

Description

Title of Invention: METHANATION DEVICE, METHANATION METHOD,
HYDROCARBON DIRECT DECOMPOSITION DEVICE, AND
HYDROCARBON DIRECT DECOMPOSITION METHOD

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Technical Field

[0001]

The present disclosure relates to a methanation device, a methanation method, a hydrocarbon direct decomposition device, and a hydrocarbon direct decomposition method.

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The present application claims priority based on JP 2023-220345 filed with the Japanese Patent Office on December 27, 2023, the contents of which are incorporated herein by reference.

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Background Art

[0002]

Currently, production of various types of energy largely depends on fossil fuels such as petroleum, coal, and natural gas, and from the viewpoint of global environmental conservation and the like, an increase in amount of carbon dioxide emitted by combustion of fossil fuels is regarded as an issue. The Paris Agreement, adopted in 2015, requires reducing the emission amount of carbon dioxide to deal with the climate change issue, and in thermal power plants and the like, reduction of the emission amount of carbon dioxide due to combustion of fossil fuels is an important issue. While a process for separating and recovering the emitted carbon dioxide has been energetically studied, a technique to produce energy without emitting carbon dioxide by using an alternative fuel to fossil fuel has also been studied.

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[0003]

Thus, hydrogen, which is a clean fuel that does not emit carbon dioxide through combustion, has attracted attention as an alternative fuel to fossil fuel. Hydrogen can be produced, for example, by steam reforming methane contained in natural gas. However, in this production method, carbon monoxide is produced as a by-product, and the carbon monoxide is finally oxidized and discharged as carbon dioxide. As a method for producing hydrogen from water without using fossil fuel, a water electrolysis method, photocatalytic method, and the like have been studied; however, these methods require a large amount of energy and are economically problematic.

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[0004]

Meanwhile, a method for producing hydrogen and carbon by directly decomposing hydrocarbon has been developed. The direct decomposition of hydrocarbon is characterized in that hydrogen fuel can be produced without emitting carbon dioxide, and while carbon as a by-product is solid and thus can be easily immobilized, carbon itself can be effectively used in a wide range of applications such as electrode materials, tire materials, and building materials. A method for directly decomposing a hydrocarbon into hydrogen and carbon by bringing a supported catalyst into contact with a hydrocarbon gas has been developed, but there has been a problem: carbon, which is a product of a direct decomposition reaction of the hydrocarbon, adheres to the catalyst, and thus that the catalytic activity is reduced in a short time.

[0005]

In view of this, the applicant of the present disclosure has developed a method for directly decomposing a hydrocarbon into carbon and hydrogen using a catalyst that is an unsupported catalyst of an aggregate of a plurality of iron particles, as described in Patent Document 1. The applicant considers that according to this method, even if carbon, which is a product of the direct decomposition reaction of a hydrocarbon, adheres to the catalyst, the activity is maintained by developing a new active site, and therefore that the activity of this reaction can be maintained for a long time.

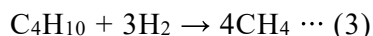
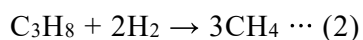
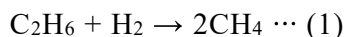
[0006]

For example, natural gas is used as a raw material gas for the direct decomposition reaction of a hydrocarbon. The natural gas contains, in addition to methane, saturated hydrocarbons having two or more carbon atoms such as ethane, propane, and butane (hereinafter referred to as "saturated hydrocarbon C2+"), and the saturated hydrocarbon C2+ has higher reactivity than methane, and therefore, at a temperature for causing the direct decomposition reaction of methane, side reactions such as thermal decomposition and polymerization reactions of the saturated hydrocarbon C2+ may cause, for example, clogging of piping. When a raw material gas containing the saturated hydrocarbon C2+ is used as a raw material for the direct decomposition reaction of a hydrocarbon, it is necessary to remove the saturated hydrocarbon C2+ from the raw material gas to suppress such a risk.

[0007]

When ethane, propane, and butane are used as examples of the saturated hydrocarbons C2+, the saturated hydrocarbons C2+ react with hydrogen to convert the saturated hydrocarbons C2+ into methane as shown in the following reaction formulas (1) to (3), and thus the saturated hydrocarbons C2+ can be

removed from the raw material gas. In general, synthesis of methane from hydrogen and carbon dioxide is often referred to as methanation, but in the present disclosure, as shown in the following reaction formulas (1) to (3), a reaction in which saturated hydrocarbon C₂+ is converted into methane by reacting the saturated hydrocarbon C₂+ with hydrogen is defined as "methanation".



Citation List

Patent Document

[0008]

Patent Document 1: JP 7089235 B

Summary of Invention

Technical Problem

[0009]

However, depending on temperature conditions of methanation, methane contained in a raw material gas or a part of converted methane may be directly decomposed into hydrogen and carbon. In this case, a methanation catalyst deteriorates due to adhesion of carbon to the methanation catalyst, resulting in a decrease in the activity of methanation, and therefore there is a risk of reducing the performance of removing the saturated hydrocarbon C₂+ from the raw material gas.

[0010]

In view of the above circumstances, it is an object of at least one embodiment of the present disclosure to provide a methanation device, a methanation method, a hydrocarbon direct decomposition device, and a hydrocarbon direct decomposition method that are capable of suppressing deterioration of a catalyst for methanation.

Solution to Problem

[0011]

In order to achieve the above object, a methanation device according to the present disclosure is a methanation device for removing a saturated hydrocarbon C₂+ having two or more carbon atoms from a raw material gas containing methane and the saturated hydrocarbon C₂+ through methanation, in

which the saturated hydrocarbon C₂⁺ is converted into methane by reacting the saturated hydrocarbon C₂⁺ with hydrogen, the methanation device including: at least two catalyst layers composed of a catalyst for the methanation, the at least two catalyst layers being provided at intervals in a flow direction of a mixed gas containing the raw material gas and a hydrogen-containing gas; a hydrogen supply line configured to supply the hydrogen-containing gas to an upstream side of a most upstream catalyst layer in the flow direction of the mixed gas; a raw material gas supply line configured to supply the raw material gas to each of the upstream side of the most upstream catalyst layer in the flow direction of the mixed gas and a space between two adjacent catalyst layers in the flow direction of the mixed gas; and a cooler provided between two adjacent catalyst layers in the flow direction of the mixed gas and cooling the mixed gas flowing out from an upstream catalyst layer in the flow direction of the mixed gas among the two adjacent catalyst layers.

