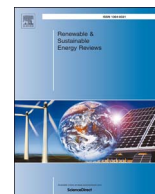




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Catalyst design for dry reforming of methane: Analysis review

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ABSTRACT

The performance of catalysts used for the dry reforming of methane can strongly depend on the selection of active metals, supports and promoters. This work studies their effects on the activity and stability of selected catalysts. Designing an economically viable catalyst that maintains high catalytic activity and stability can be achieved by exploiting the synergic effects of combining noble and/or non-noble metals to form highly active and stable bi- and tri-metallic catalysts. Perovskite type catalysts can also constitute a potent and cost effective substituent. Metal oxide supports with surface Lewis base sites are able to reduce carbon formation and yield a greater stability to the catalyst, while noble metal promoters have proven to increase both catalyst activity and stability. Moreover, a successful metal-support-promoter combination should lead to higher metal-support interaction, lower reduction temperature and enhancement of the anti-coking and anti-amalgamation properties of the catalyst. However, the effect of each parameter on the overall performance of the catalyst is usually complex, and the catalyst designer is often faced with a tradeoff between activity, stability and ease of activation. Based on the review carried out on various studies, it is concluded that a catalyst design must take into consideration not only the separate effects of the active metal, support and promoter, but should also include the combined and mutual interactions of these components.

1. Introduction

The dry reforming of methane (DRM) is a chemical process that consists of converting methane and carbon dioxide, identified as the world's most abundant greenhouse gases (GHG) [1], to syngas (hydrogen and carbon monoxide), with a H₂/CO molar ratio of 1 [2,3]. As a result, this process has the potentials to mitigate the environmental challenges associated with GHG emissions and to convert biogas and natural gas to syngas [4–6]. Moreover, the lower H₂/CO ratio syngas produced is convenient for the production of hydrocarbons via Fischer-Tropsch synthesis [7–9], in addition to the synthesis of oxygenated chemicals [10,11]. The reaction governing DRM is:



Being an extremely endothermic reaction [12,13], DRM requires high operating temperatures, usually in the range of 900–1273 K, to achieve the desirable conversion levels. The forward reaction is favored at low pressures as dictated by stoichiometry. Moreover, it has been noticed that a CO₂/CH₄ molar ratio higher than the stoichiometric requirement of 1 can also lead to high syngas yields. The positive effects of high reaction temperatures, low pressures and high CO₂/CH₄ molar

ratios on the conversion levels were investigated and confirmed in several studies [14–16].

Despite its considerable environmental potentials, DRM is not considered an industrially mature process. The extremely high endothermic reaction, coupled with rapid carbon formation eventually leads to the catalyst deactivation. In addition, the long reaction time and the requirement for pure CO₂, renders DRM an impractical process that still needs further developments [17–21].

In the present article, the performance of different catalysts used in DRM is intensively discussed. The effect of active metals, supports and promoters on the quality of the catalysts are investigated. This article gives a better understanding of catalyst design taking into consideration the effects of active metals, supports and promoters and their synergic effect.

2. Thermodynamics, reaction mechanisms and coke formation

2.1. Thermodynamics

Compared to autothermal (ATR) and steam reforming (SRM), the dry reforming of methane is the most endothermic reaction. This can be

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Table 1
Possible reactions in dry reforming of methane [13,14].

| Reaction | ΔH 298 K kJ/mol | Ln (Keq) at 573 K | Ln (Keq) at 1373 K | Favored by |
|--|-------------------------|-------------------|--------------------|-------------------|
| $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$ | 247 | -20 | 13 | High Temperatures |
| $\text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O}$ | 41 | -5 | 2 | High Temperatures |
| $2\text{CH}_4 + \text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO} + \text{H}_2\text{O}$ | 106 | -19 | -5 | High Temperatures |
| $2\text{CH}_4 + 2\text{CO}_2 \rightleftharpoons \text{C}_2\text{H}_4 + 2\text{CO} + 2\text{H}_2\text{O}$ | 284 | -36 | 0 | High Temperatures |
| $\text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$ | 136 | -14 | 4 | High Temperatures |
| $\text{CO} + 2\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH}$ | -90.6 | -10 | -20 | Low Temperatures |
| $\text{CO}_2 + 3\text{H}_2 \rightleftharpoons \text{CH}_3\text{OH} + \text{H}_2\text{O}$ | -49.1 | -12 | -20 | Low Temperatures |
| $\text{CH}_4 \rightleftharpoons \text{C} + 2\text{H}_2$ | 74.9 | -6 | 5 | High Temperatures |
| $2\text{CO} \rightleftharpoons \text{C} + \text{CO}_2$ | -172.4 | 15 | -7 | Low Temperatures |
| $\text{CO}_2 + 2\text{H}_2 \rightleftharpoons \text{C} + 2\text{H}_2\text{O}$ | -90 | 8 | -5 | Low Temperatures |
| $\text{H}_2 + \text{CO} \rightleftharpoons \text{H}_2\text{O} + \text{C}$ | -131.3 | 12 | -6 | Low Temperatures |
| $\text{CH}_3\text{OCH}_3 + \text{CO}_2 \rightleftharpoons 3\text{CO} + 3\text{H}_2$ | 258.4 | 10 | 40 | High Temperatures |
| $3\text{H}_2\text{O} + \text{CH}_3\text{OCH}_3 \rightleftharpoons 2\text{CO}_2 + 6\text{H}_2$ | 136 | 20 | 37 | High Temperatures |
| $\text{CH}_3\text{OCH}_3 + \text{H}_2\text{O} \rightleftharpoons 2\text{CO} + 4\text{H}_2$ | 204.8 | 14 | 37 | High Temperatures |
| $2\text{CH}_3\text{OH} \rightleftharpoons \text{CH}_3\text{OCH}_3 + \text{H}_2\text{O}$ | -37 | 3 | -1 | Low Temperatures |
| $\text{CO}_2 + 4\text{H}_2 \rightleftharpoons \text{CH}_4 + 2\text{H}_2\text{O}$ | -165 | 14 | -10 | Low Temperatures |
| $\text{CO} + 3\text{H}_2 \rightleftharpoons \text{CH}_4 + \text{H}_2\text{O}$ | -206.2 | 14 | -11 | Low Temperatures |

