

METHOD OF PRODUCING A METHANATION CATALYST

Field

[0001] The invention relates to production of molybdenum sulfide catalysts.

Background

[0001] The demand for natural gas increases with the economic and population growth through the world but the production of natural gas may not keep up with this increasing demand. Therefore it is necessary to produce substitute natural gas in order to meet the increasing energy demand. A possible method for producing substitute natural gas is to gasify coal to produce syngas as the raw material for methanation (i.e. production of methane). Current state of the art methanation catalysts are transition metals like nickel (Ni) which have high methanation activity. Nevertheless, these catalysts have operating limitations because of their susceptibility to poisoning by sulfur compounds present in synthesis gas obtained from coal gasification.

[0002] Molybdenum sulfide, MoS_2 , is one of the few methanation catalysts of carbon monoxide that are not affected by sulfur impurities. It is widely used for hydrodesulfurization, hydrodenitrogenation and mixed alcohol synthesis from CO hydrogenation. Sulfur-tolerant MoS_2 catalysts can overcome the disadvantage of sulfur poisoning and hence it is possible to use the feedstock from coal gasification for direct methanation without going through a sulfur removal process.

[0003] The basal plane and the edge facets of MoS_2 have very different physical and chemical properties. The surface energy for the edges is about 100 times greater than that of the basal plane (001). Therefore, the edges have been found to be active surfaces for chemical reactions. It is therefore desirable to develop a process to create a more active MoS_2 catalyst with more exposed edge sites that can achieve a high activity for synthesis gas methanation to realize the production of substitute natural gas for the growing energy market.

[0004] An effective supported MoS_2 catalyst requires good dispersion on the support while maintaining the desired morphology. For improved dispersion of the catalyst on the support, depolymerization of the precursors is desirable, while for maintaining the desired morphology

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 and in the absence of liquid solvent, and 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 in a reducing atmosphere at a temperature of 400 to 500°C 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

at a pressure of about 1 to about 2 bar, or from about 1 to 1.5, 1.5 to 2 or 1.2 to 1.7 bar, e.g. about 1, 1.1, 1.2, 1.3, 1.4, 1.5, 1.6, 1.7, 1.8, 1.9 or 2 bar.

[00011] In the event that the precursor is a thiomolybdate salt (optionally a polythiomolybdate salt), the reaction may be conducted in the absence of a liquid solvent and in the presence of a compound capable of decomposing a polythiomolybdate which may be the precursor or which may be formed *in situ* from the precursor. Suitable such compounds include common solvents, e.g. water or some other solvent, commonly one having a dielectric constant over about 30. These are described elsewhere herein. In this event reaction may comprise the step of heating the precursor and the compound capable of decomposing the intermediate in a reducing atmosphere. The reducing atmosphere may comprise hydrogen gas, and may also comprise a vapour of the compound capable of decomposing the intermediate. 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. This option may be conducted in the absence of elemental sulfur.

[00012] The catalyst produced as described above may then be exposed to a mixture of oxygen and an inert gas after said heating. In this case, the concentration of oxygen in the inert gas may be less than about 2% v/v.

[00013] In some embodiments the process may be conducted in a solvent. In this event, the reducing agent may be a borohydride, e.g. sodium borohydride. In this option, the precursor may be a thiomolybdate salt, e.g. ATM or a polythiomolybdate salt. This process may be conducted in the absence of elemental sulfur. The solvent may have a dielectric constant greater than 30. It may for example be water or dimethylformamide or a mixture of these. The heating may be at a temperature of about 180 to 220 °C. The process may be conducted in a sealed container. The pressure in this case may be that which arises naturally from heating the solvent in the sealed container. The pressure may be for example from about 2 to about 20 bar, or from about 2 to 10, 2 to 5, 5 to 20, 10 to 20, 10 to 15 or 15 to 20 bar, e.g. about 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13, 14, 15, 16, 17, 18, 19 or 20 bar.

[00014] In one 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 and elemental sulfur, said precursor being a molybdate salt.

[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 disulfide and wherein the molybdenum sulfide catalyst 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.

[00031] FIG. 2 shows the CO conversion and the methane (CH₄) selectivity of the MoS₂ catalysts, unsupported or supported on a hydrotalcite from SASOL (PURAL® MG 30, labeled as Al-Mg30), SiO₂ and Al₂O₃. The selectivity of all the catalysts reached the equilibrium at steady state, the difference in the performance is reflected only by the conversion at these reaction conditions (SV = 5000 h⁻¹, CO:H₂=1:1, reaction temperature at 550 °C).

