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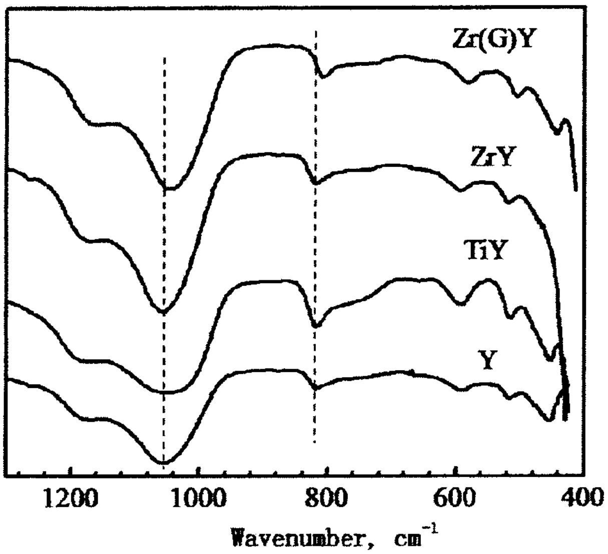

(57) Abrégé/Abstract:

The present invention relates to a metal modified Y zeolite, its preparation and use. Said zeolite contains 1-15wt% of IVB group metal as oxide and is characterized in that the ratio of the zeolite surface's IVB group metal content to the zeolite interior's NB group metal content is not higher than 0.2; and/or the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1 -0.8):1 .

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Abstract

The present invention relates to a metal modified Y zeolite, its preparation and use. Said zeolite contains 1-15wt% of IVB group metal as oxide and is characterized in that the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2; and/or the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.8):1.

A metal modified Y zeolite, its preparation and use

Technical Field

The present invention relates to a metal modified Y zeolite, its preparation and use.

Background

Along the catalytic cracking feedstock becomes heavier and heavier, it is essential for the catalytic cracking catalyst to have both higher acitivity and higher thermal and hydrothermal stabilities to increase the abilities of heavy conversion and anti-heavy metal contamination. Therefore, it is required that the main active component in the catalytic cracking catalyst, i.e. Y zeolite, has high thermal and hydrothermal stabilities, and remains a suitable contribution of acidic active centers.

The rare earth (RE) modified Y zeolite has relative high thermal and hydrothermal stabilities, and is widely used in the FCC catalyst. However, the sharp rise in the rare earth price results in the remarkable increase in the cost of the FCC catalyst. Therefore, it is desirable to introduce other metal ions to the Y zeolite, to reduce the rare earth content in the Y zeolite and to ensure a hydrothermal stability comparable to the Y zeolite with high rare earth content.

CN1350887A, CN1765492A, and US2007010698A1 propose the preparation methods for metal-modified Y zeolites. However, with comparison to the rare earth modified Y zeolite, the above metal-modified Y zeolites are poor in the thermal and hydrothermal stabilities.

CN101898144A and CN101134576A propose the modification to the framework of Y zeolites to increase the thermal and hydrothermal stabilities of Y zeolites. However, the obtained non-rare earth metal-modified Y zeolites produce a low gasoline yield in the catalytic cracking.

Summary

Aiming to the problems in the prior art, the present invention proposes a metal modified Y zeolite and its preparation method. The metal-modified Y zeolite is modified with non-rare earth metal elements, and has thermal and hydrothermal stability comparable to the rare earth modified Y zeolite. And upon being used in the catalytic cracking catalyst, the catalyst can show excellent properties in cracking activities, gasoline yield, and coke selectivity.

In one aspect, the present invention provides a metal modified Y zeolite, characterized in that: the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2; and/or the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.8):1.

In another aspect, the present invention provides a process for preparing the metal-modified Y zeolite, comprising:

(1) a Y-zeolite raw material is subjected to dewatering so that the raw material has a water content by weight of not higher than 5%;

(2) the Y zeolite obtained from step (1) is contacted with a mixture of a compound containing IVB group metal and an organic solvent, and the resulting mixture is optionally filtered and/or dried;

(3) the Y zeolite obtained from step (2) is calcined at 300-700°C, preferably for at least 0.5 hour, e.g. 0.5-5 hours;

(4) the Y zeolite obtained from step (3) is contacted with an aqueous acid solution, and then calcined at 400-800°C under 1-100% steam condition for 0.5-5 hours to produce the metal-modified Y zeolite containing the IVB group metal; the acid concentration, as H+, is 0.1-2.0mol/L.

In another aspect, the present invention provides a process for preparing the metal-modified Y zeolite, comprising:

(1) a Y zeolite is treated by contacting with an acid solution and/or an aqueous EDTA solution; wherein said acid is an organic acid and/or an inorganic acid;

(2) the product obtained from the step (1) is dewatered at a temperature below 400°C, so that the water content in the zeolite is not higher than 5wt%;

(3) the zeolite obtained from the step (2) is impregnated with a metal in an organic solvent;

(4) the metal impregnated Y zeolite obtained from the step (3) and an organic solvent are added to a vessel at a solid-to-liquid weight ratio of 1:(5-50) and mixed, an inert gas such as one or more of nitrogen and helium is introduced to the veseel, and the vessel is kept under a pressure of 0-2.0MPa (gauge pressure) at a temperature in the range from room temperature to 200°C for at least one hour, e.g. 1-48 hours; filtering and/or drying are optionally conducted, preferably filtering and drying are conducted;

(5) the zeolite obtained from the step (4) is calcined; the calcination is conducted in an inert gas atmosphere, the calcination temperature is 300-700°C, the calcination time is

at least 0.5 hour, e.g. 0.5-5 hours.

In another aspect, the present invention also provides a catalytic cracking catalyst containing the metal-modified Y zeolite and the preparation method thereof.

Specifically, the present invention involves the following technical solutions:

1. A metal modified Y zeolite, which contains 1-15wt% of IVB group metal as oxide, wherein the metal-modified Y zeolite has a ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the lattice structure of 0.1-0.8, e.g. 0.2-0.8.

2. The metal modified Y zeolite of any one of the previous solutions, which has a specific surface area of 600-850 m^2/g or 600-750m^2/g, a unit cell size a0 of 2.448-2.458 nm or 2.450-2.455nm, a crystallinity of not less than 60%, and optionally a SiO_2/Al_2O_3 molar ratio (framework Si/Al atom ratio) of 5-50, and the percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm) being 30-50% or 50%-65%.

3. The metal modified Y zeolite of any one of the previous solutions, wherein the modifying metal is Ti and/or Zr, wherein relative to the non-modified Y zeolite, the antisymmetric stretching vibration frequency (1050-1150cm^{-1}) and the symmetric stretching vibration frequency (750-820cm^{-1}) in the infrared spectrum of the metal-modified Y zeolite do not red-shift in a direction toward the lower frequency .

4. The metal-modified Y zeolite of any one of the previous solutions, which has an anhydrous chemical composition formula, as oxide and by weight, of $(0\text{-}2)Na_2O\cdot(1\text{-}15)MO_2\cdot(10\text{-}25)Al_2O_3\cdot(65\text{-}75)SiO_2$ or $(0.1\text{-}1.2)Na_2O\cdot(1\text{-}10)MO_2\cdot(20\text{-}24)Al_2O_3\cdot(67\text{-}74)SiO_2$, wherein M is a IVB group metal, selected from one or more of Ti, Zr, Hf and Rf.

5. The metal modified Y zeolite of any one of the previous solutions, wherein the IVB group metal is Ti and/or Zr, and the metal-modified Y zeolite is free of both framework Ti and framework Zr.

6. The metal modified Y zeolite of any one of the previous solutions, wherein the ratio

of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2.

7. The metal modified Y zeolite of any one of the previous solutions, wherein the content of the IVB group metal as oxide is 1-10wt%.

8. The metal modified Y zeolite of any one of the previous solutions, wherein the IVB group metal comprises Ti and/or Zr.

9. A process for preparing a metal modified Y zeolite, comprising the steps of:
(1) a Y zeolite is contacted with an acid solution and/or an aqueous EDTA solution; wherein said acid is an organic acid and/or an inorganic acid;
(2) the product obtained from the step (1) is dewatered at a temperature below 400°C, so that the water content in the zeolite is not higher than 5wt%;
(3) the zeolite obtained from the step (2) is impregnated with a metal in an organic solvent;
(4) the metal impregnated Y zeolite obtained from the step (3) and an organic solvent are added to a vessel at a solid-to-liquid weight ratio of 1:5-50, an inert gas is introduced to the vessel, and the vessel is kept under a pressure of 0-2.0MPa, preferably 0.1-2MPa (gauge pressure) at a temperature in the range from room temperature to 200°C for at least one hour; filtering and/or drying is optionally conducted;
(5) the zeolite obtained from the step (4) is calcined; the calcination is conducted in an inert gas atmosphere, the calcination temperature is 300-700°C, the calcination time is 0.5-5 hours.

10. The process of any one of the previous solutions, wherein in the step (1), the Y zeolite is one or more of NaY, NaHY, $NaNH_4Y$, NH_4Y, HY, USY, DASY zeolite, once-exchanged-once-calcined Y zeolite, twice-exchanged-twice-calcined Y zeolite, and twice-exchanged-once-calcined Y zeolite.

11. The process of any one of the previous solutions, wherein in the step (1), the Y zeolite is contacted with the acid solution in a solid-to-liquid weight ratio of 1:5-1:20 at a temperature in a range from room temperature to 100°C for at least 0.5 hour, then

filtered and washed; the acid solution has an acid concentration, as H^+, of 0.1-1mol/L.

12. The process of any one of the previous solutions, wherein the contact time is 0.5-3 hours; the acid is an inorganic acid and/or an organic acid; wherein the inorganic acid is one or more of hydrochloric acid, sulfuric acid and nitric acid; and the organic acid is one or more of formic acid, acetic acid, oxalic acid, citric acid.

13. The process of any one of the previous solutions, wherein in the step (2), the dewatering is to calcine the zeolite obtained from the step (1) at 200-400°C for 2-10 hours.

14. The process of any one of the previous solutions, wherein in the step (3), the impregnation with the metal in the organic solvent comprises the organic solvent in which a compound containing IVB group metal is solved is mixed with the zeolite obtained from the step (2), and the resulting mixture is kept for at least 0.5 hour, wherein the solid-to-liquid weight ratio of the Y zeolite and the organic solvent is 1:(0.5-5).

15. The process of any one of the previous solutions, wherein in the step (3), the resulting mixture is kept by standing or being stirred for 0.5-12 hours.

16. The process of any one of the previous solutions, wherein in the step (3), the solid-to-liquid weight ratio of the Y zeolite and the organic solvent is 1:1-2.

17. The process of any one of the previous solutions, wherein the compound containing IVB group metal is a Ti-containing compound and/or a Zr-containing compound; the Ti-containing compound is one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, and ammonium fluotitanate, and the Zr-containing compound is one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

18. The process of any one of the previous solutions, wherein in the step (4), the vessel is kept for 1-48 hours.

19. The process of any one of the previous solutions, wherein in the step (4), the pressure is 0.5-1.5MPa, the temperature is from room temperature to 150°C, the time is 4-24 hours, and the solid-to-liquid weight ratio of the zeolite and the organic organic solvent is 1:5-30.

20. The process of any one of the previous solutions, wherein in the step (5), the calcination temperature is 450-650°C, and the calcination time is 1-4 hours.

21. The process of any one of the previous solutions, wherein the organic solvent in step (3) and/or (4) has a water content of not more than 5wt%.

22. The process of any one of the previous solutions, wherein, the organic solvent in step (3) and/or (4) has a water content of not more than 3wt%; and the Y zeolite obtained from the step (2) has a water content of not more than 3wt%.

23. The process of any one of the previous solutions, wherein the organic solvent is one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, halogenated alkanes such as chloridized alkanes.

24. The process of any one of the previous solutions, wherein the organic solvent has a normal boiling point of 40-100°C.

25. The process of any one of the previous solutions, wherein the organic solvent is preferably one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone, and trichloromethane.

26. A process for preparing a metal modified Y zeolite, comprising the steps of:
(1) a Y-zeolite raw material is subjected to dewatering so that the raw material has a water content by weight of not higher than 5%;
(2) the dewatered Y zeolite obtained from step (1) is contacted with a mixture of a compound containing IVB group metal and an organic solvent, and the resulting mixture is optionally filtered and/or dried;
(3) the Y zeolite obtained from step (2) is calcined at 300-700°C;

(4) the Y zeolite obtained from step (3) is contacted with an aqueous acid solution, and then calcined at 400-800°C to produce the metal-modified Y zeolite containing the IVB group metal; the acid concentration, as H+, is 0.1-2.0mol/L.

27. The process of any one of the previous solutions, wherein in the step (2), the mixing weight ratio of the compound containing IVB group metal, the Y zeolite and the organic solvent is 0.01-0.15:1:1-50, wherein the weight of the compound containing IVB group metal is calculated as oxide, and the Y zeolite is calculated in a dry basis.

28. The process of any one of the previous solutions, wherein in the step (2), the weight ratio of the compound containing IVB group metal (as oxide): the Y zeolite (dry basis): the organic solvent is 0.01-0.1:1:5-30.

29. The process of any one of the previous solutions, wherein in the step (2), the procedure of contacting the dewatered Y zeolite obtained from step (1) with the compound containing IVB group metal and the organic solvent and optionally filtering and/or drying comprises: the compound containing IVB group metal, the organic solvent and the Y zeolite are mixed and contacted at a temperature in a range from room temperature to 100°C for at least 0.5 hour, then optionally filtered, and then optionally dried.

30. The process of any one of the previous solutions, wherein in the step (2), the procedure of contacting the dewatered Y zeolite obtained from step (1) with the mixture of the compound containing IVB group metal and the organic solvent and optionally filtering and/or drying the resulting mixture is conducted once or more than once.

31. The process of any one of the previous solutions, wherein in the step (3), the calcination temperature is 350-650°C, the calcination time is 2-4 hours, the calcination atmosphere is a dried air and/or an inert gas.

32. The process of any one of the previous solutions, wherein in the step (4), the

condition for contacting the Y zeolite obtained from step (3) and the aqueous acid solution comprises: the weight ratio (solid-to-liquid ratio) of the Y zeolite obtained from step (3) to the aqueous acid solution is 1:5-20, the contact temperature is in a range from room temperature to 100°C, the contact time is at least 0.5 hour; the aqueous acid solution has an acid concentration, as H+, of 0.1-2mol/L.

