Effective Fe-based catalysts for FTO require that the selectivity for light olefins be high and that for CH_4 to be low. However, known Fe-based catalysts have only been able to produce mainly paraffins and/or gasoline product fractions.

As such, there is a need to provide a catalyst and the preparation method thereof to overcome or at least ameliorate, one or more of the disadvantages described above. It is an object of the present disclosure to provide a one-pot synthesis method of iron-based catalysts effective for FTO.

Summary

There is provided a method of preparing a nano-sized, iron-based catalyst, the method comprising: i) mixing a solution containing an iron salt with a surfactant to form a mixture; ii) adding a basic salt solution comprising a salt of element selected from the group consisting of: alkali metals, alkaline earth metals, transition metals of groups 3 to 7 and 9 to11 of the Periodic Table of Elements, lanthanides, and combinations of elements thereof, to the mixture to form a precipitate; and iii) calcining said precipitate to form the iron-based catalyst, said iron-based catalyst at least partially comprising said element of said basic salt.

In one aspect, there is provided a method of preparing a nano-sized, iron-based catalyst, the method comprising: i) mixing a solution containing an iron salt with a surfactant to form a mixture; ii) adding a basic salt solution comprising a salt of alkali metals to the mixture to form a precipitate; and iii) without washing said precipitate, calcining said precipitate to form the iron-based catalyst, said iron-based catalyst at least partially comprising said alkali metals of said basic salt.

The presently disclosed method may involve a one-pot co-precipitation procedure to form a nano-sized Fe catalyst using a basic salt solution. Advantageously, the co-precipitation method may enable a high amount (e.g., at least about 10 % based on the total weight of catalyst) of the alkali metal, alkaline earth metal, transition metal of groups 3 to7 or 9 to 11 of the Periodic Table of Elements, lanthanides, and combinations of elements thereof to be included or impregnated in the catalyst.

Without being bound to theory, the preparation of catalysts via such methods surprisingly yields nano-sized catalysts which adopt a unique iron-based spinel crystalline phase. This may be promoted by the metal in the basic salt solution. Extended X-ray Absorption Fine structure (EXAFS) analysis of the nano-sized catalysts shows that the nano-sized catalysts form an iron-based phase which is neither Fe_2O_3 nor Fe_3O_2. It is postulated that the metal of the basic salt may be incorporated into the iron phase, leading to the unique spinel phase of the

calcined catalyst. It is also postulated that the calcination step may facilitate the formation of said spiel crystalline phase. Advantageously, the spinel phase may assist the carburization step for the formation of Fe_5C_2.

Without being bound to theory, the high loading (e.g., at least about 10 % based on the total weight of catalyst) of the promoter metals and the spinel crystalline phase in the catalyst may bring improvements on the catalyst performance. Advantageously, such iron based catalysts may provide enhanced catalytic activity for the conversion of carbon monoxide or carbon dioxide to light olefins via a Fischer Tropsch reaction. Advantageously, the conversion of carbon dioxide during the processes as described herein was found to be at least 50 mol C%.

Surprisingly, the current method may allow the precipitated catalyst to be calcined directly in air without washing, therefore reduce the impact to the environment as compared to the method of preparing said conventional fused/precipitated Fe catalyst.

Along with the improved conversion of the carbon monoxide or carbon dioxide gas, the catalyst obtained by the method may also demonstrate selectivity for light olefins comprising 2 to 4 carbon atoms over methane and long chain paraffins. Advantageously, the selectivity for methane during the processes as described herein was found to be less than 5% of the product gas stream.

There is also provided a nano-sized, iron-based catalyst comprising: 5-99 wt. % of iron based on the total weight of the nano-sized catalyst; and 1-50 wt. % of an oxide of a metal selected from the group consisting of: alkali metals, alkaline earth metals, transition metals of groups 3 to 7 and 9 to 11 of the Periodic Table of Elements, and lanthanides, wherein said metal is not iron, wherein said nano-sized catalyst has a diameter of 2 to 50 nm. In another aspect, there is provided a nano-sized, iron-based catalyst comprising: a) 5-99 wt. % of iron oxide, based on the total weight of the nano-sized catalyst; b) 1-50 wt. % of an oxide of a metal selected from the group consisting of: alkali metals, alkaline earth metals, transition metals of groups 3 to 7 and 9 to 11 of the Periodic Table of Elements, and lanthanides, wherein said metal is not iron, based on the total weight of the nano-sized catalyst; and c) oxide of a halogen, wherein said

nano-sized catalyst has a diameter of 2 to 50 nm. The catalyst may be prepared by the preparation methods disclosed herein.

In yet another aspect, there is provided a process for the production of light olefins, the process comprising the step of: i) heating the catalyst as described herein in the presence of a gas comprising one or more oxides of carbon and hydrogen to activate said catalyst; and ii) contacting said activated catalyst of step (i) with a

Claims:

1. A method of preparing a nano-sized, iron-based catalyst, the method comprising:

i) mixing a solution containing an iron salt with a surfactant to form a mixture;

ii) adding a basic salt solution comprising a salt of alkali metals to the mixture to form a precipitate; and

iii) without washing said precipitate, calcining said precipitate to form the iron-based catalyst, said iron-based catalyst at least partially comprising said alkali metals of said basic salt.

