

Catalysis to produce hydrogen

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Catalysis to produce hydrogen

Natthakich Assanee

A Thesis submitted in fulfillment of the requirements for the
degree of Master of Engineering
School of Chemical Sciences and Engineering
University of New South Wales
2008

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The present study is focused on two studies. The kinetics of methane steam reforming over a Ni/MgO catalyst at high pressure is reported in the first study. The second study is focused on the steam iron process over promoted Fe-oxide based catalyst using four different reductants; H₂, H₂ /CO mixture, CH₄ and CH₄ /CO₂ mixture.

A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure was carried out. The kinetic orders of methane and steam at 40 bars and 600 °C were found to be 0.82 and 0.62 respectively. The estimation of energy of activation of the process was found to be 106 KJ/mol. The reaction rate data was explained by a Langmuir – Hinshelwood – Hougen – Wastson model.

Four different reductants(H₂, H₂ /CO mixture, CH₄ and CH₄ /CO₂ mixture) , were applied for the study of the steam iron process. A study of the steam iron process using H₂ as reductant focused on the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂.

The first reduction was found to be composed of a two step reduction up to 550 °C. The estimation of energy of activation for the process was found to be 92.4 KJ/mol and 68.2 KJ/mol respectively.

The study of the steam iron process using H₂ /CO mixture as reductant over 4%Cr₂O₃ – 96% Fe₂O₃ found that FeO was an intermediate for the reduction of Fe₂O₃ with H₂ /CO mixture to Fe metal.

The application of methane as reductant for the steam iron process gave the worst results. As a result, NiO was added to Cr₂O₃ –Fe₂O₃ to increase the activity. Carbon formation on NiO also was found to be a serious problem

In order to minimize carbon formation on NiO, CO₂ was introduced in a mix with CH₄ for the oxidation of deposited carbon during the reduction step. Although the introduction of CO₂ can suppress carbon formation, the strong oxidation of reduced iron oxide by water formed during the reduction process coupled to the higher favorable reaction of the water gas shift reaction adversely affects the complete reduction of iron oxide to iron metal.

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Abstract

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Chapter 1

Introduction

One of the most significance issues for humanity during the twenty first century is the discovery and transformation of sustainable energy from fossil fuel. It is expected that the fossil fuel will continue to dominate Australia's primary and final consumption up to 2020[1]. Consequently, this consumption means Australia has the highest consumption per capita in the world.

An attractive alternative energy source to fossil fuel is hydrogen. Fossil fuels give off greenhouse gases on combustion while hydrogen produces only water. Furthermore, hydrogen, the simplest and most common element, has the highest energy content per unit of weight (120.7 kJ per g) when compared with other fuels[1]. Only a fraction of hydrogen production, of which approximately 95 % originates from carbonaceous raw material primarily fossil in origin, is harnessed for energy purpose; the bulk serves as a chemical feedstock for petrochemical, food, electronics and metallurgical processing industries [1]. However, the share of hydrogen in the market is increasing with the implementation of fuel cell systems and the growing demand for zero-emission fuels. Hydrogen production will need to increase with this growing market [1].

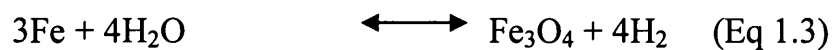
There are three major routes for hydrogen generation for meeting this hydrogen demand, steam reforming, partial oxidation and auto – thermal reforming of hydrocarbon, but the amount of CO_x as a product has to be considered for these

methods [2]. In this thesis, the steam/iron process will be studied. Due to three remarkable advantages, cheap material (ferric oxide), the quality of hydrogen product and more than one life cycle as a redox process, this steam / iron process can be a highly potential route for hydrogen production.

The original steam – iron process involved the reduction of iron oxide using synthesis gas derived from coke gasification.



Pure hydrogen was subsequently generated by reaction of iron with water



In recent years the reduction of iron oxide by natural gas has been found to be possible [3-10]. Some carbon is deposited on the catalyst but there was a window of operation where the deposited carbon did not have too great an effect on hydrogen production under different conditions. Carbon formation deactivates the catalyst, resulting in short life cycles.

In order to improve process performance, in particular minimizing catalyst deactivation caused by carbon formation and maximizing the yield of hydrogen product, the addition of the supports to catalyst is the most familiar method. Although the easiest way for this improvement is to introduce steam into the system, this increase in steam causes very high production cost. In contrast, the addition of supports is cheap. For example nickel is highly active for hydrogen production but has

a high potential for carbon formation. Due to the capacity for improving adsorption of water and promoting carbon gasification, MgO is highly suitable as promoter for hydrogen production.

Steam reforming has also been examined in the thesis. The thesis involves two areas of study.

- 1) A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure
- 2) The study of the steam iron process over promoted Fe-oxide based catalyst.

Chapter 2

A Kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure

2.1 Introduction

A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure has been conducted and is described in the first section of the thesis. Although the kinetic study of methane steam reforming at atmospheric pressure is well known, the kinetics of methane steam reforming at high pressure is rarely studied. This kinetic study is based on nickel catalyst, the most typical catalyst used for steam reforming of hydrocarbon. Although nickel metal is less active than some noble metals such as ruthenium, rhodium and platinum, nickel is the favorite choice as a result of its lower cost. However, nickel is highly active for hydrogen production and has high potentiality for carbon formation [11]. Magnesia, MgO is accepted as one of the good supports [11 -17] for the catalytic steam reforming of hydrocarbon in order to minimize carbon formation.

2.2 Literature Survey

2.2.1 Steam Reforming

Steam reforming of methane is a well – known industrial process, used in several significant chemical industries such as the production of hydrogen for ammonia synthesis, the production of synthesis gas (a mixture of CO and H₂) for the manufacture of ethanol and oxo-alcohol (aliphatic alcohol such as propanol or butanol

obtained by oxo – synthesis) and the production of pure hydrogen for fuel cell technology using natural gas or liquid hydrocarbon as feeds.

