NATURAL GAS VEHICLE POWERTRAIN WITH ONBOARD CATALYTIC REFORMER

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ABSTRACT
Catalyst compositions and methods for use of such catalyst composition in the exhaust gas recycle stream of an internal combustion engine for reforming of a methane-containing fuel are provided. A reformer incorporating such a catalyst for use in an exhaust gas recycle portion of an internal combustion engine powertrain is described. A powertrain incorporating such a reformer, a method of increasing the octane rating of an exhaust gas recycle stream, and a method of operating an internal combustion engine for methane combustion are also described.
**Figure 5**

<table>
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<tr>
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<th>Converter in</th>
<th>Converter out</th>
<th>Converter in</th>
<th>Converter out</th>
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Figure 7

Propane reforming protocol steps / Catalyst A

Time on stream, h
Figure 8

Propane reforming protocol steps / Catalyst 8

Propane Conversion, %

Time on stream, h

0 5 10 15
Figure 9

Propane reforming protocol steps / Catalyst C

- Li
- III
- IV
- V

Propane Conversion, %

0% 5% 10% 15% 20% 25% 30% 35% 40% 45% 50%

Time on stream, h

0 5 10 15
Figure 10A

Conversion, %

- Methane
- Ethane
- Propane

Temperatures: 592°C, 507°C, 485°C, 439°C
Figure 10B

The graph shows the hydrogen concentration, mol %, at different temperatures. The temperatures are 592°C, 507°C, 485°C, and 439°C. The concentration values are 25%, 15%, 10%, and 5% respectively.
Figure 11A

Conversion, %

- Methane
- Ethane
- Propane

574°C  494°C  473°C  427°C
Figure 11B

H₂ concentration, mol% vs. temperature:
- 574°C: 25 mol%
- 494°C: 15 mol%
- 473°C: 10 mol%
- 427°C: 5 mol%
NATURAL GAS VEHICLE POWERTRAIN WITH ONBOARD CATALYTIC REFORMER

CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims the benefit of provisional U.S. Application No. 61/915,555, filed on Dec. 13, 2013, the entirety of which is incorporated herein by reference.

FIELD OF THE INVENTION

[0002] Embodiments of the invention relate to catalytic reforming of a mixture of a methane-containing fuel and internal combustion engine exhaust gas. In particular, embodiments of the invention relate to catalytic reforming of such engine exhaust gas recycle that contains an amount of methane and higher molecular weight organics sufficient to sustain the formation of H2 and CO (and/or CO2) in the reformer.

BACKGROUND

[0003] Conventional internal combustion engine designs can typically include a single fuel for combustion within the engine cylinders. This can require careful selection of an appropriate fuel, so that the fuel has appropriate combustion properties, such as a suitable Research Octane Number or a suitable flame speed. This can limit the selection of fuels, as some compositions that may be suitable from an energy content standpoint can lack appropriate combustion properties.

[0004] In addition to naphtha boiling range (gasoline) and distillate boiling range (kerosene or diesel) fuels, some alternative types of fuels are available for use in internal combustion engines. For example, an engine can be configured for use with natural gas as a fuel.

SUMMARY OF THE INVENTION

[0005] In one aspect, a method for reforming a fuel in an internal combustion engine is provided, said method including: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas recycle reformer comprising a reformer inlet, a reformer outlet, and a hydrocarbon-reforming catalyst composition, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, the hydrocarbon-containing fuel comprising at least about 50 mol % methane and a weighted carbon mole percentage of carbons in C2+ compounds of at least about 5%, and (b) converting under reforming conditions at least a portion of the exhaust gas-containing mixture in the presence of the hydrocarbon-reforming catalyst composition, the reforming conditions including a reformer outlet temperature of about 435°C to about 500°C. Optionally, the reformer inlet temperature can be about 525°C to about 550°C, or about 550°C to about 625°C, or about 625°C to about 600°C.

BRIEF DESCRIPTION OF THE DRAWINGS

[0007] FIG. 1 is a schematic representation of one embodiment of the powertrain.

[0008] FIG. 2 is a schematic representation of another embodiment of the powertrain.

[0009] FIG. 3 is a schematic representation of one embodiment of an engine for combustion of a methane-containing fuel.

[0010] FIGS. 4A and 4B are graphs of conversion rates and resulting hydrogen concentrations for conversion of methane in the presence of an exemplary catalyst composition.

[0011] FIG. 5 provides examples of feed and product compositions for reforming of a natural gas composition at various conditions.

[0012] FIG. 6 is a graph showing propane conversion rates during reforming of propane in the presence of various catalyst compositions.

[0013] FIG. 7 is a graph showing propane conversion during reforming of propane under various conditions.

[0014] FIG. 8 is a graph showing propane conversion during reforming of propane under various conditions.

[0015] FIG. 9 is a graph showing propane conversion during reforming of propane under various conditions.

[0016] FIGS. 10A and 10B are graphs of conversion rates and resulting hydrogen concentrations for conversion of natural gas in the presence of an exemplary catalyst composition.

[0017] FIGS. 11A and 11B are graphs of conversion rates and resulting hydrogen concentrations for conversion of natural gas in the presence of an exemplary catalyst composition.

DETAILED DESCRIPTION OF THE INVENTION

[0018] In the following description, all numbers disclosed herein are approximate values, regardless whether the word “about” or “approximate” is used in connection therewith. They may vary by 1%, 2%, 5%, and sometimes, 10 to 20%. Whenever a numerical range with a lower limit, R¹, and an upper limit, R², is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are expressly disclosed: R¹ - R² + k, (R² - R¹), wherein k is a variable ranging from 1% to 100% with a 1% increment, i.e., k can be 1%, 2%, 3%, 4%, 5%, ..., 50%, 51%, 52%, ..., 95%, 96%, 97%, 98%, 99%, or 100%. Moreover, any numerical range defined by two R numbers as defined in the above is also expressly disclosed. It is noted for listings of R¹ or R² that begin with “about,” e.g., the presence of about prior to each number is expressly included, but the term about is provided only once in the interest of clarity.

[0019] As used herein the terms “substantially free of an oxygen-containing gas” or “does not substantially include providing an oxygen containing gas” mean that an oxygen-containing gas other than the exhaust gas of the internal
A combustion engine is not purposely provided to the catalytic reforming unit. Additionally or alternatively, these terms can mean that not more than about 0.5 mol%, not more than about 0.2 mol%, not more than about 0.1 mol%, not more than about 0.05 mol%, or not more than about 0.01 mol% of the total amount of gas supplied to the reforming unit is an oxygen-containing gas other than the exhaust gas of the internal combustion engine.

Octane ratings described herein generally refer to the Research Octane Number (RON), unless otherwise specified. RON is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for mixtures of iso-octane and n-heptane.

Overview

One potential alternative to traditional naphtha boiling range fuels for internal combustion engines can be to use natural gas. Natural gas can pose some alternative engineering challenges for use in a vehicle, such as storing the natural gas as a compressed gas to allow for additional fuel storage, but the abundant availability of natural gas can make such a trade-off worthwhile.

Methane is typically the primary component of a natural gas feed. The octane rating of methane is 129, but the flame speed of a primarily methane-containing feed can be low. One option for improving the flame speed for the overall fuel can be to reform at least a portion of the feed to make hydrogen. This can provide an at least partially reforming feed with improved characteristics for operating an engine.

An option for reforming at least a portion of the feed can be to reform at least a portion of the methane in a feed. Steam reforming of methane in the presence of a catalyst can be implemented in a reaction zone within a powertrain in the engine. However, methane steam reforming is a reversible reaction, so achieving a desired level of reforming can be dependent on operating the reforming reaction at a desired temperature, as well as other selected conditions, so that a net amount of desired hydrogen is produced. Such a temperature can be lower than a conventional steam reforming temperature. Thus, using a reforming catalyst that is effective at the desired temperature can also be beneficial.

An alternate strategy for reforming a portion of a natural gas feed can be to focus on reforming the C2+ compounds within the feed, such as C2-C4 compounds or C2-C6 compounds. A typical natural gas feed can include about 3 vol% to about 10 vol% of C2+ compounds, such as ethane and propane. Conversion of such compounds is typically less endothermic than reforming of methane on a per carbon basis.

While reforming of methane is reversible, reforming of C2+ compounds is essentially irreversible at temperatures above 400°C under typical reforming conditions as described in this invention. Therefore, it can be desirable to select conditions that allow for conversion of C2+ compounds while reducing or minimizing the reactivity for methane formation from hydrogen and CO.

In various embodiments, the invention is based in part on discovery of a catalyst composition that can effectively convert an internal combustion engine exhaust stream containing a hydrocarbon-containing fuel to a mixture comprising H2, CO, CO2, H2O, N2, and a relatively large amount of methane, CH4. The methane can correspond to methane present in the hydrocarbon-containing fuel as well as methane formed under the conversion conditions via the methanation reaction. The conversion conditions can be selected to favor reforming of methane, to favor reforming of C2+ compounds with reduced or minimized methanation, or reforming of both methane and C2+ compounds.

A reformer operating in a powertrain environment can be viewed as a reformer operating under adiabatic conditions. During adiabatic operation of a reformer, the converter bed temperature can decrease because of the endothermic nature of the steam reforming reaction. As a result, the temperature across the reformer can decrease between the reformer inlet and the reformer outlet. Since methane reforming is reversible, the conversion of methane to syngas diminishes as the temperature at the converter (reformer) outlet decreases below a critical temperature, because the back reaction of syngas to methane becomes thermodynamically favored. Due in part to this reverse reaction, methane conversion and therefore the extent of heat recovery in the on-board reforming process are thermodynamically limited.

This thermodynamic limitation can be overcome at least in part by stopping the reforming process before the temperature in the converter decreases below a critical value. The critical temperature is a function of the converter inlet temperature and gas composition. In some aspects, for on-board reforming operating conditions, e.g., inlet temperatures of about 500°C to about 650°C, such as about 600°C, or less, pressures of about 1 barg (~100 kPag) to about 4 barg (~400 kPag), and steam/carbon ratios of about 0.3-1, the converter outlet temperature can be limited to at least about 450°C. This can be achieved, for example, by controlling the amount of fuel provided to the reformer, limiting the amount of available catalyst in the reformer, limiting the activity of the reforming catalyst, or a combination thereof. Maintaining a converter outlet temperature of at least about 450°C can reduce or minimize the amount of conversion of H2 and CO to form methane via the methanation reaction.

The invention further relates to a reforming catalyst that is able to function at lower temperatures and steam/carbon ratios than typically encountered in industrial steam reforming applications. The converter outlet temperature in the on-board methane reformer can be at least about 450°C and the molecular ratio of steam contained in the EGR to carbon atoms contained in the fuel can be ~<1. Under these conditions, catalyst coking is known to be a potential issue. This invention can use a modified steam reforming catalyst that reduces or minimizes formation of coke and allows operation in the low temperature regime.

The invention further relates to increasing the fuel efficiency of an internal combustion engine in natural gas vehicles (NGV). The concept can be to selectively reform the C2+ hydrocarbons or other compounds contained in natural gas into syngas using the steam and waste heat contained in the exhaust. In addition to the heat recovery, the efficiency of the combustion process can be enhanced by the formation of H2.

In such aspects, a fuel that includes both methane and C2+ components can be injected into a reformer catalyst inserted into an exhaust gas recirculation (EGR) loop. In the reformer, the fuel can be partially converted into CO and H2 by steam reforming using the heat, water, and CO2 contained in the exhaust. The fuel reforming is described for the example of the reforming reaction with water (steam) in reaction equations 1) for methane reforming, 2) for ethane
reforming, and 3) for propane reforming. Ethane and propane make up the main constituents of the C₃+ fuel components. 

\[
\begin{align*}
\text{C₃H₆+3H₂O} & \rightarrow \text{3CO+7H₂} \quad \text{ΔH_f} = -177 \text{ kJ/mol fuel} \\
\text{C₃H₄+2H₂O} & \rightarrow \text{2CO+5H₂} \quad \text{ΔH_f} = +186 \text{ kJ/mol fuel} \\
\text{C₄H₁₀+3H₂O} & \rightarrow \text{3CO+9H₂} \quad \text{ΔH_f} = +221 \text{ kJ/mol fuel}
\end{align*}
\]

[0031] Steam and CO₂ reforming of hydrocarbons to syngas is endothermic. The endothermicity per fuel carbon decreases for paraffins with increasing carbon number. Under certain of the conditions of the present invention, e.g., in the temperature range between about 550 °C and about 400 °C, and pressure range between about 100 kgf/cm² to about 300 kgf/cm², the steam and CO₂ reforming is reversible, while reforming of C₂+ hydrocarbons (including functionalized hydrocarbons such as alcohols), having lower temperature equilibrium limits, can continue to reform as temperature drops in an adiabatic operation beyond the point that methane would be reformed. Consequently the fuel conversion in the C₂/C₃+ combined reforming process could be potentially higher than it would be for methane fuel itself under kinetic limitation conditions.

