Nanostructured Hybrid Iron-Zeolite Catalysts

Technical Field

The present invention relates to the synthesis of nanostructured hybrid Fe-zeolite catalysts that optimizes light olefin selectivity and yield. Specific examples are demonstrated through one-pot precipitation reactions and physical mixing with zeolites.

Background Art

Fischer-Tropsch Synthesis is a collection of chemical processes which use CO and H_2 as feedstock to produce longer-chain hydrocarbons. These processes usually take place over catalysts based on Co, Fe, Ru and even Ni and Re. However, conventional catalysts and processes are known to produce mainly paraffins and/or gasoline product fractions, with low yield for light olefins.

Recent interest has re-surfaced on the use of Fe in the direct Fischer-Tropsch to olefin (FTO) process due to its lower cost compared to other materials, as well as its promising selectivity to light olefin production (C2 - C4). In particular, Fe-based catalysts promoted with elements such as alkali metals, alkali earth metals, transition metals and lanthanides have shown various enhancements, such as active site dispersion, faster activation, suppression of methane and improvement to olefinicity of hydrocarbon products.

Effective Fe-based catalysts for FTO require that the selectivity for light olefins be high and that for CH_4 and C5+ (hydrocarbons comprising 5 or more carbons) to be low. However, known Fe-based catalysts have only been able to produce mainly paraffins and/or gasoline product fractions. Further, for known Fe-based catalysts, the product distribution is limited by the so-called Anderson-Schulz-Flory (ASF) theory, which shows that it is difficult to maximize the selectivity for C2-C4 olefins without concurrently increasing the selectivity for CH_4 and/or C5+.

There is therefore a need to provide a catalyst and a method of use thereof that overcomes or at least ameliorates, one or more of the disadvantages described above.

Summary

There is provided a hybrid iron nanoparticle catalyst comprising:

i) 30 to 70 wt. % of nanoparticles comprising iron and at least one of a metal M 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, lanthanides and combinations of M thereof; and

ii) 70 to 30 wt. % of an aluminosilicate or silicoaluminophosphate zeolite, based on the total weight of the catalyst

wherein said nanoparticle has a diameter of about 2 to50 nm, and the total wt.% of the nanoparticles and zeolite is 100 wt.%.

In an aspect, there is provided a hybrid iron nanoparticle catalyst consisting essentially of:

i) 30 to 70 wt. % of nanoparticles in oxide form comprising iron, at least one metal M selected from the group consisting of alkali metals, alkaline earth metals, transition metals of groups 3 to 7 or 9 to 11 of the Periodic Table of Elements, lanthanides, and combinations of M thereof, and a halogen; and

ii) 70 to 30 wt. % of an aluminosilicate or silicoaluminophosphate zeolite, based on the total weight of the catalyst,

wherein said nanoparticle has a diameter of 2 to 50 nm, and the total wt.% of the nanoparticles and zeolite is 100 wt.%.

Advantageously, the presently described hybrid iron nanoparticle catalyst may demonstrate improved activity over the Fischer Tropsch iron catalysts known in the art. High selectivity and

conversion of the gas comprising hydrogen and an oxide of carbon to the desired light olefins may be achieved utilizing the catalysts as described herein. This may be attributed to the high percentage of the alkali metals, alkaline earth metals, transition metals or lanthanide in the catalyst, as well as the porous nature of the zeolite.

In an example, the presently described catalyst may adopt a spinel crystalline phase.

Advantageously, nanoparticle catalysts having the spinel phase may demonstrate improved conversion of carbon monoxide or carbon dioxide to light olefins, particularly light olefins comprising 2 to 4 carbon atoms, with up to 24 mol.C% improvement compared to conventional catalysts. The improved yields may be attributed to the crystalline spinel phase of the nanoparticle catalysts.

