Advances in catalytic conversion of methane and carbon dioxide to highly valuable products

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Abstract
Two typical processes have been developed for the conversion of methane and carbon dioxide to higher valuable products: dry reforming of methane (DRM) and CO2-oxidative coupling of methane (CO2-OCM). Numerous articles reviewed progresses in either DRM or CO2-OCM, but no one covers both processes. In this review article, we systematically evaluated progresses in both DRM and CO2-OCM processes for conversion of methane and CO2 to highly valuable products. Critical issues, which are carbon deposition and high energy cost for DRM and the contradiction between large activity and high selectivity for CO2-OCM, were emphasized. Strategies to develop effective catalysts were evaluated, including the enhancement of metal-support interactions, the introduction of promotors, the formation of solid solutions, and the construction of core-shell structures. Plasma and photocatalysis were discussed as new promising technologies for DRM and CO2-OCM.

Keywords
CH4, CO2, dry reforming, oxidative coupling, valuable organic compounds

1 | INTRODUCTION

Methane and carbon dioxide, which are greenhouse gases, are the main components of natural gas. Methane is the most stable hydrocarbon due to its strong C-H bond (434 kJ/mol) and thus its activation needs a high temperature. There are various techniques to convert methane to more valuable chemicals and fuels,1−3 which can be classified into three types of routes5−8: (1) reforming to produce syngas including steam reforming (Equation 1), dry reforming (Equation 2), and partial oxidation (Equation 3); (2) oxidative coupling (Equation 4 and Equation 5); and (3) conversion to oxygenates such as methanol (Equation 6).

\[
\begin{align*}
\text{CH}_4 + \text{H}_2\text{O} &\rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H_{298K}^0 = +206 \text{ kJ mol}^{-1} & (1) \\
\text{CH}_4 + \text{CO}_2 &\rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298K}^0 = +247 \text{ kJ mol}^{-1} & (2)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_4 + 1/2\text{O}_2 &\rightarrow \text{CO} + 2\text{H}_2 \quad \Delta H_{298K}^0 = -36 \text{ kJ mol}^{-1} & (3) \\
2\text{CH}_4 + 1/2\text{O}_2 &\rightarrow \text{C}_2\text{H}_6 + \text{H}_2\text{O} \quad \Delta H_{298K}^0 = -177 \text{ kJ mol}^{-1} & (4) \\
2\text{CH}_4 + \text{O}_2 &\rightarrow \text{C}_2\text{H}_4 + 2\text{H}_2\text{O} \quad \Delta H_{298K}^0 = -282 \text{ kJ mol}^{-1} & (5) \\
\text{CH}_4 + 1/2\text{O}_2 &\rightarrow \text{CH}_3\text{OH} \quad \Delta H_{298K}^0 = -126.4 \text{ kJ mol}^{-1} & (6)
\end{align*}
\]

As an indirect approach for highly valuable hydrocarbon production from CH4, the first route can be followed by Fischer-Tropsch reaction (Equation 7). Although such a multi-step process has high product yield, the syngas production is expensive due to its high capital costs and it is therefore only economically viable if it is conducted on a large scale. The latter two ways can convert methane directly to other hydrocarbons.
nCO + 2nH₂ → (−CH₂)ₙ + nH₂O  ΔH°_{298K} = −165 kJ mol⁻¹

(7)

Carbon dioxide, which is a linear molecule with a C-O bond strength of 532 kJ mol⁻¹, is very stable. Furthermore, the large positive value (394.6 kJ mol⁻¹) of CO₂ formation Gibbs free energy contributes to its high inertness. Due to its being the most oxidized state of carbon, reduction is the only possible route for the conversion of CO₂ via one of the following four main methodologies⁹⁻¹²: (1) Using high-energy starting materials such as hydrogen, unsaturated compounds, small-membered ring compounds, and organometallics; (2) Choosing oxidized low-energy synthetic targets such as organic carbonates; (3) Shifting the equilibrium to the product side by removing a particular compound; and (4) Supplying physical energy such as light or electricity. So far, the catalytic hydrogenation of carbon dioxide to methanol and other oxygenates using hydrogen has attracted the most attention (Equation 8).

\[ \text{CO}_2 + 3\text{H}_2 \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad \Delta H°_{298K} = −49.5 \text{kJ mol}⁻¹ \]

(8)

Conversion of CH₄ or CO₂ individually possesses relatively lower activation energy compared with activation of both CH₄ and CO₂ in the same reaction. However, considering methane and carbon dioxide co-exist in natural gas, the conversions of both gases have significant implication toward the utilization of natural gas.¹³

The well-investigated reaction to convert these two reactants is CO₂ reforming of CH₄ (dry reforming of methane, DRM), which was thoroughly explored by Fischer and Tropsch in 1928¹⁴ and was investigated as early as 1888.⁶

Dry reforming of methane yielded a lower syngas ratio (H₂/CO 1:1) (Equation 2), which is suitable for production of oxygenated chemicals¹⁵ from Fischer-Tropsch synthesis. However, the activation of both C-H bond in CH₄ and C-O bond in CO₂, which requires efficient catalysts, is a great challenge due to their high stabilities.¹⁶⁻¹⁹ Catalysts used for DRM can be divided into two groups: earth-abundant transition metals and noble metals.²⁰ The majority of catalysts are based on Ni due to its high activity and low cost,²¹ whereas these catalysts usually undergo deactivation processes mainly due to carbon deposition²²; Noble metals²³⁻²⁶ have demonstrated much more resistance to carbon deposition than Ni catalysts, but are generally uneconomical. Furthermore, those catalysts could also be exploited to convert raw biogas (which mainly contains CH₄ and CO₂) into syngas.²⁷,²⁸ However, more attention is needed to develop sulfur-resistant catalysts, because H₂S is the main impurity in biogas.²⁹,³⁰

Oxidative coupling of methane by CO₂ (CO₂-OCM) is a direct process to convert both CH₄ and CO₂ to higher value hydrocarbons, particularly ethane and ethylene (Equations 9 and 10):

\[ 2\text{CH}_4 + \text{CO}_2 \rightarrow \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O} \quad \Delta H°_{298K} = +106 \text{kJ mol}⁻¹ \]

(9)

\[ 2\text{CH}_4 + 2\text{CO}_2 \rightarrow 2\text{CH}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O} \quad \Delta H°_{298K} = +284 \text{kJ mol}⁻¹ \]

(10)

In 1982, Keller et al.³¹ published the first report on the production of C₂ hydrocarbons from CH₄ with oxygen over catalysts (metal oxides supported on Al₂O₃) at atmospheric pressure and temperature range of 500-1000°C. O₂ as an oxidant unavoidably induces some gas-phase radical reactions, which complicate the optimization of catalyst and cause the limitation in C₂ yield due to the unavoidable, consecutive oxidation of the produced hydrocarbons to CO and finally CO₂.³² Replacing of oxygen with other oxidant is considered as a possible approach to prevent the sequential reaction of C₂ products in the gas phase.³³⁻³⁵ Carbon dioxide, which is a soft oxidant to provide extra carbon atom for the methane conversion, has been explored as an oxidant for CO₂-OCM reaction.³⁶⁻⁴⁰ Early in 1988, Aika et al. found that oxidative coupling of CH₄ by O₂ is promoted by CO₂ as a reactant. They attributed it to decrease of free energy by conversion CO₂ to CO at 800°C. However, CO₂-OCM reaction (Equations 9 and 10) is not thermodynamically favorable even at temperatures as high as 900°C.⁴¹ One way to overcome this is to introduce the solid coreactants that undergo solid-phase transformations during CO₂-OCM. It was reported that the selectivity of the methane oxidation is determined by the ability of the oxygen active species on the catalyst surface to make discrimination between a C-H bond in methane and a weaker C-H bond in the product(s).⁴² The lattice oxygen of catalysts participates in the conversion of methane, and then the reduced catalyst needs to be reoxidized for maintaining the activity of the catalyst. Furthermore, CO₂ chemoisorption requires suitable sites to form active oxygen species for recovering the reduced sites and activating methane. Therefore, it is important to develop efficient catalysts that should be capable not only of activating both CH₄ and CO₂, but also of producing C₂ hydrocarbons selectively.⁴³ As shown in Table 1, one can see that multi-component catalysts with alkali metal oxide are more effective than mono-component ones. Comparing with conventional O₂-OCM whose maximum C₂ yield ranges from 16% to 27% with selectivity 72%-82%, CO₂-OCM exhibits a lower maximum C₂ yield (6%) but comparable selectivity.⁷,⁴² Furthermore, to achieve higher methane conversion at low temperatures, nonconventional catalytic systems have also been reported, such as catalytic reactions in an electric field.⁴⁴⁻⁴⁶ catalytic reactions with discharge,⁴⁷⁻⁴⁹ and photocatalytic reactions.⁵⁰⁻⁵²

