Claims

1. ~~A~~ An apparatus for modifying a molecular sieve-based catalyst ~~modification apparatus~~ for preparing p-xylene and olefin from methanol, benzene and/or toluene, comprising: a feed unit (1), a modification unit (2) and a cooling unit (3) connected in sequence;

wherein the feed unit comprises a catalyst feed unit (11) and a modifier feed unit (12), a catalyst and a modifier are introduced into the modification unit (2) respectively by the catalyst feed unit and the modifier feed unit and are discharged from the modification unit after sufficient reaction in modification unit, and then enter the cooling unit (3) for cooling~~.~~;

~~2. The molecular sieve-based catalyst modification apparatus according to claim 1,~~

wherein the catalyst feed unit (11) comprises a feed bin (111), a conveyor (112), and the conveyor (112) is connected to the modification unit inlet (22) of the modification unit (2);

the modifier feed unit (12) includes a modifier metering pump (121) and a preheater (122), and an outlet of the preheater (122) is connected to the modification unit feed distributor (24) of the modification unit (2)~~.~~;

~~3. The molecular sieve-based catalyst modification apparatus according to claim 2,~~

wherein an inert gas pipe (123) and an air pipe (124) are disposed between the modifier metering pump (121) and the preheater (122)~~.~~;

~~4. The molecular sieve-based catalyst modification apparatus according to claim 1,~~

wherein the modification unit (2) comprises a modification unit reactor (21), a modification unit inlet (22), a modification unit outlet (23), a modification unit feed distributor (24), a heater (25) and a modification unit exhaust port (26);

wherein the modification unit reactor (21) is a fluidized bed reactor, the modification unit inlet (22) is disposed at a middle portion of the modification unit reactor (21); and the modification unit outlet (23) is disposed at the bottom of the side wall of the modification unit reactor (21); the modification unit feed distributor (24) is disposed at the bottom of the modification unit reactor (21); the heater (25) is disposed inside the modification unit reactor (21), and located below the modification unit inlet (22); the exhaust port (26) is disposed at the top of the modification unit reactor (21)~~.~~;

~~5. The molecular sieve-based catalyst modification apparatus according to claim 4,~~

wherein a modification unit gas-solid separation device (27) is disposed below the exhaust port (26) inside the reactor (21)~~.~~;

~~6. The molecular sieve-based catalyst modification apparatus according to claim 1,~~

wherein the cooling unit (3) includes a cooling unit reactor (31), a cooling unit inlet (32), a cooling unit outlet (33), a cooling unit feed distributor (34), a heat extractor (35), and a cooling unit exhaust port (36);

wherein the cooling unit reactor is a fluidized bed reactor, the cooling unit inlet (32) is disposed at a middle portion of the cooling unit reactor (31); and the cooling unit outlet (33) is disposed at the bottom of the side wall of the cooling unit reactor (31); the ~~modification~~ cooling unit feed distributor (34) is disposed at a bottom of the cooling unit reactor (31); the heat extractor (35) is

disposed inside the cooling unit reactor (31), and is located below the modification unit inlet (32); the cooling unit exhaust port (36) is disposed at the top of the cooling unit reactor (31).;

7. The molecular sieve-based catalyst modification apparatus according to claim 6,

wherein a cooling unit gas-solid separation device (37) is disposed below the cooling unit exhaust port (36) inside the cooling unit reactor (31).;

wherein the modifier is a mixture of a phosphorus reagent, a silylating reagent, and toluene, and the phosphorus reagent is trimethoxyphosphine, the silylating reagent is tetramethyl silicate or tetraethyl silicate, and the molecular sieve-based catalyst is HZSM-11 or HZSM-5 molecular sieve-based catalyst.

8.2. The apparatus for modifying a molecular sieve-based catalyst modification apparatus for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 4 1, wherein the modification unit feed distributor (24) is any one selected from a powder metallurgy sintered plate distributor, a multi-tube distributor, and a hood distributor with wind caps.

9.3. The apparatus for modifying a molecular sieve-based catalyst modification apparatus for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 4 1, wherein the heater (25) is at least one selected from an electric heater and a high temperature gas heater.

10.4. The apparatus for modifying a molecular sieve-based catalyst modification apparatus for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 5 1, wherein the modification unit gas-solid separator (27) is at least one selected from a cyclone separator and a filter.

11.5. The apparatus for modifying a molecular sieve-based catalyst modification apparatus for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 6 1, wherein the cooling unit feed distributor (34) is any one selected from a powder metallurgy sintered plate distributor, a multi-tube distributor, and a hood distributor with wind caps.

12. The molecular sieve-based catalyst modification apparatus according to claim 6, wherein the heat extractor (35) is at least one selected from a cooling water heat extractor and a cooling air heat extractor.

13.6. The apparatus for modifying a molecular sieve-based catalyst modification apparatus for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 7 1, wherein the modification cooling unit gas-solid separator (37) is at least one selected from a cyclone separator and a filter.