[0032] This invention, in one embodiment, relates to identifying a suitable catalyst and process conditions that allow for conversion of C₃+ hydrocarbons in a fuel (such as a natural gas feed) into syngas while reducing or minimizing the back reaction of syngas to methane. It has been unexpectedly determined that selective conversion of C₃+ hydrocarbons can be performed if the conversion of C₂+ compounds is conducted at a temperature where the reaction of syngas to methane is kinetically limited. This can allow reforming of C₃+ compounds to be performed at the higher temperatures near the front of a reactor in an adiabatic operation while reducing or minimizing the amount of conversion of H₂ and CO to methane (i.e., the methanation reaction) that would form as the temperature drops at the tail end of the reactor.

[0033] In a fuel reforming process for selective reforming of C₃+ compounds, the converter inlet temperatures can be between about 500 °C to 650 °C while the outlet can be below about 500 °C, such as about 400 °C to about 500 °C, or about 400 °C to about 475 °C, or about 400 °C to about 450 °C. Additionally or alternatively, the molar ratio of water contained in the exhaust gas recycle to carbon contained in the fuel can be <1. Under these conditions catalyst coking is known to be a potential issue. This invention can use a modified steam reforming catalyst that reduces or minimizing formation of coke and allows operation in the low temperature regime in which conversion of C₂+ fuel components are thermodynamically favored while methane reforming and/or methanation are kinetically limited. A preferred catalyst can be based on rhodium supported on a mixed metal oxide comprising alumina, lanthana, ceria, and zirconia.

[0034] This invention further relates to optimizing the composition of a natural gas feed as transportation fuel. In order to take advantage of the C₂+ reforming it could be beneficial to set the specification of the natural gas composition to contain a minimum amount of C₂+ content. In regions with dry natural gas resources, the C₂+ content may be elevated by blending liquefied propane gas, ethanol, or other C₂+ molecules with natural gas to obtain a fuel that meets a desired compositional specification.

Reforming of Methane

[0035] In some embodiments, the fuel used for a combustion engine can be a fuel containing at least about 50 mol % of methane, such as a fuel based on a natural gas feed (optionally modified by addition of other fuel sources containing additional C₂+ compounds). In such aspects, the reformer can be operated to reform methane, or the reformer can be operated to selectively reform the C₂+ compounds in the fuel.

[0036] In some embodiments, the reforming of methane can be performed in the presence of a reduced or minimized amount of water. During conventional reforming of methane, the ratio of the amount of water in the reaction environment to the number of carbon atoms in the feed for reforming can be at least about 3:1. It has been determined that by performing the reforming in the presence of a suitable catalyst, the ratio of water to carbon atoms in the feed can be at least about 1.0:1, or at least about 0.5:1 to at least about 1.0:1, or at least about 0.5:1 to at least about 0.9:1. Operating the reforming with a reduced amount of water can be beneficial, as this amount of water can be provided by an exhaust gas recycle stream.

[0037] In various embodiments, a hydrocarbon-containing fuel can be a fuel that contains at least about 50 mol % methane, or at least about 70 mol %, or at least about 80 mol %, or at least about 90 mol %. Natural gas is an example of a potential hydrocarbon-containing fuel that contains substantial amounts of methane. The hydrocarbon-methane containing fuel can also contain C₂-C₃ compounds, such as alkenes and/or functionalized hydrocarbons such as alcohols. The alkenes can include n-alkanes (ethane, propane, butane) and/or branched alkenes. Similarly, the alcohols or other functionalized hydrocarbons can include linear and/or branched compounds. In addition (or alternatively) to alcohols, other examples of functional groups in the functionalized hydrocarbons can include alkenes, ketones, aldehydes, carboxylic acids, alkenes, glycols, ethers, esters, and combinations thereof. A typical natural gas feed may contain only a few mole percent of C₂-C₃ alkenes (or more generally a few mole percent of C₂-C₅ compounds). For example, the total amount of C₂+ alkenes and/or C₂+ compounds in a natural gas feed can be about 0.5 mol % to about 10 mol % of the feed. In some embodiments, such as where C₂-C₃ alkenes and/or C₂-C₄ compounds are selectively reformed, it can be beneficial to use a fuel containing at least a minimum amount of C₂+ alkenes and/or C₂+ compounds, or alternatively a minimum amount of C₂-C₅ alkenes and/or C₂-C₅ compounds, or alternatively a minimum amount of C₂-C₅ alkenes and/or C₂-C₅ compounds. In such embodiments, the lower limit on the amount of C₂+ alkenes and/or C₂+ compounds can be at least about 5 mol % of the fuel, or at least about 6 mol %, or at least about 7 mol %, or at least about 8 mol % or at least about 9 mol % or at least about 10 mol % or at least about 5 mol % or about at least 5 mol % or about at least 10 mol %, or at least about 15 mol %, or at least about 20 mol %, or at least about 25 mol %, while the upper limit can be about 50 mol % or less, or about 40 mol % or less, or about 30 mol % or less, or about 25 mol % or less, or about 20 mol % or less, or about 15 mol % or less, or about 10 mol % or less. It is noted that each of the lower limits and upper limits recited above for the amount of C₂+ alkenes and/or C₂+ compounds in a fuel are expressly contemplated in conjunction with each other.

[0038] Additionally or alternatively, the lower limit on the amount of C₂-C₃ alkenes and/or C₂-C₄ compounds can be at least about 5 mol % of the fuel, or at least about 6 mol %, or at least about 7 mol %, or at least about 8 mol % or at least about 9 mol % or at least about 10 mol %, or at least about 15
mol %, or at least about 20 mol %, or at least about 25 mol %, while the upper limit can be about 50 mol % or less, or about 40 mol % or less, or about 30 mol % or less, or about 25 mol % or less, or about 20 mol % or less, or about 15 mol % or less, or at least about 10 mol % or less, or about 5 mol % or less, or about 2.5 mol % or less, or about 1 mol % or less, or about 0.5 mol % or less. It is noted that each of the lower limits and upper limits recited above for the amount of C₂-C₄ alkanes and/or C₂-C₄ compounds in a fuel are expressly contemplated in conjunction with each other.

[0039] Further additionally or alternatively, the lower limit on the amount of C₂-C₄ alkanes and/or C₂-C₄ compounds can be at least about 1 mol % of the fuel, or at least about 3 mol %, or at least about 5 mol %, or at least about 6 mol %, or at least about 7 mol %, or at least about 8 mol %, or at least about 10 mol %, or at least about 15 mol %, or at least about 20 mol %, or at least about 25 mol %, while the upper limit can be about 50 mol % or less, or about 40 mol % or less, or about 30 mol % or less, or about 25 mol % or less, or about 20 mol % or less, or about 15 mol % or less, or about 10 mol % or less. It is noted that each of the lower limits and upper limits recited above for the amount of C₂-C₄ alkanes and/or C₂-C₄ compounds in a fuel are expressly contemplated in conjunction with each other.

[0040] Still further additionally or alternatively, the amount of C₂+ compounds in a fuel, such as the amount of C₂-C₄ alkanes and/or C₂-C₄ compounds, can be described using a weighted average based on the relative amounts of carbon that are present in the fuel. In a fuel, an alkane containing 2 carbons such as ethane can be reformed to generate a larger number of hydrocarbons than a 1 carbon compound (methane). Similarly, compounds containing still larger numbers of carbon atoms can generally be reformed to generate larger amounts of hydrogen. As a result, the amount of reformable C₂+ fuel in a fuel containing 1 mol % of ethane is not as large as the amount of reformable C₂+ fuel in a fuel that contains 1 mol % of butane. One option for characterizing this can be to describe the mole percentage of carbon atoms in a fuel that are present in the C₂+ compounds (or alternatively in C₂-C₄ compounds or in C₂-C₅ alkanes) relative to the total number of carbon atoms in the fuel. As an example, a fuel containing ~90 mol % CH₄ and ~10 mol % C₂H₂ will have a weighted carbon mole percentage of ~81% carbons in CH₄ and ~19% carbons in C₂H₂. Based on weighted carbon mole percentage, the number of carbons present in a fuel as C₂+ compounds (or alternatively in C₂-C₄ compounds or in C₂-C₅ alkanes) can be a weighted carbon mole percentage corresponding to a lower limit of at least about 5%, or at least about 6%, or at least about 7%, or at least about 8% or at least about 9% or at least about 10%, or at least about 15%, or at least about 20%, or at least about 25%, while the upper limit can be about 50% or less, or about 40% or less, or about 30% or less, or about 25% or less, or about 20% or less, or about 15% or less, or about 10% or less. It is noted that each of the lower limits and upper limits recited above for the weighted carbon mole percentage of carbon atoms in C₂+ compounds and/or C₂-C₅ alkanes and/or C₂-C₄ compounds in a fuel are expressly contemplated in conjunction with each other.

[0041] In order to generate a fuel containing a desired amount of C₂+ alkanes and/or C₂+ compounds, a natural gas feed can optionally be combined with another source of C₂+ alkanes and/or C₂+ compounds prior to entering the reformer or within a reformer. Examples of other sources of C₂+ alkanes and/or C₂+ compounds include (but are not limited to) liquefied petroleum gas, liquefied propane, and alcohols such as methanol and/or ethanol.

[0042] If selective reforming of C₂+ compounds is desired, the inlet and outlet temperatures of the reformer can be controlled to allow for improved reforming of C₂+ compounds while reducing or minimizing the amount of methanation (e.g., the reverse of methane reforming). This can be achieved in part by using a lower outlet temperature for the reformer. Conventionally, a lower outlet temperature for a reformer can pose difficulties, as the thermodynamic equilibrium for methane reforming versus methane formation tends to favor methane formation at lower temperatures. However, these reactions are also kinetically limited at lower temperatures, while substantially complete reforming of C₂+ compounds can be achieved. This can allow for reforming of the C₂+ compounds without reaching the equilibrium value for the methane reforming/conversion reaction. In aspects where selective reforming of C₂+ compounds is desired, the outlet temperature of the reformer can be at least about 435°C, or at least about 450°C, or at least about 465°C, or at least about 475°C. The inlet temperature can additionally or alternatively be about 650°C or less, or about 600°C or less, or about 585°C or less, or about 575°C or less, or about 560°C or less, or about 550°C or less. Maintaining a desired temperature for the reformer can allow for an effective amount of reforming while still maintaining a desired reformer outlet temperature under adiabatic operation.

[0043] If selective reforming of C₂+ compounds is desired, both the fuel and the reformer temperatures can be controlled to allow for improved reforming while reducing or minimizing the amount of methanation. It is noted that selective reforming of C₂+ compounds can still correspond to reforming more methane than C₂+ compounds, since the overall fuel contains at least about 50 mol % methane. For example, selective reforming of C₂+ compounds can correspond to having at least 15% of the carbons converted (reformed) in the reformer correspond to carbons from C₂+ compounds, or at least about 20%, or at least about 22%, or at least about 25%, or at least about 27%. Of course, the percentage of carbon atoms corresponding to C₂+ compounds can typically be less than 100% in a real feed containing at least about 50 mol % methane.

[0044] For a fuel containing at least about 50 mol % methane, or at least about 70 mol %, or at least about 80 mol %, one option for increasing the percentage C₂+ carbons that are converted (reformed) relative to the total number of carbons converted can be to increase the mol % of C₂+ compounds. In some aspects, a fuel can contain at least about 5 mol % of an individual C₂+ component, such as at least about 5 mol % of C₂ compounds, or at least about 5 mol % of C₃ compounds, or at least about 5 mol % of C₄ compounds, or at least about 5 mol % of C₅ compounds, or at least about 5 mol % of C₆ compounds, or at least about 5 mol % of C₇ compounds, or at least about 12 mol % of C₂+ compounds, or at least about 15 mol % of C₂+ compounds, or at least about 17 mol % of C₂+ compounds, or at least about 20 mol % of C₂+ compounds.

[0045] In some cases hydrogen can be added to the natural gas feed supplementing the amount of hydrogen produced by the reforming reactions. After any optional supplementing of the hydrogen content of a fuel, the hydrogen content of the fuel can be about 20 mol % or less, or about 15 mol % or less, or about 10 mol % or less, or about 5 mol % or less, or about 2 mol % or less, or about 1 mol % or less, or about 0.1 mol %
or less (meaning the fuel is substantially free of H₂). Alternatively the H₂ content of the feed to the reformer can be increased by forming H₂ in a dedicated cylinder from which the EGR is drawn. This can be accomplished by running the cylinder under rich combustion conditions or by feeding fuel into this cylinder during the expansion stroke to form cracked products along with H₂ from the C₃+ components.

Catalyst Composition—Reforming Components

[0046] In various embodiments, the catalyst composition can include at least a metal catalyst (or metal-containing catalyst) suitable for reforming of hydrocarbons or hydrocarbon-like compounds. Often the catalyst composition can further include one or more metal oxide components that act as a support for at least a portion of the metal catalyst. The catalyst composition can optionally further include one or more molecular sieves, such as medium pore or large pore molecular sieves with cracking activity. Optionally, at least a portion of the metal catalyst (or metal-containing catalyst) can be supported on the one or more molecular sieves with cracking activity and/or supported on the small pore molecular sieve.