In this article, we will review the progress in both DRM and CO₂-OCM, with emphasis on (1) how to inhibit carbon deposition over catalysts for DRM and (2) how to increase the C₂ yield of catalysts for CO₂-OCM. Plasma and photocatalytic technologies, which were exploited as prospecting
TABLE 1  Summary of catalysts and their performances for CO2-COM

| Catalyst | Reaction condition | Products | References |
|----------|--------------------|----------|------------|
| PbO-MgO with and without CaO (K2O, Sm2O3, or BiO). | CH4−O2 (200: 1) with or without CO2 as reactants in total flow rate of 60 mL/min over 2 g catalyst at 800°C. | C2(C2H6, C2H4) yield: with CO2: 4.37%, 6 times CO; without CO2: 3.28%. | 41 |
| Unsupported metal oxides such as Co, Cu, La, Al, Sa et.al | Equimolar mixture of CH4 and CO2 with total flow rate 100 mL/min over 2 g catalyst at 850°C. | C2 yield: 0.44%, minor CO, and H2 | 38, 40, 249–252 |
| La2O3/ZnO catalysts | Molar ratio of CH4/CO2 = 2 with total flow rate of 30 mL/min as reactant gas over 0.5 g catalyst at 850°C. | C2 (C2H4/C2H6=0.7) yield: 2.8% minor CO | 37 |
| CaO-CeO2 solid solution | Total flow rate = 100 mL/min; PCH4 = 30.3 kPa with different pressures of CO2 ranging from 0 to 80 kPa over 2 g catalyst at 780-900°C. | C2 yield: 6% | 253,254 |
| CaO-MnO/CeO2 | CH4/CO2 ratio: 1.5-2; Total flow rate=100 mL/min; Total pressure = 1 atm; Wcat = 2.0 g; Temperature = 700-925°C. | Individual responses optimization: C2 yield 3.93%; multi-responses optimization: C2 yield 3.74% | 40,242,257,260 |
| CaO-ZnO | PCH4 = 30 kPa; PCO2 = 70 kPa; Wcat = 1.0 g; Total flow rate = 100 mL/min; Temperature = 850°C. | With CO2: C2 (C2H4/C2H6=1) selectivity approached 80% with a C2 yield of 4.3% Without CO2: H2 and CO as the main products with a ratio of ca. 2. | 248 |
| Nano-CeO2/ZnO | P = 1 atm; CH4 =15 mL/min; CO2=30 mL/min; Wcat=0.1 g; Temperature=740-900°C. | C2 selectivity >80%. | 261 |
| MnO-SrCO3 | PCH4 = 30.3 kPa; PCO2 = 70.7 kPa; Wcat = 3.0 g; Total flow rate = 100 mL/min; Temperature = 875°C. | C2 yield: 4.3% | 40 |
| Mn-based binary oxides (Ca-Mn, Sr-Mn, and Ba-Mn) | PCH4 = 30.3 kPa; PCO2 = 70.7 kPa; Wcat = 1.0 g (atomic ratio of M/Mn is 1.0); Total flow rate = 100 mL/min; Temperature = 850°C. | within 5-10 minutes after introduction of feed gas, CO2 as main product, H2O, and C2 as minor ones; in steady state, CO and C2 as main products with C2 yield of 4%. | 262 |

routines to reduce reaction temperature and increase activity and selectivity of catalysts for the two processes, will also be discussed.

2  |  DRY REFORMING OF METHANE

Deactivation of catalysts by coke formation, which originates from the CH4 dissociation and/or CO2 disproportionation, is a serious problem in DRM. Thermodynamic considerations suggest operation at CO2/CH4 ratios higher than 1 and high temperature to minimize carbon formation for DRM. However, from industrial viewpoint, it is desirable to operate at lower temperature and with a CO2/CH4 ratio near unity. Such an operation requires a catalyst that kinetically inhibits the carbon formation under conditions that are thermodynamically favorable for carbon deposition. Carbon deposition in DRM occurs via two main possible pathways, methane decomposition (Equation 11), and Boudouard reaction (ie, CO disproportionation) (Equation 12).

$$\text{CH}_4 \leftrightarrow \text{C}(s) + 2\text{H}_2 \quad \Delta H_{298K}^0 = +75 \text{kJ mol}^{-1} \quad (11)$$

$$2\text{CO} \leftrightarrow \text{C}(s) + \text{CO}_2 \quad \Delta H_{298K}^0 = -171 \text{kJ mol}^{-1} \quad (12)$$

The first reaction, which is endothermic, is favored at high temperature, whereas the second one prefers lower temperature due to its exothermic feature. Since a high temperature is required for methane reforming (>800°C), Boudouard reaction would not be significant. Therefore, the dissociation of methane, which may occur via four steps (CH4→*CH3→*CH2→*CH), constitutes the main
contribution to carbon deposition in DRM.\textsuperscript{55–58} Carbon formation by CH\textsubscript{4} decomposition is a structure-sensitive reaction.\textsuperscript{55,58} For example, the Ni (100) and Ni (110) surfaces are more active for the decomposition of CH\textsubscript{4} to carbon than the Ni (111) surface. Another factor affecting carbon deposition is the surface acidity of catalysts.\textsuperscript{59} Carbon formation can be diminished or even suppressed when the active metal is supported on a metal oxide carrier with Lewis basicity. The strategy to inhibit carbon deposition is to tune surface structure of a catalyst and to decrease its surface acidity.\textsuperscript{20}

It was revealed that noble metal catalysts are more resistant to carbon deposition than non-noble metal catalysts,\textsuperscript{60–67} namely, the amount of carbon deposited on metal catalysts decreased in the order Ni$>$Rh$>$Ir$>$Ru$>$Pt$\approx$Pd at 500°C and Ni$>$Pd$=$Rh$>$Ir$>$Pt$>$Ru at 650°C.\textsuperscript{68} Supports are often exploited to modify the surface structure and acidity of catalysts, leading to an increase in the resistance to carbon deposition.\textsuperscript{20} The support with high Lewis basicity, such as La\textsubscript{2}O\textsubscript{3} and CeO\textsubscript{2}, can increase the ability of catalysts to chemisorb CO\textsubscript{2}, which can react with carbon to form CO, decreasing carbon formation. The interaction of metal and support would affect dispersion and size of metal particles. The higher dispersion and smaller size of catalyst particles can inhibit carbon deposition.

### 2.1 Noble metal-based catalysts

Various supported noble metal catalysts have been explored for DRM with an activity order: Rh$\approx$Ru$>$Ir$>$Pt$>$Pd for DRM.\textsuperscript{69–71} It is generally recognized that CH\textsubscript{4} is activated on the metal of a catalysts and CO\textsubscript{2} on its support. However, Bitter et al.\textsuperscript{72} observed that CH\textsubscript{4} activation occurs at the Pt-ZrO\textsubscript{2} interfacial sites instead of Pt alone. The acidic/basic property of support has direct effect on CO\textsubscript{2} activation process: CO\textsubscript{2} activates by formation of formates with the surface hydroxyls on acidic support (like Al\textsubscript{2}O\textsubscript{3}) and on basic supports (like La\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2}) by forming oxy-carbonates.\textsuperscript{73–75} The metal particle size or metal dispersion can also be affected by support. For example, Yokota et al.\textsuperscript{76} showed that Rh dispersion increases in the order: TiO\textsubscript{2}$<$MgO$<$SiO\textsubscript{2}$<$MCM-41$<$γ-Al\textsubscript{2}O\textsubscript{3}. Whang\textsuperscript{77} found that a very small amount of Ru (0.13 wt%) supported on ZrO\textsubscript{2}-SiO\textsubscript{2} are very active and stable for DRM (Figure 1). This happened because the strong interaction between Ru and ZrO\textsubscript{2} resulted in the highly dispersed Ru with small particle size of 1.4 nm. Different from other oxide supports, TiO\textsubscript{2} possesses reducibility. As a result, TiO\textsubscript{2} can maintain the metallic nature of Rh, but it masks the catalytically active metal due to partial reduction of TiO\textsubscript{2} to TiO\textsubscript{2}, which then forms a layer over Rh in a Rh/TiO\textsubscript{2} catalyst.\textsuperscript{78,79} Noble metals on other types of supports have also been explored for DRM, including crystalline oxides (Pyrochlores, perovskite),\textsuperscript{80–87} mesoporous-structure silicate,\textsuperscript{88} ZnLaAlO\textsubscript{4},\textsuperscript{89} and NiO/MgO solid solution.\textsuperscript{90} In addition, DRM performance over Pd, Ru, or Ag metal catalyst could be enhanced using membrane reactors, which can separate the products

![FIGURE 1](Image)

\textbf{FIGURE 1} CH\textsubscript{4} and CO\textsubscript{2} conversions and H\textsubscript{2}/CO ratio for DRM reactions performed at 800°C with GHSV of 20 000 mL/h/gcat over catalysts (RS: Ru-Silica, ZS: Zr-Silica, RZS: Ru-Zr-Silica, and CRZS: Co-Ru-Zr-Silica). Reprinted with permission from \cite{77}. Copyright © 2016 Elsevier B.V. All rights reserved.
CO and H₂ from the reaction system to drive the reaction toward formation of CO and H₂ \(^{91-95}\) at a lower temperature.

