Bi-reforming of Methane from Any Source with Steam and Carbon Dioxide Exclusively to Metgas (CO−2H$_2$) for Methanol and Hydrocarbon Synthesis

George A. Olah,* Alain Goeppert, Miklos Czaun, and G. K. Surya Prakash

Loker Hydrocarbon Research Institute and Department of Chemistry, University of Southern California, University Park, Los Angeles, California 90089-1661, United States
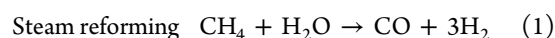
ⓈSupporting Information

ABSTRACT: A catalyst based on nickel oxide on magnesium oxide (NiO/MgO) thermally activated under hydrogen is effective for the bi-reforming with steam and CO_2 (combined steam and dry reforming) of methane as well as natural gas in a tubular flow reactor at elevated pressures (5−30 atm) and temperatures (800−950 °C). By adjusting the CO_2-to-steam ratio in the gas feed, the H_2/CO ratio in the produced syn-gas could be easily adjusted in a single step to the desired value of 2 for methanol and hydrocarbon synthesis.

Synthesis gas (syn-gas), a variable composition mixture of hydrogen and carbon monoxide (with some carbon dioxide), is the basis of Fischer−Tropsch chemistry. Syn-gas is produced by partial oxidation with steam and oxygen from virtually any carbon source, including biomass.[1] However, natural (shale) gas and methane are generally the preferred feedstocks. These are also the source for the large-scale production of synthetic fuels and chemicals including methanol, dimethyl ether, and varied hydrocarbons and their products.[2]
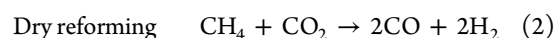
Methanol and its derivatives are becoming increasingly significant fuels and starting materials for varied chemical products. We have discussed methanol's potential role and relevant chemistry that was developed in the framework of the "Methanol Economy" in a series of publications, patents, and a monograph.[3−7] The current production of methanol is based on syn-gas following a process first developed by Mittasch et al. in 1923 and further improved over the years by companies including BASF and ICI.[8] What is needed, however, for a wider use of methanol are more efficient and economic ways of preparation.

The synthesis of methanol from syn-gas requires a H_2/CO ratio of about 2.[3] The most commonly used reforming technology for methane, steam reforming, produces a syn-gas mixture with a H_2/CO ratio close to 3 (eq 1). This means that additional steps are needed to adjust the H_2/CO ratio. Carbon dioxide reforming of methane, called dry reforming, produces a syn-gas with a H_2/CO ratio close to 1 (eq 2), which is too low and has also to be adjusted.[9] Partial oxidation of methane with oxygen can produce a H_2/CO ratio of 2, but is difficult to control and can lead to local hot spots and associated dangers of explosions (eq 3).[10] The combination of steam reforming and partial oxidation (autothermal reforming) as practiced industrially produces the H_2/CO ratio of 2 by further
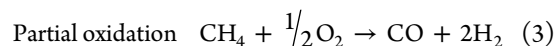
separation and adjustment steps, which makes the overall process complex and more expensive.

$$\text{Steam reforming} \quad CH_4 + H_2O \rightarrow CO + 3H_2 \quad (1)$$
$$\Delta H_{298K} = 49.1 \text{ kcal·mol}^{-1}$$

$$\text{Dry reforming} \quad CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad (2)$$
$$\Delta H_{298K} = 59 \text{ kcal·mol}^{-1}$$

$$\text{Partial oxidation} \quad CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \quad (3)$$
$$\Delta H_{298K} = -8.6 \text{ kcal·mol}^{-1}$$

We now report the exclusive preparation of a syn-gas mixture of a 2/1 H_2/CO ratio suitable for methanol synthesis in which dry and steam reforming are combined in a single step, called *bi-reforming*.[4−7] In bi-reforming, a specific ratio of methane, steam, and CO_2 of 3/2/1 produces a gas mixture with essentially a 2/1 ratio of hydrogen to carbon monoxide, which was suggested to be called "metgas" to underline its difference from the widely used syn-gas mixtures of varying H_2/CO ratio. This specific 2/1 H_2/CO gas mixture is for the preparation of methanol and subsequently derived hydrocarbon products, with complete utilization of all the hydrogen (eq 4).