[00032] FIG. 3 shows the scanning electron microscopy (SEM) images of (A) unsupported MoS₂ prepared by mixing ATM with sulfur (labeled as ATM+S method) at low magnification; (B) unsupported MoS₂ prepared by ATM+ S at high magnification; (C) 35%MoS₂/Al-Mg30 prepared by ATM+S method; (D) 35%MoS₂/Al₂O₃ prepared by ATM+S method; and (E) 35%MoS₂/SiO₂ prepared by ATM+S method.

[00033] FIG. 4 shows the CO conversion of the MoS₂ catalysts, unsupported or supported prepared using different Mo precursors. MoS₂ catalysts prepared by mixing ATM and sulfur are labeled as (ATM+S), while MoS₂ catalysts prepared by mixing ammonium molybdate tetrahydrate (AHM) are labeled as (AHM+S). CH₄ selectivity is omitted for clarity since all catalysts reached equilibrium at steady state.

[00034] FIG. 5 presents the SEM images of (A) 35% MoS₂(AHM+S)/Al-Mg30; and (B) 35%MoS₂(ATM+S)/Al-Mg30.

[00035] FIG. 6 depicts the CO conversion of the MoS₂ catalysts with different loadings from 25% to 100% (i.e. unsupported) prepared by ATM+S method.

[00036] FIG. 7 presents the SEM images of (A) 25% MoS₂(ATM+S)/Al-Mg30; (B) 35% MoS₂(ATM+S)/Al-Mg30; and (C) 50% MoS₂(ATM+S)/Al-Mg30.

[00037] FIG. 8 depicts the CO conversion of the MoS₂ catalysts prepared by hydrothermal method. The MoS₂ catalysts were supported on Al₂O₃, SiO₂, hydrotalcite (Al-Mg30), activated carbon (Act-C) and carbon nanotubes (CNT). All catalysts were prepared using dimethylformamide (DMF) as solvent except for 35%MoS₂(H₂O)/Al-Mg30-hydro which was prepared using de-ionized water as solvent.

[00038] FIG. 9 shows SEM images of (A) 35%MoS₂(H₂O)/Al-Mg30-hydro; (B) Same catalyst at higher magnification

Description of Embodiments

[00039] The method described herein for preparing the catalyst involves controlling the depolymerization of the precursor (or a polymerised form thereof) and its autoreduction, optionally on a support, so as to preserve the self-assembly of the nano-structured MoS₂ catalyst. This method yielded effective MoS₂ catalysts which are demonstrated in the examples provided herein. For example, a nano-sized molybdenum disulfide (MoS₂) catalyst supported on hydrotalcite has been prepared through methods that favour the self-assembly process during the synthesis. Specific examples have been demonstrated through a chemical vapor deposition method and a hydrothermal method.

[00040] Precursors for the reaction described herein are molybdates or thiomolybdates. These terms should be taken to include the polymeric forms of these salts, i.e. polymolybdates or polythiomolybdates respectively unless it is clear from the context that this is not intended.

[00041] Thus the present invention provides methods of synthesizing nano-sized, hydrotalcite supported MoS₂ catalysts by allowing the self-assembly process during the synthesis. One embodiment of the method begins by mixing ammonium tetrathiomolybdate, a support and large amount of elemental sulfur in a mortar. The reaction of the mixture is carried out in a reducing environment at elevated temperature in a tube furnace. Another method is carried out by mixing ammonium tetrathiomolybdate, a support and a reducing agent in a solvent. Subsequently, the mixture is transferred into a Teflon-lined autoclave and heated at elevated temperature. The self-assembly process is encouraged through control of the precursors, decomposition environment and the support materials.

[00042] Without wishing to be bound by theory, it is considered that the molybdate or thiomolybdate precursor is initially converted to a polymeric form (i.e. polymolybdate or polythiomolybdate respectively) either thermally or hydrothermally. This is subsequently depolymerised, ultimately leading to the nano-sized molybdenum sulfide catalyst described herein. It will be understood that, in the event that the precursor is initially in polymeric form (i.e. the molybdate is a polymolybdate and the thiomolybdate is a polythiomolybdate), then the step of converting to a polymeric form would not take place.

[00043] One embodiment of the invention involves a method of producing nano-sized MoS₂ catalyst. The method begins by mixing ammonium tetrathiomolybdate (ATM) and elemental

sulfur mechanically by mortar or ball-milling. The mixture is transferred into a tube furnace. The reaction of the mixture is carried out in the tube furnace at elevated temperature. In this embodiment the reaction occurs under sulfur rich and reducing environment to allow the decomposition of the precursor and self-assembled into a layered MoS₂ nanostructure.

