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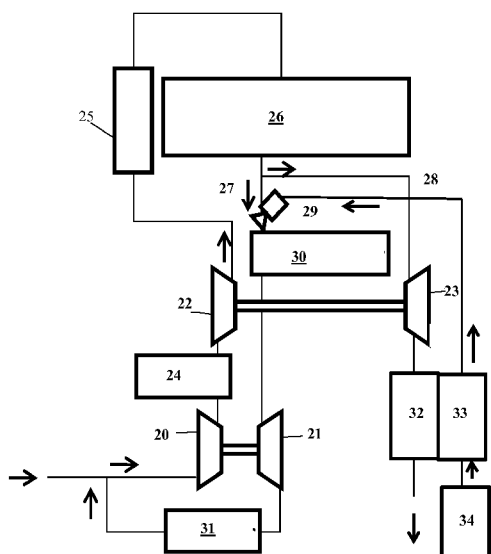
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[Continued on next page]

(54) Title: ENHANCED METHANE FORMATION IN REFORMING CATALYSTS

Figure 2.



(57) Abstract: Catalyst compositions suitable for use in the exhaust gas recycle stream of an internal combustion engine are provided. Such catalyst compositions typically provide significant amounts of methane in addition to syngas. 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 using methane-assisted combustion are also described.

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ENHANCED METHANE FORMATION IN REFORMING CATALYSTS

FIELD OF THE INVENTION

[0001] Embodiments of the invention relate to catalytic reforming of an internal combustion engine exhaust gas. In particular, embodiments of the invention relate to catalytic reforming of such engine exhaust gas that produces an amount of methane sufficient to sustain the formation of CO (and/or CO₂) and H₂ in the reformer.

BACKGROUND

[0002] 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.

[0003] 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

[0004] In one aspect, a method of increasing the octane rating of an internal combustion engine exhaust gas stream is provided, the method including: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% of a hydrocarbon-reforming catalyst selected from Co, Ru, Pt, Pd, Ni, Ir, Rh, Zn, Re, and mixtures thereof, and at least about 10 wt% of a small pore molecular sieve to form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.

[0005] In another aspect, a method of increasing the octane rating of an internal combustion engine exhaust gas stream is provided, the method including: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% Rh and at least about 10 wt% of a CHA framework type molecular sieve to form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.

[0006] In still another aspect, a reformer for use in an exhaust gas recycle portion of an internal combustion engine powertrain is provided, the reformer comprising a catalyst composition configured to convert a mixture comprising an internal combustion engine exhaust gas and a hydrocarbon-containing fuel to a gaseous mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than 1.0 mol% CH₄ based on the total moles of gas in the gaseous mixture, the catalyst composition comprising at least about 0.25 wt% of a hydrocarbon-reforming catalyst selected from Co, Ru, Pt, Pd, Ni, Ir, Rh, Zn, Re, and mixtures thereof, and at least about 10 wt% of a small pore molecular sieve.

[0007] In yet another aspect, a hydrocarbon-reforming catalyst composition is provided, the composition including about 0.25 wt% to about 10 wt% Rh, about 10 wt% to about 99.5 wt% of a CHA framework type molecular sieve, and about 0.25 wt% to about 10 wt% of one or more additional molecular sieves having a largest ring size of a 10-member ring, the CHA framework type molecular sieve optionally being chabazite, the one or more additional molecular sieves optionally being ZSM-5, MCM-68, or a combination thereof.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] Figure 1 is a schematic representation of an embodiment of a powertrain.

[0009] Figure 2 is a schematic representation of another embodiment of a powertrain.

[0010] Figure 3 is a graph of the amounts of hydrogen, methane, and carbon monoxide produced versus propane conversion for an embodiment of the present invention.

[0011] Figure 4 is a graph of the amount of heat required to maintain an example reformer at constant temperature.

[0012] Figure 5 is a graph showing ratios of methane to hydrogen versus n-heptane conversion.

[0013] Figure 6 is a graph showing heptane conversion versus residence time.

[0014] Figures 7A and 7B show reforming and methane formation rates for various catalysts.

[0015] Figures 8A and 8B show reforming rates and methane formation rates for various catalysts.

[0016] Figure 8C shows product formation selectivities for various catalysts.

[0017] Figure 9 shows methane formation rates for catalysts in the presence of syngas and n-heptane.

[0018] Figure 10 shows methane formation rates for catalysts in the presence of syngas and a multi-component naphtha feed.

[0019] Figure 11 shows product formation selectivities for various catalysts.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

[0020] 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, R^L and an upper limit, R^U , is disclosed, any number falling within the range is specifically disclosed. In particular, the following numbers within the range are expressly disclosed: $R = R^L + k * (R^U - R^L)$, 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 that for listings of R^L or R^U 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.

[0021] 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 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% (*e.g.*, 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.

[0022] 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

[0023] The invention is based in part on discovery of a catalyst composition that can effectively convert an internal combustion engine exhaust stream in the presence of a hydrocarbon-containing fuel to a mixture comprising H₂, CO₂, CO, H₂O, N₂, and a relatively large amount of methane, CH₄. Such a mixture can have the desired properties of high octane, due to the high methane content, along with a high H₂ content that can enable a flame speed high enough to maintain fuel combustion at the desired engine conditions. The invention is further based in part on discovery of a catalyst composition that can enhance the formation of methane. The catalyst composition can produce sufficient amounts of methane in the exothermic methanation reaction to sustain the reformer temperatures for the syngas producing endothermic reforming reaction, such that relatively little or no other heat may need to be added to the reformer to sustain the reforming reaction.

[0024] In various aspects, the catalyst can comprise rhodium (Rh) supported on chabazite and/or a molecular sieve having the CHA framework type. Optionally but preferably, the chabazite can be bound and/or physically mixed with another oxide, so that at least a portion of the Rh is supported on the other oxide. The oxide can be a

single metal oxide or can contain one or more metal oxides, such as a mixed metal oxide containing a plurality of metal oxides. Optionally, the catalyst can further comprise one or more additional molecular sieves, such as additional zeolites. Optionally, the catalyst can further comprise one or more additional metals. The Rh (and/or the optional one or more additional metals) can be incorporated into the catalyst as a metal or as a metal-containing compound. The Rh (and/or the optional one or more additional metals) can be incorporated into the catalyst by any convenient method, such as by ion exchange, impregnation, by incorporation into the synthesis mixture for forming the zeolite, or a combination thereof.

[0025] The catalyst composition can be capable of catalyzing hydrocarbon reforming and methane formation. The formation of CH_4 is typically exothermic, and the heat it produces may be used to supply heat to and/or to sustain a reforming reaction to produce synthesis gas or “syngas” that includes hydrogen and carbon monoxide. To improve the overall efficiency of the systems, catalysts may be optimally chosen to accomplish each reaction. Thus, in some embodiments, there may be a first catalyst composition for catalyzing a hydrocarbon reforming reaction for converting a hydrocarbonaceous feed into CO_2 , CO , H_2O , and H_2 , and a second catalyst composition capable of forming methane, whether directly from the unconverted hydrocarbonaceous feed or from the converted/reformed products. The first and second catalyst compositions may be mixed or they may be segregated within the reformer according to design parameters, *e.g.*, to efficiently distribute and/or transfer heat within the reformer. In some embodiments, the first and second catalyst compositions can be similar or identical (such that effectively a single composition effectively catalyzes both reactions).

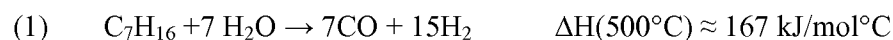
[0026] In some aspects, the catalyst can include Rh, optionally one or more additional metals, a zeolite (or other molecular sieve) having the chabazite framework structure, and optionally one or more additional molecular sieves. In such aspects, the CHA framework type molecular sieve and optional additional molecular sieves can comprise all of the support material for the catalyst, so that the weight of the Rh (plus optional additional metals) and the weight of the chabazite (plus optional additional

molecular sieves) correspond to the total catalyst weight. In certain aspects, the catalyst can further include one or more metal oxide components as support materials.

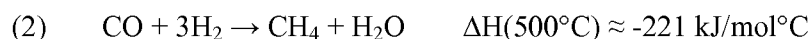
[0027] Use of a catalyst composition with activity for reforming and enhanced activity for methanation can provide advantages when reforming hydrocarbons. In particular, a catalyst composition with increased activity for methanation can reduce or minimize the need to provide additional heat to a reforming process.

[0028] Hydrocarbons and hydrocarbonaceous compounds (such as alcohols) can be reformed, such as by steam reforming, to produce syngas under appropriate conditions in the presence of a reforming catalyst. In an engine or power train environment, reforming can be used to convert hydrocarbon or hydrocarbonaceous compounds with low octane ratings into CO and H₂. The CO and H₂ provide a somewhat higher octane rating than some components in a typical naphtha boiling range fuel such as C₅+ n-alkanes. Additionally, if the reforming catalyst also has activity for forming methane from CO and H₂, the methane can serve as a still higher octane rating component in the reformed fuel stream.

[0029] Steam reforming is typically an endothermic process, so that additional heat must be provided to the reforming process to maintain the temperature of the reaction environment. Equation 1 shows the enthalpy of reaction for steam reforming of n-heptane, with the enthalpy expressed per mole of carbon in the fuel.



[0030] For reforming processes in an engine or power train environment, additional heat can be provided by combustion of fuel, but this decreases the overall efficiency of the engine. As an alternative, formation of methane from CO and H₂ is an exothermic process, as shown in Equation 2.



[0031] As shown in Equation 2, converting CO and H₂ in the reforming environment into CH₄ can provide a method for reducing or minimizing the amount of additional heat that needs to be supplied to the reforming reaction zone. As a result, a catalyst composition that is effective for both reforming of hydrocarbons while having improved activity for conversion of the resulting syngas to methane can be desirable.

Catalyst Composition

[0032] 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/or ZK-14. Chabazite can refer to a naturally occurring or a synthetic form of chabazite. Unless otherwise specified, a reference to chabazite, is understood to generally refer to the zeolite chabazite (natural or synthetic), optionally containing any of the potential various counterions and/or additional metals that can be present.

[0033] While rhodium supported on CHA framework type molecular sieve of the present invention can effectively enhance the formation of methane, additional hydrocarbon-reforming catalysts supported multi-dimensional small pore molecular sieves can also be effective. Suitable small pore molecular sieves include those having the AEI, AFT, AFX, ATT, DDR, EAB, EPI, ERI, KFI, LEV, LTA, MER, MON, MTF, PAU, PHI, RHO, and SFW framework types. Suitable hydrocarbon-reforming catalysts, as described in more detail herein, include Rh, Ru, Ir, Co, Pt, Pd, Ni, Zn, Re, and combinations thereof.

[0034] 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.

[0035] Still another additional or alternative option for characterizing small pore molecular sieves can be based on the effective size of the pore channels. Some typical small pore molecular sieves can include molecular sieves with a largest pore channel having a maximum dimension of about 5.0 Angstroms or less. A molecular sieve having elliptical pores with a slightly larger maximum dimension of about 5.1 Angstroms or about 5.2 Angstroms along the major axis may still correspond to a small pore molecular sieve, *e.g.*, particularly if the minor axis has a dimension of about 4.0 Angstroms or less. In still other additional or alternative embodiments, characterization of small pore molecular sieves can be based on the effective size of the pore channels.

In some aspects, 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 can also have a minimum dimension of at least about 3.5 Angstroms, *e.g.*, 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.

[0036] In various aspects, 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 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 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 99.0 wt%, or 99.5 wt%, or 99.75 wt%. Combinations of such lower and upper limits may be selected, *e.g.*, from about 2.5 wt% to about 95.0 wt%, from about 5.0 wt% to about 80.0wt%, from about 10.0 wt% to about 55.0 wt%, from about 20.0 wt% to about 40.0 wt%, etc.

[0037] Optionally, the catalyst composition can further comprise one or more additional molecular sieves, such as one or more additional zeolites. Any convenient molecular sieve can be used for the additional molecular sieve(s). For example, a zeolite with cracking activity such as ZSM-5 or MCM-68 can also be beneficial in some catalyst compositions. 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.

[0038] The additional 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%, 97.5 wt%, or 99.0 wt%, or 99.5 wt%, or 99.75 wt%. Combinations of such lower and upper limits may be selected and are expressly considered herein, *e.g.*, from about 2.5 wt% to about 95.0 wt%, from about 5.0 wt% to about 80.0wt%, from about 10.0 wt% to about 55.0 wt%, from about 20.0 wt% to about 40.0 wt%, etc.

[0039] When one or more additional molecular sieves different from a CHA framework type zeolite are included in the catalyst composition, the additional molecular sieve(s) can be at least one medium pore aluminosilicate zeolite having a Constraint Index of 1-12 (as defined in U.S. Patent No. 4,016,218). Suitable zeolites include zeolites having an MFI or MEL framework, such as ZSM-5 or ZSM-11. ZSM-5 is described in

detail in U.S. Patent Nos. 3,702,886 and RE 29,948. ZSM-11 is described in detail in U.S. Patent No. 3,709,979. Preferably, the zeolite is ZSM-5. Another suitable zeolite can be MCM-68, which is described in detail in U.S. Published Patent Application 2014/0140921. Other useful medium pore molecular sieves can include ZSM-12 (U.S. Patent No. 3,832,449); ZSM-22 (U.S. Patent No. 4,556,477); ZSM-23 (U.S. Patent No. 4,076,842); ZSM-34 (U.S. Patent No. 4,086,186) ZSM-35 (U.S. Patent No. 4,016,245); ZSM-48 (U.S. Patent No. 4,397,827); and ZSM-57 (U.S. Patent No. 4,873,067). Non-limiting examples of SAPO and AIPO molecular sieves include one or a combination of SAPO-11, SAPO-31, SAPO-41, AIPO-11, AIPO-31, AIPO-41, and PST-6. The additional molecular sieve(s) can also be at least one large pore aluminosilicate, aluminophosphate, or silicoaluminophosphate zeolite, such as containing 12-ring pores. Suitable large pore molecular sieves include those having AFI, AFS, ATO, ATS, *BEA, BEC, BOG, BPH, CAN, CON, EMT, EON, EZT, FAU, GME, GON, IFR, ISV, -*ITN, IWR, IWW, LTL, MAZ, MEI, MOR, MOZ, MSE, MTW, OFF, OKO, OSI, SAF, SAO, SEW, SFE, SFO, SSF, SSY, and/or USI frameworks.