The process of steam reforming of methane can be commonly divided into two reactions: the reaction of hydrocarbons with steam (Eq 2.1), and the water gas shift (WGS) reaction (Eq 2.2)

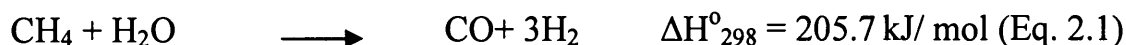


It should be emphasized that CO_2 is not only generated through the WGS reaction (Eq 2.2), but can be produced by complete oxidation (Eq. 2.3). Since steam reforming is an endothermic reaction, the necessary heat is often supplied by combustion (Eq. 2.3), the overall process being called auto thermal reforming.

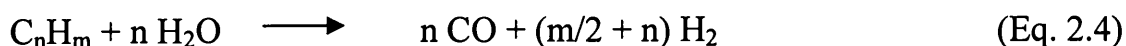
2.2.2 Methane Steam Reforming

Methane is accepted as the simplest hydrocarbon to be reformed.

The equilibrium reaction for methane reformed by steam is also well established:



The general reaction of steam reforming of hydrocarbon is described as:



where n is the number of carbon atoms in the molecule which equals one for methane

The expectation of higher conversion at higher temperatures and lower pressure is shown in Figure 2.1 and Figure 2.2

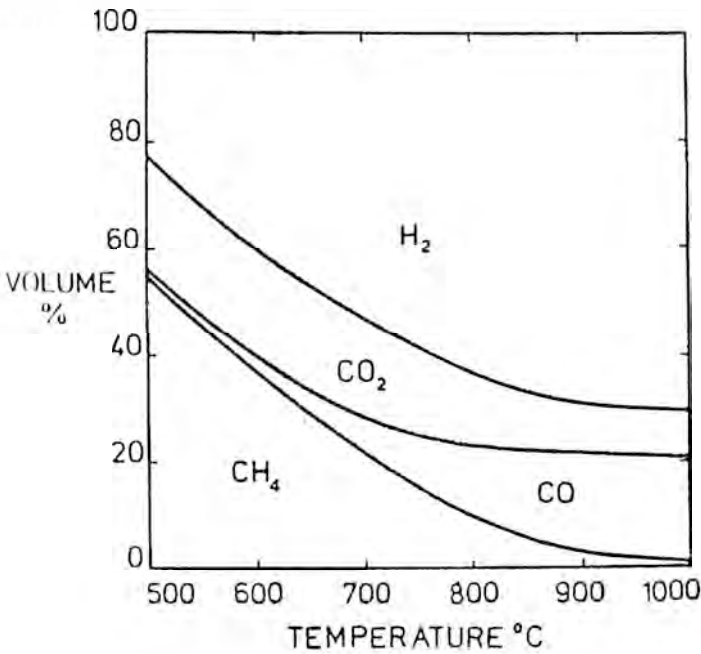


Figure 2.1: Methane reforming: effect of temperature on dry gas composition (pressure (atm)) for reactions (Eq. 2.1) and (Eq. 2.2); H₂O/C (3.0) [18]

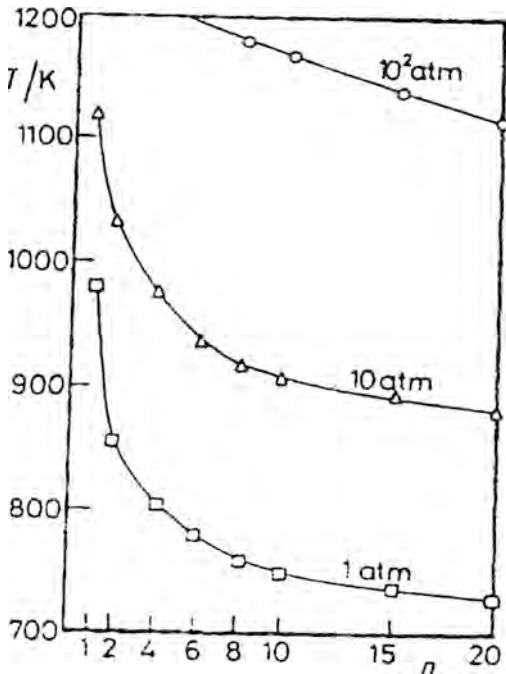
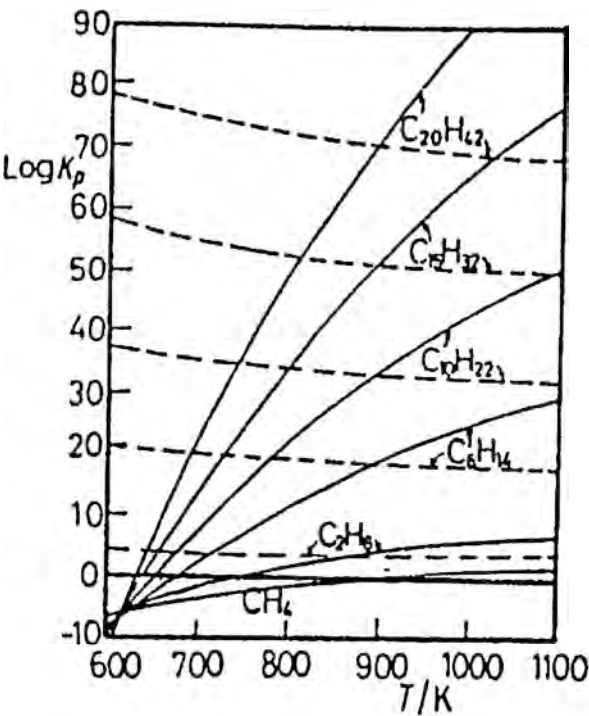


Figure 2.2: Plots of the temperature needed to give 90% conversion of a stoichiometric reaction mixture for Eq. 2.4 as a function of n, at a variety of pressures [19] (n = the number of carbon in hydrocarbon)

Another vital factor affecting steam reforming is the steam carbon ratio. The equilibrium concentration of CH_4 , CO , and CO_2 obtained in the exit dry gas by feeding different steam/ methane at various temperatures is presented in Figure 2.3.



