Claims

1. A catalytic cracking agent, having an active component consisting of a phosphorus-modified molecular sieve and a non-phosphorus-modified molecular sieve or only consisting of a phosphorus-modified molecular sieve, characterized in that with an electron probe microanalysis (EPMA), the D value of phosphorus in the catalytic cracking agent is ≥65%, preferably ≥68%, provided that the active component consists of the phosphorus-modified molecular sieve and the non-phosphorus-modified molecular sieve,

on the dry basis, said catalytic cracking agent contains:

1-25 wt% of a non-phosphorus-modified molecular sieve;

5-50 wt% of a phosphorus-modified molecular sieve;

1-60 wt% of an inorganic binder; and

optionally, 0-60 wt% of a second clay, or

the D value of phosphorus in the catalytic cracking agent is ≥82%, preferably ≥84%, provided that the active component only consists of the phosphorus-modified molecular sieve, on the dry basis, said catalytic cracking agent contains:

5-75 wt% of a phosphorus-modified molecular sieve (free of non-phosphorus-modified molecular sieve);

1-40 wt% of an inorganic binder; and

optionally, 0-65 wt% of a second clay;

the D value is determined by randomly selecting any section of the catalytic cracking agent, selecting 20 small squares with a side length of 10nm on said section, and obtaining a phosphorus content within each small square through EPMA, taking the ratio of the lowest value of the 20 phosphorus contents to the average value of the 20 phosphorus contents as a d value of the section, and taking the average value of the d values of 5 sections with a spacing greater than 50nm between each other as the D value of the catalytic cracking agent.

2. The catalytic cracking agent according to any of the previous claims, wherein

said phosphorus-modified molecular sieve is a phosphorus-modified MFI-structured molecular sieve, for example a phosphorus-modified ZSM-5 molecular sieve;

said non-phosphorus-modified molecular sieve is a FAU-structured molecular sieve, for example, a Y-type molecular sieve.

3. The catalytic cracking agent according to any of claims 1-2, wherein said catalytic cracking agent is a catalytic cracking catalyst, having an active component consisting of a phosphorus-modified molecular sieve (for example a phosphorus-modified MFI-structured molecular sieve, such as a phosphorus-modified ZSM-5 molecular sieve) and a non-phosphorus-modified

molecular sieve (for example a FAU-structured molecular sieve, such as a Y-type molecular sieve), with the electron probe microanalysis (EPMA), the D-value of the phosphorus of the catalyst is≥65%, preferably≥68%.

4. The catalytic cracking agent according to any of claims 1-2, wherein said catalytic cracking agent is a catalytic cracking auxiliary, having an active component consisting of a phosphorus-modified molecular sieve (for example a phosphorus-modified MFI-structured molecular sieve, such as a phosphorus-modified ZSM-5 molecular sieve), with the electron probe microanalysis (EPMA), the D-value of phosphorus of the auxiliary is≥82%, preferably≥84%.

5. The catalytic cracking agent according to any of claims 1-3, wherein said non-phosphorus-modified molecular sieve is at least one of a PSRY molecular sieve, a rare earth-containing PSRY molecular sieve, an USY molecular sieve, a rare earth-containing USY molecular sieve, a REY molecular sieve, a REHY molecular sieve and an HY molecular sieve.

6. The catalytic cracking agent according to any of the previous claims, wherein

the inorganic binder comprises at least one of pseudo-boehmite, alumina sol, silica-alumina sol, water glass and phosphorus-aluminum inorganic binder;

preferably, the inorganic binder contains a phosphorus-aluminum inorganic binder,

more preferably, the inorganic binder is a phosphorus-aluminum inorganic binder.

7. The catalytic cracking agent according to any of the previous claims, wherein

the phosphorus-aluminum inorganic binder is a phosphorus aluminate binder and/or a first clay-containing phosphorus-aluminum inorganic binder.

8. The catalytic cracking agent according to claim 7, wherein

the first clay-containing phosphorus-aluminum inorganic binder is based on the dry basis, the first clay-containing phosphorus-aluminum inorganic binder contains 15-40 wt% of an aluminum component (as Al_2O_3), 45-80 wt% of a phosphorus component (as P_2O_5) and greater than 0 and not more than 40 wt% of a first clay, and the first clay-containing phosphorus-aluminum inorganic binder has a P/Al weight ratio of 1.0-6.0, a pH of 1-3.5, and a solid content of 15-60 wt%; the first clay comprises at least one of kaolin, sepiolite, attapulgite, rectorite, montmorillonite and diatomite.

9. The catalytic cracking agent according to any of the previous claims, wherein

the second clay is selected from at least one of kaolin, sepiolite, attapulgite, rectorite, montmorillonite, glagerite, halloysite, hydrotalcite, bentonite and diatomite.

10. The catalytic cracking agent according to claim 3, wherein

based on the total amount of said catalytic cracking catalyst, the inorganic binder comprises, on the dry basis, 3-39 wt% of a phosphorus-aluminum inorganic binder and 1-30 wt% of at least

one inorganic binder selected from pseudo-boehmite, alumina sol, silica alumina sol and water glass.

