Claims

1. A catalytic cracking catalyst, comprising 10-70 wt% of a cracking active component, 10-60 wt% of a binder and 10-70 wt% of a clay, wherein the cracking active component comprises 5-100 wt% of a first Y-type molecular sieve and 0-95 wt% of a second molecular sieve; wherein the first Y-type molecular sieve is a modified molecular sieve based on the crystal modification of kaolin obtained from the modification treatment of a molecular sieve based on the crystal modification of kaolin, and has a sodium oxide content of less than 2 wt%,wherein for the molecular sieve based on the crystal modification of kaolin, when measured with an X-ray diffraction method, the crystallinity by the peak height method is ≥ 60%, and the ratio of the crystallinity by the peak height method to the crystallinity by the peak area method is K1, K1=0.76-0.89; the silica-alumina ratio measured with the unit cell constant a0 is 5.0-5.5, and the ratio of the silica-alumina ratio measured with the unit cell constant a0 to the silica-alumina ratio measured with the chemical method is K2, K2=0.87-0.93, the silica-alumina ratios are both the molar ratio of silica to alumina.

2. The catalytic cracking catalyst according to claim 1, wherein the crystallinity by the peak height method is ≥ 80%.

3. The catalytic cracking catalyst according to claim 1 or 2, wherein the K1=0.80-0.89, for example the K1=0.80-0.85.

4. The catalytic cracking catalyst according to any of claims 1-3, wherein the K2=0.87-0.92, for example the K2=0.88-0.90.

5. The catalytic cracking catalyst according to any of claims 1-4, wherein the K1=0.77-0.88 and the K2=0.87-0.91.

6. The catalytic cracking catalyst according to any of claims 1-5, wherein the molecular sieve based on the crystal modification of kaolin has a proportion of macropores and mesopores of 10-20% as measured with the nitrogen adsorption method RIPP151-90, wherein the pores with a pore diameter greater than 0.8nm are defined as mesopores and macropores, and the equation for the proportion of mesopores and macropores is $(V_{\text{total pores}}-V_{\text{micropores}})/V_{\text{total pores}}\times 100\%$.

7. The catalytic cracking catalyst according to any of claims 1-6, wherein the silica-alumina ratio measured with the unit cell constant a0 is 5.2-5.5.

8. The catalytic cracking catalyst according to any of claims 1-7, wherein the molecular sieve based on the crystal modification of kaolin is prepared with a process comprising the steps of:

(1) converting kaolin into metakaolin by calcining and dehydrating at 500-900°C, and pulverizing it into metakaolin powder with a particle size of less than 10 microns;

(2) adding a directing agent, sodium silicate, a sodium hydroxide solution and water to the metakaolin powder to produce a reaction raw material A, wherein the mass ratio of the directing agent to the metakaolin is 0.01-1.0, and the reaction raw material A has a composition by molar ratio of (1-2.5) $Na_2O$ : $Al_2O_3$ : (4-9) $SiO_2$ : (40-100) $H_2O$;

(3) crystallizing the reaction raw material A at 88-98°C under stirring for 1-70 hours, then supplementing a second silicon source to obtain a reaction raw material B, wherein both as

silica, the second silicon source comprises 0.1-10 wt% of the total amount of the added silicon;

(4) crystallizing the reaction raw material B under stirring at 88-98°C and recovering the product.

9. The catalytic cracking catalyst according to any of the precedent claims, wherein the modified molecular sieve based on the crystal modification of kaolin contains rare earth, and the modified molecular sieve based on the crystal modification of kaolin has the content of rare earth as $RE_2O_3$ of 10-20 wt%.