[0012]

A methanation method according to the present disclosure is a methanation method for removing a saturated hydrocarbon C₂⁺ having two or more carbon atoms from a raw material gas containing methane and the saturated hydrocarbon C₂⁺ through methanation, in which the saturated hydrocarbon C₂⁺ is converted into methane by reacting the saturated hydrocarbon C₂⁺ with hydrogen, the methanation method including: causing a hydrogen-containing gas to flow into a most upstream catalyst layer among at least two catalyst layers composed of a catalyst for the methanation, the at least two catalyst layers being provided at intervals in a flow direction of a mixed gas containing the raw material gas and the hydrogen-containing gas; causing a part of the raw material gas to flow into the most upstream catalyst layer in the flow direction of the mixed gas; supplying a remainder of the raw material gas between two adjacent catalyst layers in the flow direction of the mixed gas; cooling the mixed gas discharged from an upstream catalyst layer among the two adjacent catalyst layers; and causing the cooled mixed gas and the raw material gas supplied between the two adjacent catalyst layers in the flow direction of the mixed gas to flow into a downstream catalyst layer among the two adjacent catalyst layers.

Advantageous Effects of Invention

[0013]

According to the methanation device and methanation method of the present disclosure, a temperature of the mixed gas flowing through each

catalyst layer increases due to methanation in each catalyst layer. However, by dividing and supplying the raw material gas to each catalyst layer, the methanation in each catalyst layer can be made gentle, and further, by cooling the mixed gas flowing out from each catalyst layer, the temperature of the mixed gas flowing into the adjacent catalyst layer in the flow direction of the mixed gas can be lowered. Accordingly, even if the temperature of the mixed gas increases due to methanation in each catalyst layer, the increase can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed. As a result, deterioration of the catalyst for methanation can be suppressed.

Brief Description of Drawings

[0014]

FIG. 1 is a schematic configuration diagram of a hydrocarbon direct decomposition device including a methanation device according to an embodiment of the present disclosure.

FIG. 2 is a schematic configuration diagram of a methanation device of a simulation 1.

FIG. 3 is a schematic configuration diagram of a methanation device of simulation 2.

FIG. 4 is a schematic configuration diagram of a methanation device of simulation 3.

Description of Embodiments

[0015]

Hereinafter, a methanation device and a methanation method according to embodiments of the present disclosure will be described with reference to the drawings. The embodiments described below each illustrate one aspect of the present disclosure, do not limit this disclosure, and can be arbitrarily changed within the scope of the technical idea of the present disclosure.

[0016]

<Configuration of Methanation Device and Hydrocarbon direct decomposition device According to Embodiment of Present Disclosure>

In the following embodiment, a methanation device according to an embodiment of the present disclosure will be described as one component of a hydrocarbon direct decomposition device, but the present disclosure is not limited to this embodiment, and may be one component of any apparatus or

may be used as a single apparatus. As shown in FIG. 1, a hydrocarbon direct decomposition device 1 according to an embodiment of the present disclosure includes a methanation device 2 and a reactor 22. The methanation device 2 and the reactor 22 are communicated with each other through a processed gas supply line 5. The direct decomposition device 1 may include a gas chromatography 16 for sampling a part of the gas (processed gas described later) flowing through the processed gas supply line 5 and measuring the composition of the gas.

[0017]

The methanation device 2 includes a case 10, and a catalyst layer 11 composed of a catalyst for methanation and a cooler 13 are provided inside the case 10. The catalyst layer 11 includes two catalyst layers, that is, a first catalyst layer 11a and a second catalyst layer 11b, which are provided at intervals between both ends of the case 10. As described later, in the case 10, the gas flows in a direction from one end portion of the case 10 to the other end portion thereof, and an upstream catalyst layer in the flow direction of the gas is referred to as the first catalyst layer 11a, and a downstream catalyst layer is referred to as the second catalyst layer 11b. As the catalyst for methanation, any catalyst for methanation can be used, and examples thereof include a supported catalyst in which nickel, iron, cobalt, or a noble metal element is supported on alumina. The catalyst shape is not particularly limited, and any shape of catalyst may be used, such as a tableted shape, a ring shape, an extruded shape, or a granular pellet shape.

[0018]

In the case 10, a space 12 is formed between the first catalyst layer 11a and the second catalyst layer 11b, and the cooler 13 is provided in the space 12. The configuration of the cooler 13 is not particularly limited, but the cooler 13 may have a configuration in which the above-described gas is cooled by heat exchange with any coolant, for example.

[0019]

In the configuration of FIG. 1, two catalyst layers (i.e., the first catalyst layer 11a and the second catalyst layer 11b) and one cooler 13 provided therebetween (i.e., in the space 12) are provided in the case 10. However, three or more catalyst layers, that is, at least two catalyst layers may be provided, and in the configuration in which three or more catalyst layers are provided, the cooler 13 is provided in each of the spaces 12 between two adjacent catalyst layers in the flow direction of the above-described gas.

[0020]

The methanation device 2 further includes a hydrogen supply line 3 configured to supply a hydrogen-containing gas into the case 10 and a raw material gas supply line 4 configured to supply a raw material gas into the case 10. The hydrogen supply line 3 is connected to the case 10 on the upstream side of the first catalyst layer 11a in the flow direction of the above-described gas in the case 10. The hydrogen supply line 3 may be provided with a flow rate adjustment valve 14 configured to adjust the supply amount of the hydrogen-containing gas into the case 10. The hydrogen-containing gas flowing through the hydrogen supply line 3 may be pure hydrogen gas, or may be a mixed gas of hydrogen and a component (such as rare gas, nitrogen, or methane) that does not contribute to methanation. The raw material gas is a gas containing methane and saturated hydrocarbon C2+ having two or more carbon atoms (such as ethane, propane, or butane), and for example, natural gas, compressed natural gas (CNG), city gas, liquefied petroleum gas, and naphtha can be used as the raw material gas. Therefore, the above-described gas flowing through the case 10 is a mixed gas containing the hydrogen-containing gas supplied into the case 10 through the hydrogen supply line 3 and the raw material gas supplied into the case 10 through the raw material gas supply line 4.