[0047] The one or more metal oxide components may be selected from any suitable metal oxide(s). Exemplary metal oxides can include, but are not necessarily limited to, aluminum oxides, silicon oxides, rare-earth metal oxides, Group IV metal oxides (e.g., Al₂O₃, including θ-Al₂O₃ and/or γ-Al₂O₃), SiO₂, Y₂O₃, Sc₂O₃, La₂O₃, CeO₂, Pr₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, Tm₂O₃, ZrO₂, HfO₂, and mixtures thereof. For example, embodiments of a metal oxide mixture suitable for use in the catalyst compositions herein may include from about 1.0 wt % to about 99.0 wt %, based on the total weight of the catalyst composition, of a first metal oxide. The lower limit on the range of first metal oxide content may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, or 92.5 wt %.

The upper limit on the range of first metal oxide content may be about, e.g., 100.0 wt %, 97.5 wt %, 95.0 wt %, 92.5 wt %, 90.0 wt %, or 97.5 wt %. The upper limit on the range of second metal oxide content may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, or 92.5 wt %.

The lower limit on the range of second metal oxide content may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, or 90.0 wt %.

Combinations of such lower and upper limits may be selected, e.g., from about 1.0 wt % to about 5.0 wt %, from about 5.0 wt % to about 97.5 wt %, from about 97.5 wt % to about 95.0 wt %, from about 95.0 wt % to about 97.5 wt %, or from 97.5 wt % to 95.0 wt %.

[0048] In particular embodiments, the first metal oxide may itself be a mixture of oxides disclosed herein. For example, in an embodiment, the first metal oxide is a mixture of La₂O₃ and γ-Al₂O₃. For a mixture of La₂O₃ and γ-Al₂O₃, or more generally for a mixture of La₂O₃ and Al₂O₃, the La₂O₃ can correspond to about 0.4 wt % to about 20 wt % of the combined weight of La₂O₃ and Al₂O₃. For example, the La₂O₃ can correspond to at least about 0.4 wt % of the combined weight of La₂O₃ and γ-Al₂O₃, or at least about 1.0 wt %, or at least about 2.0 wt %, or at least about 5.0 wt %, or at least about 10.0 wt %, and/or about 20.0 wt % of less, or about 15.0 wt % or less, or about 10.0 wt % or less, or about 5.0 wt % or less, or about 2.0 wt % or less, or about 1.0 wt % or less. It is noted that all combinations for the upper and lower limit of the amount of La₂O₃ relative to the combined amount of La₂O₃ and Al₂O₃ are contemplated herein. The amount of the La₂O₃ and γ-Al₂O₃ together may be, for example, from about 20.0 wt % to about 90.0 wt %, such as from about 30.0 wt % to about 50.0 wt % or from about 32.5 wt % to about 37.5 wt %, based on the total weight of the catalyst composition. Optionally, in such embodiments, the second metal oxide may itself also be a mixture of oxides disclosed herein. For example, the second metal oxide may comprise CeO₂ and ZrO₂. The amount of the CeO₂ and ZrO₂ together may be, for example, from about 10.0 wt % to about 50.0 wt %, such as from about 15.0 wt % to about 70.0 wt % or from about 20.0 wt % to about 65.0 wt %, or from about 30.0 wt % to about 60.0 wt %, or from about 40.0 wt % to about 80.0 wt %, based on the total weight of the catalyst composition. The Ce/Zr atomic ratio may be, e.g., 10:0.5, 7.5:0.5, 5.0:1.0, 4.0:1.0, 3.0:1.0, 2.0:1.0, 1.0:1.0, or the like, or anywhere therein.

[0049] The at least one metal or metal-containing hydrocarbon reforming catalyst may be selected from the group consisting of Co, Ru, Rh, Pt, Pd, Fe, Ni, Ir, Zn, Re, and mixtures thereof. In some optional but preferred embodiments, the hydrocarbon reforming catalyst can be Rh or a mixture of metal-metal-containing catalysts that includes Rh. It will be understood that reference to the presence of such metals envisions their presence in elemental and/or compound form. Thus, amounts of such compounds refer to the total amount of metal, in the form or metal or in compound form, based on the total weight of the catalyst composition. The amount of metal-containing hydrocarbon reforming catalyst may range from about 1.0 wt % to about 50 wt %. The lower limit on the range of hydrocarbon reforming catalyst may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, or 90.0 wt %.

The upper limit on the range of metal-containing
hydrocarbon reforming catalyst content may be about, e.g., 1.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %. Combinations of such lower and upper limits may be selected, e.g., from about 1.0 wt % to about 20.0 wt %, from about 2.5 wt % to about 17.5 wt %, from about 5.0 wt % to about 15.0 wt %, from about 7.5 wt % to about 10.0 wt %, from about 1.0 wt % to about 10.0 wt %, from about 2.0 wt % to about 9.5 wt %, from about 2.5 wt % to about 9.0 wt %, from about 3.0 wt % to about 8.0 wt %, from about 4.0 wt % to about 7.7 wt %, etc., based on the total weight of the catalyst composition.

Exemplary embodiments of suitable hydrocarbon reforming catalysts or the catalyst compositions herein may include two or more such hydrocarbon reforming catalysts. For example, the catalyst composition may include a non-zero amount up to 20 wt %, based on the total weight of the catalyst composition, of a first hydrocarbon reforming catalyst. The lower limit on the range of first hydrocarbon reforming catalyst content may be about, e.g., 0.25 wt %, 0.50 wt %, 0.75 wt %, 1.0 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 4.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, or 20.0 wt %. The upper limit on the range of first hydrocarbon reforming catalyst content may be about, e.g., 0.50 wt %, 0.75 wt %, 1.0 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 4.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, or 20.0 wt %. Combinations of such lower and upper limits may be selected, e.g., from about 0.5 wt % to about 15.0 wt %, from about 1.0 wt % to about 10.0 wt %, from about 2.0 wt % to about 7.5 wt %, from about 2.5 wt % to about 5.0 wt %, etc. A second hydrocarbon reforming catalyst also may be present in an amount of >0 to about 20 wt %, based on the total weight of the catalyst composition. The lower limit on the range of second hydrocarbon reforming catalyst content may be about, e.g., 0.25 wt %, 0.50 wt %, 0.75 wt %, 1.0 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 4.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, or 20.0 wt %. Combinations of such lower and upper limits may be selected, e.g., from about 0.5 wt % to about 15.0 wt %, from about 1.0 wt % to about 10.0 wt %, from about 2.0 wt % to about 7.5 wt %, from about 2.5 wt % to about 5.0 wt %, from about 0.75 wt % to about 2.0 wt %, etc. In exemplary hydrocarbon reforming catalysts, the first hydrocarbon reforming catalyst can include or be Rh and the second hydrocarbon reforming catalyst can include or be Pt, e.g., such that the hydrocarbon reforming catalyst comprises from about 1.0 wt % to about 6.0 wt % Rh, from about 1.5 wt % to about 5.0 wt %, from about 2.0 wt % to about 4.5 wt %, from about 2.5 wt % to about 4.0 wt % Rh and from about 0.5 wt % to about 5.0 wt % Pt, from about 0.75 wt % to about 3.0 wt %, or from about 1.0 to about 2.0 wt % Pt, based on the total weight of the catalyst composition.

In some embodiments, the catalyst composition comprising the support (e.g., metal oxide(s)) and hydrocarbon reforming catalyst(s), and optionally any molecular sieves, can comprise >80.0 wt % (e.g., >82.5 wt %, >85.0 wt %, >87.5 wt %, >90.0 wt %, >92.5 wt %, >95.0 wt %, from about 95.5 wt % to about 100.0 wt %, from about 85.0 wt % to about 99.0 wt %, from about 87.5 wt % to about 95.0 wt % of particles having a size of 20-100 mesh (U.S.) (e.g., 25-90 mesh, 30-85 mesh, or 35-80 mesh). A more particular description for indicating particle size distribution using mesh size can be to use + and _ designations. A +“+” before the sieve mesh indicates the particles are retained by the sieve, while a “−” before the sieve mesh indicates the particles pass through the sieve. This means that typically ~90% or more (e.g., ~95% or more, ~96% or more, ~97% or more, ~98% or more, ~99% or more, or ~99.9% or more) of the particles will have mesh sizes between the two limits. For instance, if the particle size of a material is described as ~85+170, then ~90% or more of the material will pass through an 80 mesh sieve and be retained by a 170 mesh sieve. Thus, in some embodiments, the catalyst composition may have a particle size distribution of ~20+100 mesh, e.g., ~25+90 mesh, ~30+85 mesh, or ~35+80 mesh. It should be noted that the particle size range specified above pertains to the particular test reactor that was utilized for some of the catalytic tests of catalysts described herein. The preferred particle size range can change for different reactors and/or converter embodiments used in a vehicle application.

An additional or alternative option of describing particle size distribution refers to respective percentiles of log normal particle size distribution determined by means of a Malvern™ particle size analyzer using a hexane diluent. Thus, particles having a D50%, of, for example, 0.5 mm have a median particle size of ~0.5 mm. A D50% of 0.5 mm indicates that ~90% of the particles have a particle size of less than ~0.5 mm, and a D50% of 0.5 mm indicates that ~10% of the particles have a particle size of less than ~0.5 mm. The width or narrowness of a particle size distribution can be given by its span. The span is defined as (D90%−D10%)/(D50%), and is therefore dimensionless. In some embodiments, the catalyst composition may be characterized as having a D50%, from ~0.15 mm to ~1.0 mm (e.g., from ~0.95 mm to 0.16 mm, from ~0.60 mm to ~0.17 mm, or from ~0.50 mm to ~0.20 mm) and/or as having a span from about ~0.5 to ~10, e.g., from ~1.0 to ~6.0, from ~2.0 to ~5.0, or from ~3.0 to ~4.0.

In certain embodiments, reforming and/or cracking catalysts as described herein can be provided in a reformer (or other reaction environment) in the form of a washcoated monolithic converter. This type of catalyst embodiment for providing a supported catalyst is commonly used for automotive converters. In such an embodiment, the catalyst composition can be deposited on or otherwise supported on a flow through substrate with parallel or tortuous channels. The reactive gases can enter a plurality of channels at the front end of the converter and exit the same channels at the rear end of the converter. In another embodiment used, for example, for particulate filtration on diesel engines, half of the channels of the monolith can be plugged on the inlet side of the monolith and the alternate half of the channels can be plugged on the outlet side of the substrate. In this so-called wall flow substrate, the exhaust enters the portion of the channel system that is open on the inlet side. At least a portion of the exhaust then passes through the walls of the porous substrate and exits the substrate through the other half of the channel system. The monolith substrate can be made of, for example, ceramic or metal. Ceramic substrate materials include cordierite, SiC, alumina, titania and other oxides or mixtures of oxides. The catalyst is typically supported on the substrate in the form of a washcoat. An example of the preparation and application washcoats for monolithic catalysts is described in the literature "Catalytic Air Pollution" by Ronald M. Heck and Robert
J. Farrauto published by Van Nostrand Reinhold, 1995. The preparation of a monolith substrate typically includes the preparation of a slurry containing the catalyst powder and typically a binder material suspended in a liquid phase. The catalyst-containing slurry can then be washedcoated onto the substrate. The washedcoated substrate can then be subsequently dried and calcined in air or annealed in specified gas environments.

Catalyst Composition—Optional Cracking Component

In some embodiments, the catalyst composition can further include one or more molecular sieves, such as one or more zeolites that provide cracking activity for conversion of the C₆+ components in the feed. Any convenient molecular sieve with cracking activity can be used. For example, a molecular sieve with cracking activity such as ZSM-5 can be beneficial in some catalyst compositions. Other suitable molecular sieves can include medium pore and/or large pore molecular sieves. In some alternative aspects, instead of including a aluminosilicate type molecular sieve to provide cracking activity, a silicoaluminophosphate molecular sieve or an aluminophosphate molecular sieve can be included in the catalyst composition.

For molecular sieve(s) with cracking activity, the molecular sieve(s) can correspond to from about 1.0 wt % to about 99.75 wt %, based on the total weight of the catalyst composition. The lower limit on the range of the one or more molecular sieves added to the catalyst composition may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, 92.5 wt %, 95.0 wt %, or 97.5 wt %. The upper limit on the range of the one or more molecular sieves added to the catalyst composition may be about, e.g., 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, 92.5 wt %, 95.0 wt %, or 97.5 wt %.

ZSM-48 (U.S. Pat. No. 4,397,827); and ZSM-57 (U.S. Pat. No. 4,873,067). Non-limiting examples of SAPO and AlPO molecular sieves include one or a combination of SAPO-11, SAPO-31, SAPO-41, AlPO-11, AlPO-31, AlPO-41 and PST-6. The molecular sieve(s) can also be at least one large pore aluminosilicate, aluminophosphate, or silicoaluminophosphate zeolite containing 12-ring pores. Suitable large pore molecular sieves can include those having AFI, APS, ATO, ATS, *BEA, *BEC, BOG, BPH, CAN, CON, EMF, EON, *EZ, *FAI, GME, GON, IR, IUSV, *ITN, JWI, JWW, LTL, MAZ, MEL, MOR, MOZ, MSE, MTW, OFF, OKO, OSL, SAF, SAO, SEW, SFE, SFO, SFE, SSY, and USI frameworks, as well as combinations thereof.

