CLAIMS

1. A process for preparing a naphtha aromatization catalyst comprising:

a) detemplating a template agent-containing germanium zeolite material under a time/temperature protocol sufficient to removal all or substantially all of the templating agent in the germanium zeolite material, where the time/temperature protocol includes a detemplating time period between 1 hour and 12 hours at a detemplating temperature between 400°C and 600°C;

or

b) adding between 20 wt.% to 60 wt.% of a binder composition to a template agent-containing germanium zeolite material to form a bound germanium zeolite material and forming the bound templated germanium zeolite material to into a shaped body of germanium zeolite material and calcining the shaped body of germanium zeolite material for a time period between 1 hour and 12 hours at a calcining temperature between 400°C and 600°C;

and thereafter, performing steps (i) and (ii) in any order:

(i) ion-exchanging the detemplated germanium zeolite material with cesium (Cs) containing solution to form a non-acidic or substantially non-acidic Cs exchanged germanium zeolite material, where said step of ion-exchanging is performed at a temperature between room temperature and 100°C;

(ii) impregnating the detemplated germanium zeolite material with platinum (Pt) to form a Pt impregnated germanium zeolite material; and

heating the detemplated germanium zeolite material immediately after step (i) according to a heating time/temperature protocol, where the heating time/temperature protocol includes a heating time between 1 hour and 12 hours at a temperature from 250°C to 300°C, and heating the detemplated germanium zeolite material immediately after step (ii) according to a heating time/temperature protocol, where the heating time/temperature protocol includes a heating time between 1 hour and 12 hours at a temperature ranging from 250°C to less than 500°C;

or

after performing both steps (i) and (ii), heating the detemplated germanium zeolite material according to a heating time/temperature protocol, where the heating

time/temperature protocol includes a heating time between 1 hour and 12 hours at a temperature ranging from 250°C to less than 500°C;

with the proviso that if the process is performed using step (a), the following additional steps must be performed:

(1) adding between 20 wt.% to 60 wt.% of a binder composition to form a bound detemplated germanium zeolite material and forming bound germanium zeolite materials into shaped body; and,

(2) calcining the bound detemplated germanium zeolite material from step (1) according to a calcining time/temperature protocol including a calcining time period between 1 hour and 12 hours at a calcining temperature less than or equal to 500°C.

2. The process of Claim 1, wherein the impregnating step is a wet-incipient impregnating step.

3. The process of any of Claims 1 – 2, further comprising repeating the ion-exchanging step at least once.

4. The process of any of Claims 1 – 3, wherein the extruded germanium zeolite materials are 1/8-inch extrudates.

5. The process of any of Claims 1 – 4, wherein the detemplating temperature is between 425°C and 600°C; the heating temperature for said heating step immediately after step (i) is between 250°C and 350°C; the heating temperature for said heating step immediately after step (ii) is less than or equal to 450°C, and said step of calcining in step (2) is performed at a temperature of less than or equal to 450°C.

6. The process of any of Claims 1 – 5, wherein the detemplating temperature is between 450°C and 600°C; the heating temperature for said heating step immediately after step (i) is between 250°C and 300°C; the heating temperature for said heating step immediately after step (ii) is less than or equal to 400°C, and said step of calcining in step (2) is performed at a temperature of less than or equal to 400°C.

7. The process of any of Claims 1 – 6, wherein the detemplating temperature is between 475°C and 600°C; the heating temperature for said heating step immediately after step (i) is between 275°C and 325°C; the heating temperature for said heating step immediately after step (ii) is less than or equal to 350°C, and said step of calcining in step (2) is performed at a temperature of less than or equal to 350°C.

8. The process of any of Claims 1 – 7, wherein the detemplating temperature is between 500°C and 600°C; the heating temperature for said heating step immediately after step (i) between 275°C and 300°C; the heating temperature for said heating step immediately after step (ii) is less than or equal to 300°C, and said step of calcining in step (2) is performed at a temperature of less than or equal to 300°C.

9. The process of any of Claims 1 – 8, wherein the binder comprises a solid binder and a colloidal binder having particles between 10 nm and 30 nm.

