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Review

Methane conversion using carbon dioxide as an oxidizing agent: A review

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ABSTRACT

Recent trends on the direct conversion of methane, employing carbon dioxide as an oxidizing agent are reviewed. While oxidation using molecular oxygen involves the sequential oxidation of various intermediates to generate carbon dioxide and exhibits low selectivity for the desired products, methane activation using carbon dioxide as an oxidant eliminates this sequential oxidation and has considerable promise. In this context, supported metal catalysts can promote the dry reforming of methane, and structured oxide catalysts have been found to enable methane coupling to C_2 products, using carbon dioxide as the oxidizing agent. This review also summarizes recent research regarding the use of nonconventional processes for methane activation in conjunction with carbon dioxide.

1. Introduction: characteristics of natural gas as a feedstock

This review focuses on the direct conversion of methane (CH_4), using carbon dioxide as an oxidizing agent. Oxidation with O_2 results in the sequential oxidation to produce carbon dioxide, while the use carbon dioxide avoids this sequential oxidation.

Natural gas has attracted increasing attention as a means of reducing reliance on crude oil and addressing various environmental issues. Primarily composed of CH_4, natural gas is a flammable substance obtained from oil or gas fields and coal mines. In contrast to other fossil fuels, it is relatively evenly distributed worldwide. At present, the confirmed natural gas reserves have a total volume of 187 trillion m^3, of which 24.8% is found in the Middle East, 30.4% in Europe and Eurasia, 8.4% in the Asia Pacific region, 7.5% in Africa, 6.8% in North America and 4.1% in Middle and South America [1]. Natural gas is typically used as a fuel for power generation and for domestic heating. In 1971, global primary energy consumption was based on 48% oil, 29% coal and 18% natural gas. However, in 2015, the consumption of 13.1 billion tonnes (oil equivalent) of fuel was based on 33% oil, 30% coal and 24% natural gas [1], reflecting a shift from oil to natural gas. This transition from oil to natural gas consumption is expected to gradually increase until 2035 [1].

The current R/P ratio (R: reserves, P: production) for natural gas, which indicates how long production can be expected to continue, is predicted to allow production for another 55 years. Recent advances in technology related to gas field extraction have extended this time span based on the exploitation of unconventional natural gas sources. As a result, unconventional natural gas sources, including shale gas, have become important energy reserves, especially in North America, and the balance between demand and supply has changed such that natural gas production will increase in future. The development of other more conventional natural gas sources such as tight sand gas and coal bed methane has also progressed, and so the R/P ratio will continue to increase. From an environmental perspective, natural gas is considered greener than oil and coal, because it includes much hydrogen atom. However, the transportation and storage of natural gas are less efficient than that of oil because the energy density per unit volume of natural gas is low. Natural gas is typically transported to remote locations via pipelines or as liquefied natural gas (LNG), although the latter process is inefficient because it is costly and significant energy inputs are required in the liquefying and transportation steps. As a result, neither pipelines nor LNG transport are economically viable in the case of medium or small gas fields far from the areas where the gas will be used.

From the viewpoint of holding back global warming, how to reduce greenhouse gases (GHGs) emissions and effective utilization of GHGs have attracted more and more attentions. Fig. 1 shows the greenhouse gas emissions and sources in the world [2]. From this figure, it can be found that CO_2 and CH_4 are the main component of greenhouse gases emissions, accounting for 76.0% and 15.8% respectively. Additionally, according to the Fifth Assessment Report (AR5) of the Intergovernmental Panel on Climate Change (IPCC) in 2014, the average temperature in 2100 will become higher than now as less than 4.8 °C in the worst-case scenario. Thus, reducing GHGs emissions is an urgent strategy for all countries to solve environmental problems and collecting or converting the existing GHGs has also been an effective

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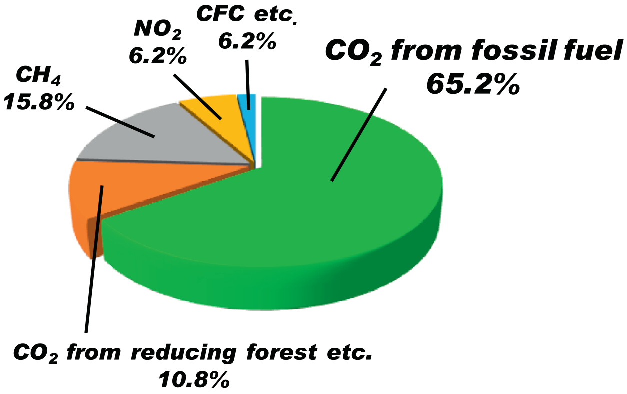

Fig. 1. Distribution of GHGs emissions to derivation sectors as in 2010.

approach to settle these issues.

In these situations, it would be helpful to develop novel methods for the conversion of CH_4 to chemical products such as syngas and C_{2+} hydrocarbons. Converting natural gas to useful chemicals, including syngas, ethylene and propylene, would increase its added value and allow effective utilization of medium/small gas fields at lower cost.