Another additional or alternative option for characterizing a zeolite (or other molecular sieve) is based on the nature of the ring channels in the zeolite. The ring channels in a zeolite can be defined based on the number of tetrahedral framework atom included in the ring structure that forms the channel. In some embodiments, a zeolite can include at least one ring channel based on a 10-member ring. In such embodiments, the zeolite preferably does not have any ring channels based on a ring larger than a 10-member ring. Examples of suitable framework structures having a 10-member ring channel but not having a larger size ring channel can include EUO, FER, HEU, IFW, ITH, IMF, LAU, MEL, MFI, MFS, MTT, MVY, MWW, NES, PCR, PON, RRO, SFT, SGF, *SFV, STT, *SVO, STY, SZR, TON, TUN, and MRE, as well as combinations thereof.

A zeolite having the desired activity can have a silicon to aluminum molar ratio of about 2 to about 300, such as about 5 to about 100 or about 20 to about 40. For example, the silicon to aluminum ratio can be at least about 2, such as at least about 5, or at least about 10, or at least about 40, or at least about 50, or at least about 60. Additionally or alternately, the silicon to aluminum ratio can be about 300 or less, such as about 200 or less, or about 100 or less, or about 80 or less, or about 60 or less, or about 50 or less.

Additionally or alternately, the one or more molecular sieves in the catalyst composition can also include and/or be enhanced by a transition metal. The transition metal can be incorporated into the zeolite by any convenient method, such as by impregnation or by ion exchange. If the transition metal is added to the molecular sieve(s) prior to incorporating the molecular sieve(s) into the catalyst composition, the amount of transition metal can be expressed as a weight percentage of the one or more molecular sieves, such as having at least about 0.1 wt % of transition metal, or at least about 0.25 wt %, or at least about 0.5 wt %, or at least about 0.75 wt %, or at least about 1.0 wt %. Additionally or alternately, the amount of transition metal can be about 20 wt % or less, such as about 10 wt % or less, or about 5 wt % or less, or about 2.0 wt % or less, or about 1.5 wt % or less, or about 1.2 wt % or less, or about 1.1 wt % or less, or about 1.0 wt % or less. It is noted that the amount of transition metal is in addition to the weight of metal or metal-containing reforming catalyst in the catalyst composition.

Further additionally or alternately, the one or more molecular sieves can include non-framework phosphorus and/or be enhanced by phosphorus treatment. Including phosphorus in the additional molecular sieve can potentially provide increased stability for the molecular sieve(s) in the reaction conditions present during reforming and/or methanation as described herein. The weight of the phosphorus can be about 0.1 wt % to about 10.0 wt % based on the weight of
the additional molecular sieve. Thus, the upper limit on the range of the phosphorus added to the one or more molecular sieves may be 10.0 wt %, 9.0 wt %, 8.0 wt %, 7.0 wt %, 6.0 wt %, 5.0 wt %, 4.0 wt %, 3.0 wt %, 2.0 wt %, 1.0 wt %, or 0.1 wt %; and the lower limit on the range added to the additional molecular sieve may be 10.0 wt %, 9.0 wt %, 8.0 wt %, 7.0 wt %, 6.0 wt %, 5.0 wt %, 4.0 wt %, 3.0 wt %, 2.0 wt %, 1.0 wt %, or 0.1 wt %. Ranges expressly disclosed include combinations of any of the above-enumerated upper and lower limits; e.g., 0.1 to 10.0 wt %, 0.1 to 8.0 wt %, 0.1 to 6.0 wt %, 0.1 to 5.0 wt %, 0.1 to 4.0 wt %, 0.1 to 3.0 wt %, 0.1 to 2.0 wt %, 0.1 to 1.0 wt %, 1.0 to 10.0 wt %, 1.0 to 9.0 wt %, 1.0 to 8.0 wt %, 1.0 to 7.0 wt %, 1.0 to 6.0 wt %, 1.0 to 5.0 wt %, 1.0 to 4.0 wt %, 1.0 to 3.0 wt %, etc. Of course, these total weights of the phosphorus shall be understood to exclude any phosphorus in the molecular sieve framework.

[0061] In embodiments where one or more molecular sieves are included in the catalyst composition, at least a portion of the metal catalyts(s) for reforming can be supported on the molecular sieve(s), or all of the metal catalyts(s) for reforming can be supported on the metal oxides.

Catalyst Composition—Optional Small Pore Zeolite

[0062] Additionally or alternatively, a small pore molecular sieve can be beneficial in the catalyst composition, such as a zeolite having the CHA framework type. In such additional or alternative embodiments, at least a portion of the metal or metal-containing catalyst can be supported on the small pore molecular sieve. In some aspects, the metal or metal-containing catalyst supported on the small pore molecular sieve can be rhodium. Supporting at least a portion of the (reforming) metal or metal-containing catalyst on the small pore molecular sieve can enhance the reforming reactivity for both methane and lower molecular weight C₂+ components.

[0063] In this discussion, unless specifically noted otherwise, references to CHA framework type zeolites are understood to generally refer to any zeolite (or other molecular sieve) having the chabazite framework type. The chabazite framework type is designated as framework type code CHA in the International Zeolite Association database of zeolite structures. Other zeolites having the CHA framework type can include AIPO-34, MCM-2, MeAPO-44, MeAPO-47, SAPO-34, SAPO-47, SSZ-13, SSZ-62, and ZK-14, as well as combinations thereof. Chabazite can refer to a naturally occurring or a synthetic form of chabazite. Unless otherwise specified, a reference to chabazite, should be understood to generally refer to the zeolite chabazite (natural or synthetic), optionally containing any of the potential various counter ions and/or additional metals that can be present.

[0064] While rhodium supported on CHA framework type molecular sieve of the present invention can effectively enhance the formation of methane, additional rhodium supported multi-dimensional small pore molecular sieves can also be effective. Suitable small pore molecular sieves can include those having the AEI, AFI, AFX, ATT, DDR, EAB, EPI, ERI, KFI, LEV, LT A, MER, MON, MTP, PAU, PHI, RHO, and/or SFW framework types.

[0065] An additional or alternative option for characterizing small pore molecular sieves can be based on the ring structures in the molecular sieves. Some suitable small pore molecular sieves can include molecular sieves having an 8-member ring channel as the largest pore size for the molecular sieve.

[0066] Another additional or alternative option for characterizing small pore molecular sieves can be based on the effective size of the pore channels. In some embodiments, a suitable small pore molecular sieve can include a largest pore channel that has a maximum dimension of about 4.8 Angstroms or less, e.g., about 4.7 Angstroms or less, about 4.6 Angstroms or less, about 4.5 Angstroms or less, about 4.4 Angstroms or less, or about 4.3 Angstroms or less. In such a molecular sieve, the largest pore channel may also have a minimum dimension of at least about 3.5 Angstroms, or at least about 3.6 Angstroms, or at least about 3.7 Angstroms. In this discussion, the maximum and minimum dimensions of a pore channel for a molecular sieve refer to the size of a sphere that can diffuse through such a pore channel, as reported in the Database of Zeolite Structures that is maintained by the International Zeolite Association.

[0067] In various embodiments, the weight of the CHA framework type molecular sieve (or small pore molecular sieve) in the catalyst composition, and/or the weight of chabazite in the catalyst composition, can be from 1.0 wt % to 99.75 wt %, based on the total weight of the catalyst composition. The lower limit on the range of CHA framework type molecular sieve (or small pore molecular sieve) content, and/or the lower limit on the chabazite content, may be about, e.g., 1.0 wt %, 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, 92.5 wt %, 95.0 wt %, or 97.5 wt %. The upper limit on the range of CHA framework type molecular sieve (or small pore molecular sieve) content, and/or the lower limit on the chabazite content, may be about, e.g., 2.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, 17.5 wt %, 20.0 wt %, 22.5 wt %, 25.0 wt %, 27.5 wt %, 30.0 wt %, 32.5 wt %, 35.0 wt %, 37.5 wt %, 40.0 wt %, 42.5 wt %, 45.0 wt %, 47.5 wt %, 50.0 wt %, 52.5 wt %, 55.0 wt %, 57.5 wt %, 60.0 wt %, 62.5 wt %, 65.0 wt %, 67.5 wt %, 70.0 wt %, 72.5 wt %, 75.0 wt %, 77.5 wt %, 80.0 wt %, 82.5 wt %, 85.0 wt %, 90.0 wt %, 92.5 wt %, 95.0 wt %, 97.5 wt %, or 100.0 wt %.

[0068] In embodiments where the catalyst composition also includes one or more metal oxides, the catalyst composition can include at least a minimum amount of chabazite (and/or a CHA framework type zeolite or other small pore molecular sieve) such as any of the lower limit amounts described above.

[0069] In some embodiments, the metal or metal-containing catalyst in a catalyst composition including a small pore molecular sieve can be any of the metal or metal-containing catalysts described above in the amounts as described above. This can include aspects where the metal or metal-containing catalyst is Rh or includes Rh. Alternatively, a first metal or metal-containing catalyst can be supported on the metal oxide support portion of the catalyst composition while a second metal or metal-containing catalyst, preferably Rh, can be supported on the small pore molecular sieve. In such embodiments, if any medium or large pore molecular sieves are also included in the catalyst composition, the medium or large
pore molecular sieves can support no metal or metal-containing catalyst, or support a portion of the metal or metal-containing catalyst present on the metal oxide support, or support a portion of the metal or metal-containing catalyst present on the small pore molecular sieve, or a combination thereof.

[0070] In embodiments where different metal or metal-containing catalysts are supported on the metal oxide portion and the small pore molecular sieve portion of a catalyst composition, the total amount of metals in the catalyst composition can correspond to any convenient combination of an amount of metal or metal-containing catalyst supported on the small pore molecular sieve and an amount of metal or metal-containing catalyst supported on the metal oxide support. As an example, a catalyst composition may include Rh as a reforming metal catalyst on the small pore molecular sieve portion of the catalyst composition while including Ru on the metal oxide support portion of the catalyst composition. For example, the catalyst composition may include a non-zero amount up to about 20 wt %, based on the total weight of the catalyst composition, of a first metal or metal-containing compound(s) such as Rh and/or an Rh-containing compound (or other metal selected from Co, Ru, Rh, Pt, Pd, Fe, Ni, Ir, and combinations thereof that is supported on the small pore molecular sieve). The lower limit on the range of the first metal content may be about, e.g., 0.05 wt %, 0.10 wt %, 0.25 wt %, 0.50 wt %, 0.75 wt %, 1.0 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 4.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, or 20.0 wt %. The upper limit on the range of the first metal content may be about, e.g., 50.0 wt %, 75.0 wt %, 100.0 wt %, 125.0 wt %, 150.0 wt %, 175.0 wt %, or 200.0 wt %. Combinations of such lower and upper limits may be selected, e.g., from about 0.5 wt % to about 15.0 wt %, from about 1.0 wt % to about 10.0 wt %, from about 2.0 wt % to about 7.5 wt %, from about 2.5 wt % to about 5.0 wt %, etc. The catalyst supported on the metal oxide support portion of the catalyst composition may also be present in an amount of >0 to about 20.0 wt %, based on the total weight of the catalyst composition. The lower limit on the range of catalyst supported on the metal oxide support may be about, e.g., 0.05 wt %, 0.10 wt %, 0.25 wt %, 0.50 wt %, 0.75 wt %, 1.0 wt %, 2.0 wt %, 2.5 wt %, 3.0 wt %, 4.0 wt %, 5.0 wt %, 7.5 wt %, 10.0 wt %, 12.5 wt %, 15.0 wt %, or 20.0 wt %. The upper limit on the range of catalyst supported on the metal oxide support may be about, e.g., 50.0 wt %, 75.0 wt %, 100.0 wt %, 125.0 wt %, 150.0 wt %, 175.0 wt %, or 200.0 wt %. Combinations of such lower and upper limits may be selected, e.g., from about 0.5 wt % to about 15.0 wt %, from about 1.0 wt % to about 10.0 wt %, from about 2.0 wt % to about 7.5 wt %, from about 2.5 wt % to about 5.0 wt %, etc. For example, an Rh or an Rh-containing compound may be supported on a small pore molecular sieve portion of the catalyst composition while Ru or an Ru-containing compound may be supported on the metal oxide portion of the catalyst composition, e.g., such that the catalyst composition comprises from about 1.0 to about 6.0 wt % Rh, from about 1.5 to about 5.0 wt %, from about 2.0 to about 4.5 wt %, or from about 2.5 to about 4.0 wt % Rh and from about 0.5 to about 5.0 wt % Ru, from about 0.75 to about 3.0 wt %, or from about 1.0 to about 2.0 wt % Ru, based on the total weight of the catalyst composition.

Reforming and Cracking in an Engine or Power Train Environment

[0071] In various embodiments, the average reformer temperature can be maintained at or above about 450°C, e.g., above about 500°C, above about 550°C, above about 600°C, above about 650°C, from about 450°C to about 650°C, from about 500°C to about 650°C, from about 550°C to about 600°C, from about 450°C to about 550°C, or from about 475°C to about 525°C.