Carbon deposition on noble metal catalysts was evaluated. Barbier et al.\(^{96,97}\) found that the carbon deposition per Pt atom decreased with increasing Pt dispersion, which was supported by work of Spivey and his coworkers.\(^{98}\) This can be explained by particle size effect of Pt, namely, the increase in Pt dispersion on a support could result in the small Pt particles, on which the assembly of carbon atoms to coke becomes difficult. The promoters also have a significant effect on carbon deposition.\(^{99-104}\) For example, it was reported that the bimetallic Pt-Au/SiO₂, Pt-Sn/SiO₂, and Pt-Sn/ZrO₂ catalysts exhibited less carbon deposition during DRM than the corresponding monometallic platinum catalysts, probably because of the formation of alloys.\(^{99}\)

Substituting a noble metal into the crystalline structure of a thermally stable oxide (such as perovskites and pyrochlores with empirical formula of ABO₃ and A₂B₂O₇) was explored to improve catalytic performance for DRM.\(^{80-87}\) In this strategy, the B sites of ABO₃ or A₂B₂O₇, which are normally occupied by a transition metal, can be substituted by noble metal isomorphically, leading to a more efficient catalysts. Recently, Spivey and his coworkers explored noble metal-substituted lanthanum zirconate pyrochlore catalysts.\(^{105-111}\) For example, they reported that a 1% Ru-substituted lanthanum strontium zirconate pyrochlore, La₁₀₀Sr₀₃Ru₀₅Zr₁₉₅O₇ (LSRuZ), exhibited higher resistance to carbon formation than 0.5% Ru/Al₂O₃ catalyst under all tested conditions.\(^{110}\) Furthermore, they evaluated two pyrochlores (LRuZ and LPtZ), which were synthesized by isomorphically partially substituting Zr in the B-site of La₂Zr₂O₇ with Ru (2.00 wt%) and Pt (3.78 wt%), respectively.\(^{106}\) It was found that LRUZ exhibited much lower activation energies than LPtZ. In addition, they demonstrated that Rh is even better than Ru and Pt to substitute B sites in both perovskites and pyrochlores, leading to excellent activity (Figure 2) and high resistance to carbon formation for DRM.\(^{108-111}\) This indicates that the three substitutes follows the order: Rh>Ru>Pt. Over the noble metal-substituted La₂Zr₂O₇ catalysts, noble metal is responsible for CH₄ activation and dissociation, while CO₂ activation takes place on La site by the formation of three polymorphs of La₂O₂CO₃, the oxidation of surface could be occurring at the Rh-La interface.\(^{109,111}\) Carbon formation decreases with increasing Rh loading.\(^{106}\)

2.2 | Supported Ni-based catalysts

Alumina is one of the most commonly used supports for nickel catalysts.\(^{112-116}\) Zhang et al. showed that the conversion of CH₄ was greater for Ni/Al₂O₃ than for Ni/La₂O₃, suggesting that acidic sites on Al₂O₃ can assist the activation of CH₄.\(^{117}\) However, these acidic sites caused carbon formation, leading to deactivation. Therefore, various methods were employed to improve Ni/Al₂O₃. Firstly, smaller Ni particles over Al₂O₃ were prepared to inhibit carbon deposition,\(^{113,116-123}\) because carbon deposition occurs more easily on larger nickel particles than smaller ones.\(^{124,125}\) For example, Shang\(^{118}\) applied atomic layer deposition (ALD) to synthesize Ni/Al₂O₃ with
high dispersion of Ni, resulting in the stable conversion of 93% at 850°C. Chen and Ren\cite{120} found that the carbon deposition over Ni/Al₂O₃ was markedly suppressed when NiO and Al₂O₃ have strong interaction, which increases the difficulty of reduction of Ni²⁺ to Ni⁰. As a result, small nickel crystallites on the catalyst surface, which are smaller than the size necessary for carbon deposition,\cite{121} were formed. Liu and coworkers reported that the glow discharge plasma-treated Ni/Al₂O₃ catalyst exhibited an excellent anticoke property for DRM.\cite{126} This happened because the plasma treated catalyst contains high concentration of close packed plane with improved Ni dispersion and enhanced Ni-alumina interaction. The change in Al₂O₃ pore structure can also tune the catalytic properties of Ni/Al₂O₃, namely, 25 wt% Ni supported on mesoporous nanocrystalline Al₂O₃ exhibited good catalytic performance in CH₄ dry reforming.\cite{127} Secondly, various types of promoters were employed to modify Ni/Al₂O₃ catalysts, including alkali, alkaline earth, transition metal, and rare earth metal oxides. The basic oxides of Na, K, Mg, and Ca were explored to decrease the acidity of Ni/Al₂O₃.\cite{112,128-134} The surface of nickel catalyst incorporating basic metal oxide is favored by CO₂ adsorption, leading to the increase in CO₂ adsorption that can enhance its reaction with carbon and thus inhibits carbon deposition. The addition of a second metal, such as Co, Cu, and Sn, can form less C-sensitive alloys.\cite{133,135-141} Choi et al. examined the effect of Co, Cu, Zr, and Mn as promoters for the Ni/Al₂O₃ catalyst.\cite{135} They found that, in comparison with unmodified Ni/Al₂O₃ catalyst, those modified with Co, Cu, and Zr exhibited slightly improved activities, whereas the Mn-promoted catalyst provided a remarkable reduction in coke deposition with only a small decrease in catalytic activity. Seok et al. demonstrated that a partial coverage of the nickel surface of Ni/Al₂O₃ by MnOₓ promoted the adsorption of CO₂, leading to the decrease in the carbon deposition.\cite{136}

Ni/Al₂O₃ catalyst can also be improved by tin and ceria, leading to enhanced conversion and stability.\cite{141} Noble metals (such as Pt, Ru, and Pd) can remarkably enhance both activity and stability due to their excellent ability to maintain Ni reduced.\cite{139,140,142,143} Furthermore, small amount of rare earth metals in Ni/Al₂O₃ exhibited promising promoting behaviors. For example, Slagtern et al. evaluated Ni/Ln/Al₂O₃ (Ln=rare earth mixture) catalysts at 800°C and 1 atm, showing that the catalyst with a rare earth content of 10.7 wt% Ln is more active and stable than the unpromoted catalyst.\cite{144-153} Promoting Al₂O₃ by Mg can also improve Ni/Al₂O₃ catalysts. As reported by Damyanova et al.,\cite{154} Ni/MgAl₂O₄ catalyst showed much better performance for DRM than Ni/Al₂O₃. Furthermore, NiFe/MgₓAlₙOₙ catalyst is even better than Ni/MgₙAl₀ₓ (Figure 3).\cite{155} The promoting effect of Fe was attributed to its dynamic redox reaction under dry reforming conditions, ensuring a close proximity of the carbon removal (FeO) and methane activation (Ni) sites. In addition, rare earth elements (Sc, Y, Ce, and Pr) exhibited promoting effect on Ni/ MgₙAl₀ₓ catalysts, leading to the improved catalytic stability and coke resistance due to the enhanced surface basicity, abundant oxygen vacancies, superior redox properties, and highly dispersed Ni particles.\cite{156}

Besides Al₂O₃, other supports were also explored. As an inert support, SiO₂ has a weak interaction with Ni, leading to relatively weak metal-support interaction and are less stable and less active compared to mildly acidic (Al₂O₃) and basic (La₂O₃, CeO₂) supports.\cite{72-75,157-177} However, the high dispersion of Ni nanoparticles in nanochannels of cerium-modified silica aerogels or in mesoporous silica can improve the catalytic activity and thermal stability.\cite{178,179} Ni/La₂O₃ catalysts were widely evaluated for DRM.\cite{180-191} Zhang and Verykios\cite{180} compared La₂O₃ and CaO with Al₂O₃ as support for Ni catalysts. They found that a Ni/La₂O₃ catalyst

