The effect of interfacial engineering on the deactivation resistance of nickel-based catalysts for dry reforming of methane

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Abstract. Methane dry reforming reaction (DRM) can convert CO₂ and CH₄, two kinds of greenhouse gases with very stable chemical properties, to produce syngas, which can be used to synthesize valuable industrial products. Nickel-based catalysts have been widely used in DRM because of their low cost and good catalytic activity. However, nickel application is limited by such as high-temperature metal sintering, carbon deposition and catalyst poisoning, which restricts the industrial application in DRM reaction. Compared with single metal nickel, the selective doping of multi metals and supports shows higher catalytic activity and anti-poisoning tolerance due to changing the chemical and structural properties of the catalyst by enhancing the alloy effect and the force between metal and support. This paper mainly reviews the catalysts with anti-coking, anti-sintering and anti-sulfur poisoning by tuning the metal-metal interaction and metal-support interaction (MSI) in DRM. The modification strategies in interfacial engineering and structure-performance relationship are discussed, and the existing difficulties and future development of Ni-based catalysts are proposed.

1. Introduction
With the increasing attention to the development of environment-friendly and renewable energy, the dry reforming of methane (DRM) is a hot spot in research and industry nowadays. It converts CO₂ and CH₄, two major greenhouse gases, into syngas (CO and H₂, H₂:CO=1:1), which is subsequently converted to higher value-added fine chemicals and fuels [1]. The main DRM process is a strong endothermic reaction, and the energy consumption is large, often accompanied by side reactions such as RWGS, CH₄ cracking and CO disproportionation reaction. The disproportionation reaction of CO is easy to occur in low temperatures, and the methane cracking is relatively active in high temperatures. CH₄ cracking and CO disproportionation are the main sources for carbon deposition. Alleviation of the side reactions in DRM is the key to the effective utilization of CH₄ and CO₂, in order to enhance the conversion of reactants and improve the anti-carbon deposition ability of the catalyst. Therefore, the selection of appropriate reaction conditions and catalysts is very important to reduce side reactions and promote the conversion of reactants.

In order to effectively reduce the required activation energy (Ea), resulting in lower energy required to reach the conversion state, a wide variety of metal catalysts are used in DRM. Noble metal-based
catalysts (Pd, Ru, Rh, Pt, Ir, etc.) exhibit high catalytic activities, but their industrial application is limited due to high cost and high processing temperature. In comparison, nickel-based catalysts have attracted much attention because of their good catalytic activities, low cost and easy availability [2]. However, at a high temperature, nickel-based catalysts suffer from several issues. For example, the migration of Ni atoms at high temperature (>500 °C) may cause the growth of large metal microcrystals, which adversely affects the metal particle size distribution and active catalytic surface area. Moreover, the agglomeration of nickel particles caused by sintering further leads to carbon deposition at the active site and accelerates the deactivation of the catalyst. In addition, biogas and natural gas, as easily available carbon sources, may contain sulfur compounds, including H2S, mercaptan, sulfide and Tetrahydrothiophene [3]. Thus, the poisoning issue of sulfur compounds chemisorption on metal catalysts to form metal sulfides is usually encountered.

Therefore, how to improve the ability of Ni to resist carbon deposition, metal sintering and catalyst poisoning has become the focus of research. In the following, the modifications to realize anti-carbon deposition, anti-sintering and anti-poisoning will be discussed in detail from two strategies: the alloy synergy and MSI effect.

2. Interfacial engineering

Interfacial engineering is a process to improve the physicochemical properties of nickel catalysts by adjusting the interaction between metals and supports due to the synergy between nickel and doped metals, and the electronic and chemical modification of Ni-support interface, which improves the catalytic activity by reducing the size of active metal, adding metal promoter, adjusting MSI, structural design and optimization of reaction parameters.

