CLAIMS

We claim:

1. A method for regenerating a spent catalyst comprising a transition metal and a catalyst support, the method comprising:

(1) contacting the spent catalyst with a chlorine-containing stream comprising a chlorine-containing compound to produce a chlorinated spent catalyst;

(2) contacting the chlorinated spent catalyst with a decoking gas stream comprising oxygen to produce a de-coked catalyst; and

(3) contacting the de-coked catalyst with a fluorine-containing solution comprising a fluorine-containing compound to produce a fluorinated catalyst.

2. The method of claim 1, wherein step (1) is conducted at a chlorination temperature in a range from 20 °C to 300 °C.

3. The method of claims 1 – 2, wherein an amount of the chlorine-containing compound in the chlorine-containing stream provides from 0.5 to 7 vol. % of chlorine (Cl) in the chlorine-containing stream.

4. The method of claim 3, wherein the chlorine-containing stream contains less than 100 ppmw of oxygen-containing compounds.

5. The method of claims 1 – 4, wherein the chlorine-containing compound comprises Cl_2, carbon tetrachloride, tetrachloroethylene, or any combination thereof.

6. The method of claims 1 – 5, wherein the chlorine-containing stream comprises Cl_2 and nitrogen.

7. The method of claims 1 – 6, further comprising a chlorine purging step prior to step (2), the chlorine purging step comprising contacting the chlorinated spent catalyst with a chlorine purging stream comprising an inert gas.

8. The method of claim 7, wherein the chlorine purging stream contains less than 100 ppmw of oxygen-containing compounds.

9. The method of claims 7 or 8, wherein the chlorine purging stream contains less than 100 ppmw of halogen-containing compounds.

10. The method of claims 7 – 9, wherein the chlorine purging step is conducted for a time period sufficient to reduce the chlorine content of the outgoing chlorine purging effluent stream, after contacting the chlorinated spent catalyst, to less than 100 ppmw of chlorine-containing compounds.

11. The method of claims 1 – 7, wherein:

step (2) is conducted at a peak decoking temperature in a range from 300 °C to 500 °C; and

the decoking gas stream comprises an inert gas and oxygen.

12. The method of claims 1 – 7, 11, wherein the decoking gas stream comprises a mole % of oxygen in a range from 0.5 to 3 mole %.

13. The method of claims 1 – 7, 11 or 12, wherein the decoking gas stream contains less than 100 ppmw of halogen-containing compounds.

14. The method of claims 1 – 7, 11 – 13, wherein the decoking gas stream contains less than 100 ppmw of water.

15. The method of claims 1 – 7, 11 - 14, wherein step (2) is started at an initial decoking temperature which is the same as a chlorination temperature in step (1).

16. The method of claims 1 – 7, 11 – 15, wherein step (3) is conducted at a fluorination temperature in a range from 20 °C to 50 °C.

17. The method of claims 1 – 7, 11 – 16, wherein an amount of the fluorine-containing compound in the fluorine-containing solution provides from 0.1 to 10 wt. % of fluorine (F) in the fluorine-containing solution.

18. The method of claims 1 – 7, 11 – 17, wherein the fluorine-containing solution comprises the fluorine-containing compound and water or a hydrocarbon solvent.

19. The method of claims 1 – 7, 11 – 18, wherein the fluorine-containing solution comprises water and at least one of ammonium fluoride and tetramethylammonium fluoride.

20. The method of claims 1 – 7, 11 – 19, wherein the fluorine-containing solution contains less than 100 ppmw of chlorine-containing compounds.

21. The method of claims 1 – 7, 11 – 20, further comprising an aging step after step (3); the aging step comprising storing the fluorinated catalyst in the fluorine-containing solution at a temperature from 20 °C to 100 °C, a pressure from ambient to 500 psig, a time period of from 1 minute to 10 days, and under conditions in which the fluorinated catalyst is stationary or moving/mixing.

22. The method of claims 1 – 7, 11 – 21, further comprising a drying step, a calcination step, or both a drying step and a calcination step, after step (3).

23. The method of claim 22, wherein the drying step comprises subjecting the fluorinated catalyst to conditions sufficient to reduce a residual solvent content of the fluorinated catalyst to less than less than 15 wt. % solvent, based on the weight of the catalyst.

24. The method of claim 23, wherein the conditions sufficient to reduce the solvent content comprise:
a drying time in a range from 1 to 48 hr;
a drying temperature in a range from 15 °C to 200 °C; and
a drying pressure equal to atmospheric pressure or equal to any suitable sub-atmospheric pressure.