![FIGURE 3](image-url) Rate of methane consumption at 650°C over catalysts: (■) Ni-MA, (▲) Ni₄Fe₁-MA, (●) Ni₃Fe₁-MA, (□) Ni₁Fe₁-MA, (△) Ni₁Fe₃-MA and (○) Fe-MA (MA: MgₓAlₙOₙ). Reprinted with permission from [155]. Copyright (2017) American Chemical Society.
exhibited a higher activity and higher stability than Ni/Al2O3 and Ni/CaO catalysts for DRM. The rate of reaction on Ni/La2O3 catalyst increased significantly with time on stream during the initial 2-5 hours of reaction, and then tended to remain unchanged for 100 operating hours. The high steady state reaction rate was attributed to the basic sites on La2O3 which assisted in the activation of CO2 and oxidation of surface carbon. The preparation method also affects the Ni/La2O3 catalysts.182,183 Hu and Ruckenstein183 investigated the role of anions NO3- or Cl- in unreduced Ni/La2O3 catalyst. Ni/La2O3 prepared from nickel nitrate showed high initial CO yield but a low stability; in contrast, the unreduced Ni/La2O3 catalyst, prepared with chloride, had a high stability. This stabilization occurred probably because a stable lanthanum chloride inhibited the formation of large ensembles of nickel atoms that are required by carbon deposition. Support precursors also showed effect on Ni/La2O3 catalysts. Li et al. synthesized a Ni/La2O3 catalyst using La2O2CO3 nanorod as a support precursor, leading to efficient Ni/La2O3 catalyst for DRM with 70% conversion for CH4 and 75% conversion of CO2 at 700°C even after 50 hours.185

Zirconia- and CeO2-supported nickel catalysts were investigated for the CO2 reforming reaction with emphasis on the stability of the catalysts.192-195 It was found that a lower nickel loading (<2 wt%) is benefit for stability of Ni/ZrO2 catalysts at temperatures between 720 and 780°C. The stabilities of Ni/ZrO2 catalysts were also dependent on preparation methods.196 Ni/ZrO2 catalyst prepared from large Zr(OH)4 particles deactivated rapidly. In contrast, a catalyst with high metal loading of nickel (27 wt%), obtained by impregnating ultrafine Zr(OH)4 particles (6 nm) with nickel nitrate, exhibited high and stable activity for DRM without deactivation. The activity of this catalyst at 757°C with a CH4/CO2=1:1 molar feed rate of 24 000 mL (g catalyst)-1 h-1 did not change for 600 hours, but exhibited oscillations in the CH4 conversion between 80 and 85%. The incorporation of Ni particles within the mesoporous zirconia was used to suppress the sintering of Ni particles and to enhance the metal-support interaction because of the formation of additional interfaces, resulting in excellent stability over 80 hours.197,198 ZrO2 with different morphologies may possess different lattice oxygen mobility and interactions between support and active metals, which can also affect the catalytic behavior of Ni/ZrO2.199,200 CeO2 nanorods (NR) and nanopolyhedra (NP) were compared as supports for Ni catalysts. Du et al. showed that the Ni/CeO2-NR catalysts possess larger catalytic activity and higher coke resistance for DRM than Ni/CeO2-NP.195 This is because the predominantly exposed planes are the unusually reactive {110} and {100} planes for the CeO2-NR, but the stable {111} one for the CeO2-NP. The {110} and {100} planes with Ni particles could generate the strong metal-support interaction (SMSI), which can inhibit the sintering of Ni particles and thus reduce the deactivation.

Zhang and his coworkers exploited 2D layer materials as support for Ni-based catalysts.201,202 They reported that Ni nanoparticles embedded on vacancy defects of hexagonal boron nitride nanosheets (Ni/h-BNNS) can optimize catalytic performance by taming two-dimensional (2D) interfacial electronic effects. Surface engineering for defects of Ni/h-BNNS catalyst can strongly influence metal-support interaction via electron donor/acceptor mechanisms and favor the adsorption and catalytic activation of CH4 and CO2, leading to superior catalytic performance during 120-h durability test [Figure 4]. This work highlights promotional mechanism of defect-modified interface. This mechanism was further supported by nickel nanoparticles on defected nanosheets of halloysites.203 The catalyst exhibited good coke and sintering resistance performance in DRM, which was reflected by negligible loss of activity after a 20 hours. This was attributed to the strong interaction between the Ni nanoparticles and the support.

**FIGURE 4** Temperature dependence of (A) CH4 conversion, (B) CH4 conversion as a function of time on stream and relevant (C) H2/CO ratio over the reduced catalysts (CO2/CH4 = 1 and GHSV = 15 000 mL/h/gcat). Reprinted with permission from [201]. Copyright © 2018 Elsevier B.V. All rights reserved.
ZSM-5 and carbon were used as supports of Ni-based catalysts for DRM by Fan and his coworkers. It was found that the addition of Ce to Ni/ZSM-5 could not only promote CH₄ decomposition for H₂ production, but also the gasification of deposited carbon with CO₂. Furthermore, the dispersion of Ni particles could be improved by Ce. They also evaluated carbon as support for Ni catalysts. The char was synthesized by pyrolysis of a long-flame coal at 1000°C and used as a support for Ni-based catalysts. It was showed that Cr could play a role of promoter in Ni/Char catalysts due to its enhancement for CO₂ adsorption. Furthermore, the promotion effect is dependent on the introduction approach of Cr, namely, the catalyst prepared by co-impregnation of Ni and Cr exhibited larger activity than that by sequential impregnation.

Mesoporous MCM-41 was also explored as a support by Damyanova et al. They found that the addition of a small amount of Pd to Ni-containing catalysts, which generated easily reducible nanostructured NiO particles, increased the activity and stability of the Ni-based catalysts. Furthermore, the PdNi catalyst with Ni/Si ratio of 0.3 reached the best performance. Hydroxyapatite-supported bimetallic Ni-Co catalysts were also evaluated for DRM. The selectivities of CO and H₂ over the catalyst reached 80%-90% with high stability.

### 2.3 | Core-shell structured Ni-based catalysts

CeO₂ was explored as a support for Ni catalysts for DRM because of its excellent redox properties and the oxygen mobility, revealing that the interaction of CeO₂ with Ni particles plays an important role. Li et al. found that the reduction of NiO/CeO₂ by H₂ in a temperature range of 500-700°C generated a strong binding between Ni and CeO₂, which can inhibit the sintering of Ni particles (8.7-9.4 nm) (Figure 5). This happened because the high-temperature (>600°C) reduction induced the encapsulation of Ni nanoparticles by a thin layer of reduced ceria support. The encapsulation effect can be exploited to improve the catalytic activity of Ni/CeO₂ and inhibits carbon deposition in DRM.

A NiCe@m-SiO₂ yolk-shell framework catalyst, in which the CeO₂-modified Ni nanoparticles are the core and the mesoporous SiO₂ is the shell, was developed. The yolk-shell framework catalyst showed high catalytic activity and stability for DRM. Its special structure and large surface area might enhance its activity, and the confinement effect of the yolk-shell framework could contribute to the stabilization of the Ni nanoparticles. The modification of the catalyst by CeO₂, which increased the active oxygen species and improved the dispersion of Ni nanoparticles, could also enhance the catalytic activity and suppressed the carbon deposition. Furthermore, NiCo@SiO₂ core-shell catalyst (ie, single NiCo alloy nanoparticle encapsulated by SiO₂ shell) was also synthesized with microemulsion technology. The catalyst exhibited larger activity and selectivity and higher stability than the Ni@SiO₂, the Co@SiO₂ core-shell catalyst, or the NiCo/SiO₂ supported catalyst (Figure 6). The encapsulation of metal nanoparticles by SiO₂ shell could effectively inhibit the agglomeration of active sites. Meanwhile, the enhanced activity of NiCo alloy catalyst could also diminish the surface carbon deposition.

The combination between SRM and DRM as the steam-CO₂ bireforming was employed to inhibit carbon deposition by the oxidation of C species with H₂O. Furthermore, the variation of CO₂/H₂O ratio can tune the produced H₂/CO ratio from 0.91 to 3.0, covering a wide range of syngas composition for various downstream hydrocarbon synthesis. So far, efforts for the bireforming have been mainly focused on Ni-based catalysts.

### 2.4 | Supported co-based catalysts

Co supported on metal oxides were explored as catalysts for DRM. It was found that 20 wt% Co/ CeO₂ exhibited high conversions up to 87.6% for CO₂ and 79.5% for CH₄ at 750°C. Furthermore, the combination of Co with Ni over AlₓMgOₓ enhanced its activity and stability, which is due to the high metal dispersion and the strong metal-support interaction as well as the synergic effect between Co and Ni.

