

CHAPTER II

BACKGROUND AND LITERATURE SURVEY

In recent years, the interest of CO₂ for the reforming of CH₄ has experienced a rapid increase due to environmental and industrial advantages. In order to develop a high performance catalyst for this reaction, many researchers attempt to elucidate the reaction mechanism and catalytic behavior. However, controversy on the mechanism and the effectiveness of catalyst still exists. This chapter, which is divided into two major parts, reviews the current status of research on the CO₂/CH₄ reforming. The first part involves methane reforming with carbon dioxide, its side reactions and also its mechanism. The second part describes the development of catalysts used for methane reforming in recently years. In the second part, details on active metals, supports, and promoters of the catalysts are also included.

2.1 Methane Reforming with Carbon Dioxide Reaction

The reforming reaction of methane with carbon dioxide is a very attractive route for the conversion of two cheapest carbon-containing materials into useful chemical products, synthesis gas (hydrogen and carbon monoxide). Unfortunately, the major problem with this dry reforming is the favorable carbon deposition occurring on the catalyst surface under severe conditions via reactions (2.1) and (2.2).

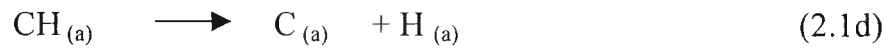
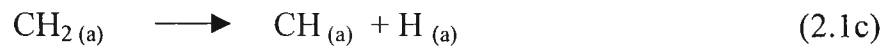
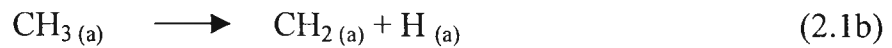
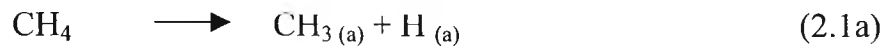
Methane decomposition:



Boudouard reaction:

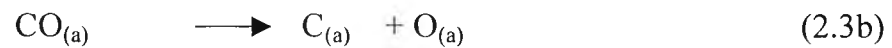
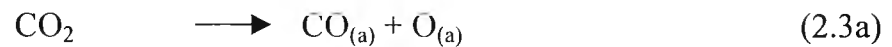


The CH₄/CO₂ reforming reaction can be seen as consisting of reaction (2.1) and the reverse of reaction (2.2). Although both reactions undergo dissociation separately, their decomposition product C, O, and CO terminate their reaction by covering the active area of the metal. Activation of methane proceeds via steps (2.1a)-(2.1d), producing short-lived CH_x residues and, at the tail-end of the chain, carbon (Alstrup *et al.*, 1992).



where *a* denotes an adsorbed species.

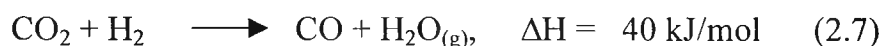
However, the dissociation of CH₄ alone is generally very limited on the reduced metal surfaces but this process is enhanced as the adsorbed O produced on the metal surface via CO₂ activation as shown in reaction (2.3a) reacts with CH₄ as in reaction (2.4).



While the dissociation of CH₄ is facilitated by the adsorbed oxygen, the dissociation of CO₂ is also promoted by the adsorbed hydrogen and possibly by other CH₄ residues as shown by reactions (2.5) and (2.6).



Other important side reactions which could also play a role on the overall product performance are reverse water gas shift,



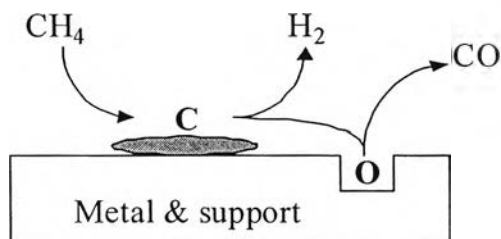
and steam/carbon gasification:



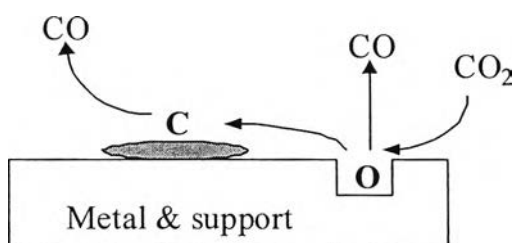
Reaction (2.7) shows the formation of undesirable H_2O product. The reaction consumes hydrogen, and, consequently, results in lower H_2/CO ratio. Apart from reactions (2.1) and (2.2), the reverse of reaction (2.8), which are favored at low temperature, is also a potential source of carbon. Ideally, if the rate of carbon deposition exceeds the rate of carbon removal, a net carbon accumulation on the metal particles leads to catalyst deactivation and reactor blockages.