[0040] An 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 atoms included in the ring structure that forms the channel. In some aspects, a zeolite can include at least one ring channel based on a 10-member ring. In such aspects, 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, SFF, SFG, *SFV, STF, -SVR, STI, SZR, TON, TUN, MRE, and combinations thereof.

[0041] Generally, 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.

[0042] Additionally or alternately, an additional molecular sieve in the catalyst composition can 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 additional molecular sieve prior to incorporating the additional molecular sieve into the catalyst composition, the amount of transition metal can be expressed as a weight percentage of the additional molecular sieve, 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.

[0043] 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.

[0044] In aspects 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) such as any of the lower limit amounts described above. In such aspects, 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 (*e.g.*, Al₂O₃, including θ -Al₂O₃ and/or γ -Al₂O₃), silicon oxides, rare-earth metal oxides, Group IV metal oxides, SiO₂, Y₂O₃, Sc₂O₃, La₂O₃, CeO₂, Pr₂O₃, Sm₂O₃, Eu₂O₃, Gd₂O₃, Tb₂O₃, Dy₂O₃, Ho₂O₃, Er₂O₃, Tm₂O₃, Yb₂O₃, Lu₂O₃, TiO₂, 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%, 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 first metal oxide 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 99.0 wt%. Combinations of such lower and upper limits may be selected, *e.g.*, from about 2.5 wt% to about 95.0 wt%, from about 5.0 wt% to about 80.0wt%, from about 10.0 wt% to about 55.0 wt%, from about 20.0 wt% to about 40.0 wt%, etc. A second metal oxide may optionally be present in an amount from about 1.0 wt% to about 99.0 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%, 90.0 wt%, 92.5 wt%, 95.0 wt%, or 97.5 wt%. The upper limit on the range of second metal oxide 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 99.0 wt%. Combinations of such lower and upper limits may be selected, *e.g.*, from about 97.5 wt% to about 5.0 wt%, from about 95.0 wt% to about 20.0wt%, from about 90.0 wt% to about 45.0 wt%, from about 80.0 wt% to about 60.0 wt%, etc.

[0045] 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 can comprise, consist essentially of, or be a mixture of La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$. For a mixture of La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$, or more generally for a mixture of La_2O_3 and Al_2O_3 , the La_2O_3 can correspond to about 0.4 wt% to about 20 wt% of the combined weight of La_2O_3 and Al_2O_3 . For example, the La_2O_3 can correspond to at least about 0.4 wt% of the combined weight of La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$, 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% or 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. It is noted that all combinations for the upper and lower limit of the amount of La_2O_3 relative to the combined amount of La_2O_3 and Al_2O_3 are expressly contemplated herein. The amount of the La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$ 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 can comprise, consist essentially of, or be a combination of CeO_2 and ZrO_2 . The amount of the CeO_2 and ZrO_2 together may be, for example, from about 10.0 wt% to about 80.0 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 about, *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 therewithin.

[0046] The amount of Rh in the catalyst composition may range from about 0.1 wt% to about 50 wt%. The lower limit on the range of Rh in 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%, or 50.0 wt%. The upper limit on the range of Rh in the catalyst composition 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%, 32.5 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.

[0047] In aspects where at least one additional metal or metal-containing compound is present in the catalyst composition, the at least one additional metal or metal-containing compound can correspond to a metal-containing hydrocarbon reforming catalyst. It is noted that Rh also serves as a hydrocarbon reforming catalyst, in addition to the role Rh serves in combination with chabazite with regard to enhancing methanation. Examples of suitable additional hydrocarbon reforming catalysts can be selected from the group consisting of Co, Ru, Pt, Pd, Fe, Ni, Ir, Zn, Re, and mixtures thereof. 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 of metal or in compound form, based on the total weight of the catalyst composition. The amount of total metal in the catalyst composition, including both Rh and any additional metal-containing hydrocarbon reforming catalyst, may range from about 1.0 wt% to about 50 wt%. The lower limit

on the range of total metal in 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%, or 50.0 wt%. The upper limit on the range of total metal in the catalyst composition 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%, 32.5 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.

[0048] In aspects where Rh and at least one additional hydrocarbon reforming catalyst are present in the catalyst composition, the total amount of metals in the catalyst composition can correspond to any convenient combination of an amount of Rh (and/or Rh-containing compound) and an amount of the one or more additional hydrocarbon reforming catalysts. 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 Rh and/or an Rh-containing compound. The lower limit on the range of Rh 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 Rh 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 wt%, from about 1.0 wt% to about 10 wt%, from about 2.0 wt% to about 7.5 wt%, from about 2.5 wt% to about 5.0 wt%, etc. The one or more additional hydrocarbon reforming catalyst also may 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 additional 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 additional 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 to about 15.0 wt%, from about 1.0 to about 10.0 wt%, from about 2.0 to about 7.5 wt%, from about 2.5 to about 5.0 wt%, from about 0.75 to about 2.0 wt%, etc. For example, in addition to Rh or an Rh-containing compound, an additional hydrocarbon reforming catalyst can include or be Pt, *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% Pt, from about 0.75 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.

[0049] In some aspects, 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 82.5 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, 99.5% or more, or 99.9% or more) of the particles will have mesh sizes between the two values. For instance, if the particle size of a material is described as -80/+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 test of catalysts described herein. The

preferred particle size range can change for different reactors and/or converter embodiments used in a vehicle application.

[0050] Another optional way 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 D_{50} of, for example, 0.5 mm have a median particle size of 0.5 mm. A D_{90} of 0.5 mm indicates that 90% of the particles have a particle size of less than 0.5 mm, and a D_{10} 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 $(D_{90}-D_{10})/(D_{50})$ and is therefore dimensionless. In some embodiments, the catalyst composition may be characterized as having a D_{50} from 0.15 mm to 1.0 mm (*e.g.*, from 0.85 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 about 10, *e.g.*, from 1.0 to 6.0, from 2.0 to 5.0, or from 3.0 to 4.0.

[0051] In certain aspects, a reforming and/or cracking and/or methanation catalyst 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 aspect, the catalyst composition can be deposited on or otherwise supported on a flow through substrate with parallel or tortuous channels. The reactive gases 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 and/or metal. Ceramic substrate materials can 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 washcoated onto the substrate. The washcoated substrate can then be subsequently dried and calcined in air or annealed in specified gas environments.

Reforming and Methanation in an Engine or Power Train Environment

[0052] The catalyst composition can advantageously be suitable for providing a sufficient amount of heat to sustain the reforming reaction to produce syngas containing hydrogen. Typically, the catalyst composition can provide, *e.g.*, greater than about 1.0 mol% CH₄, such as from about 1.0 mol% to about 6.0 mol% CH₄, or from about 1.0 mol% to about 5.0 mol% CH₄, or from about 1.0 mol% to about 4.0 mol% CH₄, or from about 1.0 mol% to about 3.5 mol% CH₄, or from about 2.0 mol% to about 6.0 mol% CH₄, or from about 2.0 mol% to about 5.0 mol% CH₄, or from about 1.0 mol% to about 4.0 mol% CH₄, or from about 1.0 mol% to about 3.5 mol% CH₄, based on the total moles of gas in the reformed gaseous mixture, thereby optionally maintaining the average reformer temperature 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. In one embodiment, the inlet temperature can be about 550°C and the outlet temperature about 450°C. In certain aspects, 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. Additionally or alternatively, the inlet temperature can 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 inlet can allow for an effective amount of reforming while still maintaining a desired reformer outlet temperature under adiabatic operation. The catalyst composition may optionally be characterized as providing a gaseous mixture having CH₄:H₂ ratio (mole/mole) of at least about 0.075 to 1.0, or from 0.1:1 to 0.9:1, or from 0.1:1 to 0.75:1, or from 0.25:1

to 0.9:1, or from 0.25:1 to 0.75:1, *e.g.*, wherein the mixture is substantially/essentially free of oxygen-containing gas other than exhaust gas from the engine and hydrocarbon-containing fuel.

[0053] 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 kinetic and or thermodynamic limitations on the reforming reactions at low temperature, using pre-combustion can allow increasing the amount of conversion before the kinetic or thermodynamically 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, for example about 525°C to about 625°C, about 525°C to about 600°C, about 550°C to about 650°C, 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 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. In some embodiments, the above amounts of CH₄ in the reformed gaseous mixture can be provided when the mixture of exhaust gas and hydrocarbon-containing fuel introduced into the reformer includes about 5.0 mol% or less of CH₄, for example about 4.0 mol% or less, about 3.0 mol% or less, about 2.0 mol% or less, or about 1.0 mol% or less. Additionally or alternatively, the above amounts of CH₄ in the reformed gaseous mixture can be provided when the hydrocarbon-containing fuel introduced into the reformer includes about 5.0 mol% or less of CH₄, for example about 4.0 mol% or less, about 3.0 mol% or less, about 2.0 mol% or less, or about 1.0 mol% or less.

[0054] 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 exhaust gas can be passed through a first heat exchanger to extract heat therefrom. The heat can be transferred to the reformer to aid in sustaining the reforming reactions therein.

[0055] An important direction in future gasoline engines is 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.

[0056] 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 media with H₂O and CO₂ as reactants for reforming of gasoline to produce H₂ rich gas to raise flame speed and/or methane to raise the octane. Typical ranges for EGR that can be used for the engine in conjunction with reforming include about 20 vol% to about 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 gasoline (or other fuel) from tankage to the reformer. The desired amount of EGR relative to feed to the reformer can depending on fuel input, engine design and engine load points. A high level of EGR increases 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.

[0057] In some embodiments, the reforming reaction can be performed in the presence of a reduced or minimized amount of water. During conventional reforming, 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 from about 0.3:1 to about 1:1, for example from about 0.5:1 to about 1:1 or from about 0.3:1 to 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.

[0058] Thus, embodiments of 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. The catalyst composition can be specifically configured to convert a mixture comprising an internal combustion engine exhaust gas and a hydrocarbon-containing fuel to a gaseous mixture comprising H₂, CO₂, CO, H₂O, N₂, and greater than about 1.0 mol% CH₄, based on the

total moles of gas in the gaseous mixture. It is noted that the output from the reformer may often contain a variety of additional components. For example, in aspects where the input flow to the reformer contains aromatic compounds and/or longer chain aliphatic compounds, the reformer output can typically include one or more types of aromatic compounds. This can include benzene formed by dealkylation of alkylated aromatics; aromatic compounds formed by dehydrocyclization of aliphatic compounds; or other types of aromatics, optionally including substituted aromatics. More generally, the output flow from the reformer can include a mixture of various aliphatic, cyclic, and/or aromatic compounds, optionally including compounds containing heteroatoms other than C and H.

[0059] Such a reformer may be used in a method of operating an internal combustion engine. The methane produced in the reformer may be used for using methane-assisted combustion in the 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) comprising CH₄, H₂, CO₂, CO, H₂O, and N₂, said CH₄ being present at a concentration greater than about 1.0 mol%, based on the total moles of gas in the reformed gaseous mixture. 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 exhaust gas can be passed through a first heat exchanger to extract heat therefrom. The heat can be transferred to the reformer (and/or to the input feed passed into the reformer) to aid in sustaining the reforming and methane-forming reactions therein.

[0060] The use of the catalyst compositions herein can serve to provide an increase in the octane rating of an internal combustion engine exhaust gas stream. 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. The first hydrocarbon-containing fuel can typically have a relatively low initial octane rating, *e.g.*, < 100 RON, < 99 RON, < 97 RON, < 95 RON, < 93 RON, < 90 RON, < 85 RON, < 80 RON, from about 65 RON to about 100 RON, from about 65 RON to about 99 RON, from about 65 RON to about 97 RON, from about 65 RON to about 95 RON, from about 65 RON to about 93 RON, from about 65 RON to about 90 RON, from about 65 RON to about 85 RON, from about 65 RON to about 80 RON, from about 70 RON to about 100 RON, from about 70 RON to about 99 RON, from about 70 RON to about 97 RON, from about 70 RON to about 95 RON, from about 70 RON to about 93 RON, from about 70 RON to about 90 RON, from about 70 RON to about 85 RON, from about 70 RON to about 80 RON, from about 75 RON to about 100 RON, from about 75 RON to about 99 RON, from about 75 RON to about 97 RON, from about 75 RON to about 95 RON, from about 75 RON to about 93 RON, from about 75 RON to about 90 RON, from about 75 RON to about 85 RON, from about 75 RON to about 80 RON, from about 80 RON to about 100 RON, from about 80 RON to about 99 RON, from about 80 RON to about 97 RON, from about 80 RON to about 95 RON, from about 80 RON to about 93 RON, from about 80 RON to about 90 RON, from about 80 RON to about 85 RON, from about 85 RON to about 100 RON, from about 85 RON to about 99 RON, from about 85 RON to about 97 RON, from about 85 RON to about 95 RON, from about 85 RON to about 93 RON, or from about 85 RON to about 90 RON. The catalyst composition in the reformer converts at least a portion of the exhaust gas-containing mixture to a reformed gaseous mixture having a second octane rating (RON) higher than the initial octane rating of the first hydrocarbon-containing fuel. Typically, the reformed gaseous mixture can comprise at least H₂, CO₂, and greater than about 0.25 mol% CH₄, or greater than about 0.4 mol% CH₄, or greater than about 1.0 mol% CH₄, or greater than about 1.5 mol% CH₄, or greater than about 2.0 mol% CH₄, and up to about 5.0 mol% CH₄, based on the total moles of gas in the reformed gaseous

mixture (and typically also CO, H₂O, and N₂), and this total mixture can advantageously have a second octane rating of > 100, *e.g.*, from about 100 to about 125. The lower limit on the range of second octane rating may be about, *e.g.*, 100, 102, 105, 107, 110, 112, 115, 120, or 122. The upper limit on the range of the second octane rating may be about, *e.g.*, 102, 105, 107, 110, 112, 115, 120, 122, or 125. Any combination of lower and upper limits may be provided by such a method, *e.g.*, from about 105 to about 125, from about 110 to about 125, from about 115 to about 125, or from about 120 to about 125.