[0072] One option for maintaining and/or increasing the temperature of a reforming reactor can be to use pre-combustion of a portion of the fuel as a source of heat for the reforming reactor. Pre-combustion can allow the inlet temperature for the reforming reactor to be varied without having to vary some other temperature within the engine. Conventionally, pre-combustion of fuel to provide heat for a reformer in an engine is not preferred, as any fuel burned to heat the reformer represents fuel that cannot be used to drive the powertrain. However, due to the thermodynamic limitation and potential kinetic limitations on the reforming reactions, using pre-combustion can allow increasing the amount of conversion before the thermodynamically limited or kinetically limited temperature is reached. For example, pre-combustion can allow the inlet temperature of the reformer to be increased to a temperature of about 525°C to about 650°C, or about 525°C to about 625°C, or about 525°C to about 600°C, or about 550°C to about 650°C, or about 550°C to about 625°C, or about 550°C to about 600°C. The resulting increase in enthalpy of the product mix due to the reforming reaction can raise the heat of combustion, which can essentially offset the loss in efficiency due to the pre-combustion. This can be desirable up to a point where raising the feed temperature by pre-combustion would lead to significant heat losses to the surrounding; e.g., a temperature over about 650°C.

[0073] In some embodiments, the invention can include a reformer for use in an exhaust gas recycle portion of an internal combustion engine powertrain, said reformer comprising at least one catalyst composition described herein. Such a reformer may be used in a method of operating an internal combustion engine. This may be accomplished, e.g., by providing an exhaust gas-containing mixture to an exhaust gas recycle reformer. The exhaust gas-containing mixture can typically comprise engine exhaust gas and a first hydrocarbon-containing fuel. At least a portion of the exhaust gas-containing mixture can be passed to the reformer and converted by the catalyst composition in the presence of heat to a reformed gaseous mixture (product) having an increased content of H₂ relative to the mixture of exhaust gas and first hydrocarbon-containing fuel. The reformed gaseous mixture and a second hydrocarbon-containing fuel may be provided to the engine for combustion. Typically, the second hydrocarbon-containing fuel can be the same as the first hydrocarbon-containing fuel (i.e., it can be convenient to draw both the first and second hydrocarbon-containing fuels from a common source or tank, in some embodiments), although this need not always be the case. Where desired, the second hydrocarbon-containing fuel may be different from the first hydrocarbon-containing fuel. The reformed gaseous mixture and second hydrocarbon-containing fuel can then be combusted in the engine to form an exhaust gas. The net exhaust gas vented from the engine can be passed through a first heat exchanger to extract heat therefrom. The heat can be transferred to the reformer feed to aid in sustaining the reforming reactions therein.
[0074] An important direction in future gasoline engines can be use of exhaust gas recycle (EGR). In some aspects, use of recycled exhaust gas as part of the input fuel mixture to the engine can lower the temperature for combustion. This can allow the engine to run at a higher compression ratio without causing knocking, which can provide increased efficiency. However, the compression ratio and amount of exhaust gas recycle are limited conventionally by practical concerns. Increasing the amount of exhaust gas recycle in a conventional engine can cause the fuel delivered to the engine to become too dilute, leading to problems with the fuel flame speed. Additionally, the compression ratio can be limited by the fuel octane rating, or resistance of a fuel to combustion prior to spark ignition.

[0075] In various embodiments, use of exhaust gas recycle with reforming of fuel prior to combustion can allow for increased use of the exhaust gas recycle. For example, use of EGR can provide a medium with H₂O and CO₂ as reactants for reforming of natural gas to produce H₂-rich gas to raise flame speed and potentially octane by reforming of lower octane C₂+ components to H₂ and CO. Typical ranges for EGR that can be used for the engine in conjunction with reforming can include about 20 vol % to 50 vol % of the engine air/EGR mix. For example, the amount of EGR can be at least about 20 vol % of the combined air and exhaust gas delivered to the engine, or at least about 25 vol %, or at least about 30 vol %, or at least about 35 vol %, and/or about 50 vol % or less, or about 45 vol % or less, or about 40 vol % or less, or about 35 vol % or less. It is noted that each of the lower limits and upper limits for the amount of exhaust gas recycle are explicitly contemplated in combination with each other. All or a portion of this EGR can be fed in conjunction with the natural gas fuel (or other fuel) from tankage to the reformer. The desired amount of EGR relative to feed to the reformer can depend on fuel input, engine design and engine load points. A high level of EGR can increase the amount of H₂O and CO₂ available for reforming, which can potentially mitigate the extent of temperature drop in the reformer. Alternatively, lowering EGR can raise the fuel concentration and thereby can enhance the kinetics for conversion.

[0076] The use of the catalyst compositions herein can serve to provide an increase in the flame speed of an internal combustion engine exhaust gas hydrocarbon mixture stream, consisting of natural gas and natural gas plus C₂+ additions as described herein. An exhaust gas-containing mixture may be provided to an exhaust gas recycle reformer including a catalyst as described herein. The exhaust gas-containing mixture can typically comprise engine exhaust gas and a first hydrocarbon-containing fuel.

[0077] In various embodiments, a hydrocarbon-containing fuel can have a laminar flame speed at stoichiometric air to fuel ratio as measured at 25°C and 1 atm of about 30 cm/sec to about 70 cm/sec. Addition of exhaust gas (such as by combining the hydrocarbon-containing fuel with an exhaust gas recycle stream) can reduce this laminar flame speed to a less than about 10 cm/sec, or less than about 5 cm/sec. Reforming of the mixture of hydrocarbon-containing fuel and exhaust gas can be used to produce a reformed mixture having a flame speed that is increased relative to the mixture prior to reforming. Thus, the reformed mixture can have a laminar flame speed of greater than about 5 cm/sec, or greater than about 7.5 cm/sec, or greater than about 10 cm/sec, or greater than about 15 cm/sec.

[0078] The reformer may also be incorporated into an internal combustion engine powertrain. Many different variations of such power trains are known. One such powertrain envisioned can include an internal combustion engine having an exhaust manifold and a fuel intake manifold. A reformer comprising a catalyst composition as described herein can fluidly connect the exhaust manifold and the fuel intake manifold. The reformer and catalyst composition can be specifically configured to convert an exhaust gas-containing mixture formed from the exhaust manifold gas and a first hydrocarbon-containing fuel to a reformed gaseous mixture comprising H₂, CO, and CH₄, along with one or more exhaust gas constituents—typically including N₂, H₂O, CO₂, trace quantities of minor species such as NOₓ and SOₓ, and the like. Conversion of a hydrocarbon feed should be understood to be calculated solely by the ratio of the difference between the mass (or number of moles) of hydrocarbon component of the feed entering the inlet of the reforming zone and the mass (or number of moles) of hydrocarbon component exiting the outlet of the reforming zone, divided by the mass (or number of moles) of hydrocarbon component of the feed entering the inlet of the reforming zone. Typically, the intake manifold can be configured to provide a reformed fuel mixture from the exhaust gas recycle unit and a second hydrocarbon-containing fuel to the internal combustion engine for combustion. As described above, the first and second hydrocarbon-containing fuels may be the same or different.

[0079] Referring now to FIG. 1, there is shown a schematic representation of an embodiment of such a powertrain. In FIG. 1, air can be drawn into the powertrain by a compressor (1). The power for compressor (1) can come from a turbine (2) that can expand the exhaust gases (3) from the engine exhaust manifold. The compressed air from the compressor can then be cooled in a cooler (4). The air flow rate can be controlled by a throttle valve (5). The air can then be mixed with the EGR stream (9) and delivered to the engine intake manifold (6). A portion of the exhaust gas (3) from the engine can be sent to an EGR stream where converter (7) and cooler means (8) can treat the EGR portion of the engine exhaust prior to reinsertion to the engine, while the remaining exhaust gas can be expanded in turbine (2) and vented to the atmosphere (10).

[0080] Hydrocarbon-containing fuel can be supplied to the powertrain in FIG. 1 by injection means (11) into the EGR stream. The EGR stream can comprise substantially components from the exhaust of the engine, which may represent a portion or substantially all the exhaust from the engine. This EGR stream can typically comprise N₂, water vapor (H₂O), CO₂, un-combusted hydrocarbons, and small amounts of CO and O₂.

[0081] Additionally or alternatively to situations where the fuel(s) correspond to a methane-containing fuel as described above, the hydrocarbon-containing fuel can be a conventional fuel, such as gasoline, and may optionally be the primary fuel supplied to the engine by direct injection into the engine. In such situations, other fuels can be used instead of or in combination with the conventional fuel (gasoline). Other such fuels can include, but are not necessarily limited to, LPG (liquefied petroleum gas), light ends, C₅-C₁₂ paraffins, naphtha, kerosene, diesel, FCC off-gases, oxygenated hydrocarbons (e.g., dialkyl ethers such as dimethyl ether, diethyl ether, methyl ethyl ether, and the like, and combinations thereof; C₇-C₁₂ alcohols such as methanol, ethanol, 1-propanol, iso-propanol, 1-butanol, 2-butanol, isobutanol, a pentanol, a hexanol, and the like, and combinations thereof; fatty acid alkyl
esters, for instance from mono-, di-, and/or tri-glyceride reaction with a C1-C4 alcohol, such as represented by FAME, FAEE, and the like, and combinations thereof; and the like; and combinations thereof), hydrocarbon-rich gas overhead from a refinery process, hydrocarbon-rich off-gas from a chemical process, or the like, or combinations thereof.

[0082] Whatever fuel is used as a feed in the methods described herein, it can advantageously have one, two, or all of the following characteristics: a relatively high paraffin content, no more than a modest aromatics content, and a relatively small content of polynuclear aromatics (PNAs), meaning compounds having two or more aromatic rings in its structure, typically two or more aromatic rings connected to each other, e.g., sharing two carbon atoms between them. The overall aromatics content of the hydrocarbon-containing fuel to be fed into the reforming zone can advantageously be no more than about 35 wt% (e.g., no more than about 30 wt%, no more than about 25 wt%, no more than about 20 wt%, no more than about 15 wt%, or no more than about 10 wt%), based on the weight of the hydrocarbon-containing fuel (optionally, the fuel can additionally have some aromatics content, e.g., at least about 0.1 wt%, at least about 0.5 wt%, at least about 1 wt%, at least about 2 wt%, at least about 3 wt%, at least about 4 wt%, at least about 5 wt%, at least about 7 wt%, at least about 10 wt%, or at least about 15 wt%, based on the weight of the hydrocarbon-containing fuel). Additionally or alternately, the PNA content of the hydrocarbon-containing fuel to be fed into the reforming zone can advantageously be no more than about 3 wt% (e.g., no more than about 2 wt%, no more than about 1 wt%, no more than about 0.5 wt%, or no more than about 0.1 wt%), based on the weight of the hydrocarbon-containing fuel (though PNAs can typically be undesirable for relatively high conversion in reforming, the fuel may nonetheless optionally have some PNA content, e.g., at least about 0.001 wt%, at least about 0.005 wt%, at least about 0.01 wt%, at least about 0.03 wt%, at least about 0.05 wt%, at least about 0.07 wt%, at least about 0.1 wt%, at least about 0.2 wt%, at least about 0.3 wt%, or at least about 0.5 wt%, based on the weight of the hydrocarbon-containing fuel). Further additionally or alternately, the paraffin content of the hydrocarbon-containing fuel to be fed into the reforming zone can advantageously be greater than about 50 wt% (e.g., at least about 55 wt%, at least about 60 wt%, at least about 65 wt%, at least about 70 wt%, at least about 75 wt%, at least about 80 wt%, at least about 85 wt%, at least about 90 wt%, at least about 95 wt%, at least about 96 wt%, at least about 97 wt%, at least about 98 wt%, or at least about 99 wt%), based on the weight of the hydrocarbon-containing fuel (though paraffinic hydrocarbons can typically be very desirable for relatively high conversion in reforming, the fuel may nonetheless optionally have some upper limit on paraffin content, e.g., up to about 99.9 wt%, up to about 99.5 wt%, up to about 99 wt%, up to about 98 wt%, up to about 97 wt%, up to about 96 wt%, up to about 95 wt%, up to about 90 wt%, up to about 85 wt%, up to about 80 wt%, up to about 75 wt%, up to about 70 wt%, up to about 65 wt%, or up to about 60 wt%, based on the weight of the hydrocarbon-containing fuel).

[0083] In FIG. 2, the fuel can be pre-heated and vaporized before its injection into the EGR stream using waste heat in the engine exhaust stream. The fuel and exhaust gas in the EGR stream can be reacted in a reformer including a catalyst composition according to embodiments of the invention to form syngas (CO/CO2 and H2) and methane (CH4). Additionally, the reformer may also be heated by combusting a hydrocarbon-containing fuel during cold starts. The EGR stream leaving the reformer, i.e., the reformed fuel stream, can optionally be cooled by passing it through a heat exchanger. The reformed fuel stream may, upon cooling, be supplied to the engine cylinders or co-mingled with a primary fuel delivered to the engine by direct injection.