33. The process of any one of the previous solutions, wherein the aqueous acid solution has an acid concentration, as H+, of 0.5-2 mol/L.

34. The process of any one of the previous solutions, wherein the organic solvent is one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, halogenated alkanes such as chloridized alkanes.

35. The process of any one of the previous solutions, wherein the organic solvent is selected from one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone, trichloromethane.

36. The process of any one of the previous solutions, wherein the organic solvent has a normal boiling point of 40-100°C.

37. The process of any one of the previous solutions, wherein the organic solvent has a water content of not more than 5wt%.

38. The process of any one of the previous solutions, wherein the organic solvent has a water content of not more than 1wt%.

39. The process of any one of the previous solutions, wherein in the step (2), the temperature for contacting the dewatered Y zeolite obtained from step (1) and the mixture of the compound containing IVB group metal and the organic solvent is such a temperature that allows the organic solvent in a liquid state.

40. The process of any one of the previous solutions, wherein the compound containing IVB group metal comprises a Ti-containing compound and/or a Zr-containing compound.

41. The process of any one of the previous solutions, wherein the Ti-containing compound is one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, ammonium fluotitanate, and the Zr-containing compound is one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

42. The process of any one of the previous solutions, wherein in the step (1), the Y zeolite raw material is one or more of NaY zeolite, NaHY zeolite, $NaNH_4Y$ zeolite, NH_4Y zeolite and HY zeolite.

43. The process of any one of the previous solutions, wherein in the step (1), the Y zeolite raw material has a water content, after dewatering, of not more than 1wt%.

44. The process of any one of the previous solutions, wherein in the step (4), the calcination is conducted in a 1-100% steam atmosphere.

45. The metal-modified Y zeolite of any one of Solutions 1-8, which is obtainable or obtained by the process of any one of Solutions 9-44.

46. A catalytic cracking catalyst, based on the total weight of the catalyst, containing 10-60wt% of a metal-modified Y zeolite, 10-60wt% of a clay and 5-50wt% of a binder, wherein said metal-modified Y zeolite is the metal-modified Y zeolite of any one of Solutions 1-8.

47. The catalytic cracking catalyst of Solution 46, wherein the catalytic cracking catalyst contains 20-55wt% of the IVB group metal-modified Y zeolite, 15-60wt% of the clay and 10-40wt% of the binder.

48. The catalytic cracking catalyst of Solution 46 wherein the catalyst further contains other molecular sieves commonly used in the catalytic cracking catalyst, said other molecular sieves include Y-type molecular sieves, MFI-structured molecular sieves, and SAPO molecular sieves.

49. The catalytic cracking catalyst of Solution 46, wherein, the content of other molecular sieves commonly used in the catalytic cracking catalyst is not more than 40wt%, such as 1-35wt%.

50. A method for preparing the catalytic cracking catalyst, which comprises the steps of preparing a metal-modified Y zeolite, mixing and slurrying the metal-modified Y zeolite and a clay and a binder, and spray-drying the resulting mixture, wherein said metal-modified Y zeolite is prepared according to the process of any one of Solutions 9-44.

51. The method of Solution 50, wherein the clay is selected from one or more of kaolin, halloysite, rectorite, diatomite, montmorillonite, bentonite and sepiolite; and the binder is selected from one or more of hydrated alumina, alumina sol, pseudobohemite, bohemite, alumina monohydrate, alumina trihydrate, and amorphous aluminum hydroxyde.

52. A solution according to any one of the above Solution 1-51, wherein the metal-modified Y zeolite substantially does not contain one or more of V、Nb、Ta、Cr、Mo、W、Mn、Tc、Re、Fe、Ru、Ir、Ni、Pd、Pt、Cu、Zn、Ag、Au、Cd、Hg、Sc and Y.

Brief Description of the Drawings

Figure 1 is a FT-IR spectra for a standard Y zeolite (Y) and the metal-modified Y zeolites prepared in Examples B.1.1.2, B.1.1.6 and B.1.2.4.

Figure 2 is a ^{27}Al-NMR spectra for a standard Y zeolite (Y) and the metal-modified Y zeolites prepared in Examples B.1.1.2, B.1.2.2 and B.1.2.5.

Detailed Description

Modified Zeolite

The first metal modified Y zeolite according to the present invention is characterized in that the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2; e.g. 0.001-0.2; or 0.02-0.18.

The second metal modified Y zeolite according to the present invention is characterized in that the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.8):1; (0.2-0.8):1; (0.2-0.6):1; (0.1-0.6):1; or (0.2-0.5):1.

The third metal modified Y zeolite according to the present invention is characterized in that the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2; e.g. 0.001-0.2; or 0.02-0.18; and the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.8):1; (0.2-0.8):1; (0.2-0.6):1; (0.1-0.6):1; or (0.2-0.5):1.

The above three metal-modified Y zeolites are further characterized by one or more of the following features:

(1) the content of IVB group metal, as oxide and based on the metal-modified Y zeolite: 1-15wt%, or 1-10wt%;

(2) the specific surface area: 600-850m^2/g, 600-750m^2/g, or 630-730m^2/g;

(3) the unit cell size (expressed as a0): 2.448-2.458nm, 2.450-2.455nm; 2.449-2.455nm; or 2.449-2.452nm;

(4) the crystallinity: not less than 60%, e.g. 60-120%, or 60-95%; and

(5) the SiO_2/Al_2O_3 molar ratio: 5-50, 5-20, 5-8, 5-6

(6) the percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm) being 30-50% or 50%-65%, e.g.35%, 40%, 45%, 50%, 55%, 60%.

According to the present invention, the IVB group metal is selected from one or more of Ti, Zr, Hf, and Rf, e.g. one or more of Ti, Zr and Hf, preferably Ti and/or Zr.

According to the present invention, as oxide and by weight, the metal-modified Y zeolite has an anhydrous chemical composition formula, as oxide and by weight, of:

$(0\text{-}2)Na_2O\cdot(1\text{-}15)MO_2\cdot(10\text{-}25)Al_2O_3\cdot(65\text{-}75)SiO_2$, or

$(0.1\text{-}1.2)Na_2O\cdot(1\text{-}10)MO_2\cdot(20\text{-}24)Al_2O_3\cdot(67\text{-}74)SiO_2$;

wherein M is a IVB group metal , selected from one or more of Ti, Zr, Hf and Rf.

In the metal-modified Y zeolite according to the present invention, most of the IVB group metal ions are located in the interior of the zeolite, and a small amount of ions are present on the surface of the zeolite. The ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2.

In the present invention, including the following Examples, the analysis methods for the zeolite are as follows:

The zeolite surface's IVB group metal content refers to the content of the IVB group metal which can be measured in the depth of 2-5 nm from the zeolite's surface by using X-ray Photoelectron Spectroscopy (XPS). The zeolite interior's IVB group metal content refers to the difference between the zeolite bulk's IVB group metal content and the zeolite surface's IVB group metal content. The zeolite bulk's IVB group metal content is the content of IVB group metal in the zeolite that can be obtained through chemical analysis method.

The ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum refers to the ratio of the spectrum peak area at a chemical shift of 40 to that at a chemical shift of 60, as measured by ^{27}Al MAS NMR.

Secondary pores are determined and measured according to the standard method RIPP151-90. A reference can be made to Analytical Methods in Petrochemical Industry (RIPP Experiment Techniques), Yang Cuiding et.al, Science Press, 1990.

The element content is determined by X-ray fluorescence spectrometry.

The specific surface area is determined by the BET method.

The unit cell size and the crystallinity are determined by X-ray diffraction according to the standard methods RIPP145-90 and RIPP146-90 respectively. A reference can be made to Analytical Methods in Petrochemical Industry (RIPP Experiment Techniques), Yang Cuiding et.al, Science Press, 1990.

The SiO_2/Al_2O_3 molar ratio (i.e. framework Si/Al atom ratio) is determined according to the standard method SH/T0339-92.

Modified Zeolite Preparation Process

The present invention provides a process for preparing the metal-modified Y zeolite, comprising:

(1) a Y-zeolite raw material is subjected to dewatering so that the raw material has a water content by weight of not higher than 5%;

(2) the dewatered Y zeolite obtained from step (1) is contacted with a mixture of a compound containing IVB group metal and an organic solvent, and the resulting mixture is optionally filtered and/or dried;

(3) the Y zeolite obtained from step (2) is calcined at 300-700°C, preferably for at

least 0.5 hours, e.g. 0.5-5 hours;

(4) the Y zeolite obtained from step (3) is contacted with an aqueous acid solution, and then calcined at 400-800°C in a 1-100% steam condition for 0.5-5 hours to produce the metal-modified Y zeolite containing the IVB group metal; the acid concentration, as H^+, is 0.1-2.0mol/L.

The metal-modified Y zeolite prepared by the above-mentioned process is characterized by one or more features selected from:

(1) most of the IVB group metal ions are located in the interior of the zeolite, while a small amount of ions are present on the zeolite surface;

(2) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2;

(3) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is 0.001-0.2;

(4) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is 0.02-0.18;

(5) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.8):1;

(6) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.6):1;

(7) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.6):1; and

(8) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.5):1.

Step (1): Dewatering

The Y zeolite raw material can be one or more of NaY zeolite, NH_4Y zeolite, HY zeolite, $NaNH_4Y$ zeolite and NaHY zeolite, preferably NaY zeolite.

The NaY zeolite can by synthesized by crystallization. After removing the mother liquor, the crystallized zeolite can be used in the present invention directly or after being washed. The NaY zeolite can be commercially available or can be prepared according to the method in the prior art, e.g. the method disclosed in USP3671191.

The $NaNH_4Y$ zeolite is one obtained by exchanging NaY zeolite with NH_4^+ to a certain extent.

The NaHY zeolite can be obtained by calcining the $NaNH_4Y$ zeolite or by exchanging the NaY zeolite with H^+ to a certain extent.

The dewatering is preferably conducted at a temperature of not more than 400°C. The dewatering can be done by drying or calcining. The drying can be a conventional drying method or a vacuum drying method. Upon using the calcination to dewater, the calcination temperature is preferably not more than 400°C, e.g. 200-400°C, usually 250-350°C. The conventional drying method includes heat-drying, air-drying, flash-drying, or spray-drying. The drying temperature is usually not higher than 200 °C, e.g. 80-200 °C. The dewatered zeolite preferably has a water content of not higher than 3wt%, preferably not higher than 1wt%.

Step (2): contact -optional filtering -optional drying

In the step (2), the dewatered Y zeolite obtained from the step (1) is contacted with a mixture of a compound containing IVB group metal and an organic solvent to introduce the modifying metal into the zeolite.

The contacting process comprises mixing and slurrying a mixture of a compound containing IVB group metal and an organic solvent and the Y zeolite, and being subjected to an ion exchange at the exchange temperature (or the contact temperature).

After the contact, a filtering is optionally conducted. Then, a drying is optionally conducted.

The contact can be done once or more than once. The so-called "more than once" contact means the zeolite obtained from the previous treatment is contacted with a mixture of an organic solvent and a compound of the modifying metal; and after each contact, the filtering is optionally done, and the drying is optionally done. In the case of "more than once" contact, it is preferable to dry after the last contact. In the case of "more than once" contact, the Y zeolite obtained through filtering can be treated directly with a compound containing IVB group metal and an organic solvent, or can be dried and/or calcined, and then treated with a compound containing IVB group metal and an organic solvent.

There can be at least one temperature point in the exchange temperature range, at which point the solvent can be present in a liquid state.

In each contact, the weight ratio of the compound containing IVB group metal (as oxide) : Y zeolite (dry basis) : the organic solvent is (0.01-0.15):1:(1-50), or (0.01-0.14):1:(5-30), or (0.02-0.11):1:(5-25), or (0.01-0.1):1:(5-30).

The contact time for example is at least 0.5 hour, e.g. 0.5-5 hours, or 1.5-3.5 hours.

The contact temperature can be such a temperature, at which the organic solvent is in a liquid state. The exchange temperature can be such a temperature range, in which the organic solvent is in a liquid state. Usually, the exchange temperature can be a temperature range, the lower point of which is higher than the solidifying point of the organic solvent, and the upper point of which is lower than the boiling point of the organic solvent. For example, the the exchange temperature is, from the room temperature to a temperature which is 20 °C lower than the normal boiling point of the organic solvent; from 0 to 100 °C; from room temperature to 100 °C; from 0 to 100 °C and 20 °C lower than the normal boiling point of the organic solvent; and from room temperature to 100 °C and 20 °C lower than the normal boiling point of the organic solvent. The room temperature is 15-40 °C. The normal boiling point means the boiling point at 1 atm.

The drying temperature is usually not more than 200°C, e.g. 0-200°C, from room temperature to 150°C, from room temperature to 120°C, from 100 to 120°C.

The drying time can be 4-48 hours, 12-48 hours.

The IVB group metal can be one or more of Ti, Zr and Hf, preferably Ti and/or Zr. The compound containing IVB group metal can be one or more of compounds containing Ti and/or Zr, e.g. a Ti-containing compound, a Zr-containing compound or a Ti- and Zr-containing compound. The compound containing IVB group metal is preferably soluble in the used organic solvent, for example, its solubility in the organic solvent is not less than 0.1g of the compound containing IVB group metal/100g of the organic solvent. The Ti-containing compound can be one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, and ammonium fluotitanate, the Zr-containing compound can be one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

The organic solvent has a water content of not more than 5wt%, preferably not more than 1wt%, e.g. not more than 0.1wt%, not more than 0.01wt%, or not more than 0.001wt%. Preferably, in the organic solvent, the content of the organic substance as solvent is not less than 95wt%, preferably not less than 99wt%. The organic solvent can be one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, halogenated alkanes such as chloridized alkanes. The normal boiling point of the organic solvent (1atm) is preferably 40-100°C, which is both favorable for the dispersion of the metal component, and favorable for removing the organic solvent. The organic solvent can be, for example, one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone and trichloromethane.

Step (3): Calcination

The calcination temperature can be for example 300-700°C, 350-650°C, 400-620°C, or 450-600°C.

The calcination time can be for example 0.5-5 hours, 1-5 hours, 2-4 hours.

The calcination atmosphere can be for example a dried air, and/or an inert gas atmosphere, preferably an inert gas atmosphere.

The inert gas can be nitrogen and/or helium. In case of the dried air, the water content therein is below 1vol%, e.g. below 0.5vol%.

Step (4): Acid treatment-calcination

The temperature for contacting the aqueous acid solution with the Y-zeolite obtained from the step (3) is in a range from room temperature to 100°C, e.g. 75-95°C.