2. The method of claim 1, wherein the basic salt solution comprises hydroxide, carbonate or bicarbonate anions.

3. The method of any of the preceding claims, wherein the basic salt is sodium hydroxide, lithium hydroxide, potassium hydroxide, cesium hydroxide, or combinations thereof.

4. The method of any of the preceding claims, wherein the adding step comprises providing a molar ratio of elemental iron to the element of the basic salt of from 1:2 to 1:10.

5. The method of claim 1, wherein the solution of step (i) comprises at least one or more additional salts of (a) a transition metal independently selected from groups 3 to 7 and 9 to 11 of the Periodic Table of Elements, (b) Mg, (c) Ca, (d) Li and (e) K.

6. The method of claim 5, wherein the transition metal is Ni, Mn, La, Co, Ce, or a combination thereof.

7. The method of claim 5, wherein the transition metal salt comprises an anion selected from the group consisting of hydroxide, carbonate,

bicarbonate, nitrate, nitrite, chloride, fluoride, bromide, iodide, phosphate, pyrophosphate, perchlorate, and mixtures thereof.

8. The method of claim 5, wherein the transition metal salt is $Mn(NO_3)_2$ or $Ni(NO_3)_2$.

9. The method of claim 5, wherein the solution of step i) comprises a molar ratio of elemental transition metal to iron of from 1:8 to 1:100.

10. The method of claim 1, wherein the adding step (ii) further comprises introducing a silicate to the mixture and precipitating said Fe-based catalyst in the presence of the silicate to thereby form a silicate-supported Fe-based catalyst.

11. The method of claim 10, wherein the silicate comprises one or more alkoxy groups of 2 to 5 carbon atoms.

12. The method of claim 10, wherein the silicate is tetraethyl orthosilicate.

13. The method of claim 10, wherein the adding step comprises providing a molar ratio of elemental iron to said silicate of from 1:5 to 1:15.

14. The method of claim 1, wherein the iron salt is an iron (II) or iron(III) salt.

15. The method of claim 1, wherein the iron salt comprises an anion selected from the group consisting of nitrate, chloride, fluoride, bromide, iodide, phosphate, pyrophosphate and perchlorate.

16. The method of claim 1, wherein the iron salt is iron (III) nitrate.

17. The method of claim 1, wherein the surfactant is an ionic surfactant.

18. The method of claim 17, wherein the surfactant is a quarternary ammonium surfactant.

19. The method of claim 1, wherein the surfactant comprises a halide anion.

20. The method of claim 1, wherein the surfactant is cetyl trimethylammonium bromide.

21. The method of claim 1, wherein the molar ratio of iron to the surfactant is 1:0.5 to 1:2.

22. The method of claim 1, wherein the calcining step is carried out at a temperature of 400°C to 600°C for 1 to 3 hours.

23. A nano-sized, iron-based catalyst comprising:

a) 5-99 wt. % of iron oxide, based on the total weight of the nano-sized catalyst;

b) 1-50 wt. % of an oxide of a metal selected from the group consisting of: alkali metals, alkaline earth metals, transition metals of groups 3 to 7 and 9 to 11 of the Periodic Table of Elements, and lanthanides, wherein said metal is not iron,

based on the total weight of the nano-sized catalyst; and

c) oxide of a halogen,

wherein said nano-sized catalyst has a diameter of 2 to 50 nm.

24. The iron-based catalyst of claim 23, wherein said oxide of a metal is present in an amount of 4-50 wt. % based on the total weight of the catalyst.

25. The iron-based catalyst of claim 23, wherein the nano-sized catalyst adopts a spinel crystalline phase.

26. The iron-based catalyst of claim 25, wherein the formula of the spinel phase catalyst is FeM_2O_4.

27. The iron-based catalyst of claim 23, wherein the catalyst further comprises an oxide of a transition metal selected from groups 3-7 and 9-11 of the Periodic Table of Elements.

28. The iron-based catalyst of claim 23, wherein the weight ratio of the transition metal to iron is 1:5 to 1:200.

29. The iron-based catalyst of claim 23, wherein the catalyst further comprises a SiO_2 matrix.

30. The iron-based catalyst of claim 23, wherein the oxide of the halogen is present in an amount of 0.1-50 wt. % based on the weight of catalyst.

31. The iron-based catalyst of claim 23, wherein the metal is alkali metals.

32. The iron-based catalyst of claim 31, prepared according to the method of claim 19.

33. A process for the production of light olefins, the process comprising the steps of:

i) heating the catalyst of any of claims 23-32 in the presence of a gas comprising one or more oxides of carbon and hydrogen to activate said catalyst; and

ii) contacting said activated catalyst of step (i) with a gas stream comprising one or more oxides of carbon and hydrogen to partially or fully convert said one or more oxides of carbon to said light olefins, said light olefins comprising between 2 to 4 carbon atoms,

wherein methane is substantially absent from said light olefins, or constitutes less than 20% of said light olefins.

34. The process of claim 33, wherein the oxide of carbon in the gas stream of step ii) is substantially carbon dioxide.