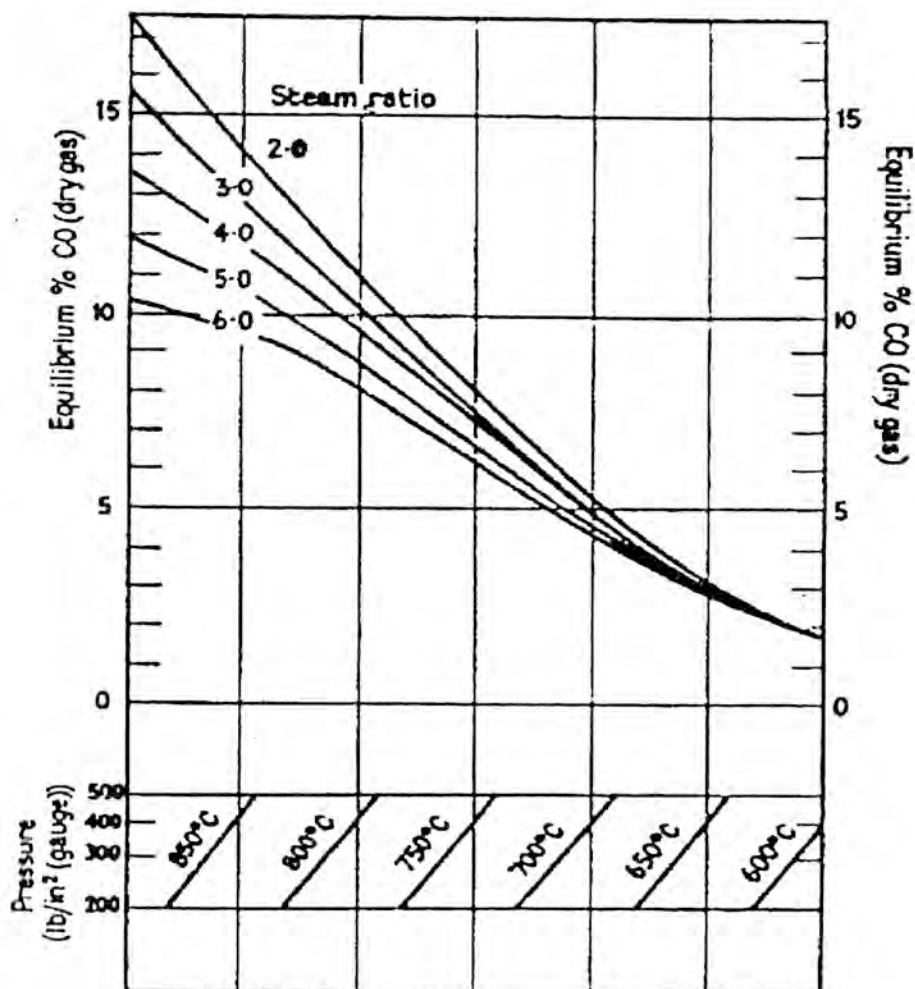


Figure 2.4: Equilibrium concentration of methane as a function of temperature, pressure and steam ratio for methane [19]

Consequently, the outcomes of steam reforming can be varied depending on process conditions and feedstock.

2.2.3 Thermodynamics

The wide spectrum of gas production depends on the reformer operating conditions.

For industrial applications, the reaction process has to be near equilibrium. Under such circumstances, the application of the knowledge of the equilibrium constants is important to determine the product stream composition [22]. Even considering only

two reactions, there are several factors affecting the equilibrium composition such as the steam/carbon ratio, the operating temperature and the pressure [20].

The two ultimate conditions in methane steam reforming are:

- 1) No methane present in the product gas – favoured by high temperature, low pressure, and high steam to carbon ratio, the reaction being endothermic;
- 2) No hydrogen present in the product gas – favored at low temperature, high pressure and low steam to carbon ratio, the reaction being exothermic. An interesting example is the production of substitute natural gas(SNG) [21]

The calculation of the equilibrium gas composition by varying the operating condition is described by Figure 2.5 [22].

