows
5 on the surface of the particle with small size and high dispersion, therefore the active component of the catalyst made from this Y-zeolite crystal may be effectively utilized. Besides, the composite material of the present invention comprises nest-like structure and may provide macropores, and facilitates to filter
10 during preparation procedure.

Description of drawings

Figure 1 is the X-ray diffraction pattern of the composite material of the present invention.

Figure 2 is the SEM image of the composite material of the
15 present invention magnified 5000 times.

Figure 3 is the SEM image of the composite material of the present invention magnified 20000 times.

Figure 4 is the SEM image of the composite material of the present invention magnified 30000 times.

20 Figure 5 is the SEM image of the composite material of the present invention magnified 20000 times.

Figure 6 is the SEM image of the composite material made from kaolin calcined at a high temperature magnified 15000 times.

Detailed embodiments of present invention

25 The composite material according to the present invention is prepared by calcining raw material comprising kaolin at a lower temperature to convert it into metakaolin, and then mixing metakaolin with sodium silicate, guide agent, solution of sodium hydroxide and water, and conducting in-situ crystallization of
30 metakaolin under stirring and a low temperature. The substance remaining after in-situ crystallization of metakaolin forms amorphous silicon/aluminum matrix and the produced Y-zeolite

after in-situ crystallization of metakaolin grows on the surface of said matrix. The crystal diameter of said Y-zeolite is in the range of about 10-400 nm, preferably in the range of 10-100 nm. And the said kaolin is selected from hard kaolin or soft kaolin.

5 The above composite material comprises nest-like structure, especially nest-like sphere, i.e. a geometric structure similar to bird's nest in appearance crosswise piled up by rodlike, flaky, and blocky crystals. There are great numbers of gaps and pores, as well as nest passages inside the nest-like structure. Said
10 pores with a diameter being about 200-1000 nm are located on the surface or interior of the nest-like structure. And the nest passages with a diameter being about 50-500 nm are located inside the structure. The equivalent diameter of said nest-like structure is in the range of about 1000-3000 nm.

15 Due to the special structure of the composite material provided by the present invention, it has a low apparent bulk density of only 0.50-0.75 g/cm³, wherein having more mesopores and macropores. And the pore volume of 17-3000 Å mesopore measured by the BET method is 0.03-0.076 ml/g, accounting for 10-35% of
20 the total volume of the pores.

Although the composite material of the present invention contains more mesopores and macropores, it still has a larger surface area, which is determined to be 280-800 m²/g by the BET method, preferably 400-750 m²/g. The silica/alumina ratio of the
25 Y-zeolite contained in the composite material is 4.0-5.5 by mole.

The Y-zeolite in the above composite material is selected from the group consisting of NaY, HY, REY or REHY. When said zeolite is REY or REHY, the content of rare-earth (RE) is 0.1-15% by weight based on oxide, preferably 8.0-12.0% by weight. The content of
30 sodium in the composite material containing REY or REHY zeolite is less than 0.3% by weight, preferably less than 0.2% by weight.

The present invention provides a process for preparing the

composite material, comprises the following steps:

(1) Calcining and dehydrating raw material comprising kaolin at 500-690°C to convert it into metakaolin, and then into a powder with diameters less than 230 μm ;

5 (2) Adding sodium silicate, guide agent, solution of sodium hydroxide, and water to metakaolin powder to make a reaction feed with a ratio of $(1-2.5)\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : (4-9)\text{SiO}_2 : (40-100)\text{H}_2\text{O}$, wherein the ratio by weight of guide agent to metakaolin is 0.1-1.0;

10 (3) Crystallizing the reaction feed made in step (2) at 88-98°C under stirring, and then filtering and drying.

The present process calcines raw material powder comprising kaolin at lower temperature to prepare metakaolin, said kaolin preferably being selected from hard kaolin or soft kaolin with an average diameter of less than 4 μm and therefore being a raw
15 earth which has not been subjected to molding treatment. The temperature for calcining said kaolin is preferably 600-690°C, more preferably 640-680°C, and the calcination time is 1-10 hours. The content of crystal in the selected kaolin should be preferably higher than 75% by weight, more preferably higher than 85% by
20 weight.

