

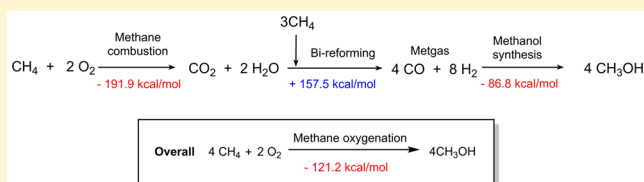
Single Step Bi-reforming and Oxidative Bi-reforming of Methane (Natural Gas) with Steam and Carbon Dioxide to Metgas (CO-2H₂) for Methanol Synthesis: Self-Sufficient Effective and Exclusive Oxygenation of Methane to Methanol with Oxygen

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S Supporting Information

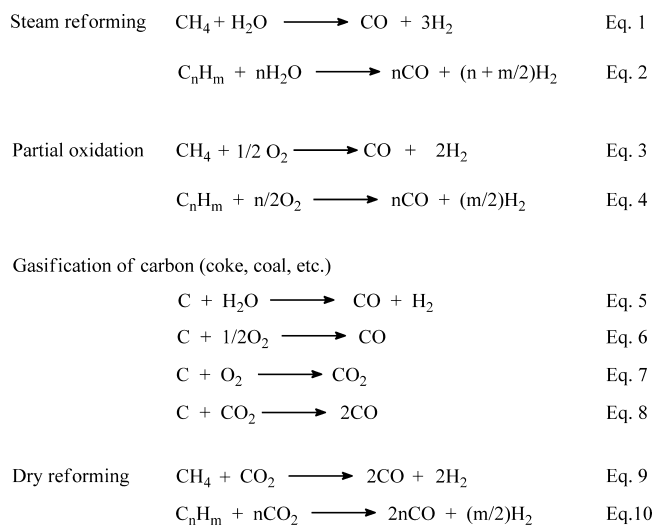
ABSTRACT: Catalysts based on suitable metal oxide supports, such as NiO/MgO and CoO/MgO, were shown to be active for single step bi-reforming, the combined steam and dry reforming of methane or natural gas with H₂O and CO₂ exclusively to metgas (CO-2H₂) for efficient methanol synthesis. Reactions were carried out in a tubular flow reactor under pressures up to 42 bar at 830–910 °C. Using a CH₄ to steam to CO₂ ratio of ~3:2:1 in the gas feed, the H₂/CO ratio of 2:1 was achieved, which is desired for subsequent methanol synthesis. The needed 2/1 steam/CO₂ feed ratio together with the reaction heat for the endothermic bi-reforming can be conveniently obtained by the complete combustion of a quarter part of the overall used methane (natural gas) with oxygen of the air (oxidative bi-reforming). Complete combustion of a part of methane followed by bi-reforming leads to the production of metgas (H₂/CO in 2:1 mol ratio) for self-sufficient exclusive methanol synthesis. The long sought after but elusive efficient and selective oxygenation of methane to methanol is thus achieved in an effective and economic way without any oxidation byproduct formation according to CH₄ + 1/2O₂ → CH₃OH.



INTRODUCTION

Synthesis gas (syngas), a variable composition mixture of hydrogen, carbon monoxide, and carbon dioxide, is the basis for the most significant Fischer–Tropsch chemicals. Syngas can be produced from virtually any carbon containing source including fossil fuels (coal, oil and natural gas) or biomass using varied reforming and gasification processes. Natural gas and methane are, however, the preferred feedstocks because of their still existing abundance as well as their well-developed transformation to syngas by steam, carbon dioxide dry reforming or partial oxidation of methane with oxygen (Scheme 1).¹ In comparison, coal and biomass require more complex and expensive industrial processes for the preparation and purification of the produced syngas to levels acceptable for downstream processes. Natural gas is also the main source for the large scale production of ammonia as well as synthetic fuels and chemicals such as methanol, dimethyl ether (DME) and alkenes.² Methanol and DME are superior fuels for spark ignition (SI) engines and modified compression ignition (CI) diesel engines, respectively. They are also excellent fuels for fuel cells. Direct methanol fuel cells (DMFC) allow the generation of electric power directly from liquid methanol close to room temperature.^{3–5} At the same time, methanol, with a current annual production capacity of 100 million tons, is also the feedstock of choice for varied chemicals and consumer products. Methanol is not only an excellent fuel and solvent

Scheme 1. Varied Syngas Production from Carbon Containing Feedstocks



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but it can also be converted to ethylene and propylene in the so-called methanol to olefin process (MTO)^{6,7} that is practiced on a large scale in the industry. Acidic zeolite catalysts such as SAPO-34 and ZSM-5 are usually used for these dehydrative coupling reactions providing ethylene and propylene with high selectivity. The obtained olefins are mainly utilized in polymerization processes to afford polyethylene and polypropylene or for the synthesis of hydrocarbons and their products. Methanol can also be converted to gasoline, in the methanol to gasoline process (MTG).⁸ Generally, all products that are presently derived from petroleum oil or natural gas can be obtained from methanol. The production and potential of methanol for replacing oil and natural gas in the framework of the "Methanol Economy" was discussed in some of our publications,^{9–12} patents¹³ and extensive monographs by our group and other researchers.^{9,12,14–17} The present comprehensive paper reports the chemistry and significance of the selective, effective oxygenation of methane (natural gas) to methanol.