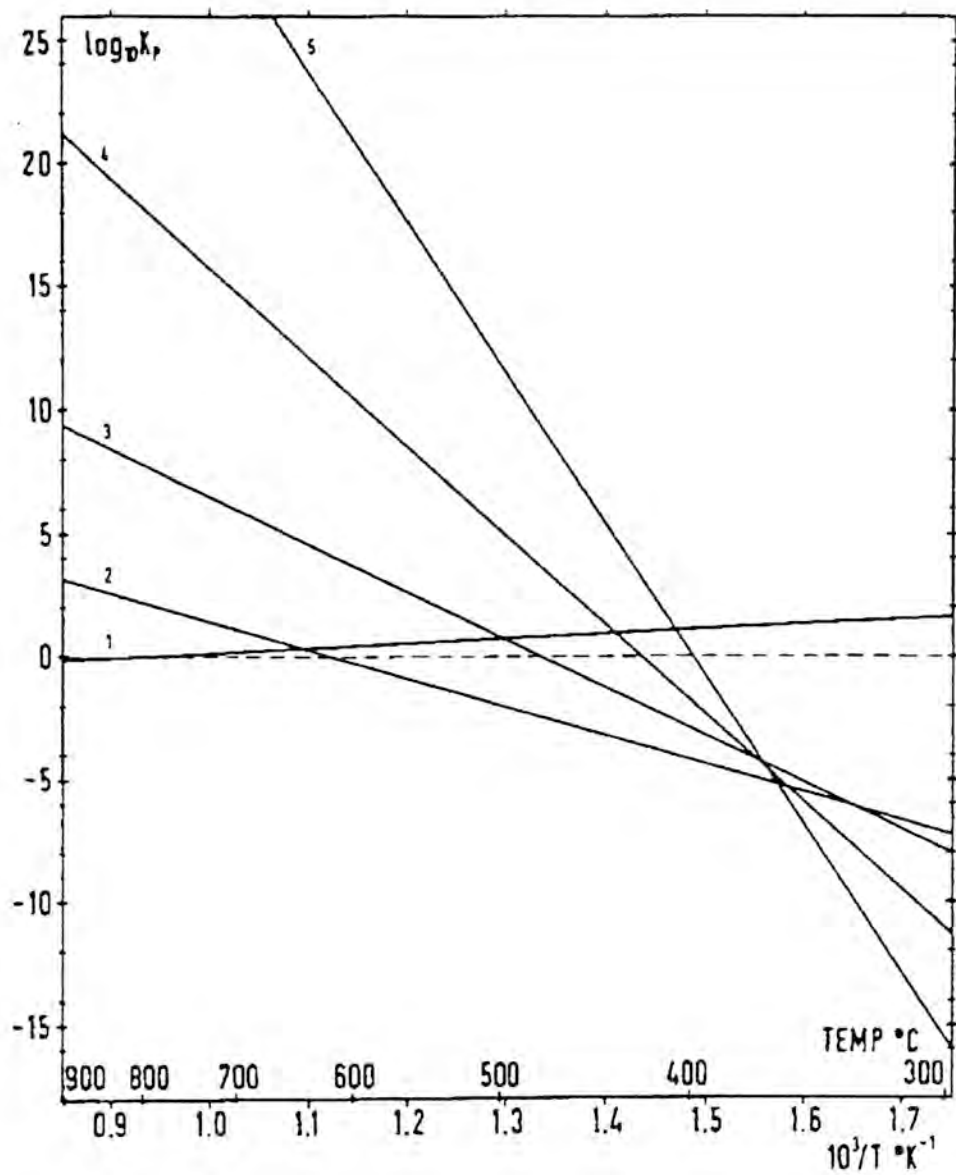


Figure 2.5: Equilibrium constants for reforming reactions [22]

			$-\Delta H^\circ (500^\circ\text{C}) \text{ kJ/mol}$	$K_p(500^\circ\text{C})$
1. $\text{CO} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CO}_2 + \text{H}_2$	37.18	4.98
2. $\text{CH}_4 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{CO} + 3\text{H}_2$	-222.19	$9.89 \times 10^3 \text{ atm}^2$
3. $\text{C}_2\text{H}_6 + 2\text{H}_2\text{O}$	$\rightleftharpoons$	$2\text{CO} + 5\text{H}_2$	-373.09	6.24 atm^4
4. $\text{n-C}_4\text{H}_{10} + 4\text{H}_2\text{O}$	$\rightleftharpoons$	$4\text{CO} + 9\text{H}_2$	-693.75	$1.21 \times 10^5 \text{ atm}^8$
5. $\text{n-C}_7\text{H}_{16} + 7\text{H}_2\text{O}$	$\rightleftharpoons$	$7\text{CO} + 15\text{H}_2$	-1174.40	$5.76 \times 10^{11} \text{ atm}^{14}$

2.2.4 Mechanisms

The mechanism of methane steam reforming on a nickel catalyst for hydrogen production has been depicted by Ross [19] as shown in Figure 2.6 and Figure 2.7

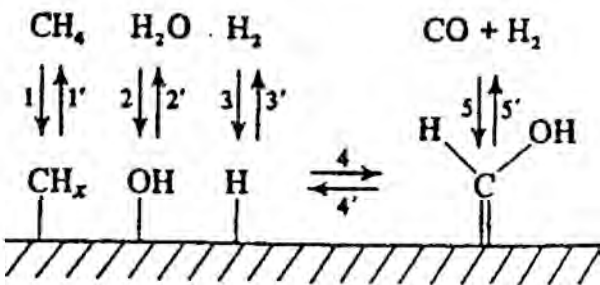


Figure 2.6: The diagram of mechanism of methane steam reforming on a nickel catalyst depicted by Ross [19]

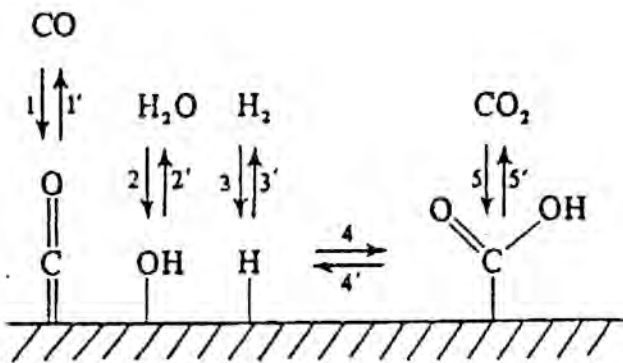
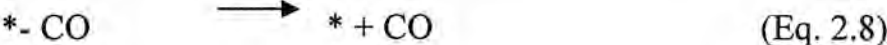
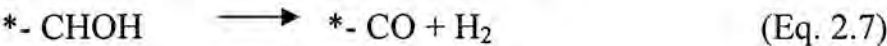
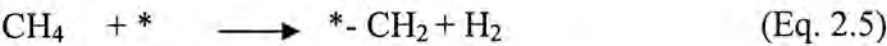
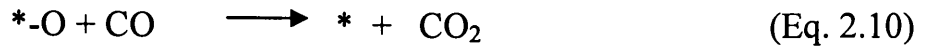
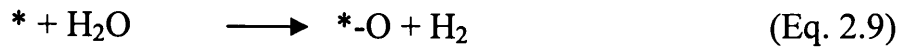


Figure 2.7: The diagram of further mechanism of methane steam reforming on a nickel catalyst for carbon dioxide production depicted by Ross [19]

Khomeko et al [23] also proposed an interesting mechanism for methane steam reforming on nickel foil without considering the production of intermediate surface carbon





where * is a nickel surface site.

2.2.5 Previous thermodynamic and kinetic studies of methane steam reforming

The kinetics of methane steam reforming has been studied by several researchers.

Bodrov et al. [24] studied the rate equation of the reaction when methane was reformed over nickel foil at 800 – 900 °C at atmospheric pressure. The rate of reaction was postulated to be:

$$r = k P_{\text{CH}_4} \quad (\text{Eq. 2.11})$$

$$r = 1 + a \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} + b P_{\text{CO}} \quad (\text{Eq. 2.12})$$

At 800 °C, values of $a = 0.5$ and $b = 2.0 \text{ atm}^{-1}$, were measured and at 900 °C the values of $a = 0.2$ and $b = 0.0 \text{ atm}^{-1}$ were documented. It also has been found that the activation energy over this temperature range was 130 kJ/mol [24]. Furthermore, it was concluded that the reaction of methane with steam was much faster than the decomposition of methane to carbon on a nickel surface. The kinetics of the methane steam reforming using nickel – alumina catalyst at 500 – 680 °C and low pressure (0 – 10 torr) was studied by Ross and Steel [25]. The result shows that the reaction rate was first order in methane and inverse half power in steam. It also was concluded that the rate of adsorption of methane and competition for the adsorption sites by steam was the rate determining step on a fully reduced catalyst.