### 2.5 | MgO-based solid-solution catalysts

MgO, which possesses high thermal stability and low cost, is an excellent catalyst support. The very high melting point (2852°C) of MgO can maintain its relatively large surface area at high temperatures compared to most oxides used as catalyst supports. Furthermore, basic metal oxide MgO has the same crystal structure as NiO (and CoO). As a result, the combination of MgO and NiO (or CoO) can easily form a solid-solution catalyst with a basic surface, which is helpful in inhibiting carbon deposition. The basic surface increases CO₂ adsorption and thus reduces or inhibits carbon deposition. The reduction of NiO (or CoO) in the NiO-MgO (or CoO-MgO) solid solution is much more difficult than that of pure NiO (or CoO), which contributes to the formation of very small Ni particles to inhibit carbon deposition. It is generally recognized that the reduction of a metal oxide is determined by its metal-oxygen bond strength. However, we demonstrated that the reduction of a metal oxide is strongly dependent on both metal-oxygen bond strength of the metal oxide and the metal-metal bond strength of its metal product. Furthermore, it is revealed that a critical factor to control the reduction of NiO (or CoO) in the solid solution is the isolation effect that NiO (or CoO) is isolated by MgO, which inhibits the metal-metal bond formation during the reduction.

Several groups reported the excellent results of CO₂ reforming of methane in the presence of NiO-MgO and CoO-MgO...
solid-solution catalysts. In 1995, we invented a highly efficient NiO/MgO solid-solution catalyst for DRM, which was prepared by impregnation and was calcined at 800°C and atmosphere pressure.\textsuperscript{223} The reduced solid-solution catalyst exhibited almost 100% conversion of CO\textsubscript{2}, >91% conversion of CH\textsubscript{4}, and >95% selectivity to CO and H\textsubscript{2} at 790°C and a very high space velocity of 60 000 mL (g catalyst)\textsuperscript{-1} h\textsuperscript{-1} with a CH\textsubscript{4}/CO\textsubscript{2} molar ratio of 1.0 (Figure 7). To the best of our knowledge, this would be the best performance among all reported results for DRM. In contrast to MgO, the other alkaline earth oxides (such as CaO, SrO, and BaO) were found to be poor supports for NiO probably due to sintering. The excellent catalytic performance of NiO/MgO was attributed to the formation of a solid solution.\textsuperscript{222,223} Furthermore, the conversion, selectivity, and stability characteristic of NiO/MgO solid-solution catalysts were found to be dependent on their composition, preparation conditions, and even the properties of MgO.\textsuperscript{24,224–227} For example, we found that high and stable CO yields (>95%) occurred with NiO/MgO catalysts having NiO contents between 9.2 and 28.6 wt%.\textsuperscript{24} No activity was observed for a NiO content of 4.8 wt%. At the high NiO content of 50 wt%, the CO yield decreased from 91% to 53% after 40 hours, and the catalyst became black, because of carbon deposition. In contrast, the other NiO/MgO solid-solution catalyst maintained their initial color, and no carbon deposition was detected by TEM even after 120 hours of reaction.\textsuperscript{219,220} This happened because too small amount of NiO in the NiO/MgO catalyst provided too-small numbers.
of Ni sites, and too-high amounts provided a big number of nickel metal particles that could easily sinter, generating large particles that facilitated carbon deposition.

Fujimoto et al.\textsuperscript{228–231} demonstrated that water treatment of the Ni\textsubscript{0.03}Mg\textsubscript{0.97}O solid-solution catalyst increased the catalytic activity and stability for CO\textsubscript{2} reforming of CH\textsubscript{4}. The excellent anticoking performance of the reduced NiO/MgO solid solution-catalyst can be attributed to the high dispersion of the reduced nickel species, the basicity of the support surface, and the nickel-support interactions. Zanganeh\textsuperscript{232} synthesized nanocrystal Ni\textsubscript{0.1}Mg\textsubscript{0.9}O with high surface area by surfactant assisted coprecipitation method. The catalyst showed stable catalytic performance for 122 hours at high temperatures. To correlate the structures of NiO/MgO solid-solution catalysts with their catalytic performances, other techniques, such as sol-gel and microemulsion synthesis approaches, were also employed to prepare NiO/MgO solid-solution catalysts.\textsuperscript{233–235}

CoO/MgO solid-solution catalysts exhibited similar catalytic performance to those of NiO/MgO.\textsuperscript{236–238} For example, an effective 12 wt% CoO/MgO solid-solution catalyst had a CO yield of 93\% and a H\textsubscript{2} yield of 90\% at the high space velocity of 60 000 mL (g of catalysts)\textsuperscript{−1} h\textsuperscript{−1} and 900°C, which remained unchanged during 50 hours.

3 | CO\textsubscript{2} OXIDATIVE COUPLING OF METHANE

Conventional oxidative coupling of methane has been realized by adding oxygen as oxidant, which is called OCM. The OCM follows complicated homogeneous (gas-phase) and heterogeneous (surface-catalyzed) reaction pathways. In the presence of oxygen, solid oxide catalysts can form active surface oxygen species that selectively abstract one hydrogen from methane to release free methyl radicals(CH\textsubscript{3}·) in the gas phase, which subsequently couples to form ethane. The reaction is followed by the dehydrogenation of ethane to form ethylene or by

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure6.png}
\caption{Stability test of core-shell catalysts at (A, B) 800°C and (C, D) 900°C and the supported catalysts at 800°C (E, F) in DRM reactions (Reaction conditions: CH\textsubscript{4}:CO\textsubscript{2}:N\textsubscript{2} = 1:1:1). Reprinted with permission from [211]. Copyright © 2017 Published by Elsevier Ltd.}
\end{figure}
the irreversible formation of oxidation products (CO or CO₂). Furthermore, it was reported that electrophilic lattice oxygen species and the facile filling of surface lattice oxygen vacancies by gas-phase oxygen are key factors to design efficient catalysts for the oxidative coupling of methane. Aika and Nishiyama are the first researchers to introduce CO₂ into the catalytic oxidative coupling of CH₄. They combined Equation 5 with Equation 12 to decrease free energy loss and utilize the oxygen of CO₂, leading to negative ∆G of the total reaction and 6.1% of theoretical yield for C₂ hydrocarbons. The following mechanism was proposed for the CO₂-promoted CH₄ coupling with O₂ (Equations 13-16):

\[
\begin{align*}
\text{CO}_2 & \rightarrow \text{CO} + \text{O}_{\text{ads}} \quad \text{(13)} \\
\text{O}_{\text{ads}} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{OH}_{\text{ads}} \quad \text{(14)} \\
2\text{CH}_3 & \rightarrow \text{C}_2\text{H}_6 \quad \text{(15)} \\
2\text{OH}_{\text{ads}} & \rightarrow \text{H}_2\text{O} + \text{O}_{\text{ads}} \quad \text{(16)}
\end{align*}
\]

Effective surface activation of CO₂ plays an important role in coupling of CH₄. Isotope and kinetic evaluations revealed that the oxygen atoms of CO₂ participate the CH₄ coupling through the reverse shift reaction of CO₂, and C₂ hydrocarbons can further react with the oxygen from CO₂ under conditions of high conversion. If oxygen is replaced with CO₂ to realize CO₂-oxidative coupling of methane (CO₂-OCM), the conversion mechanism of methane involves following steps:

1. oxygen-assisted breakage of a C-H bond of CH₄ on catalyst surface;
2. heterogeneous decomposition of CO₂ to CO and oxygen active species on catalyst surface;
3. homogeneous recombination of CH₃· radicals released from the surface;
4. homogeneous oxidative or radical dehydrogenation of C₂H₆ to C₂H₄.

In this mechanism, (a) and (b) are surface reactions for activation of CH₄ and CO₂, in which produced O radical intermediate can attack CH₄ molecular to attain CH₃· intermediate. Two CH₃· radicals can combine to form C₂H₆ (reaction c), followed by dehydrogenation to C₂H₄ (reaction d) or adding another CH₃· to generate a higher hydrocarbon. However, CH₄ activation may also include lattice oxygen of catalyst. Therefore, CO₂-OCM would have two kinds of oxidant: lattice oxygen and oxygen active species from CO₂ decomposition, both of them are involved in the surface reaction associated with active sites of catalyst. It was shown that the selectivity of the methane oxidation reaction is determined by the ability of the oxygen active species on the catalyst surface to discriminate between a C-H bond in methane and a weaker C-H bond in the product(s). Those are strongly
dependent on the properties of catalysts, which has promoted intensive research to explore efficient catalysts for CO2-OCM (Table 1).