[00044] One embodiment involves the use of suitable support material for the nano-sized MoS₂ catalyst. The support serves to reduce the loading of MoS₂ used in the methanation while maintaining the nano-sized, layered morphology of the catalyst as well as the activity. For example, a suitable support material could be a basic support. It is thought that this might enhance depolymerization of an intermediate polymolybdate or polythiomolybdate and reduce autoreduction on the support which could interfere with the decomposition and self assembly of layered and dispersed nano-sized MoS₂ catalyst.

[00045] In another embodiment, the supported MoS₂ catalyst can be prepared under hydrothermal conditions. The method starts by mixing ammonium tetrathiomolybdate, a support and a reducing agent in a suitable solvent then the mixture is transferred into a Teflon-lined autoclave and heated at 200 °C for 10 h. This provides a low cost route for preparing MoS₂ catalyst at lower temperature. The suitable solvent could help to reduce polymerization of the precursor which enhances the dispersion of MoS₂ on the support and prevents strong chemical interaction between the precursor and the support that leads to autoreduction. The depolymerisation of an intermediate polythiomolybdate or polymolybdate from the decomposition of the precursor may be achieved by selecting a suitable solvent that can effectively disperse the precursor. It is thought that sulfur is able to act as an agent for the depolymerisation of polymolybdate or thiomolybdate intermediates. However, the depolymerisation agent may be replaced by a solvent, e.g. water. In a solvent-free system, a suitable vapour, e.g. water vapour, may serve a similar role. Thus for example a low concentration (e.g. about 0.5 to about 5% w/w or v/v, or about 0.5 to 2, 1 to 2, 1 to 3, 3 to 4 or 2-4%, e.g. about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5%) may be used in the gas in which the reaction is conducted. This gas may be static, in an enclosed chamber, or may be flowed through a vessel or reaction chamber in which the reaction is conducted.

[00046] The nano-sized MoS₂ catalyst shows significant improvements over conventional catalysts due to its unique morphology. The use of suitable support material is able to maintain this nano-morphology and its high activity even though the loading of MoS₂ is lower. The CO

conversion obtained by the use of these catalysts can achieve 69% using hydrothermal synthesized catalyst and greater than 80% using the catalysts produced by the chemical vapor method in the syngas direct methanation.

[00047] Unprocessed syngas which typically consists of carbon monoxide (CO) and hydrogen (H₂) in equal molar concentration can be methanized directly by the nano-sized MoS₂ catalyst. Therefore the H₂/CO ratio of the feedstock does not require adjustment to higher ratio using water gas shift reaction as required by Ni catalyst, and this will help in reducing the operation cost. Furthermore the sulfur tolerant property of MoS₂ catalyst also helps in lowering the capital cost of the acid gas removal unit.

[00048] Thus the process of the invention relates to production of a molybdenum sulfide catalyst. In the method, a precursor containing molybdenum is heated in the presence of a reducing agent. In cases where the precursor contains no sulfur, e.g. a molybdate salt precursor, it is necessary to include a sulfur containing reagent. A convenient way to achieve this is to conduct the reaction in the presence of elemental sulfur. However in cases where the precursor contains sulfur, e.g. a thiomolybdate precursor, the presence of an additional sulfur containing reagent may be not necessary, although in some instances it may be used. In an embodiment the invention relates to production of a molybdenum sulfide catalyst by heating either a molybdate salt or a thiomolybdate salt in the presence of elemental sulfur and a separate reducing agent. The reducing agent, depending on experimental details, may for example be hydrogen gas or may be a borohydride salt.

[00049] Convenient precursors, therefore, are molybdate or thiomolybdate salts. These may conveniently be ammonium salts, however may alternatively be any other such salt, e.g. alkaline metal or alkaline earth salts. Particular examples include sodium, potassium, magnesium, calcium or rubidium salts. The salts may be anhydrous, or may be in the form of a hydrate. As noted earlier, the molybdate or thiomolybdates may be in polymeric form. The processing of these may be under similar conditions to those used for monomeric molybdate salts and thiomolybdate salts respectively. In some instances, higher pressures and/or higher temperatures may be used. These conditions have been discussed elsewhere herein.

[00050] As it is generally convenient to have the product catalyst supported, the reaction may be conducted in the presence of a support. This will result in a supported catalyst. Suitable supports

include metal oxides or mixed metal oxides and hydrated forms thereof, for example silica, magnesia, dolomite, diatomaceous earth, hydrotalcite. Other suitable supports include activated carbon, carbon nanotubes, graphite, graphene and other carbon forms.

[00051] The reducing agent may be a solid reducing agent. It may be a borohydride, e.g. sodium borohydride. It may be used in solution, e.g. aqueous solution.

