

CHAPTER II

LITERATURE SURVEY

2.1 CH₄ Reforming Reactions

Catalytic reforming of methane with carbon dioxide to synthesis gas was first proposed by Fischer and Tropsch using nickel- and cobalt-based catalysts as shown in eq. [1] (Fischer and Tropsch, 1928).



This reaction produces a synthesis gas with a H₂/CO ratio of approximately 1. There are a number of potentially very large new applications requiring a feed gas with a H₂/CO ratio of 1:1. One of these is for the production of dimethyl ether (DME) as show in eq. [2].



In addition to being an industrially important chemical in its own right, DME is an intermediate for the production of synthetic gasoline and it can also be converted via isobutanol in eq. [3] to isobutene in eq. [4] from which the octane enhancer methyl tertiary butyl ether (MTBE) is produced by reacting with methanol as shown in eq. [5] (Brown et al., 1991).





CH_4 reforming with CO_2 is also used as a chemical energy storage and energy transmission system (CETS) because of the high endothermicity of this reaction. Figure 2.1 shows that solar energy is used to drive the endothermic forward reaction and the energy is stored in the synthesis gas which can be transported via pipeline to a location where the energy is released by the exothermic backward reaction (Richardson and Paripatyadar, 1990).

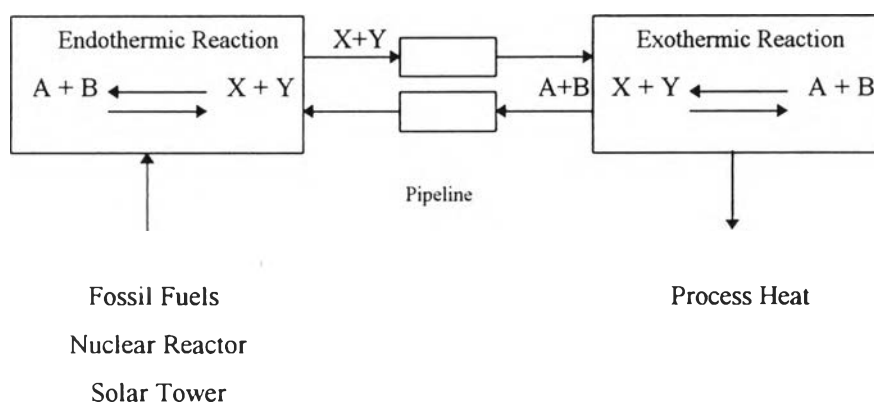


Figure 2.1 Schematic diagram of the chemical energy transmission system (CETS).

The main reaction [1] is accompanied by several secondary processes [6-9], of which the reverse water-gas shift reaction appears to be the most important one because of its dependence on the product hydrogen of reaction [1] (Rostrup-Nielsen and Bak Hansen, 1993).

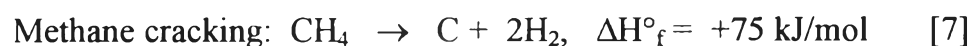
Reverse water-gas shift:



It can be seen that water always form in the reaction system. The formation of water is reflected by lower hydrogen concentration than CO due

to the reverse water-gas shift reaction which is the main water formation route. Then the amount of CO is always higher than that of hydrogen.

Moreover, depending on the reaction conditions and on the composition of feed gas, carbon build up can occur due to the Boudouard reaction and methane cracking (Gadalla and Bower, 1988).



Thus, the CH₄/CO₂ reforming reaction [1] can be seen as consisting of reaction [7] and the reverse of reaction [8]. Ideally the carbon formed in the reaction [7] should be rapidly consumed by the reverse of reaction [8] and, to a lesser extent, by the steam/carbon gasification reaction [9].

Steam/carbon gasification:



Reaction [9] can play a role in CH₄/CO₂ reforming because steam is almost always formed via the reverse water-gas shift (RWGS) reaction [6]. If reaction [7] is faster than the carbon removal rates [8,9], there will be a net build-up of carbon to pose serious problems in the overall reaction concept which in practice would lead to catalyst deactivation and reactor blockage. Apart from reaction [7], reaction [8] and the reverse of reaction [9], both of which are favoured at low temperatures, are also potential sources of carbon. (Edwards and Maitra, 1995).