The contact time is not less than 0.2 hour, e.g. 0.5-5 hours,

The contact solid-to-liquid ratio (the weight ratio of zeolite to the aqueous acid solution) is 1:5-20, e.g. 1:6-14.

The concentration of the used aqueous acid solution, as H^+, is 0.1-2mol/L, 0.5-2mol/L, 0.5-1.5mol/L. After contact, the filtering is done. After filtering, the acid-contacted zeolite is washed with water to remove free acid, and then dried and calcined. The calcination temperature is 400-800°C, 500-600°C. The calcination atmosphere is a 1-100% steam condition. The calcination time is 0.5-5 hours, or 1-3 hours. The acid used in the step (4) is selected from one or more of hydrochloric acid, sulfuric acid, nitric acid, oxalic acid, acetic acid, formic acid, preferably one or more of hydrochloric acid, oxalic acid, and formic acid.

In another aspect, the present invention provides a process for preparing the metal-modified Y zeolite, which comprises:

(1) a Y zeolite is treated by contacting with an acid solution and/or an aqueous EDTA solution; wherein said acid is an organic acid and/or an inorganic acid;

(2) the product obtained from the step (1) is dewatered at a temperature below 400°C,

so that the water content in the zeolite is not higher than 5wt%;

(3) the zeolite obtained from the step (2) is impregnated with a metal in an organic solvent;

(4) the metal impregnated Y zeolite obtained from the step (3) and an organic solvent are added to a vessel at a solid-to-liquid weight ratio of 1:5-50, an inert gas such as nitrogen and/or helium is introduced to the vessel, and the vessel is kept under a pressure of 0-2.0MPa (gauge pressure) at a temperature in the range from room temperature to 200°C for at least one hour, e.g. 1-48 hours; filtering and/or drying is optionally conducted, and filtering and drying are preferably conducted;

(5) the zeolite obtained from the step (4) is calcined; the calcination is conducted in an inert gas atmosphere, the calcination temperature is 300-700°C, the calcination time is 0.5-5 hours, or more than 0.5 hour.

The metal-modified Y zeolite prepared by the above-mentioned process is characterized by one or more features selected from:

(1) most of the IVB group metal ions are located in the interior of the zeolite, while a small amount of ions are present on the zeolite surface;

(2) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2;

(3) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is 0.001-0.2;

(4) the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is 0.02-0.18;

(5) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.8):1;

(6) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.6):1;

(7) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.1-0.6):1; and

(8) the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the zeolite lattice structure is (0.2-0.5):1.

Step (1): Contact

The Y zeolite as starting material can be one or more of NaY, NaHY, $NaNH_4Y$, NH_4Y, HY, USY, once-exchanged-once-calcined Y zeolite, DASY zeolite, twice-exchanged-twice-calcined Y zeolite, twice-exchanged-once-calcined Y zeolite.

The once-exchanged-once-calcined Y zeolite for example can be the Y zeolite obtained by subjecting a NaY zeolite to once-exchanging-once-calcination; DASY zeolite for example can be the Y zeolite obtained by subjecting a Y zeolite to calcination in presence of steam; The twice-exchanged-twice-calcined Y zeolite for example can be the Y zeolite obtained by subjecting a NaY zeolite to twice-exchanging-twice-calcination; The twice-exchanged-once-calcined Y zeolite for example can be the Y zeolite obtained by subjecting a NaY zeolite to twice-exchanging-once-calcination; and preferably, the exchange is conducted with H^+ and/or NH_4^+.

The weight ratio between the Y zeolite (dry basis) and the acid solution (the aqueous acid solution) or the aqueous EDTA solution (the solid-to-liquid ratio) is 1:5-20. The contact temperature is in a range from room temperature to 100°C. The contact time is at least 0.5 hour, e.g. 0.5-3 hours. After the contact, the filtering and washing can be done. The acid concentration of the acid solution, as H^+, is 0.1-1mol/L, 0.2-0.5mol/L or 0.5-1mol/L. The acid can be an inorganic acid and/or an organic acid. The inorganic acid can be one or more of hydrochloric acid, sulfuric acid and nitric acid; the organic acid can be one or more of formic acid, acetic acid, oxalic acid, citric acid. In the step (1), the washing can be done with water such as deionized water and distillated water to remove the acid in the zeolite. For example, the weight ratio of water to zeolite can be 5-20:1. The treated zeolite obtained from the step (1) has a Na_2O content of not higher than 4.0wt% and preferably not higher than 2.0wt%.

Step (2)-Calcination

The treated zeolite obtained from the step (1) can be calcined to remove the adsorbed water. Through the calcination, the water content in the zeolite is not higher than 5wt%, for example not higher than 3wt%.

The calcination temperature can be 200-400°C, e.g. 300-350°C.

The calcination time can be 2-10 hours, e.g. 2-4 hours.

The solid content of the calcined zeolite is not less than 95wt%, not less than 97wt%, or 97-99.9wt%.

Step (3)

The zeolite being impregnated with a metal in an organic solvent comprises mixing the compound containing IVB group metal in the organic solvent and the zeolite, and keeping the mixture for at least 0.5 hours, e.g. 0.5-12 hours with stirring or without stirring (by standing). For example, the mixture was kept with stirring for 0.5-12 hours. Then, the next step can be conducted, for example, by proceeding with the step (4), or repeating the step (3). The introduction of modifying metal(s) into the Y zeolite can be done through one or more than one impregnations. The solid-to-liquid weight ratio of the Y zeolite to the organic solvent can be 1:(0.5-5), 1:(1-2), 1:(1-4), or 1:(1.1-1.6). The impregnation temperature is one that can make the organic solvent be in a liquid state. The impregnation can be done in a manner of isometric impregnation or excessive impregnation. The impregnation temperature is not particularly limited, for example, the impregnation can be done at room temperature.

The IVB group metal is selected from one or more of Ti, Zr, Hf and Rf, preferably Ti and/or Zr. The compound containing IVB group metal can be one or more of a Ti-containing compound, a Zr-containing compound, a Hf-containing compound, a Rf-containing compound, e.g. a Ti-containing compound and/or a Zr-containing compound. The compound containing IVB group metal can be an inorganic salt and/or an organometallic compound of IVB group metal, for example, the Ti-containing compound can be one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, and ammonium fluotitanate. The Zr-containing compound can be one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

The organic solvent has a water content of not higher than 5wt%, or not higher than 3wt%, or not higher than 1wt%. The organic solvent can be one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, halogenated alkanes such as chloridized alkanes. The organic solvent can have a normal boiling point of 40-100°C. The organic solvent is preferably one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone, trichloromethane.

Step (4) Introducing an inert gas-optional filtering - optional drying

The impregnated zeolite and the organic solvent are placed in a reaction vessel such as autoclave. The solid-to-liquid weight ratio of the zeolite to the organic solvent is 1:(5-50), e.g. 1:(5-30) or 1:(5-10). Generally, the organic solvent used in the step (4) is identical to that used in the step (3). An inert gas such as nitrogen and helium can be introduced to the reaction vessel. The reaction vessel pressure (gauge pressure) is 0.0-2.0MPa, or 0.5-1.5MPa. The reaction vessel temperature is from room temperature to 200°C, from room temperature to 150°C, or from room temperature to 90°C. The substances in the reaction vessel can be kept by standing or under stirring for at least 1 hour, usually 1-48 hours, 2-24 hours, or 4-24 hours.

Then, the filtering and/or drying can be optionally conducted. The filtering and the drying are preferably conducted so that the zeolite can be separated from the organic solvent. The filtering and the drying can be conventionally conducted. The existing drying process can be adopted, such as air-drying, flash-drying and spray-drying. For example, the drying temperature can be 100-200 °C. For example, the drying time can be 1 second to 2 days, e.g. 6-24 hours.

Step (5) Calcination

The zeolite obtained from the step (4) is calcined; the calcination is conducted in an inert gas atmosphere, the calcination temperature is 300-700°C, the calcination time is 0.5-5 hours, or more than 0.5 hour.

The calcination is conducted in an inert gas atmosphere. The calcination temperature is 300-700°C, 450-650°C or 500-600°C. The calcination time is 0.5-5 hours, or 1-4 hours. The inert gas comprises one or more of nitrogen and helium.

Catalytic cracking catalyst

The present invention further provides a catalytic cracking catalyst, based on the total weight of the catalyst, containing 20-60wt% of the IVB group metal modified Y zeolite according to the present invention, 10-60wt% of a clay and 5-50wt% of a binder .

Method for preparing catalytic cracking catalyst

The present invention also provides a method for preparing the catalytic cracking catalyst, which comprises the steps of mixing and slurrying the metal-modified Y zeolite according to the present invention and a clay and a binder, and spray-drying the resulting mixture. For example, deionized water , the clay and the binder can be mixed and slurried, and to the resulting slurry is added the modified Y zeolite. The technology of spray-drying and calcination are well known in the prior art, and therefore would not be discussed in detail.

According to the present invention, the clay is selected from one or more of kaolin, halloysite, rectorite, diatomite, montmorillonite, bentonite, and sepiolite, which are well known in the art.

According to the present invention, the binder refers to a substance, which can form a heat-resistant inorganic oxide after calcination. The heat resistant inorganic oxide comprises one or more of alumina, silica, amorphous silica-alumina, preferably alumina. The binder is preferably selected from one or more of hydrated alumina, alumina sol, pseudobohemite, bohemite, alumina trihydrate, alumina monohydrate, and amorphous aluminum hydroxide. These different binders can transfer to the form of γ-Al_2O3 after calcination. These binders are well known in the art.

The IVB metal-modified Y zeolite according to the present invention has high crystallinity, large specific surface area, and high thermal and hydrothermal stability.

According to the present invention, Y zeolite is modified with the IV group metal, without using the costly rare earth material. And the modified Y zeolite according to the present invention can provide a comparable or better thermal and hydrothermal stability than the rare earth modified Y zeolite.

The modified Y zeolite according to the present invention can be used in the catalytic cracking catalyst to substitute the rare-earth modified Y zeolite. The catalyst cost can be remarkably reduced.

The catalytic cracking catalyst according to the present invention shows excellent performance in cracking activities, gasoline yield, and coke selectivity.

Example

In the following Examples, the used room temperature is 15-40°C such as 26°C.

The light oil micro-activity (MA) is measured according to the standard method RIPP92-90, wherein 5g of the catalyst is used. The reaction temperature is 460 °C. The feedstock is a straight run light diesel having a distillation range of 235-337°C. The product composition is analyzed by gas chromatography. According to the product composition, the micro-activity is calculated, as follows:

light oil micro-activity (MA) =(the gasoline output (<216°C) + gas output +coke output)/feedstock input×100%

In the Examples and Comparative Examples, the used starting materials are commercially available and their detailed specifications are as follows.

Zeolite raw materials, industrial product, available from Sinopec Catalyst Company, Qilu Division.

$ReCl_3$ (Mixed rare earth chloride), industrial grade, available from Sinopec Catalyst Company, Qilu Division.

Other Agents: Chemically pure, unless indicated to the contrary

The secondary pore volume is measured according to the standard method RIPP151-90. A reference can be made to Analytical Methods in Petrochemical Industry (RIPP Experiment Techniques), Yang Cuiding et.al, Science Press, 1990. According to the adsorption isotherm, the total pore volume of the zeolite is measured. Then the micro-pore volume of the zeolite is measured from the adsorption isotherm according to the T plotting method. The total pore volume minus the micro-pore volume leaves the secondary pore volume, and the percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm) is calculated from the secondary pore distribution of the zeolite.

A.1 Zeolite Modification

Example A.1.1.1

200g of NaY zeolite was calcined at 300°C for 3 hours (after calcination, the water content was 1wt%). After being cooled to room temperature, it was placed in 2000g of ethanol (the ethanol content = 99.9wt%). The resulting slurry was stirred homogenously. To the slurry was added 10.5g of zirconium nitrate ($Zr(NO_3)_4 \cdot 5H_2O$). Then, the resulting mixture was stirred at room temperature for 2 hours, and filtered. The filter cake was dried in a baker at 100°C for 24 hours, and then calcined at 600°C for 2 hours.

The above calcined Y zeolite was added to 2000g of an aqueous inorganic acid solution with an acid concentration of 1.0mol/L (a diluted hydrochloric acid solution). The resulting mixture was mixed homogenously, stirred at 80°C for 3 hours, then filtered, washed with deionized water (the weight of washing water was 15 times larger than the dry basis weight of the zeolite), and filtered. The filter cake was removed, and calcined in a 100% steam at 600°C for 1 hour. Finally, the Zr-modified zeolite was obtained and named as Zr(2)Y, the properties of which were shown in Table A1.

Example A.1.1.2

200g of NaY zeolite was vacuumized at 200°C under 0.001Pa for 4 hours. After being cooled to room temperature (water content = 0.5wt%), it was placed in 1500g of ethanol (ethanol content = 99.9wt%). The resulting slurry was stirred homogenously. To the slurry was added 15.7g of zirconium oxychloride ($ZrOCl_2 \cdot 8H_2O$). Then, the resulting mixture was stirred at room temperature for 3 hours, and filtered. The filter cake was dried in a baker at 100°C for 24 hours, and then calcined at 500°C for 3 hours.

The above calcined Y zeolite was added to 1500g of an aqueous oxalic acid solution with an acid concentration of 2.0mol/L. The resulting mixture was mixed homogenously, warmed upto 90°C, stirred for 1 hour, then filtered, and washed with deionized water (the weight of washing water was 15 times larger than the dry basis weight of the zeolite). The filter cake was removed, and calcined in a 100% steam at 500°C for 2 hour. Finally, the Zr-modified zeolite was obtained and named as Zr(4)Y, the properties of which were shown in Table A1.

Example A.1.1.3

200g of NaY zeolite was calcined at 300°C for 3 hours. After being cooled to room temperature (water content = 1wt%), it was placed in 1000g of n-hexane (n-hexane content = 99.5wt%). The resulting slurry was stirred homogenously. To the slurry was added 37.8g of zirconium isopropoxide. The resulting mixture was stirred at room temperature for 3 hours, and filtered. The filter cake was dried in a baker at 120°C for 48 hours, and then calcined at 500°C (in a dried air atmosphere, the water content in the air was not more than 0.2vol%) for 4 hours.