[00052] The reaction may conveniently be conducted in the absence of a solvent. This avoids the need for solvents which may be costly, hazardous (e.g. flammable and/or toxic) and which may pose a disposal or recycling problem. To achieve this, the precursor may simply comprise heating the precursor and elemental sulfur in a reducing atmosphere. The reducing atmosphere may for example comprise hydrogen. The hydrogen may be neat or may be in combination with a second gas which does not react with hydrogen under the conditions of the reaction. Suitable mixing gases include nitrogen, argon, helium, neon or mixtures of the two. The hydrogen (or some other reducing gas or vapour) may be present in the reducing atmosphere in a proportion of from about 1 to about 100%, or about 10 to 100, 50 to 100, 80 to 100, 1 to 50, 1 to 20, 1 to 10, 10 to 50, 20 to 80 or 50 to 80%, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90 or 100% by volume or mass. Prior to the heating, the precursor and the sulfur may be intimately mixed. A convenient way to achieve this is to simply grind the two together, e.g. in a ball mill. The ratio of sulfur to molybdenum may be from about 2:1 to about 10:1 on a molar basis, or about 2:1 to 5:1, 2:1 to 3:1, 2.5:1 to 10:1, 3:1 to 10:1, 5:1 to 10:1, 2.5:1 to 5:1 or 2.1:1 to 2.5:1, e.g. about 2:1, 2.1:1, 2.2:1, 2.3:1, 2.4:1, 2.5:1, 3:1, 3.5:1, 4:1, 4.5:1, 5:1, 6:1, 7:1, 8:1, 9:1 or 10:1. This ratio should be at least 2:1, but may be substantially greater than this, e.g. at least 5:1, at least 10:1, at least 20:1 or more. Thus sulfur may be in at least a twofold molar excess over molybdenum so as to allow for a high yield of MoS_2 .

[00053] The heating may be at a temperature of about 350 to about 550 °C, or about 350 to 500, 350 to 450, 400 to 550, 450 to 450, 400 to 500, 400 to 450 or 450 to 500 °C, e.g. about 350, 400, 450, 500 or 550 °C. The reaction may be conducted for sufficient time to achieve at least 90% conversion to MoS_2 . The sufficient time may be from about 1 to about 10 hours, or about 1 to 5, 1 to 2, 2 to 10, 5 to 10 or 2 to 5 hours, e.g. about 1, 2, 3, 4, 5, 6, 7, 8, 9 or 10 hours. It will be understood that the lower the temperature, the longer the required time of reaction.

[00054] Following formation of the catalyst, it may be cooled, e.g. to about ambient temperature (e.g. between about 20 and about 30 °C. It may be then subjected to an atmosphere containing oxygen. The oxygen may be mixed with a gas which is non-oxidisable under the conditions of the subjecting. This may serve to passivate the catalyst. The oxygen may be in a concentration of from about 0.5 to about 5% by volume, or about 0.5 to 2, 0.5 to 1, 1 to 5, 2 to 5 or 1 to 2%, e.g. about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5%. In some instances the concentration may be less than about 2%, or less than about 1.5 or 1%. This step may be performed at ambient temperature. It may be performed at a temperature between about 20 and about 40 °C, or about 20 to 30, 30 to 40 or 25 to 30 °C, e.g. about 20, 25, 30, 35 or 40 °C. It may be performed for about 0.5 to 5 hours, or about 0.5, 1, 1.5, 2, 2.5, 3, 3.5, 4, 4.5 or 5 hours.

[00055] If the reaction is conducted in a solvent, suitable solvents include solvents for the reagents. These typically have high dielectric constants, e.g. over about 30, optionally over 40, 50, 60, 70 or 80. The dielectric constant may be between about 30 and about 90, or about 30 to 80, 30 to 60, 40 to 90, 60 to 90 or 40 to 60, e.g. about 30, 40, 50, 60, 70, 80 or 90. These include water, DMF and mixtures thereof. More generally, many dipolar aprotic solvents may be suitable either alone, in mixtures with each other or in mixtures with water. Such solvents include DMSO, HMPT, HMPA, dioxane, THF etc. In this event, temperatures of about 150 to 250 °C may be used, or about 150 to 200, 200 to 250, 180 to 250, 180 to 220, 150 to 220 or 190 to 210 °C, e.g. about 150, 160, 170, 180, 190, 200, 210, 220, 230, 240 or 250 °C. Suitably such reactions may be conducted in a sealed container. This allows the temperature to exceed the normal boiling point of the solvent, or of any of the solvents in a mixed solvent used for the reaction.