A further study of the pore diffusion effect on methane steam reforming by Bodrov [26] (porous nickel catalyst of various sizes at 700 – 900 °C and atmospheric pressure)

has been reported. The reaction was reported to be first order with respect to methane and, due to the effect of pore diffusion, the rate of reaction of methane was directly proportional to the geometric surface area of the catalyst. Similarly, at lower temperature (400 - 600 °C), the reaction was also first order with respect to methane and inhibited by hydrogen [27]. At high temperature this inhibition disappeared. The rate equation was revealed to be:

$$r = k \frac{P_{CH_4}}{P_{H_2}} \quad (\text{Eq. 2.13})$$

The measured value of activation energy was 130 kJ/mol, which agreed with the results reported by Kemball [28], who studied the activation energy of the exchange of methane with deuterium over nickel film. It also was found by Wright et al [29] that the activation energy of methane cracking was the same (130 kJ/mol)

Wei and Iglesia [30] studied the mechanism of reaction of CH₄ with H₂O to produce synthesis gas and carbon on nickel catalysts. It was proposed that energy of activity of methane steam reforming using Ni on MgO at 550 – 750°C was 105 kJ/mol. The rate of reaction could be written as

$$r_f = k P_{CH_4} \quad (\text{Eq. 2.14})$$

Song and Pan [31] reported the energy of activation of methane steam reforming to be 69.1±20.2 kJ/mol on Ni/Al₂O₃(ICI), 165.7±26.4 kJ/mol on Ni/MgO/CeZrO and 160.1± 32.2 kJ/mol on Ni/MgO at 700 -850°C. It was suspected that the lower value resulted from mass transfer effects.

A kinetic mechanism for production of CO and H₂ through the initial step of CH₂ radical formation was proposed by Song and Pan [31] and Bodrov et al [27]. This step

was assumed to be rate determining. Similarly, it was postulated by Gordon et al [32] that this step was the rate determining step over nickel-kieselguhr catalyst at 638°C and atmospheric pressure.

The reaction of methane and steam in the absence of catalyst at 1000 – 1100°C and atmospheric pressure was studied by Gordon et al [32]. It was concluded that the reaction was possibly a combination of methane decomposition while steam behaved as an inert gas (diluent) until methane decomposed into carbon.

As has been shown, several vital factors such as catalysts, supports, pressure and temperature have remarkable effects on the result of study of the thermodynamic and kinetic study of reactions in methane steam reforming.

2.2.6 Carbon Formation

The primary problem for all hydrogen production processes from methane reforming is carbon formation. Carbon is a significant cause of catalyst deactivation and plant shutdown as it leads to reactor fouling and / or blocking of the active sites on the catalyst. This accumulation of carbon results from a greater rate of carbon formation as compared with the rate of carbon gasification. Although the addition of excess steam or oxygen is applied industrially for the prevention of carbon formation as shown in Figure 2.8, this solution can lead to high production costs. Therefore, the challenge is to expand understanding of carbon formation and to develop economic techniques for its minimization.

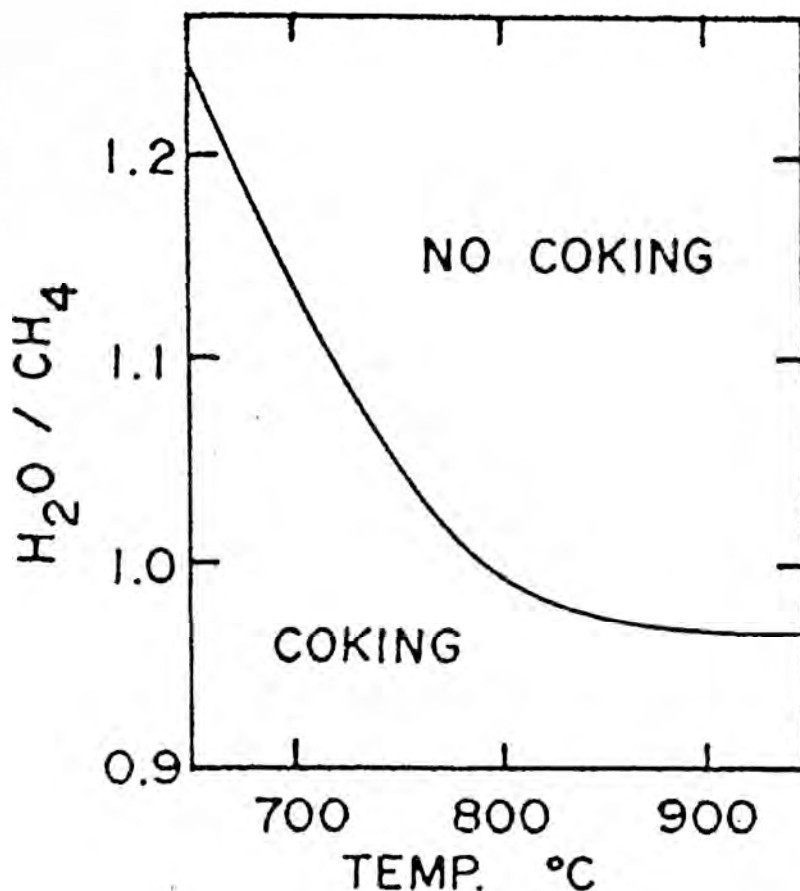


Figure 2.8: The minimum steam to methane ratio versus temperature, at which no carbon deposition will take place at equilibrium [33]

2.2.6.1 Types of carbon

The exact structure, morphology and location of the coke are possibly much more important than the total quantity of coke on the catalyst. The formation of each different type depends on temperature and reaction conditions [34].

Rostrup-Nielsen [35] classified carbon on nickel catalysts in steam reforming or reactions of pure hydrocarbons on nickel foils into three types, which are summarized in Table 2.1 [34].