$$\text{Steam reforming} \quad 2CH_4 + 2H_2O \rightarrow 2CO + 6H_2$$
$$\text{Dry reforming} \quad CH_4 + CO_2 \rightarrow 2CO + 2H_2$$
$$\text{Bi-reforming} \quad 3CH_4 + 2H_2O + CO_2 \xrightarrow{\text{Ni/MgO}}$$
$$4CO + 8H_2 \xrightarrow[\text{synthesis}]{\text{methanol}} 4CH_3OH \quad (4)$$
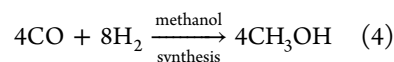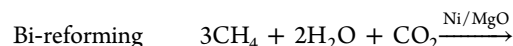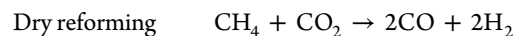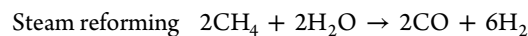
The feed is purified when needed before being introduced into the reforming vessel to remove impurities, mainly H_2S and SO_2, which would poison the Cu-based catalyst in the subsequent methanol synthesis step. The needed heat for the bi-reforming process can be provided by any external energy source (conventional or alternative energy sources including hydro, solar, wind, etc. as well as atomic energy).

Bi-reforming to produce metgas is also advantageous in the use of varied natural gas sources even containing significant amounts of CO_2. Some natural gas as well as biogas sources

---

contain CO_2 concentration up to 50−70%. Bi-reforming can also be used to recycle CO_2 emissions from sources such as flue gases from fossil fuel (coal, petroleum, natural gas, etc.)-burning power plants, exhaust of cement factories, and varied industries.

Bi-reforming to metgas is also adaptable for reforming shale gas. Dry shale gas is essentially methane (>98%). Wet shale gas also contains ethane, propane (which can be dehydrogenated to ethylene and propylene), and some higher hydrocarbon homologues (eq 5).

$$3C_nH_{(2n+2)} + (3n − 1)H_2O + CO_2 \rightarrow$$

$$(3n + 1)CO + (6n + 2)H_2 \rightarrow (3n + 1)CH_3OH \quad (5)$$
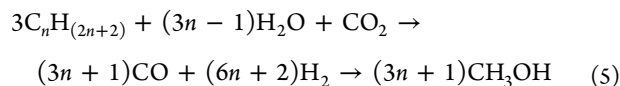
Metgas can also be obtained from other natural carbon sources including coalbed methane and methane hydrates as well as biomass. Recent findings of significant shale gas (methane) deposits considerably increased the overall reserves of natural gas. Shale gas production is made possible by horizontal drilling and rock fracking using high-pressure water, chemical additives, and sand. The environmental consequences of these techniques are still under debate.[11]

Preferentially, bi-reforming is carried out under 5−30 atm of pressure and 830-950 °C temperature, producing metgas, which can be directly used in the methanol synthesis.[12] Most of the reported studies on dry and combinations of dry[9,13] and steam[14−17] reforming have been conducted at atmospheric pressure and mostly with pure methane. In order to approach conditions closer to practical applications, we studied bi-reforming of methane as well as of natural gas at pressures up to 30 atm.[6,7] The reactions were conducted in a tubular flow reactor system built specially for this purpose and suitable to withstand pressures up to 100 atm and needed temperatures of 800−1000 °C provided by external heating. All the surfaces in contact with the catalyst and reacting gases at the high temperatures were made of alumina to avoid any side reactions or possible deterioration of the reactor materials. Quartz, which is often used in reforming studies at atmospheric pressure, was inadequate, leading to coke formation and eventually reactor clogging. The preferred catalyst used was based on NiO deposited on magnesium oxide, i.e., NiO/MgO, which was active and stable over extended continuous durations (320 h), as are related supported metal oxides. The NiO content in NiO/MgO can be between 5 and 35%. A gas feed composition of $CH_4/CO_2/H_2O$ with a molar ratio of 3/1.2/2.4 was typically used with nitrogen as an internal reference. Ni deposited on MgO had been previously shown to be an effective and stable catalyst for dry reforming reaction.[13]

Reforming is frequently affected by coking, involving the deposition of carbon in the form of soot or coke on the catalyst (reducing strongly its activity), as well as parts of the equipment. Carbon may be formed by both CH_4 (natural gas) decomposition and CO disproportionation (Boudouard reaction). The relative contributions depend on the reaction conditions and catalyst used. The undesired formation of carbon is, however, largely prevented by the presence of steam and short residence times in the flow reactor.