[00056] As noted above, when the precursor contains sulfur, there may be no necessity to separately add sulfur. Therefore in this instance the reaction may be conducted in the absence of sulfur (i.e. elemental sulfur). A suitable precursor for sulfur-free MoS₂ synthesis is thiomolybdate salt such as ammonium thiomolybdate. However in an embodiment, thiomolybdate may be used in the presence of elemental sulfur.

[00057] The catalyst produced by the process described above may be nanosized. This refers to catalysts that have at least one dimension, optionally 2 or 3 dimensions, that is within the range of 1 to 999nm, i.e. that is a nano-dimension. The nano-dimension, or each nano-dimension independently, may be in the range of about 1 to about 500, 1 to 200, 1 to 100, 1 to 50, 1 to 20, 1

to 10, 10 to 999, 20 to 999, 50 to 999, 100 to 999, 200 to 999, 500 to 999, 10 to 500, 10 to 100, 10 to 50, 50 to 500, 50 to 100 or 100 to 500 nm, e.g. about 1, 2, 3, 4, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, 100, 150, 200, 250, 300, 350, 400, 450, 500, 600, 700, 800, 900, 95 or 999nm.

[00058] The MoS₂ produced by the process may be pure. This should not preclude the presence of a catalyst support (as discussed above), which is not accounted for in determining the purity of the catalyst. The purity of the catalyst may be at least about 80% or a weight or mole basis, optionally at least about 85, 90, 95, 96, 97, 98, 99, 99.5 or 99.9%.

[00059] In the event that the MoS₂ is supported, the support may be as discussed earlier. The ratio of MoS₂ to support may be from about 1:1 to about 1:3 on a weight basis, or about 1:1 to 1:2, 1:2 to 1:3 or 2:3 to 2:5, e.g. about 1:1, 2:3, 1:2, 2:5, 1:3 or 35:65.

[00060] The catalyst of the invention, either supported or unsupported, may be used for generating methane from carbon monoxide and hydrogen. The carbon monoxide and hydrogen may be in a ratio of about 1:1 to about 1:4 on a mole or volume basis, or about 1:1 to 1:3, 1:1 to 1:2, 1:2 to 1:4 or 1:2 to 1:3, e.g. about 1:1, 2:3, 1:2, 2:5, 1:3, 2:7 or 1:4. However the catalysts of the present invention are quite tolerant to varying ratios, and ratios other than those described may also be used. The reaction may be conducted at a suitable temperature, for example about 400 to about 700 °C, or about 400 to 600, 400 to 500, 500 to 700, 600 to 700 or 500 to 600 °C, e.g. about 400, 450, 500, 550, 600, 650 or 700 °C. The catalyst of the invention is remarkably resistant to poisoning by sulfur containing substances. Therefore the feed gas mixture may comprise a sulfur containing gas, e.g. hydrogen sulfide.

[00061] Prior to being used as a catalyst as described above, the material of the invention may be treated with a reducing agent, e.g. hydrogen sulfide. Suitable conditions are for example 5% H₂S in H₂ for 1 h. This pretreatment may serve to remove surface oxides

[00062] EXAMPLE 1

[00063] Unsupported MoS₂ catalyst was prepared by mixing ammonium tetrathiomolybdate (ATM) with elemental sulfur and subsequently transferred into a tube furnace. The reaction was carried out in a mixture of hydrogen and nitrogen environment at a temperature of 450 °C for 5 h. The catalyst was passivated with 1% O₂ in N₂ at a flow rate of 30 mL/min for 1 h before

retrieving the catalyst. The resultant catalyst is in the form of black powder. This method is identified as ATM+S method.

[00064] Supported MoS₂ catalysts were prepared through chemical vapor reaction method using a tube furnace. ATM was used as the precursor and the thermal decomposition was carried out in a quartz tube reactor. Typically, 1.0 g of support, 1.461 g of ATM and 4.3828 g of sulfur powder were mixed in mortar before transferring the mixture to a ceramic boat which is placed inside a quartz tube. The mixture was heated in H₂/N₂ (1:2) atmosphere with a total gas flow rate of 30 mL/min and with a heating rate of 5 °C/min to 450 °C for 5 h. After the reactor has cooled down to room temperature. The catalyst was passivated with 1% O₂ in N₂ at a flow rate of 30 mL/min for 1 h before retrieving the catalyst. The catalyst was collected and tested in a fixed-bed microreactor.

[00065] The reducing environment during the synthesis of the MoS₂ catalyst was to make sure MoS₂ was formed instead of forming MoS₃ when only inert gas was used. Sulfur is considered to be important in the formation of nano-structure MoS₂. The role of sulfur is not just as a donor for sulfur since ATM contains sulfur, but to provide saturated sulfur vapor during the reaction which is thought to be important for the self-assembly of nano-sized MoS₂ flowers in the gas phase.