[0021]

The raw material gas supply line 4 is branched into branch lines 4a and 4b, and one branch line 4a is connected to the case 10 on the upstream side of the first catalyst layer 11a in the flow direction of the above-described mixed gas in the case 10, and the other branch line 4b is connected to the case 10 between the first catalyst layer 11a and the second catalyst layer 11b. The branch line 4a may be connected to the case 10 without merging with the hydrogen supply line 3, or may merge with the hydrogen supply line 3 as shown in FIG. 1. The branch line 4b may be connected to the case 10 so as to communicate with the space 12, and the raw material gas flowing into the space 12 through the branch line 4b may flow in on the upstream side of the cooler 13, may flow into the downstream side of the cooler 13, or may flow into a region where the cooler 13 is provided. The branch lines 4a and 4b may be provided with flow rate adjustment valves 15a and 15b configured to adjust the supply amount of the raw material gas supplied into the case 10 through the branch lines 4a and 4b, respectively. The hydrogen supply line 3 may include a branch line like the raw material gas supply line 4, and each of the branch lines of the hydrogen supply line 3 may be connected to the case 10 on the upstream side of the first catalyst layer 11a and between the first catalyst layer 11a and the second catalyst layer 11b.

[0022]

A catalyst 20 for direct decomposition reaction of a hydrocarbon is accommodated in the reactor 22. The reactor 22 is provided with a heater 21 (for example, a jacket through which steam flows) configured to increase the temperature inside the reactor 22, in particular, the temperature of the catalyst 20. A product gas flow line 6 is connected to the reactor 22 on the opposite side of the catalyst 20 from a position where the processed gas supply line 5 is connected to the reactor 22.

[0023]

The catalyst 20 is not particularly limited, but may be, for example, an unsupported catalyst of an aggregate of a plurality of iron particles. In the reactor 22, each particle of the catalyst 20 may be in a stationary state, or may be in a fluidized bed state in which the particles are suspended and floated in the raw material gas by injecting the processed gas described later upward. When the hydrocarbon is reacted by the catalyst 20, carbon and hydrogen are produced, and the carbon adheres to the particles of the catalyst 20. In the case where the catalyst 20 forms a fluidized bed, the particles of the catalyst 20 rub against each other so that the carbon adhering to the particles of the catalyst 20 is physically removed from the particles. In the case where a fixed bed reactor is used as the reactor 22, for example, a carbon remover may be provided outside the reactor 22 in order to remove the carbon adhered to the catalyst 20 from the catalyst 20.

[0024]

The direct decomposition device 1 may further include a hydrogen recycle line 7 communicating the product gas flow line 6 with the hydrogen supply line 3. The hydrogen recycle line 7 may be provided with a valve 8 which may be either an on-off valve or a flow rate adjustment valve.

[0025]

<Operation of Methanation Device According to Embodiment of Present Disclosure>

Next, an operation of the methanation device according to an embodiment of the present disclosure (a methanation method) will be described. The hydrogen-containing gas flows into the case 10 through the hydrogen supply line 3 on the upstream side of the first catalyst layer 11a. A part of the raw material gas flowing through the raw material gas supply line 4 flows into the case 10 on the upstream side of the first catalyst layer 11a through the branch line 4a.

[0026]

The hydrogen-containing gas and the raw material gas flowing into the case 10 on the upstream side of the first catalyst layer 11a flow into the first catalyst layer 11a. In the first catalyst layer 11a, the saturated hydrocarbon C2+ in the raw material gas reacts with hydrogen in the hydrogen-containing gas by action of the catalyst for methanation to produce methane, and a mixed gas containing methane, unreacted saturated hydrocarbon C2+, and unreacted hydrogen flows out from the first catalyst layer 11a and flows into the space 12. Although the temperature of the mixed gas increases by the reaction heat due to the methanation as described above, the methanation in the first catalyst layer 11a becomes mild (the reaction amount of the methanation is reduced) in the above-described operation as compared with a case where the entire amount of the raw material gas flowing through the raw material gas supply line 4 is supplied into the case 10 on the upstream side of the first catalyst layer 11a, and therefore the temperature increase of the mixed gas flowing out from the first catalyst layer 11a can be suppressed.

[0027]

In the methanation device 2 having the configuration shown in FIG. 1, the catalyst layer 11 is divided into two to supply the raw material gas in two. However, if the number of divisions of the catalyst layer 11 (i.e., the number of divisions of the raw material gas) is increased, the flow rate of the raw material gas flowing through the first catalyst layer 11a is reduced, and therefore the methanation in the first catalyst layer 11a becomes more gentle, and the temperature increase of the mixed gas flowing out from the first catalyst layer 11a can be further suppressed. If the temperature increase of the mixed gas flowing out from the first catalyst layer 11a can be suppressed to such an extent that direct decomposition of methane does not occur, the direct decomposition reaction of methane can be suppressed from occurring in the first catalyst layer 11a, and carbon can be suppressed from adhering to the catalyst for methanation constituting the first catalyst layer 11a, and therefore deterioration of the catalyst for methanation can be suppressed.

[0028]

The mixed gas flowing into the space 12 is cooled by heat exchange with a coolant flowing in the cooler 13. The cooled mixed gas and the raw material gas flowing through the branch line 4b flow into the second catalyst layer 11b. Even in the second catalyst layer 11b, the saturated hydrocarbon C2+ reacts with hydrogen to produce methane on the same principle as in the first catalyst layer 11a. Since the mixed gas cooled by the cooler 13 flows into the second catalyst layer 11b, even if the temperature of the mixed gas in the

second catalyst layer 11b increases due to such methanation, the temperature of the mixed gas can be suppressed to a temperature at which direct decomposition of methane does not occur. As a result, the direct decomposition reaction of methane can be suppressed from occurring in the second catalyst layer 11b, and carbon can be suppressed from adhering to the catalyst for methanation constituting the second catalyst layer 11b, and therefore deterioration of the catalyst for methanation can be suppressed.