Syngas with a H₂/CO ratio of about 2 (called metgas) is optimal for the synthesis of methanol.¹⁴ Steam reforming, which is the most commonly used reforming technology for methane, produces syngas with a H₂/CO ratio around 3. Additional steps are therefore required to adjust the H₂/CO ratio to 2/1. Carbon dioxide reforming of methane, also called dry reforming, produces a syngas with a H₂/CO ratio of about 1, which is too low for methanol production and has also to be adjusted.¹⁸ Partial oxidation of methane with oxygen to give a H₂/CO ratio of ≈ 2 is difficult to control. Potentially, it leads to the formation of local hot spots resulting in catalyst deactivation from sintering, which further decreases the selectivity for syngas and makes the process highly exothermic, raising safety concerns.¹⁹ The combination of steam reforming and partial oxidation (autothermal reforming) usually produces a H₂/CO ratio higher than 2.¹

The production of a syngas mixture with a H₂/CO ratio of 2/1 suitable for methanol synthesis in which dry reforming is combined with steam reforming of natural gas in a single step was considered difficult. It was stated in a monograph on syngas chemistry¹ that the one step combination of steam and CO₂ reforming to a 2:1 ratio syngas is even more challenging under elevated pressures. On the basis of our studies, herein we describe a successful single step reforming reaction to achieve this elusive goal, which we have called bi-reforming.^{9,10,15}

In the literature, the overwhelming majority of studies on dry^{18,20} and some combinations of dry and steam reforming^{21–24} and partial oxidation²⁵ have been conducted at atmospheric pressure and with pure methane. Some studies were also carried out under low-temperature plasma conditions and atmospheric pressure, although with only low methane conversions.²⁶ In order to provide conditions closer to practical operations it is, however, preferable to perform experiments under pressure. The advantage of operating bi-reforming under higher pressure is also that the produced metgas could be directly used in the methanol synthesis unit with little or no need for further compression to reach the typical operating pressure of 50 to 100 bar.²⁷ Because of experimental difficulties, reforming studies of methane under pressure and elevated temperature are challenging to carry out compared with those at atmospheric pressure. Only a limited number of studies under such conditions have been reported compared with those at atmospheric pressure. Ni, Co, Pt, Ir, Rh, Pd and Ru based catalysts on various supports such as Al₂O₃, MgO, TiO₂, SiO₂,

ZrO₂ as well as carbides of W, Mo, V, Nb, and Ta have been reported as catalysts for higher pressure dry reforming with CO₂.^{28–38} The combination of dry and steam reforming of CH₄ under pressure was also reported. CeO₂ promoted Ni/MgAl₂O₄ catalyst was tested for this reaction and showed relatively stable activity for 20h at 10 bar.^{39,40} The Chiyoda corporation in Japan recently disclosed a catalyst based on "noble metals," at a conference, which was active for extended periods of time (up to 10000 h) under 19–20 bar pressure⁴¹ under conditions somewhat similar to our reported¹⁰ conditions for methane bi-reforming. Details about the composition of the used catalyst were, however, not discussed. The patent literature indicates that it contains Ru and/or Rh on a basic support⁴² thus essentially different from our catalysts.

After preliminary communications,^{10,11} we herein report results obtained for bi-reforming of pure methane as well as natural gas at pressures of up to 42 bar for extended reaction times excluding noble metal containing catalysts. We also discuss the advantage of oxidative bi-reforming to produce metgas.

■ EXPERIMENTAL SECTION

Chemicals and Gases Used. Nickel nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.999% trace metal basis) and cobalt nitrate hexahydrate (Co(NO₃)₂·6H₂O, 99.999%) were purchased from Aldrich. Magnesium oxide (MgO, 99.5% Mg) was purchased from Strem Chemicals. Methane (UHP), CO₂ (instrument grade), N₂ (prepurified grade), hydrogen (UHP, or any >99%) and natural gas were obtained from Airgas and Gilmore Gas.

Preparation of Catalysts (15-NiO-MgO). 15.00 g of MgO support was mixed with 100 mL methanol. 10.305 g of Ni(NO₃)₂·6H₂O dissolved in methanol was then added to the dispersion and stirred overnight. Subsequently, methanol was removed under reduced pressure on a rotavap and the obtained solid was dried overnight at 120 °C in an oven. The sample was then transferred to a box furnace, heated to 550 °C and maintained at this temperature for 5 h. After cooling, the catalyst was pulverized. The surface area of the obtained catalyst was determined by the BET method giving an area of 54.1 m²/g. The thermogravimetric and XRD analysis of the catalyst, 15-NiO-MgO is shown in Figure S1–S2. The catalysts with a higher and lower NiO content as well as the one based on cobalt oxide were prepared using a similar procedure.

Pressurized Flow Reactor. The reactor for the bi-reforming experiments was designed in collaboration with the Parr Instrument Company and further modified after delivery to our specific requirements. A schematic of this pressurized system (up to 100 bar and 800–1000 °C) is shown in Figure S3–S4. The flow rate of the feed gases are regulated by mass flow controllers (MFC). After a mixing chamber, the gases are sent to the tubular reactor. The reaction occurs in the alumina tube where the catalyst is placed. This is essential to maintain the integrity of the metal parts of the reactor under these harsh conditions (high carbon activity).^{43–44} All the gases exiting at the bottom of the alumina tube are directed to a condenser followed by a gas/liquid separator and a back pressure regulator modulating the reaction pressure in the system. The gas/liquid separator is also connected via a forward pressure regulator to a gas transfer line to a GC for online gas analysis. The entire system is controlled remotely by a process controller connected to a computer.

The arrangement inside the catalytic reactor is shown in Figure 1. All parts, except for the catalyst, in contact with the reactive gases at high temperature are composed of nonporous and very low surface area alumina. The catalyst is held in place by the alumina particles. Alumina particles and spheres are also placed on top of the catalyst to improve the heat exchange with the entering gases before reaching the catalyst. The reaction gases are fed into the reactor directly into the alumina tube. From the side of the alumina tube, a N₂ "blanket" (generally 20 mL min⁻¹) is introduced. Therefore, the hot reactive

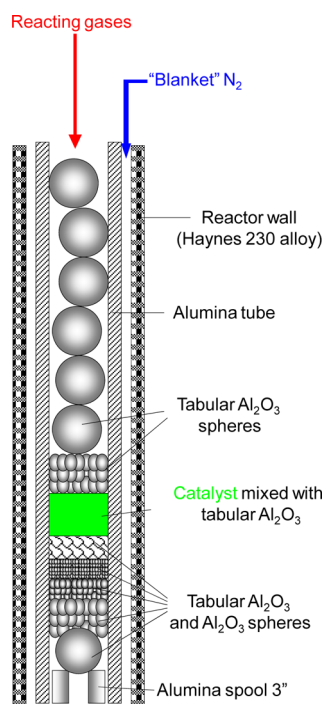


Figure 1. Arrangement of the catalyst and filling material in the tubular reactor.

gases are never in contact with the metallic wall of the reactor, protecting it from possible deterioration due to metal dusting⁴⁵ or carburization.