Obviously, the role of suitable catalysts would be not only to speed up the overall reaction but also to adjust the appropriate elementary steps in a way which prevents both net carbon deposition and water formation. It is known

that most of the group VIII metals are efficient at catalysing the methane reforming with CO_2 . Thus, many researcher have focused on the development of noble metals for this relation.

2.2 Catalytic Effects on Surface Intermediate

2.2.1 Support

Erdohelyi et al. (1994) paid great attention to the effects of the support and to the identification of surface intermediates in the low-temperature interaction and high-temperature reaction of carbon dioxide and methane. Four supported Pd catalysts, Pd/TiO₂, Pd/Al₂O₃, Pd/SiO₂ and Pd/MgO, were studied in the experiment. They observed the following:

Dissociation of CO₂: The dissociation of CO₂ was monitored by IR spectroscopy. Carbon monoxide bands indicative of the dissociation of carbon dioxide, appeared only at and above 373-473 K. The specific activities of the catalysts agreed with their activity order towards the dissociation of carbon dioxide. Then, the order of activity of palladium samples is as follows: Pd/TiO₂, Pd/Al₂O₃, Pd/SiO₂ and Pd/MgO.

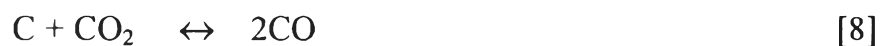
Deposition of CH₄ and reactions of the formed carbon: the dissociation of methane has been observed even in the low-temperature range of 473-573 K, when hydrogen and a small amount of ethane were produced with the deposition of surface carbon. In the temperature range of CH₄ + CO₂ reaction (673-773K), the extent of methane decomposition was greater and a much larger amount of surface carbon was produced. Moreover they also observed no significant support effect in the decomposition of methane on the Pd catalysts.

CH₄ + CO₂ surface interaction: They examined how the addition of methane to carbon dioxide influenced the dissociation of carbon dioxide. They

found that the promotion of the dissociation of carbon dioxide is attributed to the effect of hydrogen formed in the decomposition of methane on Pd catalysts.

Catalytic reaction between CH_4 and CO_2 : Although both compounds undergo dissociation separately even at much lower temperatures, their decomposition products C, O and CO terminate their reactions by covering the active areas of Pd metal. However, when both compounds are present, particularly at high temperatures, their self-decomposition is greatly accelerated. The probable reasons are: (i) promotion of the dissociation of carbon dioxide by hydrogen, and perhaps by CH_x fragments, too, and (ii) facilitation of the dissociation of methane by adsorbed O formed in the decomposition of carbon dioxide.

Whereas the decomposition of methane on supported Pd in the absence of carbon dioxide produces a multilayer of carbon at 773 K, in the high-temperature reaction of $\text{CH}_4 + \text{CO}_2$ only a limited amount of surface carbon was produced, because the possibility of decomposition of CH_x to surface carbon is limited. Alternatively, the carbon formed in the methane dissociation reacts with carbon dioxide and/or water immediately after its production, before its aging and transformation into a less reactive form.



Furthermore, the variation of the CO / H_2 with the catalyst sample and with temperature is probably due to the differences in the activation energy of the secondary reaction.