The calcined metakaolin must be crushed to make the diameter of all particles less than 230 μm , otherwise there would exist very rigid solid particle with a larger size in the products to be synthesized directly without crushing the calcined metakaolin,
25 which is unfavorable to the application of the product in catalytic process.

The guide agent used in the above step (2) may be synthesized according to conventional processes, such as those disclosed in USP 3,574,538, USP 3,639,099, USP 3,671,191, USP 4,166,099. The
30 composition of said guide agent is $(10-17)\text{SiO}_2 : (0.7-1.3)\text{Al}_2\text{O}_3 : (11-18)\text{Na}_2\text{O} : (200-350)\text{H}_2\text{O}$, and in synthesis the guide agent is obtained by aging the raw material at 4-35°C, preferably at

4-20°C.

In the above raw materials for synthesis, sodium silicate may be industrial water glass or other raw materials containing silica, and sodium aluminate is sodium meta-aluminate. The concentration of the solution of sodium hydroxide is 1-10% by weight, preferably 4-6% by weight. In step (2), an auxiliary accounting for 0.1-2.5% by weight of the total reactive raw material (reactants) may be added, the auxiliary being selected from the group consisting of sodium dodecyl sulfonate, hexadecyl trimethyl ammonium bromide, polyethylene glycol, oxalic acid, citric acid, sodium tartrate, or ethylenediamine tetraacetic acid (EDTA). The auxiliary is preferably added to the synthesis feed after adding guide agent.

The composite material according to the present invention is a product obtained by crystallization under stirring. The stirring rate in crystallization of step (3) is 200-1000 rpm, preferably 400-600 rpm, and the time is 16-48 hours, preferably 24-32 hours. The temperature for drying the composite material after crystallization is 100-120°C.

In order to apply said composite material to the catalytic cracking reaction of heavy oils, the NaY zeolite therein should be converted into H-type or rare earth (RE) ion-exchanged zeolite. The process for preparing HY zeolite is to conduct ion-exchanging of NaY with a solution of soluble ammonium salts, and then drying and calcining. The solution of soluble ammonium salts is selected from solution of ammonium chloride or ammonium nitrate, and the concentration is 4-10% by weight. The calcination temperature after drying is 500-600°C.

The process of the present invention for preparing REY is exchanging the HY zeolite made by ammonium-exchanging with a solution of soluble RE compound once, drying, calcining at 500-600°C, and then conducting ammonium exchange once to three times and drying. The soluble RE compound is preferably chloride

of mixed RE, or chloride or nitrate of other RE elements. The RE element is preferably selected from lanthanum, cerium, praseodymium, neodymium, europium, or ytterbium. The property of yttrium is close to RE, so it can also be used for ion-exchange.

5 The composite material according to present invention is suitable for various reactions catalyzed by solid acid, especially, it can be used as an active component of the catalyst for fluidized bed catalytic cracking of heavy oils or resid. The zeolite in the composite material has higher hydrothermal
10 stability and anti-coking ability after exchange with RE. The suitable conditions for cracking heavy oil or resid using the composite material of the present invention as a catalyst are 460-520°C, a catalyst/oil ratio of 1.0-5.0 by weight, and a mass space velocity of the feed of 16-45 h⁻¹.

15 The present invention will be described in detail below by the examples, but will not be limited by them.

The content of NaY and the unit cell constant a_0 of the composite material in the examples are measured according to methods in ASTM D-3906 and D-3942 respectively, and the content
20 of RE₂O₃ is determined by using the method of X-ray fluorescent spectroscopy.

The silica/alumina ratio in zeolite is obtained by first measuring the unit cell constant a_0 and then calculating based on the following formula:

25
$$\text{SiO}_2/\text{Al}_2\text{O}_3 \text{ (mole ratio)} = 2 \times (25.858 - a_0) / (a_0 - 24.191)$$

The specific surface area and pore volume are measured by using the low temperature nitrogen adsorption method (BET) according to ASTM D-3663 and D-4365 respectively, and the collapse temperature of the zeolite is determined according to
30 differential thermal analysis (DTA).

EXAMPLE 1

Preparing Y-zeolite-containing composite material of the

present invention.