[0029]

According to such a methanation method, although the temperature of the mixed gas flowing through each of the first catalyst layer 11a and the second catalyst layer 11b increases due to methanation in each of the first catalyst layer 11a and the second catalyst layer 11b, by supplying the raw material gas divided to each of the first catalyst layer 11a and the second catalyst layer 11b, the methanation in each of the first catalyst layer 11a and the second catalyst layer 11b can be made gentle. Furthermore, by cooling the mixed gas flowing out from the first catalyst layer 11a, the temperature of the mixed gas flowing into the adjacent second catalyst layer 11b in the flow direction of the mixed gas can be lowered. Accordingly, even if the temperature of the mixed gas increases due to methanation in each of the first catalyst layer 11a and the second catalyst layer 11b, the increase can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed. As a result, deterioration of the catalyst for methanation can be suppressed.

[0030]

In such a methanation method, since the raw material gas is divided and supplied through the branch lines 4a and 4b, the flow rate of the mixed gas flowing through the second catalyst layer 11b is larger than the flow rate of the mixed gas flowing through the first catalyst layer 11a. Therefore, the amount of the catalyst constituting the second catalyst layer 11b is preferably larger than the amount of the catalyst constituting the first catalyst layer 11a. Accordingly, the amount of the catalyst in each of the first catalyst layer 11a and the second catalyst layer 11b can be set to an appropriate amount according to the amount of the mixed gas flowing through each of the first catalyst layer 11a and the second catalyst layer 11b, and therefore methanation in each of the first catalyst layer 11a and the second catalyst layer 11b can be performed under appropriate conditions. In the case where the catalyst layer 11 is composed of three or more catalyst layers, the amount of the catalyst constituting each catalyst layer is

preferably increased as the catalyst layer is disposed further downstream in the flow direction of the mixed gas.

[0031]

In such a methanation method, when the hydrogen-containing gas contains a component that does not contribute to methanation, the concentrations of hydrogen and saturated hydrocarbon C₂+ in each catalyst layer are lower than those when the hydrogen-containing gas contains only hydrogen, and therefore the temperature increase of the mixed gas due to heat generated during methanation in each catalyst layer is suppressed, so that the methanation in each catalyst layer can be made gentle. As a result, the temperature increase of the mixed gas in each catalyst layer can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed, and deterioration of the catalyst for methanation can be suppressed.

[0032]

In such a methanation method, the supply amount of the hydrogen-containing gas is preferably adjusted so that a concentration ratio of hydrogen to the saturated hydrocarbon C₂+ in the mixed gas is 1 or more. To convert ethane, which has the lowest number of carbon atoms, among the saturated hydrocarbons C₂+, into methane, one molecule of hydrogen is required for one molecule of ethane. Therefore, by adjusting such conditions, the saturated hydrocarbons C₂+ in the raw material gas can be stoichiometrically converted into methane.

[0033]

In the configuration in which the gas chromatography 16 and the flow rate adjustment valve 14 are provided, a decrease in the activity of methanation in the methanation device 2 can be detected from the measurement result of the gas chromatography 16, and when a decrease in the activity of methanation is detected, the supply amount of the hydrogen-containing gas can be increased by the flow rate adjustment valve 14. When the supply amount of the hydrogen-containing gas increases, the concentration of hydrogen in the mixed gas rises. In this case, carbon, a polymerization reaction product, or the like adhered to the catalyst for methanation easily reacts with hydrogen, and therefore the adhered carbon, polymerization reaction product, or the like can be converted into a gas such as methane to remove adherents from the catalyst. That is, it is possible to suppress the deterioration of the catalyst for methanation due to a product produced by side reactions such as thermal decomposition and

polymerization reactions of the saturated hydrocarbon C₂+, or it is possible to regenerate the deteriorated catalyst.

[0034]

5 If the sulfur content is contained in the raw material gas, the catalyst for methanation may be deteriorated by the sulfur content. Therefore, it is preferable to remove the sulfur content from the raw material gas before the raw material gas flows into the case 10 by providing a desulfurization device in the raw material gas supply line 4.

[0035]

10 Operation of Hydrocarbon Direct Decomposition Device According to Embodiment of Present Disclosure

Next, an operation of the hydrocarbon direct decomposition device according to an embodiment of the present disclosure (a hydrocarbon direct decomposition method) will be described. The mixed gas flowing out from the second catalyst layer 11b flows out from the case 10, flows through the processed gas supply line 5 as a processed gas, and flows into the reactor 22. The processed gas flowing into the reactor 22 passes through the catalyst 20 while contacting the catalyst 20. At this time, the hydrocarbon in the processed gas is directly decomposed into hydrogen and carbon. For example, when methane is used as the hydrocarbon in the direct decomposition reaction, a reaction represented by the following reaction formula (4) occurs in the reactor 22.

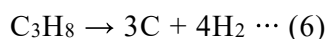
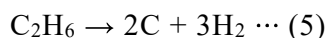


25 [0036]

The carbon produced by the direct decomposition method adheres to the catalyst 20, and the produced hydrogen flows out from the reactor 22 as a product gas together with an unreacted hydrocarbon and flows through the product gas flow line 6. The recovery of carbon can be performed by recovering the catalyst 20 from the reactor 22 after the supply of the processed gas to the reactor 22 is stopped, and if necessary, removing carbon adhered to the catalyst 20 with a carbon remover. The hydrogen is recovered by recovering a reaction gas flowing through the product gas flow line 6. Hydrogen can be purified by providing a hydrogen refiner in the product gas flow line 6. In this case, when the conversion rate of the hydrocarbon is low, the hydrogen concentration in the processed gas is low, but the concentration of hydrogen as a final product can be increased with the hydrogen refiner.

