Processes for producing hydrogen from hydrocarbon feed sources

Figure 4

Abstract: Processes are provided for producing hydrogen wherein at least a metal halide and a hydrocarbon feed source and/or a gas stream comprising methane are combined.
Declarations under Rule 4.17:
— as to applicant’s entitlement to apply for and be granted a patent (Rule 4.17(U))
— as to the applicant’s entitlement to claim the priority of the earlier application (Rule 4.17(iii))
— of inventorship (Rule 4.17(iv))

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BACKGROUND

[0001] Hydrogen is useful in the production of ammonia, methanol, gasoline, heating oil, and rocket fuel. It is also used to make fertilizers, glass, refined metals, vitamins, cosmetics, semiconductor circuits, soaps, lubricants, cleaners, and even margarine and peanut butter.

[0002] Other possible uses for hydrogen include fueling internal combustion engine vehicles or fuel-cell vehicles.

[0003] In spite of technologies that are currently described and available, a need exists for commercially feasible means for production of hydrogen.

THE INVENTION

[0004] This invention meets the above-described needs by providing processes for producing H₂.

[0005] We have discovered that H₂ can be produced directly from methane and/or other hydrocarbon feed sources by processes that comprise combining at least gaseous methane and/or a hydrocarbon feed source and a metal halide suitable for catalyzing polymerization of the methane. A benefit of processes of this invention is that usable H₂ is produced, as is described in greater detail below. A component suitable for absorbing hydrogen can be used in processes of this invention for recovery of the usable H₂. Alternatively, H₂ can be recovered by techniques familiar to those skilled in the art, such as by pressure swing absorption, distillation, and the like. The availability of usable H₂ is advantageous in that it can be used as a clean-burning fuel with reduced CO₂ emissions as compared to traditional fuels.

[0006] Also provided by this invention are processes for producing H₂, the process comprising combining at least a hydrocarbon feed source and a metal halide at a temperature of at least 100°C and yielding at least H₂; such processes wherein the metal halide comprises aluminum bromide, aluminum chloride, aluminum fluoride, titanium bromide, or aluminum iodide; such processes wherein the hydrocarbon feed source comprises a paraffin wax, polyethylene, plastic grocery bags, C₁₀ straight chain paraffins, isopentane, cyclohexane, heptane, acetylene, or ethylene; such processes
further comprising combining an additional component with the at least hydrocarbon feed source and metal halide, wherein the additional component comprises methyl iodide, titanium bromide, a branched hydrocarbon, ethane, hydrogen, an alkyl halide, an olefin, or a metal halide comprising Li, Na, K, Mg, Ca, Sc, Y, Zr, Cu, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and bromine, chlorine, fluorine, or iodine; such processes further comprising combining a halogen with the at least hydrocarbon feed source and metal halide; such processes further comprising combining a hydrogen halide with the at least hydrocarbon feed source and metal halide; such processes further comprising combining a hydrogen halide and an additional component with the at least hydrocarbon feed source and metal halide, wherein the additional component comprises methyl iodide, titanium bromide, a branched hydrocarbon, ethane, hydrogen, an alkyl halide, an olefin, or a metal halide comprising Li, Na, K, Mg, Ca, Sc, Y, Zr, Cu, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and bromine, chlorine, fluorine, or iodine; and such processes further comprising combining gaseous methane with the at least hydrocarbon feed source and metal halide.

[0007] Also provided are processes for producing H₂ comprising: combining at least a hydrocarbon feed source and a metal halide at about 350°C, cracking at least some of the hydrocarbon feed source to C₁ or higher hydrocarbons; and polymerizing at least some of the C₁ or higher hydrocarbons; yielding at least H₂ and C₂ and higher hydrocarbons.

[0008] Also provided are processes for producing H₂, the processes comprising combining at least a gas stream comprising methane and a metal halide at a temperature of at least 100°C and yielding at least H₂; such processes wherein the gas stream comprises at least about 50 vol% methane; such processes wherein the gas stream comprises at least about 75 vol% methane; such processes wherein the metal halide comprises aluminum bromide, aluminum chloride, aluminum fluoride, titanium bromide, or aluminum iodide; such processes wherein the metal halide comprises aluminum bromide; and such processes wherein the process comprises combining at least the gas stream comprising methane, the metal halide, and a component suitable for absorbing hydrogen.

