Claims

1. A phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve, which is characterized in that in its 27AlMAS-NMR, the ratio of peak area for the resonance signal having a chemical shift of 39±3ppm to peak area for the resonance signal having a chemical shift of 54ppm±3ppm is ≥ 1;
in its surface XPS elemental analysis, the value of n1/n2 is ≤ 0.1;
wherein n1 represents the mole number of phosphorus, n2 represents the total mole number of silicon and aluminum.

2. The phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 1, which is characterized in that the phosphorus-containing or phosphorus-modified molecular sieve is a phosphorus-containing hierarchical ZSM-5 molecular sieve.

3. The phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 1 or 2, which is characterized in that after the molecular sieve has undergone a hydrothermal aging under a condition of 800°C and 100% steam for 17h, in its NH3-TPD spectrum, for the desorption temperature of 200°C or higher, the proportion of the peak area for the strong acid center relative to the peak area for the total acid center is ≥ 40%.

4. The phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 1, which is characterized in that when both phosphorus and aluminum are on a molar basis, the ratio of the two is 0.01-2.

5. A process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 1-4, which is characterized in that the preparation process comprises: treating a ZSM-5 molecular sieve by contacting a phosphorus-containing compound, drying the treated ZSM-5 molecular sieve, hydrothermally calcining the dried ZSM-5 molecular sieve in an atmosphere condition where an external pressure is applied and water is externally added, and recovering the resulting product;
the contacting is to make an aqueous solution of the phosphorus-containing compound at a temperature of 0-150°C and the ZSM-5 molecular sieve at a temperature of 0-150°C in contact (by mixing) at substantially the same temperature for at least 0.1 hours through the immersion method, or,
the contacting is to vigorously mix and stir the phosphorus-containing compound, the ZSM-5 molecular sieve and water and then keep the mixture at 0-150°C for at least 0.1 hours;
with respect to the atmosphere condition, its gauge pressure is 0.01-1.0MPa and it contains 1-100% water vapor;
the ZSM-5 molecular sieve is an HZSM-5 molecular sieve or a hydrogen-type hierarchical ZSM-5 molecular sieve.

6. The process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 5, which is characterized in that the phosphorus-containing compound is selected from an organic phosphorus compound and/or an inorganic phosphorus compound.

7. The process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 5, which is characterized in that in the ZSM-5 molecular sieve, Na2O < 0.1wt%.

8. The process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 5, which is characterized in that the molar ratio of the phosphorus-containing compound as phosphorus to the ZSM-5 molecular sieve as aluminum is 0.01-2.

9. The process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 5, which is characterized in that with respect to the contacting, the weight ratio of water/molecular sieve is 0.5-1, and the contacting is performed at 50-150°C.

10. The process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to claim 5, which is characterized in that with respect to the atmosphere condition, its gauge pressure is 0.1-0.8 MPa, it contains 30-100% water vapor;

the hydrothermal calcining treatment is performed at 200-800°C.

11. A catalytic cracking auxiliary, which is characterized in that based on the dry basis of the catalytic cracking auxiliary, the catalytic cracking auxiliary contains 5-75 wt% of the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 1-4.

12. The catalytic cracking auxiliary according to claim 11, which is characterized in that based on the dry basis of the catalytic cracking auxiliary, it further contains 1-40 wt% of a binder and 0-65 wt% of a second clay.

13. The catalytic cracking auxiliary according to claim 12, which is characterized in that the binder includes or is a phosphorus-aluminum inorganic binder.

14. The catalytic cracking auxiliary according to claim 13, which is characterized in that the phosphorus-aluminum inorganic binder is a phosphorus-aluminum glue and/or a first clay-containing phosphorus-aluminum inorganic binder.

15. A process of preparing the catalytic cracking auxiliary according to any of claims 11-14, which is characterized in that the preparation process comprises a phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve, a binder and optionally a second clay are vigorously mixed and stirred with water and spray-dried to produce the catalytic cracking auxiliary,

wherein the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve is the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 1-4, or is prepared with the process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 5-10.

16. The process of preparing the catalytic cracking auxiliary according to claim 15, which is characterized in that the binder comprises a phosphorus-aluminum inorganic binder and/or other inorganic binders.

17. The process of preparing the catalytic cracking auxiliary according to claim 16, which is characterized in that the phosphorus-aluminum inorganic binder is a phosphorus-aluminum glue and/or a first clay-containing phosphorus-aluminum inorganic binder;

based on the dry basis weight of the first clay-containing phosphorus-aluminum inorganic binder, the first clay-containing phosphorus-aluminum inorganic binder contains 10-40 wt% of an aluminum component as Al_2O_3, 45-90 wt% of a phosphorus component as P_2O_5 and greater than 0 and not more than 40 wt% of a first clay on a dry basis, 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, smectite and diatomite;

the other inorganic binder comprises at least one of pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

18. The process of preparing the catalytic cracking auxiliary according to any of claims 15-17, which is characterized in that the second clay is at least one selected from kaolin, sepiolite, attapulgite, rectorite, smectite, giagerite, halloysite, hydrotalcite, bentonite and diatomite.

19. The process of preparing the catalytic cracking auxiliary according to claim 16, which is characterized in that based on the total weight of the catalytic cracking auxiliary, the binder comprises based on the dry weight, 3-39 wt% of the phosphorus-aluminum inorganic binder and based on the dry weight, 1-30 wt% of the other inorganic binder, the other inorganic binder comprises at least one of pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

20. The process of preparing the catalytic cracking auxiliary according to any of claims 15-19, which is characterized in that the process further comprises: the spray-dried product is subjected to a first calcining, and then washed, and optionally dried to produce the catalytic cracking auxiliary; wherein for the first calcining, the calcining temperature is 300-650°C, the calcining time is 0.5-8h; the drying temperature is 100-200°C, the drying time is 0.5-24h.

