Claims

1. A phosphorus-modified MFI-structured molecular sieve, which is characterized in that the molecular sieve has a K value, satisfying 70% ≤ K ≤ 90%;

wherein, K=P1/P2×100%,

P1 represents the mass content of phosphorus within a region having an area of 100 square nanometers and a vertical depth from 0 to 2 nm at any crystal surface of the crystal grain of a molecular sieve, as measured by the XPS method,

P2 represents the mass content of phosphorus within a region having an area of 100 square nanometers and a vertical depth from 5 to 10 nm at any crystal surface of the crystal grain of a molecular sieve, as measured by the EPMA method.

2. The molecular sieve according to claim 1, wherein the molar ratio of the phosphorus content as P2O5 to the alumina content is ≥ 0.01.

3. The molecular sieve according to claim 1 or 2, wherein the phosphorus-modified MFI-structured molecular sieve is a micropore ZSM-5 molecular sieve or a hierarchical ZSM-5 molecular sieve.

4. The molecular sieve according to claim 3, wherein the micropore ZSM-5 molecular sieve has a silica/alumina molar ratio of 15-1000.

5. The molecular sieve according to claim 3, wherein 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 diameter of 2-20nm, and a silica/alumina molar ratio of 15-1000.

6. A catalytic cracking auxiliary, based on the dry basis of the catalytic cracking auxiliary, the catalytic cracking auxiliary contains 5-75 wt% of the phosphorus-modified MFI-structured molecular sieve according to any of claims 1-5, 1-40 wt% of a binder and 0-65 wt% of a second clay.

7. The catalytic cracking auxiliary according to claim 6, wherein the binder comprises a phosphorus-aluminum inorganic binder and/or other inorganic binder(s),

the phosphorus-aluminum inorganic binder is a phosphorus-aluminum glue and/or a first clay-containing phosphorus-aluminum inorganic binder, the first clay-containing phosphorus-aluminum inorganic binder contains 10-40 wt%, of aluminum component (as Al2O3), 45-90 wt% of 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 second clay is selected from kaolin, sepiolite, attapulgite, rectorite, smectite, diatomite, giagerite, halloysite, hydrotalcite, and bentonite;

the other inorganic binder(s) is selected from pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

8. A catalytic cracking catalyst containing phosphorus-modified MFI-structured molecular sieve(s), based on the dry basis of the catalyst, the catalytic cracking catalyst contains 1-25 wt% of Y zeolite, 5-50 wt% of the phosphorus-modified MFI-structured molecular sieve according to any of claims 1-5, 1-60 wt% of an inorganic binder and optionally 0-60 wt% of a second clay.

9. The catalytic cracking catalyst according to claim 8, wherein the inorganic binder comprises a phosphorus-aluminum inorganic binder and/or other inorganic binder(s),

the phosphorus-aluminum inorganic binder is a phosphorus-aluminum glue and/or a first clay-containing phosphorus-aluminum inorganic binder, the first clay-containing phosphorus-aluminum inorganic binder contains 10-40 wt%, of aluminum component (as Al_2O_3), 45-90 wt% of 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 second clay is selected from kaolin, sepiolite, attapulgite, rectorite, smectite, diatomite, giagerite, halloysite, hydrotalcite, and bentonite;

the other inorganic binder(s) is selected from pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

10. The catalytic cracking catalyst according to claim 8, wherein the Y zeolite comprises at least one of PSRY zeolite, PSRY-S zeolite, rare earth-containing PSRY zeolite, rare earth-containing PSRY-S zeolite, USY zeolite, rare earth-containing USY zeolite, REY zeolite, REHY zeolite, and HY zeolite.

11. A process of preparing the phosphorus-modified MFI-structured molecular sieve according to any of claims 1-5, which is characterized in that the phosphorus-modified MFI-structured molecular sieve is obtained through an immersion method, comprising: the contact by mixing an aqueous solution of the phosphorus-containing compound at a temperature of 40-150°C and an MFI-structured molecular sieve at 40-150°C at substantially the same temperature for at least 0.1 hours, then the drying, and the calcining at 200-600°C, air or water vapor for at least 0.1 hours; or, vigorously mixing and stirring a phosphorus-containing compound, an MFI-structured molecular sieve and water, adjusting the temperature to 40-150°C, maintaining for at least 0.1 hours, then drying, and calcining at 200-600°C, air or water vapor for at least 0.1 hours.

12. The process of preparing the phosphorus-modified MFI-structured molecular sieve according to claim 11, wherein the phosphorus-containing compound is selected from organic phosphorous compounds and/or inorganic phosphorous compounds; the organic phosphorous 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, 1,3-bis((triethyl-phosphaneyl)methyl)benzene, the inorganic phosphorous compound is selected from phosphoric acid, ammonium hydrogen phosphate, diammonium hydrogen phosphate, ammonium phosphate, boron phosphate.