[0009] Also provided are processes for producing H₂, comprising: (a) heating a metal halide to a melt temperature at least high enough to melt the metal halide; (b) combining at least a gas stream comprising methane and the heated metal halide; (c) producing C₂ and higher hydrocarbons; and (d) producing H₂.
[0010] Also provided are processes for producing \( \text{H}_2 \), comprising: (a) heating a metal halide to a melt temperature at least high enough to melt the metal halide; (b) combining at least a gas stream comprising methane, a halogen, and the heated metal halide; (c) producing \( \text{C}_2 \) and higher hydrocarbons; and (d) producing \( \text{H}_2 \).

[0011] Also provided are processes comprising combining at least gaseous methane and a Lewis acid at at least \( 100^\circ \text{C} \), yielding at least \( \text{H}_2 \) and \( \text{C}_2 \) and higher hydrocarbons. Suitable Lewis acids include, without limitation, metal halides such as aluminum bromide. As is familiar to those skilled in the art, a Lewis acid is defined as a compound capable of accepting an electron pair.

[0012] Also provided are processes comprising combining at least gaseous methane and a Lewis acid at at least a temperature at which at least some of the Lewis acid is gaseous, yielding at least \( \text{H}_2 \) and \( \text{C}_2 \) and higher hydrocarbons.

[0013] Also provided are processes comprising combining at least gaseous methane, a Lewis acid, and a Bronsted acid, e.g., \( \text{HBr} \), at at least \( 100^\circ \text{C} \), yielding at least \( \text{H}_2 \) and \( \text{C}_2 \) and higher hydrocarbons. As is familiar to those skilled in the art, a Bronsted acid is defined as a compound capable of donating a proton.

[0014] Also provided are processes comprising combining at least gaseous methane, a Lewis acid, and a Bronsted acid, e.g., \( \text{HBr} \), at at least a temperature at which at least some of the Lewis acid is gaseous, yielding at least \( \text{H}_2 \) and \( \text{C}_2 \) and higher hydrocarbons.

[0015] These and other aspects of the invention are described herein and by reference to the Figures, in which:

- Figure 1 illustrates a batch process according to this invention; and
- Figure 2 illustrates a batch process according to this invention; and
- Figure 3 illustrates a batch process according to this invention; and
- Figure 4 illustrates a continuous process according to this invention.

[0018] \( \text{C}_2 \) and higher hydrocarbons produced according to processes of this invention can include without limitation \( \text{C}_2 \) to \( \text{C}_{30} \) hydrocarbons, particularly \( \text{C}_2 \) to \( \text{C}_{12} \) hydrocarbons or \( \text{C}_4 \) to \( \text{C}_8 \) hydrocarbons. The \( \text{C}_2 \) and higher hydrocarbons produced according to this invention can include normal and iso alkanes (\( \text{C}_n \text{H}_{2n+2} \)), cyclic alkanes (\( \text{C}_n \text{H}_{2n} \)), alkenes (\( \text{C}_n \text{H}_{2n+2} \)), alkynes (\( \text{C}_n \text{H}_{2n+2} \)), aromatics, and the like.

[0017] The gaseous methane can be provided by a natural gas stream co-produced with oil or otherwise produced, or a natural gas stream from any other suitable source. For example, the gas stream can be produced from coal beds (e.g., anthracite or
bituminous), biogas produced by the anaerobic decay of non-fossil organic material from swamps, marshes, landfills, and the like, biogas produced from sewage sludge and manure by way of anaerobic digesters, biogas produced by enteric fermentation particularly in cattle and termites, and from other gas sources. \( \text{H}_2 \) can be added with the gas stream.

[0018] The gas stream can comprise at least about 50 vol% methane, or at least about 75 vol% methane. Other components can be present in the gas stream, for example, ethane, butane, propane, carbon dioxide, nitrogen, helium, hydrogen sulfide, water, odorants, mercury, organosulfur compounds, etc. Such components can be removed as needed from the gas stream prior to, during, or after processing according to this invention using techniques familiar to those skilled in the art. The gas stream can consist essentially of methane, e.g., can be zero grade, or essentially pure, methane.