The use of a suitable catalyst is the most effective way to solve carbon deposition problem for the dry reforming reaction (Bitter *et al.*, 1997). Obviously, the role of the suitable catalyst would be not only to speed up the overall reaction but also to adjust the appropriate elementary steps in the way that prevents both net carbon deposition and water formation (Edwards and Maitra, 1995). Moreover, the addition of a modifier, such as support and promoter could enhance the effectiveness of the catalyst. A suitable support aids the CO_2 dissociation, which, in turn, helps to remove carbon deposited on the metal during the decomposition of CH_4 (Stagg and Resasco, 1998). The addition of promoters improves catalyst stability by stabilizing the surface area for high temperature operation, increasing density of CO_2 adsorption sites near the metal particles, and reducing particles growth under severe reaction conditions (Stagg and Resasco, 1998). All of these promotional effects are believed to have a large impact on the cleaning mechanism, which is the process that can reduce the amount of carbon deposition from metal surface. This mechanism is schematically shown in Figure 2.1.

a) Methane decomposition



b) Carbon dioxide dissociation



c) Concerted mechanism

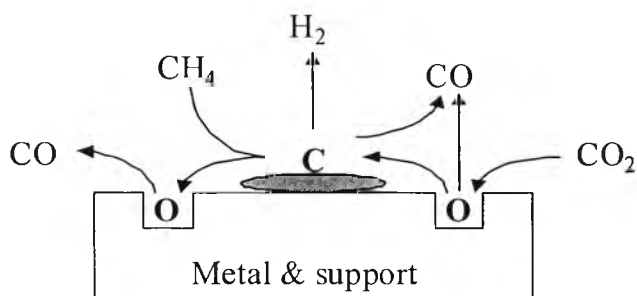


Figure 2.1 Cleaning mechanism scheme

Initially, the methane decomposition takes place on the metal, resulting in the production of hydrogen and the formation of carbonaceous deposits, which can partially oxidize support to form CO and generating oxygen vacancies. CO_2 adsorbed near the metal-support interface and dissociates to form CO and fill the vacancies by adsorbed O . This adsorbed O then reacts with carbon deposits on the metal particles to form an additional CO and clean the metal surface (Stagg *et al.*, 1998).

2.2 Catalyst Development

2.2.1 Active Metals

As early as 1928, the first report of carbon dioxide reforming of methane was published by Fischer and Tropsch (1928). The authors reported that different metals have different activities for the CO₂/CH₄ reforming and that most Group VIII metals, especially Ni, Ru, Rh, Pt, Ir, Pd, when distributed in a reduced form on suitable supports, displayed an appreciable activity for this reaction. This work showed that Co and Mo were also catalytically active for the CO₂/CH₄ reforming while Fe appeared to be the only inactive Group VIII element. However, Cu and W, which were not detected any activity by Fischer and Tropsch, cannot be totally ruled out to be effective catalysts when put on suitable supports.

Despite a controversial debate about the most suitable metal for the CO₂/CH₄ reforming, Rh was unanimously observed to be among the most suitable and active of the Group VIII metals due to the good overall performance, e.g., high activity, high H₂ selectivity and carbon-free operation. Furthermore, this catalyst gives near equilibrium conversions over a wide range of space velocity with H₂/CO ratio close to unity (Richardson and Paripatyadar, 1990; Basini *et al.*, 1991). However, the limited supply of this metal when compared to others reduces the potential to become commercially feasible.

Rostrup-Nielsen and Bak Hansen (1993) studied the performance of Ru for both steam reforming and dry reforming reactions. The results showed that Ru was the most active catalysts for both reforming reactions. Takayasu *et al.* (1991) also supported this idea. They reported that Ru had an almost ideal performance. However, these results are in contrast with others, such as those from Solymosi *et al.* (1991) and Ashcroft *et al.*

(1991). Both of them found that Ru had less activity and H₂ selectivity than Rh, Pt, Pd, and Ni.

There also has been some debate over the results of using Ir as a catalyst by Ashcroft *et al.* (1991) and Solymosi *et al.* (1991). The former authors reported high methane and carbon dioxide conversions with the Ir catalyst, but very low activity and product yield were found by the latter authors.

Considering the cost of Rh, Ni catalyst deserves closer attention. Many authors (Hally *et al.*, 1994; Rostrup-Nielsen and Bak Hansen, 1993; Qin and Lapszewicz, 1994) investigated the activity and stability of Ni for the CO₂ reforming reaction under conditions favorable towards carbon formation. The results are commercially more interesting compared to other noble metals but its main drawback is the high rate of coke formation. Development on these catalysts and identifying reaction conditions for carbon-free operation will help to improve the stability of these catalysts.

From an economic point of view, Pt is a reasonable compromise with its has relatively low price and good availability when compared to Rh. Moreover, several works have shown that Pt is more stable than Ni, Pd, Ir, and Ru when using suitable supports (Hally *et al.*, 1994).

However, research on using Pt as a catalyst has been limited due to deactivation observed from carbon deposition. The use of suitable modifiers, which can minimize the rate of carbon deposition could give Pt a chance to become an effective carbon dioxide reforming catalysts.