### 3.1 Mono-component catalysts for CO2-OCM

It is generally recognized that the activation of CO2 requires electron transfer from the catalyst probably through an anionic CO2− precursor. Although CO2 is easily adsorbed on alkaline earth metals (such as CaO), it is unable to activate CO2 over CaO because CaO cannot donate electrons. However, CO2 can be activated by ZnO due to its defects, which are generated by reducing Zn2+ with electrons from CH3 formed by splitting of methane. The existence of defect sites such as Zn1+ or oxygen vacancy centers has been reported for ZnO, which may be responsible for CO2 activation. Nevertheless, C2 selectivity is less than 5% and thus its yield is very low over ZnO alone. This happened probably because ZnO is not efficient for CH4 splitting.

Asami et al. evaluated various unsupported metal oxides for C2 production by CH4 and CO2 reaction at 850°C. As shown in Figure 8, C2 yield and selectivity vary with different metal oxide. Rare earth metal (yttrium, lanthanum, and samarium) catalysts exhibited high selectivity of about 30%. Although C2 yield over manganese is comparable to that over yttrium, its C2 selectivity is considerably lower than that of yttrium. They also examined catalytic effectiveness of other unsupported metal oxides (including alkaline earth, rare earth, and transition metals) for C2 formation from CO2-OCM. For CO2-OCM over Pr oxide catalyst, the unstable lattice oxygen may participate in C2 formation through a redox mechanism.

### 3.2 Multi-component catalysts

Various metal oxides were combined as binary catalysts to improve catalytic performance for CO2-OCM. The binary oxides of rare earth and alkaline earth metals constitute the best type of catalysts. CaO/CeO2 mixed oxides, which form solid solutions with highly mobile lattice oxygen, are applied as model catalysts to evaluate the role of oxygen mobility in C2 production. In the CaO/CeO2 catalyst, oxygen ion conductivity can be tuned by changing the CaO content, whereas electron conductivity is negligible compared to anion conductivity. Although lower CH4 conversion and C2 selectivity were observed over CaO alone, the introduction of CaO to CeO2 can remarkably increase C2 selectivity. Wang’s group reported high C2 yield of more than 5% with C2 selectivity of 60%−70% for CaO-CeO2 catalysts. It was found that CO and H2 are the main products in the conversion of CH4 with the lattice oxygen of CaO-CeO2 without CO2, while the presence of CO2 induced the formation of C2 hydrocarbons that increased with increasing partial pressure of CO2. They proposed that CO2 adsorbs on Ca2+ sites and subsequently yield active oxygen species on neighboring Ce3+ or other metal sites, which work as an oxidant to convert CH4 to C2 hydrocarbons. The similar results were obtained by Litawa et al.251 The synergistic effect of catalytic basicity and reducibility in CaO-MnO/CeO2 on CO2-OCM were evaluated by Amin’s group with CO2-TPD and H2-TPR. It was demonstrated that the introduction of CaO into MnO/CeO2 could increase the basicity, leading to enhancement in CO2 adsorption. The proper amount of CO2 adsorbed on the CaO-MnO/CeO2 catalyst may inhibit the redox reaction involving the lattice oxygen and promote the defect sites or oxygen vacancy on Mn2.7+ (mainly due to Mn3O4) and/or Ce3+. In this process, basic Ca2+ sites are responsible for absorbing CO2, and then the Ce3+ and Mn2.7+ sites activate CO2 to generate CO and active oxygen species (possibly O−). The oxygen species can convert CH4 to CH3 radical. Furthermore, they created Response Surface Methodology (RSM) to optimize process parameters and catalyst compositions for CO2-OCM, leading to the maximum selectivity of 82.62% for C2 hydrocarbons over the CaO-MnO/CeO2 (with 8.2 wt% CaO and 6.8 wt% MnO) at 1.9 ratio of CO2/CH4 and reactor temperature of 807°C. The solid-solution feature of CeO2/CaO catalyst may play a role in the above activation process. CaO can partially dissolve in CeO2 to form a fluorite-type solid solution, creating a synergistic effect between CaO and CeO2 on the C2 selectivity. Although the increase of P(CO2) did not affect the C2 selectivity over individual CaO or CeO2,
the selectivity increased with increasing $P(\text{CO}_2)$ over CaO-CeO$_2$ catalyst. This indicates that CO$_2$ plays a crucial role in the selective formation of C$_2$ hydrocarbons over the catalyst. The formation of solid solution, which possesses neighboring Ca$^{2+}$ and Ce$^{3+}$ sites, is efficient for CO$_2$ adsorption and its subsequent activation. Furthermore, the incorporation of bivalent Ca$^{2+}$ cation into CeO$_2$ lattice generates defect sites, which promote redox reactions between Ce$^{4+}$ and Ce$^{3+}$. This may be the reason why the formation of CaO-CeO$_2$ solid solution can increase in the rate of CH$_4$ conversion.

For CO$_2$-OCM, Zn$^{2+}$ in ZnO can accept electrons from CH$_4$ formed by splitting of methane and the subsequent reduction of adsorbed oxygen to O$_2$ lattice oxygen by electron transfer from Zn$^{1+}$ or Zn. The existence of defect sites in ZnO (such as Zn$^{1+}$ or oxygen vacancy centers) may be responsible for CO$_2$ activation. However, C$_2$ selectivity is less than 5% over ZnO alone. To improve catalytic performance, ZnO$_2$ was combined with other metal oxides for more efficient catalysts. Chen’s group prepared ZnO/La$_2$O$_3$ by impregnating ZnO with lanthanum nitrate solution and evaluated its catalytic performance with a fixed-bed reactor. The ZnO/La$_2$O$_3$ catalysts exhibited a high C$_2$ selectivity of 90%, which is larger than that of pure ZnO (7.6%) or La$_2$O$_3$ (56.8%). The interaction between ZnO and La$_2$O$_3$ was proposed to generate synergic sites at La$_2$O$_3$-ZnO interfacial area, which are responsible for converting CH$_4$ and CO$_2$ into C$_2$ hydrocarbon. Furthermore, Grzybek et al. demonstrated that doping ZnO into NaOH-CaO catalyst can increase C$_2$ selectivity. This was supported by experimental results from Wang’s group, namely, CaO/ZnO with a Ca/Zn ratio of 0.5 exhibited the highest C$_2$ selectivity (80%) and yield (4.3%) for CO$_2$-OCM, which are higher than those of CaO/CeO$_2$. In the absence of CO$_2$, ZnO was reduced to Zn after the reaction, which was proved by XRD patterns of deposit downstream on the wall of the reactor. The main products are CO and H$_2$. In contrast, when CO$_2$ existed, XRD diffraction peaks remained almost unchanged and no deposit was detected. This indicates that the catalyst reduced by CH$_4$ is instantly reoxidized by CO$_2$ to form CO and the active oxygen species. Zinc sites associated with the reduced state or oxygen vacancies connected to the zinc sites are responsible for CO$_2$ activation. Raouf et al. employed CaO-ZnO catalyst as the secondary bed to combine the main bed of Li$_2$MgO, leading to the increase in selectivity and yield of C$_2$ hydrocarbons at relatively low temperature. The combination between CeO$_2$ and ZnO without alkaline earth metal oxide exhibited promising catalytic performance for CO$_2$-OCM. He et al. prepared CeO$_2$/ZnO nanocatalyst by a novel approach, in which homogeneous precipitation was combined with microemulsion. CO$_2$-TPD exhibited a larger peak of CO$_2$ desorption, implying that the nanocatalyst had a higher density of basic sites. ZnO could modulate the intensity of the surface basicity through adjusting the intensity of the strong basic sites and weak basic sites. The conversion of methane over the CeO$_2$/ZnO nanocatalyst showed 83.6% selectivity and 4.76% yield for C$_2$, which are higher than those over the CeO$_2$/ZnO catalysts prepared by conventional method. Furthermore, the nanostructured CeO$_2$/ZnO catalyst also exhibited a high stability.