[0019] This invention also provides processes for producing \( \text{C}_2 \) and higher hydrocarbons comprising combining at least a hydrocarbon feed source and a metal halide within a temperature range in which at least some of the metal halide is gaseous. Suitable hydrocarbon feed sources include without limitation, paraffin waxes, high density polyethylene, plastic grocery bags, \( \text{C}_{16} \) straight chain paraffins, isopentane, cyclohexane, heptane, acetylene, ethylene, etc.

[0020] Other components can be present in the hydrocarbon feed source, for example, oxygen, nitrogen, helium, hydrogen sulfide, water, odorants, mercury, organosulfur compounds, etc. Such components can be removed as needed from the hydrocarbon feed source prior to, during, or after processing according to this invention using techniques familiar to those skilled in the art. A stream comprising gaseous methane can be combined with the hydrocarbon feed source.

[0021] The metal halide or other Lewis acid can be suitable for catalyzing polymerization of methane and can comprise aluminum bromide (e.g., \( \text{AlBr}_3 \) or \( \text{AlBr}_4 \)), aluminum chloride, aluminum fluoride, aluminum iodide, titanium bromide, and the like, including mixtures thereof. For example, titanium bromide in the form of \( \text{TiBr}_2 \), \( \text{TiBr}_4 \), and the like can be used. Without limiting this invention, metal halides comprising a metal such as Li, Na, K, Mg, Ca, Sc, Y, Zr, Cu, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and a halogen such as bromine, chlorine, iodine, or fluorine may also be used in processes of this invention. The metal halide can have a purity of 100% or less than 100%. For example, the metal halide can be of a commercial grade, can have a...
purity of at least about 95%, or at least about 98%, or at least about 99%, or at least about 99.9%. Impurities can be present on the surface of the metal halide(s); and such impurities can participate in reactions that occur during processes of this invention.

[0022] The metal halide can be heated such that it is at a temperature, or is within a temperature range, that is at least high enough to gasify at least some of the metal halide. When the metal halide comprises aluminum bromide, the temperature can be at least about 100°C, and can be from about 100°C to about 400°C, or about 250°C to about 350°C.

[0023] When a hydrogen halide is used in processes of this invention, any suitable hydrogen halide can be used, for example hydrogen bromide. When a hydrogen halide, such as hydrogen bromide for example, is used, it can have a purity of about 100% or less than about 100%. For example, the hydrogen halide can be of a commercial grade, can have a purity of at least about 95%, or at least about 98%, or at least about 99%, or about 99.9%. Additionally, the hydrogen halide can have a purity of at least about 50% or at least about 90% and can comprise various impurities such as H₂O, CO, CO₂, O₂, HCl, HF, Br₂, Cl₂, fluoride, or iodine, to name a few. The same is true when another hydrogen halide is used, such as hydrogen fluoride, or hydrogen chloride, or hydrogen iodide.

[0024] The component suitable for absorbing hydrogen can comprise Raney nickel, platinum, palladium, tantalum, niobium, yttrium, platinum on carbon, palladium on carbon, platinum on activated carbon, palladium on activated carbon, etc. Raney nickel can be comprised of aluminum-nickel alloy. Given the teachings of this disclosure, one skilled in the art can select an suitable component for absorbing hydrogen.

[0025] Processes according to this invention for producing C₂ and higher hydrocarbons can comprise combining at least gaseous methane, a metal halide, and an additional component. Without limiting this invention, the additional component (sometimes referred to herein as a promoter) can comprise a halogen such as bromine, chlorine, fluorine, or iodine; methyl iodide; titanium bromide; metal halides comprising a metal such as Li, Na, K, Mg, Ca, Sc, Y, Zr, Cu, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and a halogen such as bromine, chlorine, fluorine, or iodine; branched hydrocarbons such as isopentane, neopentane, and the like; ethane; hydrogen; alkyl halides such as methyl bromide, ethyl bromide, and the like; and/or olefins such as propene, butene, and the like. One or more additional components can be combined. Such additional components can be generated in situ. For example, combined
methane and bromine can generate methyl bromide in situ; combined hydrogen bromide and ethylene can generate ethylene bromide in situ, etc..  