[0084] In one embodiment, the generation of hydrogen in the powertrain of FIG. 1 can be accomplished by an initial endothermic reaction to produce syngas. Alternatively, start-up hydrogen may be supplied by stored hydrogen (not shown), which optionally may be replenished after start-up by operation of the reforming reaction.

[0085] Referring now to FIG. 2, there is shown a schematic representation of another embodiment of a powertrain having a reformer of the present invention in the EGR loop. A feature of this second embodiment is that two turbine-compressor systems are used. In FIG. 2, air and exhaust gas from the EGR stream can be mixed and compressed by compressor (20). The power for compressor (20) can come from a turbine (21) that can expand the EGR stream. The compressed mixture from (20) can be cooled in a cooler (24) and compressed by a second compressor (22). The power for compressor (22) can come from a turbine (23) that can expand the exhaust gas vented to the atmosphere. The compressed air and EGR gas can be cooled at (25) and then delivered to the engine (26). A portion of the exhaust gas from the engine can be sent to an EGR stream (27), while the remaining exhaust gas (28) can be expanded in turbine (23), fed over a three-way catalyst in a catalytic converter (32) and vented to the atmosphere. Fuel can be provided from a fuel tank (34), injected into the EGR stream (29), and the stream can then be passed to reformer (30), substantially identical to that described in the embodiment of the invention depicted in FIG. 1. The stream exiting the reformer can be expanded in turbine (21), cooled in a cooler (31), and finally mixed with the air stream supplying the powertrain. Optionally, fuel may be preheated and/or vaporized prior to injection into the EGR stream, e.g., by means of a heat exchanger (33). Heat can be derived from the net exhaust by first raising the exhaust temperature by combustion of residual hydrocarbons and CO over a three-way catalyst. The heat transfer from the three-way catalyst to the hydrocarbon feed is merely one potential mechanism for heat integration. There are other ways of attaining heat integration than described in FIG. 2 that derive heat from the net engine exhaust gas, and any one or more of them may be used in tandem with the invention, in addition or alternatively to the configuration shown in FIG. 2.

[0086] FIG. 3 shows an example of an engine configuration that can be adapted for use with a natural gas feed or other type of fuel containing less than 50 mol% of methane. In the configuration shown in FIG. 3, a compressed natural gas fuel reservoir (301) can be used to provide a hydrocarbon-containing fuel. The natural gas fuel reservoir (301) can provide fuel stream (302) directly to intake manifold (310) and can provide a secondary fuel stream (304) that can be combined with exhaust gas (343) from exhaust manifold (340). The intake manifold can receive both fuel stream (302) and combined exhaust gas and fuel stream (352) from reformer (350). The fuel can be combusted with air (inlet not shown) in engine cylinders (320). The exhaust from cylinders (320) can be passed into exhaust manifold (340). In addition to exhaust gas stream (343) that can be used for the exhaust gas recycle loop, exhaust manifold (340) can also produce a primary exhaust stream (347). In the con-
Additional Embodiments

Embodiment 1

A method for reforming a fuel in an internal combustion engine, said method comprising: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer; the exhaust gas recycle reformer comprising a reformer inlet, a reformer outlet, and a hydrocarbon-reforming catalyst composition, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, the hydrocarbon-containing fuel comprising at least about 50 mol % methane, and (b) converting under reforming conditions at least a portion of the exhaust gas-containing mixture in the presence of a hydrocarbon-reforming catalyst composition comprising at least about 0.1 wt % of a hydrocarbon-reforming metal catalyst supported on a mixed metal oxide support, the mixed metal oxide support comprising at least about 20 wt % of a mixture of lanthanum oxide and aluminum oxide and at least about 10 wt % of a mixture of cerium oxide and zirconium oxide, the aluminum oxide optionally being γ-alumina oxide.

Embodiment 2

The method of Embodiment 1, wherein the mixed metal oxide support consists essentially of the mixture of lanthanum oxide and aluminum oxide and the mixture of cerium oxide and zirconium oxide.

Embodiment 3

The method of Embodiments 1 or 2, wherein the mixture of lanthanum oxide and aluminum oxide comprises about 0.4 wt % to about 15 wt % of lanthanum oxide based on the combined weight of lanthanum oxide and aluminum oxide.

Embodiment 4

A method for reforming a fuel in an internal combustion engine, said method comprising: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer comprising a reformer inlet, a reformer outlet, and a hydrocarbon-reforming catalyst composition, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, the hydrocarbon-containing fuel comprising at least about 50 mol % methane and a weighted carbon mole percentage of carbons in \( C_2+ \) compounds of at least about 5%, and (b) converting under reforming conditions at least a portion of the exhaust gas-containing mixture in the presence of the hydrocarbon-reforming catalyst composition, the reforming conditions including a reformer outlet temperature of about 435°C to about 500°C.

Embodiment 5

The method of Embodiment 4, wherein the reformer inlet temperature is about 525°C to about 650°C, or about 535°C to about 625°C, or about 550°C to about 600°C.

Embodiment 6

The method of any of the above embodiments, wherein the hydrocarbon-containing fuel comprises at least about 70 mol % methane, or at about 80 mol % methane, or at least about 90 mol % methane.

Embodiment 7

The method of any of the above embodiments, wherein the hydrocarbon-containing fuel comprises at least about 5 mol %, or at least about 10 mol %, of ethane, ethanol, propane, propane isomers, butane, butane isomers, \( C_3 \) compounds, \( C_4 \) compounds, or combinations thereof.

Embodiment 8

The method of any of the above embodiments, wherein the hydrocarbon-containing fuel comprises at least about 10 mol % (or at least about 15 mol %) of \( C_2+ \) compounds, or at least about 10 mol % (or at least about 15 mol %) of \( C_2 \) to \( C_4 \) compounds, or at least about 10 mol % (or at least about 15 mol %) of \( C_2 \) to \( C_4 \) compounds.

Embodiment 9

The method of any of the above embodiments, wherein the hydrocarbon-containing fuel comprises at least about 50 mol % of \( C_2+ \) compounds of at least about 5%, or at least about 10%, or a weighted carbon mole percentage of carbons in \( C_3 \) to \( C_4 \) compounds of about 5%, or at least about 10%, or a weighted carbon mole percentage of carbons in \( C_3 \) to \( C_4 \) alkanes of at least about 5%, or at least about 10%.

Embodiment 10

The method of any of the above embodiments, wherein the hydrocarbon-containing fuel comprises at least about 5 mol % or less of \( H_2 \) prior to converting at least a portion of the exhaust gas mixture under reforming conditions, wherein converting the at least a portion of the exhaust gas-containing mixture generates a reformed gas product comprising at least about 20 mol % to about 20 mol % \( H_2 \), or a combination thereof.

Embodiment 11

The method of any of the above embodiments, wherein the hydrocarbon-reforming catalyst composition comprises a hydrocarbon-reforming metal catalyst loading from 0.5 wt % to 10.0 wt %, based on the total weight of the catalyst composition.

Embodiment 12

The method of any of the above embodiments, wherein the hydrocarbon-reforming metal catalyst is selected from the group consisting of Co, Ru, Rh, Pt, Pd, Ni, Ir, Zn, Re, and mixtures thereof, the hydrocarbon-reforming metal catalyst optionally comprising Rh.

Embodiment 13

The method of any of the above embodiments, wherein the hydrocarbon-reforming catalyst composition further comprises at least one medium pore molecular sieve or large pore molecular sieve, the at least one medium pore
molecular sieve or large pore molecular sieve optionally comprising ZSM-5, phosphorus-modified ZSM-5, MCM-68, or a combination thereof.

**Embodiment 14**

[0100] The method of any of the above embodiments, wherein the hydrocarbon-reforming catalyst composition further comprises at least one small pore molecular sieve, the at least one small pore molecular sieve optionally comprising chabazite, a CHA framework molecular sieve, or a combination thereof.

**Embodiment 15**

[0101] The method of any of the above embodiments, wherein providing an exhaust gas-containing mixture to an exhaust gas recycle reformer comprises: passing at least a portion of the first hydrocarbon-containing fuel into a cylinder of the internal combustion engine after the combustion of the reformed gaseous mixture and second hydrocarbon-containing fuel to form a portion of the exhaust gas; cracking the at least a portion of the first hydrocarbon-containing fuel in the cylinder to form a cracked hydrocarbon-containing fuel; and providing the portion of the exhaust gas and the cracked hydrocarbon-containing fuel to the exhaust gas recycle reformer.

**Embodiment 16**

[0102] The method of Embodiment 15, further including prior to introducing the reformed gaseous mixture into the internal combustion engine, cooling the gaseous mixture by passing the gaseous mixture through the first heat exchanger or a second heat exchanger.

**Embodiment 17**

[0103] The method of any of the above embodiments, further comprising combusting a portion of the exhaust gas mixture prior to converting the at least a portion of the exhaust gas mixture under reforming conditions.

**EXAMPLES**

**Example 1**

**General Temperature Profile for Adiabatic Reforming**

[0104] A series of tests was performed using a reforming catalyst composition in a plug flow reactor to simulate the reaction conditions that may be expected in a reforming reactor or engine or powertrain environment. The reforming catalyst composition used in the tests (Catalyst A) included ~3.5 wt % Rh supported on a mixed metal oxide comprising La2O3–Al2O3 (25 wt % of total) and CeO2–ZrO2 (70 wt % of total). The La2O3–Al2O3 support was prepared separately by impregnation of an aqueous La(NO3)3 solution onto γ-Al2O3 followed by drying and calcination at ~600 °C. CeO2–ZrO2 was co-precipitated from an aqueous Ce(NO3)3 and Zr(NO3)4 solution onto the La2O3–Al2O3 support using urea as a base. The Ce/Zr atomic ratio was ~4:1. The La–γ-Al2O3–CeO2–ZrO2 support was calcined at ~600 °C prior to incipient wetness impregnation with an aqueous solution containing Rh(NO3)3. After the precious metal impregnation the catalyst was calcined for ~6 hours in air at ~600 °C.

[0105] In the tests, ~0.01 g of catalyst powder (Catalyst A) sized to ~25-40 mesh was diluted with ~1.88 g of silica. The diluted catalyst was loaded into a vertically mounted cylindrical quartz plugged flow reactor (~6 mm id×15 mm long) which was heated by a furnace. The temperature was measured in the front catalyst bed (~¼ inch from catalyst inlet) and in the rear catalyst bed (~¼ inch from the catalyst outlet). The average catalyst bed temperature was defined as the arithmetic average between the catalyst front bed and rear bed temperatures. A feed gas comprising ~16.1 mol % methane, ~15.3 mol % H2O, and ~8.13 mol % CO2 in N2 (balance of feed gas) was fed over the catalyst to achieve a gas hourly space velocity of ~26 khr⁻¹ at ~1.3 barg (~130 kPag). This corresponded to a fuel delivery rate of ~2.76 g methane/g Rh/s. The concentration of hydrocarbons was monitored by GC/FID (gas chromatography-flame ionization detection), while the concentration of reaction products carbon monoxide and hydrogen was detected by GC/TCD analyzers (gas chromatography-thermal conductivity detector). Data were collected for ~6 hours on stream at each temperature. The reforming reaction was investigated at different temperatures using the same catalyst. After completing the test at each temperature, the catalyst in the reactor was subjected to a stream containing ~5% O2 at ~550 °C for ~10 min to remove any carbonaceous deposits that may have formed on the catalyst during the NG reforming step.

[0106] Table 1 below shows furnace set temperatures and the measured temperatures for the front and back of the catalyst bed at each furnace set temperature. It was noted that the catalyst bed temperatures tended to be slightly higher than the furnace set temperatures. This was because the heat flux from the furnace to the catalyst bed was larger than the heat consumed by the endothermic methane steam reforming reaction. The average of the front and back bed temperatures is shown as the temperature in FIGS. 4A and 4B.

<table>
<thead>
<tr>
<th>Furnace Temp °C</th>
<th>Top bed Temp °C</th>
<th>Bottom bed Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>~600</td>
<td>~608</td>
<td>~616</td>
</tr>
<tr>
<td>~500</td>
<td>~514</td>
<td>~520</td>
</tr>
<tr>
<td>~475</td>
<td>~493</td>
<td>~499</td>
</tr>
<tr>
<td>~450</td>
<td>~468</td>
<td>~473</td>
</tr>
<tr>
<td>~425</td>
<td>~442</td>
<td>~448</td>
</tr>
</tbody>
</table>

[0107] FIGS. 4A and 4B show results from the tests at the various temperatures. For the results in FIGS. 4A and 4B, the methane conversion and hydrogen production values shown at each temperature corresponded to an average of the values measured between ~1 hour and ~6 hours on stream at the corresponding temperature. As shown in FIG. 4A, the amount of methane converted by the reforming catalyst was reduced as the temperature in the reactor was reduced. FIG. 4B shows a similar drop in the hydrogen concentration in the effluent from the reactor as the temperature was reduced.