[0061] The reformer may also be incorporated into an internal combustion engine powertrain. Many different variations of such powertrains 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 a branch of the exhaust manifold and the fuel intake manifold. The reformer and catalyst composition can be specifically configured to convert an exhaust gas-containing mixture 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 NO_x and SO_x, and the like. The reformed gaseous mixture may be characterized by one or more of the following: (i) a Research Octane Number (RON) of > 100, *e.g.*, from about 100 to about 130, or more typically from about 100 to about 125 (the lower limit on the range of second octane rating may be about 100, about 102, about 105, about 107, about 110, about 112, about 115, about 120, or about 122; additionally or alternatively, the upper limit on the range of the second octane rating may be about 102, about 105, about 107, about 110, about 112, about 115, about 120, about 122, or about 125; if a range is desired, the range can be, *e.g.*, from about 105 to about 125, from about 110 to about 125, from about 115 to about 125, or from about 120 to about 125); (ii) a CH₄ content of greater than about 1.0 mol% (*e.g.*, from about 1.0 mol% to about 6.0 mol% CH₄, from about 1.5 mol% to about 5.0 mol% CH₄, or from about 2.0 mol% to about 4.0 mol% CH₄, based on the number of moles of gas in the reformed fuel mixture); and (iii) a mixture of H₂, CO, CO₂, H₂O, and CH₄ (optionally also N₂) characteristic of at least about 50% (*e.g.*, at

least about 80%, at least about 85%, at least about 90%, or at least about 95%) conversion in the reforming zone. 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.

[0062] Referring now to Figure 1, there is shown a schematic representation of an embodiment of such a powertrain. In Figure 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 reinjection to the engine, while the remaining exhaust gas can be expanded in turbine (2) and vented to the atmosphere at (10).

[0063] Hydrocarbon-containing fuel can be supplied to the powertrain in Figure 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. 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. However, 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, C₂-C₁₂ paraffins, naphtha, kerosene, diesel, FCC off-gas, oxygenated hydrocarbons (*e.g.*, dialkyl ethers such as dimethyl ether, diethyl ether, methyl ethyl ether, and the like, and combinations thereof; C₁-C₁₂ alcohols such as methanol, ethanol, 1-propanol, isopropanol, 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.

[0064] 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).

[0065] In Figure 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). Optionally, 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.

[0066] In one embodiment, the generation of hydrogen in the powertrain of Figure 1 can be accomplished by an initial endothermic reaction to produce syngas. The syngas-containing hydrogen can then be used to conduct the methane-producing exothermic reaction described above, to thereafter sustain the temperature high enough for the endothermic reforming processes of reactor during operation. Alternatively, start-up hydrogen for the methane formation reaction may be supplied by stored

hydrogen (not shown), which optionally may be replenished after start-up by operation of the reforming reaction.

[0067] Referring now to Figure 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 Figure 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), led 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 Figure 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 attain heat integration than described in Figure 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 Figure 2.

Additional Embodiments

[0068] Embodiment 1. A method of increasing the octane rating of an internal combustion engine exhaust gas stream, said method comprising: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-

containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% of a hydrocarbon-reforming catalyst selected from Co, Ru, Pt, Pd, Ni, Ir, Rh, Zn, Re, and mixtures thereof, and at least about 10 wt% of a small pore molecular sieve to form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.

[0069] Embodiment 2. The method of Embodiment 1, wherein the hydrocarbon-reforming catalyst composition comprises about 0.25 wt% to about 10 wt% of the hydrocarbon-reforming catalyst, or about 0.5 wt% to about 10 wt%, or wherein the hydrocarbon-reforming catalyst composition comprises about 10 wt% to about 99.75 wt% of the small pore molecular sieve, or about 10 wt% to about 75 wt%, or about 10 wt% to about 50 wt%, or a combination thereof.

[0070] Embodiment 3. The method of any of the above embodiments, wherein the small pore molecular sieve comprises a molecular sieve having the framework type AEI, AFT, AFX, ATT, DDR, EAB, EPI, ERI, KFI, LEV, LTA, MER, MON, MTF, PAU, PHI, RHO, or SFW, or wherein the small pore molecular sieve comprises a molecular sieve having a largest pore size corresponding to an 8-member ring.

[0071] Embodiment 4. The method of any of the above embodiments, wherein the small pore molecular sieve is chabazite and/or has a CHA framework type molecular sieve, and/or wherein the hydrocarbon-reforming catalyst comprises Rh.

[0072] Embodiment 5. A method of increasing the octane rating of an internal combustion engine exhaust gas stream, said method comprising: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% Rh and at least about 10 wt% of a CHA framework type molecular sieve to

form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.

[0073] Embodiment 6. The method of any of Embodiments 4-5, wherein the hydrocarbon-reforming catalyst composition further comprises about 0.25 wt% to about 10 wt% of an additional metal selected from the group consisting of Co, Ru, Pt, Pd, Ni, Ir, Zn, Re, and mixtures thereof, a total weight of Rh and the additional metal being about 20 wt% or less.

[0074] Embodiment 7. The method of any of the above embodiments, wherein said converting supplies heat sufficient to maintain the reformer at an average reformer temperature above about 450°C.

[0075] Embodiment 8. The method of any of the above embodiments, wherein said exhaust gas-containing mixture is substantially free of oxygen-containing gas other than the exhaust gas and the first hydrocarbon-containing fuel.

[0076] Embodiment 9. The method of any of the above embodiments, wherein the hydrocarbon-reforming catalyst composition further comprises a metal oxide composition, the metal oxide composition optionally comprising and/or being selected from aluminum oxides, silicon oxides, rare-earth metal oxides, Group IV metal oxides, and mixtures thereof, for example a mixture of an aluminum-containing oxide and a cerium-containing oxide.

[0077] Embodiment 10. The method of any of the above embodiments, wherein the hydrocarbon-reforming catalyst composition further comprises about 5 wt% to about 50 wt% of one or more additional molecular sieves, the one or more molecular sieves optionally having a largest ring size of a 10-member ring, and/or the one or more additional molecular sieves optionally being ZSM-5, MCM-68, or a combination thereof.

[0078] Embodiment 11. The method of any of the above embodiments, wherein the reformed gaseous mixture has an octane rating (RON) from about 100 to about 125.

[0079] Embodiment 12. The method of any of the above embodiments, further comprising: introducing the reformed gaseous mixture and a second hydrocarbon-containing fuel into the engine, wherein said second hydrocarbon-containing fuel may

be the same or different from the first hydrocarbon-containing fuel; combusting the reformed gaseous mixture and second hydrocarbon-containing fuel in the engine to form an exhaust gas; and passing the exhaust gas through a first heat exchanger to extract heat from the exhaust gas, wherein, prior to introducing the reformed gaseous mixture into the internal combustion engine, the gaseous mixture can optionally be cooled by passing the gaseous mixture through the first heat exchanger or a second heat exchanger.

[0080] Embodiment 13. The method of any of the above embodiments, further comprising pre-combusting a portion of exhaust gas-containing mixture prior to providing the exhaust gas-containing mixture to the exhaust gas recycle reformer, the exhaust gas recycle reformer having a reformer inlet temperature of about 525°C to about 625°C.

[0081] Embodiment 14. The method of any of the above embodiments, wherein the reformed gaseous mixture comprises from about 2.0 mol% to about 5.0 mol% CH₄, the reformed gaseous mixture has a CH₄:H₂ ratio (mol/mol) of at least about 0.05:1, or a combination thereof.

[0082] Embodiment 15. A reformer for use in an exhaust gas recycle portion of an internal combustion engine powertrain, said reformer comprising a catalyst composition configured to convert a mixture comprising an internal combustion engine exhaust gas and a hydrocarbon-containing fuel to a gaseous mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than 1.0 mol% CH₄ based on the total moles of gas in the gaseous mixture, the catalyst composition comprising a hydrocarbon-reforming catalyst composition described in any of Embodiments 1-14.

[0083] Embodiment 16. The reformer of Embodiment 15, further comprising an internal combustion engine having an exhaust manifold comprising an exhaust gas recycle unit and a fuel intake manifold, the reformer being fluidly connected to the exhaust manifold and the fuel intake manifold, the fuel intake manifold being 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, wherein the first and second hydrocarbon-containing fuels may be the same or different.

[0084] Embodiment 17. A hydrocarbon-reforming catalyst composition comprising about 0.25 wt% to about 10 wt% Rh, about 10 wt% to about 99.5 wt% of a CHA framework type molecular sieve, and about 0.25 wt% to about 10 wt% of one or more additional molecular sieves having a largest ring size of a 10-member ring, the CHA framework type molecular sieve optionally being chabazite, the one or more additional molecular sieves optionally being ZSM-5, MCM-68, or a combination thereof.

[0085] Embodiment 18. The hydrocarbon-reforming catalyst composition of Embodiment 17, wherein the hydrocarbon-reforming catalyst composition further comprises 0.25 wt% to 10 wt% of an additional metal selected from the group consisting of Co, Ru, Pt, Pd, Ni, Ir, Zn, Re, and mixtures thereof.

[0086] Embodiment 19. The hydrocarbon-reforming catalyst composition of any of Embodiments 17-18, wherein the hydrocarbon-reforming catalyst composition further comprises a metal oxide composition, the metal oxide composition optionally being selected from aluminum oxides, silicon oxides, rare-earth metal oxides, Group IV metal oxides, and mixtures thereof, or optionally comprising a mixture of an aluminum-containing oxide and a cerium-containing oxide.

EXAMPLES

Catalyst Preparation Examples

Preparation of catalysts A and A':

[0087] Catalyst A included ~3.5 wt% Rh supported on a mixed metal oxide comprising La_2O_3 - γ - Al_2O_3 (~40 wt% of total support) and CeO_2 - ZrO_2 (~60 wt% of total support). Catalyst A' included ~3.5wt% Rh supported on a mixed metal oxide comprising La_2O_3 - γ - Al_2O_3 (~38.5wt% of total support) and CeO_2 - ZrO_2 (~58 wt% of total support). The La_2O_3 - Al_2O_3 support was prepared separately by impregnation of an aqueous $\text{La}(\text{NO}_3)_3$ solution onto γ - Al_2O_3 , followed by drying and calcination at ~600°C. The La:Al atomic ratio was ~1.5:100. CeO_2 - ZrO_2 was co-precipitated from an aqueous $\text{Ce}(\text{NO}_3)_4$ and $\text{Zr}(\text{NO}_3)_4$ solution onto the La_2O_3 - Al_2O_3 support using urea as base. The Ce:Zr atomic ratio was ~4:1. The La_2O_3 - γ - Al_2O_3 - CeO_2 - ZrO_2 support was calcined at ~600°C prior to incipient wetness impregnation with an aqueous solution

containing $\text{Rh}(\text{NO}_3)_3$. After the precious metal impregnation, the catalyst was calcined in air at $\sim 600^\circ\text{C}$.

Preparation of catalyst B:

[0088] Catalyst B included ~ 3.5 wt% Rh supported on a mixed metal oxide comprising La_2O_3 and $\gamma\text{-Al}_2\text{O}_3$. The $\text{La}_2\text{O}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ support was prepared by impregnation of an aqueous $\text{La}(\text{NO}_3)_3$ solution onto $\gamma\text{-Al}_2\text{O}_3$, followed by drying and calcination at $\sim 600^\circ\text{C}$. The La:Al ratio was $\sim 1.5:100$. The calcined $\text{La}_2\text{O}_3\text{-}\gamma\text{-Al}_2\text{O}_3$ support was subsequently impregnated with an aqueous solution of $\text{Rh}(\text{NO}_3)_3$. After the precious metal impregnation, the catalyst was calcined in air at $\sim 600^\circ\text{C}$.

Preparation of catalyst C:

[0089] Catalyst C included ~ 0.62 wt% Rh supported on zeolite Chabazite. The zeolite was prepared from a synthesis mixture having the stoichiometry: ~ 3 SDAOH: ~ 10 Na_2O : Al_2O_3 : ~ 35 SiO_2 : ~ 1000 H_2O , where SDAOH was N,N,N-trimethyladamantylammonium hydroxide. To a ~ 125 ml Teflon autoclave were added ~ 8.86 g of ~ 25 wt% SDAOH, ~ 0.70 g $\sim 50\%$ NaOH, ~ 21.0 g of sodium silicate solution ($\sim 30\%$ SiO_2 , $\sim 9\%$ Na_2O), ~ 42.3 g deionized water, and ~ 2.1 g of USY zeolite (Si/Al ~ 2.5 , 17% Al_2O_3), and the mixture was heated for 4 days at $\sim 140^\circ\text{C}$ in a tumbling oven at ~ 20 rpm. The product was recovered by vacuum filtration and washed with de-ionized water. Phase analysis by powder X-ray diffraction showed that the sample appeared to be pure chabazite having a Si/Al ratio of ~ 8 (ICP-AES analysis).

[0090] The Na-form of the chabazite was subsequently ion exchanged with an aqueous solution of $\text{Rh}(\text{NH}_3)_5\text{Cl}_3$ for ~ 48 hours at $\sim 85^\circ\text{C}$ using a ~ 0.03 molar Rh solution, ~ 5 g dry zeolite, and a liquid/solid weight ratio of $\sim 175:1$. After the ion exchange, the slurry was filtered, and the filter cake was washed with ~ 500 ml of deionized water. The washed Rh-CHA filter cake was subsequently dried for ~ 12 hours at $\sim 110^\circ\text{C}$ and then calcined for ~ 2 hours at $\sim 500^\circ\text{C}$ in air using a ramp rate of $\sim 2^\circ\text{C}/\text{min}$.

Preparation of catalyst D:

[0091] Catalyst D included ~ 1.37 wt% Rh supported on zeolite CHA. A synthesis mixture was prepared having the stoichiometry: ~ 0.11 Rh: ~ 1.4 K_2O : Al_2O_3 : ~ 5.1 SiO_2 :

~110 H₂O. To a plastic beaker were added ~15.5 g deionized water, ~1.94 g KOH·½H₂O, and ~4.84 g of an amorphous silica-alumina gel (~22.5% Al₂O₃, ~67.5% SiO₂). About 4.97 g of 10 wt% Rh(en)₃Cl₃·3H₂O solution (en = ethylenediamine) solution was added dropwise with stirring and then stirred for an additional ~20 mins. The mixture was transferred to a ~45 ml Teflon autoclave and then heated for ~12 days at ~100°C in a tumbling oven at ~25 rpm. The product was recovered by vacuum filtration and washed with de-ionized water. Phase analysis by powder X-ray diffraction showed that the sample appeared to be pure chabazite. The sample was finally calcined in air for ~2 hours at ~560°C using a ramp rate of ~4.5°C/min.