There is provided a method of preparing a hybrid nanoparticle iron catalyst, the method comprising

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

ii) adding a basic salt solution comprising a salt of an element selected from the group consisting of alkali metals, alkaline earth metals, transition metals of groups 3 to7 or 9 to11 of the Periodic Table of Elements, lanthanides, and combinations of elements thereof; to the mixture of step (i) to form a precipitate;

iii) heating the precipitate of step (ii) in the presence of air and oxygen; and

iv) mixing the precipitate of step (iii) with an aluminosilicate or a silicoaluminophosphate zeolite to yield a hybrid iron catalyst.

In another aspect, there is provided a method of preparing a hybrid iron nanoparticle catalyst, the method comprising

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

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

iii) heating the precipitate of step (ii) in the presence of air and oxygen at a temperature of 300ºC to 600ºC; and

iv) mixing the precipitate of step (iii) with an aluminosilicate or a silicoaluminophosphate zeolite to yield a hybrid iron nanoparticle catalyst.

Advantageously, the presently disclosed method of preparing the hybrid iron nanoparticle catalyst may involve the co-precipitation of an iron nanoparticle catalyst with a basic salt solution. The co-precipitation method may enable a high concentration of the alkali metal, alkaline earth metal, transition metal of groups 3 to7 or 9 to11 of the Periodic Table of Elements, lanthanides, and combinations of elements thereof to be included in the nanoparticle. Such iron nanoparticles may surprisingly demonstrate enhanced catalytic activity for the conversion of carbon monoxide or carbon dioxide to light olefins via a Fischer Tropsch reaction. Along with the improved

conversion of the carbon monoxide or carbon dioxide gas, the catalyst may also demonstrate selectivity for light olefins comprising 2 to 4 carbon atoms over methane and long chain paraffins.

Further advantageously, the hybrid iron catalyst and zeolite disclosed herein may also reduce the activation time of the catalyst in the Fischer-Tropsch reaction, with an activation speed of 2 to 16 hours as compared to conventional catalysts with induction times of 40 to 100 hours. As such, high yields of the light olefin may be achieved within a shorter period of time, without compromising the selectivity of the catalysts for the C2 - C4 light olefins.

In another aspect, there is provided a process for the production of light olefins, the process comprising the step of:

i) heating the catalyst as defined above in the presence of a gas comprising one or more oxides of carbon and hydrogen to activate said catalyst; and

Claims

1. A hybrid iron nanoparticle catalyst consisting essentially of:
   i) 30 to 70 wt. % of nanoparticles in oxide form comprising iron, at least one metal M selected from the group consisting of alkali metals, alkaline earth metals, transition metals of groups 3 to 7 or 9 to 11 of the Periodic Table of Elements, lanthanides, and combinations of M thereof, and a halogen; and

   ii) 70 to 30 wt. % of an aluminosilicate or silicoaluminophosphate zeolite, based on the total weight of the catalyst,

   wherein said nanoparticle has a diameter of 2 to 50 nm, and the total wt.% of the nanoparticles and zeolite is 100 wt.%.

2. The catalyst of claim 1, wherein said metal M is the alkali metal.

3. The catalyst of claim 1, wherein said metal M comprises 10 to 50 wt. % based on the weight of the iron nanoparticle.

4. The catalyst of any of the preceding claims, wherein the nanoparticles adopt a spinel crystalline phase, or a spinel crystalline phase having the formula FeM_2O_4.

5. The catalyst of any of the preceding claims, wherein the zeolite is an aluminosilicate zeolite, a pentasil zeolite or faujasite zeolite, or the zeolite is selected from the group consisting of zeolite X, ZSM-5, zeolite Y, ZSM-12, ZSM-22, and HY zeolite.

6. The catalyst of any of the preceding claims, wherein the mole ratio of alumina to silica in the zeolite is 1:2 to 1:90.

7. The catalyst of any of the preceding claims, wherein the zeolite is a silicoaluminophosphate zeolite, SAPO 11 or SAPO 34.