[0026] Referring, for example, to Figure 1, in processes of this invention, the metal halide 114 can catalyze polymerization of methane in gaseous methane stream 118 to C₂ and higher hydrocarbons. Gaseous methane stream 118 can comprise ethane, butane, olefins, etc., in addition to the methane. The metal halide 114 can be in a container 112. The container 112 can be heated by any suitable means, e.g., by a heated sand bed 116, so that the metal halide 114 is heated, e.g., at least to its melting temperature. The gaseous methane stream 118 can be injected into (or otherwise put into) the container 112 such that the metal halide 114 catalyzes polymerization of the methane. For example, the residence time of methane in the gaseous methane stream 118 within the container 112 and other conditions, such as temperature, can be adequate to initiate polymerization of the methane. For example, the residence time of methane in the gaseous methane stream 118 within the container 112 and other conditions, such as temperature, can be adequate to initiate polymerization of the methane. For example, residence time can be up to about one minute. Longer residence times can be used. For example, residence time of methane in the gaseous methane stream 118 within the container 112 can be longer than about one minute, for example from about one minute to about five minutes, or up to about two minutes. A substantial portion of the polymerization can occur in vapor phase 119. Simultaneously with the polymerization in vapor phase 119, some of the polymerized higher hydrocarbons can be cracked, e.g., by thermal cracking, acid cracking, etc.. At appropriately high temperatures, olefins are formed and hydrogen given off can assist in the cracking process. For example, the temperature can be above about 350°C, or can be from about 350°C to about 400°C. At lower temperatures, cracking can be achieved without the assistance of olefins by addition of hydrogen. For example, at a temperature of up to about 350°C, or at about 110°C, cracking can be assisted by addition of hydrogen under pressure. Thermal reforming of hydrocarbons, isomerization of hydrocarbons, and other reactions can also occur in vapor phase 119 and/or elsewhere in container 112. Skeletal or bond isomerization can occur. The metal halide can catalyze polymerization of the methane by action as a Lewis acid. Although not illustrated in Figure 1, hydrogen given off during the polymerization of the methane can be recovered for sale or use, e.g., by being absorbed by a component suitable for absorbing hydrogen, which component
may be in the container 112 with the metal halide 114 or may be in a separate container through which the gaseous methane stream 118 (or a resulting product/product stream (not shown in Figure 1)) is subsequently passed. Produced C2 and higher hydrocarbons can be recovered from container 112 by means known to those skilled in the art (not illustrated in Figure 1). Given the teachings of this disclosure, those skilled in the art can determine appropriate temperatures, pressures, and other process parameters as desired to achieve desired results using processes of this invention.

[0027] Referring, for example, to Figure 2, in processes of this invention, metal halide 214 can catalyze polymerization of methane in gaseous methane stream 218 to C2 and higher hydrocarbons. The metal halide 214 can be in a container 212. Also, component 215 (e.g., packing) can be put into container 212, e.g., for the purpose of increasing surface area within container 212 and/or for supporting the metal halide 214. One benefit of component 215 is that additional surface area is provided for surface activated polymerization reactions. Gas/vapor phase polymerization reactions can also occur. Suitable packing materials will be well known to those skilled in the art, given the teachings of this disclosure, and can include, for example, glass beads, aluminum oxides, and zeolites. The container 212 can be heated by any suitable means, e.g., by a heated sand bed 216, so that the metal halide 214 is heated, e.g., to at least its melting temperature. The gaseous methane stream 218 can be injected into (or otherwise put into) the container 212 such that the metal halide 214 catalyzes polymerization of the methane. For example, the residence time of methane in the gaseous methane stream 218 within the container 212 and other conditions, such as temperature, can be adequate to initiate polymerization of the methane. A substantial portion of the polymerization can occur on the surface of component 215 and/or in vapor phase 219. Simultaneously with the polymerization on the surface of component 215 and/or in vapor phase 219, some of the polymerized higher hydrocarbons can be cracked by, e.g., thermal cracking, acid cracking, or the like. ThermaS reforming of hydrocarbons, isomerization of hydrocarbons, and other reactions can also occur in vapor phase 219 and/or elsewhere in container 212. Although not illustrated in Figure 2, hydrogen given off during the polymerization of the methane can be recovered for sale or use, e.g., by being absorbed by a component suitable for absorbing hydrogen, which component may be in the container with the metal halide or may be in a separate container through which the gaseous methane stream is subsequently passed.
Produced C\textsubscript{2} and higher hydrocarbons can be recovered from container 212 by means known to those skilled in the art (not illustrated in Figure 2).