[00066] The use of sulfur in excess (S/Mo >> 2) and decomposition of ATM in reducing gas (H₂) greatly affects the morphology of the MoS₂ catalyst. Decomposition of ATM in inert gas will only produce MoS₂ catalyst with smooth surface (Fig. 1A). Including sulfur will create roughness on the surface of MoS₂ but not produce the desired nano-flower-like morphology (Fig. 1B). Decomposition of ATM without sulfur but with H₂ gas will produce other types of nanostructures as shown in Fig. 1C. Previous workers have also reported the observation of MoS₂ nanotubes or fibers when ATM was decomposed in H₂, but these are not the desired nanoflower morphology as shown in Fig. 1D which can be achieved by decomposing ATM in H₂ and with the addition of large quantity of elemental sulfur.

[00067] For activity evaluation, 0.8 g of MoS₂ catalyst was loaded into a stainless steel reactor. Prior to the activity test, the catalyst was treated with 5% H₂S in H₂ for 1 h to remove surface oxides. During the activity test, a syngas ratio (H₂/CO) of 1.0 was selected and a reaction temperature of 550 °C was used. H₂ and CO flow was 23.33 sccm, and the remaining inert gas

was N₂ which was flowing at 20 sccm. 3000 ppm of H₂S was fed into the reactant stream. Main products obtained from the reaction using this catalyst were CH₄ and CO₂.

[00068] Fig. 2 shows the CO conversion and CH₄ selectivity of the MoS₂ catalysts, unsupported or supported on different catalyst supports. Three supports: hydrotalcite from SASOL (PURAL® MG 30, labeled as Al-Mg30), SiO₂ and Al₂O₃ were used to compare the activity of MoS₂ catalyst on support. The CH₄ selectivity for all these MoS₂ catalysts testing at the present condition is able to reach the equilibrium selectivity therefore the discussion will concentrate on the CO conversion. The average CO conversion of the catalysts are calculated after the reaction had reached the steady state, which is around 3 h after the reactor reached the temperature and pressure set points. The average CO conversion of MoS₂(ATM+S)-unsupported was 81.9%, while it was 81.6% for 35%MoS₂(ATM+S)/Al-Mg30, 80.5% for 35%MoS₂(ATM+S)/SiO₂ and 78.1% for 35%MoS₂(ATM+S)/Al₂O₃. The activity of 35%MoS₂(ATM+S)/Al-Mg30 is similar to that of MoS₂(ATM+S)-unsupported even though the loading of MoS₂ was lower by 1/3, while the other two materials (SiO₂ and Al₂O₃) were less efficient as the support for MoS₂ catalyst prepared by the present method. C. The isoelectric points (IEP) of MgO, Al₂O₃ and SiO₂ are known and it has been found that MgO is strongly basic (IEP = 11.6), Al₂O₃ is slightly basic (7.2) while SiO₂ is acidic (2.8). It is considered that the IEP of the support determines the principle interaction of the supported molybdenum ion. There is evidence that the higher IEP of the support, the stronger depolymerization of the precursor. Therefore, MoS₂ supported on Al-Mg30, which consists of 30% MgO and 70% Al₂O₃, is expected to have better dispersion compared with the catalyst supported on Al₂O₃ and SiO₂. This is confirmed by the observation using scanning electron microscopy (SEM).

[00069] Fig. 3 shows the SEM images of the catalysts. The bulk morphology of MoS₂(ATM+S)-unsupported is presented in Fig. 3A. The MoS₂ particles in Fig. 3A typically have dimensions of around 30 to 40 microns. Fig. 3B shows the morphology of MoS₂(ATM+S)-unsupported at higher magnification. From the SEM image, the surfaces of the MoS₂ slabs are decorated with nano-flowers with petals of less than 100 nm. This nano-structure formed through the self-assembly during decomposition of the precursor is the reason for the high activity of the MoS₂ catalyst. However, the formation of large slabs of MoS₂ from these nanoflowers limited the utilization of the active sites in the center of the MoS₂ blocks. Therefore a suitable support is needed for better dispersion of the MoS₂ catalyst. Fig. 3C depicts 35 wt% MoS₂ supported by Al-Mg30. Small flakes of MoS₂ nanoflowers can be observed on Al-Mg30.

As shown in Fig. 3D and 3E, Al_2O_3 and SiO_2 are not effective for dispersing MoS_2 because slabs of MoS_2 similar to that of the unsupported MoS_2 are still observable.