Preparation of catalyst E:

[0092] Catalyst E included ~0.35 wt% Rh supported on zeolite CHA. A reaction mixture having the stoichiometry: ~0.064 Rh: ~3 SDAOH: ~10 Na₂O: Al₂O₃: ~35 SiO₂: ~1000 H₂O, where SDA was N,N,N-trimethyladamantylammonium, was prepared by mixing the following ingredients together in a Teflon liner of a ~125 ml autoclave: ~9.49 g of ~25% SDAOH, ~0.46 g of ~50% NaOH, ~43.74 g deionized water, and ~23.1 g sodium silicate (~28.2% SiO₂, ~9.3% Na₂O). A ~1.02 g solution of ~10 wt% Rh(en)₃Cl₃·3H₂O (en = ethylenediamine) was slowly added while mixing with a magnetic stir bar. Then ~2.18 g of USY zeolite (~17.5% Al₂O₃, Si/Al ≈ ~2.5) was added and the mixture reacted for ~5 days at ~140 °C in a tumbling oven (~40 rpm). The product was recovered by vacuum filtration, washed with deionized water and then dried in a ~115°C oven. Phase analysis by powder X-ray diffraction showed the sample to be pure chabazite. Analysis by X-ray fluorescence showed the sample to contain about ~0.35% Rh. The sample was finally calcined in air for ~2 hours at ~560°C using a ramp rate of ~4.5°C/min.

Preparation of catalyst F:

[0093] Catalyst F included ~1.31 wt% Rh encapsulated in zeolite CHA. A synthesis mixture was prepared having the stoichiometry: ~0.2 Rh: ~2.15 SDAOH: ~7 Na₂O: Al₂O₃ : ~25 SiO₂ : ~715 H₂O, where SDAOH was N,N,N-trimethyladamantylammonium hydroxide. For preparation of the synthesis mixture, to a plastic beaker were added ~20.7 g sodium silicate (~28.2% SiO₂, ~9.3% Na₂O), ~38.0 g deionized water, ~0.5 g ~50% NaOH, and ~8.8 g ~25% SDAOH. The mixture was

stirred with a magnetic stirrer. About 4.14 g of ~10 wt% Rh(en)₃Cl₃·3H₂O solution (en = ethylenediamine) solution was added drop wise with stirring and then stirred until homogenous. The mixture was divided between three ~23 ml Teflon autoclaves and then ~0.94 g of USY zeolite (~60 wt% SiO₂, ~17 wt% Al₂O₃) was mixed in each liner. The autoclaves were heated for ~7 days at ~140°C in a tumbling oven at ~25 rpm. The product was recovered by vacuum filtration and washed with de-ionized water. Phase analysis by powder X-ray diffraction showed that the sample appeared to be pure chabazite. The sample was finally calcined in air for ~3 hours at ~560°C using a ramp rate of ~4.5°C/min. Analysis by X-ray fluorescence showed the sample contained ~1.31 wt% Rh.

Preparation of Catalyst G:

[0094] A self-bound ZSM-5 sample (Si/Al ~ 30) was contacted with an aqueous solution of H₃PO₄ to the point of incipient wetness. The impregnated material was dried overnight at ~121°C in stagnant air, and treated subsequently in flowing dry air (~5 volumes air/volume solids/min) for ~3 hours at ~538°C. The calcined sample was analyzed to contain ~1.2 wt% P.

Preparation of Catalyst H:

[0095] Catalyst H was composed of a physical mixture of Catalyst A and C, where equal amounts of Rh were supported on the support of catalyst A (consisting of alumina, lanthana, ceria, zirconia) and on the support of catalyst C (consisting of chabazite). Based on the individual Rh loadings on catalyst components A and C, their weight ratio in catalyst G was chosen to be ~1 part by weight of catalyst A and ~5.6 parts by weight of catalyst C. This resulted in a catalyst composition having about 1 wt% Rh, about 15 wt% of the mixed oxide support from catalyst A, and about 84 wt% of chabazite.

Preparation of Catalyst I:

[0096] Catalyst I was composed of a physical mixture of Catalyst A and D, where equal amounts of Rh were supported on the support of catalyst A (consisting of alumina, lanthana, ceria, zirconia) and on the support of catalyst D (consisting of chabazite). Based on the individual Rh loadings on catalyst components A and D, their weight ratio in catalyst H was chosen to be ~1 part by weight of catalyst A and ~2.6

parts by weight of catalyst D. This resulted in a catalyst composition of about 2 wt% Rh, about 28 wt% of the mixed oxide support from catalyst A, and about 70 wt% of chabazite.

Preparation of Catalyst J:

[0097] Catalyst J was composed of a physical mixture of Catalyst A and E where equal amounts of Rh were supported on the support of catalyst A (consisting of alumina, lanthana, ceria, zirconia) and on the support of catalyst E (consisting of chabazite). Based on the individual Rh loadings on catalyst components A and E, their weight ratio in catalyst I was chosen to be ~1 part by weight of catalyst A and ~10 parts by weight of catalyst E. This resulted in a catalyst composition of about 0.6 wt% Rh, about 9 wt% of the mixed oxide support from catalyst A, and about 90.4 wt% of chabazite.

Preparation of Catalyst K:

[0098] Catalyst K was composed of a physical mixture of Catalyst A and F, where equal amounts of Rh were supported on the support of catalyst A (consisting of alumina, lanthana, ceria, zirconia) and on the support of catalyst F (consisting of chabazite). Based on the individual Rh loadings on catalyst components A and F, their weight ratio in catalyst K was chosen to be ~1 part by weight of catalyst A and ~2.7 parts by weight of catalyst F.

Preparation of Catalyst L:

[0099] Catalyst L was composed of a physical mixture of reforming catalysts A and C and cracking catalyst G. Equal amounts of Rh were supported on the support of catalyst A (consisting of alumina, lanthana, ceria, zirconia) and on the support of catalyst C (consisting of chabazite). Based on the individual Rh loadings on catalyst components A and C, their weight ratio in catalyst L was chosen to be ~1 part by weight of catalyst A and ~5.6 parts by weight of catalyst C. The amount of the cracking catalyst G was chosen to be ~1 part by weight.

Preparation of catalyst M:

[00100] Catalyst M included ~3.75 wt% Rh and ~1.25wt% Pt supported on a mixed metal oxide comprising La_2O_3 - γ - Al_2O_3 (~40 wt% of total support) and CeO_2 - ZrO_2 (~60 wt% of total support). The La_2O_3 - Al_2O_3 support was prepared separately by

impregnation of an aqueous $\text{La}(\text{NO}_3)_3$ solution onto $\gamma\text{-Al}_2\text{O}_3$. The impregnated $\gamma\text{-Al}_2\text{O}_3$ was dried and calcined at $\sim 600^\circ\text{C}$. The La:Al atomic ratio was $\sim 1.5:100$. $\text{CeO}_2\text{-ZrO}_2$ was co-precipitated from an aqueous $\text{Ce}(\text{NO}_3)_4$ and $\text{Zr}(\text{NO}_3)_4$ solution onto the $\text{La}_2\text{O}_3\text{-Al}_2\text{O}_3$ support using urea as base. The Ce:Zr atomic ratio was $\sim 4:1$. The La- $\gamma\text{-Al}_2\text{O}_3\text{-CeO}_2\text{-ZrO}_2$ support was calcined at $\sim 600^\circ\text{C}$ prior to incipient wetness impregnation with an aqueous solution containing $\text{Rh}(\text{NO}_3)_3$ and $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$. After the precious metal impregnation, the catalyst was calcined in air at $\sim 600^\circ\text{C}$.

Preparation of catalyst N:

[00101] Catalyst N consisted of rhodium supported on γ -alumina. A nominal metal loading of ~ 2.0 wt% rhodium was attained. For the preparation of catalyst N, an aqueous solution containing $\text{Rh}(\text{NO}_3)_3$ was impregnated onto the γ -alumina support in one step. The powder was dried after the impregnation for ~ 12 hours at $\sim 110^\circ\text{C}$ in air. After drying, the powder catalyst was calcined for ~ 4 hours at $\sim 450^\circ\text{C}$ in air. After the calcination, the catalyst powder was pelletized and reduced for ~ 4 hours at $\sim 350^\circ\text{C}$ in a flow of $\sim 10\%$ H_2 , balance N_2 , followed by a ~ 1 hour purge in a flow of pure N_2 gas at $\sim 350^\circ\text{C}$.

Preparation of catalyst O:

[00102] Catalyst O consisted of rhodium supported on silica. About 0.99 grams of an aqueous rhodium nitrate solution (~ 10 wt% Rh), ~ 1.35 grams of arginine, and about 6 drops of $\sim 60\%$ nitric acid were added to deionized water, so that the total solution volume reached ~ 10.0 cm^3 . The impregnated solution was added onto ~ 10.0 grams of a silica support (Davisil™ 646) by incipient wetness. The catalyst was dried at $\sim 100^\circ\text{C}$ overnight ($\sim 8\text{-}16$ hours). The catalyst was calcined in air at $\sim 425^\circ\text{C}$ for ~ 4 hours. The final Rh loading was about 1wt%.

Preparation of catalyst P

[00103] Catalyst P consisted of rhodium and ruthenium supported on γ -alumina. Nominal metal loadings of ~ 3.5 wt% rhodium and of ~ 1.71 wt% ruthenium were attained. For the preparation of catalyst P, an aqueous solution containing $\text{Rh}(\text{NO}_3)_3$ and $\text{Ru}(\text{NO})(\text{NO}_3)_3$ was impregnated onto the γ -alumina support in two steps. An incipient wetness volume of $\sim 90\%$ was achieved in the first impregnation step and of $\sim 85\%$ in the second impregnation step. Powders were dried between impregnations

and after the second impregnation for ~12 hours at ~110°C in air. After drying, the powder catalyst was calcined for ~4 hours at ~450°C in air. After the calcination, the catalyst powder was pelletized and reduced for ~4 hours at ~350°C in a flow of ~10% H₂, balance N₂, followed by a ~1 hour purge in a flow of pure N₂ gas at ~350°C.

Table 1 – Composition of Catalysts A-P

Catalyst	Support	Rh loading, wt%	Type
A, A'	La ₂ O ₃ -Al ₂ O ₃ -CeO ₂ -ZrO ₂	~3.5	Reforming
B	La ₂ O ₃ -Al ₂ O ₃	~3.5	Reforming
C	CHA	~0.62	Reforming+ Methanation
D	CHA	~1.37	Reforming+ Methanation
E	CHA	~0.35	Reforming+ Methanation
F	CHA	~1.31	Reforming+ Methanation
G	P-ZSM-5	0.0	Acid Cracking
Composite catalysts	Catalysts	Catalyst wt ratio	
H	A + C	A:C ≈ 1:5.6	Reforming+ Methanation
I	A + D	A:D ≈ 1:2.6	Reforming+ Methanation
J	A + E	A:E ≈ 1:10	Reforming+ Methanation
K	A + F	A:F ≈ 1:2.7	Reforming+ Methanation
L	A + C + G	A:C:G ≈ 1:5.6:2	Reforming + Methanation + Cracking
Additional catalysts	Support	Rh (and other metals) loading, wt%	
M	La ₂ O ₃ -Al ₂ O ₃	~3.75 (+ ~1.25 Pt)	Reforming
N	γ-alumina	2.0	Reforming
O	Silica	1.0	Reforming
P	γ-alumina	~3.5 (+ ~1.71 Ru)	Reforming

Example 1 - Propane steam reforming test of catalyst M:

[00104] Propane was used as a model fuel compound for determining reforming and methanation rates in the presence of a catalyst composition with two hydrocarbon reforming catalysts (~3.75 wt% Ru, ~1.25 wt% Pt). For the catalytic test, ~0.08 grams of catalyst powder M sized to about ~25-40 mesh was diluted with silica at a ratio of ~1:15. The diluted catalyst was loaded into a vertically mounted cylindrical quartz plugged flow reactor (~6 mm id x ~15 mm long), which was heated by a furnace. The temperature was measured in the front catalyst bed (~¼" from catalyst inlet) and in the rear catalyst bed (~¼" 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, ~26.6 mol% CO₂, and N₂ balance

was fed over the catalyst to achieve gas hourly space velocities of $\sim 26 \text{ hr}^{-1}$ and $\sim 52 \text{ hr}^{-1}$. The conversion of propane and the concentration of the reaction product methane were monitored by FID (flame ionization detection), while the concentration of reaction products, carbon monoxide, and hydrogen were detected by GC/TCD (gas chromatography/thermal conductivity detector) analyzers.

[00105] Figure 3 shows the amounts of H_2 (31), CH_4 (32), and CO (33) produced by the example reformer at various levels of fuel conversion. The mole fraction of CH_4 in the reformer product appeared to increase from about 0.04 at $\sim 12\%$ fuel conversion to about 0.06 at $\sim 44\%$ fuel conversion to about 0.13 at $\sim 75\%$ fuel conversion.

[00106] Referring now to Figure 4, trace (41) shows the amount of heat needed to maintain the reformer at about constant temperature when the reforming catalyst produced substantially only syngas and no methane. The heat requirement appeared to increase from about 1.5 kJ/g fuel at $\sim 12\%$ fuel conversion to about 5.3 kJ/g fuel at $\sim 44\%$ conversion to about 9.1 kJ/g fuel at $\sim 75\%$ fuel conversion in this case. Trace (42) shows the amount of heat needed to maintain the reformer at constant temperature when the reforming catalyst produces the levels of methane shown in Figure 3. The heat requirement appeared to be much lower in this case, varying from about 1.2 kJ/g fuel at $\sim 12\%$ fuel conversion to about 2.8 kJ/g fuel at $\sim 44\%$ conversion to about 2.8 kJ/g fuel at $\sim 75\%$ fuel conversion.