2.2.2 Active Metals

Solymosi et al. (1991) studied the catalytic efficiencies of alumina-supported Pt metals in the $\text{CH}_4 + \text{CO}_2$ reaction. Five different active metals used in this experiment were : Ru/ Al_2O_3 , Rh/ Al_2O_3 , Pd/ Al_2O_3 , Ir/ Al_2O_3 and Pt/ Al_2O_3 . Before kinetic measurements, they investigated the high-temperature interaction of methane and carbon dioxide with a catalyst surface by the pulse method. On exposure of the reduced surface to methane pluses, they observed the formation of ethane and traces of ethylene, which indicates the occurrence of the dissociation of methane and the recombination of CH_3 and CH_2 species. Moreover the dissociation of carbon dioxide to CO and O also occurred on this surface. On repetition of these measurements on oxidized surface, the total oxidation of methane was experienced until the consumption of surface oxygen and no dissociation of carbon dioxide was observed. About kinetic measurement, the supported Pt metals exhibited great differences in catalytic behaviour as concerns the $\text{CH}_4 + \text{CO}_2$ reaction given below,



The reaction occurred at the highest rate on Rh, followed by Pt, Pd, Ru and Ir.

The conversion of carbon dioxide exceeded that of methane for every catalyst sample indicating that the reaction was followed by several secondary processes, including the methanation of carbon dioxide and carbon monoxide, reverse water gas shift reaction and Boudouard reaction. The amount of surface carbon formed was determined by its oxidation to CO_2 . The largest amount of carbon formed on Rh and Pt, and the least on Pd. Finally, the comparison of Rh, Pd and Pt were studied. For the formation of ethane supported Ru and Pd exhibited the highest activity.

Mark and Maier (1996) studied the CO₂ reforming of methane under conditions of stoichiometric feed composition on Rh, Ru, and Ir catalyst. The activity of these effective catalysts can be correlated with the accessible metal surface area. Over a wide range of catalyst and supports studied, the rate per unit surface area did not depend significantly on dispersion, indicating that CO reforming at high temperatures is structure insensitive. No direct influence of the microstructure of the support on the reaction rates was detected. The influence of the support seems limited to the stabilization of the metal surface area, which in turn is responsible for catalyst activity. The study, limited to reaction controlled conditions, shows that in preparation of highly active catalysts accessible metal surface area is an important parameter. To optimize catalyst performance (high yield at low cost), metal dispersion has to be maximized and has to be stable. This can be achieved by selected oxidation reduction pretreatments of catalysts. Both γ -Al₂O₃ and the binary oxide ZrO₂(5%)/SiO₂ are especially good catalyst supports: Rh catalysts based on these supports not only showed high activity but also showed promise to be thermally stable even after long reaction times. Product composition can be easily controlled over a wide range of CO/H₂ ratios by partial substitution of CO₂ by H₂O or O₂ in the feed.

2.3 Carbon Deposition

However, carbon deposition accompanies the with the CO₂ + CH₄ reaction.

Tang et al. (1995) investigated the effect of support on carbon deposition. Two nickel catalysts on different supports, Ni/SiO₂ and Ni/ α -Al₂O₃, were studied. They also examined how the addition of CaO and MgO which increased the basicity of the catalysts influenced the carbon

deposition. They observed that the use of SiO₂ as a support gave a high content of carbon deposition, and the addition of MgO and CaO resulted in less carbon deposition. As the surface basicity of the catalysts increases, carbon dioxide is more easily adsorbed, which leads to increased carbon dioxide concentration on the surface of the catalysts. As a result the equilibrium, will move towards the left, which will inhibit and partially remove carbon deposition on the surface of catalysts.



Catalysts supported on $\alpha\text{-Al}_2\text{O}_3$ showed little carbon deposition, whereas the presence of MgO and CaO increased the formation of carbon.

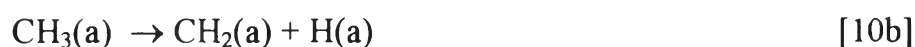
Zhang and Verykios (1994) found that the carbon deposits comprise various forms of carbon which are different in terms of reactivity. Three types of carbonaceous species, $\alpha\text{-c}$, $\beta\text{-c}$ and $\gamma\text{-c}$ species exist on the Ni catalysts. While the $\alpha\text{-c}$ species is suggested to be responsible for CO formation, the less active $\beta\text{-c}$ and $\gamma\text{-c}$ species are presumed to cause catalyst deactivation. It is known that among the deposited carbons, only a stable form, possibly arising from the CO disproportionation, would poison the Ni particles and that other less stable forms arising from methane activation are rapidly accumulated on the catalyst poisoning the catalysts to a lesser extent.