2. Methane to syngas using carbon dioxide as an oxidizing agent

2.1. Syngas production

A number of catalytic processes have been reported for the chemical conversion of CH_4 [3–9] and these are summarized in Fig. 2. Recent catalyst researches on Ni-based catalyst in DRM reaction are also summarized in Table 1 (because some good reviews have already summarized recent works before 2017) [10–13]. These technologies can generally be divided into two types: indirect and direct conversion processes. During an indirect conversion, the CH_4 is converted to syngas, mixed with CO and H_2, and subsequently converted to various chemical products such as FT oil, dimethyl ether and methanol. [7–9,14] The main techniques used to produce the initial syngas are steam reforming (SR), dry reforming (DR), autothermal reforming (ATR) and partial oxidation (PO_x).

In the case of indirect conversion, oxidizing agents such as O_2, CO_2 or H_2O are often used to obtain either H_2 or syngas.

Since the 1960s, the majority of syngas and H_2 production from CH_4 has been by the steam reforming of CH_4 (SRM) [15–17]. The reaction equation for this process is as follows.

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206.1\ \mathrm{kJ \cdot mol^{-1}} \tag{1}$$

The dry reforming of CH_4 (DRM: Eq. (2)) has also attracted attention because it also allows the elimination of CO_2, a well-known greenhouse gas.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \quad \Delta H^0_{298} = 247.2\ \mathrm{kJ \cdot mol^{-1}} \tag{2}$$

The change in the Gibbs free energy (G) with temperature (T) for this dry reforming reaction is as in Eq. (3).

$$\Delta G_T\,(\mathrm{kJ \cdot mol^{-1}}) = 2.31 \times 10^2 - 0.0702T \cdot \ln T + 0.185T + 5.19 \times 10^{-5}T^2 + 5.65 \times 10^{-9}T^3 \tag{3}$$

Equilibrium conversion values can be calculated from Eq. (3) and these demonstrate that, on a thermodynamic basis, temperatures above 1173 K are required for the DRM to proceed efficiently. However, the use of such high temperatures can lead to sintering of supported metals and catalyst support.

In the DRM process, the order of catalytic activities is known to be Ru > Rh > Ni > Pt > Pd on a SiO_2 support, Ru > Rh > Ni > Pd > Pt on a MgO support and Rh > Ni > Pt > Ir > Ru > Co on an Al_2O_3 support [18]. In recent years, Ni or Co supported catalysts have become of interest because they are less expensive than noble metals [19–28], and Ni catalysts supported on oxides have been found to give the best results during the DRM. Although Ni supported catalysts exhibit high DRM activity, these catalysts tend to undergo sintering and lose their activity soon after the onset of C deposition [29]. To overcome this problem, the second metal addition to Ni supported catalysts has been investigated by many researchers and summarized in some good reviews [30,31]. In Ni–transition-metal bimetallic systems,

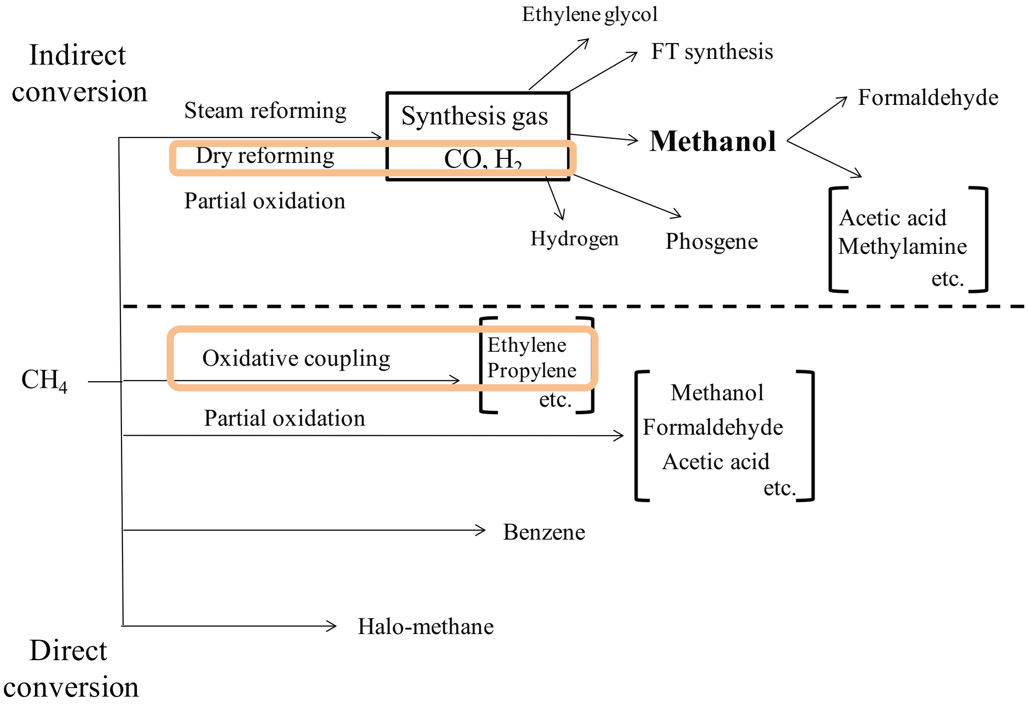

Fig. 2. The scheme of methane conversion.