The above calcined Y zeolite was added to 1000g of an aqueous inorganic acid (sulfuric acid) solution with an acid concentration of 0.5mol/L. The resulting mixture was stirred at 80°C for 3 hours, then filtered, and washed with deionized water (the weight of washing water was 20 times larger than the dry basis weight of the zeolite). The filter cake was removed, and calcined at 500°C, under a 100% steam atmosphere for 3 hours. Finally, the Zr-modified zeolite was obtained and named as Zr(8)Y, the properties of which were shown in Table A1.

Example A.1.1.4

200g of NaY zeolite was calcined at 300°C for 3 hours. After being cooled to room temperature, it was placed in 1000g of butanone (butanone content = 99.5wt%). The resulting slurry was stirred homogenously. To the slurry was added 14.2g of titanium tetrachloride. The resulting mixture was stirred at room temperature for 2 hours, and filtered. The filter cake was dried in a baker at 120°C for 24 hours, and then calcined at 450°C in a nitrogen atmosphere for 4 hours.

The above calcined Y zeolite was added to 1000g of an aqueous inorganic acid (hydrochloric acid) solution with an acid concentration of 0.5mol/L. The mixture was mixed homogenously, stirred at 80°C for 2 hours, then filtered, and washed with deionized water (the weight of washing water was 10 times larger than the dry basis weight of the zeolite). The filter cake was removed, and calcined at 500°C in a 100% steam atmosphere for 2 hours. Finally, the Ti-modified zeolite was obtained and named as Ti(4)Y, the properties of which were shown in Table A1.

Example A.1.1.5

200g of NaY zeolite was vacuumized at 300°C under 0.001Pa for 4 hours. After being cooled to room temperature, it was placed in 2000g of cyclohexane (cyclohexane content=99.9wt%). The resulting slurry was stirred homogenously. To the slurry was added 63.9g of tetrabutyl titanate. The resulting mixture was stirred at room temperature for 3 hours, and filtered. The filter cake was dried at 100°C in a baker for 48 hours, and then calcined at 600°C in a nitrogen atmosphere for 2 hours.

The above calcined Y zeolite was added to 2000g of an aqueous oxalic acid solution with an acid concentration of 1.5mol/L. The mixture was mixed homogenously, stirred at 90°C for 1 hour, then filtered, and washed with deionized water (the weight of washing water was 20 times larger than the dry basis weight of the zeolite). The filter cake was removed, and calcined at 600°C in a 100% steam atmosphere for 2 hours. Finally, the Ti-modified zeolite was obtained and named as Ti(10)Y, the properties of which were shown in Table A1.

Example A.1.1.6

200g of NaY zeolite was vacuumized at 300°C under 0.001Pa for 4 hours. After being cooled to room temperature, it was placed in 3000g of ethanol (ethanol content = 99.9wt%). The resulting slurry was stirred homogenously. To the slurry were added 3.6g of titanium tetrachloride and 31.5g of zirconium nitrate. The resulting mixture was stirred at room temperature for 3 hours, and filtered. The filter cake was dried at 100°C in a baker for 48 hours, and then calcined at 550°C in a nitrogen atmosphere for 3 hours.

The above calcined Y zeolite was added to 3000g of an aqueous inorganic acid (nitric acid) solution with an acid concentration of 1.0mol/L. The mixture was mixed homogenously, stirred at 80°C for 2 hours, then filtered, and washed with deionized water (the weight of washing water was 20 times larger than the dry basis weight of the zeolite). The filter cake was removed, and calcined at 550°C under a 100% steam atmosphere for 3 hours. Finally, the Ti- and Zr-modified zeolite was obtained and named as Ti-Zr-Y, the properties of which were shown in Table A1.

Example A.1.1.7

A modified zeolite was prepared according to Example A.1.1.4, except that after being treated with the inorganic acid, the filter cake was firstly dried, and then calcined at 500°C in an air atmosphere to produce the modified zeolite named as Ti(4)Y-1.

Example A.1.2.1

200g of NaY zeolite and 2000g of deionized water were mixed and slurried. To the resulting slurry was added 45mL of a solution of 270g/l $RECl_3$. The mixture was adjusted with a diluted hydrochloric acid to pH=3.8, and warmed upto 80°C to exchange for 1 hour. After filtering and washing, the resulting filter cake was calcined at 500 °C for 3 hours. Then, the resulting Y zeolite and 2000g of deionized water were mixed and slurried. To the slurry was added 45g of ammonium sulfate. The mixture was adjusted with a diluted hydrochloric acid to pH=4.0, and warmed upto 80°C to exchange for 1 hour. After filtering and washing, the resulting filter cake was calcined at 600°C, under a 100% steam atmosphere for 3 hours. Finally, a RE-modified zeolite was obtained and named as RE(8)Y, the properties of which were shown in Table A1.

Example A.1.2.2

200g of NaY zeolite was placed in 2000g of deionized water. The resulting slurry was stirred homogenously. To the slurry was added 31.4g of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$. The mixture was warmed upto 90°C, stirred for 3 hours, and filtered. The filter cake was dried at 100°C in a baker for 12 hours, and calcined at 500°C for 3 hours. Then the calcined Y zeolite and 2000g of deionized water were mixed and slurried. To the resulting slurry was added 45g of ammonium sulfate. The mixture was adjusted with a diluted hydrochloric acid to pH=4.0, and warmed upto 80°C to exchange for 1 hour. After filtering and washing, the filter cake was calcined at 500°C in a 100% steam atmosphere for 2 hours. Finally, the Zr-modified zeolite was obtained and named as Zr(W)Y, the properties of which were shown in Table A1.

Example A.1.2.3

A modified zeolite was prepared according to Example A.1.2.2, except that 14.2g of titanium tetrachloride was used in place of 31.4g of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$. Finally, the Ti-modified zeolite was obtained and named as Ti(W)Y, the properties of which were shown in Table A1.

Example A.1.2.4

A Zr-modified Y zeolite was prepared according to Example 1 of CN101134576A. Finally, the Zr-modified zeolite was obtained and named as Zr(G)Y, the properties of which were shown in Table A1.

Example A.1.2.5

200g of NH_4USY (Si/Al atom ratio=5.2) was added to 500 g of absolute ethanol under a violent stirring to form a suspension, to which was added 50 g/L of a solution of butyl titanate-absolute ethanol (as TiO_2) under a violent stirring. The mixture was air-dried overnight under stirring. The resulting sample was calcined at 500 °C for 5 hours to produce Ti-modified zeolites with titanium content of 2.4wt% and 9.1wt%, named as DT2 and DT9.

Table A1 Physical and chemical properties of metal-modified Y zeolites

Example A.1.1.X	1	2	3	4	5	6	7
Sample	Zr(2)Y	Zr(4)Y	Zr(8)Y	Ti(4)Y	Ti(10)Y	Ti-Zr-Y	Ti(4)Y-1
α0,nm	2.452	2.450	2.449	2.451	2.449	2.449	2.455
crystallinity,%	77.6	73.7	70.3	72.6	69.1	68.8	73.0
Na_2O,wt%	1.0	0.9	0.7	0.9	0.8	1.0	0.9
Al_2O_3,wt%	22.8	22.5	21.8	22.8	21.3	20.9	22.8
SiO_2,wt%	73.6	72.5	69.7	72.1	68.8	70.5	72.0
ZrO_2,wt%	2.1	3.8	7.3	0	0	5.5	0
TiO_2,wt%	0	0	0	3.7	8.6	1.9	3.7
RE_2O_3,wt%	0	0	0	0	0	0	0
specific surface area, m^2/g	676	710	690	726	702	640	722
lattice collapse temperature, °C	1048	1044	1051	1046	1050	1051	1045
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	0.05	0.10	0.12	0.08	0.16	0.15	0.10
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	0.4	0.3	0.5	0.4	0.6	0.5	0.3
The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)	48.2	50.6	57.8	52.4	62.4	64.5	51.8

Table A1 (continued)

Example A.1.2.X	1	2	3	4	5	
Sample	RE(8)Y	Zr(W)Y	Ti(W)Y	Zr(G)Y	DT2	DT9
α0,nm	2.451	2.450	2.452	2.451	2.458	2.448
crystallinity,%	62.7	50.6	53.9	64.2	69.9	63.0
Na_2O,wt%	1.0	0.8	1.0	0.8	1.1	1.2
Al_2O_3,wt%	21.7	21.9	21.8	20.8	21.2	21.8
SiO_2,wt%	70.5	69.9	72.8	70.7	74.8	67.2
ZrO_2,wt%	0	7.0	0	7.5	0	0
TiO_2,wt%	0	0	3.9	0	2.4	9.1
RE_2O_3,wt%	6.6	0	0	0	0	0
specific surface area, m^2/g	640	548	526	624	535	520
lattice collapse temperature, °C	1043	1028	1015	1030	1036	1036
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	-	1.8	1.2	-	1.0	1.3
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	-	0.05	0.06	0.02	0.01	0.04

A.2 Stability of the modified zeolite

Modified Y zeolites prepared according to Examples A.1.1.1-A.1.1.7 and A.1.2.1-A.1.2.5 were aged at 800°C under a 100% steam condition for 8 hours to determine the crystallinity and the specific surface area, and the crystallinity retention and the specific surface area retention were calculated. The results were listed in Table A2. The aged zeolites were subjected to the light oil micro-activity (MA) test. The results were listed in Table A2.

Table A2 Physical and chemical properties of the metal-modified Y zeolites after the hydrothermal aging

Example A.2.1.X	1	2	3	4	5	6	7
Y zeolite	Zr(2) Y	Zr(4) Y	Zr(8) Y	Ti(4) Y	Ti(10) Y	Ti-Zr-Y	Ti(4)Y-1
Crystallinity retention,%	60.5	62.1	64.7	63.9	65.9	66.3	63.2
Specific surface area retention, %	62.4	65.0	66.7	64.1	67.8	68.0	65.2
800°C/8h, activity	81	84	86	85	86	87	84

Table A2 (continued)

Example A.2.2.X	1	2	3	4	5	
Y zeolite	RE(8)Y	Zr(W)Y	Ti(W)Y	Zr(G)Y	DT2	DT9
Crystallinity retention,%	63.2	45.5	50.2	60.8	60.2	62.0
Specific surface area retention, %	65.5	50.8	51.6	64.9	61.6	62.9
800°C/8h, activity	84	75	75	80	70	72

Example A.2.1.8

According to Example A.1.1.5, Ti-modifed Y zeolites having Ti contents (as TiO_2) of 1wt%, 2wt%, 7wt%, 12wt%, 15wt% were prepared. The physical and chemical properties were listed in Table A3. These Ti-modifed Y zeolites were aged at 800°C under a 100% steam condition for 8 hours to determine the crystallinity and the specific surface area, and the crystallinity retention and the specific surface area retention were calculated. The aged zeolites were subjected to the light oil micro-activity (MA) test. The results were listed in Table A3.

Example A.2.2.6

According to Example A.1.2.1, RE-modifed Y zeolites having RE contents of 1wt%, 2wt%, 12wt%, 15wt% were prepared. The physical and chemical properties were listed in Table A3. These RE-modifed Y zeolites were aged at 800°C under a 100% steam condition for 8 hours to determine the crystallinity and the specific surface area, and the crystallinity retention and the specific surface area retention were calculated. The aged zeolites were subjected to the light oil micro-activity (MA) test. The results were listed in Table A3.

Table A3

	Example A.2.1.8					Example A.2.2.6			
TiO_2,wt%	1.0	2.0	7.0	12.0	15.0	0	0	0	0
RE_2O_3,wt%	0	0	0	0	0	1.0	2.0	12.0	15.0
Na_2O,wt%	1.1	0.9	1.1	0.9	0.9	0.8	1.0	1.0	0.9
Al_2O_3,wt%	23.2	22.8	21.4	19.2	16.5	22.0	21.8	20.2	17.2
SiO_2,wt%	73.3	72.8	68.7	66.9	67.1	74.5	73.5	66.0	66.2
α0, nm	2.449	2.450	2.452	2.455	2.455	2.455	2.457	2.458	2.460
Crystallinity, %	71.2	70.6	72.8	71.1	69.8	70.2	68.4	62.2	60.8
specific surface area , m^2/g	674	680	690	666	645	620	653	560	490
Lattice collapse temperature, °C	1042	1045	1050	1046	1046	1030	1044	1045	1045
the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content	0.02	0.05	0.12	0.15	0.17				
Zeolite No.	Ti(1)Y	Ti(2)Y	Ti(7)Y	Ti(12)Y	Ti(15)Y				
After the hydrothermal aging									
Crystallinity retention,%	62.2	61.2	63.6	66.0	64.5	60.0	63.4	66.2	65.0
Specific surface area retention, %	61.9	63.8	63.4	67.7	66.6	62.2	64.5	67.0	65.9
800°C/8h, activity	82	85	87	85	85	80	82	83	83

A.3 Catalyst

Example A.3.1.1

The modified Y zeolite prepared according to the present invention, Zr(8)Y, was used as active component to prepare the catalyst according to the conventional preparation method of the catalytic cracking catalyst. The preparation was as follows. According to the ratio of zeolite (dry basis):kaolin (dry basis):pseudobohemite (as Al_2O_3):alumina sol (as Al_2O_3) being 38:34:20:8, kaolin and decationized water were mixed and slurried. To the resulting slurry was added alumina sol, and further added pseudoboehmite under a continuous stirring. After 30 minutes of stirring, a liquor containing zeolite was added to the colloid. The resulting mixture was mixed homogenously, spray-dried and shaped to produce a catalyst, named as C1.

The catalyst was pretreated at 800 °C in a 100% steam condition for 17 hours. Then the pretreated catalyst was tested on a small-scale fixed fluidised bed (ACE) for catalyst evaluation. The feedstock for evaluation was Wuhun III, the properties of which were shown in Table A4. Reaction temperature, catalyst-to-oil ratio, WHSV and evaluation result were listed in Table A5.

wherein,

conversion=gasoline yield+liquefied gas yield+Dry gas yield+coke yield

coke selectivity =coke yield*100/conversion

Example A.3.2.1

A catalyst was prepared according to Example A.3.1.1, except that the same amount of RE(8)Y zeolite was used in place of Zr(8)Y zeolite to produce a catalyst named as DC1. Then DC1 was evaluated according to Example A.3.1.1. The evaluation result was listed in Table A5.

Example A.3.2.2

A catalyst was prepared according to Example A.3.1.1, except that the same amount of Zr(W)Y zeolite was used in place of Zr(8)Y zeolite to produce a catalyst named as DC2. Then DC2 was evaluated according to Example A.3.1.1. The evaluation result was listed in Table A5.

