

CHAPTER II

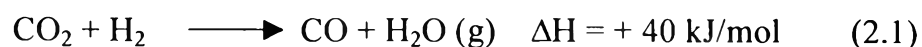
BACKGROUND AND LITERATURE SURVEY

Before the development of catalysts for the CO₂/CH₄ reforming will be mentioned, understanding of the reaction, side reaction, and its mechanism can not be ignored. So, this chapter begins with the CH₄ reforming reaction, its side reaction, and possible mechanism for the reaction. Since this work involves the addition of oxygen to the CH₄ reforming as another promoter, the partial oxidation of methane and its possible mechanism will be discussed. The catalyst development will then follow.

2.1 CH₄ Reforming Reaction

As mentioned before, the CH₄ reforming, reaction (1.3), is likely to be conducted under conditions where carbon or coke can easily form via reactions (1.4) and (1.5). Other reactions, which could have an important role on the overall product, are

Reverse water gas shift (RWGS)



Steam/carbon gasification reaction

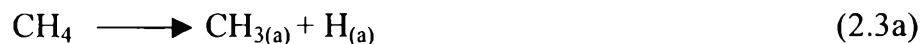


Hydrogen from the methane reforming is consumed by reaction (2.1). To maintain the overall stoichiometry of the dry reforming products, reaction (2.2), must be controlled so that the amount of H₂ produced from the methane reforming is not used up by reaction (2.1) (Edwards and Maitra, 1995).

Reaction mechanism

Although several mechanisms exist for reaction (1.3), a possible mechanism consists of two reaction paths, CH₄ decomposition on the metal

particle and CO_2 dissociation on the support (Stagg *et al.*, 1998). First, CH_4 decomposes on the metal particle via steps 2.3(a) to 2.3(d) producing short-lived CH_x residues and carbon.



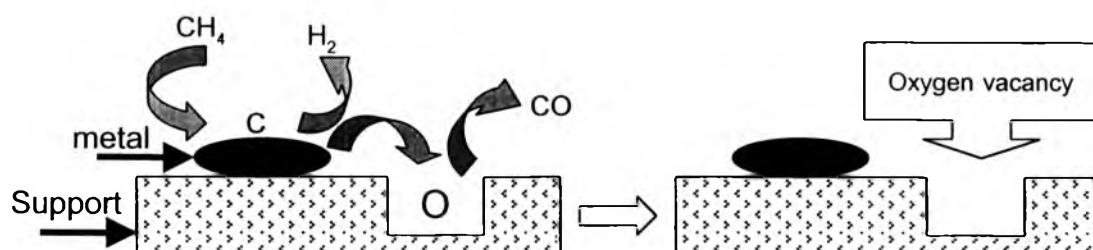
where the subscript a represents an adsorbed species.

When CO_2 is present, it adsorbs near the metal–support interface and dissociates to form CO and adsorbed O as shown in reaction (2.4) (Edwards and Maitra, 1995; Hai-You and Chak-Tong, 1996).

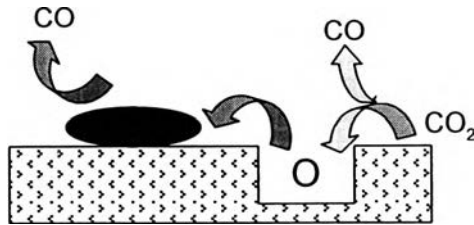


This adsorbed O then reacts with the carbon deposits on the metal particle to form additional CO and clean the metal surface. This step is called “*cleaning*”. Another possibility for the cleaning mechanism is that the oxygen that reacts with the carbon comes from the support. In this case, the support acts as a source or sink of oxygen, the mechanism can be presented as the following (Stagg *et al.*, 1998).

