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Self-Sufficient and Exclusive Oxygenation of Methane and Its Source Materials with Oxygen to Methanol via Metgas Using Oxidative Bi-reforming

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ABSTRACT: A combination of complete methane combustion with oxygen of the air coupled with *bi-reforming* leads to the production of metgas (H_2/CO in 2:1 mole ratio) for exclusive methanol synthesis. The newly developed *oxidative bi-reforming* allows direct oxygenation of methane to methanol in an overall economic and energetically efficient process, leaving very little, if any, carbon footprint or byproducts.

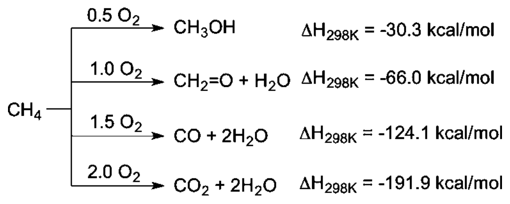
One of the major challenges of hydrocarbon chemistry is to convert methane to methanol by the overall insertion of a single oxygen atom (oxygenation)[1] in high yield and selectivity without the formation of other oxidation products (eq 1).

$$CH_4 + 0.5O_2 \rightarrow CH_3OH$$
$$\Delta H_{298K} = -30.3\ \text{kcal/mol} \qquad (1)$$

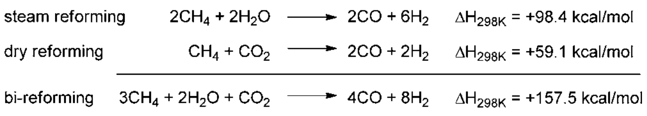
Over the years, extensive attempts have been carried out, and still are, on the selective direct oxygenation of methane to methanol. Numerous publications and patents claimed some success but only under extreme conditions (very high dilution with excess methane, short contact time, low temperature, etc.) and generally only in low conversions.[2−8] Attempts to increase yields inevitably resulted in loss of selectivity. Therefore, effective oxidative synthesis of methanol by direct methane oxidation is considered not feasible. During the course of direct methane oxidation, the thermodynamically as well as kinetically favored formation of further oxidation products, i.e., formaldehyde, formic acid, and eventually carbon dioxide, is inevitable (Scheme 1).

The practical synthesis of methanol was developed on the basis of syn-gas (a mixture of CO and H_2) in the 1920s in Germany in the context of the so-called Fischer−Tropsch chemistry.[9] It was originally based on coal but subsequently shifted to more convenient natural gas. The conversion of natural gas by steam or dry (CO_2) reforming as well as partial oxidation produces H_2/CO mixtures with a molar ratio generally between 3 and 1 (Scheme 2). However, to produce methanol, a specific 2:1 H_2:CO mixture is needed, which we have named *metgas*.[10] This is rarely achieved in conventional reforming processes. When H_2 is present in excess, CO_2 is added to the syngas mixture for the subsequent methanol synthesis.

Scheme 1. Direct Oxidation of Methane



Scheme 2. Reforming Processes



Furthermore, the overall reforming process is strongly endothermic. In modern processes (Haldor−Topsøe, Lurgi, Linde and others), part of the natural gas is combusted *in situ* to provide the needed heat energy (autothermal reforming). This renders, however, the needed metgas production even more complex and costly (up to some 60% of the overall cost of a methanol plant),[10] involving separation, purification, and adjustments such as the water−gas shift reaction.

In extensive studies,[11−16] effective metgas formation with a combination of endothermic steam and dry (CO_2) reforming providing also the required reaction heat was found not to be feasible.[17]

We have recently reported a facile new way called *bi-reforming* to produce metgas from methane (natural or shale gas) in a single step combining the steam and dry reforming reactions by reacting methane, CO_2, and steam in a 3:1:2 ratio over Ni/MgO or related catalysts at 800−950 °C in a pressurized tubular flow-reactor at 5−30 atm (Scheme 2).[18,19]

We now report a significant further advance of exclusive self-sufficient conversion of methane and its source materials such as natural (shale) gas, coal-bed methane, tight-sand gas, biogas, or methane hydrates to metgas for methanol synthesis by selective *oxygenation* of methane using a process we call *oxidative bi-reforming*. Oxygenation (i.e., oxygen functionalization) as defined and discussed means substitution or insertion of oxygen into a C−H or C−C bond of a hydrocarbon, thus essentially different from conventional oxidations.[1] *Bi-reforming*[18,19] of methane (from natural or shale gas) is highly endothermic, necessitating substantial external energy as well as multi-step feed preparation. Traditionally practiced partial

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oxidation and reforming (autothermal reforming) also necessitates costly separation steps and adjustments.[17] In contrast, the complete combustion of 1 equiv of methane with O_2 from the air gives the needed reaction and process heat for the subsequent *bi-reforming* step. Furthermore, it also provides the required $CO_2{-}2H_2O$ mixture, which is mixed with 3 equiv of methane (natural gas), giving the needed specific feed for bi-reforming to produce exclusively metgas for the subsequent methanol synthesis step (Scheme 3).[20]

Scheme 3. Oxidative Bi-reforming for Methanol Synthesis

methane combustion

$$\mathrm{CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O} \qquad \Delta H_{298K} = -191.9\ \mathrm{kcal/mol}$$

after admixing fresh methane, bi-reforming is carried out

$$\mathrm{3CH_4 + 2H_2O + CO_2 \longrightarrow \underbrace{4CO + 8H_2}_{metgas}} \qquad \Delta H_{298K} = +157.5\ \mathrm{kcal/mol}$$

methanol synthesis

$$\mathrm{4CO + 8H_2 \longrightarrow 4CH_3OH} \qquad \Delta H_{298K} = -86.8\ \mathrm{kcal/mol}$$

overall reaction

$$\mathrm{4CH_4 + 2O_2 \longrightarrow 4CH_3OH} \qquad \Delta H_{298K} = -121.2\ \mathrm{kcal/mol}$$

The self-sufficient *oxidative bi-reforming* of methane to metgas can be carried out in a single bundled multi-tubular reactor or in two separate reactors. It allows separate combustion of 1 equiv of methane with the oxygen of the air to give a $CO_2{-}2H_2O$ flue gas mixture. After admixing of 3 equiv of fresh methane upstream of the flame followed by *bi-reforming*,[18−20] the formed metgas is then converted to methanol in a well-known and industrially practiced synthesis step using $Cu/ZnO/Al_2O_3$ or related catalysts. Furthermore, the exothermic heat of reaction of methane combustion is more than sufficient for the subsequent endothermic *bi-reforming* process.[18,19,21] Thus, methanol produced from the still-abundant natural or shale gas resources that can last well into the next century can be used as a replacement for petroleum oil and its derived products while also decreasing their environmental harm (global warming) via CO_2 capture and recycling (CCR) in a feasible, economic way for use in our previously developed *Methanol Economy*.[10]

The presently developed *oxidative bi-reforming* followed by methanol synthesis thus achieves the long-sought-after goal of transforming methane to methanol in high yield and selectivity (eq 1) with no other oxidation products formed in this overall economic and energetically efficient process, leaving very little, if any, carbon footprint.

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Notes

The authors declare no competing financial interest.

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