Initially, the bi-reforming reactions were conducted directly in the metallic tubular reactors (Haynes 230) without protection of any inner parts from the high carbon activity of the reaction gases. After a few reactions under these conditions, the presence of a coke “ring” around the spool holding the catalyst in place was observed (Figure S5–S9). The formation of coke progressively impedes the gas passage resulting in reactor clogging and an increase in pressure. After less than 40 h the reactor was often clogged and severe metal dusting was observed. (Details are given in the Supporting Information.)

The system described is able to operate up to three reactions in parallel using three distinct tubular reactors. The reaction conditions (pressure, temperature, flow rate) can be modulated independently. For example three reactions can be run at different pressures at the same time (see Figure S4 for more details).

Testing of the Catalysts. The results of a blank experiment indicated that no reforming reactions took place in the absence of the catalyst (Figure S10). The catalyst (generally 100 mg) was mixed with 900 mg tabular alumina (60–200 mesh obtained from Almatix, called diluent) and placed on top of tabular alumina in an alumina tube (inner diameter of 0.8 cm) inserted into the metallic tubular reactor with an inner diameter of 1.25 cm. During activation, the catalyst was heated under a hydrogen/nitrogen mixture (1/1) to 850 °C in 1.5 h and kept at this temperature for 3 h. The gas was then switched to nitrogen, set to the desired reaction pressure and temperature. The reaction gas mixture composed of CO₂, CH₄ and N₂ used as a reference was then introduced. Water, necessary for bi-reforming was introduced into the system using a high pressure pump and vaporized to steam in the upper part of the reactor before being mixed with the other feed gases. Downstream of the reactor, the cooled products were analyzed by online GC using a TCD detector (argon was used as a carrier gas): A Varian 450 series GC equipped with a gas handling valve system. Two packed columns were used in series for the gas analysis: a 5 Å molecular sieve column and a Hayesep column.

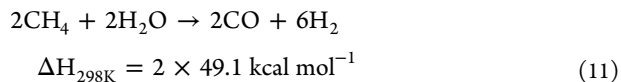
RESULTS AND DISCUSSION

The bi-reforming reactions were conducted in the described pressurized tubular flow reactor system (Figure S3 and S4). Ni deposited on MgO has been used previously as an effective and stable catalyst for the dry reforming reaction.²⁰ The high activity was believed to be the result of the formation of a solid solution. Because of the favorable characteristics of NiO/MgO for dry reforming,^{46–47} this catalyst was selected and found to be active under our conditions for the bi-reforming reaction.

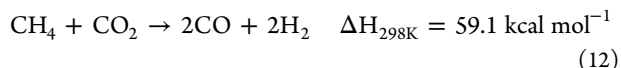
Our studies directed to a new efficient production of methanol led to a successful single step reforming reaction of methane as well as of natural or shale gas to the needed syngas mixture (2H₂+CO), which we have named bi-reforming.^{10,14} The studied catalysts including varied metals such as V, Ti, Ga, Ca, Mo, Bi, Fe, Mn, Co, Nb, Zr, La and Sn and their corresponding oxides were proved efficient on different supports including silica and alumina,¹³ but preferentially NiO deposited on magnesium oxide was found ideal for the bi-reforming reaction.

In bi-reforming, a syngas with an exclusive 2/1 ratio of hydrogen to carbon monoxide is obtained by the reaction of methane, steam and CO₂ in a ratio of 3/2/1 in high yield with no oxidative byproducts. We call the gas mixture with a ratio of H₂/CO of 2/1 as “metgas” to differentiate it from syngas, which is used to describe any gas mixtures of varying H₂/CO ratio. These specific 2/1 H₂/CO gas mixture (metgas) is suitable for the sole purpose of preparing methanol (and its derived materials) with complete utilization of the hydrogen of the gas feed as shown in eq 13.

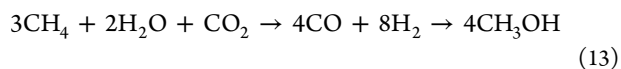
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Dry reforming:

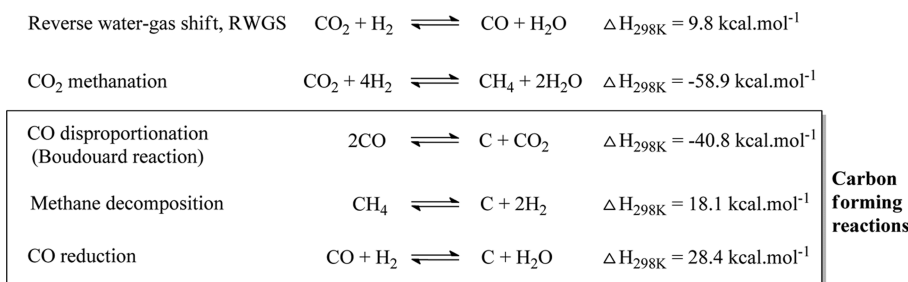


Bi-reforming:



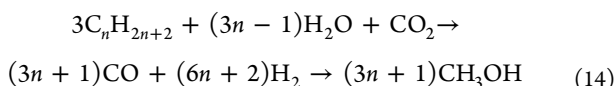
Bi-reforming is also directly applicable to various methane sources such as natural gas, biogas, shale gas or coalbed methane containing varied amounts of CO₂. Some natural gas fields and biogas contain substantial amounts of CO₂ in concentrations up to 50% or even higher.⁴⁸ This CO₂ is, otherwise, separated and vented into the atmosphere (or in some cases captured and stored, CCS) to allow further processing of the natural gas or biogas. CO₂ emissions from diverse sources such as flue gases from various fossil fuel (coal, oil, natural gas, etc.) burning power plants, exhaust of cement factories, other industries, natural sources and eventually from the air⁴⁹ can also be recycled to methanol through bi-reforming.^{49–54} The bi-reforming also helps in recycling of carbon dioxide (carbon capture and recycling, CCR) to synthesize methanol, a valuable fuel and feed-stock. Mechanistic studies showed that the formation of methanol is inhibited from a syngas that is carefully purified from CO₂ and H₂O, indicating that methanol forms most probably via hydrogenation of CO₂.^{55–59} Therefore, the role of CO is to scavenge the oxygen atom from H₂O and serve as a CO₂ source through water gas shift reaction.⁵⁵ Isotope labeling studies have

Scheme 2. Possible Side Reactions of Methane Bi-reforming



also confirmed that CO₂ is indeed the main source of carbon in methanol synthesized from syngas.⁶⁰

Bi-reforming to metgas is readily adaptable for reforming varied natural and shale gas sources, which contain higher (mainly C2–C5) hydrocarbon homologues.