[0037]

When the saturated hydrocarbon C₂+, such as ethane or propane, is contained as a hydrocarbon in a processed gas in addition to methane, for example, ethane or propane is also directly decomposed into hydrogen and carbon as in the following reaction formulas (5) and (6). However, at a temperature for causing a direct decomposition reaction of methane (preferably from 600°C to 900°C), a side reaction such as thermal decomposition of the saturated hydrocarbon C₂+ and a polymerization reaction (tar generation) accompanying the thermal decomposition may also occur, and such a side reaction may cause, for example, clogging of piping.



[0038]

However, in the hydrocarbon direct decomposition method according to an embodiment of the present disclosure, in the methanation device 2, the processed gas, from which at least a part of the saturated hydrocarbon C₂+ has been removed by conversion of the raw material gas into methane, is used as the raw material gas of the direct decomposition reaction. That is, the concentration of the saturated hydrocarbon C₂+ in the processed gas used as the raw material gas for the direct decomposition reaction is lower than that of the initial raw material gas supplied to the methanation device 2. Therefore, as compared with the case where the initial raw material gas supplied to the methanation device 2 is used as the raw material gas for the direct decomposition reaction, in the hydrocarbon direct decomposition method according to an embodiment of the present disclosure, it is possible to suppress a side reaction such as a polymerization reaction (tar generation) accompanying the thermal decomposition of the saturated hydrocarbon C₂+, and thus, it is possible to reduce the risk of causing clogging of piping, for example.

[0039]

In the case where the hydrogen recycle line 7 is provided, at least a part of the product gas is supplied to the hydrogen supply line 3, and therefore the hydrogen-containing gas flowing through the hydrogen supply line 3 flows into the case 10 on the upstream side of the first catalyst layer 11a together with the product gas. That is, at least a part of the product gas can be used as at least a part of the hydrogen-containing gas. Accordingly, since the amount of hydrogen to be directly supplied to the direct decomposition device 1 can be reduced, the operation cost of the direct decomposition device 1 can be reduced.

[0040]

When the valve 8, which is an on-off valve, is provided in the hydrogen recycle line 7, by closing the valve 8, the entire amount of the product gas can be transferred to a storage unit or hydrogen consuming facility, which is not shown, without using the product gas as at least a part of the hydrogen-containing gas. When the valve 8 is a flow rate adjustment valve, the amount of the product gas used as at least a part of the hydrogen-containing gas can be adjusted.

[0041]

<Simulation for Verifying Effect of Methanation Method of Present Disclosure>

Next, a simulation performed to verify the effect of the methanation method of the present disclosure will be described. According to the study of the present inventors in the present disclosure, a preferred temperature range of the above-described methanation is from 250°C to 360°C, while the preferred temperature range of the direct decomposition reaction of methane is from 600°C to 900°C as described above. Therefore, in the methanation method of the present disclosure, it is considered that the effect can be appropriately exhibited if the temperature of the mixed gas flowing out from each catalyst layer can be controlled to 360°C or less.

[0042]

(Simulation 1)

As shown in FIG. 2, a simulation was performed with a methanation device configured such that five catalyst layers of catalyst layers I to V were provided in a case, a raw material gas was divided and supplied to each catalyst layer as shown in (1) to (5), and a hydrogen gas was supplied to the upstream side of the most upstream catalyst layer I. The composition of the raw material gas was set at 89 vol% methane, 6 vol% ethane, 4 vol% propane, and 1 vol% butane. The adiabatic temperature rise is about 180°C when saturated hydrocarbon C2+ (ethane, propane, or butane) in such raw material gas is converted into methane by methanation in the entire catalyst layers I to V. In simulation 1, the ratio of the concentration of hydrogen to the concentration of saturated hydrocarbon C2+ was set to 1.5, and the condition of each gas flowing into each catalyst layer was calculated such that the adiabatic temperature rise in each of the catalyst layers I to V was 60°C. At this time, the mixed gas whose temperature has been increased by the heat generated during the methanation is cooled by heat exchange with the coolant in the cooler

between the adjacent catalyst layers to decrease the temperature by 60°C. The results thereof are shown in Table 1 below.

[0043]

[Table 1]

Catalyst layer into which each gas flows	Flow rate of mixed gas [Nm ³ /hr]	Flow rate of hydrogen [Nm ³ /hr]	Flow rate of hydrocarbon [Nm ³ /hr]			Content of saturated hydrocarbon C2+ [vol%]	Temperature increase [°C]
			Methane	Saturated hydrocarbon C2+	Total		
I	393	283	108	12	110	3.0	60
II	543	259	134	16	150	3.0	60
III	753	227	187	23	210	3.0	60
IV	1043	181	258	32	290	3.1	60
V	1439	95	351	43	394	3.0	60
Entirety	1439	283	1028	128	1156	8.9	180

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[0044]

According to Table 1, the temperature of the mixed gas flowing out from each catalyst layer can be controlled to 360°C or less by setting the supply amounts of the raw material gases (1) to (5) to 110 Nm³/hr in (1), 150 Nm³/hr in (2), 210 Nm³/hr in (3), 290 Nm³/hr in (4), and 394 Nm³/hr in (5).

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[0045]

(Simulation 2)

As shown in FIG. 3, a simulation was performed with a methanation device configured such that two catalyst layers of catalyst layers I and II were provided in a case, a raw material gas was divided and supplied to each catalyst layer as shown in (1) and (2), and a hydrogen gas was supplied to the upstream side of the most upstream catalyst layer I. In simulation 2, it is assumed that methane is supplied at a flow rate of 1121 Nm³/hr to the hydrogen gas supplied to the upstream side of the catalyst layer I on the assumption that a component that does not contribute to methanation is contained in the hydrogen-containing gas. The adiabatic temperature rise is about 100°C in simulation 2 when the saturated hydrocarbon C2+ in the raw material gas having the same composition as that in simulation 1 is converted into methane by methanation in the entire catalyst layers I and II. In simulation 2, similarly to simulation 1, the ratio of the concentration of hydrogen to the concentration of saturated hydrocarbon C2+ was set to 1.5, and the condition of each gas flowing into each catalyst layer was calculated such that the adiabatic temperature rise in

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each of the catalyst layers I and II was 60°C. At this time, the mixed gas of the raw material gas and the hydrogen gas is cooled by heat exchange with the coolant in the cooler between the catalyst layers I and II to decrease the temperature by 60°C. The results thereof are shown in Table 2 below. The supply amount of hydrogen in Table 2 is a flow rate excluding the supply amount of methane.