Table 2.1: Formation and effects of species in steam reforming of hydrocarbon

[34]

	Whiskerlike	Encapsulating film	Pyrolytic carbon
Formation	Diffusion of C through Ni crystal, nucleation and whisker growth with Ni crystal at top	Slow polymerization of C_nH_m radicals on Ni surface into encapsulating film	Thermal cracking of hydrocarbon, Deposition of C precursors on catalyst
Effects	No deactivation of Ni surface, Breakdown of catalyst and increasing ΔP	Progressive deactivation	Encapsulation of catalyst particle, Deposition of C precursors on catalyst
Temperature range, °C	>450	<500	>600
Critical parameters	High temperature, Low H_2O/C_nH_m . No enhanced H_2O adsorption, Low activity, Aromatic feed	Low temperature, Low H_2O/C_nH_m . Low H_2O/C_nH_m . Aromatic feed	High temperature. High void fraction. Low H_2O/C_nH_m . High pressure. Acidity of catalyst

The relationship between types of carbon and their structure as formed on a metal catalyst is shown in Table 2.2 [35]

Table 2.2: The relationship between types of carbon and their structure as formed on a metal catalyst [35]

<u>Catalyst</u>	<u>Reaction</u>	<u>Poisons</u>
Silica/alumina	Cracking	Organic bases; hydrocarbons; heavy metals
Nickel, platinum, copper	Hydrogenation; dehydrogenation	Compounds of S, Se, Te, P, As, Zn, Hg; halides; Pb; NH ₃ ; C ₂ H ₂
Nickel	Steam reforming of methane, naphtha	H ₂ S
Nickel, cobalt, iron	CO hydrogenation of coal-derived gases	H ₂ S; COS; As; HCl
Cobalt	Hydrocracking	NH ₃ ; S, Se, Te, P
Silver	Ethylene → Ethylene-oxide	Ethane
Vanadium oxide	Oxidation	As
Iron	Ammonia synthesis, hydrogenation; oxidation	O ₂ ; H ₂ O; CO; S; C ₂ H ₂ ; Bi; Se; Te; P; VSO ₄
Platinum, Palladium	Automotive oxidation of CO and hydrocarbons	Pb; P; Zn
Cobalt and molybdenum sulfides	Hydrotreating of petroleum residua	Asphaltenes; N Compounds; Ni; V

Goodman [36] used Auger electron spectroscopy in order to study the kinetics of surface carbide (C α) build up from CO and its removal with hydrogen on a nickel (100) surface. It has been found that the p (pi electron) divided into 2 sectors; a carbide region in which C/Ni process coverage was less than 0.28 and a graphite region in which coverage was more than 0.28 and favored at temperature above 600°C (Figure 2.9).

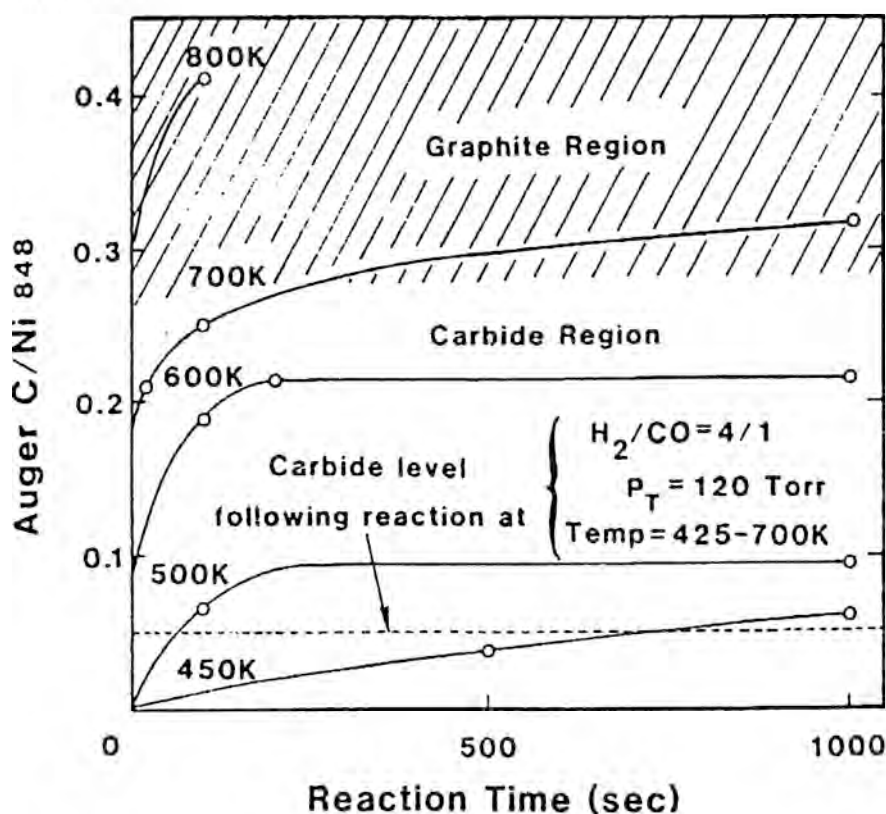


Figure 2.9: The rate of carbon buildup on Ni(100) catalyst by reaction with 24 torr CO. Ordinate values for carbon have been normalized to the 848 Auger transaction intensity

The apparent energy of activation for CO dissociation was estimated to be approximately 92 – 102 kJ/mole and the reaction was executed at a total pressure of 16 kPa and between 425°C and 720°C with a H₂/CO ratio of 4:1.

2.2.6.2 Mechanism of Carbon formation on Ni catalyst

Catalyst deactivation by carbon formation is caused by accumulating of inactive carbon on the metal surface. This deactivation is formed by less reactive β – carbon or by condensed polymer [37 and 38] at low temperatures (300 – 375°C). At higher temperature, encapsulation of the metal surface [39 and 40] can involve graphitic carbon [36, 41 and 42]. The steps of the mechanism of catalytic carbon formation have been described by Rostrup – Nieson and Trimm [43]:

- i) Adsorption of the hydrocarbon on the metal surface.
- ii) Formation of surface/ bulk metal carbide.
- iii) Dissolution of the adsorbed carbon atoms or metal carbide in the metal crystallite.
- iv) Diffusion through the metal.
- v) Precipitation of carbon atoms at the rear of the metal particle to form a polymeric carbon filament.
- vi) Lifting of metal particles from the support material with continuing carbon precipitation behind the metal particle on the support.