(1) Preparation of guide agent: 120 g solution of sodium meta-aluminate (containing 3.15% by weight of Al_2O_3 , 21.1% by weight of Na_2O) was slowly added to 250 g solution of sodium silicate (containing 20.05% by weight of SiO_2 and 6.41 % by weight of Na_2O) at 30°C under rapid stirring, and the mixture was stirred for 1 hour and then aged at 20°C for 48 hours, yielding a guide agent having a composition of $16\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 15\text{SiO}_2 : 320\text{H}_2\text{O}$.

(2) Preparation of composite material

Kaolin with an average particle diameter of $4\text{ }\mu\text{m}$ (Suzhou, Yangshan brand, China Kaolin Company, containing 80% by weight of crystal) was calcined at 660°C for 3 hours, yielding metakaolin powder, which was crushed into metakaolin powder with particle diameters of less than $230\text{ }\mu\text{m}$.

Under stirring, to 500 g crushed metakaolin powder was added 2000 g solution of sodium silicate (containing 20.05% by weight of SiO_2 and 6.41 % by weight of Na_2O), 300g guide agent prepared in step (1), 500 g solution of sodium hydroxide with a concentration of 5% by weight, yielding a mixture with a composition of $1.39\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5.38\text{SiO}_2 : 54.7\text{H}_2\text{O}$. This mixture was heated up to 90°C and crystallized for 28 hours with the temperature maintaining constant under stirring, the stirring speed during feeding and crystallizing is 1000 rpm. After crystallization, the crystallization tank was quenched, filtered and washed until the pH value of the washing liquor was lower than 10, then dried at 120°C for 2 hours, yielding composite material Y-1. X-ray diffraction determination shows that the content of NaY in Y-1 was 35.4% by weight, the unit cell constant was 24.67, and the silica/alumina ratio was 4.96.

EXAMPLE 2

Composite material Y-2 was prepared according to the process of Example 1, except that the kaolin was calcined at 680°C for

4 hours and the stirring speed was 600 rpm in the crystallization of the reaction feed. The content of NaY in Y-2 was measured by X-ray diffraction to be 52.4% by weight and the physico-chemical properties are shown in Table 1. The X-ray diffraction pattern is shown in Figure 1 and the images of field emission scanning electron microscope (SEM) with different magnification factors are shown in Figures 2-5.

It can be seen from the X-ray diffraction pattern in Figure 1 that the composite material of the present invention possesses characteristic peaks of NaY, showing that it contains NaY, and the content of NaY can be calculated from the area of the characteristic peaks.

It is clear from the SEM image of Y-2 magnified 5000 times in Figure 2 that the composite material of the present invention consists of nest-like structure with equivalent diameters less than 3000 nm. The SEM image magnified 20000 times in Figure 3 shows that the nest-like structure contains at least 70% of rodlike crystal with the remainder being flaky and blocky crystals, wherein the diameter of the rodlike crystal is about 50-200 nm and length thereof is about 100-600 nm, the thickness of the flaky crystal is less than about 50-200 nm, and the equivalent diameter of the blocky crystal is about 100-500 nm. The SEM image magnified 30000 times in Figure 4 shows that there are a great number of NaY crystals on the rodlike crystals with diameters less than about 100 nm and the flaky crystals also contain a great number of NaY crystals with diameters of about 40-100 nm. The SEM image magnified 20000 times in Figure 5 is the cross section of Y-2, showing that the cross section of the nest-like structure is similar to grotto and the linkages of rodlike crystal with rodlike crystal, rodlike crystal with flaky crystal, and rodlike crystal with blocky crystal in the nest-like structure are realized by bonding. Figures 4 and 5 further clearly show that a great number

of pores, holes and nest passages exist in the composite material of the present invention.

EXAMPLE 3

Composite material Y-3 was made according to the process of Example 1, except that the amount of added sodium silicate was 4000 g to make the composition of the feed be $2.2\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 8.4\text{SiO}_2 : 80.2\text{H}_2\text{O}$. Obtained Y-3 has a NaY content of 32.8% by weight, a unit cell constant of 24.68, and a silica/alumina ratio of 4.82.