[0046]

[Table 2]

Catalyst layer into which each gas flows	Flow rate of mixed gas [Nm ³ /hr]	Flow rate of hydrogen [Nm ³ /hr]	Flow rate of hydrocarbon [Nm ³ /hr]			Content of saturated hydrocarbon C2+ [vol%]	Temperature increase [°C]
			Methane	Saturated hydrocarbon C2+	Total		
I	2070	283	413	51	463	3.0	60
II	2560	259	616	77	693	2.9	60
Entirety	2560	283	1156	128	1156	5.0	100

[0047]

According to Table 2, the temperature of the mixed gas flowing out from each catalyst layer can be controlled to 360°C or less by setting the supply amounts of the raw material gases (1) and (2) to 463 Nm³/hr in (1) and 693 Nm³/hr in (2).

[0048]

(Simulation 3)

As shown in FIG. 4, a simulation was performed with a methanation device configured such that three catalyst layers of catalyst layers I to III were provided in a case, a raw material gas was divided and supplied to each catalyst layer as shown in (1) to (3), and a hydrogen gas was supplied to the upstream side of the most upstream catalyst layer I. Similarly to simulation 2, it is assumed in simulation 3 that methane is supplied at a flow rate of 720 Nm³/hr to the hydrogen gas supplied to the upstream side of the catalyst layer I on the assumption that a component that does not contribute to methanation is contained in the hydrogen-containing gas. The adiabatic temperature rise is about 120°C in simulation 2 when the saturated hydrocarbon C2+ in the raw material gas having the same composition as that in simulation 1 is converted into methane by methanation in the entire catalyst layers I to III. In simulation3, the ratio of the concentration of hydrogen to the concentration of saturated hydrocarbon C2+ was set to 1.5, and the condition of each gas

flowing into each catalyst layer was calculated such that the adiabatic temperature rise in each of the catalyst layers I to III was 60°C or less. At this time, the mixed gas of the raw material gas and the hydrogen gas is cooled by heat exchange with the coolant in the cooler between the adjacent catalyst layers to decrease the temperature by 60°C. The results thereof are shown in Table 3 below. The supply amount of hydrogen in Table 3 is a flow rate excluding the supply amount of methane.

[0049]

[Table 3]

Catalyst layer into which each gas flows	Flow rate of mixed gas [Nm ³ /hr]	Flow rate of hydrogen [Nm ³ /hr]	Flow rate of hydrocarbon [Nm ³ /hr]			Content of saturated hydrocarbon C2+ [vol%]	Temperature increase [°C]
			Methane	Saturated hydrocarbon C2+	Total		
I	1259	283	226	28	254	2.2	45
II	1648	255	347	43	391	2.6	52
III	2159	212	453	56	509	2.6	52
Entirety	2159	283	1028	128	1156	5.9	120

[0050]

According to Table 3, the temperature of the mixed gas flowing out from each catalyst layer can be controlled to 360°C or less by setting the supply amounts of the raw material gases (1) to (3) to 254 Nm³/hr in (1), 391 Nm³/hr in (2), and 509 Nm³/hr in (3).

[0051]

From the simulations 1 to 3, the catalyst layer composed of the catalyst for methanation is divided into a plurality of layers, the raw material gas is divided and supplied to each catalyst layer, and the mixed gas flowing out from each catalyst layer is cooled in the cooler. Thus, even if the temperature of the mixed gas increases due to the methanation in each catalyst layer, the temperature can be suppressed to such an extent that direct decomposition of methane does not occur.

[0052]

The content described in each of the embodiments described above is understood, for example, as follows.

[0053]

[1] A methanation device according to one aspect is a methanation device (2) for removing a saturated hydrocarbon C2+ having two or more

carbon atoms from a raw material gas containing methane and the saturated hydrocarbon C₂+ through methanation, in which the saturated hydrocarbon C₂+ is converted into methane by reacting the saturated hydrocarbon C₂+ with hydrogen, the methanation device including: at least two catalyst layers (11a, 11b) composed of a catalyst for methanation, the at least two catalyst layers (11a, 11b) being provided at intervals in a flow direction of a mixed gas containing the raw material gas and a hydrogen-containing gas; a hydrogen supply line (3) configured to supply the hydrogen-containing gas to an upstream side of a most upstream catalyst layer (11a) in the flow direction of the mixed gas; a raw material gas supply line (4) configured to supply the raw material gas to each of the upstream side of the most upstream catalyst layer (11a) in the flow direction of the mixed gas and a space between two adjacent catalyst layers (11a, 11b) in the flow direction of the mixed gas; and a cooler (13) provided between two adjacent catalyst layers (11a, 11b) in the flow direction of the mixed gas and cooling the mixed gas flowing out from an upstream catalyst layer (11a) in the flow direction of the mixed gas among the two adjacent catalyst layers (11a, 11b).

[0054]

According to the methanation device of the present disclosure, a temperature of the mixed gas flowing through each catalyst layer increases due to methanation in each catalyst layer. However, by dividing and supplying the raw material gas to each catalyst layer, the methanation in each catalyst layer can be made gentle, and further, by cooling the mixed gas flowing out from each catalyst layer, the temperature of the mixed gas flowing into the adjacent catalyst layer in the flow direction of the mixed gas can be lowered.

Accordingly, even if the temperature of the mixed gas increases due to methanation in each catalyst layer, the increase can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed. As a result, deterioration of the catalyst for methanation can be suppressed.

[0055]

[2] A methanation device according to another aspect is the methanation device according to [1], wherein an amount of the catalyst constituting each of the at least two catalyst layers (11a, 11b) is larger as the catalyst layer (11b) is disposed further downstream in the flow direction of the mixed gas.

[0056]

With the configuration [1] above, by dividing and supplying the raw material gas to each catalyst layer, the amount of the mixed gas flowing

through the catalyst layer on the downstream side increases. Therefore, according to the above configuration, the amount of the catalyst in each catalyst layer can be set to an appropriate amount corresponding to the amount of the mixed gas flowing through each catalyst layer, and therefore methanation in each catalyst layer can be performed under appropriate conditions.