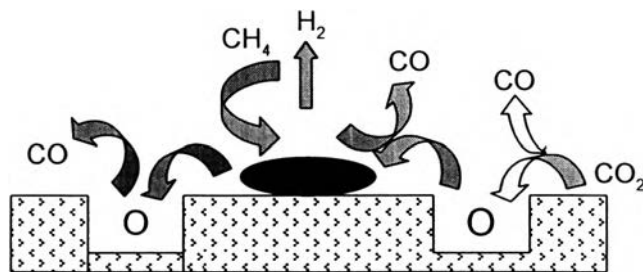
a) Methane decomposition on the metal particle generates oxygen vacancies.



- b) CO₂ adsorption on the support and dissociation at the metal – support interface to fill the vacancies and generate CO.

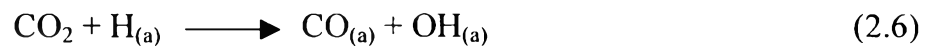


- c) Overall mechanism.



From this mechanism, catalyst stability depends on the balance between the two paths. If the CH₄ decomposition is much faster than the rate of cleaning by the CO₂ dissociation, the deposition of carbon takes place. On the other hand, if the CH₄ decomposition becomes too slow, the CO₂ dissociation is inhibited.

The dissociation of CO₂ can be promoted by adsorbed hydrogen via reaction (2.6)



Hydroxyl groups can recombine and form H₂O or react further with CH₄ to form CO and H₂ (steam reforming) (Bitter *et al.*, 1999).

2.2. Partial Oxidation of Methane

The partial oxidation of methane, reaction (1.2), is mildly exothermic and yields a synthesis gas mixture with the H₂/CO ratio of two.

A possible mechanism for this reaction involves the oxidation of CH₄ primarily to H₂O and CO₂ via methane combustion, reaction (2.5), followed by the reforming of CH₄ with H₂O and CO₂ (O'Conner and Ross, 1998; Chak-Tong *et al.*, 1999).

Methane combustion



Another mechanism is the direct oxidation. This has been claimed to occur over Rh and Pt coated monoliths in an ultra short contact time reactor above 1000°C. The direct partial oxidation was also reported over Ru/TiO₂, Ni/CaO.2Al₂O₃, and yttria/ zirconia (Steghuis *et al.*, 1998).

O'Conner and Ross (1998) found that Pt/Al₂O₃ was the most active catalyst for the partial oxidation compared with Pt/ZrO₂ and Ni/Al₂O₃ catalysts. Only slight deactivation of the catalyst occurred. The authors also found that when oxygen was added to the system of the CO₂ reforming, methane conversion increased with the amount of oxygen. This was most probably due to less carbon being formed on the catalyst. The mechanism for this combined system is like the indirect partial oxidation. In addition, the authors suggested that all of the oxygen is utilized in the combustion at the start of the reactor bed.

2.3 Catalyst Development

2.3.1 Active Metals and Supports

As mentioned before, the deactivation of catalysts by coking is a critical criterion in designing suitable catalysts for the CO₂ reforming. In

fact, the deactivation of CO₂ reforming catalysts is explained by two independent processes, i.e., covering of the active sites by carbonaceous deposits or sintering of the metal particles. However, the latter case has been seen to be minimal (Bitter *et al.*, 1999).

Group VIII metals in their reduced forms, especially, Ni, Ru, Rh, Pd, Ir, and Pt seem to be the effective catalytic components for the CO₂ reforming (Edwards and Maitra, 1995; Zhenxing *et al.*, 1996). Many catalysts, which consist of these metals supported on various supports, were studied for their activity and stability. Ni catalysts are commercially more feasible but its major drawback is high carbon deposition (Hally *et al.*, 1994). On the other hand, although Rh and Pt are more stable and active than Ni, Rh is likely to be too expensive for use in an industrial process, especially if large quantities of metal are required. Even though the current Rh price is approximately the same as that of Pt, the supply of this metal is limited and a significant increase in price would probably occur (Ross *et al.*, 1996). Therefore, from economic point of view, Pt is a reasonable compromise.