EXAMPLE 4

Composite material Y-4 was made according to the process of Example 1, except that adding 5 g metakaolin powder, 20 g solution of sodium silicate, 2 g guide agent, 20 g in a concentration of 10% by weight of solution of sodium hydroxide, and then 0.8 g EDTA to make the composition of the feed be $2.29\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5.33\text{SiO}_2 : 87.1\text{H}_2\text{O}$, and then crystallizing for 29 hours. The content of NaY in Y-4 was 79.6% by weight and the unit cell constant was 24.68. The physico-chemical properties of Y-4 are shown in Table 1.

EXAMPLE 5

Composite material Y-5 was made according to the process of Example 1, except that adding 1.1 g sodium tartrate to the reaction feed, the temperature increasing to 90°C and crystallizing for 30 hours under stirring. Obtained Y-5 has a NaY content of 66.2% by weight, a unit cell constant of 24.73, and a silica/alumina ratio of 5.26. The physico-chemical properties of Y-5 are shown in Table 1.

EXAMPLE 6

Composite material Y-6 was made according to the process of Example 1, except that adding 5 g metakaolin powder, 20 g solution of sodium silicate, 4 g guide agent, 15 g solution of sodium hydroxide, and 0.15 g dodecyl sodium sulfonate to make the composition of the feed be $1.77\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 5.44\text{SiO}_2 : 80.4\text{H}_2\text{O}$. The content of NaY in Y-6 was 82.5% by weight and the unit cell constant

was 24.71. The physico-chemical properties of Y-6 are shown in Table 1.

EXAMPLE 7

Composite material Y-7 was made according to the process of Example 1, except that adding 5 g metakaolin powder, 15 g solution of sodium silicate, 1.7 g guide agent, 15 g solution of sodium hydroxide to make the composition of the feed be $1.32\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4.55\text{SiO}_2 : 67.7\text{H}_2\text{O}$. Obtained Y-7 has a NaY content of 63.3% by weight, a unit cell constant of 24.65, and a silica/alumina ratio of 5.26.

EXAMPLE 8

Composite material Y-8 was made according to the process of Example 1, except that adding 5 g metakaolin powder, 15 g solution of sodium silicate, 3.0 g guide agent, 15 g solution of sodium hydroxide to make the composition of the feed be $1.44\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 4.63\text{SiO}_2 : 71.1\text{H}_2\text{O}$. Obtained Y-8 has a NaY content of 75.0% by weight, a unit cell constant of 24.68, and a silica/alumina ratio of 4.82.

COMPARATIVE EXAMPLE

Kaolin was calcined at 870°C for 2 hours according to the process of CN 1334142A and then Y-9 was made according to the process of Example 1. The content of NaY in Y-9 was 80% by weight and the silica/alumina ratio was 4.72. The SEM image of Y-9 is shown in Figure 6, which indicates that Y-9 has no nest-like structure.

EXAMPLES 9-13

Preparing REY-containing composite material of the present invention

100 g NH_4Cl and 1000 g deionized water were added to 100 g composite material containing NaY zeolite prepared according to the present invention, and the mixture was stirred at 90°C for 2 hours, followed by being washed and filtered, and then dried

at 120°C for 2 hours, yielding a composite material containing NH_4Y zeolite.

Deionized water was added to 100 g composite material containing NH_4Y zeolite in a ratio of $\text{NH}_4\text{Y} : \text{RE}_2\text{O}_3 : \text{H}_2\text{O}$ of 1: 0.1: 10 and the pH value was adjusted to 4.5 with dilute hydrochloric acid. Then solution of mixed RE chloride was added and ion-exchange proceeded at 90°C under stirring for 2 hours. After washing and filtering, the collected solid was calcined at 560°C for 2 hours. A calcined stock with a ratio of $\text{REY} : \text{NH}_4\text{Cl} : \text{H}_2\text{O} = 1: 0.3: 10$ was fed and subjected to ammonium-exchange at 90°C under stirring for 1 hour. Followed by being filtered, washed, and dried at 120°C for 2 hours. The ammonium-exchange was repeated once under the same condition yielding REY-zeolite-containing composite material with a content of sodium oxide below 0.3% by weight. The content of REY in the composite material prepared from each example, corresponding number thereof, and the number of the feed used in preparation processes are shown in Table 2.