[00107] As shown in Figure 4, a reforming catalyst on a metal oxide support can generate some methane under reforming conditions, so that the amount of heat required for the reforming reaction can be reduced. As a comparison, trace (43) shows the amount of heat released by cooling the recycled exhaust gas by $\sim 100^\circ\text{C}$ and by combusting fuel with residual oxygen, present at about a 1% level in the exhaust gas. Trace (43) also shows that this amount of heat appeared to be enough to supply the additional heat needed for the reforming reactions. However, the additional fuel used to supply heat for the reforming reactions can represent an additional fuel debit against the overall efficiency of the engine.

Example 2 - n-Heptane steam reforming test:

[00108] An n-heptane feed was used to for determining reforming and methanation rates for a model feed based on a hydrocarbon that was representative of a compound

present in a typical naphtha boiling range fuel. About 50 mg to about 1250 mg of catalysts A', N, O, and P were sized to ~40-60 mesh and blended with quartz sized to ~60-80 mesh to obtain ~4 cm³ of catalyst-quartz mixture. The catalyst diluent mixture was loaded into a stainless steel reactor tube of ~4" length and ~0.3" inner diameter. The reactor tube was heated by a furnace to maintain a constant temperature of ~450°C, ~500°C, or ~550°C in the catalyst throughout the length of the catalyst bed. A thermocouple in the bed was used to confirm that all experiments were performed approximately isothermally. A gas mixture comprising ~2.5 mol% n-heptane, ~13 mol% H₂O, ~11 mol% CO₂, and balance N₂ was fed to the catalyst at a pressure of ~2 barg (~200 kPag) or ~4 barg (~400 kPag). The total gas flow rate was varied between about 70 mL/min and about 400 mL/min to achieve different levels of fuel conversion.

[00109] The ratio of methane and hydrogen as a function of conversion at ~500°C catalyst bed temperature was measured for catalyst A' (71), N (72), O (73), and P (75) at ~2 barg (~200 kPag) pressure, as well as for catalyst O (74) at ~4 barg (~400 kPag) pressure. It was apparent that catalysts N, O, and P appeared to exhibit a higher CH₄/H₂ ratio compared to the reference catalyst A'. The CH₄/H₂ ratio also appeared to be higher when the pressure was raised from ~2 barg (~200 kPag) to ~4 barg (~400 kPag). These are shown in the graph at Figure 5. The catalyst and conditions in trace (74), corresponding to Catalyst O at the higher pressure, appeared to be the most effective at maintaining high catalyst temperatures.

[00110] Figure 6 shows n-heptane conversion versus contact time for (81) Catalyst A' at ~550°C, (82) Catalyst A' at ~500°C, (83) Catalyst A' at ~450°C, (84) Catalyst N at ~500°C, (85) Catalyst O at ~500°C, and (86) Catalyst P at ~500°C. The conditions were ~2.5 mol% n-heptane, ~13 mol% H₂O, ~11 mol% CO₂, balance N₂, at ~2 barg (~200 kPag) pressure. Although Catalyst O was most effective in producing a high ratio of CH₄ to H₂ (as shown in Figure 5), Figure 6 shows that the conversion rate of Catalyst O for reforming n-heptane appeared substantially slower than Catalyst A', N, or P. This suggests that the high ratio of CH₄ to H₂ for Catalyst O may be related to a reduced level of H₂ production rather than an increased level of CH₄ production.

Example 3 – Reforming of n-heptane and Methanation

[00111] Catalysts A and H were tested in a laboratory reactor in the steam reforming reaction of n-heptane. For the tests, ~50-1250 mg of catalyst were sized to ~40-60 mesh and blended with quartz sized to ~60-80 mesh to obtain ~4 cm³ of catalyst-quartz mixture. The catalyst diluent mixture was loaded into a stainless steel reactor tube of 4” length and 0.3” inner diameter. The reactor tube was heated by a furnace to maintain a constant temperature of ~500°C in the catalyst throughout the length of the catalyst bed. A thermocouple in the bed was used to confirm that experiments were performed isothermally. A gas mixture comprising ~2.5 mol % n-heptane, ~13 mol % H₂O, and ~11 mol % CO₂ in N₂ (balance of gas mixture) was fed to the catalyst at a pressure of ~2 barg (~200 kPag). The total gas flow rate was varied between ~70 ml/min and ~400 ml/min to achieve different levels of fuel conversion. Reaction products CO, CO₂, H₂, were analyzed by GC-TCD, CH₄ was analyzed by GC-FID. N-heptane reforming rates were defined as mol fuel carbon converted/mol Rh/s. Methane formation rates were defined as mol CH₄ formed/mol Rh/s. Tests were conducted at a residence time of ~10 g Rh*s/g fuel.

[00112] FIGS 7A and 7B show the n-heptane conversion rates and the methane formation rates, respectively, in the reforming reaction of Example 3 for catalysts A and H. While catalysts A and H appeared to display similar n-heptane conversion rates, the methane formation rate was unexpectedly substantially higher over catalyst H. Thus, catalyst H can provide both a desirable level of conversion (reforming) of naphtha boiling range fuel components like n-heptane, while also providing an improved amount of methane formation.

Example 4 – Reforming of multi-component model fuel and Methanation

[00113] Catalysts A, C, H, I, J, and K were tested on a surrogate gasoline type fuel containing ~45 vol% 3-methyl pentane, ~15 vol% n-hexane, ~10 vol% 2,2,4-trimethyl pentane (iso-octane), ~20 vol% toluene, and ~10 vol% ethanol. The same reactor and procedures as described in Example 3 were used for the multi-component model fuel reforming test. A gas mixture comprising ~1.4 mol% 3-methyl pentane, ~0.46 mol% n-hexane, ~0.25 mol% 2,2,4 trimethyl pentane, ~0.76 mol% toluene, ~0.69 mol% ethanol, ~13.1 mol% H₂O, and ~12.6 mol% CO₂ in N₂ (balance of gas mixture) was fed into a

reactor at ~2 barg (~200 kPag) pressure and ~500°C catalyst bed temperature. Reaction products CO, CO₂, H₂, were analyzed by GC-TCD, CH₄ was analyzed by GC-FID. The global reforming rates were defined as mol fuel carbon converted/mol Rh/s. Methane formation rates were defined as mol CH₄ formed/mol Rh/s. Tests were conducted at a residence time of ~10 g Rh*s/g fuel.

[00114] FIGS 8A and 8B show the global multi component fuel conversion rates and the methane formation rates, respectively, for the reforming reaction of Example 4 for catalysts A, C, H, I, J, and K. It was apparent that catalyst C showed a lower reforming activity than catalyst A. It was unexpectedly found that catalyst H, which was a physical mixture of catalysts A and C, had a similar reforming activity to catalyst A alone. Catalyst J, which was a physical mixture of catalysts A and E, also unexpectedly showed a reforming activity comparable to catalyst A alone. Catalyst K, which was a physical mixture of catalysts A and F, also unexpectedly showed a reforming activity comparable to and possibly greater than catalyst A alone.

[00115] Catalyst C showed a higher methanation activity than catalyst A. It was unexpectedly found that catalyst H, which was a physical mixture of catalyst A and C, showed a substantially higher methane formation rate than its individual constituents A and C alone. Catalyst I, which was a physical mixture of catalysts A and D, also showed a higher methanation rate than catalyst A alone. It was noted that Catalyst I was similar in Rh content to Catalyst H, but had a lower concentration of the CHA framework type zeolite. As shown in FIG. 8B, reducing the amount of CHA framework type zeolite appeared to result in a reduced amount of methanation. By contrast, Catalyst J, which was a physical mixture of catalysts A and E, and Catalyst K, which was a physical mixture of catalysts A and F, displayed the highest methanation rates. Catalyst J had an increased amount of CHA framework type zeolite relative to Catalyst H. Similar to catalyst I, catalyst K had a lower amount of CHA framework type zeolite than catalyst H. However, unlike catalyst I, catalyst K appeared to show a higher methane formation rate than H. The methanation catalyst component in Catalyst K was formed by an alternative method.

[00116] The product selectivities expressed as mol% carbon converted into products CO_x (CO + CO₂), benzene, and methane are shown in Figure 8C for the tests in

Example 4. In Figure 8C, the CO_x selectivity is shown as the left bar for each catalyst, the benzene selectivity is the middle bar, and the methane selectivity is the right bar. Catalyst C had higher CO_x selectivity, lower benzene selectivity, and higher methane selectivity compared to catalyst A. It was unexpectedly found that mixing of catalysts A and C (such as to form catalyst H) resulted in a significant reduction of CO_x selectivity and an increase in methane selectivity relative to catalyst A. It was noted that, in line with their high methane formation rates, catalysts J and K also appeared to show the highest methane selectivity. Catalysts J and K also appeared to show the lowest CO_x selectivities.

Example 5 – CO Hydrogenation

[00117] The methanation rate was measured for various feed streams containing CO and H₂ over catalysts B and C. In a first test, the methane formation rate for a feed containing just syngas (H₂, CO, CO₂) was tested. The same reactor and procedure as described for Example 1 was used for the CO hydrogenation test. A gas mixture comprising ~8.3 mol% CO, ~15.9 mol% H₂, ~5.7 mol% CO₂ in N₂ (balance of gas mixture) was fed at ~2 barg (~200 kPag) pressure and ~500°C catalyst bed temperature. Catalyst B (Rh-LaAl₂O₃) was run at a residence time of ~8.8 g Rh*s/g CO, while catalyst C (Rh-CHA) was run at a residence time of ~11.1 g Rh*s/g CO. It was noted that water was not included in the gas mixture. The absence of water in the initial gas mixture was believed to reduce/minimize the opportunity for steam reforming to occur in the reaction environment as a complementary reaction.

[00118] The effect of n-heptane co-feed on the CO hydrogenation activity was also tested. The same reactor and test procedure as described above were used to test CO hydrogenation in the presence of n-heptane. A gas mixture comprising ~8.4 mol% CO, ~16 mol% H₂, ~5.3 mol% n-heptane, and ~5.8 mol% CO₂ in N₂ (balance of gas mixture) was fed at ~2 barg (~200 kPag) pressure and ~500°C catalyst bed temperature. Catalyst B (Rh-LaAl₂O₃) was run at a residence time of ~3.9 g Rh*s/g heptane and ~8.8 g Rh*s/g CO.

[00119] The effect of a multi-component hydrocarbon fuel co-feed on the CO hydrogenation activity was also tested. The same reactor and test procedure as described above were used for the CO hydrogenation test in the presence of the multi

component hydrocarbon fuel. A gas mixture comprising ~8.1 mol% CO, ~15.6 mol% H₂, ~2.44 mol% 3-methyl pentane, ~0.81 mol% n-hexane, ~0.43 mol% 2,2,4 tri-methyl pentane, ~1.32 mol% toluene, ~1.2 mol% ethanol, and ~5.6 mol% CO₂ in N₂ (balance of gas mixture) was fed at ~2 barg (~200 kPag) pressure and ~500°C catalyst bed temperature. Catalyst C (Rh-CHA) was run at a residence time of ~5.0 g Rh*s/g fuel and ~11.1 g Rh*s/g CO.

[00120] FIG. 9 shows the methane formation rate from testing catalyst B in the presence of the syngas feed (H₂ and CO) and the feed of syngas plus n-heptane. As shown in FIG. 9, the n-heptane co-feed appeared to strongly deplete the ability of catalyst B to convert syngas into methane. This indicated that catalyst B had some activity for methanation. However, in an engine environment, the goal of reforming can typically be to convert a lower octane rating fuel to a higher octane fuel. Such lower octane fuels can typically correspond to hydrocarbons, such as linear or branched alkanes. FIG. 9 shows that low octane feed components typically present in a naphtha boiling range fuel can substantially reduce/minimize the methanation activity of Catalyst B.

[00121] FIG. 10 shows the methane formation rate from testing Catalyst C in the presence of the syngas feed (H₂ and CO) and the feed of syngas plus the multi-component model fuel. As described above, the multi-component model fuel includes a variety of types of compounds that can be present in a fuel, including both low octane components such as n-hexane and higher octane components such as toluene. As shown in FIG. 10, Catalyst C actually had a lower methane formation rate than Catalyst B for the syngas feed without any additional fuel components. However, in the presence of the fuel components of the multi-component model fuel, Catalyst C unexpectedly showed a substantially higher methane formation rate.

Example 6 – Reforming, Methanation, and Cracking

[00122] In order to test the effect of an acid cracking catalyst on reforming, a blend of catalysts H and G (corresponding to catalyst L) was tested. The product selectivity of catalyst L for reforming the multi-component fuel feed of Example 4 is shown in Figure 11. The product selectivity for catalyst H is also shown in Figure 11 to provide a comparison. As shown in Figure 11, the addition of a cracking function (such as P-

ZSM-5 zeolite) appeared to decrease the selectivity for CO_x and increase the selectivity for methane. This result was unexpected, because no significant amounts of methane were observed in fuel cracking experiments over the acid cracking catalyst G alone. The methane selectivity for catalyst L, as shown in FIG. 11, also appeared to be slightly greater than the methane selectivity for catalyst J in FIG. 8C.

[00123] 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.

[00124] As should be 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 this art in light of the above detailed description. All such variations can be 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.

CLAIMS:

1. A method of increasing the octane rating of an internal combustion engine exhaust gas stream, said method comprising:
 - (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-containing mixture comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% of a hydrocarbon-reforming catalyst selected from Co, Ru, Pt, Pd, Ni, Ir, Rh, Zn, Re, and mixtures thereof, and at least about 10 wt% of a small pore molecular sieve to form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.
2. The method of claim 1, wherein the hydrocarbon-reforming catalyst composition comprises about 0.25 wt% to about 10 wt% of the hydrocarbon-reforming catalyst, or about 0.5 wt% to about 10 wt%, or wherein the hydrocarbon-reforming catalyst composition comprises about 10 wt% to about 99.75 wt% of the small pore molecular sieve, or about 10 wt% to about 75 wt%, or about 10 wt% to about 50 wt%, or a combination thereof.
3. The method of any of the above claims, wherein the small pore molecular sieve comprises a molecular sieve having the framework type AEI, AFT, AFX, ATT, DDR, EAB, EPI, ERI, KFI, LEV, LTA, MER, MON, MTF, PAU, PHI, RHO, or SFW, or wherein the small pore molecular sieve comprises a molecular sieve having a largest pore size corresponding to an 8-member ring.
4. The method of any of the above claims, wherein the small pore molecular sieve is chabazite and/or has a CHA framework type molecular sieve, and/or wherein the hydrocarbon-reforming catalyst comprises Rh.
5. A method of increasing the octane rating of an internal combustion engine exhaust gas stream, said method comprising: (a) providing an exhaust gas-containing mixture to an exhaust gas recycle reformer, the exhaust gas-containing mixture

comprising engine exhaust gas and a first hydrocarbon-containing fuel, said engine exhaust gas having an initial octane rating, 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 0.25 wt% Rh and at least about 10 wt% of a CHA framework type molecular sieve to form a reformed gaseous mixture, the reformed gas mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than about 1.0 mol% CH₄ based on the total moles of gas in the reformed gaseous mixture.