Van Keulen *et al.* (1995) investigated the activity and stability of Pt on ZrO₂, TiO₂, and Al₂O₃. At high temperatures it can be seen clearly that Pt/ZrO₂ is the most active and stable catalyst. Pt/Al₂O₃ catalyst deactivated due to carbon deposition, and large amounts of carbon were detected on the material after use. The titania-supported material exhibited an intermediate behavior. Bitter *et al.* (1999) examined the stability of Pt supported on these supports. The same result was reported. Furthermore, the authors found that two regimes of deactivation existed with Pt/Al₂O₃ and Pt/TiO₂. One of the regimes is accounted for the slow deactivation while the other is for the rapid deactivation. The slow deactivation was attributed to a singular blocking of active metal sites with unreactive carbon or oxidic sites for CO₂ activation at the metal-support boundary. The rapid deactivation is explained by the overgrowth of the metal perimeter with carbon of low activity. This showed

that carbon on Pt/ZrO₂ catalyst must be more reactive than those on Pt/Al₂O₃ and Pt/TiO₂. Therefore, ZrO₂ seems to be the very well suited support for Pt.

Even though ZrO₂ has been widely investigated, many authors proposed that ZrO₂ facilitates the CO₂ dissociation, which when takes place near the metal particle, aids in the removal of carbon formed on the metal from the decomposition of CH₄ (Bitter *et al.*, 1997, 1999; Stagg and Resasco, 1998). In addition, van Keulen *et al.* (1995) proposed that ZrO₂ has an anchoring effect, which helps to maintain a high Pt dispersion. Hegarty *et al.* (1998) also found that the activity for Pt/ZrO₂ catalyst is reasonable active for CO₂ reforming at 800 °C

As mentioned above, roles of the support in CO₂/CH₄ reforming are:

1. To adsorb CO₂ and facilitate its dissociation at the metal-support interface. This help cleaning the carbon deposited from the CH₄ decomposition.
2. To influence the growth of carbon possible by controlling the type of metallic clusters, which are the sites of carbon formation. The various supports have different amount of the reactive forms of carbon. The more reactive form of carbon the easier the carbon migration from the metal to the support, producing a free metal surface for catalysis.

Furthermore, the morphology of the support can be greatly altered at high temperatures, causing a large reduction of surface area, which would explains the large activity loss observed (Stagg *et al.*, 1998).

2.3.2 Promoters

In previous work, Stagg and Resasco (1997) and Stagg *et al.* (1998) investigated the effects of adding Sn as a promoter into Pt/ZrO₂. The results show that the presence of Sn disrupted the metal-support interactions, thus inhibiting the dissociation of CO₂ and eliminating the cleaning mechanism. However, adding Sn into Pt/ZrO₂, using surface reduction

deposition techniques, can result in increased activity and stability at high temperatures and high CH₄:CO₂ ratio. The chosen preparation technique is necessary to maximize the Pt-Sn interaction while minimizing the interaction between the promoter and the support. It is believed that these bimetallic catalysts reduce the amount of carbon deposited from the CH₄ decomposition without significantly altering the effect of the support.

Stagg and Resasco (1998) also investigated the effects of adding cation such as Ce⁴⁺ and La³⁺ into the zirconia support. The results show that the promoters increased the surface area by stabilizing the tetragonal form of ZrO₂ and increased the density of CO₂ adsorption sites near the metal particle. Both of these effects were believed to have a large impact on the cleaning mechanism. Another effect of cerium and lanthanum promoters is that their presence retards the Pt particle growth and the role of the support is not hindered at high temperatures. All of these promotional effects lead to an increase in catalyst stability. Furthermore, promotion of ZrO₂ with Ce has been shown to improve the oxygen storage capacities of the support, which can possibly result in enhanced cleaning ability and higher catalyst stability. In addition, in the steam reforming, cerium has very favorable influence on the nickel dispersion and its resistance for sintering.

Trovarelli *et al* (1997, 1999) studied the exhaust catalysts containing ceria doped with ZrO₂ and/or rare earth oxides, which is the new generation catalyst of automobiles. These new catalysts have higher oxygen storage capacity, higher thermal stability, and six times the surface area of the unpromoted catalyst.