EXAMPLE 14

REY-containing composite material of the present invention was aged at 810°C for 8 and 17 hours respectively with 100% steam, and then dried and evaluated for its catalytic performance with light oil having a boiling range of 239–351°C in a micro-reactor. The results are shown in Table 3.

It can be seen from Table 3 that the composite material according to the present invention still has a preferable hydrothermal stability after severe aging treatment. This is reflected by the high activity in the micro-reactor. This is because that the composite material of the present invention has a nest-like structure, various crystals can not completely pile up between each other and there exit many gaps and spaces, which are favorable to the diffusion and transfer of heat, meanwhile, as zeolite crystal grows on the surface of the amorphous

silica/alumina matrix formed after crystal transformation of kaolin, which matrix not only can disperse the heat on the zeolite crystal, but also can dilute the concentration of sodium oxide on the crystal, thereby enhancing the thermal stability.

5 **EXAMPLE 15**

The present example illustrates the catalytic performance of the composite material of the present invention for cracking heavy oil in a micro-reactor.

REY-1, REY-3, and REY-5 using as catalysts, were aged at 810°C
10 for 17 hours with 100% steam, and then evaluated for catalytic performance of aged catalysts in a micro-reactor device of heavy oil. The loading of the catalyst was 2 g. The properties of the feed oil used are shown in Table 4. The results obtained at a reaction temperature of 500°C, catalyst/oil ratio of 1.18, and
15 mass space velocity of 43.71 h^{-1} are shown in Table 5, wherein the end point of gasoline was 220°C and that of diesel oil was 330°C.

The data in Table 5 indicate that compared to the comparative catalyst REY-5, the composite materials according to the present invention exhibited higher conversion, high yield of light oils,
20 low yield of dry gas and coke even after subjecting to extremely sever aging treatment, showing that the composite materials according to the present invention have a high hydrothermal stability, and a strong ability to crack heavy oils.

Table 1

No. of composite material	Y-2	Y-4	Y-5	Y-6
NaY content, wt%	52.4	79.6	86.6	82.5
Silica/alumina, mole ratio	5.2	4.8	4.96	4.4
Unit cell constant, Å	24.65	24.68	24.67	24.71
Specific surface area, m ² /g	470.5	558.3	750.3	623.0
BET total pore volume, ml/g	0.22	0.25	0.37	0.34
17-3000Å pore volume, ml/g	0.061	0.039	0.040	0.07
Apparent bulk density, g/cm ³	0.65	0.55	0.40	0.60
Structure collapse temperature, °C	896	902	923	893.8

Table 2

Example No.	9	10	11	12	13
Feed No.	Y-2	Y-6	Y-7	Y-8	Y-9
No. of composite material	REY-1	REY-2	REY-3	REY-4	REY-5
Contents of substances in composite material, wt%					
Na ₂ O	0.25	0.17	0.13	0.16	0.23
RE ₂ O ₃	9.5	10.7	10.0	10.0	10.0
SiO ₂	65	64	65	63	65
Al ₂ O ₃	25	24	24	23	24

5

Table 3

Activity, wt%	No. of material				
	REY-1	REY-2	REY-3	REY-4	REY-5
Treating condition					
810°C, steam, 8 hours	80	72	86	82	70
810°C, steam, 17 hours	75	66	79	72	61

Table 4

20°C density, g/cm ³	0.8916
Viscosity, mm ² /s	9.629 (80°C)
	6.312 (100°C)
Freezing point, °C	47
Carbon residue, wt%	0.28
Distillation range, °C	
Initial Boiling Point	288
90%	518

Table 5

Catalyst No.	REY-1	REY-3	REY-5
Material balance, wt%			
Dry gas	0.56	0.84	1.2
LPG	9.6	8.77	14.4
Gasoline	60.98	57.97	51.8
Diesel oil	15.01	15.82	13.8
Heavy oil	12.56	15.67	17.0
Coke	1.3	0.98	1.8
Conversion, wt%	72.43	68.51	69.0
Light oil, wt%	75.99	73.79	65.6
Light oil + LPE, wt%	85.59	82.56	80.0
Coke/conversion	0.018	0.014	0.026

CLAIMS

1. A Y-zeolite-containing composite material, characterized in that said composite material comprises nest-like structure.