2.2.2 Supports

The use of suitable supports has a profound effect on activity and stability of a catalyst. Alumina, magnesia, and europia have been successfully employed to support most of the high performing Group VIII element (Basini *et al.*, 1991; Perera *et al.*, 1991; Takayasu *et al.*, 1991). For

Pt, other supports such as ZrO_2 (Inui, 1993; Seshan *et al.*, 1994), TiO_2 (Bitter *et al.*, 1997), MgO (Rostrup-Nielsen and Bak Hansen, 1993; Qin *et al.*, 1996) have also been used with good results.

The most commonly used support for Pt is Al_2O_3 . Gonzalez-Velasco *et al.* (1994) studied activity of platinum catalysts for automotive exhaust control. The results showed that, under normal operating conditions, Pt/Al_2O_3 catalysts promoted by rare earth oxides were able to achieve high hydrocarbon and carbon monoxide conversion. Several works reported that the addition of some oxides such as MgO and CaO to Al_2O_3 support could enhance the catalyst stability under long reaction time (Fischer and Tropsch, 1928; Gadalla and Sommer, 1989).

Bradford and Vannice (1998) compared the activity and stability of Pt on three different supports, TiO_2 , ZrO_2 , and Cr_2O_3 at low temperature reactions. Although the absence of any significant metal-support interaction in Pt/Cr_2O_3 resulted in substantial carbon deposition and rapid deactivation within 15 hours onstream, the Pt/ZrO_2 and Pt/TiO_2 catalysts exhibited much higher stability even after long periods of time onstream. The results also showed a little higher activity and stability of Pt/TiO_2 when compared to Pt/ZrO_2 . However, Van Keulen *et al.* (1997) compared the activity of Pt supported with ZrO_2 , TiO_2 , and Al_2O_3 at high temperature operations. The result showed that, at high temperature, the alumina-based material had distinct deactivation with time, and the titania-based material had somewhat lower rate of deactivation. In contrast, the platinum-zirconia material gave a seemingly steady behavior.

The comparison between SiO_2 and ZrO_2 supported Pt were studied by Stagg *et al.* (1998). They found that the Pt/ZrO_2 catalyst had much higher activity and stability than the Pt/SiO_2 catalyst. The low activity observed on the Pt/SiO_2 catalyst could be due to sintering of the Pt particles and subsequent carbon formation on the large Pt agglomerates. On the other

hand, the ability of ZrO_2 to anchor Pt particles promoted the CO_2 dissociation, so that it led to a decrease in the rate of carbon deposition and promoted the cleaning mechanism. The research work by Van Keulen *et al.* (1997) substantiated the above ideas. The authors found that zirconia-based material resisted extensive carbon lay-down, probably because any carbon formed on the catalyst was readily gasified once more by the reaction with CO_2 (reverse of reaction (2.2)). In contrast to the behavior of the zirconia-supported catalyst, the resistance to carbon deposition was significantly less marked with the other supports.

2.2.3 Promoters

Modifications to the support are sometimes made by the addition of promoters. The effect of adding Sn to SiO_2 and ZrO_2 supported Pt catalysts for dry reforming were studied by Stagg *et al.* (1998). On the SiO_2 support, alloy formation between the metal and promoter decreased the coke formation. This led to an increase in the activity and stability of the catalyst. The use of ZrO_2 as a support in the presence of excess Sn resulted in decreasing the performance of the catalyst because of the Pt-Sn alloy segregation, which, in turn, blocked the interaction between the metal particles and the support. This inhibited the dissociation of CO_2 and eliminated the cleaning mechanism. However, controlling the addition of Sn to Pt/ ZrO_2 resulted in activity and stability increase under severe deactivating conditions by choosing a suitable preparation technique, such as surface reduction deposition or co-impregnation.

Development of a new generation of automotive oxidation catalysts containing CeO_2 doped with ZrO_2 or other rare earth oxides such as PrO_x , Y_2O_3 , and La_2O_3 were studied by Trovarelli *et al.* (1997). The results showed that these new catalysts possess high oxygen storage capacity, improved thermal stability, and enhanced catalytic properties. Stagg and

Resasco (1998) focused on the addition of Ce and La as promoters to Pt/ZrO₂ catalysts for the CO₂ reforming of CH₄. The results of this study showed that both promoted catalysts had higher surface areas and CO₂ desorption capacity than the unpromoted catalyst. Furthermore, the results from the EXAFS study showed that the promoted catalysts exhibited only modest particle growth, while the unpromoted catalyst had greater growth and faster rate of deactivation. All of these results indicated that the addition of cerium and lanthanum to the support could improve the catalytic performance by increasing stability of the catalysts.

Besides Sn, Ce, and La, Y has been investigated as a good promoter by Duchet *et al.* (1991). It is well established that adding Y³⁺ cations enhance the surface and thermal stability of ZrO₂.