The formation of whisker or filamentous carbon occurs for the temperature range 375 -650°C. Although the mechanism of filamentous or whisker carbon has been previously described, there also are controversies about the driving force behind carbon whisker formation and the rate determining step. Two different driving forces have been proposed. On one hand, it is suggested by Rostrup–Nielson that the driving force is a concentration gradient of carbon atoms across the metal particle and this concentration is lower at the growing filament / metal interface [43]. On the other hand, Harris and Baker [37] suggest that the presence of a temperature gradient, as a result of the exothermicity of hydrocarbon dissociation at the metal surface, drives

the reaction. Alternatively, the driving force can combine both concentration and temperature when some hydrocarbon decomposition reaction results in carbon filaments [44].

Similarly, two different models of the mechanism of carbon transformation for the formation of carbon whiskers have been proposed. The former model involves the bulk diffusion of carbon through the metal whereas the later describes surface migration of adsorbed carbon atoms to the carbon / metal interface [43 and 45]. The previous model is supported by evidence that metal carbide is a reaction intermediate [37, 46 and 47]. Indeed, it has been found that the apparent activation energy for the growth of carbon whisker is comparable with this energy for carbon diffusion in nickel [48].

Although whisker carbon has little effects on the activity of the catalyst, formation creates pressure drop across the reactor [13, 49 and 50]. The catalyst and reactor voids are plugged and Rostrup – Nielsen [13] reports that the system is blocked by this plugging [13].

2.2.6.3 The application of Magnesia (MgO) as a support and the removal of carbon formation

As coke formation is a major problem for hydrogen production from hydrocarbon, the selection of a support which favors coke removal is necessary. Due to the capacity for improving adsorption of water and promoting carbon gasification [51 and 52], the application of MgO as a support is a good choice. In addition, a study by Borowiecki [53 and 54] states that the use of MgO as support led to a high dispersion of nickel

and to an increase in resistance to carbon formation, since the metal dispersion increased for butane steam reforming. Indeed, Armor and Martenak [15] indicate that methane steam reforming at high pressure using NiO/MgO shows a lower carbon deposit rates than over a traditional Ni/Al₂O₃ reforming catalyst.

The applications of magnesia as a support for steam reforming catalyst require certain fixed precautions. Under some circumstances, the catalyst can be hydrated and markedly weakened, as shown in following equation:



Figure 2.10 reveals the relationship between temperature and the partial pressure of water equilibrium with Mg(OH)₂. It can be seen that hydration can be avoided by controlling pressure during steam reforming. Furthermore, kinetic studies of hydration have shown a liquid phase reaction, where water condenses in the internal pores [55 and 56]. Consequently, the relative humidity of the atmosphere has a complete influence the hydration and hydration failure; hydration is not a problem except where the catalyst based on magnesia is exposed to liquid water or is operated near water condensation (dotted line in Figure 2.10) [11].

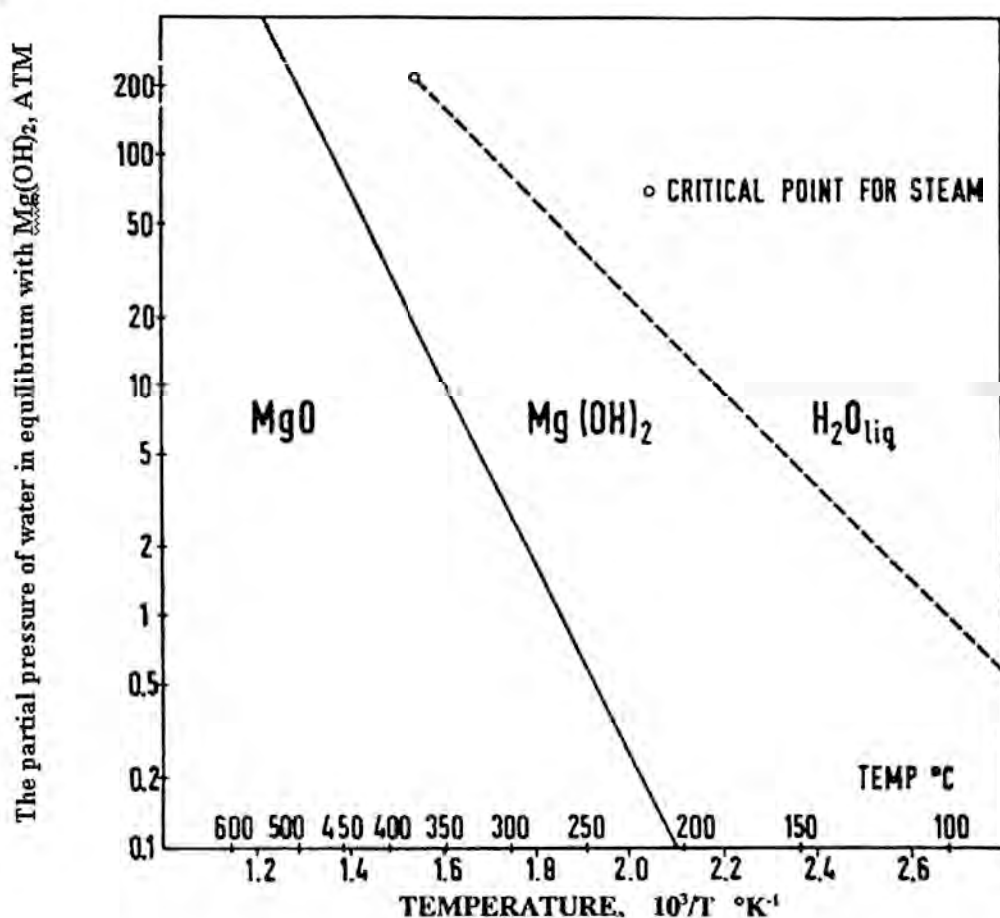


Figure 2.10: Equilibrium steam pressure for $\text{Mg(OH)}_2 = \text{MgO} + \text{H}_2\text{O}$

Dotted curve: Pressure of saturated steam [11]

2.2.7 NiO –MgO interaction

Boudart [57] reported that there are two kinds of metal-support interaction. The first interaction results in bifunctional catalysis. Bifunctional catalysis is apparent when there is a reaction on the metal to generate an intermediate which further reacts on the support. The product obtained on the support metal can not be formed only on the metal or on the support alone. The second interaction, which includes an interface between the metal and support, is less obvious. The metal particle, especially small

particles, can be insulated by semi conducting supports. The insulation results in different chemical properties.