[0108] It was noted that the results in FIG. 4A indicated that the reaction conditions used in the tests appeared to result in a kinetically limited reaction. To determine this, model simulations were performed using an adiabatic Gibbs reactor simulation of a comparable reactor. The simulations were performed using a pressure of ~1 barg (~100 kPag), and a feed to the reformer was simulated as a mixture of a pure methane feed with about 30% exhaust gas recycle from a combustion
engine. Because the simulations were adiabatic, the temperature of the reforming reactor decreased across the reactor. At an inlet temperature of −600°C, the resulting outlet temperature was −449°C. In the simulation with an outlet temperature of −449°C, the amount of methane converted was about 17%. By contrast, FIG. 4A shows that only about 9% of methane was converted at an average reactor temperature of −445°C. This indicated that methane conversion was kinetically limited.

Example 2

Simulation of C₂+ Conversion in a Natural Gas Feed

Table 2 shows an example for a fuel composition of natural gas fuel containing methane and C₂+ components comprising ethane, propane, iso-butan e, n-butan e, and iso-pentane. As shown in Table 2, an example of a potential natural gas composition was substantially composed of methane (more than 90 mol%), with less than 5 mol% of each of propane and ethane.

<table>
<thead>
<tr>
<th>Example of a Natural Gas Composition</th>
<th>Mol %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>94.1</td>
</tr>
<tr>
<td>Ethane</td>
<td>1.77</td>
</tr>
<tr>
<td>Propane</td>
<td>−3.29</td>
</tr>
<tr>
<td>2-methylpropane</td>
<td>−0.66</td>
</tr>
<tr>
<td>n-butane</td>
<td>−0.42</td>
</tr>
<tr>
<td>2-methylbutane</td>
<td>−0.02</td>
</tr>
</tbody>
</table>

The example of a natural gas composition shown in Table 2 was used as the basis for performing simulations for reforming of natural gas fuel. The reforming was simulated at a ~600°C and a ~500°C inlet temperature at ~1 barg (~100 kPag) of pressure. A Gibbs adiabatic reactor model was used to simulate the product composition produced from steam reforming of the natural gas composition when combined with ~30% exhaust gas recycle with equilibrium being reached.

FIG. 5 shows the results from an adiabatic Gibbs reactor simulation of reforming the mixture of exhaust gas and natural gas at the ~600°C and ~500°C inlet temperatures. As shown in FIG. 5, the outlet temperature for the ~600°C simulation was almost 150°C lower than the inlet temperature. At a starting temperature of ~500°C, a more modest temperature reduction of about 90°C was predicted. This was due in part to the reduced conversion rate for methane at lower temperatures due to the equilibrium limitation.

One feature of the simulation results shown in FIG. 5 was that a ~500°C inlet temperature appeared to result in the net formation of methane by about 2%, while about 4% of the methane was converted at the ~600°C inlet temperature. By contrast, substantially all of the ethane, propane, and butane present in the natural gas feed appeared to be converted at either temperature. It was noted that the mole fraction values shown in FIG. 5 represented the total composition. Thus, even though the absolute number of moles of N₂ did not change during the simulation, the relative mole fraction can change if the product has greater (or fewer) moles. In order to arrive at the net formation or conversion values for the simulation results shown in FIG. 5, the mole fraction of methane needed to be normalized based on the mole fraction of nitrogen in the products. The results in FIG. 5 demonstrated that the C₂+ components in a fuel containing a majority of methane can be reformed with high selectivity relative to the amount of methane reformed. In order to take further advantage of reforming of a fuel at temperatures between about 550°C and about 400°C, one can use a catalyst having suitable activity for reformating C₂+ compounds in the desired temperature range, a low activity for reforming methane in the temperature range, and a reduced or minimized activity for methanation in the temperature range.

Example 3

Propane Steam Reforming

Propane steam reforming was performed using three different types of catalyst compositions including Rh as a reforming catalyst. It was noted that Catalyst A corresponded to a catalyst composition made using a mixture of the oxide supports used for Catalyst B and Catalyst C.

Catalyst A included ~3.5 wt % Rh supported on a mixed metal oxide comprising La₃O₇–γ-Al₂O₃ (~35 wt % of total) and CeO₂–ZrO₂ (~60 wt % of total). The La₃O₇–Al₂O₃ support was prepared separately by impregnation of an aqueous La(NO₃)₃ solution onto γ-Al₂O₃, followed by drying and calcination at ~600°C. CeO₂–ZrO₂ was co-precipitated from an aqueous Ce(NO₃)₃ and Zr(NO₃)₄ solution onto the La₃O₇–Al₂O₃ support using urea as base. The Ce/Zr atomic ratio was ~4:1. The La₃–γ-Al₂O₃–CeO₂–ZrO₂ support was calcined at ~600°C prior to incipient wetness impregnation with an aqueous solution containing Rh(NO₃)₃. After the precious metal impregnation the catalyst was calcined for ~6 hours in air at ~600°C.

Catalyst B included ~3.5 wt % Rh supported on a La₃O₇–γ-Al₂O₃ mixed metal oxide. The La₃O₇–γ-Al₂O₃ support was prepared separately by impregnation of an aqueous La(NO₃)₃ solution onto γ-Al₂O₃, followed by drying and calcination at ~600°C. An aqueous solution of Rh(NO₃)₃ was impregnated onto the La₃O₇–γ-Al₂O₃ support by incipient wetness impregnation as described for catalyst A, followed by drying and calcination for ~6 hours in air at ~600°C.

Catalyst C included ~3.5 wt % Rh supported on a CeO₂–ZrO₂ mixed metal oxide. CeO₂–ZrO₂ was prepared by co-precipitation from an aqueous Ce(NO₃)₃ and Zr(NO₃)₄ solution using urea as base. The Ce/Zr atomic ratio was ~4:1. The CeO₂–ZrO₂ support was calcined at ~600°C prior to incipient wetness impregnation with an aqueous solution containing Rh(NO₃)₃. After the precious metal impregnation the catalyst was calcined for ~6 hours in air at ~600°C.

Using Catalysts A-C, a series of propane reforming tests were conducted in order to test the catalysts activity for reforming one of the C₂+ components. The sequence consisted of four steps denoted as test protocols II (step 1), III (step 2), IV (step 3), and V (repeat of step 1). Each protocol is described below.

Test Protocol II (Propane Reforming, No Syngas Components Added)...

For the propane reforming test in test protocol II, ~0.088 g of catalyst powders A, B, and C were each sized to ~25–40 mesh and diluted with silica at a ratio ~1:15. The diluted catalyst was loaded into a vertically mounted cylindrical quartz plugged flow reactor (~6 mm id×15 mm long) which was heated by a furnace. The temperature was measured in the front catalyst bed (~1/4 inch from catalyst inlet) and in rear catalyst bed (~1/4 inch from the catalyst outlet).
The average catalyst bed temperature was calculated from the catalyst bed temperatures at the inlet and outlet. A feed gas comprising -13.3 mol % propane, -27.4 mol % H₂O, and -26.6 mol % CO₂ in N₂ (balance of gas composition) was fed over the catalyst to achieve a gas hourly space velocity of ~26 khr⁻¹ at a furnace set temperature of ~400°C. The conversion of propane and the concentration of the reaction product methane were monitored by FID, while the concentration of reaction products carbon monoxide and hydrogen were detected by GC/TCD analyzers. Prior to the reforming test, catalysts were reduced for ~20 minutes in a stream containing ~20% hydrogen balance N₂, followed by a N₂ sweep for ~20 minutes at ~400°C. After ~3 hours of reforming test II, catalysts were subjected to a stream containing ~5% O₂ (balance N₂) for ~5 minutes at ~400°C furnace set temperature in order to remove carbonaceous deposits that were formed during the reforming test II. The oxidation step was followed by a N₂ sweep for ~15 minutes at ~400°C.

[0120] Test Protocol III (Propane Reforming, Addition of H₂)

[0121] After completing test protocol II, including the oxidation and reduction steps at the end of the protocol, test protocol III was applied. In test protocol III, a feed similar to the propane-containing feed in test protocol II was used, except that ~17% of the feed N₂ was replaced with H₂ in order to study the effect of hydrogen on the reforming of propane. After ~3 hours of reforming test III, catalysts were subjected to a stream containing ~5% O₂ (balance N₂) for ~5 minutes at ~400°C in order to remove carbonaceous deposits that were formed during the reforming test III. The oxidation step was followed by a N₂ sweep for ~15 minutes at ~400°C.


[0123] After completing test protocol III, including the oxidation and reduction steps at the end of the protocol, test protocol IV was applied. In test protocol IV, a feed similar to the propane-containing feed in test protocol II was used, except that ~23% of the feed N₂ was replaced with ~17% H₂ and ~6% CO in order to study the effect of hydrogen and CO on the reforming of propane. After the reforming test IV, catalysts were subjected to a stream containing ~5% O₂ (balance N₂) for ~5 minutes at ~400°C in order to remove carbonaceous deposits that were formed during the reforming test IV. The oxidation step was followed by a N₂ sweep for ~15 minutes at ~400°C.

[0124] Test Protocol V (Repeat of Test Protocol II)

[0125] After completing test protocol IV, including the oxidation and reduction steps at the end of the protocol, test protocol V was applied. Test protocol V was a repeat of the conditions from test protocol II.

[0126] The results from applying test protocols II, III, IV, and V to Catalysts A, B, and C are shown in FIGS. 6-9. In FIG. 6, the rate of propane reforming is shown for Catalysts A, B, and C under the conditions of test protocol V. As shown in FIG. 6, Catalyst A appeared to have a higher propane steam reforming activity than either Catalyst B or Catalyst C. This result was unexpected, as Catalyst A has a similar reforming catalyst (Rh) content to Catalyst B and Catalyst C. The main difference between Catalyst A and Catalyst B or Catalyst C was that Catalyst A had a mixture of the support oxides used for Catalyst B and Catalyst C.

[0127] FIGS. 7-9 provide further details regarding the differences in activity for the catalysts. In FIG. 7, the activity of Catalyst A was shown for the full sequence of test protocols II, III, IV, and V. As shown in FIG. 7, introducing H₂ (test III) or H₂ and CO (test IV) into the reactor substantially increased the rate of propane conversion. During exposure to propane in the presence of syngas components, the rate of propane conversion was shown to be reduced. This was believed to be due to coking of the catalyst, which was expected behavior during reforming in the presence of syngas components. As shown in test V, the Catalyst A appeared to retain its activity after exposure to reforming environments that included syngas components and subsequent regeneration cycles.

[0128] FIG. 8 shows the results of performing test protocols II, III, IV, and V on Catalyst B. Similar to Catalyst A, the initial activity for conversion of propane appeared to increase when exposed to syngas components (or at least H₂), as shown in tests III and IV. However, the activity of Catalyst B for propane reforming appeared to drop more sharply than Catalyst A. As shown in tests III and IV in FIG. 8, the rate of propane reforming appeared to have leveled off at about 15% by about halfway through each of tests III and IV. This was in contrast to FIG. 7, where more than ~20% of the propane was being converted at the end tests III and IV. It was noted that the overall activity of Catalyst B also appeared to be lower for propane reforming. The rate of propane reforming without syngas components was lower than Catalyst A, and the rate when both H₂ and CO were present (test IV) was also clearly lower.

[0129] FIG. 9 shows the results of performing test protocols II, III, IV, and V on Catalyst C. Catalyst C appeared to show different behavior than Catalysts A or B, in that introducing syngas components into the reforming environment did not appear to substantially change the activity of Catalyst C for propane conversion. However, in tests II and V, where no syngas components were present, Catalyst C appeared to have a higher baseline activity for propane reforming. Also, Catalyst C did not show a significant reduction in catalyst activity over time when exposed to syngas components.

[0130] Based on the results shown in FIGS. 6-9, it appeared that using a mixture of the oxide supports from Catalyst B and Catalyst C resulted in a catalyst composition (Catalyst A) that received the benefits of the two different support oxides while reducing or minimizing the disadvantages. Catalyst A appeared to have a higher baseline activity (test V) as shown in FIG. 6) than either Catalyst B or Catalyst C. Catalyst A also appeared to have received the higher activity in the presence of syngas components of Catalyst B, while receiving at least some of the resistance to activity loss in the presence of syngas components that was observed for Catalyst C. Additionally, it was noted that Catalyst A appeared to be superior to either Catalyst B or Catalyst C for propane reforming in the presence of both H₂ and CO. During test IV, relative to tests II or V without syngas components, Catalyst B showed a small increase in activity, followed by a sharp decline back to a level modestly above tests II or V, while Catalyst C showed almost no activity change at all. By contrast, Catalyst A showed a larger initial increase in activity during test IV and a more shallow decline in activity over time.