[0057]

[3] A methanation device according to still another aspect is the methanation device according to [1] or [2], wherein the catalyst is a supported catalyst in which nickel, iron, cobalt, or a gas metal element is supported on alumina.

[0058]

According to such a configuration, methanation can be appropriately performed in each catalyst layer.

[0059]

[4] A hydrocarbon direct decomposition device according to one aspect includes:

the methanation device according to any one of [1] to [3];

a reactor (22) containing a catalyst (20) for direct decomposition reaction of a hydrocarbon; and

a processed gas supply line (5) configured to supply a processed gas, which is a gas flowing out from the methanation device (2), to the reactor (22).

[0060]

According to the hydrocarbon direct decomposition device of the present disclosure, the content of the saturated hydrocarbon C₂⁺ in the processed gas is reduced as compared with the raw material gas, making it possible to suppress the risk caused by side reactions such as thermal decomposition and polymerization reaction of the saturated hydrocarbon C₂⁺.

[0061]

[5] A hydrocarbon direct decomposition device according to another aspect is the hydrocarbon direct decomposition device according to [4] including:

a product gas flow line (6) through which a product gas containing hydrogen generated by direct decomposition of hydrocarbon in the reactor (22) flows after flowing out from the reactor; and

a hydrogen recycle line (7) communicating the product gas flow line (6) with the hydrogen supply line (3).

[0062]

According to such a configuration, at least a part of hydrogen in the product gas is used as at least a part of hydrogen to be supplied to the methanation device, and therefore, the amount of hydrogen to be supplied to the direct decomposition device can be reduced, and as a result, the operation
5 cost of the hydrocarbon direct decomposition device can be reduced.

[0063]

[6] A methanation method according to one aspect is a methanation method for removing a saturated hydrocarbon C₂+ having two or more carbon atoms from a raw material gas containing methane and the saturated
10 hydrocarbon C₂+ through methanation, in which the saturated hydrocarbon C₂+ is converted into methane by reacting the saturated hydrocarbon C₂+ with hydrogen, the methanation method including: causing a hydrogen-containing gas to flow into a most upstream catalyst layer (11a) among at least two catalyst layers (11a, 11b) composed of a catalyst for the methanation, the at
15 least two catalyst layers (11a, 11b) being provided at intervals in a flow direction of a mixed gas containing the raw material gas and a hydrogen-containing gas; causing a part of the raw material gas to flow into the most upstream catalyst layer (11a) in the flow direction of the mixed gas; supplying a remainder of the raw material gas between two adjacent catalyst layers (11a,
20 11b) in the flow direction of the mixed gas; cooling the mixed gas discharged from an upstream catalyst layer (11a) among the two adjacent catalyst layers (11a, 11b); and causing the cooled mixed gas and the raw material gas supplied between the two adjacent catalyst layers (11a, 11b) in the flow direction of the mixed gas to flow into a downstream catalyst layer (11b) among the two
25 adjacent catalyst layers (11a, 11b).

[0064]

According to the methanation method of the present disclosure, a temperature of the mixed gas flowing through each catalyst layer increases due to methanation in each catalyst layer. However, by dividing and supplying the
30 raw material gas to each catalyst layer, the methanation in each catalyst layer can be made gentle, and further, by cooling the mixed gas flowing out from each catalyst layer, the temperature of the mixed gas flowing into the adjacent catalyst layer in the flow direction of the mixed gas can be lowered. Accordingly, even if the temperature of the mixed gas increases due to
35 methanation in each catalyst layer, the increase can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed. As a result, deterioration of the catalyst for methanation can be suppressed.

[0065]

[7] A methanation method according to another aspect is the methanation method according to [6], wherein a supply amount of the hydrogen-containing gas is adjusted so that a concentration ratio of hydrogen to the saturated hydrocarbon C2+ in the mixed gas is 1 or more.

[0066]

To convert ethane, which has the lowest number of carbon atoms, among the saturated hydrocarbons C2+, into methane, one molecule of hydrogen is required for one molecule of ethane. Therefore, according to such a method, the saturated hydrocarbons C2+ in the raw material gas can be stoichiometrically converted into methane.

[0067]

[8] A methanation method according to still another aspect is the methanation method according to [6] or [7]

The hydrogen-containing gas contains hydrogen and a component that does not contribute to the methanation.

[0068]

According to such a method, the concentrations of hydrogen and saturated hydrocarbon C2+ in each catalyst layer are lower than those when only hydrogen is supplied, and therefore the temperature increase of the mixed gas due to heat generated during methanation in each catalyst layer is suppressed, so that the methanation in each catalyst layer can be made gentle. As a result, the temperature increase of the mixed gas in each catalyst layer can be suppressed to such an extent that direct decomposition of methane does not occur, and therefore, adhesion of carbon to the catalyst for methanation can be suppressed, and deterioration of the catalyst for methanation can be suppressed.

[0069]

[9] A methanation method according to still another aspect is the methanation method according to any one of [6] to [8] including:

detecting a decrease in activity of the methanation; and
increasing a supply amount of the hydrogen-containing gas when the decrease in the activity is detected.

[0070]

According to such a method, it is possible to suppress the deterioration of the catalyst for methanation due to a product produced by side reactions such as thermal decomposition and polymerization reactions of the saturated hydrocarbon C2+, or it is possible to regenerate the deteriorated catalyst.

[0071]

[10] A methanation method according to still another aspect is the methanation method according to any one of [6] to [9], wherein

the raw material gas is natural gas, compressed natural gas, city gas, liquefied petroleum gas, or naphtha.

5 [0072]

According to such a method, a generally available hydrocarbon gas can be used as a raw material gas without separately preparing the raw material gas.

[0073]

10 [11] A hydrocarbon direct decomposition method according to one aspect includes:

converting the saturated hydrocarbon C₂⁺ in the raw material gas into methane by the methanation method according to any one of [6] to [10]; and

15 directly decomposing methane in a processed gas, which is a gas after conversion of the saturated hydrocarbon C₂⁺ into methane, into hydrogen and carbon by contacting the processed gas with a catalyst (20) for direct decomposition reaction of a hydrocarbon.