Table A4

Feedstock	Wuhun III
Density (20°C), g/cm^3	0.9044
Refraction (20°C)	1.5217
Viscosity (100°C), mm^2/s	9.96
Freezing point, °C	40
Aniline point, °C	95.8
C,wt% H,wt% S,wt% N,wt%	85.98 12.86 0.55 0.18
Residual Carbon, wt%	3.0
Distillation range, °C Initial distillation point 5% 10% 30% 50% 70% 90%	 243 294 316 395 429 473 -

Table A5

Example	A.3.1.1	A.3.2.1	A.3.2.2
Catalyst	C1	DC1	DC2
Reaction Temp, °C	500	500	500
Catalyst-to-oil weight ratio	5	5	5
WHSV, h^{-1}	16	16	16
Production Distribution, wt%			
Dry gas	1.15	1.10	1.18
liquefied gas	11.15	11.66	12.03
coke	4.02	5.45	4.65

gasoline	56.40	53.08	50.30
diesel	20.17	21.46	23.02
Heavy oil	7.11	7.25	8.82
Conversion, wt%	72.72	71.29	68.16
Coke selectivity	5.53	7.64	6.82

Example A.3.1.2

According to Example A.1.1.1, the used amount of zirconium nitrate was adjusted to prepare a Zr-modified Y zeolite, named as Zr(6)Y, wherein the ratio of the used amount of zirconium nitrate (as ZrO_2) to the weight amount of the zeolite was 6:100 by weight.

323g of pseudobohemite (having a solid content of 62wt%) and 1343g of deionized water were mixed. The mixture was stirred for 15 minutes and mixed homogenously to produce a pseudoboehmite slurry, the pH value of which was adjusted with diluted hydrochloric acid to 3.5. The resulting slurry was aged at room temperature for 6 hours. To the aged slurry were added 447g of kaolin (having a solid content of 76wt%) and 372g of alumina sol (having an alumina content of 21.5wt%). The resulting slurry was stirred for 60 minutes. To the above slurry was added a slurry formed by slurrying 380g (dry basis) of the above modified Zr(6)Y zeolite and 880g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 550°C for 1 hour to produce a catalytic cracking catalyst, named as C11. The ZrO_2 content of the catalyst C11, measured by XRF, was 2.2wt%.

Example A.3.1.3

A Zr-modified Y zeolite was prepared according to Example A.1.1.2, named as Zr(10)Y, wherein ZrO2:zeolite = 10:100.

421g of kaolin (having a solid content of 76wt%), 465g of alumina sol (having an alumina content of 21.5wt%) and 732g of deionized water were added to and slurried in a slurry vessel, to which was added 1667g of an acidified pseudoboehmite (being acidified with hydrochloric acid, the mole ratio of hydrochloric acid / alumina = 0.15, and having a solid content of 12wt%). After stirring for 60 minutes, to the vessel was added a slurry formed by slurrying 380g (dry basis) of the above modified Zr(10)Y zeolite and 880g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 550°C for 1 hour to produce a catalytic cracking catalyst, named as C21. The ZrO_2 content of the catalyst C21, measured by XRF, was 3.5wt%.

Example A.3.1.4

447g of kaolin, 372g of alumina sol and 800g of deionized water were mixed and slurried for 60 minutes. After adding 1667g of an acidified pseudobohemite, the resulting slurry was further stirred for 60 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified Ti(2)Y zeolite and 880g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 650°C for 2 hours to produce a catalytic cracking catalyst, named as C31. The TiO_2 content of the catalyst C31, measured by XRF, was 0.75wt%.

Example A.3.1.5

447g of kaolin, 372g of alumina sol and 800g of deionized water were mixed and slurried for 60 minutes. After adding 1667g of an acidified pseudobohemite, the resulting slurry was further stirred for 60 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified Ti(4)Y zeolite and 880g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 650°C for 2 hours to produce a catalytic cracking catalyst, named as 41. The TiO_2 content of the catalyst C41, measured by XRF, was 1.5wt%.

Example A.3.1.6

A catalyst was prepared according to Example A.3.1.5, except that the same amount of Ti(4)Y-1 was used in place of the Ti(4)Y zeolite to produce the catalyst, named as C41-1.

Example A.3.1.7

A catalyst was prepared according to Example A.3.1.5, except that a REY zeolite prepared according to the prior method (SiO_2/Al_2O_3 molar ratio=5.1, rare earth content=3.8wt%, Na2O content=0.4wt%) was used in place of a part of the Ti(4)Y zeolite. The weight ratio of the REY zeolite prepared according to the prior method to the Ti(4)Y zeolite was 1:1 to produce a catalyst, named as C41-2.

Example A.3.1.8

According to Example A.1.1.4, the used amount of titanium tetrachloride was adjusted to prepare a Ti-modified Y zeolite, named as Ti(8)Y, wherein the ratio of the used amount of titanium tetrachloride (as TiO_2) to the weight amount of the zeolite was 8:100 by weight.

421g of kaolin, 698g of alumina sol and 900g of deionized water were mixed and slurried for 60 minutes. After adding 1250g of an acidified pseudobohemite, the resulting slurry was further stirred for 60 minutes.

To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified Ti(8)Y zeolite and 800g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 700°C for 2 hours to produce a catalytic cracking catalyst, named as C51. The TiO_2 content of the catalyst C51, measured by XRF, was 3.0wt%.

Example A.3.1.9

The same starting materials as those used in Example A.3.1.2 were used, except for the metal-modified Y zeolite.

355g of pseudoboehmite and 1478g of deionized water were mixed and stirred for 30 minutes to produce a pseudoboehmite slurry, the pH of which was adjusted with a suitable amount of diluted hydrochloric acid to 3.8. The resulting slurry was aged at

60°C for 2 hours. To the aged slurry were added 395g of kaolin and 465g of alumina sol. The resulting mixture was stirred for 60 minutes. Then to the slurry was added a slurry formed by slurrying 380g (dry basis) of the above modified Ti-Zr-Y zeolite and 880g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 600°C for 3 hours to produce a catalytic cracking catalyst, named as C61.

Example A.3.2.3

A catalyst was prepared according to Example A.3.1.8, except that the same amount of RE(8)Y zeolite was used in place of Ti(8) Y zeolite to produce a catalyst, named as DC11. The RE_2O_3 content of the catalyst DC11, measured by XRF, was 2.32wt%.

Example A.3.2.4

A catalyst was prepared according to Example A.3.1.8, except that the same amount of Ti(W)Y zeolite was used in place of Ti(8)Y zeolite to produce a catalyst, named as DC21. The TiO_2 content of the catalyst DC21, measured by XRF, was 2.40wt%.

Example A.3.2.5

A catalyst was prepared according to Example A.3.1.2, except that the same amount of Zr(W)Y zeolite was used in place of Zr(6)Y zeolite to produce a catalyst, named as DC31. The ZrO_2 content of the catalyst DC31, measured by XRF, was 2.18wt%.

The catalysts C11-C61 and DC11-DC31 were pretreated at 800 °C in a 100% steam condition for 8 hours. Then the pretreated catalyst was tested on a small-scale fixed fluidised bed (ACE) for catalyst evaluation. The feedstock for evaluation was Wuhun III, the properties of which were shown in Table A4. Reaction temperature, catalyst-to-oil ratio, WHSV and evaluation result were listed in Table A6.
wherein, conversion=gasoline yield+liquefied gas yield+Dry gas yield+coke yield

Table A6 Evaluation Result

Example	A.3.1.2	A.3.1.3	A.3.1.4	A.3.1.5	A.3.1.6	A.3.1.7	A.3.1.8	A.3.1.9	A.3.2.3	A.3.2.4	A.3.2.5
Catalysts	C11	C21	C31	C41	C41-1	C41-2	C51	C61	DC11	DC21	DC31
Zeolites	Zr(6)Y	Zr(10)Y	Ti(2)Y	Ti(4)Y	Ti(4)Y-1	Ti(4)Y REY	Ti(8)Y	Ti-Zr-Y	RE(8)Y	Ti(W)Y	Zr(W)Y
Reaction Temp, °C	500	500	500	500	500	500	500	500	500	500	500
Catalyst-to-oil weight ratio	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04	8.04
WHSV, h^{-1}	16	16	16	16	16	16	16	16	16	16	16
Production Distribution, wt%											
Dry gas	1.35	1.32	1.33	1.34	1.33	1.3	1.32	1.35	1.34	1.34	1.35
liquefied gas	14.04	13.61	13.30	14.43	14.21	13.96	14.52	14.26	13.58	13.35	13.72
coke	6.71	6.86	7.52	7.05	7.13	7.42	6.76	6.71	8.02	7.29	7.12
gasoline	54.11	53.52	52.98	53.44	53.25	53.51	53.24	53.87	52.22	49.87	50.55
diesel	16.76	16.84	16.96	16.65	16.94	16.71	16.94	16.84	16.89	17.19	17.37
Heavy oil	7.03	7.85	7.91	7.09	7.14	7.1	7.22	6.97	7.95	10.96	9.89
Total	100	100	100	100	100	100	100	100	100	100	100
Conversion, wt%	76.21	75.31	75.13	76.26	75.92	76.19	75.84	76.19	75.16	71.85	72.74
coke /conversion	0.08805	0.09109	0.10009	0.09245	0.09391	0.09739	0.08914	0.08807	0.10671	0.10146	0.09788

B.1 Zeolite Modification

Example B.1.1.1

(1) At room temperature, 200g of NaY zeolite (dry basis, 75wt%) and 1500ml of a hydrochloric acid solution having a molar concentration of 0.5mol/L were mixed and stirred for 30 minutes. After filtering, the filter cake was washed with 1500ml deionized water to produce an acid-treated NaY zeolite, which had a Na2O content of 3.5wt%;

(2) The acid-treated NaY zeolite was calcined at 300 °C for 3 hours to produce a zeolite having a solid content of 96wt%, named as F1;

(3) 5.23 g of zirconium nitrate $Zr(NO_3)_4 \cdot 5H_2O$ was dissolved in 200g of ethanol (analytically pure, ethanol content = 99.9wt%) to produce an impregnation liquor. The impregnation liquor and the treated Y zeolite F1 were mixed homogenously and kept by standing at room temperature for 1 hour.

(4) The product from the step (3) and 800ml of ethanol were mixed and transferred to an autoclave, to which nitrogen was introduced. The pressure was kept at 0.5MPa. Then the mixture was kept by standing at room temperature for 12 hours. After filtering, the filter cake was heat-dried at 100°C for 24 hours.

(5) The product from the step (4) was calcined in a nitrogen atmosphere at 500°C for 4 hours to produce a Zr-modified Y zeolite, named as ZrY(1), the properties of which were shown in Table B2.

Example B.1.1.2 to Example B.1.1.7

With reference to Example B.1.1.1, modified zeolites were prepared according to the process of the present invention. The operation conditions and the product properties were shown in Table B2.

Example B.1.1.8

A modified zeolite was prepared according to Example B.1.1.1, except that in the step (4), nitrogen was introduced and the pressure (gauge pressure) was kept at 0 MPa. The obtained modified zeolite was named as ZrY(1)-1, the properties of which were shown in Table B2.

Example B.1.1.9

A modified zeolite was prepared according to Example B.1.1.1, except that in the step (1):

(1) At room temperature, 200g of NaY zeolite (dry basis, 75wt%) and 1500ml of a EDTA solution having a molar concentration of 0.5mol/L were mixed and stirred for 30 minutes. After filtering, the filter cake was washed with 1500ml deionized water to produce an acid-treated NaY zeolite, which had a Na2O content of 3.5wt%;

Steps (2)-(5) were identical to those in Example B.1.1.1. The obtained modified zeolite was named as ZrY(1)-2, the properties of which were shown in Table B2.

Example B.1.2.1

200g of NaY zeolite (the same as that in Example B.1.1.1) and 2000g of deionized water were slurried. To the slurry was added 60g of ammonium sulfate. The resulting slurry was adjusted with diluted hydrochloric acid to pH=4.0, warmed upto to 80°C and exchanged for 1 hour. After filtering and washing with water, the filter cake was calcined at 550°C in a 100% steam atmosphere for 2 hours. The above procedure was repeated twice to produce a modified Y zeolite.

Then, the resulting Y zeolite and 2000g of deionized water were slurried. To the slurry was added 45ml of a $RECl_3$ solution (270g/l). The resulting slurry was adjusted with diluted hydrochloric acid to pH=3.8, warmed upto to 80°C and exchanged for 1 hour. To the mixture was added 45g of ammonium sulfate, and the resulting mixture was stirred for 1 hour. After filtering and washing, the filter cake was calcined at 550°C in a 100% steam atmosphere for 2 hours. Finally, a rare earth modified REY zeolite was obtained and named as REY, the properties of which were shown in Table B3.

Example B.1.2.2

The modified zeolite was prepared according to B.1.1.2, except that the same amount of zirconium oxychloride $ZrOCl_2 \cdot 8H_2O$ was dissolved in 200g of deionized water. Finally, a Zr-modified zeolite was obtained and named as Zr(W)Y, the properties of which were shown in Table B3.

Example B.1.2.3

200g of NaY zeolite and 2000g of deionized water were slurried. To the resulting slurry was added 60g NH4Cl. The slurry was adjusted to a pH of 3.8, warmed upto 80 °C, and exchanged for 2 hours. After filtering and washing with water, the filter cake was calcined at 600 °C in a 100% steam condition for 2 hours.

The calcined zeolite and 2000g of deionized water were slurried. To the resulting slurry was added 45g NH4Cl and 31.4g zirconium oxychloride $ZrOCl_2$•$8H_2O$ to conduct a second ion-exchange substantially at the same temperature and for the same time as the first exchange. After filtering and washing with water, the filter cake was calcined at 600 °C in a 100% steam condition for 2 hours. Finally, a Zr-modified zeolite was obtained and named as Zr(J)Y, the properties of which were shown in Table B3.

Example B.1.2.4

A Zr-modified Y zeolite was prepared according to Example 1 of CN101134576A. Finally, the Zr-modified zeolite was obtained and named as Zr(G)Y, the properties of which were shown in Table B3.

Example B.1.2.5

200g of DASY0.0 zeolite was added to 500 g of absolute ethanol under a violent stirring to form a suspension, to which was added 50 g/L of a solution of butyl titanate-absolute ethanol (as TiO_2) under a violent stirring. The mixture was air-dried overnight under stirring. The resulting sample was calcined at 500 °C for 5 hours to produce Ti-modified zeolites with titanium content of 7.9wt%, named as Ti(D)Y.