[0028] The vapor phase (e.g., 119 in Figure 1 or 219 in Figure 2) can comprise ionic species in that the pressure and temperature conditions allow a substantial portion of the metal halide to remain available as a salt in the vapor phase. A vapor phase containing such ionic species can be conducive to reactions such as alkylation, isomerization, and the like.

[Q029] Byproducts of processes according to this invention can include red oil or red oil like substances. Red oil is a clathrate of at least olefinic hydrocarbon(s), aluminum halide(s), and, in some cases, Bronsted acid(s) and/or other Lewis acid(s).

[0030] A benefit of processes of this invention is that components having a catalytic effect on the polymerization reactions taking place, e.g., aluminum bromide and hydrogen bromide, for example, either do not require regeneration, e.g., when conditions are maintained to minimize tar formation during processes of this invention, or can be regenerated in situ with hydrogen pressure at the appropriate temperature.

Examples

[0031] The following examples are illustrative of the principles of this invention. It is understood that this invention is not limited to any one specific embodiment exemplified herein, whether in the examples or the remainder of this patent application.

[0032] At an offshore oil production site, natural gas comprising at least about 50 vol\% methane is being co-produced with oil. Given the remote location of the production site and limited available space on the offshore platform, the natural gas is being flared. None of the valuable energy potential of the methane is being utilized.

[0033] To improve the situation, a process according to the present invention is used to produce higher hydrocarbons from the methane. The higher hydrocarbons as well as the hydrogen produced during the process are utilized as fuel at the platform, thus providing a substantial economic benefit to the site.

[0034] Referring to Figure 3, natural gas stream 318 comprises on average from about 70 vol\% to about 85 vol\% methane, and also includes other components such as ethane, butane, propane, carbon dioxide, nitrogen, helium, and hydrogen sulfide. Instead of being flared, at least a portion of natural gas stream 318 is passed through container 312. Device 313 in container 312 is supported by inert material 310. Device 313 is made from glass, an inert material. Inert material 310 is glass beads; and in
addition to supporting device 313, inert material 310 fills at least some of the otherwise empty space in container 312. In general, inert materials 310 used in this invention can include glass and other suitable inert materials. A slurry 317 of about 3 grams to about 5 grams of aluminum bromide 314 and about 0.5 grams to about 2 grams platinum-on-activated-charcoal 315 is in device 313. The temperature inside container 312 is maintained between about 250°C and 400°C by heated sand bed 316. Residence time of methane (in natural gas stream 318) within container 312 is from about 1 minute to about 30 minutes. The conditions in container 312 are adequate to catalyze polymerization of methane to C2 and higher hydrocarbons. A substantial portion of the polymerization occurs in vapor phase 319. Simultaneously with the polymerization in vapor phase 319, some of the polymerized higher hydrocarbons are thermally cracked. During the polymerization, produced hydrogen is absorbed by platinum-on-activated-charcoal 315, or another suitable hydrogen absorber. Outlet gas stream 320, exiting container 312 and comprising produced C2 and higher hydrocarbons and any unreacted methane, is input to device 330. Within device 330, recycle stream 334 comprising any unreacted methane is separated from product stream 332 comprising liquefied C2 and higher hydrocarbons. Recycle stream 334 comprising methane is input into container 312 along with natural gas stream 318. Product stream 332 comprising liquefied C2 and higher hydrocarbons is removed from device 330 and is put into storage containers (not illustrated in Figure 3) for use as fuel and for chemical feedstock needed at the offshore production site, or is used directly without being stored. Intermittently, platinum-on-activated-charcoal 315 is removed from device 313 in container 312 and replaced with fresh platinum-on-activated-charcoal 315. Hydrogen is recovered as removed platinum-on-activated-charcoal 315 is regenerated for reuse within container 312, using means known to those skilled in the art. The replacement and regeneration of platinum-on-activated-charcoal 315, and recovery of hydrogen therefrom, are not illustrated in Figure 3. Recovered hydrogen is stored for use as fuel, or used directly without being stored.

