by preserving the self-assembly process during decomposition, autoreduction on the support due to strong chemical interaction should be suppressed.

[0005] The present invention provides a process for achieving this.

Summary

[0006] There is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a precursor in the presence of a reducing agent, said precursor being a molybdate salt or a thiomolybdate salt, wherein if the precursor is a molybdate salt, the reaction is conducted in the presence of elemental sulfur.

[0006a] In one aspect, there is provided a process for making a supported molybdenum sulfide catalyst, said process comprising heating a precursor in the presence of a reducing agent and a support, said precursor being a molybdate salt or a thiomolybdate salt, wherein:

if the precursor is a molybdate salt, the reaction is conducted in the presence of elemental sulfur in a reducing atmosphere at a temperature of 400 to 500°C; and

if the precursor is a thiomolybdate salt the reaction is conducted either (a) in the absence of liquid solvent and in the presence of elemental sulfur or (b) in the absence of elemental sulfur and in the presence of liquid solvent at 180 to 220°C.

[0007] The following options may be used in conjunction with the above aspect, either individually or in any suitable combination.

[0008] The salt may be an ammonium salt. Thus the molybdate salt may be an ammonium molybdate and the thiomolybdate salt may be an ammonium thiomolybdate. The ammonium molybdate may be ammonium heptamolybdate tetrahydrate (AHM). The ammonium thiomolybdate may be ammonium tetrathiomolybdate (ATM).

[0009] The heating may be conducted in the presence of a support. In this case, the process produces a supported molybdenum sulfide catalyst. The support may be selected from the group consisting of alumina, magnesium oxide, silica, aluminium oxide/magnesium oxide, hydrotalcite, activated carbon and carbon nanotubes and mixtures of any two or more of these, or some other support may be used.

[00010] The reaction may be conducted in the absence of solvent and in the presence of elemental sulfur. In this event reaction may comprise the step of heating the precursor and the elemental sulfur in a reducing atmosphere. The sulfur may be capable of decomposing a polymolybdate or polythiomolybdate which may be used as the precursor or which may be formed *in situ* from the precursor. The process may comprise the step of grinding the precursor and the elemental sulfur together prior to the step of heating. The reducing atmosphere may comprise hydrogen gas. The hydrogen gas may be mixed with an inert gas, e.g. nitrogen. The heating may be to a temperature of from about 400 to about 500°C. The reaction may be conducted at approximately atmospheric pressure, i.e. about 1 atmosphere. It may be conducted

[00015] In another embodiment there is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a precursor in the presence of a reducing agent, said precursor being a thiomolybdate salt. In this embodiment, the heating may be in the presence of sulfur or it may be in the absence of sulfur.

[00016] In another embodiment there is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a molybdate salt in the presence of elemental sulfur in the absence of solvent in a reducing atmosphere comprising hydrogen at temperature of about 400 to about 500°C.

[00017] In another embodiment there is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a thiomolybdate salt in the presence of elemental sulfur in the absence of liquid solvent in a reducing atmosphere comprising hydrogen at temperature of about 400 to about 500°C.

[00018] In another embodiment there is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a thiomolybdate salt in a solvent in the presence of a borohydride reducing agent at a temperature of about 180 to about 220°C.

[00019] In a further embodiment there is provided a process for making a molybdenum sulfide catalyst, said process comprising heating a thiomolybdate salt in the presence of a substance, e.g. water vapour, capable of depolymerising a polymeric thiomolybdate, optionally in the absence of elemental sulfur, in the absence of liquid solvent, in a reducing atmosphere comprising hydrogen at temperature of about 400 to about 500°C. The pressure in this instance may be about 1 atmosphere, or may be from about 1 to about 2bar.

[00020] There is also provided a molybdenum sulfide catalyst which is makeable by, or made by, the process as defined herein.

[00020a] In another aspect, there is provided a supported molybdenum sulfide catalyst made by the process as defined herein, wherein the molybdenum sulfide catalyst is on a support and is at least 90% molybdenum sulfide and wherein the molybdenum sulfide comprises nanosized molybdenum sulphide.

[00021] The following options may be used in conjunction with the above aspect, either individually or in any suitable combination.

[00022] The catalyst may comprise nanosized molybdenum sulfide. It may comprise molybdenum sulfide particles, each having at least one dimension, optionally 2 dimensions or 3

dimensions, in the range of about 1 to about 999 nm. It may be in the form of molybdenum sulfide flowers.

[00023] The molybdenum sulfide may be high purity. It may be at least 90%, optionally about 100%, molybdenum disulfide, i.e. at least 90%, optionally about 100% pure.

[00024] The catalyst may comprise molybdenum disulfide on a support. The support may be selected from the group consisting of alumina, magnesium oxide, silica, aluminium oxide/magnesium oxide, hydrotalcite, activated carbon and carbon nanotubes and mixtures of any two or more of these. It may be hydrotalcite. The ratio of molybdenum sulfide to support may be about 35:65 on a w/w basis.

[00025] In another aspect, there is provided a method for generating methane comprising exposing a gaseous mixture containing carbon monoxide and hydrogen to a catalyst according to the second aspect.