Metgas can also be made from such abundant sources as methane hydrates and biomass. Methane from shale gas deposits, the economic exploitation of which was made recently viable through the implementation of new technologies such as horizontal drilling and rock fracking using high pressure water, sand and chemical additives (hydrofracking) has particularly increased the overall availability of methane. The environmental effects of some of these technologies remains, however, unclear.⁶¹ We recently suggested a CO₂ based dry fracking approach⁶² that eliminates many of the problems associated with hydrofracking.

The combined reactions involved in bi-reforming can also be performed in two separate steps, one for dry reforming and another for steam reforming of natural (shale) gas, combining the two effluent product streams to obtain the needed 2:1 ratio before sending it to the methanol synthesis unit. However, it is of great advantage to be able to combine them into a single step allowing lower capital and operating costs as well as decreased process complexity. The catalyst applied, need to be active at elevated temperature, stable over extended reaction times and should be easily reactivated.

Most side reactions, including CO disproportionation, CO₂ and CO methanation (reverse of steam reforming) and reductive coke (carbon) formation, are favored at lower temperatures and are suppressed under the conditions used (Scheme 2). Methane reforming could be affected by coking involving the deposition of carbon in the form of soot, whiskers or coke on the surface of the catalyst (reducing its activity) as well as on parts of the reformer and downstream equipment, resulting in clogging and deterioration. The amount of carbon formed by CH₄ decomposition and/or CO disproportionation (Boudouard reaction) varies with the reaction conditions and the catalyst used. At higher temperatures (750 °C and above), it is suggested that most of the carbon deposited on the catalyst originates from the CH₄ decomposition reaction.¹

The undesired formation of carbon deposits (coking) can be mostly alleviated by the use of excess steam and short residence times in the reactor.¹ Carbon deposition can also be suppressed through formulation of catalysts that are more resistant to coking.

In a typical experiment the catalyst composed of 15% NiO on MgO (15-NiO-MgO) was first activated at 850 °C under a

H₂/N₂ mixture. (The catalyst is also self-activated under the bi-reforming conditions.) The bi-reforming reactions were initially carried out at atmospheric pressure at 830 °C applying a flow rate of 100 mL/min using a gas feed composition of CH₄/CO₂/H₂O/N₂ with a molar ratio of 3/1.0/2.0/2.25. Nitrogen served as an internal reference and did not participate in the reaction. Although high conversions of CH₄ and CO₂ were achieved (86 and 94.1% respectively, Figure S11) it is not practical due to the relatively low amount of gases that could be reacted in the industrial reformer at atmospheric pressure. In accordance with the Le Chatelier principle, methane conversion decreases as a function of pressure in the bi-reforming reaction. In order to partially compensate for the loss in methane conversion, an excess of CO₂ and H₂O was used. At elevated pressures, the typical reaction was performed using a gas feed composition of CH₄/CO₂/H₂O/N₂ with a molar ratio of 3/1.2/2.4/2.25. Applying an excess of steam is also advantageous because a part of H₂O is converted in water gas shift reaction, which is a typical (side) reaction taking place in reformers. Further, the excess of steam decreases coking and thus helps maintaining the stable performance of the catalyst.

The catalyst (15-NiO-MgO) showed stable activity for the bi-reforming reaction at 830 °C, 7 bar and a flow rate of 100 mL min⁻¹ for the duration of the experiment (320 h) giving a stable CH₄ and CO₂ conversion of 71 and 62%, respectively (Figure 2a). Because of excess CO₂ in the gas feed (CH₄/CO₂ ratio of 3/1.2 instead of 3/1 theoretically), the CO₂ conversion was lower than the CH₄ conversion. The corrected CO₂ conversion based on the theoretical CH₄/CO₂ ratio of 3/1 is however very close to the obtained CH₄ conversion (Figure 2b). The yields of CO and H₂ based on methane conversion were about 71% and remained constant for the duration of the experiment (Figure S12). The calculated selectivity for CO and H₂ were close to 100% (Figure S12) as was the overall carbon balance.

The H₂/CO ratio was close to 2 and remained stable over the reaction period of 320 h (Figure 2c) and the catalyst maintained its activity for the combined steam and CO₂ reforming reactions (bi-reforming) giving a metgas mixture of H₂/CO with a ratio of 2. This is in line with the accepted view that CO₂ reforming on nickel catalyst can be described by the same kinetics as found in steam reforming.^{20,63,64}

Effect of Temperature and Pressure. To study the bi-reforming reaction, the effect of parameters such as temperature, pressure and CH₄/steam/CO₂ ratio were investigated.

When the temperature was increased from 830 to 910 °C, the conversion of both CH₄ and CO₂ increased (Figure 3a). Methane conversion increased by 15% to reach 86% at 910 °C. CO₂ conversion, on the other hand, increased by 17 to 79%. The H₂/CO ratio decreased slightly going from 1.99 to 1.97

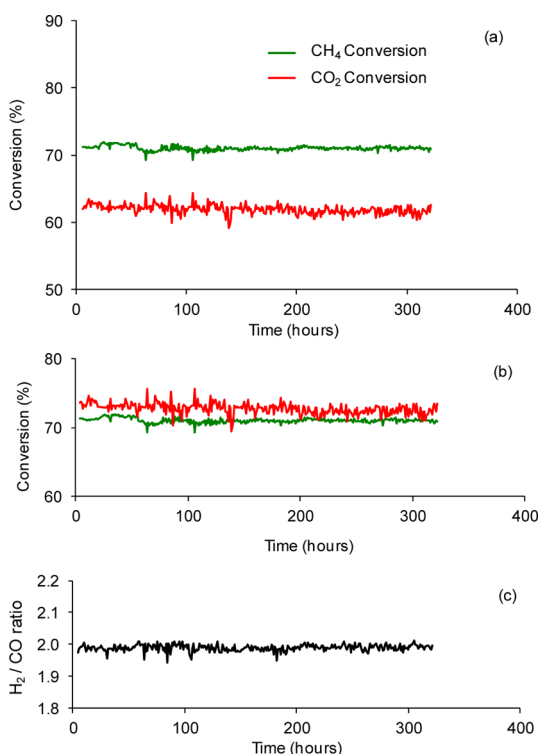


Figure 2. Bi-reforming of methane over 15-NiO-MgO at 7 bar. (a) Raw CH₄ and CO₂ conversion data. (b) CO₂ conversion based on the equivalent amount of CO₂ that can be converted in bi-reforming. (c) H₂/CO ratio.