6. The method of any of claims 4-5, wherein the hydrocarbon-reforming catalyst composition further comprises about 0.25 wt% to about 10 wt% of an additional metal selected from the group consisting of Co, Ru, Pt, Pd, Ni, Ir, Zn, Re, and mixtures thereof, a total weight of Rh and the additional metal being about 20 wt% or less.

7. The method of any of the above claims, wherein said converting supplies heat sufficient to maintain the reformer at an average reformer temperature above about 450°C.

8. The method of any of the above claims, wherein said exhaust gas-containing mixture is substantially free of oxygen-containing gas other than the exhaust gas and the first hydrocarbon-containing fuel.

9. The method of any of the above claims, wherein the hydrocarbon-reforming catalyst composition further comprises a metal oxide composition, the metal oxide composition optionally comprising and/or being selected from aluminum oxides, silicon oxides, rare-earth metal oxides, Group IV metal oxides, and mixtures thereof, for example a mixture of an aluminum-containing oxide and a cerium-containing oxide.

10. The method of any of the above claims, wherein the hydrocarbon-reforming catalyst composition further comprises about 5 wt% to about 50 wt% of one or more additional molecular sieves, the one or more molecular sieves optionally having a largest ring size of a 10-member ring, and/or the one or more additional molecular sieves optionally being ZSM-5, MCM-68, or a combination thereof.

11. The method of any of the above claims, wherein the reformed gaseous mixture has an octane rating (RON) from about 100 to about 125.

12. The method of any of the above claims, further comprising:

introducing the reformed gaseous mixture and a second hydrocarbon-containing fuel into the engine, wherein said second hydrocarbon-containing fuel may be the same or different from the first hydrocarbon-containing fuel;

combusting the reformed gaseous mixture and second hydrocarbon-containing fuel in the engine to form an exhaust gas; and

passing the exhaust gas through a first heat exchanger to extract heat from the exhaust gas, wherein, prior to introducing the reformed gaseous mixture into the internal combustion engine, the gaseous mixture can optionally be cooled by passing the gaseous mixture through the first heat exchanger or a second heat exchanger.

13. The method of any of the above claims, further comprising pre-combusting a portion of exhaust gas-containing mixture prior to providing the exhaust gas-containing mixture to the exhaust gas recycle reformer, the exhaust gas recycle reformer having a reformer inlet temperature of about 525°C to about 625°C.

14. The method of any of the above claims, wherein the reformed gaseous mixture comprises from about 2.0 mol% to about 5.0 mol% CH₄, the reformed gaseous mixture has a CH₄:H₂ ratio (mol/mol) of at least about 0.05:1, or a combination thereof.

15. A reformer for use in an exhaust gas recycle portion of an internal combustion engine powertrain, said reformer comprising a catalyst composition configured to convert a mixture comprising an internal combustion engine exhaust gas and a hydrocarbon-containing fuel to a gaseous mixture comprising H₂, CO, CO₂, H₂O, N₂, and greater than 1.0 mol% CH₄ based on the total moles of gas in the gaseous mixture, the catalyst composition comprising a hydrocarbon-reforming catalyst composition described in any of claims 1-14.

16. The reformer of claim 15, further comprising an internal combustion engine having an exhaust manifold comprising an exhaust gas recycle unit and a fuel intake manifold, the reformer being fluidly connected to the exhaust manifold and the fuel intake manifold, the fuel intake manifold being 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, wherein the first and second hydrocarbon-containing fuels may be the same or different.

17. A hydrocarbon-reforming catalyst composition comprising about 0.25 wt% to about 10 wt% Rh, about 10 wt% to about 99.5 wt% of a CHA framework type molecular sieve, and about 0.25 wt% to about 10 wt% of one or more additional molecular sieves having a largest ring size of a 10-member ring, the CHA framework type molecular sieve optionally being chabazite, the one or more additional molecular sieves optionally being ZSM-5, MCM-68, or a combination thereof.

18. The hydrocarbon-reforming catalyst composition of claim 17, wherein the hydrocarbon-reforming catalyst composition further comprises 0.25 wt% to 10 wt% of an additional metal selected from the group consisting of Co, Ru, Pt, Pd, Ni, Ir, Zn, Re, and mixtures thereof.

19. The hydrocarbon-reforming catalyst composition of any of claims 17-18, wherein the hydrocarbon-reforming catalyst composition further comprises a metal oxide composition, the metal oxide composition optionally being selected from aluminum oxides, silicon oxides, rare-earth metal oxides, Group IV metal oxides, and mixtures thereof, or optionally comprising a mixture of an aluminum-containing oxide and a cerium-containing oxide.

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Figure 1.

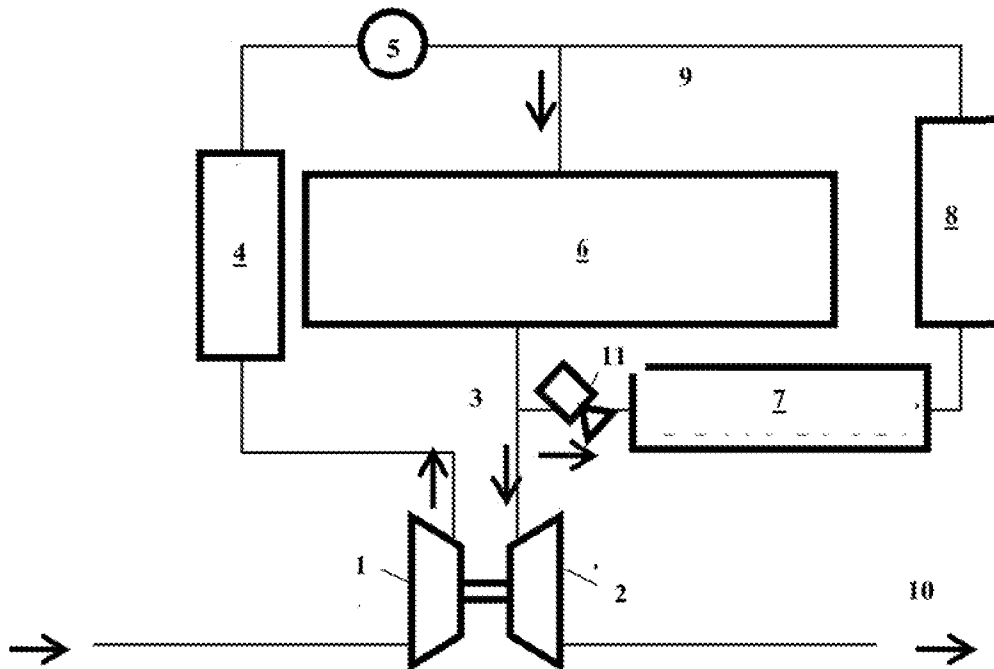
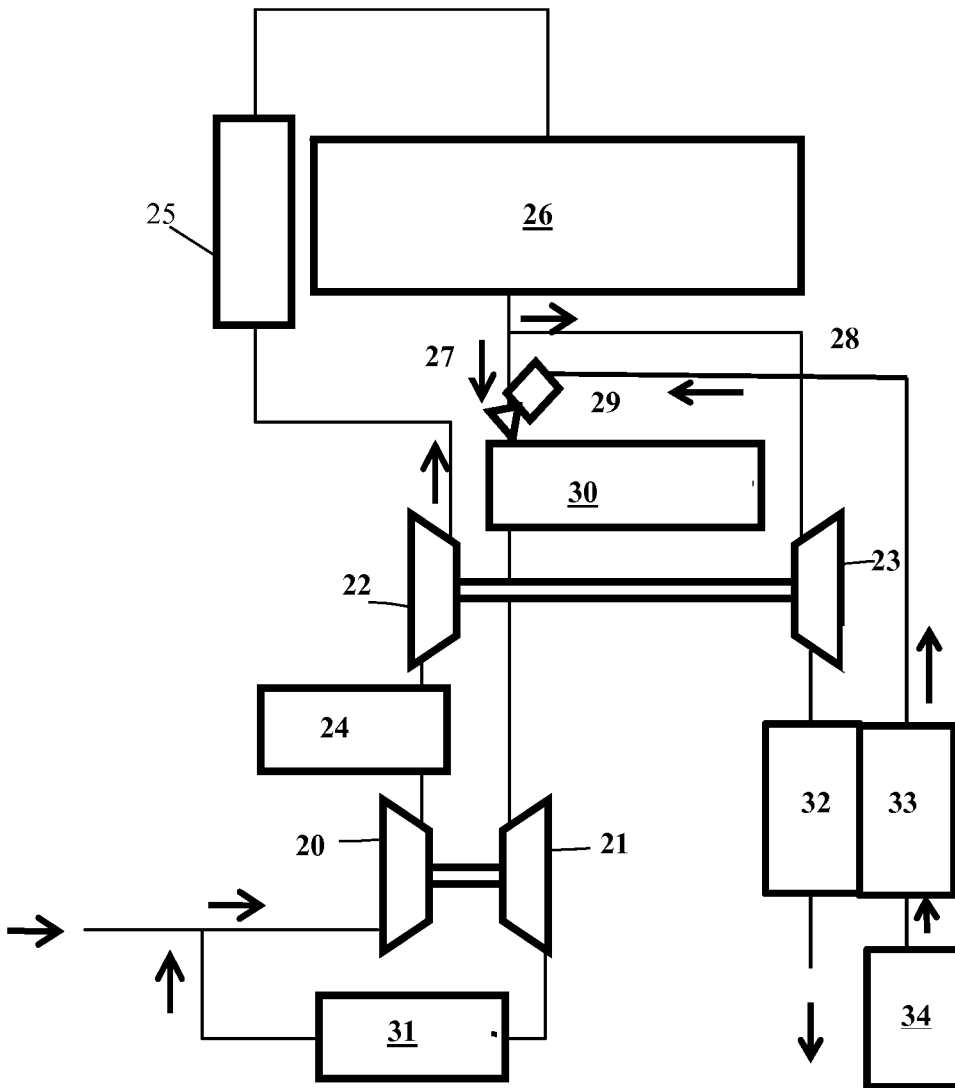
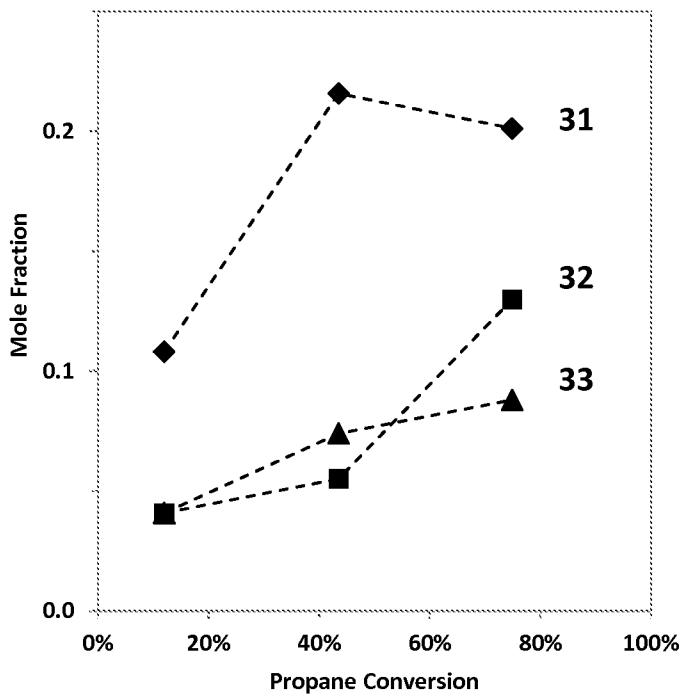


Figure 2.



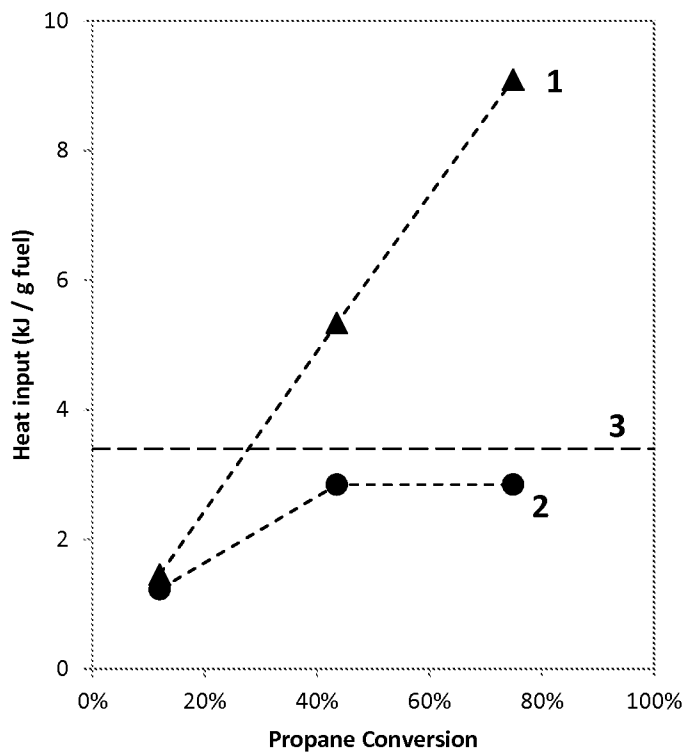
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Figure 3.