5 2. The composite material according to claim 1, characterized in that said composite material is made from materials comprising kaolin by in-situ crystallization.

3. The composite material according to claim 2, characterized in that said composite material comprises Y-zeolite in the content of 30-85% by weight and matrix formed after in-situ crystallization of the materials comprising kaolin.

4. The composite material according to claim 3, characterized in that the content of Y-zeolite is in the range of 30-70% by weight.

15 5. The composite material according to claim 1, characterized in that said nest-like structure is comprised of at least 70% of rodlike crystal, wherein said rodlike crystal has a diameter of 50-200 nm and a length of 100-600 nm.

6. The composite material according to claim 5, characterized in that said nest-like structure further comprises flaky crystal and blocky crystal, wherein blocky crystal has an equivalent diameter of 50-500 nm and flaky crystal has a thickness of 50-200 nm.

7. The composite material according to claim 1, characterized in that the crystal diameter of said Y-zeolite is in the range of 10-400 nm, and the equivalent diameter of said nest-like structure is in the range of 1000-3000 nm.

8. The composite material according to claim 5 or 6, characterized in that said rodlike crystal, flaky crystal and blocky crystal are formed of matrix formed after in-situ crystal transformation of the materials comprising kaolin and Y-zeolite on the surface of said matrix.

9. The composite material according to claim 2, characterized in that said materials comprising kaolin is selected from hard kaolin or soft kaolin.

10. The composite material according to claim 1, characterized in that the apparent bulk density of the composite material is 0.50–0.75 g/cm³ and the surface area is 280–800 m²/g.

11. The composite material according to claim 1, characterized in that the pore volume of 17–3000 Å mesopore measured by the BET method is 0.03–0.076 ml/g, accounting for 10–35% of the total volume of the pore.

12. The composite material according to claim 1, characterized in that the SiO₂/Al₂O₃ ratio in Y-zeolite is 4.0–5.5 by mole.

13. The composite material according to claim 1, characterized in that said Y-zeolite is selected from the group consisting of NaY, HY, REY and REHY.

14. A process for preparing the composite material according to claim 1, comprising the following steps:

(1) Calcining and dehydrating raw material comprising kaolin at 500–690°C to convert it into metakaolin, and then into a powder with particle diameters less than 230 μm;

(2) Adding sodium silicate, guide agent, solution of sodium hydroxide, and water to metakaolin powder to make a reaction feed with a ratio of (1–2.5) Na₂O: Al₂O₃: (4–9) SiO₂: (40–100) H₂O, wherein the ratio by weight of guide agent to metakaolin is 0.1–1.0;

(3) Crystallizing the reaction feed made in step (2) at 88–98°C under stirring, and then filtering and drying.

15. The process according to claim 14, characterized in that the composition of said guide agent in step (2) is (10–17) SiO₂: (0.7–1.3) Al₂O₃: (11–18) Na₂O: (200–350) H₂O, and the guide agent is made by aging at 4–20°C.

16. The process according to claim 14, characterized in that the temperature for calcining raw material in step (1) is in the

range of 600-690°C.

17. The process according to claim 14, characterized in that the stirring rate for crystallization in step (3) is 200-1000 rpm and the crystallization time is 16-48 hours.

5 18. The process according to claim 14, characterized in that the concentration of the added solution of sodium hydroxide in step (2) is 1-10% by weight.

19. The process according to claim 14, characterized in that said kaolin in step (1) is selected from hard kaolin or soft kaolin,
10 containing more than 75% by weight of crystal.

20. The process according to claim 14, characterized in that an auxiliary accounting for 0.1-2.5% by weight of the total reaction feed is further added to the feed in step (2), and the auxiliary is selected from the group consisting of sodium dodecyl
15 sulfonate, hexadecyl trimethyl ammonium bromide, polyethylene glycol, oxalic acid, citric acid, sodium tartrate, or ethylenediamine tetraacetic acid.