It could be seen from the FT-IR spectra of modified Y zeolites in Fig. 1 that the antisymmetric stretching vibration frequency (1050-1150cm^{-1}) and the symmetric stretching vibration frequency (750-820cm^{-1}) of the Zr(G)Y zeolite provided in the prior art (e.g. Example B.1.2.4) had a red-shift in a direction toward the lower frequency, showing that Zr entered the framework structure of the Y zeolite. The modified Y zeolites provided by the present invention (e.g. ZrY and TiY) did not show the red shift, showing that Zr and Ti did not enter the framework structure of the zeolite.

It could be seen from the ^{27}Al-NMR spectra of modified Y zeolites in Fig. 2 that the modified Y zeolite had much tetrahedral-coordinated framework aluminum (chemical shift 60) and little hexahedral-coordinated framework aluminum (chemical shift 0). Compared to the Y zeolite, the peak of tetrahedral-coordinated framework aluminum of the ZrY zeolite prepared by organic solution impregnation method became wider and moved towards the lower chemical shift, showing that Zr entering the interior of the zeolite interacted with the zeolite framework [AlO4]. This interaction caused the spectrum peak of tetrahedral-coordinated framework aluminum moves to higher field, meanwhile the spectrum peak of the distorted tetrahedral-coordinated framework aluminum was remarkable (chemical shift 40). The ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum could be e.g. 0.1-0.6. Zr(W)Y and Ti(D)Y zeolites, prepared according to Example B.1.2.2 (aqueous solution impregnation) and Example B.1.2.5, had no remarkable change in the peak of distorted tetrahedral-coordinated framework aluminum, showing that Zr or Ti had little interaction with the zeolite's framework [AlO4], and the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum was less than 0.1. It could be seen that the modification method according to the present invention was more favorable for the metal ions to enter the interior of the zeolite, interact with the zeolite's framework [AlO4], and have an effect of stabilizing the zeolite framework structure.

Table B1

Raw Material	NaY	DASY(0.0)	Once-exchanged-once-calcined
Elemental composition, wt%			
Na_2O	12.8	1.2	3.7
Al_2O_3	21.9	23.6	23.4
SiO_2	64.4	71.7	72.0
Unit cell size, nm	2.466	2.448	2.453
crystallinity, %	81.6	65.6	78.0
Total specific surface area , m^2/g	762	620	644
Total pore volume, ml/g	0.377	0.353	0.352

Table B2

	Example	B.1.1.1	B.1.1.2	B.1.1.3	B.1.1.4	B.1.1.5
Step (1)	Y zeolite raw material	NaY	DASY(0.0)	Once-exchanged-once-calcined	Once-exchanged-once-calcined	NaY
	Acid solution concentration, mol/L	0.5	0.1	1.0	0.2	0.5
	Acid	Hydrochloric acid	hydrochloric acid	Oxalic acid	Sulfuric acid	Hydrochloric acid
	Acid solution:zeolite weight ratio	10	10	10	10	10
	The content of Na_2O after treatment, wt%	3.5	0.6	1.2	0.8	3.5
Step (2)	Calcination Temperature, °C	300	300	350	350	300
	Calcination time, hours	3	3	3	3	3
	Water content, wt%	4	3	1.5	1.5	4
Step (3)	Compound containing IVB group metal	zirconium nitrate	zirconium oxychloride	zirconium isopropoxide	zirconium isopropoxide	titanium tetrachloride
	Solvent	ethanol	ethanol	n-hexane	n-hexane	butanone
	Water content in solvent, wt%	0.1	0.1	0.2	0.2	0.3
	Solvent:Zeolite weight ratio	1.3	1.5	1.5	1.2	1.3
	Metal salt (as oxide):zeolite weight ratio	0.01	0.03	0.06	0.10	0.02
Step (4)	Used solvent	ethanol	ethanol	n-hexane	n-hexane	butanone
	Solvent:Zeolite weight ratio	5.1	10.0	10.0	10.0	5.1
	Introduced Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen	nitrogen
	Pressure, MPa	0.5	1.0	0.5	0.8	0.5
	Temperature, °C	26	25	60	25	25
	Time, hour	12	8	5	8	5
	Manner	By standing	Being stirred	Being stirred	By standing.	being stirred

Step (4)	Drying Temperature, °C	100	120	120	120	100
	Drying Time, hour	24	6	6	6	12
Step (5)	Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen	nitrogen
	Calcination Temperature, °C	500	550	550	550	500
	Calcination Time, hour	4	2	3	3	3
Metal-modified Y zeolite, No.		ZrY(1)	ZrY(3)	ZrY(6)	ZrY(10)	TiY(2)
Na_2O,wt%		1.0	0.5	0.8	0.6	1.2
Al_2O_3,wt%		23.3	23.5	22.2	20.5	22.8
SiO_2,wt%		73.8	72.8	70.5	67.8	73.1
ZrO_2,wt%		0.9	2.8	6.1	10.5	
TiO_2,wt%						2.2
α0, nm		2.456	2.448	2.450	2.452	2.451
Crystallinity, %		78.8	64.7	70.6	72.2	76.9
Specific surface area ,m^2/g		710	616	624	635	702
lattice collapse temperature, °C		1048	1050	1045	1047	1044
The ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum		0.2	0.3	0.5	0.6	0.2
The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)		32.5	42.8	48.7	50.3	38.6

Table B2 (continued)

	Example	B.1.1.6	B.1.1.7	B.1.1.8	B.1.1.9
Step (1)	Y zeolite raw material	Once-exchanged once-calcined	Once-exchanged- once-calcined	NaY	NaY
	Acid solution concentration, mol/L	1.0	1.0	0.5	0.5
	Acid	acetic acid	oxalic acid	hydrochloric acid	EDTA
	Acid solution:zeolite weight ratio	10	10	10	10
	The content of Na_2O after treatment, wt%	1.0	1.0	3.5	3.5
Step (2)	Calcination Temperature, °C	350	350	300	300
	Calcination time, hours	3	3	3	3
	Water content, wt%	1.8	1.5	4	4
Step (3)	Compound containing IVB group metal	butyl titanate	butyl titanate+zirconium nitrate	zirconium nitrate	zirconium nitrate
	Solvent	cyclohexane	ethanol	ethanol	ethanol
	Water content in solvent,wt%	0.2	0.1	0.1	0.1
	Solvent:Zeolite weight ratio	1.5	1.5	1.3	1.3
	Metal salt (as oxide):zeolite weight ratio	0.10	0.08	0.01	0.01
Step (4)	Used solvent	cyclohexane	Ethanol	ethanol	ethanol
	Solvent:Zeolite weight ratio	10.0	8.0	5.1	5.1
	Introduced Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen
	Pressure, MPa	0.5	1.5	0.0	0.5
	Temperature, °C	25	80	26	26
	Time, hour	10	24	12	12
	Manner	Being stirred	Being stirred	By standing	By standing
Step (4)	Drying Temperature, °C	120	120	100	100
	Drying Time, hour	6	24	24	24

Step (5)	Inert Gas	nitrogen	nitrogen	nitrogen	nitrogen
	Calcination Temperature, °C	550	550	500	500
	Calcination Time, hour	2	3	4	4
	Metal-modified Y zeolite, No.	TiY(10)	Ti-Zr-Y	ZrY(1)-1	ZrY(1)-2
	Na_2O,wt%	1.0	0.8	1.0	0.9
	Al_2O_3,wt%	21.5	21.9	23.2	23.4
	SiO_2,wt%	67.1	69.0	73.9	73.6
	ZrO_2,wt%		3.8	0.9	0.9
	TiO_2,wt%	9.8	4.0		
	α0, nm	2.455	2.455	2.454	2.455
	crystallinity, %	73.5	72.9	71.5	77.7
	specific surface area ,m^2/g	642	639	700	699
	lattice collapse temperature, °C	1045	1050	1045	1048
	the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum	0.5	0.5	0.2	0.2
	The percent of the secondary pores (pore diameter of 6-20 nm) to the total secondary pores (pore diameter of 2-100 nm)	49.8	44.4	35.4	33.9

Table B3

Example	B.1.2.1	B.1.2.2	B.1.2.3	B.1.2.4	B.1.2.5
Y zeolite No.	REY	Zr(W)Y	Zr(J)Y	Zr(G)Y	Ti(D)Y
Na_2O,wt%	1.2	0.8	0.6	0.5	1
Al_2O_3,wt%	21.4	20.6	21.8	20.8	21.5
SiO_2,wt%	70.5	70.2	71	70.7	69.3
ZrO_2,wt%		8	6.2	7.5	
TiO_2,wt%					7.9
RE_2O_3,wt%	6.6				
α0, nm	2.451	2.45	2.452	2.451	2.453
crystallinity, %	62.7	51.9	55.7	60.2	59.6
specific surface area ,m^2/g	640	536	548	624	610
lattice collapse temperature, °C	1043	1027	1028	1041	1033
the ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum		0.05	0.01	0.02	0.01

B.2 Stability of the modified zeolite

Modified Y zeolites prepared according to Example B.2.1.1-B.2.1.9 and B.2.2.1-B.2.2.5 were aged at 800°C under a 100% steam condition for 8 hours and 17hours respectively to determine the crystallinity and the specific surface area, and the crystallinity retention and the specific surface area retention were calculated. The aged zeolites were subjected to the light oil micro-activity (MA) test. The results were listed in Table B4.

Table B4

Example B.2.1.X	1	2	3	4	5	6	7	8	9
Y zeolite	ZrY(1)	ZrY(3)	ZrY(6)	ZrY(10)	TiY(2)	TiY(10)	Ti-Zr-Y	ZrY(1)-1	ZrY(1)-2
800°C/8h crystallinity retention, %	61.2	62.8	63.7	68.4	63.1	67.5	68.6	62.0	61.8
800°C/17h crystallinity retention, %	55.5	57.0	56.7	62.5	57.6	60.1	60	56.5	56.1
800°C/8h specific surface area retention,%	62.0	61.3	62.9	69.6	66.1	68	69.6	62.8	61.0
800°C/17h specific surface area retention,%	57.2	56.7	57.6	63.9	59.6	62.2	62.8	57.0	56.4
800°C/8h activity,%	80	82	84	87	85	86	87	80	80
800°C/17h activity,%	76	77	79	82	79	80	81	75	77

Table B4 (continued)

Example B.2.2.X	1	2	3	4	5
Y zeolite	REY	Zr(W)Y	Zr(J)Y	Zr(G)Y	Ti(D)Y
800°C/8h crystallinity retention, %	63.2	50.4	50.5	60.8	61.6
800°C/17h crystallinity retention, %	56.5	45.8	42.5	52.9	53
800°C/8h specific surface area retention,%	67.1	58	54.2	64.9	62.4
800°C/17h specific surface area retention,%	61.2	52.6	49.8	58.2	59.1
800°C/8h activity,%	85	75	72	80	72
800°C/17h activity,%	79	68	65	75	66

B.3 catalyst

Example B.3.1.1

The modified Y zeolite prepared according to the present invention, Zr(6)Y, was used as active component to prepare the catalyst according to the conventional preparation method of the catalytic cracking catalyst. The preparation was as follows.

According to the ratio of zeolite (dry basis):kaolin (dry basis):pseudobohemite (as Al_2O_3):alumina sol (as Al_2O_3) being 38:34:20:8, kaolin and decationized water were mixed and slurried. To the resulting slurry was added alumina sol, and further added pseudoboehmite under a continuous stirring. After 30 minutes of stirring, a liquor containing zeolite was added to the colloid. The resulting mixture was mixed homogenously, spray-dried and shaped to produce a catalyst, named as C1.

Evaluation of heavy oil cracking performance:

The catalyst was pretreated at 800 °C in a 100% steam condition for 8 hours. Then the pretreated catalyst was tested on a small-scale fixed fluidised bed (ACE) for catalyst evaluation. The feedstock for evaluation was a mixed oil of ZhengHai VGO and DaQing atmospheric residue (80:20 by weight), the properties of which were shown in Table B5. Reaction Temp=500°C, WHSV=16h^{-1}, Catalyst-to-oil weight ratio=45. The evaluation result was listed in Table B6.

wherein,

conversion = gasoline yield+liquefied gasyield+Dry gasyield+coke yield

coke selectivity =coke yield×100/conversion

Table B5

Feedstock	ZhengHai VGO	DaQing Atmospheric Residue
Density (20°C), g/cm^3	0.9154	0.8906
Refraction (70°C)	1.4926	1.4957(20°C)
Viscosity (100°C) mm^2/s	6.962	24.84
SARA composition, %		
Saturated hydrocarbons	64.0	51.2
Aromatic hydrocarbons	32.0	29.7
Resin	4.0	18.3
Asphaltene	0.0	0.8
Freezing point,°C	35	43
Aniline point,°C	82.0	>105
C, wt%	85.38	86.54
H ,wt%	12.03	13.03
S ,wt%	2.0	0.13
N ,wt%	0.16	0.3
Residual Carbon %	0.18	4.3
Distillation range, °C		
Initial distillation point	329	282
5%	363	351
10%	378	370
30%	410	482
50%	436	553
70%	462	-
90%	501	-

Example B.3.1.2

A catalyst was prepared according to Example B.3.1.1, except that the same amount of TiY(2) zeolite was used in place of ZrY(6) zeolite to produce a catalyst C2. Then the evaluation of C2 was done according to Example B.3.1.1. The evaluation result was listed in Table B6.

Example B.3.2.1 to Example B.3.2.3

A series of catalysts were prepared according to Example B.3.1.1, except that the same amount of REY zeolite, the same amount of Zr(W)Y zeolite, and the same amount of Ti(D)Y zeolite were respectively used in place of ZrY(6) zeolite to produce the catalysts DC1, DC2 and DC3. Then the evaluation of DC1-DC3 was done according to Example B.3.1.1. The evaluation result was listed in Table B6.

Table B6

Example	B.3.1.1	B.3.1.2	B.3.2.1	B.3.2.2	B.3.2.3
Zeolite No.	ZrY(6)	TiY(2)	REY	Zr(W)Y	Ti(D)Y
Catalyst	C1	C2	DC1	DC2	DC3
Reaction Temp, °C	500	500	500	500	500
Catalyst-to-oil weight ratio	5	5	5	5	5
WHSV, h^{-1}	16	16	16	16	16
Production Distribution, wt%					
Dry gas	1.40	1.39	1.38	1.39	1.37
liquefied gas	17.15	16.92	16.53	16.44	16.98
coke	4.52	4.75	5.35	5.16	5.33
gasoline	50.80	49.98	49.70	45.62	48.29
diesel	17.85	18.76	18.64	19.97	18.73
Heavy oil	8.28	8.20	8.40	11.42	9.30
Conversion, wt%	73.87	73.04	72.96	68.61	71.97
Total liquid yield, wt%	85.80	85.66	84.87	82.03	84.00
Coke selectivity	6.12	6.50	7.33	7.52	7.41

Example B.3.1.3

A Zr-modified Y zeolite was prepared according to Example B.1.1.1, named as Zr(2)Y, wherein the weight ratio of zirconium nitrate(as ZrO_2):Y zeolite= 0.02:1.