14.7. A method for modifying molecular sieve-based catalyst for preparing p-xylene and olefin from methanol, benzene and/or toluene, wherein at least one of the apparatus for modifying a molecular sieve-based catalyst modification apparatuses for preparing p-xylene and olefin from methanol, benzene and/or toluene according to anyone of claim 1 to claim 13 is used in the method;

comprising: introducing a catalyst and a modifier into the modification unit (2) respectively through the feed unit (1), wherein the catalyst is modified by the modifier in the modification unit (2), and then discharged to the cooling unit (3) to cool until the temperature is lower than 50 ºC, and then the cooled modified catalyst is transferred to any storage device.;

15. The method for modifying molecular sieve-based catalyst according to claim 14,

wherein the introduced catalyst is subjected to an activation treatment in the modification unit (2) before the modification, and the activation treatment specifically comprises:

a) introducing air into the modification unit through the modifier feed unit;

b) heating the catalyst to an activation treatment temperature, wherein the activation treatment temperature is in a range of 400 ºC to 650 ºC;

c) activating the catalyst for an activation time in a range of 0.5 h to 3 h at an activation treatment temperature.

16.8. The method for modifying molecular sieve-based catalyst for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 15 7, wherein the air in the modification unit (2) is replaced with an inert gas after finishing the activation, and the replacement time is greater than 5 min;

Preferably, when the gas phase oxygen concentration is less than 1 vol.%, the replacement is completed.

17. The method for modifying molecular sieve-based catalyst according to claim 16, wherein a modifier is introduced after finishing the replacement, which is heated and vaporized before being introduced and carried into the modification unit (2) by inert gas.

18.9. The method for modifying molecular sieve-based catalyst for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim 14 7, wherein the modification is carried out under an inert gas atmosphere at a temperature in a range of 150 ºC to 600 ºC with a modification time in a range of 0 h to 10 h.

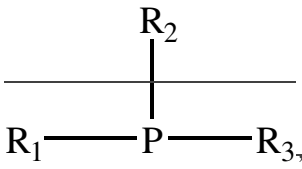
19. The method for modifying molecular sieve-based catalyst according to claim 14, wherein the modified catalyst is first calcined after finishing the modification and then discharged to the cooling unit.

20. The method for modifying molecular sieve-based catalyst according to claim 19, wherein the calcination is carried out under an air atmosphere at a calcination temperature in a range of 400 ºC to 700 ºC with a calcination time in a range of 1 h to 6 h.

21. The method for modifying molecular sieve-based catalyst according to anyone of claim 14 to claim 20, wherein the molecular sieve-based catalyst is any one selected from HZSM-5 and HZSM-11 molecular sieve-based catalysts.

22. The method for modifying molecular sieve based catalyst according to claim 14, wherein the modifier is at least one selected from a phosphorus reagent, a silylating reagent, and toluene.

~~23. The method for modifying molecular sieve-based catalyst according to claim 22, wherein the phosphorus reagent is at least one selected from the compounds with the formula I:~~



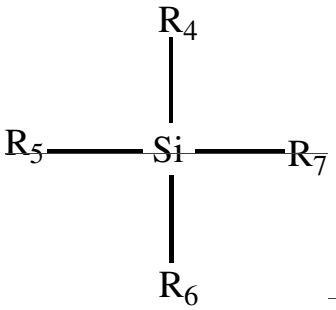
~~, formula I, wherein~~

~~R_1, R_2, R_3 is independently selected from C_1-C_{10} alkyl or C_1-C_{10} alkoxy.~~

~~24. The method for modifying molecular sieve-based catalyst according to claim 23, wherein at least one of R_1, R_2, R_3 in formula I is selected from C_1-C_{10} alkoxy.~~

~~25. The method for modifying molecular sieve-based catalyst according to claim 23, wherein the phosphorus reagent is at least one selected from trimethoxyphosphine, triethoxyphosphine, tripropoxyphosphine, tributoxyphosphine, and methyldiethoxyphosphine.~~

~~26. The method for modifying molecular sieve-based catalyst according to claim 22, wherein the silylating reagent is at least one selected from the compounds with the formula II:~~



~~, formula II,~~

~~wherein R_4, R_5, R_6, R_7 are independently selected from C_1-C_{10} alkyl or C_1-C_{10} alkoxy.~~

~~27. The method for modifying molecular sieve-based catalyst according to claim 26, wherein at least one of R_4, R_5, R_6, R_7 in formula II is selected from C_1-C_{10} alkoxy.~~

~~28. The method for modifying molecular sieve-based catalyst according to claim 22, wherein the silylating reagent is at least one selected from tetramethyl silicate, tetraethyl silicate, tetrapropyl silicate, and tetrabutyl silicate.~~

~~29.~~10. The method for modifying molecular sieve-based catalyst for preparing p-xylene and olefin from methanol, benzene and/or toluene according to claim ~~22~~ 7, wherein the modifier has a phosphorus reagent content in a range of 1% to 10% by weight based on the total mass of the mixture~~.~~;

~~30. The method for modifying molecular sieve-based catalyst according to claim 22,~~

wherein the modifier has a silylating reagent content in a range of 1% to 40% by weight based on the total mass of the mixture.