Example 4

Reforming of C₂⁺ Components of Natural Gas

[0131] Additional characterization of Catalyst A was performed by using Catalyst A for steam reforming of a natural gas feed. During reforming of the natural gas feed, ~0.1 g of catalyst powder A sized to ~25-40 mesh was diluted with ~1.8
g of silica. The diluted catalyst was loaded into a vertically mounted cylindrical quartz plugged flow reactor (~6 mm idx~15 mm long), which was heated by a furnace. The temperature was measured in the front catalyst bed (~¼ inch from catalyst inlet) and in the rear catalyst bed (~¼ inch from the catalyst outlet). The average catalyst bed temperature was defined as the arithmetic average between the catalyst front bed and rear bed temperatures. A feed gas comprising ~16.1 mol % methane, ~0.30 mol % ethane, 0.74 mol % propane, ~15.3 mol % H₂O, and ~8.1 mol % CO₂ in N₂ balance was fed over the catalyst to achieve gas hourly space velocities of ~10 khr⁻¹ and ~20 khr⁻¹ at ~1.3 barg (~130 kPa). The total fueling rate was ~0.26 g fuel/g Rh/s. The concentration of hydrocarbons was monitored by GC/FID, while the concentration of reaction products carbon monoxide and hydrogen was detected by GC/TCD analyzers. Data were collected for ~6 hours on stream at each temperature and average conversions between ~1 hour and ~6 hours on stream were reported. After each temperature step, the catalyst was subjected to a stream containing ~5% O₂ at ~500° C. for ~10 minutes to remove any carbonaceous deposits that may have formed on the catalyst during the NO reforming step.

Tables 3 and 4 show the furnace set temperatures, the catalyst bed temperatures at the top and bottom, and the average catalyst bed temperatures measured for tests using the natural gas reforming test protocol over catalyst A for space velocities of ~10 khr⁻¹ and ~20 khr⁻¹, respectively.

**TABLE 3**

<table>
<thead>
<tr>
<th>Furnace Temp °C</th>
<th>Top bed Temp °C</th>
<th>Bottom bed Temp °C</th>
<th>Avg bed Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>~600</td>
<td>~571</td>
<td>~541</td>
<td>~587</td>
</tr>
<tr>
<td>~500</td>
<td>~434</td>
<td>~515</td>
<td>~475</td>
</tr>
<tr>
<td>~475</td>
<td>~475</td>
<td>~495</td>
<td>~485</td>
</tr>
<tr>
<td>~425</td>
<td>~432</td>
<td>~446</td>
<td>~439</td>
</tr>
</tbody>
</table>

**TABLE 4**

<table>
<thead>
<tr>
<th>Furnace Temp °C</th>
<th>Top bed Temp °C</th>
<th>Bottom bed Temp °C</th>
<th>Avg bed Temp °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>~600</td>
<td>~557</td>
<td>~591</td>
<td>~574</td>
</tr>
<tr>
<td>~500</td>
<td>~484</td>
<td>~505</td>
<td>~494</td>
</tr>
<tr>
<td>~475</td>
<td>~463</td>
<td>~483</td>
<td>~473</td>
</tr>
<tr>
<td>~425</td>
<td>~417</td>
<td>~437</td>
<td>~427</td>
</tr>
</tbody>
</table>

Fig. 10A shows methane, ethane, and propane conversions as a function of the average catalyst bed temperature for natural gas reforming over catalyst A at a space velocity of ~10 khr⁻¹ at the temperatures shown in Table 3. As shown in Fig. 10A, conversions appeared to decrease with decreasing temperature, with methane having a noticeably larger drop in the amount of conversion relative to ethane or propane. For example, at temperatures near ~500° C., over 95% of the ethane and propane was converted, while about 20% or less of the methane was converted. Even at the lowest temperature of ~450° C., the ethane conversion was about 70%, while propane conversion was about 90%. Fig. 10A shows that controlling the conditions in a reforming reactor at temperatures below about 550° C. can be an effective way for selectively reforming C₃+ components in a natural gas feed.

Fig. 10B shows the resulting H₂ concentration in the output from the reforming reaction under the conditions from Table 3. Although the amount of methane conversion had been dramatically reduced, Fig. 10B shows that the amount of H₂ present in the reformer output fell off only modestly. This demonstrated that a suitable amount of H₂ can be generated in the reformer output by selectively reforming the C₃+ components in a suitable natural gas-type feed.

Figs. 10A and 11B were similar to Figs. 10A and 10B, but show results from reforming at ~20 khr⁻¹ at the conditions shown in Table 4. In Fig. 11A, the amount of ethane and propane reforming at various temperatures was shown to be lower due to the increased space velocity, but, qualitatively, the results in Fig. 11A were similar to Fig. 10A. Fig. 11B is also similar to Fig. 10B, with lower amounts of H₂ in the reformer effluent due to the increased space velocity.

Calculations were also performed to determine how the reaction product concentrations from the tests correlated to Table 4 related to expected equilibrium concentrations based on thermodynamics. The approach to equilibrium for the tests shown in Table 4 was characterized using the following formula:

\[ \eta = \frac{P_{CH₄} P_{H₂O}}{P_{CO} P_{H₂}} \left( \frac{1}{K_e} \right) \]

where \( P_{CH₄} \), \( P_{H₂O} \), \( P_{CO} \), and \( P_{H₂} \) represented the respective partial pressures of methane, water, carbon monoxide, and hydrogen at the reactor outlet, and \( K_e \) represented the equilibrium constant for the methanation reaction.

Table 5 lists the values for \( \eta \) and the fraction of C₃+ conversion relative to the total fuel conversion in the natural gas reforming tests at ~20 khr⁻¹ for the temperatures in Table 4. In Table 5, the fraction of C₃+ conversion refers to the amount of hydrocarbons from C₃+ compounds that were reformed relative to the total number of fuel hydrocarbons that were reformed.

**TABLE 5**

<table>
<thead>
<tr>
<th>Reactor avg Temp °C</th>
<th>( \eta )</th>
<th>Fraction of fuel C converted from C₃+</th>
</tr>
</thead>
<tbody>
<tr>
<td>~600</td>
<td>~591</td>
<td>~3.0</td>
</tr>
<tr>
<td>~500</td>
<td>~505</td>
<td>~3.0</td>
</tr>
<tr>
<td>~483</td>
<td>~483</td>
<td>~3.0</td>
</tr>
<tr>
<td>~437</td>
<td>~437</td>
<td>~3.0</td>
</tr>
</tbody>
</table>

As shown in Table 5, at temperatures of about 500° C. or less, the composition produced by selectively reforming the C₃+ components started to diverge more substantially from the equilibrium composition. This was believed to be due to kinetic differences between conversion (reforming) of C₃+ compounds versus conversion of methane. At temperatures of about 500° C. or less, reforming of C₃+ compounds (such as C₂ to C₃ compounds) to form typical syngas components can have sufficiently favorable kinetics to allow for substantially complete reforming of C₃+ compounds under the reforming conditions. By contrast, the reactions for
reforming of methane and/or the reverse reaction for methane formation can be kinetically limited under the reforming conditions. As a result, at temperatures between about 435°C to about 500°C, the output composition from reforming of a fuel mixture containing both methane and C2+ compounds can exit the reformer with product mixtures increasingly far from the thermodynamic equilibrium concentrations, as shown by the increasing value of η in Table 5. Due to such kinetic limitations, for a given input fuel composition, an increasing percentage of the hydrogen in the reformer output can correspond to hydrogen derived from reforming of C2+ compounds.

[0139] All patents, test procedures, and other documents cited herein, including priority documents, are fully incorporated by reference to the extent such disclosure is not inconsistent with this invention and for all jurisdictions in which such incorporation is permitted. Should the disclosure of any of the patents and/or publications that are incorporated herein by reference conflict with the present specification to the extent that it might render a term unclear, the present specification shall take precedence.

[0140] As is apparent from the foregoing general description and the specific embodiments, while forms of the invention have been illustrated and described, various modifications can be made without departing from the spirit and scope of the invention. Accordingly, it is not intended that the invention be limited thereby. Many variations will suggest themselves to those skilled in the art in light of the above detailed description. All such variations are within the full intended scope of the appended claims. Certain embodiments and features have been described using a set of numerical upper limits and a set of numerical lower limits. It should be appreciated that ranges from any lower limit to any upper limit are contemplated unless otherwise indicated. Certain lower limits, upper limits and ranges appear in one or more claims below. All numerical values are “about” or “approximately” the indicated value, and take into account experimental error and variations that would be expected by a person having ordinary skill in the art.

What is claimed is:

1. A method for reforming a fuel in an internal combustion engine, said method comprising:
   (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas recycle reformer comprising a reformer inlet, a reformer outlet, and a hydrocarbon-reforming catalyst composition, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, the hydrocarbon-containing fuel comprising at least about 50 mol % methane, and
   (b) converting under reforming conditions at least a portion of the exhaust gas-containing mixture in the presence of the hydrocarbon-reforming catalyst composition comprising at least about 0.1 wt % of a hydrocarbon-reforming metal catalyst supported on a mixed metal oxide support, the mixed metal oxide support comprising at least about 20 wt % of a mixture of lanthanum oxide and aluminum oxide and at least about 10 wt % of a mixture of cerium oxide and zirconium oxide.

2. The method of claim 1, wherein the mixture of lanthanum oxide and aluminum oxide comprises about 0.4 wt % to about 15 wt % of lanthanum oxide based on the combined weight of lanthanum oxide and aluminum oxide, wherein the mixed metal oxide support consists essentially of the mixture of lanthanum oxide and aluminum oxide and the mixture of cerium oxide and zirconium oxide, or a combination thereof.

3. The method of claim 1, further comprising combusting a portion of the exhaust gas mixture prior to converting the at least a portion of the exhaust gas mixture under reforming conditions.

4. The method of claim 1, wherein the hydrocarbon-containing fuel comprises at least about 70 mol % methane.

5. The method of claim 1, wherein the hydrocarbon-containing fuel comprises at least about 5 mol % of ethane, ethanol, propane, propane isomers, butane, butane isomers, C3 compounds, C4 compounds, or a combination thereof.

6. The method of claim 1, wherein the hydrocarbon-containing fuel comprises at least about 10 mol % of C2+ compounds, or at least about 10 mol % of C2 to C4 compounds, or at least about 10 mol % of C2 to C4 compounds.

7. The method of claim 6, wherein the hydrocarbon-containing fuel comprises at least about 15 mol % of C2+ compounds or C2 to C4 compounds or C2 to C4 compounds.

8. The method of claim 1, wherein the hydrocarbon-containing fuel comprises a weighted carbon mole percentage of carbons in C2+ compounds of at least about 10%, or a weighted carbon mole percentage of carbons in C2 to C4 compounds of at least about 10%, or a weighted carbon mole percentage of carbons in C2 to C3 alkanes of at least about 10%.

9. The method of claim 1, wherein the hydrocarbon-containing fuel comprises about 5 mol % or less of H2 prior to converting at least a portion of the exhaust gas mixture under reforming conditions, wherein converting the at least a portion of the exhaust gas-containing mixture generates a reformed gas product comprising about 5 mol % to about 20 mol % H2, or a combination thereof.

10. The method of claim 1, wherein the hydrocarbon-reforming catalyst composition comprises a hydrocarbon-reforming metal catalyst loading from 0.5 wt % to 10.0 wt %, based on the total weight of the catalyst composition.

11. The method of claim 1, wherein the hydrocarbon-reforming metal catalyst is selected from the group consisting of Co, Ru, Rh, Pt, Pd, Ni, Ir, Zn, Re and mixtures thereof.

12. The method of claim 11, wherein the hydrocarbon-reforming metal catalyst comprises Rh.

13. The method of claim 1, wherein the hydrocarbon-reforming catalyst composition further comprises at least one medium pore molecular sieve or large pore molecular sieve.

14. The method of claim 13, wherein the at least one medium pore molecular sieve or large pore molecular sieve comprise ZSM-5, phosphorus-modified ZSM-5, MCM-68 or a combination thereof.

15. The method of claim 1, wherein the hydrocarbon-reforming catalyst composition further comprises at least one small pore molecular sieve.

16. The method of claim 15, wherein the at least one small pore molecular sieve comprises chabazite, a CHA framework molecular sieve, or a combination thereof.

17. The method of claim 1, wherein providing an exhaust gas-containing mixture to an exhaust gas recycle reformer comprises:
   passing at least a portion of the first hydrocarbon-containing fuel into a cylinder of the internal combustion engine after the combusting of the reformed gaseous mixture and second hydrocarbon-containing fuel to form a portion of the exhaust gas;
cracking the at least a portion of the first hydrocarbon-containing fuel in the cylinder to form a cracked hydrocarbon-containing fuel; and
providing the portion of the exhaust gas and the cracked hydrocarbon-containing fuel to the exhaust gas recycle reformer.

18. The method of claim 1, further including prior to introducing the reformed gaseous mixture into the internal combustion engine, cooling the gaseous mixture by passing the gaseous mixture through the first heat exchanger or a second heat exchanger.

19. A method for reforming a fuel in an internal combustion engine, said method comprising:
(a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer comprising a reformer inlet, a reformer outlet, and a hydrocarbon-reforming catalyst composition, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, the hydrocarbon-containing fuel comprising at least about 50 mol % methane and a weighted carbon mole percentage of carbons in C₂⁺ compounds of at least about 5%, and
(b) converting under reforming conditions at least a portion of the exhaust gas-containing mixture in the presence of the hydrocarbon-reforming catalyst composition, the reforming conditions including a reformer outlet temperature of about 435°C to about 500°C.

20. The method of claim 19, wherein the reformer inlet temperature is about 535°C to about 625°C.

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