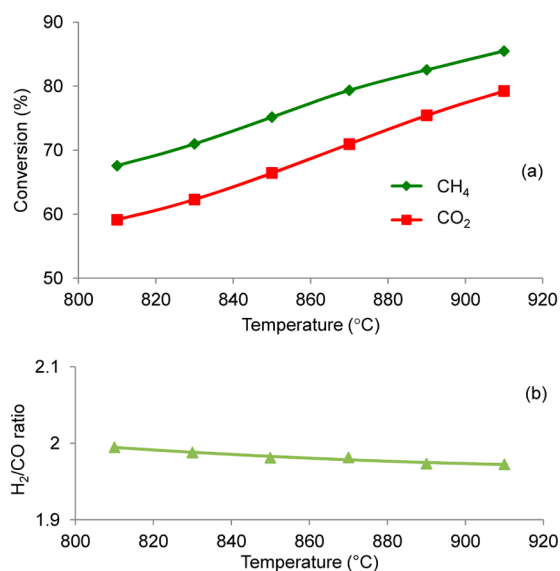


Figure 3. Effect of temperature on the bi-reforming of methane over 15-NiO-MgO catalyst. (a) Methane and CO₂ conversion. (b) H₂/CO ratio.

when the temperature was increased from 830 to 910 °C (Figure 3b). As expected from thermodynamic considerations, the conversion of CH₄ decreased with increasing pressure (Le Chatelier's principle), from 71% at 7 bar to about 42% at 42 bar, as shown in Figure 4a. On the other hand, the H₂/CO ratio increased slightly from 1.99 to 2.03 when the pressure was increased from 7 to 42 bar (Figure 4b). Doubling the amount of water and CO₂ (CH₄/CO₂/H₂O with a molar ratio of 3/2.4/

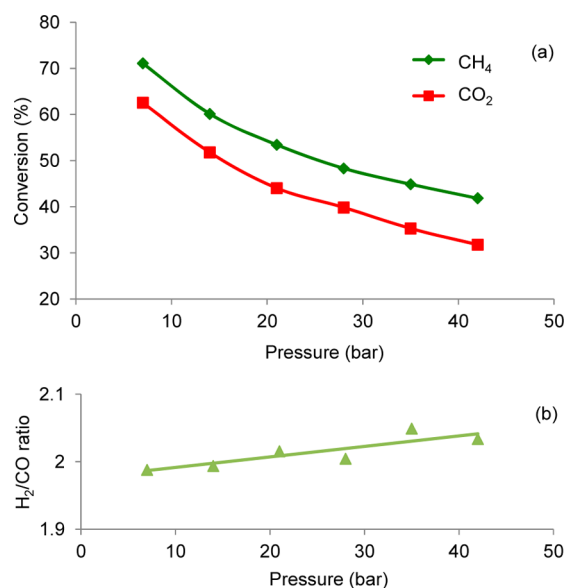


Figure 4. Effect of pressure on the bi-reforming of methane over 15-NiO-MgO catalyst. (a) Methane and CO₂ conversion. (b) H₂/CO ratio.

4.8) at 7 bar substantially increased the CH₄ conversion from 71 to 85%. At the same time, the desirable H₂/CO ratio stayed at ≈ 2 . It should also be added here that although the coke formation did not result in continuous deterioration of the catalytic activity even at lower CH₄ to H₂O ratio (3.0/2.4), doubling the amount of steam (CH₄/H₂O of 3.0/4.8) further decreased coking from 2.35 to 0.47 weight% of the catalyst and diluent material. Carbon content of the used catalysts was determined by thermogravimetric analysis by gradually heating the sample to 800 °C in a flow of air (30 mL min⁻¹) and monitoring the weight loss.

Effect of Gas Hourly Space Velocity (GHSV). In order to study the activity of the catalyst, the ratio between the amount of feed gas entering the reactor and the amount of catalyst was varied (variation of gas hourly space velocity). Reforming reactions being endothermic, increasing the gas flow would progressively reduce the temperature over the catalyst bed. The temperature profile of the reactor during a bi-reforming reaction over 15-NiO-MgO showed that with a gas flow rate of 100 mL min⁻¹ (GHSV of 6×10^4 mL h⁻¹ g⁻¹), the temperature decreased to a minimum of about 800 °C (Figure S13). When the flow was doubled to 200 mL min⁻¹ (GHSV of 12×10^4 mL h⁻¹ g⁻¹), the temperature decreased further with an apex at about 782 °C. On the other hand, by varying the catalyst amount and keeping the flow rate at 100 mL min⁻¹, the temperature decrease is relatively similar as long as the activity of the catalyst is maintained.

Accordingly, the gas hourly space velocity (GHSV) was increased 10-fold from 6×10^4 to 6×10^5 mL h⁻¹ g⁻¹ by decreasing the amount of catalyst used from 0.1 to 0.01 g but keeping the same gas feed and flow rate. Compared to the reaction with a GHSV of 6×10^4 mL h⁻¹ g⁻¹, methane conversion practically did not change and remained stable for more than 170 h (Figure 5). Carbon dioxide conversion also remained similar to the one observed with a lower GHSV whereas the H₂/CO ratio decreased to about 1.95–1.97. On the other hand, increasing the amount of catalyst to 1g to obtain a GHSV of 6×10^3 mL h⁻¹ g⁻¹ resulted in a somewhat