10. The catalytic cracking catalyst according to any of the preceding claims, wherein the second molecular sieve is selected from faujasite, BEA structure molecular sieve, MFI structure molecular sieve, and mordenite; for example, the faujasite is one or more of HY, REY, REHY, USY, REUSY, DASY and REDASY; the binder is one or more of zirconia sol, silica sol, alumina sol, acidified pseudo-boehmite, and metal-modified pseudo-boehmite; the clay is one or more of kaolin, montmorillonite, diatomite, halloysite, metahalloysite, saponite, rectorite, sepiolite, attapulgite, hydrotalcite and bentonite; or

the catalytic cracking catalyst contains 10-70 wt% of the cracking active component, 1-20 wt% of a silica-alumina material, 10-60 wt% of a binder and 10-70 wt% of a clay; wherein the cracking active component comprises 25-100 wt% of a first Y-type molecular sieve and 0-75 wt% of a second molecular sieve; the first Y-type molecular sieve is a Y-type molecular sieve synthesized by in-situ crystallization having a sodium oxide content of less than 2 wt%; the silica-alumina material has an anhydrous chemical formula by weight of (0-1) $Na_2O$ • (15-50) $Al_2O_3$ • (85-50) $SiO_2$, a pore size of 10-100nm, a specific surface area of 150-600 m2/g, a pore volume of 0.5-1.5 mL/g, and a proportion of the pore volume of the pores having a pore diameter of greater than 10 nm to the total pore volume of 70-98%; or

the catalytic cracking catalyst comprises 10-60 wt% of the cracking active component, 20-60 wt% of a binder, and 10-70 wt% of a clay; wherein the binder comprises 1-50 wt% of a zirconia sol, and 50-99 wt% of a second binder, the zirconia sol comprises 0.5-20 wt% of $ZrO_2$, a stabilizer, an alkali cation and water, wherein the molar ratio of the stabilizer to Zr is 1-6, the pH value of the zirconia sol is 1-7; preferably, the cracking active component comprises 70-100 wt% of a Y-type molecular sieve and 0-30 wt% of a second molecular sieve; or

the catalytic cracking catalyst comprises 10-60 wt% of the cracking active component on the dry basis, 20-60 wt% of a binder on the dry basis, and 0-70 wt% of a second clay on the dry basis; wherein, based on the dry basis weight of the binder, on the dry basis, the binder comprises 1-50 wt% of a zirconia sol, 50-99 wt% of a phosphorus-aluminum inorganic binder and 0-45 wt% of a third binder; the cracking active component comprises a first molecular sieve and optionally a second molecular sieve, the first molecular sieve is a pentasil molecular sieve; on the dry basis, the first molecular sieve comprises 70 wt% or more of the cracking active component; preferably, the cracking active component contains 70-100 wt% of the first molecular sieve, and 0-30 wt% of the second molecular sieve; the zirconia sol comprises 0.5-20 wt% of $ZrO_2$, a stabilizer, an alkali cation and water, wherein the molar ratio of the stabilizer to Zr is 1-6, the pH value of the zirconia sol is 1-7; the

phosphorus-aluminum inorganic binder contains 15-40 wt% of an aluminum source component as $Al_2O_3$, 45-80 wt% of a phosphorus component (as $P_2O_5$) and 0-40 wt% of a first clay on the dry basis, and has a P/Al weight ratio of 1-6, a pH value of 1-3.5 and a solid content of 15-60 wt%; or

based on the dry basis weight of the catalytic cracking catalyst, the catalytic cracking catalyst comprises 10-70 wt% of the cracking active component, 1-20 wt% of a zirconia binder, 1-20 wt% of a silica sol binder, 0-50 wt% of an alumina-based binder and 10-70 wt% of a clay, the zirconia binder is a zirconia sol, the zirconia sol comprises 0.5-20 wt% of $ZrO_2$, a stabilizer, an alkali cation and water, wherein the molar ratio of the stabilizer to Zr is 1-6, the pH value of the zirconia sol is 1-7; or

the catalytic cracking catalyst comprises a molecular sieve, an alumina-based binder, a clay and a composite, based on the total amount of the catalyst, the content of the molecular sieve is 10-70 wt%, the content of the alumina-based binder is 5-30 wt%, the content of the clay is 10-70 wt%, the content of the composite is 6-50 wt%; the molecular sieve comprises a first molecular sieve and an optional second molecular sieve, based on the total amount of the molecular sieve, the content of the first molecular sieve is 70-100 wt%, the content of the second molecular sieve is 0-30 wt%; the composite comprises a zirconia sol and a silica-alumina material, the zirconia sol comprises 0.5-20 wt% of $ZrO_2$, a stabilizer, an alkali cation and water, wherein the molar ratio of the stabilizer to Zr is 1-6, the pH value of the zirconia sol is 1-7; the first molecular sieve is a Y-type molecular sieve, wherein the content of the rare earth element in the Y-type molecular sieve is 0-20 wt%; the second molecular sieve is a pentasil molecular sieve.