attributed to the fact that CO_2 , the oxidizing agent used in DRM, is the most stable compared to oxygen and steam used in ATM and SRM respectively [18–22].

Although DRM is mainly governed by the reaction between CH_4 and CO_2 (reaction 1), several other reactions can also occur during the process. Nikoo and Amin [14] presented these different reactions (Table 1), their equilibrium constants as a function of temperature (Fig. 1) and carried out the corresponding thermodynamics analysis. The equilibrium composition of the reaction system was analyzed based on the Gibbs free energy minimization method.

The authors concluded that the main reaction of dry reforming (reaction 1) is thermodynamically favored at reaction temperatures higher than 1000 K. Similar conclusions were reached by Bradford and Vannice [5], Wang et al. [13] and Istadi et al. [23].

Nikoo and Amin [14] identified that methane decomposition (reaction 8), carbon monoxide disproportionation (i.e. Boudouard reaction) (reaction 9), hydrogenation of carbon dioxide (reaction 10), and hydrogenation of carbon monoxide (reaction 11) are the four reactions responsible for carbon formation during DRM. Among these reactions, it was found that only (reaction 8) is favored at high temperatures, while the other three are favored when operating at reaction temperatures lower than 800 K. Furthermore, it was found that the Reverse Water Gas-Shift RWGS (reaction 2), which is the reaction that leads to a H_2/CO ratio less than unity, is dependent on the equilibrium at a certain temperature range and is usually present during DRM.

On the other hand, Wang et al. [13] reported that the RWGS and Boudouard reaction will not occur at temperatures exceeding 1093 K, and that the Boudouard reaction and methane decomposition will be

mostly responsible for the formation of carbon at temperatures ranging from 830 K to 973 K (Table 2).

Zhang et al. [24] reported an increase of the equilibrium constants of methane decomposition and RWGS with temperature and its decrease for the Boudouard reaction.

Concerning the remaining reactions shown in (Table 1), the oxidative coupling of methane (reaction 3 and 4) were found to be only possible at very high temperatures. Similarly, the dehydrogenation of ethane (reaction 5) is also favored at high temperatures. On the other hand, the reverse of reaction 6 and 7 are more favored at high temperatures. Conversely, reactions 12, 13 and 14 are favored at any temperature range and reaction 15 is dependent on equilibrium limitations. Finally, due to their exothermic nature and negative $\ln(K)$ values, reactions 16 and 17 have the possibility of occurring at temperatures lower than 800 K.

2.2. Reaction mechanism

The mechanism of methane dry reforming is detailed by Papadopoulou et al. [25]. It can be summarized in four steps as follows:

1. Dissociative adsorption of methane: although the dissociation energy of $\text{CH}_x\text{-H}$ bonds is dependent on the surface properties, it is generally agreed that the dissociation of methane on the catalyst is the rate determining step. Each partially dissociated CH_x species adsorbs preferentially on a site which completes its tetravalency, with CH_3 adsorbing on top of metal atoms while CH_2 adsorbs between two metal atoms (bridged adsorption). Step sites are more

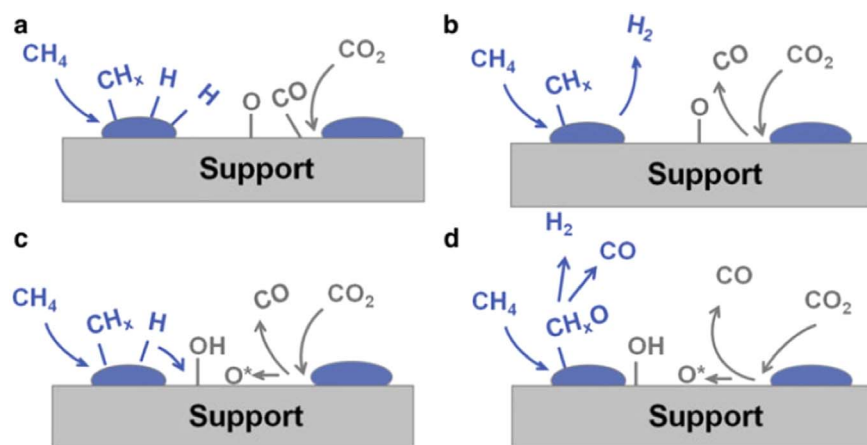


Fig. 1. Reaction steps for the dry reforming of methane [25]: (a) Dissociative adsorption of CO_2 on the metal and metal-support interface respectively. (b) Fast desorption of CO and hydrogen. (c) Formation of surface hydroxyls and oxygen spillover. (d) Surface hydroxyls and oxygen species oxidize hydrogen depleted S- CH_x species and formation of CO and H_2 .

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