[0035] Referring to Figure 4, which illustrates continuous process system 599 according to this invention, gaseous feedstock in container 500 comprises gaseous methane, HBr, ethane and hydrogen. The gaseous feedstock is fed via conduit 510 to conduit 520. Pressure regulator 530 is used to regulate the pressure within container 500. Flow valve 540 is used to control flow through rotometer 545. Container 550 contains aluminum bromide 560. Aluminum bromide 560 is heated to about 100°C by
heat provided by a heating source, e.g., a heating mantle (not shown in Figure 4) with heat from the heating source being transferred through a heat transfer material 555, e.g., sand. Nitrogen from a nitrogen source (not shown in Figure 4) is fed through conduit 570 (via flow valve 572 and rotometer 574) through the aluminum bromide in container 550. Pressure indicator 565 indicates the pressure within container 550. Gaseous nitrogen and aluminum bromide exit container 550 via conduit 580. Both the gaseous feedstock from conduit 510 and the gaseous nitrogen and aluminum bromide from conduit 580 flow into conduit 520 in container 521. Each of conduits 580 and 520 is insulated, e.g., with heating tape. The contents of conduit 520 are fed to stainless capillary coil 590, which is heated to a temperature of about 325°C by heat provided by a heating source, e.g., a heating mantle (not shown in Figure 4) with heat from the heating source being transferred through sand bed 592 in container 591. Stainless capillary coil 590 is about 100 yards long. Product comprising C2 and higher hydrocarbons exits container 591 (coil 590) via conduit 600. Device 610 is an all-in-one condenser, separator, collector, and sight glass). Flow valve 611 is used to control flow of product comprising C2 and higher hydrocarbons to storage and/or end use facilities (not shown in Figure 4). Flow valve 620 in conduit 625 controls flow of gaseous fluid through rotometer 640 that is used to regulate flow through continuous process system 599. Gaseous fluid in conduit 625 is vented via vent 623; samples of gaseous fluid in conduit 625 can be taken through valve 645.

[0686] Given the teachings of this disclosure, those skilled in the art can determine appropriate temperatures, pressures, and other process parameters as desired to achieve desired results using processes of this invention.

[0037] It is to be understood that the reactants and components referred to by chemical name or formula anywhere in the specification or claims hereof, whether referred to in the singular or plural, are identified as they exist prior to being combined with or coming into contact with another substance referred to by chemical name or chemical type (e.g., another reactant, a solvent, or etc.). It matters not what chemical changes, transformations and/or reactions, if any, take place in the resulting mixture or solution or reaction medium as such changes, transformations and/or reactions are the natural result of bringing the specified reactants and/or components together under the conditions called for pursuant to this disclosure. Thus the reactants and components are identified as ingredients to be brought together in connection with performing a desired chemical reaction or in forming a mixture to be used in conducting a desired
reaction. Accordingly, even though the claims hereinafter may refer to substances, components and/or ingredients in the present tense ("comprises", "is", etc.), the reference is to the substance, component or ingredient as it existed at the time just before it was first contacted, combined, blended or mixed with one or more other substances, components and/or ingredients in accordance with the present disclosure. Whatever transformations, if any, which occur in situ as a reaction is conducted is what the claim is intended to cover. Thus the fact that a substance, component or ingredient may have lost its original identity through a chemical reaction or transformation during the course of contacting, combining, blending or mixing operations, if conducted in accordance with this disclosure and with the application of common sense and the ordinary skill of a chemist, is thus wholly immaterial for an accurate understanding and appreciation of the true meaning and substance of this disclosure and the claims thereof. As will be familiar to those skilled in the art, the terms "combined", "combining", and the like as used herein mean that the components that are "combined" or that one is "combining" are put into a container with each other. Likewise a "combination" of components means the components having been put together in a container.

[0038] While the present invention has been described in terms of one or more preferred embodiments, it is to be understood that other modifications may be made without departing from the scope of the invention, which is set forth in the claims below.
What is claimed is:

1. A process for producing $H_2$, the process comprising combining at least a hydrocarbon feed source and a metal halide at a temperature of at least 1000°C and yielding at least $H_2$.

2. The process of claim 1 wherein the metal halide comprises aluminum bromide, aluminum chloride, aluminum fluoride, titanium bromide, or aluminum iodide.

3. The process of claim 1 wherein the hydrocarbon feed source comprises a paraffin wax, polyethylene, plastic grocery bags, $d_6$ straight chain paraffins, isopentane, cyclohexane, heptane, acetylene, or ethylene.