[00070] EXAMPLE 2

[00071] Ammonium heptamolybdate tetrahydrate (AHM) can be used as precursor to mix with sulfur and subsequently react under similar conditions to produced unsupported MoS_2 catalyst. The catalyst obtained was labeled as $\text{MoS}_2(\text{AHM}+\text{S})$ -unsupported. The CO conversion $\text{MoS}_2(\text{AHM}+\text{S})$ -unsupported is presented in Fig. 4. The average CO conversion for this catalyst is 81.8 %, which is comparable to that of $\text{MoS}_2(\text{ATM}+\text{S})$ -unsupported and 35% $\text{MoS}_2(\text{ATM}+\text{S})/\text{Al-Mg30}$. However, the supported catalyst prepared by AHM+S method, which is labeled as 35% $\text{MoS}_2(\text{AHM}+\text{S})/\text{Al-Mg30}$ shows significantly lower activity.

[00072] Fig. 5 compares the SEM image of 35% $\text{MoS}_2(\text{AHM}+\text{S})/\text{Al-Mg30}$ with that of 35% $\text{MoS}_2(\text{ATM}+\text{S})/\text{Al-Mg30}$. In Fig. 5A, the MoS_2 formed nanowalls with thicker edges on Al-Mg30 when AHM is used as the precursor. This morphology is very different from the MoS_2 flakes with nanoflowers on its surface as observed in 35% $\text{MoS}_2(\text{ATM}+\text{S})/\text{Al-Mg30}$ (Fig. 5B). The structure of MoS_2 in 35% $\text{MoS}_2(\text{AHM}+\text{S})/\text{Al-Mg30}$ is not favorable for methanation and therefore lower activity as shown in Fig. 4. The interaction of the precursor (AHM) with the support (Al-Mg30) is apparently too strong and hence led to the formation of the MoS_2 nanowalls. On the other hand, the interaction of ATM with Al-Mg30 appears to be enough to disperse the MoS_2 catalyst through depolymerization of the precursor but not too strong to react chemically with the support. Therefore a suitable precursor with the desired interaction strength with the support appears to be important in the synthesis of active MoS_2 catalyst. The reason for the stronger interaction of the AHM precursor with the support is thought to lie in the polymolybdate species. The Mo-O-Mo species in the AHM precursor interacts more strongly with the oxide support compared with the ATM precursor which has no oxygen. Furthermore, AHM precursor would have higher degree of polymerization than ATM, since oxygen is more electronegative than sulfur. Higher polymerization might lead to autoreduction of the AHM precursor which is not considered to be favourable for the self-assembly of MoS_2 layered structure.

[00073] EXAMPLE 3

[00074] Fig. 6 shows the CO conversion of MoS₂ catalysts with different loadings prepared by ATM+S method. The activity of the catalysts increased from 68.5% to 81.6% as the MoS₂ loading increased from 25% to 35% and slightly dropped to 80.5% when the loading increased to 50%. Consequently 35% is a suitable loading for the supported catalysts. Fig. 7A shows the SEM images of 25%MoS₂(ATM+S)/Al-Mg30, 35%MoS₂(ATM+S)/Al-Mg30 and 50%MoS₂(ATM+S)/Al-Mg30. The lower loading of 25%MoS₂(ATM+S)/Al-Mg30 allowed the precursor to have stronger interaction with the support, therefore the formation of undesired MoS₂ nanowalls are found on the support (Fig. 7A). At higher loading (35%), MoS₂ flakes with nanoflower morphology are dispersed on the support (Fig. 7B), but as the loading increased to 50%, the MoS₂ flakes clustered together, which somehow lowered the surface available for reaction.

[00075] EXAMPLE 4

[00076] Alternatively, hydrotalcite supported MoS₂ catalyst can be prepared in a low temperature environment, i. e. through hydrothermal method which is less costly. The method begins with dissolving 1.461 g of ATM in 80 ml of solvent by sonication for 20 min. 1 g of support is added after the molybdenum source was fully dissolved. The mixture was sonicated for another 20 min and 0.01 g of NaBH₄ was added to the mixture before transferring the mixture into a Teflon-lined autoclave. The autoclave was heated to 200 °C for 10 h. After the reaction, the mixture was washed with de-ionized water and filtered. The catalyst collected was in the form of black powder.

[00077] For the activity evaluation, 0.8 g of MoS₂ catalyst was loaded into a stainless steel reactor. The reaction conditions are similar to the description given in Example 1.