11. A process for preparing the catalytic cracking catalyst according to any of the precedent claims, comprising the following steps:

(1) preparing a modified molecular sieve based on the crystal modification of kaolin;

(2) making a clay, a cracking active component and a binder form a slurry; the cracking active component comprises the modified molecular sieve based on the crystal modification of kaolin and an optional second molecular sieve;

(3) spray-drying the slurry obtained in step (2), wherein the process for preparing the modified molecular sieve based on the crystal modification of kaolin comprises the following steps:

(1) converting kaolin into metakaolin by calcining and dehydrating at 500-900°C, and pulverizing it into metakaolin powder with a particle size of less than 10 microns;

(2) adding a directing agent, sodium silicate, a sodium hydroxide solution and water to the metakaolin powder to produce a reaction raw material A having a composition of (1-2.5) $Na_2O$ : $Al_2O_3$ : (4-9) $SiO_2$ : (40-100) $H_2O$, wherein the mass ratio of the directing agent to the metakaolin is 0.01-1.0;

(3) crystallizing the reaction raw material A at 88-98°C under stirring for 1-70 hours, then supplementing a second silicon source to obtain a reaction raw material B, wherein both as silica, the second silicon source comprises 0.1-10 wt% of the total amount of the added silicon;

(4) crystallizing the reaction raw material B under stirring at 88-98°C and recovering the product;

(5) ion-exchanging the recovered product.

12. The catalytic cracking catalyst according to claim 8 or the process for preparing the catalytic cracking catalyst according to claim 11, wherein the directing agent has a composition of (10-17) $SiO_2$ : (0.7-1.3) $Al_2O_3$ : (11-18) $Na_2O$ : (200-350) $H_2O$.

13. The preparation process according to claim 11, wherein the second silicon source has the sodium content as $Na_2O$ of< 1 wt%.

14. The process for preparing the catalytic cracking catalyst according to any of claims 11-13, wherein the second silicon source is a solid silica gel.

15. The process for preparing the catalytic cracking catalyst according to claim 14, wherein the solid silica gel has an average pore size of 1.5-2.0 nm, or the solid silica gel has an average pore size of 4.0-5.0 nm, or the solid silica gel has an average pore size of 10.0 nm or more, or the solid silica gel has an average pore size of 0.8 nm or less.

16. The process for preparing the catalytic cracking catalyst according to any of claims 11-15, wherein the second silicon source is a liquid silica gel.

17. The process for preparing the catalytic cracking catalyst according to claim 16, wherein the liquid silica gel has the $SiO_2$ content by weight of 1-30%.

18. The process for preparing the catalytic cracking catalyst according to any of claims 11-17, wherein both as silica, the second silicon source comprises 4-10 wt% of the total amount of the added silicon.

19. The process for preparing the catalytic cracking catalyst according to any of claims 11-18, wherein the ion-exchanging in step (5) is the ammonium ion exchanging and/or the rare earth ion exchanging.

20. The process for preparing the catalytic cracking catalyst according to any of claims 11-19, wherein the ion-exchanged product obtained from step (5) is further calcined.

21. The process for preparing the catalytic cracking catalyst according to any of claims 11-20, wherein the ion-exchanging comprises the rare earth ion exchanging, and the modified molecular sieve based on the crystal modification of kaolin obtained from step (5) has the rare earth content as $RE_2O_3$ of 10-20 wt%, and the sodium oxide content of less than 2 wt%.

22. A catalytic cracking process, which comprises a step of contacting a hydrocarbon oil with the catalytic cracking catalyst according to any of claims 1-10 to react.