4. The process of claim 1 further comprising combining an additional component with the at least hydrocarbon feed source and metal halide, wherein the additional component comprises methyl iodide, titanium bromide, a branched hydrocarbon, ethane, hydrogen, an alkyl halide, an olefin, or a metal halide comprising Li, Na, K, Mg, Ca, Sc, Y, Zr, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and bromine, chlorine, or iodine.

5. The process of claim 1 further comprising combining a halogen with the at least hydrocarbon feed source and metal halide.

6. The process of claim 1 further comprising combining a hydrogen halide with the at least hydrocarbon feed source and metal halide.

7. The process of claim 1 further comprising combining a hydrogen halide and an additional component with the at least hydrocarbon feed source and metal halide, wherein the additional component comprises methyl iodide, titanium bromide, a branched hydrocarbon, ethane, hydrogen, an alkyl halide, an olefin, or a metal halide comprising Li, Na, K, Mg, Ca, Sc, Y, Zr, Hf, V, Nb, Ta, Fe, Ru, Co, Ni, Pb, B, Ga, Ge, Sn, or Sb and bromine, chlorine, or iodine.
8. The process of claim 1 further comprising combining gaseous methane with the at least hydrocarbon feed source and metal halide.

9. A process for producing H₂ comprising:
   - combining at least a hydrocarbon feed source and a metal halide at at least about 350°C,
   - cracking at least some of the hydrocarbon feed source to C₁ or higher hydrocarbons; and
   - polymerizing at least some of the C₁ or higher hydrocarbons;
   - yielding at least H₂ and C₂ and higher hydrocarbons.

10. A process for producing H₂, the process comprising combining at least a gas stream comprising methane and a metal halide at a temperature of at least 100°C and yielding at least H₂.

11. The process of claim 10 wherein the gas stream comprises at least about 50 vol% methane.

12. The process of claim 10 wherein the gas stream comprises at least about 75 vol% methane.

13. The process of claim 10 wherein the metal halide comprises aluminum bromide, aluminum chloride, aluminum fluoride, titanium bromide, or aluminum iodide.

14. The process of claim 10 wherein the metal halide comprises aluminum bromide.

15. The process of claim 10 wherein the process comprises combining at least the gas stream comprising methane, the metal halide, and a component suitable for absorbing hydrogen.

16. A process for producing H₂, comprising: (a) heating a metal halide to a melt temperature at least high enough to melt the metal halide; (b) combining at least gaseous methane and the heated metal halide; (c) producing C₂ and higher hydrocarbons; and (d) producing H₂.
17. A process for producing H₂, comprising: (a) heating a metal halide to a melt temperature at least high enough to melt the metal halide; (b) combining at least gaseous methane, a halogen, and the heated metal halide; (c) producing C₂ and higher hydrocarbons; and (d) producing H₂.

18. A process comprising combining at least gaseous methane and a Lewis acid at at least 100°C, yielding at least H₂ and C₂ and higher hydrocarbons.

19. A process for producing H₂, the process comprising combining at least a hydrocarbon feed source and a Lewis acid at at least a temperature at which at least some of the Lewis acid is gaseous, yielding at least H₂.

20. A process for producing H₂, the process comprising combining at least a hydrocarbon feed source, a Lewis acid, and a Bronsted acid at at least a temperature at which at least some of the Lewis acid is gaseous, yielding at least H₂.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
INV. C07C2/76  C10G50/00  C10G11/08

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C07C  C10G  C10B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal  CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>X</td>
<td>OSTERWALDER N ET AL: &quot;Direct coupling of bromine-mediated methane activation and</td>
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<td>carbon deposit gasification&quot; CHEMPHYSCHEM - A EUROPEAN JOURNAL OF</td>
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<td>CHEMICAL PHYSICS &amp; PHYSICAL CHEMISTRY, Dbewley, weinheim, vol. 8, 1 January 2007</td>
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<td>(2007-01-01), pages 297-303, XP002489549</td>
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<td>BREED ET AL: &quot;Natural gas conversion to liquid fuels in a zone reactor&quot;</td>
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<td>pages 301-304, XP005161450 ISSN: 0920-5861</td>
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| X | Further documents are listed in the continuation of Box C. |
| X | See patent family annex |

"A" document defining the general state of the art which is not considered to be of particular relevance

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Date of the actual completion of the international search

1 October 2008

Date of mailing of the international search report

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<td>US 3 257 333 A (ALLAN BLAIR EDGAR)</td>
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