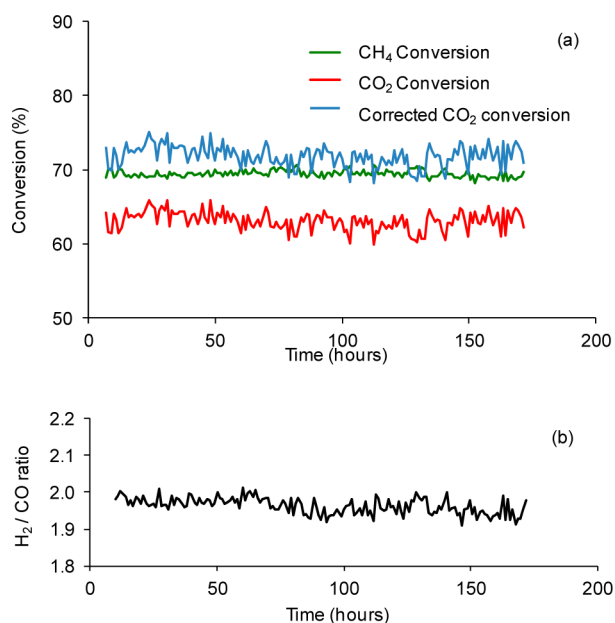


Figure 5. Bi-reforming of methane over 15-NiO-MgO catalyst at 7 bar. GHSV of 6×10^5 mL h⁻¹ g⁻¹ catalyst. (a) Raw CH₄ and CO₂ conversion data as well as corrected CO₂ conversion. (b) H₂/CO ratio.

higher methane conversion of 77% and a H₂/CO ratio close to 2 (Figure S14).

It can be concluded that even with 10 or 100 times higher GHSVs, the catalyst still remains highly active for the bi-reforming reaction.

Effect of NiO Loading of the NiO/MgO Catalyst.

Although nickel is a more cost-effective metal than noble metals, the nickel loading of the applied catalyst still affects its final cost for a given process. Varying nickel loading from 5 to 35% NiO on MgO had only a minimal effect on the bi-reforming reaction at 7 bar (Figure S15). Methane conversion was stable in all cases at around 70–72%. It can be concluded that increasing the NiO loading from 5 to 35% did not result in higher activity or selectivity under the present conditions.

Bi-reforming of Natural Gas. In order to study conditions adaptable to practical application, the 15-NiO-MgO catalyst was also tested under pressure for the bi-reforming of natural gas. While containing predominantly methane, the natural gas mixture used for these experiments contained also ethane, propane, butane as well as higher hydrocarbons (please see Table S3 for more details about the composition). No hydrocarbons other than methane were detected in the gaseous products, indicating that all higher hydrocarbons were also converted on the metallic sites of the catalyst to metgas and some methane.¹ They could also contribute to form some carbonaceous deposits. From Figure 6a, it can be seen that at 7 bar, an essentially stable CO₂ and natural gas conversion was observed for the duration of the experiment (160 h). Natural gas (mainly methane) and CO₂ conversions were about 70 and 67%, respectively.

As observed in the case of pure methane, natural gas and carbon dioxide conversion decreased with increasing pressure. From ≈70% at 7 bar, natural gas conversion decreased to 61% at 14 bar, 55% at 21 bar and 51% at 28 bar (Figure S16). The catalyst showed, however, no noticeable decline in its activity over time depending on the pressure.

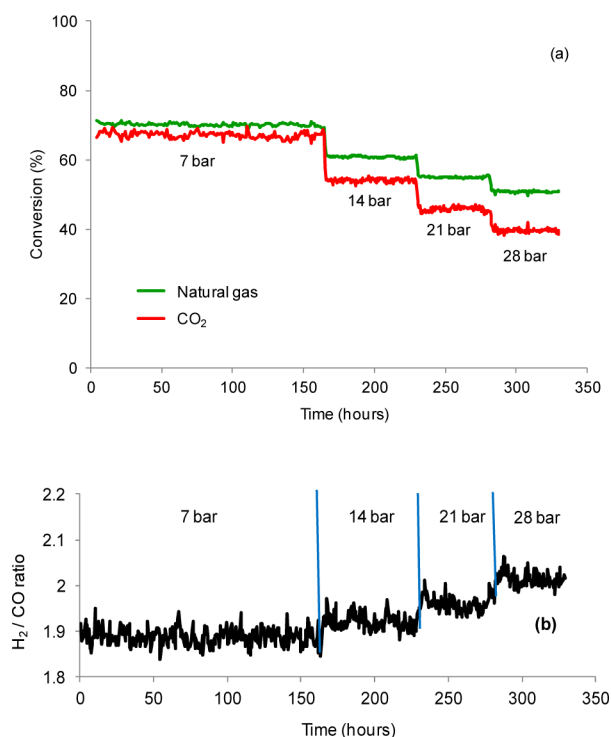


Figure 6. Bi-reforming of natural gas over 15-NiO-MgO catalyst from 7 to 28 bar. (a) Raw CH₄ and CO₂ conversion data. (b) H₂/CO ratio.

The H₂/CO ratio did only slightly increase with increasing pressure from about 1.90 at 7 bar to 1.92 at 14 bar, 1.96 at 21 bar and 2.01 at 28 bar (Figure 6b) indicating that the increase in pressure seemed to actually have a positive effect on the H₂/CO ratio. A similar trend, although less pronounced, was also observed when using pure methane instead of natural gas (vide supra). This observation correlates with the lower relative conversion of CO₂ with increasing pressure and could indicate that at higher pressure, the steam reforming reaction is somewhat favored compared to the dry reforming reaction. In the water gas shift (WGS) reaction, the mole number remains unchanged. Therefore, the equilibrium composition should not be affected by the pressure. However, in the case of lower conversion, more water is present in the gas mixture, which could possibly favor the WGS reaction leading to higher hydrogen content in the products.

At 7 bar, the H₂/CO ratio remained stable for more than 160 h at around 1.9 (Figure 6b). The somewhat lower H₂/CO ratio compared to the reaction with pure methane is in line with the presence of higher hydrocarbons exhibiting a lower hydrogen/carbon (H/C) ratio. As the alkane chain length increases, the H/C ratio is getting closer to 2. Whereas methane has the highest possible H/C ratio of 4, ethane, propane and butane have a decreasing H/C ratio of 3, 2.7 and 2.5, respectively. When the ratio of water and CO₂ compared to the hydrocarbon feed is kept identical, this leads to a lower H₂/CO ratio. However, when the amount of water in the gas feed is increased, a H₂/CO ratio of 2 according to eq 14, should be relatively easily achievable and this was indeed observed when the water flow rate was increased by approximately 10%.

