

Review

Low-temperature catalytic CO₂ dry reforming of methane on Ni-based catalysts: A review



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ABSTRACT

CO₂ dry reforming of methane (DRM) not only utilized the two greenhouse gases, CO₂ and CH₄, but also produced synthesis gas, which could be used for Fischer-Tropsch synthesis. Besides, DRM reaction could utilize marsh gas and the gaseous products from pyrolysis of biomass, consequently increasing their value for businesses and reducing environment pollution, thereby providing ways for sustainable development. Nickel based catalyst was widely used in DRM reaction. This paper reviewed the recent progresses of the DRM reaction at low temperature. Suitable supports and promoters improved the catalytic performance by adjusting the interaction between nickel and the support. Besides, the temperature of calcination, the order of materials loading on support, the reduction temperature, and the nickel particle size also altered the performance of the catalysts. It was suggested that by investigating the interaction of supports, promoters with nickel, as well as their structural adjustment, the development of low temperature DRM catalysts was feasible.

1. Importance of the CO₂ dry reforming of methane

Carbon dioxide reforming of methane also called dry reforming of methane (DRM) is of significant importance because of at least the following reasons. Firstly, since CO₂ and CH₄ were both greenhouse gases, the utilization of CO₂ and CH₄ could provide a way to reduce the greenhouse effect [1–4]. Secondly, CO₂ and CH₄ were also produced in the pyrolysis of biomass, then the utilization of CO₂ and CH₄ could also make more valuable the pyrolysis gases, enhancing the whole process more practical [5–7]. Thirdly, because the main components of the marsh gas from digestion were CO₂ and CH₄, the utilization of CO₂ and CH₄ could provide a way to make the biogas value-added [8,9]. However, if pyrolysis gases and biogas were directly used as fuel, the purification of the gases to remove CO₂ was generally needed, since CO₂ could not contribute to combustion, providing heat. Gases with high content of CH₄ could also be used in fuel cells for electricity generation, and synthesizing organic compounds such as CHFCl₂, CCl₄, CH₃OH and HCOOH [10–13]. On the other hand, in addition to the use of CO₂ in beverage additives, CO₂ could be used in supercritical extraction agent and synthesizing polyketide and polycarbonate [14–16]. Whereas DRM reaction utilizes directly both CO₂ and CH₄ simultaneously, which reduces the step of separation. Hence the DRM reaction is an effective way for the protection of environment and the effective utilization of energy resource, thereby providing ways for sustainable development

[3,17,18].

It is well known that the C–H bond in CH₄ is difficult to be activated [19,20], while CO₂ is the utmost oxidized state of carbon, which is also very stable [21–23]. The co-activation of both C–H bond in CH₄ and C–O bond in CO₂ faced challenging difficulties. Besides, because of the thermodynamics limitation, DRM reaction was usually performed at high temperature (~800 °C) [24–28]. Much progresses and significant achievements have been made for high temperature DRM [29–33], whereas the development of catalysts for the DRM reaction at low temperatures reaction (below 700 °C) was relatively scarce. In addition to high operating costs, high-temperature operation usually caused metal Ni sintering and coke formation, which would lead to catalyst deactivation [32,34–37]. Although many efforts, such as core-shell structure catalyst, have been made in solving the problems, the solution was far from being perfect [35,38–42]. Sibudjing Kawi [43] reviewed the advances in synthesis of high activity and stability Ni-based catalysts for DRM with emphasis on in-depth mechanism and reaction pathways on high stability and activity. Yasotha Kathiraser [44] underlined the importance of the kinetics and mechanistics in DRM reaction over Ni-based catalysts for the optimization of catalyst design and synthesis. Ziwei Li [45] also stressed the importance of the kinetic and mechanistic on DRM reaction over core/yolk-shell nanocatalysts.

According to detailed theoretical thermodynamic calculation of DRM reaction [46], as shown in Fig. 1a, the equilibrium conversions of

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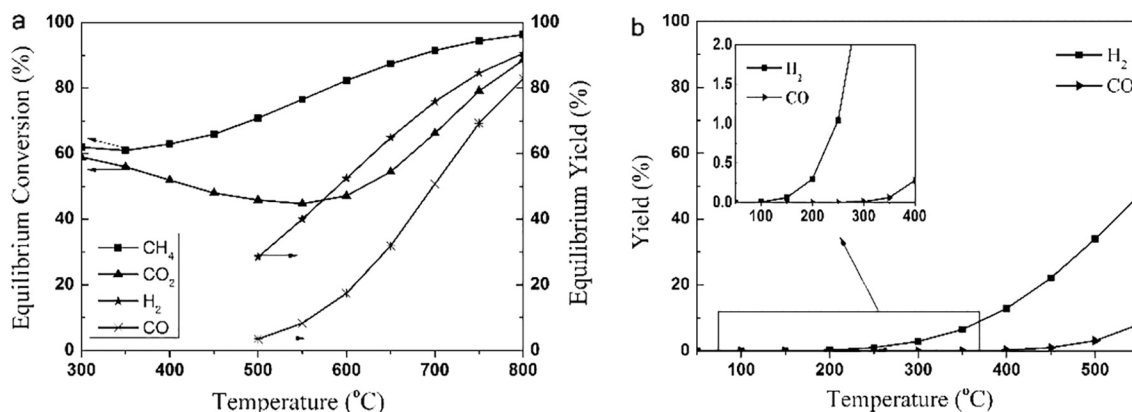
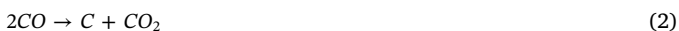


Fig. 1. The detailed theoretical thermodynamics calculation of DRM reaction. Condition: $F(\text{CH}_4) = F(\text{CO}_2)$; $p = 1$ atm.