10. The process of any of Claims 1 – 8, wherein the binder comprises a solid binder and a mixture of colloidal binders including at least 10 wt.% of a first colloidal binder having particles between 10 nm and 30 nm and the remainder being a second colloidal binder having particles less than 10 nm.

11. The process of any of Claims 1 – 10, wherein the solid binder is selected from the group consisting of silica, alumina, magnesia, calcium oxide, and any combination thereof.

12. The of any of Claims 1 – 11, wherein the first colloidal binder has a particle size between 10 nm and 25 nm.

13. The process of any of Claims 1 – 12, wherein the first colloidal binder has a surface area less than or equal to 250 m^2/g.

14. The process of any of Claims 1 – 13, wherein the first colloidal binder has a surface area between 250 m^2/g and 100 m^2/g.

15. The process of any of Claims 1 – 14, wherein:

the amount of germanium is adjusted such that the final catalyst has germanium in a range of from 0.1 wt.% to 10wt.% based on the total catalyst weight;

the amount of platinum is adjusted such that the final catalyst has platinum in a range of from 0.05 wt.% to 3 wt.% based on the total catalyst weight; and

the amount of cesium is adjusted such that the final catalyst has cesium in a range of from 2 wt.% to 8 wt.% based on the total catalyst weight.

16. The process of any of Claims 1 – 15, wherein the exchange metal is an alkali metal selected from the group consisting of Na, K, Rb, Cs; an alkaline earth metal selected from the group consisting of Mg, Ca, Sr, Ba, and any combination thereof, and, further wherein the noble metal is selected from the group consisting of Pt, Pd, Ir, Rh, Ru, and any combination thereof.

17. The process of any of Claims 1 – 16, wherein the germanium zeolite material is a medium pore zeolite having an average pore size in the range from 5Å to 7Å, has a Si/Al_2 atomic ratio of 40-500 and has a germanium content in the range from 0.1 wt.% to 10wt.%.

18. The process of any of Claims 1 – 17, wherein the germanium zeolite material comprises a zeolite having a structure selected from the group consisting of MTW, FER, MEL, TON, MRE, MWW, MFI, BEA, MOR, LTL and MTT.

19. The process of any of Claims 1 – 18, wherein the germanium zeolite material comprises germanium ZSM-5 material.

20. A process for aromatizing a light naphtha hydrocarbon feed comprising:

contacting a light naphtha feed comprising C_6-C_{12} alkanes with a catalyst prepared by the process of any of Claims 1 – 19; and

thereafter, recovering a hydrocarbon product comprising aromatics hydrocarbons.

21. The process of Claim 20, wherein the contacting between the feed and the catalyst is at a liquid hourly space velocity in the range between 0.1 h^{-1} and 100 h^{-1}, at a temperature higher than 450°C, at a pressure in the range between 1 psia and 315 psia, and the feed comprises at least 30% C_6-C_{10} alkanes.

22. The process of any of Claims 20 – 21, wherein the contacting between the feed and the catalyst is at a liquid hourly space velocity in a range between 0.1 h^{-1} and 100 h^{-1}, at a temperature in a range between 450°C and 550°C, at a pressure in a range between 5 psia and 315 psia, and the feed comprises at least 50% C_6-C_{10} alkanes.

23. The process of any of Claims 20 – 22, wherein the feed comprises sulfur at levels up to 1000 ppm.

CLAIMS

1. A process for preparing a naphtha aromatization catalyst comprising:

preparing a detemplated germanium ZSM-5 material from a germanium ZSM-5 material containing a templating agent by a) or b)

a) detemplating germanium ZSM-5 material containing the templating agent under a detemplating time/temperature protocol sufficient to remove all or substantially all of the templating agent in the germanium ZSM-5 material to form the detemplated germanium ZSM-5 material, where the detemplating time/temperature protocol includes a detemplating time period between 1 hour and 12 hours at a detemplating temperature between 400°C and 600°C; or

b) adding between 20 wt.% to 60 wt.% of a binder composition to the germanium ZSM-5 material containing the templating agent to form a bound germanium ZSM-5 material, shaping the bound germanium ZSM-5 material, and calcining the bound germanium ZSM-5 material for a time period between 1 hour and12 hours at a calcining temperature between 400°C and 600°C to form the detemplated germanium ZSM-5 material; and thereafter,

performing steps (i) and (ii) in any order

(i) ion-exchanging the detemplated germanium ZSM-5 material with a cesium (Cs) containing solution, where said step of ion-exchanging is performed at an ion-exchanging temperature between room temperature and 100°C;