Oxide catalysts of Mn and alkaline earth metals (Ca, Sr, and Ba) were explored for the coupling of CH$_4$ to C$_2$ hydrocarbons (C$_2$H$_6$ and C$_2$H$_4$) using CO$_2$ as oxidant. The binary oxides showed different behaviors in different range of reaction temperature, which may be caused by different phase composition. The Ca-Mn oxide catalyst exhibited similar catalytic performances to those of other Ca-containing binary oxides at 840°C. However, reducing reaction temperature to 825°C caused rapid decrease in CH$_4$ conversion and C$_2$ selectivity. This was attributed to the phase transformation of Ca$_{0.48}$Mn$_{0.52}$O to CaCO$_3$. Furthermore, in the temperature range of 700-900°C, the Sr-Mn oxide catalyst showed the highest C$_2$ selectivity, the Ca-Mn oxide catalyst the lowest, and the Ba-Mn oxide catalyst in between. The Sr-Mn oxide catalyst provided a high C$_2$ yield of 63.5% with C$_2$ selectivity of 64% at 900°C. It was found that SrMnO$_{2.5}$ and BaMnO$_{2.5}$ are the main phase compositions for Sr-Mn and Ba-Mn oxide catalysts in the reaction, respectively. These species with Mn$^{3+}$ probably catalyze the activation of CH$_4$. In addition, MnO-SrCO$_3$ was prepared by simultaneously adding solutions of Mn(NO$_3$)$_2$ and Sr(NO$_3$)$_2$ with aqueous solution of K$_2$CO$_3$. The catalyst showed the maximum C$_2$ yield of 5.1% with a C$_2$ selectivity of 68.1% at 900°C. The excellent performance of the MnO-SrCO$_3$ catalyst for the CH$_4$-CO$_2$ reaction could be attributed to both the dissociation of SrCO$_3$ to form CO$_2$ and the formation of an Mn$^{3+}$/Mn$^{2+}$ couple to activate CO$_2$, and thus to activate CH$_4$. A possible mechanism for CH$_4$ and CO$_2$ to produce C$_2$ hydrocarbons over Mn-SrCO$_3$ was proposed by as follows:

$$\text{SrCO}_3 \xrightarrow{\Delta} \text{SrO} + \text{CO}_{2\text{ads}} \quad (17)$$

$$\text{CO}_{2\text{ads}} + \text{Mn}^{3+} \rightarrow \text{Mn}^{2+} + \text{CO} + \text{O}^- \quad (18)$$

$$\text{O}^- + 2\text{CH}_4 + \text{Mn}^{3+} \rightarrow 2\text{CH}_3 + \text{H}_2\text{O} + \text{Mn}^{2+} \quad (19)$$

$$2\text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad (20)$$

$$\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_4 + \text{H}_2 \quad (21)$$

$$\text{SrO} + \text{CO}_2 \rightarrow \text{SrCO}_3 \quad (22)$$

### 4 | PLASMA-ASSISTED CONVERSION OF CH$_4$ AND CO$_2$

Nonthermal plasma (NTP) is considered as a promising alternative process for the conversion of CH$_4$ and CO$_2$ due to its ability to initiate reactions at near ambient temperature. NTP configurations, which have been exploited for dry reforming configurations.
reaction, include gliding arc discharges, dielectric barrier discharge (DBD), corona discharges, and glow discharges. The most promising one is DBD due to its high electron density and ability to produce highly reactive species at room temperature. Furthermore, to improve the selectivity to desired syngas, DBD would be combined with heterogeneous catalysts, such as Pd (Cu, Ni, Co, Mn, or Ag) supported on γ-Al₂O₃. So far, most of the catalysts used for plasma-assisted DRM are Ni-based catalysts, especially Ni/Al₂O₃. However, the conversions of CH₄ and CO₂ in plasma-assisted DRM are usually lower than those from conventional DRM. This means that the coupling of the plasma with the catalyst did not generate a plasma-catalytic synergy in NTP process. Nevertheless, Tu and Whitehead observed the plasma-catalyst synergetic effect on DRM, which is dependent on packing methods. They found that, when the 10 wt% Ni/Al₂O₃ catalyst in flake form calcined at 300°C was partially packed in the plasma, the synergy of plasma-catalysis was clearly observed, leading to the doubled CH₄ conversion and H₂ yield (17.5%). This synergistic effect also contributes to a significant enhancement in the energy efficiency of feed gas conversion. This synergistic effect from the combination of low temperature plasma and solid catalyst can be attributed to both strong plasma-catalyst interactions and high activity of the Ni catalyst calcined at low temperature (300°C). A higher conversion was also obtained by plasma with NiO/Al₂O₃ (or NiO-MnO₂/Al₂O₃) catalyst compared to plasma alone, whereas the best syngas ratio was achieved with plasma alone. The increase in CO₂ and CH₄ conversions were obtained by plasma over Ni, Co, or Cu catalyst. Furthermore, the plasma-assisted DRM is able to achieve coke free. This may be attributed to highly reactive radicals which can easily react with carbon atoms to inhibit coke formation.

As shown above, previous work on DRM with NTPs mainly focused on syngas production, whereas very limited efforts were devoted to CO₂-OCM for the synthesis of liquid fuels and chemicals. This is because plasma-catalytic CO₂-OCM systems possess low selectivity with various products, including syngas, higher hydrocarbons, and oxygenates. The use of NaX zeolite could inhibits the formation of the undesired solid carbonaceous species and increases the selectivity of hydrocarbons (ethane, ethylene, acetylene, propane, propene, butane et al. with syngas). Higher CH₄ conversion and C₂ selectivity could be obtained by Pd/Al₂O₃ catalyst. Furthermore, Na-ZSM-5 exhibited a selectivity for production of liquid aromatic hydrocarbons from CH₄-CO₂. The product distribution in solid catalyst-plasma system can also be adjusted by introducing third gas (such as O₂ and Ar) into CH₄/CO₂. Very recently, Tu and coworkers reported the synthesis of liquid fuels and chemicals from CO₂ and CH₄ at room temperature and atmospheric pressure using a novel DBD plasma reactor with a water electrode. For the DBD plasma process
without a catalyst, a total liquid selectivity of 59.1% was achieved with selectivities of 33.7, 11.9, 11.9, and 1.6% for acetic acid, ethanol, methanol, and acetone, respectively (in Figure 9A). The selectivity was only about 20.0% for CO (Figure 10B), and the conversion is 18.3% for CH₄ and 15.4% for CO₂ (Figure 9C). Furthermore, catalysts were exploited for the plasma process to tune the production of different oxygenates under ambient conditions. Cu/γ-Al₂O₃ catalyst packed in the DBD reactor enhanced the selectivity for acetic acid to 40.2%, which is higher than those of the plasma-only mode (about 34%) and the plasma reaction using γ-Al₂O₃ only (20.2%). The major product was acetic acid regardless of the catalyst used, followed by methanol and ethanol (Figure 9A). Formaldehyde (HCHO) was formed only when the noble metal catalysts were used in the plasma reaction, and the highest selectivity for HCHO was obtained with Pt/γ-Al₂O₃. The plasma processes with and without catalysts exhibited similar gaseous product distributions with H₂, CO, and C₂H₆ as major gaseous products (Figure 9B). However, combining the plasma with the catalysts resulted in 10%-20% increase for H₂ selectivity, slight increase for C₂H₆, and negligible effect on CO production with exception for Cu/γ-Al₂O₃. Compared to the plasma-only mode, the conversion of CO₂ and CH₄ slightly decreased with packing catalysts. This phenomenon was attributed to the change in discharge behavior induced by the catalyst, which had a negative effect on the reaction.

The density functional theory (DFT) was used to evaluate the synthesis reaction mechanism of hydrocarbons from CH₄ and CO₂ under cold plasmas. It was proposed that the main obstacle for the synthesis is the dissociation of CH₄ and CO₂, the cold plasma can supply the necessary energy for this dissociation through the use of its energetic electrons without extra heating gas. The electrons, which are the main species to initiate the discharge reactions, can activate CH₄ directly into methyl radical CH₃· without assistance of CO₂ (Equation 23). The methyl radical, which is the key species for the formation of hydrocarbons, can be further dissociated into CH₃ and CH₂, and even carbon. Dissociation of CO₂ can also be enhanced by electron attack (Equations 24 and 25), and oxygen species can terminate activating CH₄. There are two possible ways for CO₂ dissociation, namely, one is via CO₂⁺ and the other via CO. The chemical activation of CO₂⁺ is more facile. The pathways for syngas and hydrocarbons are similar to catalytic system without plasma. Carbon monoxide (CO) is principally generated from the dissociation of CO₂. The recombination of the H atoms, which comes from the hydrocarbon reaction with O species produced from CO₂ dissociation (Equations 26-28), produces H₂. Formation of higher hydrocarbon is via carbon chain growth initiated with methane dissociation by the electrons or hydrogen abstraction by some active species (O, H, and OH) (Equation 29).