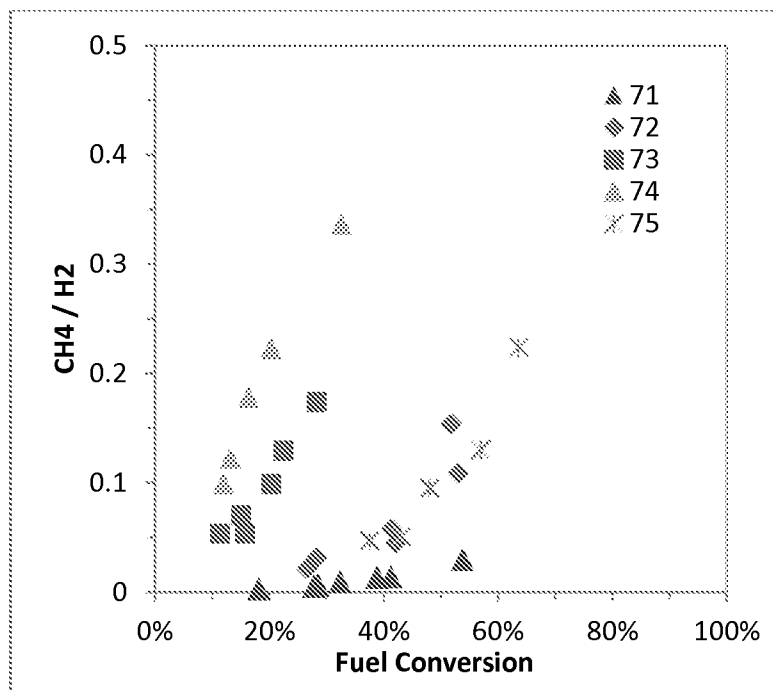
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Figure 4



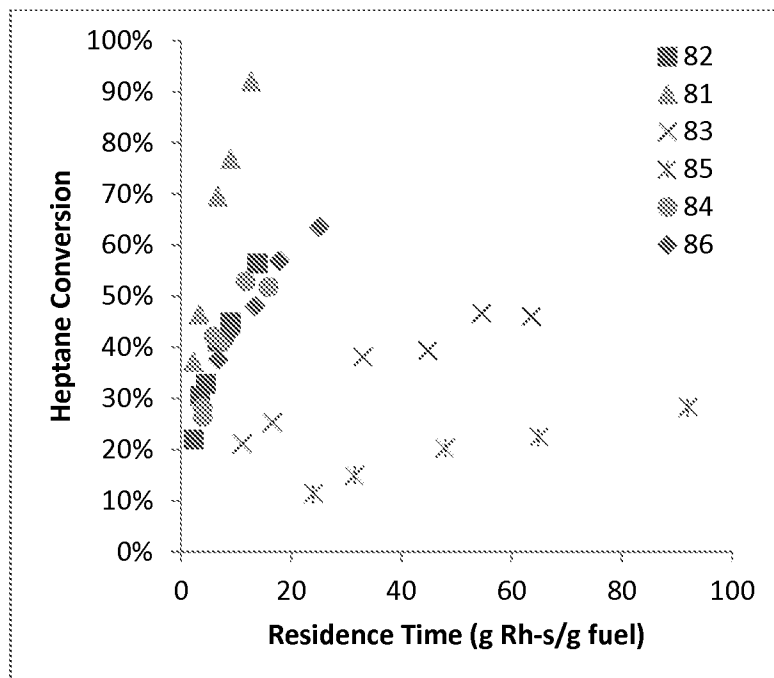
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Figure 5



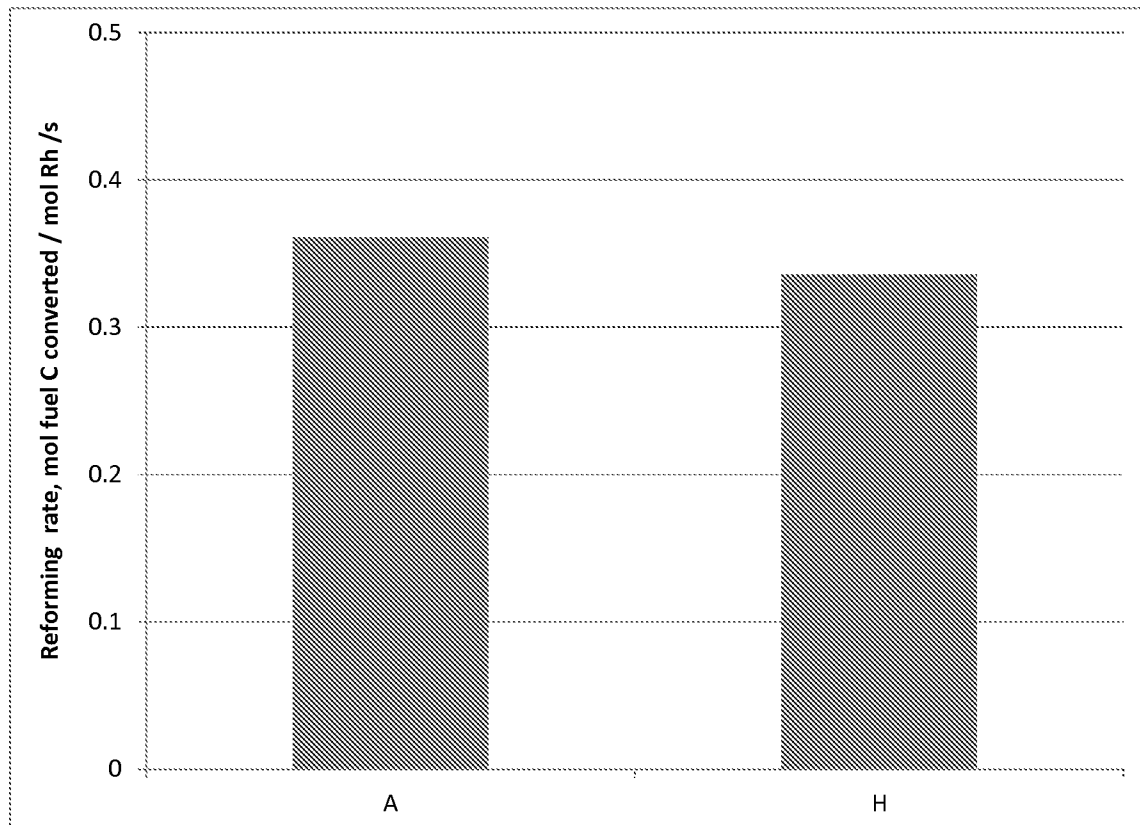
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Figure 6



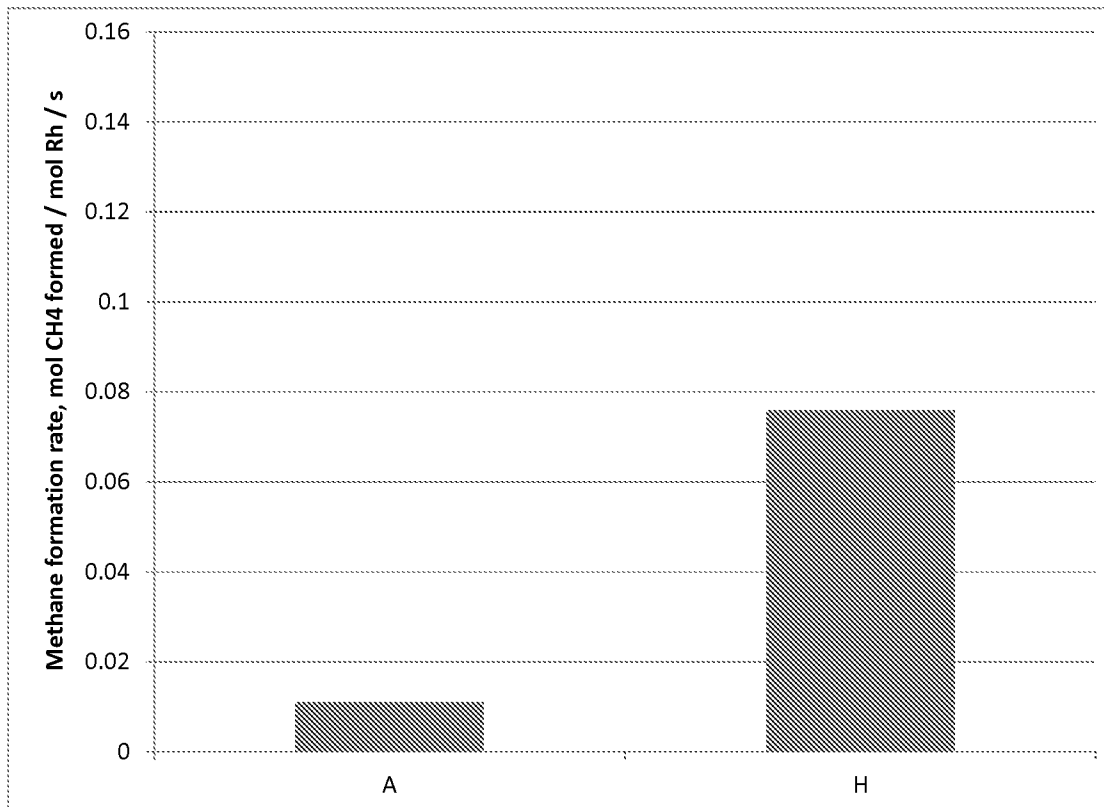
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Figure 7A



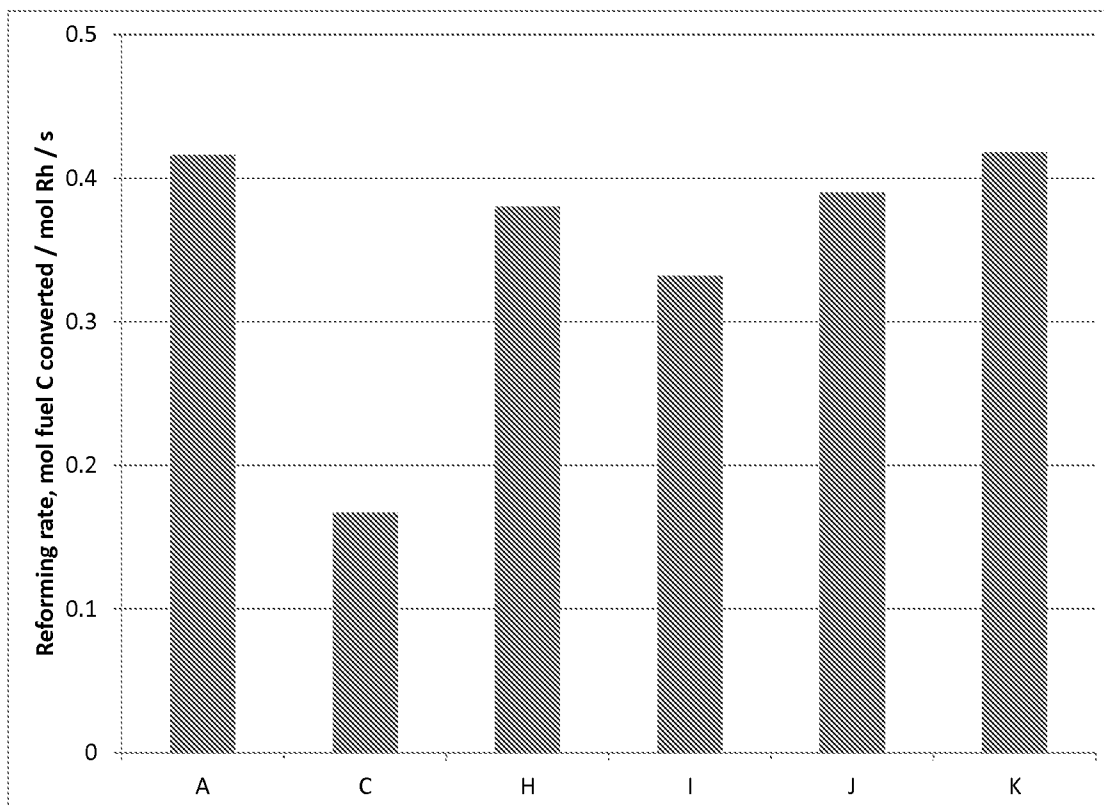
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Figure 7B



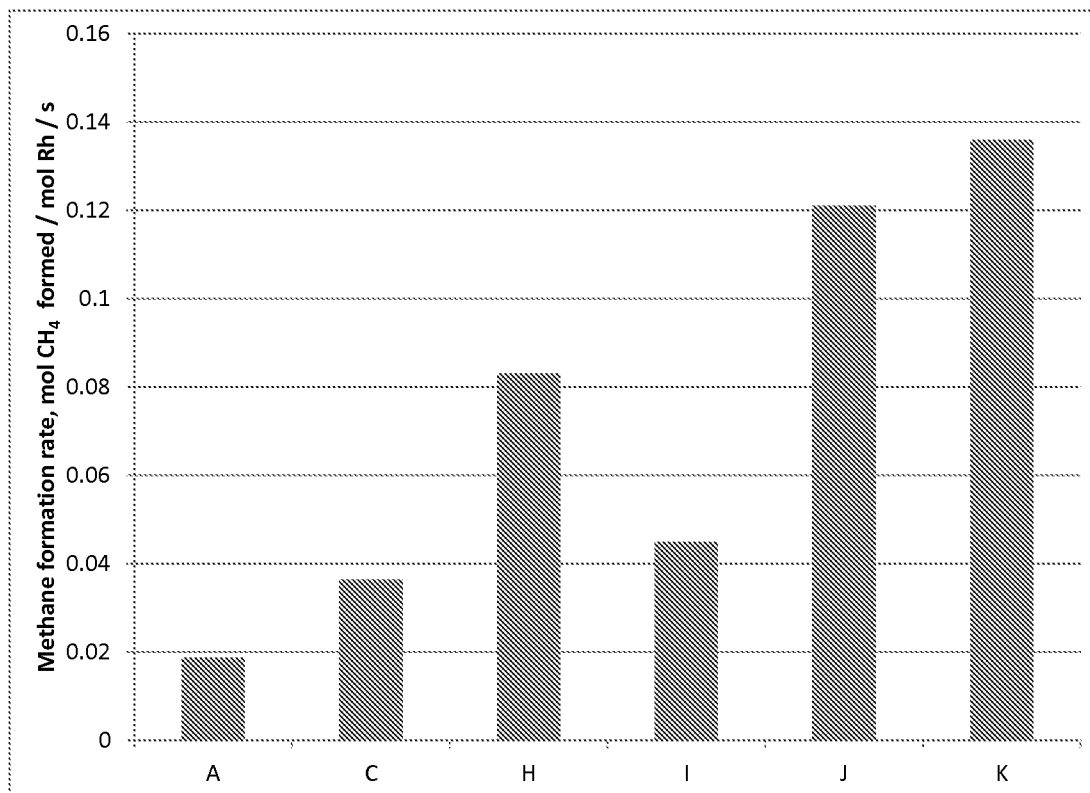
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Figure 8A