(ii) impregnating the detemplated germanium ZSM-5 material with platinum (Pt); and

forming the naphtha aromatization catalyst by heating according to I) and II)

I) heating the detemplated germanium ZSM-5 material immediately after step (i) according to a cesium heating time/temperature protocol, where the cesium heating time/temperature protocol includes a cesium heating time between 1 hour and 12 hours at a cesium heating temperature from 250°C to 300°C, and heating the detemplated germanium ZSM-5 material immediately after step (ii) according to a platinum heating time/temperature protocol, where the platinum heating time/temperature protocol includes a platinum heating time between 1 hour and 12 hours at a platinum heating temperature ranging from 250°C to less than 500°C to form the naphtha aromatization catalyst; or

II) after performing both steps (i) and (ii), heating the detemplated germanium ZSM-5 material according to a cesium-platinum heating time/temperature protocol to form the naphtha aromatization catalyst, where the cesium-platinum heating time/temperature protocol includes a cesium-platinum heating time between 1 hour and 12 hours at a cesium-platinum temperature ranging from 250°C to less than 500°C;

with the proviso that if the process is performed using step (a), the following additional steps (1) and (2) must be performed after step (a)

(1) adding between 20 wt.% to 60 wt.% of the binder composition to the detemplated germanium ZSM-5 material and shaping the detemplated germanium ZSM-5 material; and,

(2) calcining the detemplated germanium ZSM-5 material from step (1) according to a bound calcining time/temperature protocol including a bound calcining time period between 1 hour and 12 hours at a bound calcining temperature less than or equal to 500°C; and

wherein the binder composition comprises

a solid binder and a colloidal binder having particles between 10 nm and 30 nm, or

the solid binder and a mixture of colloidal binders including at least 10 wt.% of a first colloidal binder having particles between 10 nm and 30 nm and the remainder being a second colloidal binder having particles less than 10 nm.

2. The process of claim 1, wherein the impregnating is a wet-incipient impregnating step.

3. The process of claim 1, further comprising repeating the ion- exchanging at least once.

4. The process of claim 1, wherein the shaping forms a shaped body, and wherein the shaped body comprises 1/8-inch extrudates.

5. The process of claim 1, wherein the detemplating temperature is between 425°C and 600°C; the cesium heating temperature is between 250°C and 350°C; the platinum heating

temperature is less than or equal to 450°C, and the bound calcining temperature is less than or equal to 450°C.

6. The process of claim 1, wherein the detemplating temperature is between 450°C and 600°C; the cesium heating temperature is between 250°C and 300°C; the platinum heating temperature is less than or equal to 400°C, and the bound calcining temperature is less than or equal to 400°C.

7. The process of claim 1, wherein the detemplating temperature is between 475°C and 600°C; the cesium heating temperature is between 275°C and 325°C; the platinum heating temperature is less than or equal to 350°C, and the bound calcining temperature is less than or equal to 350°C.

8. The process of claim 1, wherein the detemplating temperature is between 500°C and 600°C; the cesium heating temperature is between 275°C and 300°C; the platinum heating temperature is less than or equal to 300°C, and the bound calcining temperature is less than or equal to 300°C.

9. The process of claim 1, wherein the solid binder is selected from silica, alumina, magnesia, calcium oxide, and any combination thereof.