When NiO/MgO with a NiO content of 35% was tested for the bi-reforming of natural gas at 100 psi with a slightly higher water flow rate, stable activity was observed for more than 240 h. The natural gas conversion was almost constant at about

72% (Figure S17) and a H_2/CO ratio around 2 was obtained, which remained stable for the duration of the experiment (240 h, Figure 7). Using the same catalyst, the conversion of natural

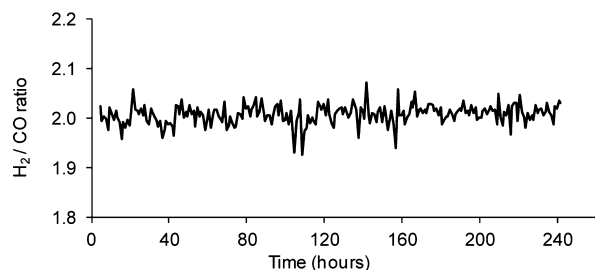


Figure 7. H_2/CO ratio of bi-reforming of natural gas over 35-NiO-MgO with higher flow rate of water at 7 bar.

gas was similar to the conversion of pure methane (see Figure S17). The H_2/CO ratio was also similar. The conversion of CO_2 , however, was slightly lower (57%) than in the case of methane (63%). A lower conversion of CO_2 is to be expected from the reaction of CO_2 with natural gas, which contains beside methane also higher alkanes. Regardless of the alkane, only one mole of CO_2 for three moles of alkane is required to obtain a H_2/CO ratio of 2 according to eq 14. *Only the amount of water has to be increased with higher alkanes to achieve a H_2/CO ratio of 2.* By modulating the ratio of steam and CO_2 compared to the alkane mixture in the gas feed, the H_2/CO ratio could therefore be easily adjusted to the desired one, indicating that the method can be adapted to natural gas resources with various hydrocarbon compositions and CO_2 content.

Effect of a Higher GHSV over 35-NiO-MgO Catalyst.

Keeping the same flow rate (100 mL min^{-1}) and ratio of $CO_2/CH_4/H_2O$ but decreasing the amount of catalyst (35-NiO-MgO) 5-fold, the GHSV effectively increased 5-fold from 6×10^4 to $3 \times 10^5 \text{ mL h}^{-1} \text{ g}^{-1}$. At this higher GHSV, the conversion of natural gas was stable at about 70% over the duration of the experiment (Figure S18a). The natural gas conversion was only slightly lower than the one observed at a higher catalyst loading. The CO_2 conversion also decreased only slightly from 57 to 55% at a higher GHSV. On the other hand, the H_2/CO ratio increased somewhat to 2.03 from 2.00 compared to the reaction with a lower GHSV (Figure S18b).

Similar to the results obtained with pure methane, a lower catalyst loading did not result in a significant lowering of activity or selectivity in the conversion of natural gas.

Bi-reforming over CoO/MgO Catalyst. We also studied the use of CoO catalyst instead of NiO on MgO. Cobalt has often been studied previously for reforming reactions.⁶⁵ The behavior of cobalt on basic supports (MgO, CaO, SrO and BaO) in the dry reforming reaction was described by Ruckenstein et al.^{66–68} Among these basic supports, only

MgO displayed a high and stable activity.⁶⁸ Accordingly, we performed the reaction of bi-reforming on a catalyst based on cobalt supported on MgO prepared in the same way as the one containing nickel. The catalyst contained 15% CoO on MgO and was consequently named 15-CoO-MgO. In the bi-reforming of methane, this catalyst had a relatively stable activity for the duration of the reaction ($\approx 100 \text{ h}$, Figure S19a). The conversion of methane (71%) was comparable to the one obtained with the catalyst containing the same nickel oxide loading, but the conversion of CO_2 on the other hand was higher, about 66% compared to 62% on 15-NiO-MgO, resulting in a lower H_2/CO ratio of about 1.93. The use of natural gas instead of pure methane had a detrimental effect on 15-CoO-MgO, with initial natural gas and CO_2 conversion lower than in the equivalent reaction with 15-NiO-MgO (Figure S19b). Furthermore, the activity of the catalyst decreased progressively during the reaction to end at about 63% CH_4 conversion and 56% CO_2 conversion after 100 h on stream. The cobalt-based catalyst seems therefore to suffer from some deactivation, which was not observed in the case of nickel. On the other hand, even as the conversions of both methane and CO_2 decreased, the H_2/CO ratio remained relatively stable at around 1.95 (Figure S19c). Although the H_2/CO ratio remained stable and the natural gas conversion increased from 64% at $830 \text{ }^\circ\text{C}$ to 77% at $870 \text{ }^\circ\text{C}$ and 82% at $890 \text{ }^\circ\text{C}$, the deactivation pattern of 15-CoO-MgO is a major drawback for prolonged operation.

Self-Sufficient Oxidative Bi-reforming of Methane or Natural Gas.

Similar to steam and dry reforming, bi-reforming is an endothermic reaction which requires heat input. While it is possible to heat the reaction via any external heat, it is advantageous to have a self-sufficient way to supply the heat required for the bi-reforming reaction. This is achieved by initial complete combustion of one-quarter of overall methane or natural gas used with oxygen. Besides heat, it also produces a 2:1 ratio of H_2O/CO_2 (Figure 8) needed for the bi-reforming reaction. The gaseous 2:1 H_2O/CO_2 feed from the complete combustion reaction is then mixed with three equivalents of fresh methane to perform the bi-reforming reaction and obtain metgas for subsequent methanol synthesis.⁶⁹ Besides providing the 2:1 ratio H_2O/CO_2 mixture, the burning of methane also provides the energy required for the subsequent endothermic bi-reforming reaction. We name this reaction, *oxidative bi-reforming*.¹¹ The overall process is self-sufficient and converts methane or natural gas exclusively to metgas for subsequent methanol synthesis without any byproducts.

Significance of Exclusive and Effective Oxygenation of Methane or Natural Gas to Methanol.