As an example, after activation at 850 °C under hydrogen, a catalyst composed of 15% NiO on MgO (15-NiO-MgO) showed a stable activity in a typical bi-reforming reaction at 830 °C and 7 atm for the duration of continuous experiment up to 320 h (Figure 1). The H_2/CO ratio remained essentially 2 and also remained stable over the reaction time. Under the studied
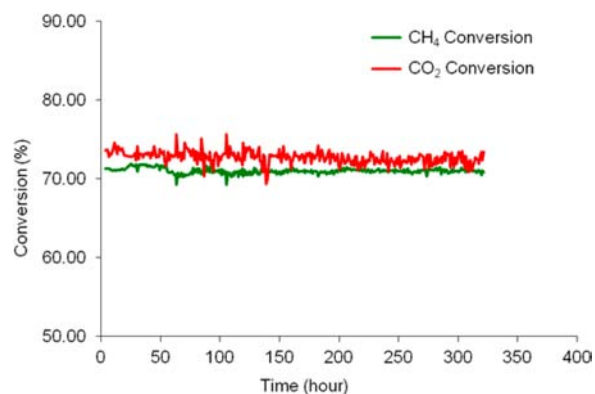
Figure 1. Single pass CH_4 and CO_2 conversion in bi-reforming of methane over 15-NiO-MgO catalyst at 7 atm and 830 °C: 100 mL·min^{-1} of $CH_4/CO_2/H_2O$ with a molar ratio of 3/1.2/2.4 and GHSV of 6×10^4 mL·h^{-1}·g^{-1} catalyst.

conditions, the catalytic system is able to perform both dry and steam reforming simultaneously with ease. This indicates that steam and CO_2 reforming on nickel catalyst involve similar kinetics.[1,13,18,19] The selectivity for CO and H_2 were 100% and 98%, respectively. When the temperature was increased from 830 to 910 °C, the conversion of both methane and CO_2 increased. Methane conversion increased about 15% to reach 86% at 910 °C. The H_2/CO ratio decreased only very slightly from 1.99 to 1.97. As expected, however, from the thermodynamics of endothermic reactions, with an increase in number of moles (Le Chatelier's principle), the conversion of methane decreased with increasing pressure (from 71% at 7 atm to about 52% at 28 atm). On the other hand, the H_2/CO ratio increased slightly from 1.99 to 2.02 when the pressure was increased from 7 to 28 atm. Doubling the amount of steam and CO_2 ($CH_4/CO_2/H_2O$ with a molar ratio of 3/2.4/4.8) at 7 atm increased the methane conversion from 71% to 85%. The experiments were carried out in a single pass mode, but the unreacted feed gases can be recycled to improve the overall conversion.

When the gas hourly space velocity (GHSV) was increased 10-fold to 6×10^5 mL·min^{-1}·g^{-1}, methane conversion decreased only by about 2% but remained stable. CO_2 conversion also slightly decreased, as did the H_2/CO ratio to about 1.95−1.97.

The same 15-NiO-MgO catalyst was also tested under the studied pressures for the bi-reforming of natural gas (composed of methane containing ethane, propane, butane, and higher hydrocarbons). No hydrocarbons other than unreacted methane were detected in the products, indicating that all higher hydrocarbons had reacted. At 7 atm, again stable CO_2 and CH_4 conversion was observed for the duration of the experiment (160 h). The conversion of natural gas was about 70%, and the H_2/CO ratio remained stable at around 1.9. This somewhat lower H_2/CO ratio compared to the reaction with pure methane is consistent with the presence of higher hydrocarbons having a lower H/C ratio. The H/C ratio will get closer to 2 as the alkane chain length increases. Whereas methane has a H/C ratio of 4, ethane, propane, and butane have a H/C ratio of 3, 2.7, and 2.5, respectively. Keeping the same ratio of steam and CO_2 to the hydrocarbon feed results in a lower H_2/CO ratio. However, when the amount of steam in the gas feed was increased by 10%, a constant H_2/CO ratio of 2 was obtained. The H_2/CO ratio can therefore be easily

modulated by adjusting the ratio of steam and CO_2 in the gas feed.