Sacco et al. (1989) investigated carbon deposition and filament growth on Fe, Ni and CO foils. All three metals were observed to have similar slow rates of carbon deposition in the metal phase field. The source of carbon deposited on Ni is CH₄ whereas on Fe and CO it appears to be CO.

2.4 Reaction Mechanism

Although the complexity of this reaction and the occurrence of several secondary processes make it difficult to determine the mechanism of the $\text{CH}_4 + \text{CO}_2$ reaction, some conclusions can be drawn on the reaction of CO_2 and CH_4 on metal surfaces.

Alstrup and Tavares (1992) proposed that the activation of methane proceeds via step 10(a)-10(d) producing short-lived CH_x residues and, at the tail-end of the chain, carbon.

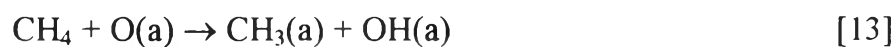
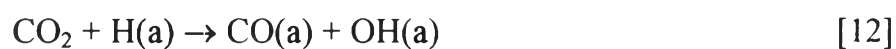


When sufficient carbon is formed on the catalyst surface it blocks the active sites and hinders dissociation of CH_4 . Generally, the carbon deposits comprise various forms of carbon which are different in terms of reactivity: adsorbed atomic carbon (highly reactive, surface carbidic form), amorphous carbon, vermicular carbon, bulk nickel carbide, and crystalline graphitic carbon. The reactivity of carbon deposit or its transformation is sensitive to the type of catalyst surface, the temperature of its formation and the duration of thermal treatment. Similar considerations also apply to carbon formed from CO as the precursor as shown by eq. [11b].



The dissociation of CH₄ alone is generally very limited on the reduced metal surfaces but this process is enhanced by adsorbed O produced on the metal surface via CO₂ activation (when it is also present) as shown in eq. [11a].

Although both CH₄ and CO₂ undergo dissociation separately, their decomposition products terminate the respective dissociation by covering the metal surfaces. When both CH₄ and CO₂ are present, their self-decomposition is enhanced via reactions [12]-[14]. Thus, whilst the dissociation of CH₄ is facilitated by adsorbed oxygen, the dissociation of CO₂ is also promoted by adsorbed hydrogen and possibly by other CH_x residues.



Apart from the selective reactions of the surface species producing the desired reforming reaction products, eq. [15] shows the formation of undesired H₂O which competes with CO₂ for subsequent reactions with carbon formed by the dissociation of CH₄.



However, the kinetics for CO₂ reforming depends on the type of catalyst and probably the mechanism is changing with temperature.

2.5 Economical Catalyst

Up to present, there is no established industrial technology for methane reforming with carbon dioxide, in spite of potentially attractive incentives with economical and environmental benefits. The principal reason for this is the carbon-forming reaction, which quickly deactivate conventional reforming catalysts. Furthermore, considering the high cost and limited availability of noble metals exploring other catalyst system is also important.

Osaki et al. (1997) described the catalyst performance of metal sulfide of Mo and W by comparing with that of Ni/SiO₂ catalyst. Catalyst deactivation due to carbon deposition was not observed on MoS₂ and WS₂ during CO₂-reforming, although the rate was smaller than that on Ni. From the dependence of reaction rate on the partial pressures of CH₄ and CO₂, it could be deduced that the MoS₂ and WS₂ surface was covered with CO₂(ads) (or O(ads)) during the steady-state CH₄-CO₂ reaction. The abundance of adsorbed CO₂ was also considered an unfavorable condition for the direct decomposition of methane and as a result, carbon deposition was very much suppressed on the sulfides. No catalyst deactivation was also observed on the sulfide catalysts by the admission of H₂S during the reforming.

Some scientists have investigated the conventional form of tungsten with this reaction. In order to avoid complications that might result from the presence of a support material, this research described here was carried out over a tungsten wire.