323g of pseudoboehmite and 1343g of deionized water were mixed and stirred for 15 minutes to produce a pseudoboehmite slurry. The slurry was adjusted with diluted hydrochloric acid (having a concentration of 15wt%) to a pH of 3.5, and aged at room temperature for 6 hours. To the aged slurry were added 421g of kaolin and 465g of alumina sol. After stirring for 60minutes, to the resulting slurry was added a slurry formed by slurrying 380g (dry basis) of the above modified ZrY(2) zeolite and 800g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 550°C for 2 hours to produce a catalytic cracking catalyst, named as C17. The ZrO_2 content of the catalyst C17, measured by XRF, was 0.75wt%.

Example B.3.1.4

421g of kaolin, 465g of alumina sol and 732g of deionized water were added to and slurried in a slurry vessel, to which was added 1667g of an acidified pseudoboehmite. After stirring for 60 minutes, to the vessel was added a slurry formed by slurrying 380g (dry basis) of the above modified Zr(6)Y zeolite and 800g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 550°C for 1 hour to produce a catalytic cracking catalyst, named as C18. The ZrO_2 content of the catalyst C18, measured by XRF, was 2.18wt%.

Example B.3.1.5

421g of kaolin, 558g of alumina sol and 800g of deionized water were mixed and slurried for 60 minutes. After adding 1500g of an acidified pseudobohemite, the resulting slurry was further stirred for 60 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified ZrY(10) zeolite and 800g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 650°C for 2 hours to produce a catalytic cracking catalyst, named as C19. The ZrO_2 content of the catalyst C19, measured by XRF, was 3.52wt%.

Example B.3.1.6

According to Example B.2.1.5, a Ti-modified Y zeolite was prepared and named as TiY(8), wherein during the impregnation of the step (3), the weight ratio of titanium tetrachloride (as TiO_2) to zeolite was 0.08:1.

421g of kaolin and 380g of deionized water were mixed and slurried for 60 minutes. After adding 1667g of an acidified pseudobohemite, the resulting slurry was further stirred for 30 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified TiY(8) zeolite and 800g of deionized water. After stirring for 60 minutes, to the resulting slurry was added 465g of alumina sol. The resulting mixture was stirred for 30 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 700°C for 2 hours to produce a catalytic cracking catalyst, named as C20. The TiO_2 content of the catalyst C20, measured by XRF, was 3.02wt%.

Example B.3.1.7

According to Example B.2.1.5, a Ti-modified Y zeolite was prepared and named as TiY(4), wherein during the impregnation of the step (3), the weight ratio of titanium tetrachloride (as TiO_2) to zeolite was 0.04:1.

323g of pseudoboehmite and 1478g of deionized water were mixed. The mixture was stirred for 30 minutes to produce a pseudoboehmite slurry, the pH value of which was adjusted with a suitable amount of diluted hydrochloric acid to 3.8. The resulting slurry was aged at 60°C for 2 hours. To the aged slurry were added 421g of kaolin and 465g of alumina sol. The resulting slurry was stirred for 60 minutes. To the above slurry was added a slurry formed by slurrying 380g (dry basis) of the above modified TiY(4) zeolite and 800g of deionized water. The resulting mixture was stirred for 60 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 600°C for 3 hours to produce a catalytic cracking catalyst, named as C21. The TiO_2 content of the catalyst C21, measured by XRF, was 1.48wt%.

Example B.3.1.8

According to Example B.2.1.5, a Hf-modified Y zeolite was prepared and named as

HfY(6), wherein during the impregnation of the step (3), the weight ratio of hafnium nitrate (as HfO_2) to zeolite was 0.06:1.

421g of kaolin and 380g of deionized water were mixed and slurried for 60 minutes. After adding 1667g of an acidified pseudobohemite, the resulting slurry was further stirred for 30 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified HfY(6) zeolite and 800g of deionized water. After stirring for 60 minutes, to the resulting slurry was added 465g of alumina sol. The resulting mixture was stirred for 30 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 700°C for 2 hours to produce a catalytic cracking catalyst, named as C22. The HfO_2 content of the catalyst C22, measured by XRF, was 2.11wt%.

Example B.3.1.9

421g of kaolin and 380g of deionized water were mixed and slurried for 60 minutes. After adding 1667g of an acidified pseudobohemite, the resulting slurry was further stirred for 30 minutes. To the resulting mixture was added a slurry formed by slurrying 380g (dry basis) of the above modified Ti-Zr-Y zeolite and 800g of deionized water. After stirring for 60 minutes, to the resulting slurry was added 465g of alumina sol. The resulting mixture was stirred for 30 minutes to produce a catalyst slurry, which was spray-dried and shaped, and calcined at 700°C for 2 hours to produce a catalytic cracking catalyst, named as C23. The TiO_2 and ZrO_2 contents of the catalyst C23, measured by XRF, were 1.50wt% and 1.48wt% respectively.

Example B.3.1.10 to Example B.3.1.12

A series of catalysts were prepared according to Example B.3.1.3, except that the same amount of ZrY(1), the same amount of ZrY(1)-1 and the same amount of ZrY(1)-2 were respectively used in place of ZrY(2) zeolite to produce the catalysts C24, C25 and C26.

Example B.3.2.4

A catalyst was prepared according to Example B.3.1.4, except that the same amount of Zr(W)Y zeolite was used in place of ZrY(6) zeolite to produce the catalyst DC14. The ZrO_2content of the catalyst DC14, measured by XRF, was 2.19wt%.

Example B.3.2.5

500g of NaY zeolite (dry basis) and 6000g of deionized water were mixed and slurried. To the resulting slurry was added 200g of NH_4Cl. The mixture was adjusted to pH=3.8, warmed upto 80°C to exchange for 2 hours, filtered and washed with water. The above procedure was repeated for three times. The resulting filter cake was calcined at 600 °C under a 100% steam atmosphere for 2 hours. Then, the calcined Y zeolite and 6000g of deionized water were mixed and slurried. To the slurry was added 150g NH4Cl and 95.1g of titanium tetrachloride. The mixture was warmed upto 80°C to exchange for 3 hours. After filtering and washing, the resulting filter cake was calcined at 600°C, under a 100% steam atmosphere for 2 hours. Finally, a zeolite was obtained and named as Ti(J)Y zeolite.

A catalyst was prepared according to Example B.3.1.6, except that the same amount of Ti(J)Y zeolite was used in place of TiY(8) zeolite to produce the catalyst DC15. The TiO_2content of the catalyst DC15, measured by XRF, was 1.72wt%.

Example B.3.2.6

200g of NaY zeolite and 2000g of deionized water were mixed and slurried. To the resulting slurry was added 45mL of a solution of 270g/l $RECl_3$. The mixture was adjusted with a diluted hydrochloric acid to pH=3.8, and warmed upto 80°C to exchange for 1 hour. After filtering and washing, the resulting filter cake was calcined at 500 °C for 3 hours. Then, the resulting Y zeolite and 2000g of deionized water were mixed and slurried. To the slurry was added 45g of ammonium sulfate. The mixture was adjusted with a diluted hydrochloric acid to pH=4.0, and warmed upto 80°C to exchange for 1 hour. After filtering and washing, the resulting filter cake was calcined at 600°C, under a 100% steam atmosphere for 3 hours. Finally, a RE-modified zeolite was obtained and named as REY(8).

According to the ratio of zeolite (dry basis):kaolin (dry basis):pseudobohemite (as Al_2O_3):alumina sol (as Al_2O_3) being 38:34:20:8, kaolin and decationized water were mixed and slurried. To the resulting slurry was added alumina sol, and further added pseudoboehmite under a continuous stirring. After about 30 minutes of stirring, a liquor containing zeolite was added to the colloid. The resulting mixture was mixed homogenously, spray-dried and shaped to produce a catalyst, named as DC16.

The catalysts C17-C26 and DC14-DC16 were pretreated at 800 °C in a 100% steam condition for 17 hours. Then the pretreated catalysts were tested on a small-scale fixed fluidised bed (ACE) for catalyst evaluation. The feedstock for evaluation was Wuhun III, the properties of which were shown in Table B7. Reaction temperature = 500°C, and the catalyst-to-oil weight ratio = 5. The evaluation result was listed in Table B8.

wherein,

conversion=gasoline yield + liquefied gas yield + Dry gas yield + coke yield

coke selectivity =coke yield/conversion

Table B7 Feedstock's properties

Feedstock	Wuhun III
density (20°C), g/cm^3	0.9044
Refraction (20°C)	1.5217
Viscosity (100°C), mm^2/s	9.96
Freezing point, °C	40
Aniline point, °C	95.8
C,wt%	85.98
H,wt%	12.86
S,wt%	0.55
N,wt%	0.18
Residual Carbon, wt%	3.0
Distillation range, °C	
Initial distillation point	243
5%	294
10%	316
30%	395
50%	429
70%	473
90%	-

Table B8 Evaluation Result

Example	B.3.1.3	B.3.1.4	B.3.1.5	B.3.1.6	B.3.1.7	B.3.1.8	B.3.1.9
Catalyst No.	C17	C18	C19	C20	C21	C22	C23
Modified Y Zeolite No.	ZrY(2)	ZrY(6)	ZrY(10)	TiY(8)	TiY(4)	HfY(6)	Ti-Zr-Y
Reaction Temp,°C	500	500	500	500	500	500	500
Catalyst-To-Oil Ratio (Weight)	5	5	5	5	5	5	5
WHSV, h^{-1}	16	16	16	16	16	16	16
Production Distribution,wt%							
Dry Gas	1.25	1.12	1.29	1.22	1.10	1.18	1.20
Liquefied Gas	12.04	13.05	11.53	12.09	12.41	12.48	12.35
Coke	5.09	4.26	4.95	4.96	5.01	4.85	4.99
Gasoline	53.99	54.61	54.59	54.44	54.07	53.95	54.11
Diesel	21.41	20.98	21.58	21.34	21.84	21.69	21.36
Heavy Oil	6.22	5.98	6.06	5.95	5.57	5.85	5.99
Total	100	100	100	100	100	100	100
Conversion, wt %	72.37	73.04	72.36	72.71	72.59	72.46	72.65
Coke /Conversion	0.07033	0.05832	0.06841	0.06822	0.06902	0.06693	0.06869

Table B8: Evaluation Result (continued)

Example	B.3.1.10	B.3.1.11	B.3.1.12	B.3.2.4	B.3.2.5	B.3.2.6
Catalyst No.	C24	C25	C26	DC14	DC15	DC16
Modified Y Zeolite No.	ZrY(1)	ZrY(1)-1	ZrY(1)-2	Zr(W)Y	Ti(J)Y	RE(8)Y
Reaction Temp, °C	500	500	500	500	500	500
Catalyst-To-Oil Ratio (Weight)	5	5	5	5	5	5
WHSV, h^{-1}	16	16	16	16	16	16
Production Distribution, wt%						
Dry Gas	1.21	1.22	1.23	1.32	1.18	1.10
Liquefied Gas	11.81	11.79	11.89	11.78	12.03	11.66
Coke	4.62	4.52	4.71	5.88	5.25	5.45
Gasoline	54.15	54.21	54.48	50.57	50.30	53.08
Diesel	21.88	21.91	21.28	22.01	22.12	21.46
Heavy Oil	6.33	6.35	6.41	8.44	9.12	7.25
Total	100	100	100	100	100	100
Conversion,wt%	71.79	71.74	72.31	69.55	68.76	71.29
Coke/Conversion	0.06435	0.06301	0.06514	0.08454	0.07635	0.0764

CLAIMS:

1. A metal modified Y zeolite, which contains 1-15wt% of IVB group metal as oxide, wherein the metal-modified Y zeolite has a ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the lattice structure of 0.1-0.8.

2. The metal modified Y zeolite of claim 1, which has a specific surface area of 600-850 m^2/g or 600-750m^2/g, a unit cell size a0 of 2.448-2.458 nm or 2.450-2.455nm, a crystallinity of not less than 60%, and optionally a SiO_2/Al_2O_3 molar ratio of 5-50 and the percent of the secondary pores having a pore diameter of 6-20 nm to the total secondary pores having a pore diameter of 2-100 nm being 30-50% or 50%-65%.

3. The metal modified Y zeolite of claim 1, wherein the modifying metal is Ti and/or Zr, wherein relative to the non-modified Y zeolite, the antisymmetric stretching vibration frequency at 1050-1150cm^{-1} and the symmetric stretching vibration frequency at 750-820cm^{-1} in the infrared spectrum of the metal-modified Y zeolite do not red-shift in a direction toward the lower frequency .

4. The metal-modified Y zeolite of claim 1 or 3, which has an anhydrous chemical composition formula, as oxide and by weight, of $(0\text{-}2)Na_2O\bullet(1\text{-}15)MO_2\bullet(10\text{-}25)Al_2O_3\bullet(65\text{-}75)SiO_2$ or $(0.1\text{-}1.2)Na_2O\bullet(1\text{-}10)MO_2\bullet(20\text{-}24)Al_2O_3\bullet(67\text{-}74)SiO_2$, wherein M is a IVB group metal, selected from one or more of Ti, Zr, Hf and Rf.

5. The metal modified Y zeolite of claim 1, wherein the IVB group metal is Ti and/or Zr, and the metal-modified Y zeolite is free of both framework Ti and framework Zr.

6. The metal modified Y zeolite of claim 1, wherein the ratio of the zeolite surface's IVB group metal content to the zeolite interior's IVB group metal content is not higher than 0.2.

7. The metal modified Y zeolite of claim 1, wherein the content of the IVB group metal as oxide is 1-10wt%.

8. The metal modified Y zeolite of claim 1, wherein the IVB group metal comprises Ti and/or Zr.

9. The metal modified Y zeolite of claim 1, wherein the metal-modified Y zeolite has a ratio of the distorted tetrahedral-coordinated framework aluminum to the tetrahedral-coordinated framework aluminum in the lattice structure of 0.2-0.8.