2.1. Interaction between alloys

2.1.1. Anti-coking. On the precious metal surface, the dissociation rate of methane is much lower than that of C oxidation, which hinders coke formation. Therefore, doping noble metals into Ni catalyst shows a significant improvement in the limitation of carbon deposition. The increase of methane activation barrier renders the Ni-Pt catalyst a better coke resistance. The formation of alloy plays an essential role in the change of electronic structure, which abates the adsorption of methane. Compared with nickel (111) and platinum (111), bimetallic Ni-Pt produces lower adsorption energy of H* and carbonaceous substances such as CO*, C* and CH*, which weakens hydrogen dissociation and enhances hydrogen formation, resulting in inhibited RWGS and higher H2/CO [4]. Similar to noble metals, transition metals can enhance the coking resistance of nickel catalysts by forming alloys. Compared with Pt, Fe-Ni alloys reduce coke through redox cycle. At the metal-support interface, Fe is partially oxidized by CO2 to FeO, and then FeO reacts with carbon deposits on the nickel surface to form CO through redox mechanism, resulting in less coke deposition. Also, Ni-Cu exhibits a promising anti-coking capability in DRM reaction. Density functional calculation reveals that the energy barrier of carbon adsorption increases, which promotes the removal of deposited carbon. The new active center also helps to weaken the interaction between the adsorbed coke species and the Ni active sites. Another transition metal Co facilitates the movement of coke on the catalyst surface, and reduces the chance of coke deposition on the Ni active center compared with pure Ni and Co surfaces [5]. In addition, the close proximity of W6+ and Ni2+ ions changes the electronic environment of Ni2+ ions, forming a "NiWAIO" phase, which hinders the diffusion of carbon in its lattice and removes the remaining carbon on the surface through the carbonization and gasification mechanism of tungsten carbide [6].

2.1.2. Anti-sintering. The alloying of nickel with other metals can finely tune the surface structure of nickel, so as to inhibit thermal sintering. When noble metals are added to nickel-based catalysts, the oxidation of nickel can be reduced due to the oxidation resistance of noble metals. Owing to the dilution effect of precious metals, when the platinum atom layer covering nickel body is heated, Pt
monolayer and Ni form a core-shell structure, which was conducive to the oxidation of CH, the removal of carbon and enhancement of the Ni dispersion. However, for cost-effective catalyst manufacturing, precious metals are rarely considered as the second metal in nickel alloy catalyst system. Transition metals have recently been used to form alloys with nickel. Adding a small amount of Ta can dilute the nickel on the surface, generating a small Ni particle size [7]. However, high content of Ta has a negative effect on the reducibility of nickel, because the lattice structure of nickel is saturated and the synergy of Ni-Ta is limited at a high concentration (Fig. 1). For Ni-Fe alloy, redox cycle is applied to oxidize Fe to FeOₓ to stabilize metal Ni. Different from Fe, Cu and Ni have similar face centered cubic metal crystal structures and lattice constants, which promotes the formation of a stable Ni alloy, thus leading to a high dispersion of nickel and reduced agglomeration.

Figure 1 (Ⅰ) Sketch map of Ni-Ta/ZSM-5 catalytic dry reforming of methane. (Ⅱ) H₂-TPR curve of catalyst. (a) 10Ni, (b) 7Ni-3Ta, (c) 5Ni-5Ta, (d) 3Ni-7Ta and (e) 10Ta. Reproduced with permission from [7], Copyright 2020, Elsevier.

2.1.3. Anti-poisoning. Transition metal molybdenum has been widely used as active sites or promoters in different desulfurization processes because of its excellent absorption and resistance to sulfur components. The interaction between MoOₓ and NiOₓ through electronic effect makes the oxygen in the catalyst "inactive", which leads to the continuous sulfur adsorption of H₂S and improves the catalytic activity of NiMo alloy [8]. In another case, Ni₄ clusters on the surface of YSZ are easy to deform under sulfur adsorption. In contrast, when Ni-Re alloy clusters are formed on YSZ, the deformation under sulfur adsorption and the subsequent loss of catalytic activity are both inhibited, benefiting the activation of reactant molecules not occupied by sulfur atoms, so as to enhance the stability in DRM reaction [9].

2.2. Interaction between metal and support

2.2.1. Anti-coking. One of the main problems of DRM is serious carbon deposition on the Ni catalyst. Therefore, by adding promoters, the interaction between metal and support can be enhanced and carbon deposition could be inhibited. For example, the addition of K hinders the accumulation of carbon on the catalyst surface and changes the MSI. The addition of Mn, Zn and Ca leads to a increase in methane conversion and a decrease in carbon deposition. Rare earth metal additives contribute to the formation of small nickel particles and inhibition of carbon formation. With the help of mesoporous support La₂O₃ₓ, Ni dispersion is enhanced due to the strong MSI, which also promotes the formation of bicontact carbonate and coke removal [10], despite the side reactions in the presence of La₂O₃, such as the direct decomposition of methane. Similar to La, finely dispersed nickel particles are confined by ceria particles and quite scattered on the surface of silica. The small nickel particles are in close contact with the small cerium oxide particles, which is conducive to the gasification of
carbon species. Furthermore, Ni/ZrO\textsubscript{2} is doped with rare earth metals (Ce, La, Sm, Y) and its effect on coking process is observed. The results show that the oxygen adsorbed on the surface can significantly promote the dissociation of methane and the activation of CO\textsubscript{2}. Yttrium promoter showed the best surface oxygen adsorption catalyst activity, followed by Sm, La, Ce and undoped catalyst [11]. Apart from the rare earth metal, the addition of the transition metal Co strengthens the interaction between Ni and $\gamma$-Al\textsubscript{2}O\textsubscript{3}-HY zeolite support, which increases the formation of new active sites [12]. In Ni/Al\textsubscript{2}O\textsubscript{3}, doped TiO\textsubscript{2} furnishes a mesoporous structure with high specific surface area and promotes the high dispersion of Ni particles. Moreover, the close contact between free NiO and Al\textsubscript{2}O\textsubscript{3} matrix promotes the formation of aluminate phase. The synergistic effect of titanium dioxide and alumina provides high coke resistance.