13. The process of preparing the phosphorus-modified MFI-structured molecular sieve according to claim 11 or 12, wherein the molar ratio of the phosphorus-containing compound as P_2O_5 to the MFI-structured molecular sieve as Al_2O_3 is 0.01-2.

14. The process of preparing the phosphorus-modified MFI-structured molecular sieve according to any of claims 11-13, wherein the phosphorus-containing compound is a mixture of boron phosphate and one or more selected from trimethyl phosphate, triphenylphosphine, trimethyl phosphite, phosphoric acid, ammonium hydrogen phosphate, diammonium hydrogen phosphate, and ammonium phosphate, in the mixture, boron phosphate comprises 10%-80% by weight.

15. The process of preparing the phosphorus-modified MFI-structured molecular sieve according to any of claims 11-14, wherein the weight ratio of water/molecular sieve in the contacting is 0.5-1, and the contacting time is 0.5-40 hours.

16. The process of preparing the phosphorus-modified MFI-structured molecular sieve according to any of claims 11-15, wherein the calcining is performed at 450-550°C, under the water vapor atmosphere.

17. A process of preparing the catalytic cracking auxiliary according to claim 6 or 7, wherein the process comprises, a phosphorus-modified MFI-structured molecular sieve, a binder, and optionally a second clay are vigorously mixed and stirred with water, and then spray-dried to produce the catalytic cracking auxiliary.

18. The process of preparing the catalytic cracking auxiliary according to claim 17, wherein the binder includes or is a phosphorus-aluminum inorganic binder.

19. The process of preparing the catalytic cracking auxiliary according to claim 18, wherein 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 on a dry basis, 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, smectite and diatomite.

20. The process of preparing the catalytic cracking auxiliary according to any of claims 17-19, wherein the second clay is at least one selected from kaolin, sepiolite, attapulgite, rectorite, smectite, giagerite, halloysite, hydrotalcite, bentonite, and diatomite.

21. The process of preparing the catalytic cracking auxiliary according to claim 18, wherein 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 other inorganic binder(s).

22. The process of preparing the catalytic cracking auxiliary according to claim 21, wherein the other inorganic binder may also include at least one of pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

23. The process of preparing the catalytic cracking auxiliary according to any of claims 17-22, wherein 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.

24. The process of preparing the catalytic cracking auxiliary according to claim 19, wherein 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.

25. A process of preparing the catalytic cracking catalyst according to any of claims 8-10, wherein the process comprises a Y zeolite, the phosphorus-modified MFI-structured molecular sieve according to any of the previous claims, an inorganic binder and optionally a second clay are vigorously mixed and stirred with water, and spray-dried to produce the catalytic cracking catalyst.

26. The process of preparing the catalytic cracking catalyst according to claim 25, wherein the inorganic binder includes or is a phosphorus-aluminum inorganic binder.

27. The process of preparing the catalytic cracking catalyst according to claim 26, wherein 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 aluminum component (as Al2O3), 45-90 wt% of 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.

28. The process of preparing the catalytic cracking catalyst according to claim 25, wherein the second clay is at least one selected from kaolin, sepiolite, attapulgite, rectorite, smectite, giagerite, halloysite, hydrotalcite, bentonite, and diatomite.

29. The process of preparing the catalytic cracking catalyst according to claim 26, wherein based on the catalytic cracking catalyst, the inorganic binder comprises on the dry basis 3-39 wt% of the phosphorus-aluminum inorganic binder and on the dry basis 1-30 wt% of other inorganic binder, the other inorganic binder is at least one selected from pseudo-boehmite, alumina sol, silica-alumina sol, and water glass.

30. The process of preparing the catalytic cracking catalyst according to any of claims 25-29, wherein 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 catalyst; 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.

31. The process of preparing the catalytic cracking catalyst according to claim 27, wherein 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.

32. The catalytic cracking auxiliary that is obtained with the process of preparing the catalytic cracking auxiliary according to any of claims 17-24.

33. The catalytic cracking catalyst that is obtained with the process of preparing the catalytic cracking catalyst according to any of claims 25-31.

34. 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 claim 6, 7 or 32 or the catalytic cracking catalyst according to any of claims 8-10, 33 under a catalytic cracking condition.

35. The process for catalytically cracking the hydrocarbon oil according to claim 34, wherein the process comprises: the hydrocarbon oil is reacted by contacting a catalyst mixture containing the catalytic cracking auxiliary according to any of the previous claims and a catalytic cracking catalyst under the catalytic cracking condition; in the catalyst mixture, the content of the catalytic cracking auxiliary is 0.1-30 wt%.

36. The process for catalytically cracking the hydrocarbon oil according to claim 34 or 35, 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.