10. A process for preparing a metal modified Y zeolite according to any one of claims 1-9, comprising the steps of:
(1) a Y zeolite is contacted with an acid solution and/or an aqueous EDTA solution; wherein said acid is an organic acid and/or an inorganic acid;
(2) the product obtained from the step (1) is dewatered at a temperature below 400°C, so that the water content in the zeolite is not higher than 5wt%;
(3) the zeolite obtained from the step (2) is impregnated with a metal in an organic solvent;
(4) the metal impregnated Y zeolite obtained from the step (3) and an organic solvent are added to a vessel at a solid-to-liquid weight ratio of 1:5-50, an inert gas is introduced to the vessel, and the vessel is kept under a gauge pressure of 0-2.0MPa at a temperature in the range from room temperature to 200°C for at least one hour; filtering and/or drying is optionally conducted;
(5) the zeolite obtained from the step (4) is calcined; the calcination is conducted in an inert gas atmosphere, the calcination temperature is 300-700°C, the calcination time is 0.5-5 hours.

11. The process of claim 10, wherein in the step (1), the Y zeolite is one or more of NaY, NaHY, NaNH$_4$Y, NH$_4$Y, HY, USY, DASY zeolite, once-exchanged-once-calcined Y zeolite, twice-exchanged-twice-calcined Y zeolite, and twice-exchanged-once-calcined Y zeolite.

12. The process of claim 10, wherein in the step (1), the Y zeolite is contacted with the acid

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solution in a solid-to-liquid weight ratio of 1:5-1:20 at a temperature in a range from room temperature to 100°C for at least 0.5 hour, then filtered and washed; the acid solution has an acid concentration, as H^+, of 0.1-1mol/L.

13. The process of claim 12, wherein the contact time is 0.5-3 hours; the acid is an inorganic acid and/or an organic acid; wherein the inorganic acid is one or more of hydrochloric acid, sulfuric acid and nitric acid; and the organic acid is one or more of formic acid, acetic acid, oxalic acid, citric acid.

14. The process of claim 10, wherein in the step (2), the dewatering is to calcine the zeolite obtained from the step (1) at 200-400°C for 2-10 hours.

15. The process of claim 10, wherein in the step (3), the impregnation with the metal in the organic solvent comprises the organic solvent in which a compound containing IVB group metal is solved is mixed with the zeolite obtained from the step (2), and the resulting mixture is kept for at least 0.5 hour, wherein the solid-to-liquid weight ratio of the Y zeolite and the organic solvent is 1:(0.5-5).

16. The process of claim 15, wherein in the step (3), the resulting mixture is kept by standing or being stirred for 0.5-12 hours.

17. The process of claim 15, wherein in the step (3), the solid-to-liquid weight ratio of the Y zeolite and the organic solvent is 1:1-2.

18. The process of claim 15, wherein the compound containing IVB group metal is a Ti-containing compound and/or a Zr-containing compound; the Ti-containing compound is one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, and ammonium fluotitanate, and the Zr-containing compound is one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

19. The process of claim 10, wherein in the step (4), the metal impregnated Y zeolite obtained from the step (3) and an organic solvent are added to a vessel at a solid-to-liquid weight ratio of 1:5-50, an inert gas is introduced to the vessel, and the vessel is kept under a gauge pressure of 0.1-2MPa at a temperature in the range from room temperature to 200°C for at least one hour; filtering and/or drying is optionally conducted.

20. The process of claim 10, wherein in the step (4), the vessel is kept for 1-48 hours.

21. The process of claim 10, wherein in the step (4), the pressure is 0.5-1.5MPa, the temperature is from room temperature to 150°C, the time is 4-24 hours, and the solid-to-liquid weight ratio of the zeolite and the organic solvent is 1:5-30.

22. The process of claim 10, wherein in the step (5), the calcination temperature is 450-650°C, and the calcination time is 1-4 hours.

23. The process of claim 10, wherein the organic solvent has a water content of not more than 5wt%.

24. The process of claim 23, wherein, the organic solvent has a water content of not more than 3wt%; and the Y zeolite obtained from the step (2) has a water content of not more than 3wt%.

25. The process of any one of claims 10-24, wherein the organic solvent is one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, and halogenated alkanes.

26. The process of any one of claims 10-24, wherein the organic solvent is a chloridized alkane.

27. The process of claim 25 or 26, wherein the organic solvent has a normal boiling point

of 40-100°C.

28. The process of claim 25 or 26, wherein the organic solvent is one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone, and trichloromethane.

29. A process for preparing a metal modified Y zeolite according to any one of claims 1-9, comprising the steps of:
(1) a Y-zeolite raw material is subjected to dewatering so that the raw material has a water content by weight of not higher than 5%;
(2) the dewatered Y zeolite obtained from step (1) is contacted with a mixture of a compound containing IVB group metal and an organic solvent, and the resulting mixture is optionally filtered and/or dried;
(3) the Y zeolite obtained from step (2) is calcined at 300-700°C;
(4) the Y zeolite obtained from step (3) is contacted with an aqueous acid solution, and then calcined at 400-800°C to produce the metal-modified Y zeolite containing the IVB group metal; the acid concentration, as H+, is 0.1-2.0mol/L.

30. The process of claim 29, wherein in the step (2), the mixing weight ratio of the compound containing IVB group metal, the Y zeolite and the organic solvent is 0.01-0.15:1:1-50, wherein the weight of the compound containing IVB group metal is calculated as oxide, and the Y zeolite is calculated in a dry basis.

31. The process of claim 29, wherein in the step (2), the weight ratio of the compound containing IVB group metal as oxide: the Y zeolite on the dry basis: the organic solvent is 0.01-0.1:1:5-30.

32. The process of claim 29, wherein in the step (2), the procedure of contacting the dewatered Y zeolite obtained from step (1) with the compound containing IVB group metal and the organic solvent and optionally filtering and/or drying comprises: the compound

containing IVB group metal, the organic solvent and the Y zeolite are mixed and contacted at a temperature in a range from room temperature to 100°C for at least 0.5 hour, then optionally filtered, and then optionally dried.

33. The process of claim 29 or 32, wherein in the step (2), the procedure of contacting the dewatered Y zeolite obtained from step (1) with the mixture of the compound containing IVB group metal and the organic solvent and optionally filtering and/or drying the resulting mixture is conducted once or more than once.

34. The process of claim 29, wherein in the step (3), the calcination temperature is 350-650°C, the calcination time is 2-4 hours, the calcination atmosphere is a dried air and/or an inert gas.

35. The process of claim 29, wherein in the step (4), the condition for contacting the Y zeolite obtained from step (3) and the aqueous acid solution comprises: the solid-to-liquid weight ratio of the Y zeolite obtained from step (3) to the aqueous acid solution is 1:5-20, the contact temperature is in a range from room temperature to 100°C, the contact time is at least 0.5 hour; the aqueous acid solution has an acid concentration, as H+, of 0.1-2mol/L.

36. The process of claim 29, wherein the aqueous acid solution has an acid concentration, as H+, of 0.5-2 mol/L.

37. The process of claim 29, wherein the organic solvent is one or more of alkanes, aromatic hydrocarbons, alcohols, ketones, ethers, esters, and halogenated alkanes.

38. The process of claim 29, wherein the organic solvent is a chloridized alkane.

39. The process of claim 29, wherein the organic solvent is selected from one or more of n-hexane, cyclohexane, heptane, benzene, toluene, methanol, ethanol, isopropanol, acetone, butanone, and trichloromethane.

40. The process of claim 29, wherein the organic solvent has a normal boiling point of 40-100°C.

41. The process of any one of claims 29-40, wherein the organic solvent has a water content of not more than 5wt%.

42. The process of claim 29, wherein the organic solvent has a water content of not more than 1wt%.

43. The process of any one of claims 29-42, wherein in the step (2), the temperature for contacting the dewatered Y zeolite obtained from step (1) and the mixture of the compound containing IVB group metal and the organic solvent is such a temperature that allows the organic solvent in a liquid state.

44. The process of claim 29, wherein the compound containing IVB group metal comprises a Ti-containing compound and/or a Zr-containing compound.

45. The process of claim 44, wherein the Ti-containing compound is one or more of titanium sulfate, titanyl sulfate, titanium tetrachloride, titanium trichloride, tetrabutyl titanate, ammonium fluotitanate, and the Zr-containing compound is one or more of zirconium tetrachloride, zirconium sulphate, zirconium nitrate, zirconium oxychloride, zirconium acetate, and zirconium isopropoxide.

46. The process of claim 29, wherein in the step (1), the Y zeolite raw material is one or more of NaY zeolite, NaHY zeolite, $NaNH_4Y$ zeolite, NH_4Y zeolite and HY zeolite.

47. The process of claim 29, wherein in the step (1), the Y zeolite raw material has a water content, after dewatering, of not more than 1wt%.

48. The process of claim 29, wherein in the step (4), the calcination is conducted in a 1-100%

steam atmosphere.

49. A catalytic cracking catalyst, based on the total weight of the catalyst, containing 10-60wt% of a metal-modified Y zeolite, 10-60wt% of a clay and 5-50wt% of a binder, wherein said metal-modified Y zeolite is the metal-modified Y zeolite of any one of claims 1-9.

50. The catalytic cracking catalyst of claim 49, wherein the catalytic cracking catalyst contains 20-55wt% of the IVB group metal-modified Y zeolite, 15-60wt% of the clay and 10-40wt% of the binder .

51. The catalytic cracking catalyst of claim 49 wherein the catalyst further contains other molecular sieves commonly used in the catalytic cracking catalyst, said other molecular sieves include Y-type molecular sieves, MFI-structured molecular sieves, and SAPO molecular sieves.

52. The catalytic cracking catalyst of claim 49, wherein, the content of other molecular sieves commonly used in the catalytic cracking catalyst is not more than 40wt%.

53. The catalytic cracking catalyst of claim 49, wherein, the content of other molecular sieves commonly used in the catalytic cracking catalyst is 1-35wt%.

54. A method for preparing a catalytic cracking catalyst, which comprises the steps of preparing a metal-modified Y zeolite, mixing and slurrying the metal-modified Y zeolite and a clay and a binder, and spray-drying the resulting mixture, wherein said metal-modified Y zeolite is prepared according to the process of any one of claims 10-48.

55. The method of claim 54, wherein the clay is selected from one or more of kaolin, halloysite, rectorite, diatomite, montmorillonite, bentonite and sepiolite; and the binder is selected from one or more of hydrated alumina, alumina sol, pseudobohemite, bohemite,

alumina monohydrate, alumina trihydrate, and amorphous aluminum hydroxyde.

Drawings

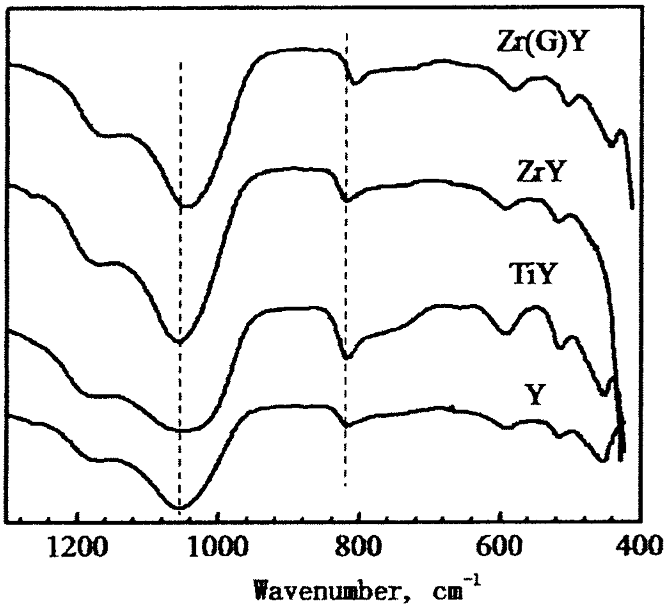


Figure 1

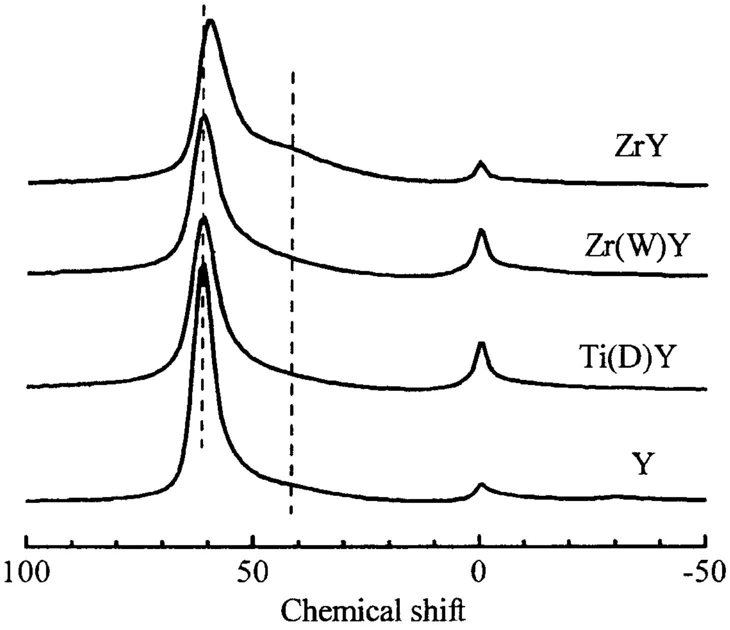
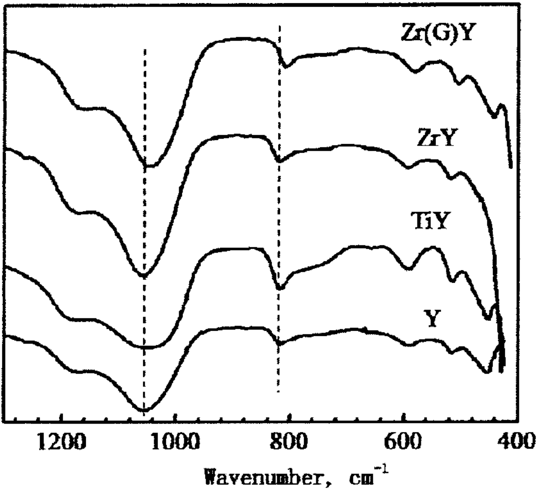


Figure 2


Zr(G)Y
ZrY
TiY
Y
1200
1000
800
600
400
Wavenumber, cm^{-1}