10. The process of claim 1, wherein the first colloidal binder has a particle size between 10 nm and 25 nm.

11. The process of claim 1, wherein the first colloidal binder has a surface area less than or equal to 250 m^2/g.

12. The process of claim 1, wherein the first colloidal binder has a surface area between 250 m^2/g and 100 m^2/g.

13. The process of claim 1, wherein the naphtha aromatization catalyst comprises 0.1 wt.% to 10wt.% germanium; 0.05 wt.% to 3 wt.% platinum; and 2 wt.% to 8 wt.% cesium; based on a total weight of the naphtha aromatization catalyst

14. A process for preparing a naphtha aromatization catalyst comprising:

preparing a detemplated germanium zeolite material from a germanium zeolite material containing a templating agent by one of a) or b)

a) detemplating the germanium zeolite material containing the templating agent under a detemplating time/temperature protocol sufficient to remove all or substantially all of the templating agent in the germanium zeolite material to form the detemplated germanium zeolite material, where the detemplating time/temperature protocol includes a detemplating time period between 1 hour and 12 hours at a detemplating temperature between 400°C and 600°C; or

b) adding between 20 wt.% to 60 wt.% of a binder composition to the germanium zeolite material containing the templating agent to form a bound germanium zeolite material, shaping the bound templated germanium zeolite material, and calcining the bound germanium zeolite for a time period between 1 hour and12 hours at a calcining temperature between 400°C and 600°C to form the detemplated germanium zeolite material; and thereafter,

performing steps (i) and (ii) in any order

(i) ion-exchanging the detemplated germanium zeolite material with an exchange metal containing solution , where said step of ion-exchanging is performed at an ion-exchanging temperature between room temperature and 100°C;

(ii) impregnating the detemplated germanium zeolite material with a noble metal; and

forming the naphtha aromatization catalyst by heating according to I) or II)

I) heating the detemplated germanium zeolite material immediately after step (i) according to an exchanged heating time/temperature protocol, where the exchanged heating time/temperature protocol includes an exchange heating time between 1 hour and 12 hours at an exchange temperature from 250°C to 300°C, and heating the detemplated germanium zeolite material immediately after step (ii) according to an impregnated heating time/temperature protocol, where the impregnated heating time/temperature protocol includes an impregnated

heating time between 1 hour and 12 hours at an impregnated temperature ranging from 250°C to less than 500°C to form the naphtha aromatization catalyst; or

II) after performing both steps (i) and (ii), heating the detemplated germanium zeolite material according to a combined heating time/temperature protocol to form the naphtha aromatization catalyst, where the combined heating time/temperature protocol includes a combined heating time between 1 hour and 12 hours at a combined temperature ranging from 250°C to less than 500°C;

with the proviso that if the process is performed using step (a), the following additional steps (1) and (2) must be performed after step (a)

(1) adding between 20 wt.% to 60 wt.% of the binder composition to form detemplated germanium zeolite material and shaping the detemplated germanium zeolite materials; and

(2) calcining the detemplated germanium zeolite material from step (1) according to a bound calcining time/temperature protocol including a bound calcining time period between 1 hour and 12 hours at a bound calcining temperature less than or equal to 500°C;

wherein the exchange metal is an alkali metal selected from of Na, K, Rb, Cs and any combination thereof; and alkaline earth metal selected from Mg, Ca, Sr, Ba, and any combination thereof, and, further wherein the noble metal is selected from Pt, Pd, Ir, Rh, Ru, and any combination thereof;

wherein the germanium zeolite material comprises a zeolite having a structure selected from MTW, FER, MEL, TON, MRE, MWW, ZSM-5, BEA, MOR, LTL, and MTT; and

wherein the binder composition comprises

a solid binder and a colloidal binder having particles between 10 nm and 30 nm, or

the solid binder and a mixture of colloidal binders including at least 10 wt.% of a first colloidal binder having particles between 10 nm and 30 nm and the remainder being a second colloidal binder having particles less than 10 nm.

15. The process of claim 14, wherein the impregnating is a wet-incipient impregnating step.

16. The process of claim 14, wherein the solid binder is selected from silica, alumina, magnesia, calcium oxide, and any combination thereof.

17. The process of claim 14, wherein the germanium zeolite material is a medium pore zeolite having an average pore size in the range from 5Å to 7Å, has a Si/Al_2 atomic ratio of 40-500 and has a germanium content in the range from 0.1 wt.% to 10 wt.%.