21. The process of preparing the catalytic cracking auxiliary according to claim 17, which is characterized in that,

the process further comprises: the first clay-containing phosphorus-aluminum inorganic binder is prepared with the following steps: an alumina source, the first clay and water are vigorously mixed and stirred to disperse into a slurry having a solid content of 5-48 wt%; wherein the alumina source is aluminum hydroxide and/or alumina that can be peptized by an acid, relative to 10-40 parts by weight of the alumina source (as Al2O3), 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 the simple substance in phosphoric acid, Al is the weight of aluminum as the simple substance in the alumina source.

22. A catalytic cracking catalyst, which is characterized in that based on the dry basis of the catalytic cracking catalyst, the catalytic cracking catalyst contains on a dry basis, 1-25 wt% of a Y zeolite, on a dry basis, 5-50 wt% of the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 1-4, on a dry basis, 1-60 wt% of an inorganic binder and optionally on a dry basis, 0-60 wt% of a second clay, the inorganic binder comprises a phosphorus-aluminum inorganic binder and/or other inorganic binder(s).

23. The catalytic cracking catalyst according to claim 22, which is characterized in that the Y zeolite comprises at least one of a PSRY-S zeolite, a rare earth-containing PSRY-S zeolite, a PSRY zeolite, a rare earth-containing PSRY zeolite, a USY zeolite, a rare earth-containing USY zeolite, a REY zeolite, a REHY zeolite and an HY zeolite.

24. A process of preparing the catalytic cracking catalyst according to any of claims 22-23, which is characterized in that the process comprises: a reaction material including a Y zeolite, a phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve and an inorganic binder is vigorously mixed and stirred with water and spray-dried, and optionally calcined to produce the catalytic cracking catalyst; wherein, a second clay is optionally added to the reaction material; on a dry basis, the used amount ratio by weight of the Y zeolite : the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve :

the inorganic binder : the second clay is (1-25):(5-50):(1-60):(0-60);
wherein the inorganic binder comprises a phosphorus-aluminum inorganic binder and/or other inorganic binder(s),
the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve is the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 1-4, or is prepared with the process of preparing the phosphorus-containing or phosphorus-modified ZSM-5 molecular sieve according to any of claims 5-10.

25. The process of preparing the catalytic cracking catalyst according to claim 24, which is characterized in that the phosphorus-aluminum inorganic binder is a phosphorus-aluminum glue and/or a first clay-containing phosphorus-aluminum inorganic binder;
based on the dry basis weight of the first clay-containing phosphorus-aluminum inorganic binder, the first clay-containing phosphorus-aluminum inorganic binder contains 10-40 wt% of an aluminum component as Al2O3, 45-90 wt% of a phosphorus component as P2O5 and greater than 0 and not more than 40 wt% of a first clay on a dry basis, 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, smectite and diatomite;
the other inorganic binder comprises at least one of pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

26. The process of preparing the catalytic cracking catalyst according to any of claims 24-25, which is characterized in that the second clay is at least one selected from kaolin, sepiolite, attapulgite, rectorite, smectite, giagerite, halloysite, hydrotalcite, bentonite and diatomite.

27. The process for preparing the catalytic cracking catalyst according to any of claims 24-26, which is characterized in that based on the dry basis of the catalytic cracking catalyst, the catalyst contains, based on the dry weight, 3-40 wt% of a phosphorus-aluminum inorganic binder and 1-30 wt% of other inorganic binder(s), the other inorganic binder comprises at least one of pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

28. The process for preparing the catalytic cracking catalyst according to claim 24, which is characterized in that the Y zeolite comprises at least one of a PSRY-S zeolite, a rare earth-containing PSRY-S zeolite, a PSRY zeolite, a rare earth-containing PSRY zeolite, a USY zeolite, a rare earth-containing USY zeolite, a REY zeolite, a REHY zeolite and an HY zeolite.

29. The process for preparing the catalytic cracking catalyst according to any of claims 24-28, which is characterized in that the process further comprises: the calcined product is washed and optionally dried to produce the catalytic cracking catalyst; wherein with respect to the first calcining, the calcining temperature is 300-650°C, the calcining time is 0.5-12h.

30. The process for preparing the catalytic cracking catalyst according to claim 25, which is characterized in that the process further comprises: the first clay-containing phosphorus-aluminum inorganic binder is prepared with the following steps: an alumina source, the first clay and water are vigorously mixed and stirred to disperse into a slurry having a solid content of 5-48 wt%; wherein the alumina source is aluminum hydroxide and/or alumina that can be peptized by an acid, relative to 10-40 parts by weight

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 the simple substance in phosphoric acid, Al is the weight of aluminum as the simple substance in the alumina source.

31. 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 auxiliary according to any of claims 11-14 under a catalytic cracking condition.

32. The process for catalytically cracking the hydrocarbon oil according to claim 31, which is characterized in that the process comprises: the hydrocarbon oil is reacted by contacting a catalyst mixture containing the catalytic cracking auxiliary and a catalytic cracking catalyst under a catalytic cracking condition; in the catalyst mixture, the content of the catalytic cracking auxiliary is 0.1-30 wt%.

33. The process for catalytically cracking the hydrocarbon oil according to any of claims 31-32, 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.

34. A method of application of the catalytic cracking catalyst according to any of claims 22-23.

35. The method of application according to claim 34, which comprises reacting the hydrocarbon oil by contacting the catalytic cracking catalyst under a catalytic cracking reaction condition, wherein the catalytic cracking reaction condition includes: the reaction temperature is 500-800°C.

36. The method of application according to claim 35, wherein 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.