[00078] Fig. 8 shows the CO conversion of the catalysts prepared using hydrothermal method. The MoS₂ catalysts were supported on Al₂O₃, SiO₂, hydrotalcite (Al-Mg30), activated carbon (Act-C) and carbon nanotubes (CNT). All catalysts were prepared using dimethylformamide (DMF) as solvent except for 35%MoS₂(H₂O)/Al-Mg30-hydro which was prepared using de-ionized water as solvent. Carbon supports are generally not effective compare to the other support which can be observed from the low CO conversion (~30%). Al-Mg30 was found to be the most effective support, with a CO conversion of about 60% compared with all hydrothermal catalysts prepared using DMF as solvent. When the solvent changed to water, the MoS₂ catalyst

using the same support (Al-Mg30), the performance improved by nearly 10%. This shows that by combining the right support and solvent, the MoS₂ prepared can be more effective.

[00079] Fig. 9 shows the SEM images of 35%MoS₂(H₂O)/Al-Mg30-hydro. From the images, it can be observed that the MoS₂ formed on the support exhibit two different types of morphologies, one resembles nanowalls on the support, while the other resembles nanoplates scattered on top of the support. Both of structures exposed the edge sites of the MoS₂ catalyst, therefore the catalyst is effective for CO methanation as shown in Fig. 8.

[00080] The difference in the performance between the 35%MoS₂/Al-Mg30-hydro prepared using DMF and water can be explained by the polarity index of the solvent. ATM is highly soluble in polar solvents. The polarity of water (dielectric constant = 80) is significantly higher than that of DMF (dielectric constant = 38), therefore ATM is more soluble in water. This led to weaker interaction of the precursor with the support, and reduce autoreduction which may cause by the support. Consequently this helps in the self-assembly of MoS₂ catalyst. Better solubility in the solvent also reduces the polymerization of the precursor, which might help in the formation of smaller clusters and more dispersed MoS₂ catalyst.

[00081] In one form, the present invention provides a method of producing a nano-sized MoS₂ catalyst. The method begins by mixing ammonium tetrathiomolybdate (ATM) and elemental sulfur in a mortar. The reaction of the mixture is carried out in a reducing environment at elevated temperature in a tube furnace. This demonstrated the preservation of the self-assembly process that led to desired morphology under sulfur-rich and reducing environment.

[00082] In a second form, the MoS₂ catalyst can be also produced by mixing ATM, elemental sulfur and a suitable support in a mortar. The mixture is then transfer to a tube furnace and the reaction is carried out in a mixture of hydrogen and nitrogen environment at a temperature of 450 °C for 5 h. The support serves to reduce the loading of MoS₂ used in the methanation while maintaining the nano-sized morphology of the catalyst as well as its activity. A suitable support material was chosen to enhance dispersion and suppress the chemical interaction of precursor with the support.

[00083] In another form, the present invention provides another method of reacting ATM and a support under hydrothermal conditions. The method starts by mixing ammonium tetrathiomolybdate, a support and a reducing agent in a solvent. Subsequently, the mixture is

transferred into a Teflon-lined autoclave and heated at 200 °C for 10 h. Suitable solvent and support were chosen to enhance depolymerization and reduce autoreduction of the precursors

[00084] Thus, described herein is a method that facilitates the self-assembly of nano-sized molybdenum disulfide catalyst with or without support prepared using chemical vapor deposition in a saturated sulfur source and reducing environment. A suitable support is PURAL® MG 30 from SASOL. The temperature of the reaction may be 450 °C. The sulfur source may be the vapor from elemental sulfur. The reducing gas may be H₂. The MoS₂ catalyst may have a total CO conversion in syngas direct methanation greater than 80%.

[00085] There is also described a method that facilitates the self-assembly of nano-sized molybdenum disulfide catalyst using hydrothermal method. As above, in this method the support may be PURAL® MG 30 from SASOL. The temperature of the reaction may be 200 °C. The solvent may be water.

[00086] There is also described the use of hydrotalcite support accompanied by the flow of H₂ in the preparation of a MoS₂ catalyst from ammonium tetrathiomolybdate via sulfur vapor synthesis.

[00087] Further, there is described the use of hydrotalcite support in the hydrothermal synthesis of MoS₂ catalyst from ammonium tetrathiomolybdate with water as solvent.

An advantage of the present invention is the tolerance of the catalyst to H₂S. As a result, syngas can be used without purification. This can result in higher CO conversion compared with conventional impregnation methods. The process of the invention results in unique morphologies as observed in the SEM images. These include clusters of nanoflowers, nanowalls or nanoplates for the hydrothermal catalyst. High CO conversion, e.g. 70% to 80% at 550 °C, has been achieved.

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 and in the absence of liquid solvent, and 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 in a reducing atmosphere at a temperature of 400 to 500°C 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 disulfide and wherein the molybdenum sulfide catalyst 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.