2.2.2. Anti-sintering. Similarly, different MSI have different effects on the sintering of active Ni. Alkaline earth metals Ca and Mg as dopants can strengthen the interaction between Ni and support. The interaction between Ni and MgO in NiO-MgO solid solution restricts the growth of nickel particles. On the other hand, the doping of rare earth metal Ce can induce strong MSI, stabilizing the Ni nanoparticles against thermal sintering, thus benefiting the selective activation of the first C-H bond in methane and resulting in a high activity and stability within 100 hours [13]. Besides the alkali earth metal, when rare earth metal oxide Y\textsubscript{2}O\textsubscript{3} is doped in Ni catalysts, the flake structure composed of nickel particles on the surface controls the size and dispersion of nickel. However, the addition of promoter may reduce the surface area of the support, resulting in poor interaction between nickel particles and the support. The addition of La\textsubscript{2}O\textsubscript{3} improves the reduction of nickel, but Ni mainly locates near the orifice and some NiO species fail to firmly bind to the support, resulting in the blockage of the pores of the catalyst [14]. In some cases, strong MSI leads to the reduction of nickel active sites covered by oxides.

2.2.3. Anti-poisoning. Due to the inevitable generation of impurities in the process of methane production, the deactivation of nickel catalyst is obvious when sulfur impurities exist in the feed stream. Even the existence of trace sulfur content after purification may lead to the deactivation of nickel catalyst. Other compounds such as oxygen or nitrogen have little or negligible negative effects on the stability of the catalyst.

The results of the research indicates that the chemical adsorption between sulfur and nickel is easy to form metal sulfide, covering the surface active sites of the catalyst and resulting in the deactivation of the catalyst. Therefore, the key factor of sulfur deactivation and regeneration on nickel catalyst is the formation and removal of Ni\textsubscript{7}S\textsubscript{6} [15]. La\textsubscript{2}O\textsubscript{3} is susceptible to H\textsubscript{2}S poisoning and generates stoichiometric nickel sulfide and lanthanum sulfide (LaS and La\textsubscript{2}S\textsubscript{3}). Also, CeO\textsubscript{2} is selected as a sacrificial body to provide active oxygen anions to reduce sulfur poisoning and deactivation of the active phase by promoting the formation of sulfur oxide. Considering the Gibbs free energy of cerium sulfide and nickel sulfide, compared with the formation of NiS (s), the formation of Ce\textsubscript{2}O\textsubscript{2}S (s) is more spontaneous in thermodynamics, which is conducive to maintaining the number of active sites of Ni [16].

3. Conclusion
For the synergistic effect in alloys, doping precious metals can enhance the reduction of nickel and prevent metal oxidation. Transition metals with oxygen affinity or redox cycle selectively expose specific sites, thus improving the carbon deposition resistance. The strong interaction between support and Ni can enhance the dispersion by anchoring active Ni particles, providing abundant catalytic active sites. The addition of rare earth metal oxides can reduce sulfur poisoning and deactivation of active Ni and improve reaction efficiency by providing oxygen anion for the formation of sulfur oxide. However, there are still some work for further improvement in the future: Strategies can be explored in order to develop multi-functional anti-deactivation catalyst systems with a high conversion. Interfacial engineering plays a certain role in the inhibition of sulfur poisoning in reforming reaction.
Therefore, the mechanisms of reducing sulfur poisoning can be studied in depth by using advanced characterization techniques. In addition to alloy formation and addition of promoters, other factors can be put into consideration to optimize the interfacial property, such as thermal treatment parameters.

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