[0074]

20 According to the hydrocarbon direct decomposition method of the present disclosure, the content of the saturated hydrocarbon C₂⁺ in the processed gas is reduced as compared with the raw material gas, making it possible to suppress the risk caused by side reactions such as thermal decomposition and polymerization reaction of the saturated hydrocarbon C₂⁺.

[0075]

25 [12] A hydrocarbon direct decomposition method according to another aspect is the hydrocarbon direct decomposition method according to [11], wherein at least a part of a product gas containing hydrogen generated by directly decomposing methane in the processed gas into hydrogen and carbon is used as at least a part of the hydrogen-containing gas supplied to an most upstream catalyst layer (11a) among at least two catalyst layers (11a, 11b)
30 provided at intervals in a flow direction of the mixed gas.

[0076]

35 According to such a method, at least a part of hydrogen in the product gas is used as at least a part of hydrogen to be used in the methanation method, and therefore, the amount of hydrogen to be used in the methanation method can be reduced, and as a result, the operation cost of the hydrocarbon direct decomposition device can be reduced.

Reference Signs List

[0077]

1: Direct decomposition device

2: Methanation device

3: Hydrogen supply line

5 4: Raw material gas supply line

5: Processed gas supply line

6: Product gas flow line

7: Hydrogen recycle line

11a: First catalyst layer (catalyst layer)

10 11b: Second catalyst layer (catalyst layer)

13: Cooler

20: Catalyst

22: Reactor

Claims

[Claim 1]

A methanation device for removing a saturated hydrocarbon having two or more carbon atoms from a raw material gas containing methane and the saturated hydrocarbon through methanation, in which the saturated hydrocarbon is converted into methane by reacting the saturated hydrocarbon with hydrogen, the methanation device comprising:

at least two catalyst layers composed of a catalyst for the methanation, the at least two catalyst layers being provided at intervals in a flow direction of a mixed gas containing the raw material gas and a hydrogen-containing gas;

a hydrogen supply line configured to supply the hydrogen-containing gas to an upstream side of a most upstream catalyst layer in the flow direction of the mixed gas;

a raw material gas supply line configured to supply the raw material gas to each of the upstream side of the most upstream catalyst layer in the flow direction of the mixed gas and a space between two adjacent catalyst layers in the flow direction of the mixed gas; and

a cooler provided between two adjacent catalyst layers in the flow direction of the mixed gas and cooling the mixed gas flowing out from an upstream catalyst layer in the flow direction of the mixed gas among the two adjacent catalyst layers.

[Claim 2]

The methanation device according to claim 1, wherein an amount of the catalyst constituting each of the at least two catalyst layers is larger as the catalyst layer is disposed further downstream in the flow direction of the mixed gas.

[Claim 3]

The methanation device according to claim 1 or 2, wherein the catalyst is a supported catalyst in which nickel, iron, cobalt, or a noble metal element is supported on alumina.

[Claim 4]

A hydrocarbon direct decomposition device comprising:
the methanation device according to claim 1 or 2;

a reactor containing a catalyst for direct decomposition reaction of a hydrocarbon; and

a processed gas supply line configured to supply a processed gas, which is a gas flowing out from the methanation device, to the reactor.

[Claim 5]

The hydrocarbon direct decomposition device according to claim 4, comprising:

a product gas flow line through which a product gas containing hydrogen generated by direct decomposition of hydrocarbon in the reactor flows after flowing out from the reactor; and

a hydrogen recycle line communicating the product gas flow line with the hydrogen supply line.

[Claim 6]

A methanation method for removing a saturated hydrocarbon having two or more carbon atoms from a raw material gas containing methane and the saturated hydrocarbon through methanation, in which the saturated hydrocarbon is converted into methane by reacting the saturated hydrocarbon with hydrogen, the methanation method comprising:

causing a hydrogen-containing gas to flow into a most upstream catalyst layer among at least two catalyst layers composed of a catalyst for the methanation, the at least two catalyst layers being provided at intervals in a flow direction of a mixed gas containing the raw material gas and the hydrogen-containing gas;

causing a part of the raw material gas to flow into the most upstream catalyst layer in the flow direction of the mixed gas;

supplying a remainder of the raw material gas between two adjacent catalyst layers in the flow direction of the mixed gas;

cooling the mixed gas flowing out from an upstream catalyst layer among the two adjacent catalyst layers; and

causing the cooled mixed gas and the raw material gas supplied between the two adjacent catalyst layers in the flow direction of the mixed gas to flow into a downstream catalyst layer among the two adjacent catalyst layers.

[Claim 7]

The methanation method according to claim 6, wherein a supply amount of the hydrogen-containing gas is adjusted so that a concentration ratio of hydrogen to the saturated hydrocarbon in the mixed gas is 1 or more.

[Claim 8]

The methanation method according to claim 6 or 7, wherein the hydrogen-containing gas contains hydrogen and a component that does not contribute to the methanation.

[Claim 9]

The methanation method according to claim 6 or 7, comprising:
detecting a decrease in activity of the methanation; and
increasing a supply amount of the hydrogen-containing gas when the decrease in the activity is detected.

[Claim 10]

The methanation method according to claim 6 or 7, wherein the raw material gas is natural gas, compressed natural gas, city gas, liquefied petroleum gas, or naphtha.

[Claim 11]

A hydrocarbon direct decomposition method comprising:
converting the saturated hydrocarbon in the raw material gas into methane by the methanation method according to claim 6 or 7; and
directly decomposing methane in a processed gas, which is a gas after conversion of the saturated hydrocarbon into methane, into hydrogen and carbon by contacting the processed gas with a catalyst for direct decomposition reaction of a hydrocarbon.

[Claim 12]

The hydrocarbon direct decomposition method according to claim 11, wherein at least a part of a product gas containing hydrogen generated by directly decomposing methane in the processed gas into hydrogen and carbon is used as at least a part of the hydrogen-containing gas supplied to an most upstream catalyst layer among at least two catalyst layers provided at intervals in a flow direction of the mixed gas.