The activated NiO/MgO catalyst was thus shown to be equally active for the bi-reforming of pure methane and natural gas or other sources. The conversion of methane as well as carbon dioxide was constant for extended periods of time in the pressurized (5–30 atm) flow reactor at temperatures of 800–950 °C. The reaction of CH_4/natural gas and CO_2 conversion decreased with increasing pressure. This effect can, however, be in part countered by increasing the amount of steam and CO_2 in the gas feed and increasing the reaction temperature. The H_2/CO ratio can be successfully and easily adjusted to the desired value of 2 ideal for methanol synthesis by adjusting the CO_2 to steam ratio in the gas feed.

In conclusion, the reported bi-reforming effectively converts methane and its natural sources (natural or shale gas, coal-bed methane, methane hydrates) to metgas, a 2/1 H_2/CO mixture directly applicable for subsequent well-studied methanol synthesis with high selectivity. A typical single pass conversion at 7 atm is about 70–75%, which can be increased to 80–85% by adjusting the feed gas composition. Unreacted feed gases can be readily recycled. The efficient conversion of methane and its varied sources to methanol via metgas can also be utilized for subsequent synthesis of varied hydrocarbons and their products through zeolite-based chemistry[12] or over various bi-functional acidic–basic catalytic routes[20] giving alkenes (mainly ethylene and propylene) and their derived products, replacing petroleum oil as the source material.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information
Experimental details and procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author
olah@usc.edu

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ REFERENCES

(1) Rostrup-Nielsen, J.; Christiansen, L. J. *Concepts in Syngas Manufacture*; Imperial College Press: London, 2011.

(2) Arpe, H.-J. *Industrial Organic Chemistry*, 5th ed.; Wiley-VCH: Weinheim, 2010.

(3) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *Beyond Oil and Gas: The Methanol Economy*, 2nd ed.; Wiley-VCH: Weinheim, 2009.

(4) Olah, G. A.; Goeppert, A.; Prakash, G. K. S. *J. Org. Chem.* **2009**, *74*, 487.

(5) Olah, G. A.; Prakash, G. K. S.; Goeppert, A. *J. Am. Chem. Soc.* **2011**, *133*, 12881.

(6) Olah, G. A.; Prakash, G. K. S. U.S. Patent 7,906,559, 2011.

(7) Olah, G. A.; Prakash, G. K. S. U.S. Patent 8,133,926, 2012.

(8) Weissermel, K.; Arpe, H.-J. *Industrial Organic Chemistry*, 4th ed.; Wiley-VCH: Weinheim, 2003.

(9) Fan, M.-S.; Abdullah, A. Z.; Bhatia, S. *ChemCatChem* **2009**, *1*, 192.

(10) Choudhary, T. V.; Choudhary, V. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 1828.

(11) Kerr, R. A. *Science* **2010**, *328*, 1624.

(12) *Methanol Production and Use*; Cheng, W.-H., Kung, H. H., Eds.; Marcel Dekker: New York, 1994.

(13) Bradford, M. C. J.; Vannice, M. A. *Catal. Rev.-Sci. Eng.* **1999**, *41*, 1.

(14) Roh, H.-S.; Koo, K. Y.; Jeong, J. H.; Seo, Y. T.; Seo, D. J.; Seo, Y.-S.; Yoon, W. L.; Park, S. B. *Catal. Lett.* **2007**, *117*, 85.

(15) Roh, H.-S.; Koo, K. Y.; Joshi, U. D.; Yoon, W. L. *Catal. Lett.* **2008**, *125*, 283.

(16) Koo, K. Y.; Roh, H.-S.; Jung, U. H.; Yoon, W. L. *Catal. Lett.* **2009**, *130*, 217.

(17) Koo, K. Y.; Roh, H.-S.; Seo, Y. T.; Seo, D. J.; Yoon, W. L.; Park, S. B. *Int. J. Hydrogen Energ.* **2008**, *33*, 2036.

(18) Wei, J.; Iglesia, E. *J. Catal.* **2004**, *224*, 370.

(19) Rostrup-Nielsen, J. R.; Bak Hansen, J.-H. *J. Catal.* **1993**, *144*, 38.

(20) Olah, G. A.; Doggweiler, H.; Felberg, J. D.; Frohlich, S.; Grdina, M. J.; Karpeles, R.; Keumi, T.; Inaba, S.-I.; Ip, W. M.; Lammertsma, K.; Salem, G.; Tabor, D. C. *J. Am. Chem. Soc.* **1984**, *106*, 2143.