25. The method of claims 23 – 24, wherein the drying step comprises drying stationary fluorinated catalyst, fluidizing the fluorinated catalyst, or drying the fluorinated catalyst in a rotary dryer.

26. The method of claims 23 – 25, wherein the calcination step comprising subjecting the fluorinated catalyst to a calcination temperature in a range from 200 °C to 800 °C for a calcination time in a range from 30 min to 48 hours.

27. The method of claims 1 – 7, 11 – 22, wherein the method further comprises an oxygen purging step after step (2), the oxygen purging step comprising contacting the de-coked catalyst with an oxygen purging stream an inert gas.

28. The method of claim 27, wherein the oxygen purging stream contains less than 100 ppmw of oxygen-containing compounds.

29. The method of claims 27 or 28, wherein the oxygen purging stream contains less than 100 ppmw of halogen-containing compounds.

30. The method of claims 27 – 29, wherein the oxygen purging step is conducted for a time period sufficient to reduce the oxygen content of the outgoing oxygen purging effluent stream, after contacting the de-coked catalyst, to less than 100 ppmw of oxygen-containing compounds.

31. The method of claims 1 – 7, 11 – 22, or 27, further comprising:

a partial decoking step prior to step (1), the partial decoking step comprising contacting the spent catalyst with a partial decoking gas stream comprising oxygen; and

a pre-drying step prior to step (1), the pre-drying step comprising contacting the spent catalyst with a pre-drying gas stream comprising an inert gas.

32. The method of claims 1 – 7, 11 – 22, 27, or 31, wherein:

the transition metal comprises platinum;

the catalyst support comprises a KL-zeolite and a binder comprising alumina, silica, a mixed oxide thereof, or a mixture thereof; and

the spent catalyst further comprises chlorine and fluorine.

33. The method of claims 1 – 7, 11 – 22, 27, 31, or 32, further comprising:

a calcining step after step (3), the calcining step comprising calcining the fluorinated catalyst to produce a calcined catalyst; and

a reducing step after step (3), the reducing step comprising contacting the calcined catalyst with a reducing gas stream comprising molecular hydrogen.

34. A method for regenerating a spent catalyst comprising a transition metal and a catalyst support, the method comprising:

(a) contacting the spent catalyst with a pre-drying gas stream comprising an inert gas;

(b) contacting the spent catalyst with a chlorine-containing stream comprising a chlorine-containing compound to produce a chlorinated spent catalyst;

(c) contacting the chlorinated spent catalyst with a decoking gas stream comprising oxygen to produce a de-coked catalyst;

(d) contacting the de-coked catalyst with a fluorine-containing solution comprising a fluorine-containing compound to produce a fluorinated catalyst; and

(e) drying, calcining, or both drying and calcining the fluorinated catalyst.

35. The method of claim 34, wherein:

the pre-drying gas stream consists essentially of nitrogen;

the decoking gas stream comprises nitrogen and oxygen; and

the fluorine-containing solution comprises water and at least one of ammonium fluoride and tetramethylammonium fluoride.

36. The method of claim 34, wherein the chlorine-containing compound comprises Cl_2, carbon tetrachloride, tetrachloroethylene, or a combination thereof.

37. The method of claim 34, further comprising a step of contacting the spent catalyst, prior to step (b), with a partial decoking gas stream comprising oxygen at a partial decoking temperature in a range from 125 °C to 450 °C.

38. A reforming process comprising:

(A) contacting a hydrocarbon feed with an aromatization catalyst comprising a transition metal and a catalyst support under reforming conditions in a reactor system to produce an aromatic product;

(B) performing step (A) for a time period sufficient to form a spent catalyst;

(C) contacting the spent catalyst with a chlorine-containing stream comprising a chlorine-containing compound to produce a chlorinated spent catalyst;

(D) contacting the chlorinated spent catalyst with a decoking gas stream comprising oxygen to produce a de-coked catalyst; and

(E) contacting the de-coked catalyst with a fluorine-containing solution comprising a fluorine-containing compound to produce a fluorinated catalyst.

39. The process of claim 38, wherein the reforming process is an *in-situ* process.

40. The process of claim 38, wherein step (E) is performed external to the reactor system of steps (A)–(D).

41. The process of claim 38, further comprising a step of reducing the catalyst after step (E).