[00026] The following options may be used in conjunction with the above aspect, either individually or in any suitable combination.

[00027] The method may be conducted at a temperature of from about 500 to about 600°C.

[00028] The gaseous mixture may additionally comprise a sulfur containing gas, e.g. hydrogen sulfide. In this event, the catalyst may be not poisoned by the sulfur containing gas, e.g. hydrogen sulfide.

[00028a] In another aspect, there is provided use of a catalyst as defined herein for catalysing a methanation reaction.

Brief Description of Drawings

[00029] The invention may best be understood by reference to the following description when considered in conjunction with the non-limiting examples and the accompanying drawings.

[00030] FIG. 1 shows the scanning electron microscopy (SEM) images of (A) Sample prepared by decomposition of ATM in inert gas (N_2); (B) Sample prepared by decomposition of ATM in N_2 with elemental sulfur; (C) Sample prepared by decomposition of ATM in reducing gas (H_2); (D) Sample prepared by decomposition of ATM in H_2 with elemental sulfur.

Claims:

1. A process for making a supported molybdenum sulfide catalyst, said process comprising heating a precursor in the presence of a reducing agent and a support, said precursor being a molybdate salt or a thiomolybdate salt, wherein:

if the precursor is a molybdate salt, the reaction is conducted in the presence of elemental sulfur in a reducing atmosphere at a temperature of 400 to 500°C; and

if the precursor is a thiomolybdate salt the reaction is conducted either (a) in the absence of liquid solvent and in the presence of elemental sulfur or (b) in the absence of elemental sulfur and in the presence of liquid solvent at 180 to 220°C.

2. The process of claim 1 wherein the salt is an ammonium salt, whereby the molybdate salt is an ammonium molybdate and the thiomolybdate salt is an ammonium thiomolybdate.

3. The process of claim 2 wherein the ammonium molybdate is ammonium heptamolybdate tetrahydrate (AHM) and the ammonium thiomolybdate is ammonium tetrathiomolybdate (ATM).

4. The process of claim any one of claims 1 to 3 wherein the support is selected from the group consisting of alumina, magnesium oxide, silica, aluminium oxide/magnesium oxide, hydrotalcite, activated carbon and carbon nanotubes and mixtures of any two or more of these.

5. The process of any one of claims 1 to 4 wherein the reaction is conducted in the absence of solvent and in the presence of elemental sulfur, and wherein the reaction comprises the step of heating the precursor and the elemental sulfur in a reducing atmosphere.

6. The process of claim 5 comprising the step of grinding the precursor and the elemental sulfur together prior to the step of heating.

7. The process of claim 5 or claim 6 wherein the reducing atmosphere comprises hydrogen gas.

8. The process of claim 7 wherein the hydrogen gas is mixed with an inert gas.

9. The process of claim 8 wherein the inert gas is nitrogen.

10. The process of any one of claims 5 to 9 comprising the step of exposing the catalyst to a mixture of oxygen and an inert gas after said heating, the concentration of oxygen in said inert gas being less than 2% v/v.

11. The process of any one of claims 1 to 4 which is conducted in a solvent and the reducing agent is a borohydride.

12. The process of claim 11 wherein the borohydride is sodium borohydride.

13. The process of claim 11 or claim 12 wherein the precursor is ATM.

14. The process of any one of claims 11 to 13 wherein the solvent has a dielectric constant greater than 30.

15. The process of claim 14 wherein the solvent is water or dimethylformamide or a mixture of these.

16. The process of any one of claims 11 to 15 which is conducted in a sealed container.

17. A supported molybdenum sulfide catalyst made by the process of any one of claims 1 to 16, wherein the molybdenum sulfide catalyst is on a support and is at least 90% molybdenum sulfide and wherein the molybdenum sulfide comprises nanosized molybdenum sulfide.

18. The catalyst of claim 17 wherein the catalyst comprises molybdenum sulfide particles, each having at least one dimension in the range of 1 to 999nm.

19. The catalyst of claim 17 or 18 wherein the molybdenum sulfide is about 100% molybdenum disulfide.

20. The catalyst of any one of claims 17 to 19 wherein the support is selected from the group consisting of alumina, magnesium oxide, silica, aluminium oxide/magnesium oxide, hydrotalcite, activated carbon and carbon nanotubes and mixtures of any two or more of these.

21. The catalyst of claim 20 wherein the support is hydrotalcite.

22. The catalyst of any one of claim 17 to 21 wherein the ratio of molybdenum sulfide to support is 35:65 on a w/w basis.

23. A method for generating methane comprising exposing a gaseous mixture containing carbon monoxide and hydrogen to a catalyst according to any one of claim 17 to 22.

24. The method of claim 23 which is conducted at a temperature of from 500 to 600 °C.

25. The method of claim 23 or claim 24 wherein the gaseous mixture additionally comprises hydrogen sulfide.

26. The method of claim 25 wherein the catalyst is not poisoned by the hydrogen sulfide.

27. Use of a catalyst according to any one of claims 17 to 22 for catalysing a methanation reaction.