\[
e + \text{CH}_4 \rightarrow \text{CH}_3 + H + e' \quad (23)
\]
\[
e + \text{CO}_2 \rightarrow \text{O}^- + \text{CO} \quad (24)
\]
\[
e + \text{CO}_2 \rightarrow O + \text{CO} + e' \quad (25)
\]
\[
\text{CH}_3 + O \rightarrow \text{CH}_3O \quad (26)
\]
\[
\text{CH}_2O \rightarrow \text{H} + \text{H}_2\text{CO} \quad (27)
\]
\[
\text{CH}_3O \rightarrow \text{H}_2\text{COH} \rightarrow \text{H} + \text{H}_2\text{CO} \text{ (or H}_2 + \text{HOC) } (28)
\]
\[
\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6 \quad (29)
\]
\[
* e' repesent electron with less energy
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5 | PHOTOCATALYTIC CONVERSION OF CH₄ AND CO₂

The conversion of CH₄ and CO₂ at low temperature is thermodynamically unfavorable. Furthermore, large energy requirement of dry reforming of methane (DRM) has obstructed its application. Solar energy would be a solution for the energy issue. Therefore, photocatalysis was exploited to break this thermodynamic limitation and to solve the issue of large energy requirement. Shimura and Yoshida explored Ga₂O₃ as a photocatalyst for CH₄ and CO₂ at lower temperature. They found that, under UV irradiation, DRM could not occur at temperature below 200°C. In contrast, CO₂ oxidative coupling of methane is the main reaction at room temperature under UV irradiation, producing ethane and hydrogen. However, when 200°C was used as operating temperature, both the photocatalytic CO₂ oxidative coupling of methane and the photocatalytic dry reforming of methane (PDRM) took place over β-Ga₂O₃ upon UV irradiation. Several Ga₂O₃ photocatalysts with the different crystal phase and specific surface area were evaluated. It was revealed that the product selectivity is largely depended on the surface structure of the Ga₂O₃ photocatalyst. Furthermore, the selectivity for products was also determined by the type of catalysts. For example, acetone with high selectivity (92%) is the main product over Cu/CdS-TiO₂/SiO₂ photocatalyst and C₂H₆ and CO over La-promoted TiO₂ photocatalyst. So far, there has been a very limited exploration for PDRM. Most reported PDRM processes exploited only UV light (which is about 4% of the total solar energy), leading to very low H₂ and CO yields (at the level of μmol/h/gcat). Recently, we reported a novel approach, in which the combination of Pt/blackTiO₂ catalyst with a light-diffuse-reflection-surface of a SiO₂ substrate
created an efficient visible light PDRM.\textsuperscript{292} Under visible light illumination by filtering UV from AM 1.5 G sunlight, H\textsubscript{2} and CO yields reached 71 and 158 mmol/h/g cat with quantum efficiency of 32.3\% at 550°C and 129 and 370 mmol/h/g cat with quantum efficiency of 57.8\% at 650°C (Figure 10). In contrast, without light irradiation, H\textsubscript{2} and CO yields were negligible at 550°C and very small (9 and 99 mmol/h/g cat, respectively) at 650°C. This indicates that the PDRM exhibited much better performance than the conventional thermocatalytic DRM. Furthermore, those H\textsubscript{2} and CO yields from the PDRM with the Pt/black-TiO\textsubscript{2} catalyst on the light-diffuse-reflection-surface of a SiO\textsubscript{2} substrate are three orders of magnitude larger than previously reported PDRM values. In this work, the black TiO\textsubscript{2}, which is a novel semiconductor with efficient absorption for visible light, played a role of photocatalyst and Pt (as cocatalyst) possesses an excellent activity to break C-H bonds of methane. Furthermore, the dispersion of Pt/black-TiO\textsubscript{2} catalyst on the light-diffuse-reflection-surface of a SiO\textsubscript{2} substrate could increase the light absorption of the photocatalyst by 100 times.

6 | TECHNOCO-ECONOMIC ANALYSIS

The economic analysis coupled with process simulation is called techno-economic analysis, and Aspen Plus is usually selected for simulating the reforming process.\textsuperscript{295} Furthermore, the techno-economic analysis of DRM is often compared with mature steam reforming of methane (SRM) that has been commercialized for several decades.\textsuperscript{296,297}
to DRM, SRM needs two reformers and extra desulfurizer unit, leading to its higher cost. However, if biogas or landhill gas is used as CH$_4$ and CO$_2$ sources for DRM, desulfurization is also needed. The furnace or combustion of natural gas can be used as heating units. There are two types of reformer reactors: the conventional packed-bed (PBR) reactor and the membrane reactor (MR). The latter reactor can produce syngas with lower cost due to the absence of compressor and pressure swing adsorption for gas purification. The running cost and the price of unit product can be valued by simulating process. For synthesis of methanol via syngas, DRM cost ($1066/MT$ methanol) is less than that of SRM ($1087/MT$ methanol), indicating that DRM is competitive to SRM. For a smaller production scale, the total cost of DRM is around $51533$/year with production of $7$ m$^3$/h H$_2$ using a conventional packed-bed reactor. However, as an emerging technology for direct conversion of CH$_4$ and CO$_2$ to highly valuable hydrocarbons, CO$_2$-OCM has not yet been evaluated by techno-economic analysis.

7 | CONCLUSION AND PROSPECTS

We discussed two routes to convert CH$_4$ and CO$_2$ into higher-valued products: Dry reforming of methane (DRM) for syngas production and the CO$_2$ oxidative coupling of methane (CO$_2$-OCM) for the formation of hydrocarbons.

For DRM, there are two types of catalysts: noble metal and non-noble metals. Noble metal catalysts (such as Pt, Pd, Rh, and Ru) possess excellent catalytic activity and selectivity as well as high stability with less carbon deposition, but they are expensive with limited source. Non-noble metals (such as Ni and Co) also exhibited excellent activity and selectivity for DRM to produce syngas at low cost. However, those non-noble metal catalysts suffered deactivation due to carbon deposition. Therefore, intensive efforts were made to inhibit the carbon deposition for the non-noble metal catalysts by employing three strategies: (1) increasing the interactions between metals and supports, (2) introducing promoters, (3) forming solid solutions to create isolation effect, and (4) generating core-shell structures. The target was successfully achieved by several types of catalysts, among which NiO/MgO solid-solution catalysts would be the best.

Three types of catalysts were explored for the production of C$_2$ hydrocarbons from CO$_2$-OCM: (1) the binary oxides of rare earth and alkaline earth metals, such as CaO/CeO$_2$ catalysts, (2) ZnO-based catalysts, such as La$_2$O$_3$/ZnO and CaO/ZnO, and (3) the binary oxides of Mn and alkaline earth metals (Ca, Sr, and Ba), such as Ca/Mn oxide catalysts and Sr/Mn oxide catalysts. Among them, the combination between the rare earth metal oxides and the alkaline earth metal oxides is the best. Furthermore, the increased attention was paid to the activation of CO$_2$ on the catalyst surface, because it plays a key role to increase C$_2$ selectivity. Therefore, most catalysts contain the component of alkaline metal oxides to increase the basicity of catalysts for CO$_2$ adsorption. Future research is necessary to design and synthesize highly efficient catalysts, which must possess unique ability to activate the C-H bond of methane without breaking the weak C-H bond of hydrocarbon products.

The critical issue for DRM, which has limited its commercialization, is large energy requirement. Solar energy is considered as its solution, which requires an efficient PDRM. However, most catalysts explored for PDRM are not efficient, because they can use only UV light (about 4% of the total solar energy). Recently, a progress was made by combining Pt/blackTiO$_2$ catalyst with a light-diffuse-reflection-surface of a SiO$_2$ substrate, which created an efficient visible light PDRM at relatively low temperature (much lower than the temperatures used in conventional DRM). This would open a new direction for the development of efficient DRM approaches. The increase in photocatalyst stability for PDRM would attract great attention in the future research.

Several catalysts were developed for photocatalytic CO$_2$ oxidative coupling of methane (CO$_2$-OCM) for hydrocarbons. However, their efficiency is quite low due to their feasibility only for UV light. The future research is required for the development of advanced catalysts, which can efficiently use visible light for photocatalytic CO$_2$ oxidative coupling of methane.

Plasma was exploited for the conversion of CH$_4$ and CO$_2$ at low temperature, and a broad distribution of products was obtained, including syngas and various hydrocarbons. Although the plasma-assisted processes could provide a high conversion rate, but a very low selectivity. This issue will stimulate future research to develop selectivity-controlled plasma processes for the conversion of CH$_4$ and CO$_2$.

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**How to cite this article:** Cai X, Hu YH. Advances in catalytic conversion of methane and carbon dioxide to highly valuable products. *Energy Sci Eng*. 2019;7:4–29. [https://doi.org/10.1002/ese3.278](https://doi.org/10.1002/ese3.278)