In studies in the late 1970s, Olah et al. discovered that if methane was reacted with hydrogen peroxide in a superacidic media, the methyloxonium ion is formed selectively without further oxidation products (eq 15). The reason is that the insertion

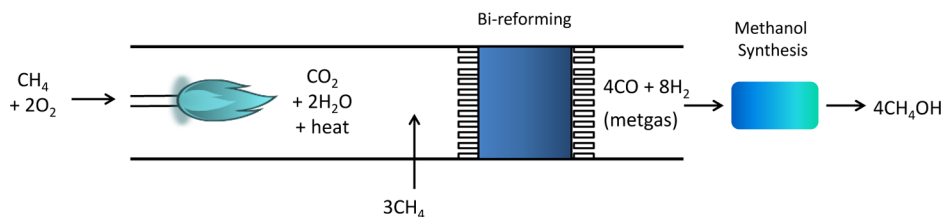
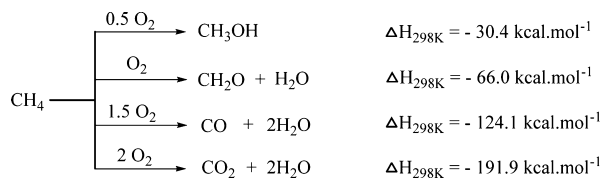


Figure 8. Oxidative bi-reforming.

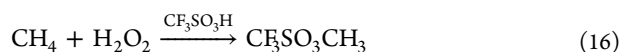
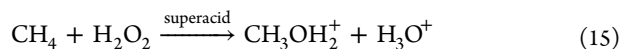
Scheme 3. Methane Oxidation Products



of incipient “+OH” derived from H₃O₂⁺ (protonated hydrogen peroxide) into a methane C–H bond via electrophilic oxygenation results in methanol in its protonated form, CH₃OH₂⁺, protecting it from thermodynamically favored further oxidation and accounting for the observed high selectivity.^{70,71} Using hydrogen peroxide in superacids is, however, not suited for practical applications.

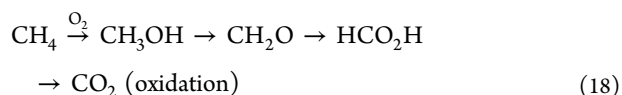
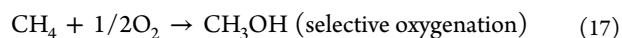
When triflic acid was used as a superacid, methyl triflate was formed, protecting methanol from further oxidation. This reaction with subsequent hydrolysis is applicable to smaller scale laboratory preparation of methanol (eq 16).

Periana, Taube et al. subsequently developed, a method, wherein the oxidation of methane takes place in concentrated sulfuric acid or oleum with Hg and Pt-based catalysts forming methyl hydrogen sulfate. The obtained methyl hydrogen sulfate is also not prone to further oxidation and can be subsequently hydrolyzed to methanol.^{72–75} However, the use of sulfuric acid or oleum and related high cost of the process make it impractical.



Given the fundamental difficulty mentioned in direct selective oxidation of methane to methanol, the combination of bi-reforming or oxidative bi-reforming of methane or natural gas to metgas for subsequent methanol synthesis is a new, highly efficient and economical way to achieve the long sought after efficient exclusive conversion of methane to methanol.

The described oxidative bi-reforming of methane with subsequent conversion of metgas to methanol is essentially a complete exclusive oxygenation of methane or natural gas to methanol. The pathway shown in Figure 8 represents the efficient oxygenation of methane with insertion of a single oxygen atom exclusively to methanol in contrast to any oxidation of methane (Eqs. 17, 18). It thus differs fundamentally from the previously much studied partial oxidation of methane, which inevitable proceeds to the more thermodynamically favored oxidation byproducts from formaldehyde to formic acid and CO and finally carbon dioxide, the fully oxidized product of methane (Scheme 3).



Direct selective oxidation of methane, despite extensive studies, is only able to produce methanol in extremely low yield (generally 1–3%). Attempts to increase yields while keeping high selectivity were unsuccessful, preventing any practical scale application.^{76–80} In the forgoings, we have thus achieved via oxidative bi-reforming of methane (or natural gas) an efficient and selective production of metgas for exclusive methanol synthesis in high yields without further oxidation side-products. The overall reaction is thus exclusive oxygenation of methane to methanol (Scheme 4).

CONCLUSIONS

We have shown that NiO/MgO and related catalysts are active in a pressurized tubular flow reactor at 7–42 bar and 830–910 °C for bi-reforming to convert methane or natural gas in a single step exclusively to metgas, a mixture of hydrogen and carbon monoxide with a specific H₂/CO ratio of 2/1 for subsequent widely practiced methanol synthesis. Furthermore, the direct conversion of methane (natural gas) is made self-sufficient by combustion of one-quarter of used methane (or natural gas) produces not only the needed reaction heat but also the necessary 2H₂O/CO₂ mixture for the bi-reforming reaction.

A long elusive but never reached goal of hydrocarbon chemistry for the effective selective oxygenation of methane (natural gas) with oxygen of the air, to methanol without any oxidation byproducts favored by thermodynamics was thus achieved. The reported bi-reforming allows the captured CO₂ of coal burning power plants, and cement plants and other industries to be recycled (CCR) instead of just sequestered (CCS). It thus can render CO₂ producing industries to continue their essential contribution to our life in an economic and environmentally favorable way while safeguarding the environment.

ASSOCIATED CONTENT

Supporting Information

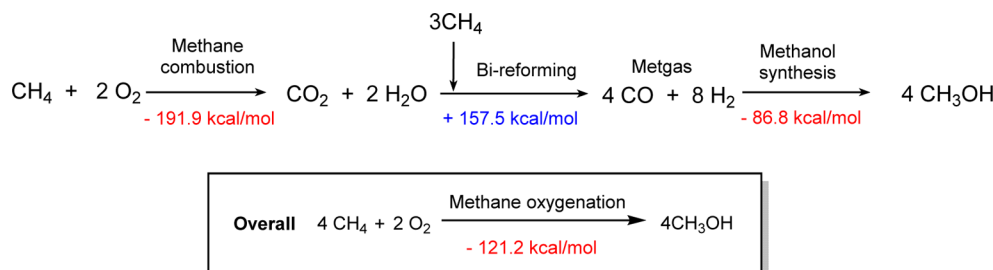
Additional experimental details. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b02029.

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Scheme 4. Oxidative Bi-reforming of Methane to Metgas for Methanol Synthesis



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Notes

The authors declare no competing financial interest.

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