8. The catalyst of any of the preceding claims, wherein the weight ratio of the zeolite to the iron nanoparticle is 1:0.5 to 1:2.

9. The catalyst of claim 1, wherein the oxide of the halogen is present in an amount of 0.1 to 50 wt. %, based on the weight of the nanoparticles.

10. The catalyst of any of the preceding claims, wherein the iron nanoparticles further comprise a transition metal of groups 3 to 7 and 9 to 11 of the Periodic Table of Elements.

11. The catalyst of claim 10, wherein the molar ratio of iron to the transition metal is 1:1 to 50:1.

12. The catalyst of any of the preceding claims, wherein the iron nanoparticles further comprises a SiO_2 matrix.

13. A method of preparing a hybrid iron nanoparticle catalyst, the method comprising

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

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

iii) heating the precipitate of step (ii) in the presence of air and oxygen at a temperature of 300°C to 600°C; and

iv) mixing the precipitate of step (iii) with an aluminosilicate or a silicoaluminophosphate zeolite to yield a hybrid iron nanoparticle catalyst.

14. The method of claim 13, wherein said salt of the element comprises hydroxide, carbonate or bicarbonate anions.

15. The method of claim 13 or 14, wherein the molar ratio of the iron to the element of the basic salt is 1:2 to 1:25.

16. The method of any of claims 13-15, wherein the heating step is carried out for 1 to 10 hours.

17. The method of any of claims 13-16, wherein the iron salt is an iron (II) or iron (III) salt or the iron salt comprises an anion selected from the group consisting of nitrate, chloride, fluoride, bromide, iodide, phosphate, pyrophosphate and perchlorate.

18. The method of any of claims 13-17, wherein the surfactant is an ionic surfactant, or the surfactant comprises an anion selected from the group consisting of: halides, sulfonates, sulfates, phosphates and carboxylates.

19. The method of claim 17, wherein the surfactant comprises the halide anion.

20. The method of any of claims 13-19, wherein the molar ratio of iron to the surfactant is 1:0.5 to 1:15.

21. The method of any of claims 13-20, further comprising, prior to step (iii), the steps of:

collecting the precipitate; and

drying said precipitate in air.

22. The method of claim 21, wherein the collection of the precipitate is by centrifugation and/ or filtration.

23. The method of any of claims 13-22, further comprising, prior to step (ii), adding a solution of a salt of a transition metal to the mixture of step (i).

24. The method of any of the claims 13-22, further comprising:

prior to step ii), introducing a solution of a silicate to the mixture of step (i).

25. The method of claim 24, wherein the silicate comprises alkoxy groups of 2 to 15 carbon atoms.

26. The method of claim 24 or 25, wherein the molar ratio of iron to said silicate is 1:1 to 1:50.

27. The catalyst of claim 2, prepared according to the method of claim 19, or the catalyst of any of claims 10-11, prepared according to the method of claim 23, or the catalyst of claim 12, prepared according to the method of any of claims 24-26.

28. A process for the production of light olefins, the process comprising the step of:

    i) heating the catalyst of any of claims 1-12 or 27 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.

29. The process of claim 28, wherein the step (i) is carried out at a temperature of 200°C–350°C, or wherein step (ii) is carried out at a temperature of 200°C-450°C, or wherein step (i) is carried out at a pressure of 5-30 bar, or wherein step (ii) is carried out at a pressure of 5 to 50 bar.

30. The process of claim 28 or 29, wherein the space velocity of the gas stream in step (ii) is 1500 ml/g.h to 5000 ml/g.h.

31. The process of any of claims 28-30, wherein the molar ratio of hydrogen to the one or more oxides of carbon in the gas is 4:1 to 1:3.

32. The process of any of claims 28-31, further comprising, prior to step (i), reducing the catalyst of any of claims 1-12 or 27 by contacting said catalyst with a stream of hydrogen gas.

33. The process of any of claims 28-32, wherein the oxide of carbon in the gas stream of step (ii) is substantially carbon dioxide.