11. A process for preparing the catalytic cracking agent according to any of claims 1-10, which is characterized in that the process comprises:

(1) mixing the following components as raw material and slurrying the raw material, and shaping into shaped bodies:

a phosphorus-modified molecular sieve,

optionally, a non-phosphorus-modified molecular sieve,

an inorganic binder, and

optionally, a second clay;

(2) a hydrothermal calcining treatment is performed on the shaped bodies under an atmosphere condition in which an external pressure is applied and an aqueous solution is externally added;

said phosphorus-modified molecular sieve is obtained through contacting a molecular sieve to be phosphorus-modified having a temperature of 0-150°C with an aqueous solution of a phosphorus-containing compound having a temperature of 0-150°C by impregnation;

said hydrothermal calcining treatment is performed under a gauge pressure of 0.01-1.0MPa at a temperature of 200-800°C in an atmosphere of 100% water vapor or in an air atmosphere having a moisture content of at least 1%.

12. The process according to claim 11, wherein said molecular sieve to be phosphorus-modified is a micropore ZSM-5 molecular sieve or a hierarchical ZSM-5 molecular sieve;

preferably, the micropore ZSM-5 molecular sieve has a silica/alumina molar ratio of 15-1000, preferably 20-200;

preferably, the hierarchical ZSM-5 molecular sieve has a proportion of the mesopore volume relative to the total pore volume of greater than 10%, an average pore size of 2-20nm, and a silica/alumina molar ratio of 15-1000, preferably 20-200.

13. The process according to any of claims 11-12, wherein the molar ratio of the phosphorus-containing compound (as phosphorus) to the molecular sieve to be phosphorus-modified (as aluminum) is 0.01-2; preferably, 0.1-1.5; more preferably, 0.2-1.5.

14. The process according to any of claims 11-13, wherein the phosphorus-containing compound is selected from an organic phosphorus compound and/or an inorganic phosphorus compound;

preferably, the organic phosphorus compound is selected from trimethyl phosphate, triphenylphosphine, trimethyl phosphite, tetrabutylphosphonium bromide, tetrabutylphosphonium chloride, tetrabutylphosphonium hydroxide, triphenylethylphosphonium bromide, triphenylbutylphosphonium bromide, triphenylbenzylphosphonium bromide,

hexamethylphosphoric triamide, dibenzyl diethylphosphoramidite, and 1, 3-bis((triethyl-phosphaneyl)methyl)benzene;

preferably, the inorganic phosphorus compound is selected from phosphoric acid, ammonium hydrogen phosphate, diammonium hydrogen phosphate, ammonium phosphate, and boron phosphate.

15. The process according to any of claims 11-14, wherein in said molecular sieve to be phosphorus-modified, Na_2O<0.1wt%.

16. The process according to any of claims 11-15, the process further comprises: the inorganic binder is a phosphorus-aluminum inorganic binder, the phosphorus-aluminum inorganic binder is a phosphorus aluminate binder and/or a first clay-containing phosphorus-aluminum inorganic binder, the first clay-containing phosphorus-aluminum inorganic binder is prepared with the following steps: an alumina source, a first clay and water are slurried to disperse into a slurry having a solid content of 5-48 wt%; wherein said alumina source is aluminum hydroxide that can be peptized with an acid and/or alumina, relative to 15-40 parts by weight of the alumina source as Al_2O_3, the used amount of the first clay based on the dry weight is greater than 0 part by weight and not more than 40 parts by weight; a concentrated phosphoric acid is added to the slurry under stirring according to the weight ratio of P/Al = 1-6, and the resulting mixed slurry is reacted at 50-99°C for 15-90 minutes; wherein P in the P/Al is the weight of phosphorus as simple substance in the phosphoric acid, Al is the weight of aluminum as simple substance in the alumina source.

17. The process according to any of claims 11-16, wherein said shaping is pelleting by spray-drying.

18. The process according to any of claims 11-17, wherein

the conditions of said hydrothermal calcining treatment comprise:

gauge pressure: 0.1-0.8 MPa, preferably 0.3-0.6 MPa;

atmosphere: an atmosphere of 100% water vapor or an air atmosphere having a moisture content of at least 30%, preferably, an atmosphere of 100% water vapor or an air atmosphere having a moisture content of at least 60%;

temperature: 200-800°C, preferably 300-500°C;

the conditions of said contacting by impregnation comprise:

the weight ratio of water/molecular sieve: 0.5-1;

temperature: 50-150°C, preferably 70-130°C;

time: 0.5- 40 hours.

19. A process for catalytically cracking a hydrocarbon oil, which is characterized in that the

process comprises: the hydrocarbon oil is reacted by contacting the catalytic cracking agent according to any of claims 1-10 under a catalytic cracking condition.

20. The process for catalytically cracking the hydrocarbon oil according to claim 19, wherein the process comprises the hydrocarbon oil is reacted by contacting a mixture containing the catalytic cracking auxiliary according to claim 4 and the catalytic cracking catalyst according to claim 3 under a catalytic cracking condition; in the mixture, the content of the catalytic cracking auxiliary is 0.1-30 wt%.

21. The process for catalytically cracking the hydrocarbon oil according to any of claims 19-20, wherein

the catalytic cracking condition includes: the reaction temperature is 500-800°C; the hydrocarbon oil is one or more selected from crude oil, naphtha, gasoline, atmospheric residue, vacuum residue, atmospheric gas oil, vacuum gas oil, straight-run gas oil, propane light/heavy deasphalted oil, coker gas oil and coal liquefication product.