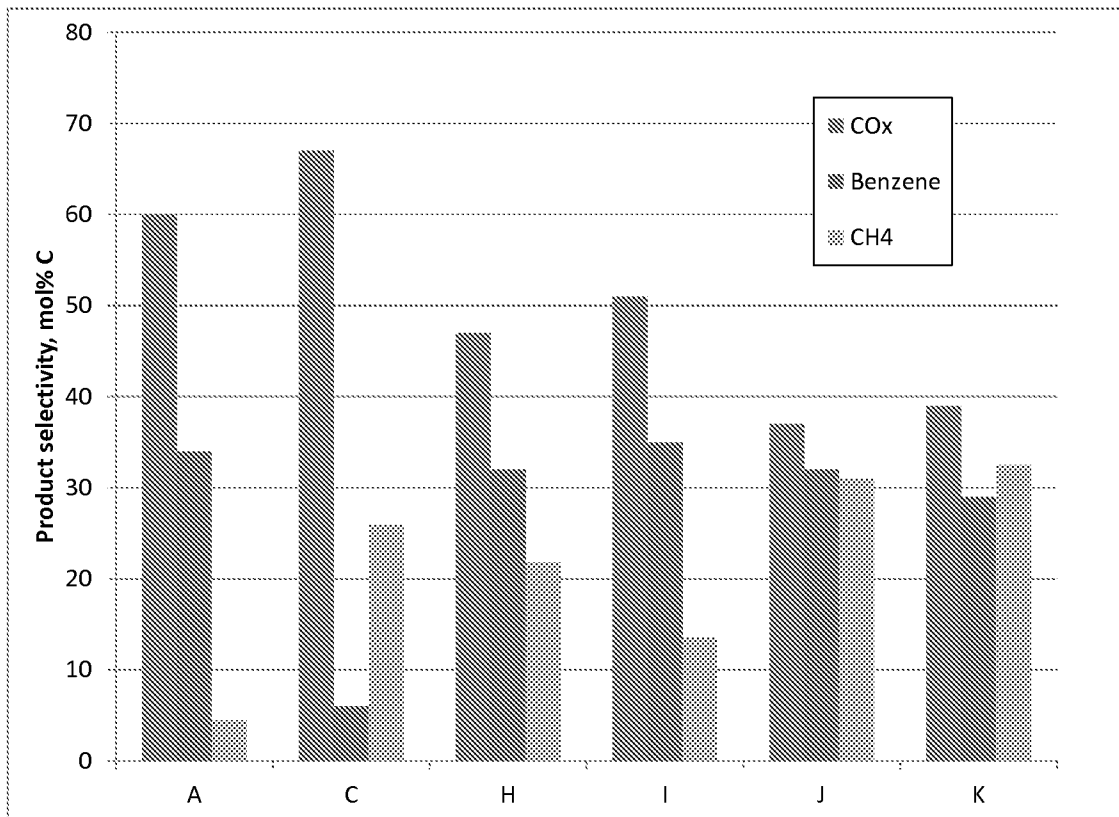
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Figure 8B



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Figure 8C



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Figure 9

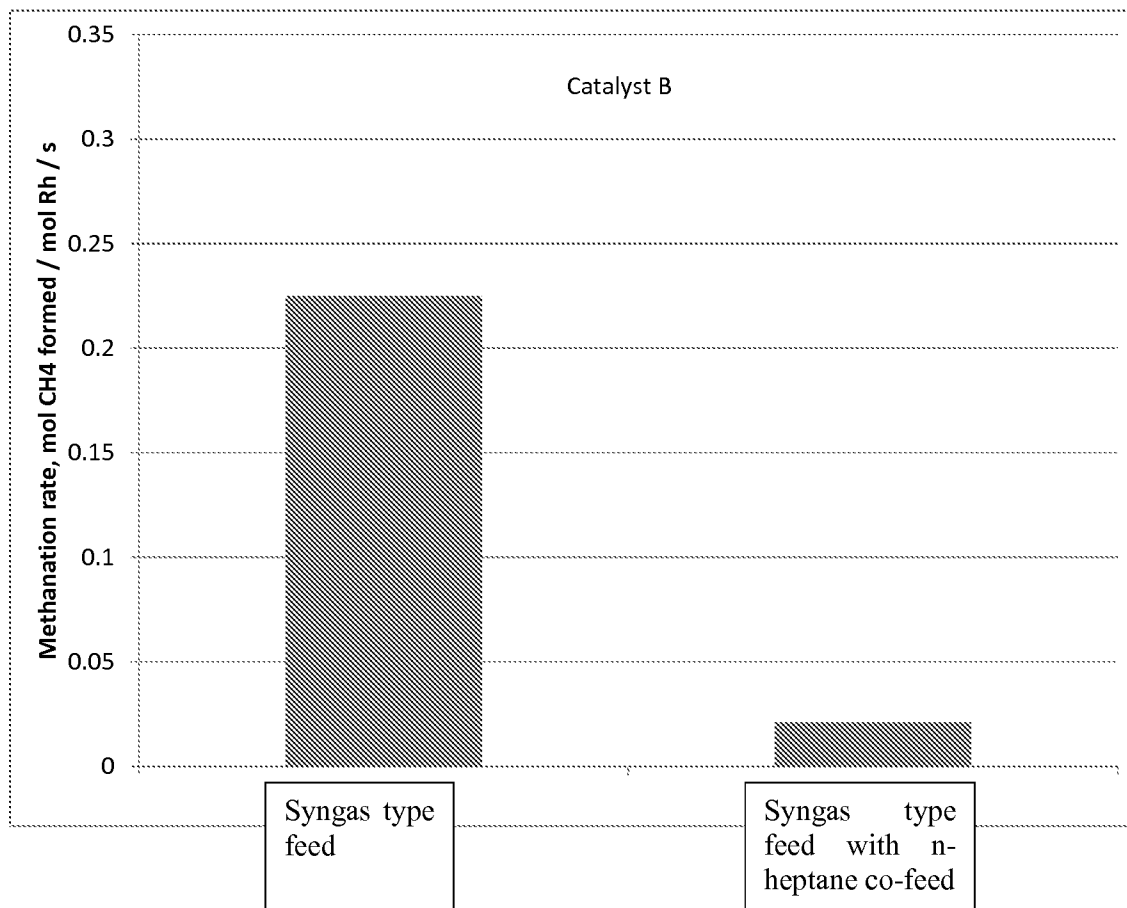


Figure 10

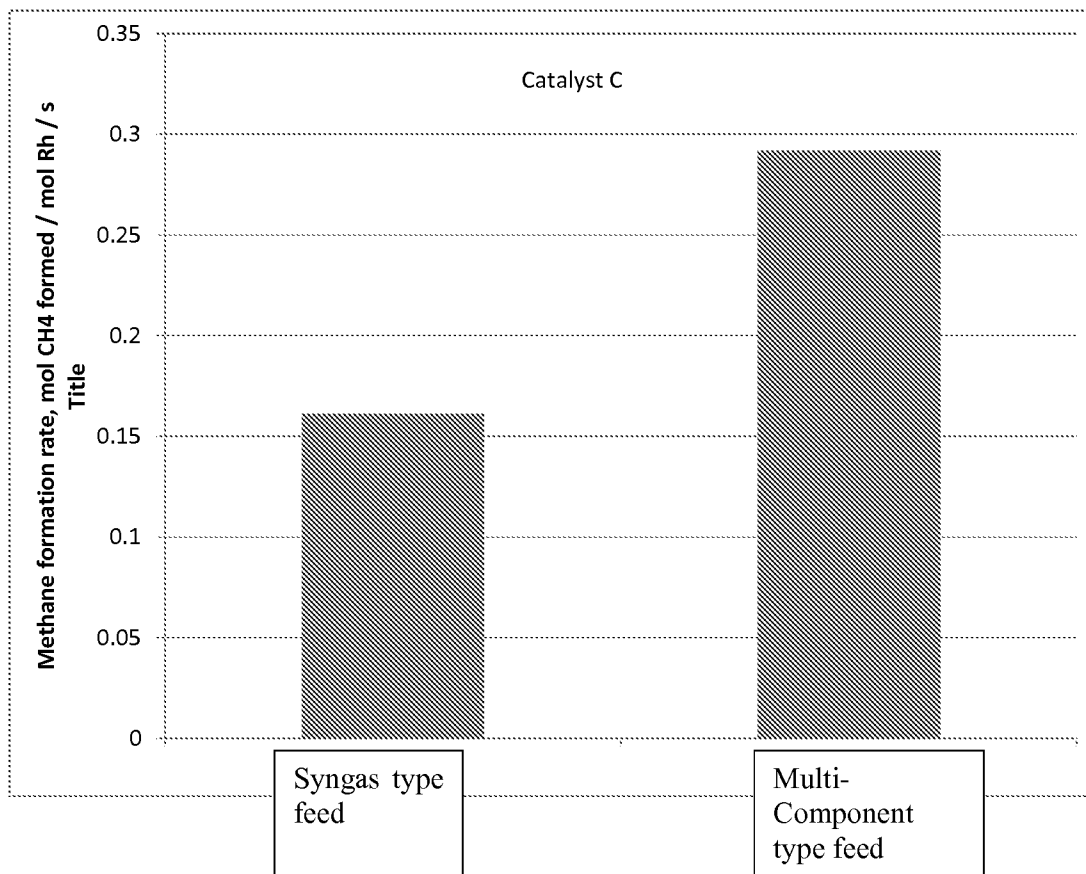
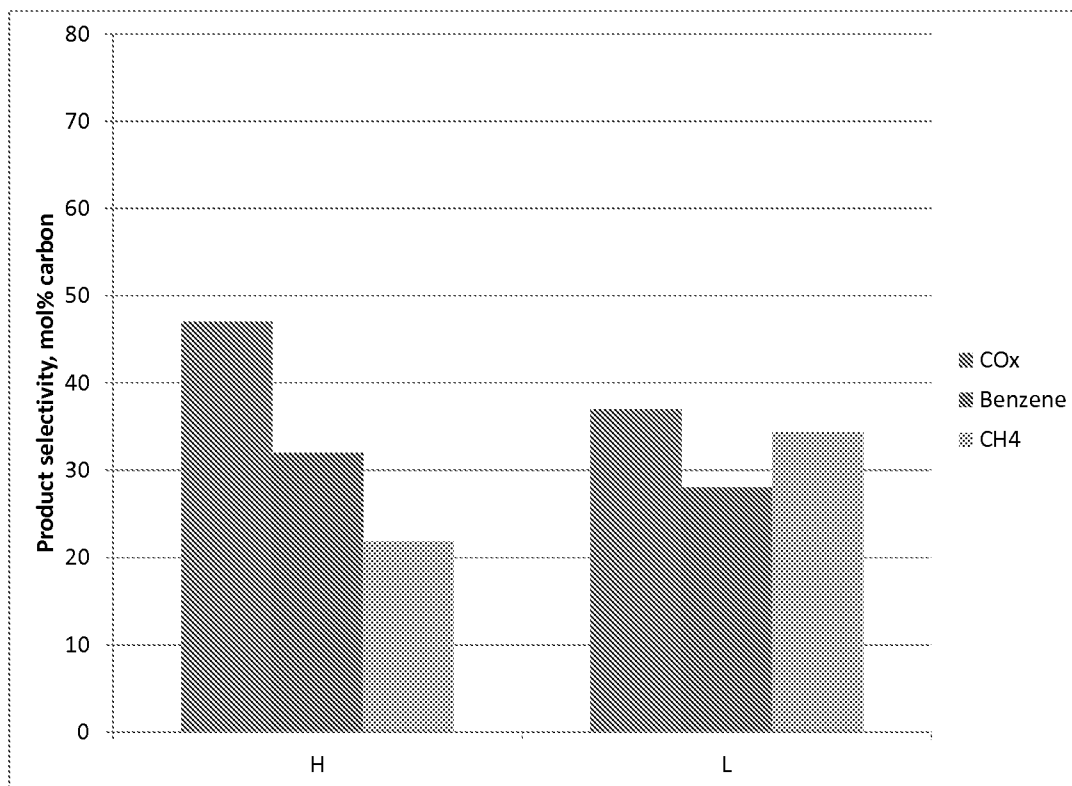


Figure 11



INTERNATIONAL SEARCH REPORT

International application No PCT/US2014/069677

A. CLASSIFICATION OF SUBJECT MATTER INV. C01B3/40 F02M25/12 B01J29/80 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01J C01B F02M		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data, COMPENDEX, API Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 753 143 A (BHAT RAMANATH [US] ET AL) 19 May 1998 (1998-05-19)	15, 16
Y	claims	1-14
X	US 6 242 380 B1 (PARK SANG-EON [KR] ET AL) 5 June 2001 (2001-06-05)	15, 16
Y	DE 10 2012 204649 A1 (VOLKSWAGEN AG [DE]) 26 September 2013 (2013-09-26) paragraph [0002] paragraph [0008] paragraph [0014] paragraph [0033] - paragraph [0040] figures	1-14
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<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents :		
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone	
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Date of the actual completion of the international search	Date of mailing of the international search report	
19 March 2015	27/03/2015	
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer Van der Poel, Wim	

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2014/069677

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2013/050964 A1 (BASF SE [DE]; BASF CHINA CO LTD [CN]; STIEBELS SUSANNE [DE]; WENDT CLA) 11 April 2013 (2013-04-11) claims; example 1 -----	17-19
A	US 2004/035395 A1 (HEYWOOD JOHN B [US] ET AL) 26 February 2004 (2004-02-26) abstract; claims -----	5
A	US 2009/035192 A1 (HWANG HERNG SHINN [US]) 5 February 2009 (2009-02-05) claims -----	1,5,15

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