CH₄ and CO₂ at 300 °C for DRM reaction were about 60% and 50%, respectively. Another detailed theoretical thermodynamic calculation of DRM reaction by Patrick Da Costa [2], showed that hydrogen could be generated starting at about 100 °C, while carbon monoxide might be produced starting at about 300 °C, as shown Fig. 1b. So the activation of both CH₄ and CO₂ at low temperature was thermodynamically feasible, which required the development of new efficient catalyst. Therefore, it is necessary to develop catalysts for low temperature DRM reaction, and more and more researchers [1,2,20,47–76] started to study low temperature (under 700 °C) CO₂ dry reforming of methane. Noble metal catalysts such as Pt [2,47], Rh [51,58,64], Ir [56] were widely explored, due to the high activity and preference resistance to deactivation. These active materials showed high activity and stability at low temperature (about 450 °C) for DRM reaction [51]. Taking the cost into account, more and more researchers turned their interests to nickel based catalyst on DRM reaction [77].

However, if nickel catalyst is applied at low temperature for DRM reaction, several challenges arise. Firstly, the activity was very low on the presently investigated nickel based catalysts [20,48,50,51,75]. Secondly, the catalyst deactivates rapidly due to formation of NiO shells covering Ni particles [69,78]. Thirdly, the coke deposition on the active metal owing to the methane direct decomposition reaction (1) and CO disproportionation reaction (2) [32,36,52,53,79,80] also deactivates the catalysts.



In the present work, we reviewed the recent advances in the development of Ni-based catalysts for low temperature DRM, with emphasis on the relationship between composition structure and performance of the catalyst. The effects of supports, promoter and several other preparation parameters on the low temperature DRM reaction were also discussed. Several suggestions for further development of low temperature DRM catalysts were provided.

2. The effect of several parameters on low temperature DRM

Many attempts had been made to achieve activation of both CH₄ and CO₂ on Ni-based catalysts at relatively low temperature. The activity of most of the previously reported Ni-based catalysts for low temperature DRM reaction is shown in Table 1.

2.1. The effect of nickel-support interaction on the performance of DRM

Researchers investigated mechanistically the interaction between nickel and various supports. The interaction of metal and support would have effect on the electronic effects, dispersion and size of nickel

particle. Bradford et al. [50] prepared different Ni based catalysts for low temperature DRM reaction, and found that the Ni/TiO₂ catalyst showed the highest activity with CH₄ conversion of 3.2% at 450 °C, due to the strong interaction of the metal and support, which would increase the electron density in the metal crystallites, thereby enhance the ability to activate C–H bond of methane. They also found that during the reduction process, TiO_x species would form, and the interaction of the nickel and TiO_x would increase the activity of the catalyst [51]. Ni/MgO [50] catalyst showed the lowest activity and highest stability. XRD and chemisorption results showed that Ni/MgO possessed strong Ni–O bond. It could be verified that the solid solution NiO–MgO formed, which directly increased the stability of the Ni–Ni bonds, due to excessive strength of strong electron donor. Besides, Ni/ZrO₂ [60] catalyst showed higher activity than Ni/CeO₂ at 700 °C due to the high surface area and controlled porosity. The small nickel particles deposited in the hole rather than on the surface of ZrO₂, thus achieving nanoparticles and better nickel dispersion. Ni/CeO₂ [60] and Ni/SiO₂ [69] also possessed high surface area, however they showed lower activity on DRM reaction. It was observed that the interaction of nickel and SiO₂ on Ni/SiO₂ catalyst was weak, whereas the strong interaction of the nickel and CeO₂ did not contribute to the enhancement of activity of Ni/CeO₂ catalyst. The reverse water-gas shift reaction took place preferably at low temperature on Ni/CeO₂ catalyst during the process of DRM reaction, which led to decrease of hydrogen selectivity. Zhang et al. [72] reported that the novel Ni/La₂O₃ catalyst exhibited an excellent activity at 550 °C reaction temperature and the activity increased within 5 h, which suggested that new active site formed under reaction conditions. However, because of the weaker interaction of the nickel and support SiO₂ or C [20,50,75], Ni/SiO₂ and Ni/C catalysts formed filamentous carbon under reaction conditions leading to the deactivation of the catalysts [50].

The above reports indicated that the nature and strength of the interaction of nickel with the supports would alter the performance of the catalysts. For example, the formation of solid solution NiO–MgO could enhance the stability of the catalyst. Ni/TiO₂ catalyst showed high activity attributing to the strong interaction of nickel and TiO₂, however, the strong interaction of the nickel and CeO₂ did not contribute to the enhancement of activity of Ni/CeO₂ catalyst.

To adjust the interaction of the nickel and supports, composite carriers were used to obtain higher activity for low temperature DRM reaction. Li et al. [62] prepared a series of Ni/BaTiO₃-Al₂O₃ catalysts with different content of BaTiO₃ for low-temperature DRM. At 690 °C, the Ni/32.4%BaTiO₃-Al₂O₃ catalysts showed the best activity and stability during 50 h time-on-stream. It was deemed that BaTiO₃ improved the dispersion of the active nickel and the NiO_x species with weakened electronic donor intensity, and then enhanced the stability of the catalyst. The initial CH₄ conversion on Ni/32.4%BaTiO₃-Al₂O₃, Ni/BaTiO₃

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