Trimm [12] stated that the role of the support in chemical reaction with the catalyst is vital. It is different from bifunctional catalysis as the support acts as a co – catalyst. Consequently, it affects the effect of the interactions between the support and the catalyst and modifies catalyst performance [12].

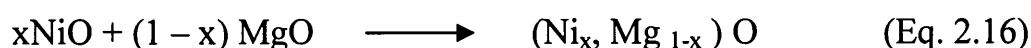
There are four categories of catalyst – support interaction [12].

- 1) The possible effect of geometrical interaction involves catalyst and support on a molecular scale or by electron transfer.
- 2) The appearance of support – catalyst influence in alloys (or in solid solution of two metals) by the effect of a catalytically interactive material (e.g. support) on the structure of the active catalyst.
- 3) The possible deactivation of a catalyst caused by a chemical reaction between catalyst and support.
- 4) The appearance of catalyst – support interaction resulting from the transfer of an adsorbed gas across the surface from the catalyst to the support.

It is well known that the formation of a NiO – MgO solid solution by the calcination of a mixed oxide at high temperature [58] is highly favorable and much attention has been paid to its specific properties [59 - 62]. Moreover, it was illustrated by Parmaliana et al [61] that the activity of Ni (17.9%)/MgO catalyst calcined at 800°C was low for the steam reforming. They described their result as due to Ni^{2+} in the solid solution, with reduction in rate resulting from the formation of solid solution.

However, the strong interaction between NiO and MgO leads to a highly stable performance of Ni/MgO, resulting in the suppression of coke formation. Due to the strong interaction between NiO and MgO solid solution, the reduction was slower and the reduction temperature window is wide when compared with pure NiO. Hence, relatively small and finely dispersed metallic Ni particles were obtained during reduction. In this case, the metal surface becomes more resistant to coke formation, as the ensemble size necessary for carbon formation is larger than that for methane reforming [63].

Interaction between nickel and magnesium oxide is also observed under steaming condition at high temperatures.



The formation of the green solid solution of nickel and magnesium oxide is favorable at high temperature while less well-crystallized structures occur at low temperature.

Furthermore, the support interaction can be affected by calcination of the catalyst. The effect of calcination and reduction temperatures on the metal dispersion of magnesia – supported nickel catalyst from 400 – 800°C as measured by hydrogen chemisorption measurements was studied by Arena et al [64]. The results were compared with the physical mixture of a nickel oxide – magnesia. They applied XPS to determine the role of the bulk $\text{Ni}_x, \text{Mg}_{1-x}\text{O}$ solid solution in controlling NiO reducibility and the metal dispersion in Ni/MgO. They proposed the mechanism of NiO-MgO interaction at different calcinations temperatures (T_c) as shown below:

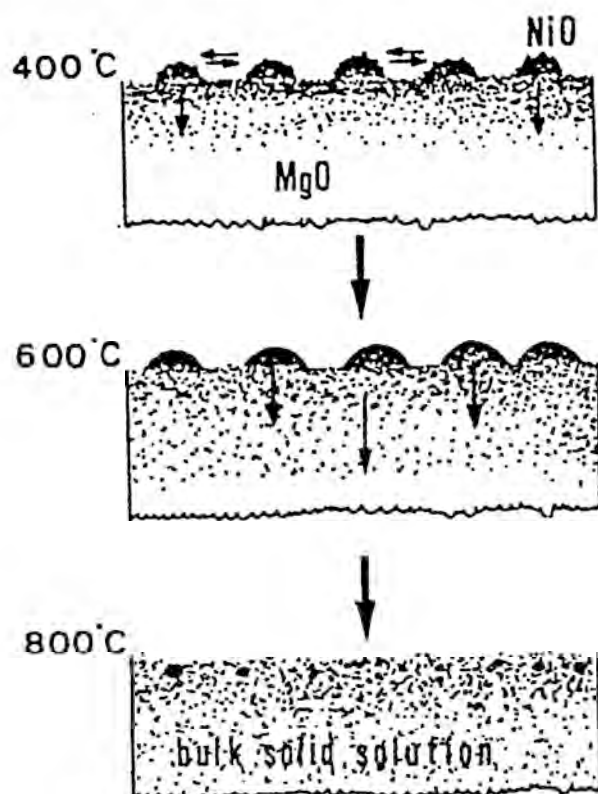


Figure 2.11: Mechanism scheme of NiO-MgO interaction at different calcination temperature [64]

It was inferred that, when T_c increases from 400°C to 600°C, the agglomeration of surface “free” NiO clusters occurs in larger particles, reducing the “lattice distortion” and the reduction rate. Whereas over T_c 600°C, the diffusion of Ni^{2+} ions into the matrix is very fast and the system significantly develops via an equilibrium state corresponding to the bulk $\text{Ni}_x\text{MgO}_{(1-x)}$ solid solution.

The surface properties of the NiO/MgO system substantially rely on the possible formation of solid solutions. XPS and ISS data, indicates that, at calcinations temperature over 600°C, there is a change in the structure and the surface properties of Ni/MgO catalysts. Both the reducibility of the NiO and the sintering of Ni particles (without altering the general pattern) are controlled by metal loading. It is considered

that calcination at 400°C is the optimal temperature resulting in the highest metal surface area in magnesia-supported nickel catalysts.

Parmaliama et al [65] studied the properties and reactivity of the surface in methane steam reforming over magnesia-supported nickel catalysts, which were calcined by passing air at temperature from 400 – 800°C. They applied Transmission Electron Microscope (TEM), Infra Red (IR) spectroscopy of adsorbed CO and catalytic measurements for the analysis of the surface properties and the reactivity of magnesia – supported nickel. The formation of irreducible NiO-MgO solid solution was promoted by calcination at over 600°C and a nickel loading lower than 11 %. In addition, due to a volcano – shape relationship and the adverse effect of high metal dispersions (higher than 15 %) on both the activity and stability of Ni/MgO, the reduction temperature was strongly influenced by both the metal surface area and the catalytic activity.

2.2.8 The effect of high pressure on methane steam reforming

Fedders et al. [66] showed the methane conversions at chemical equilibrium for methane steam reforming when the pressure was increased at different temperature and when the temperature was increased at 40 atm at different methane steam ratios as shown in Figure 2.12.

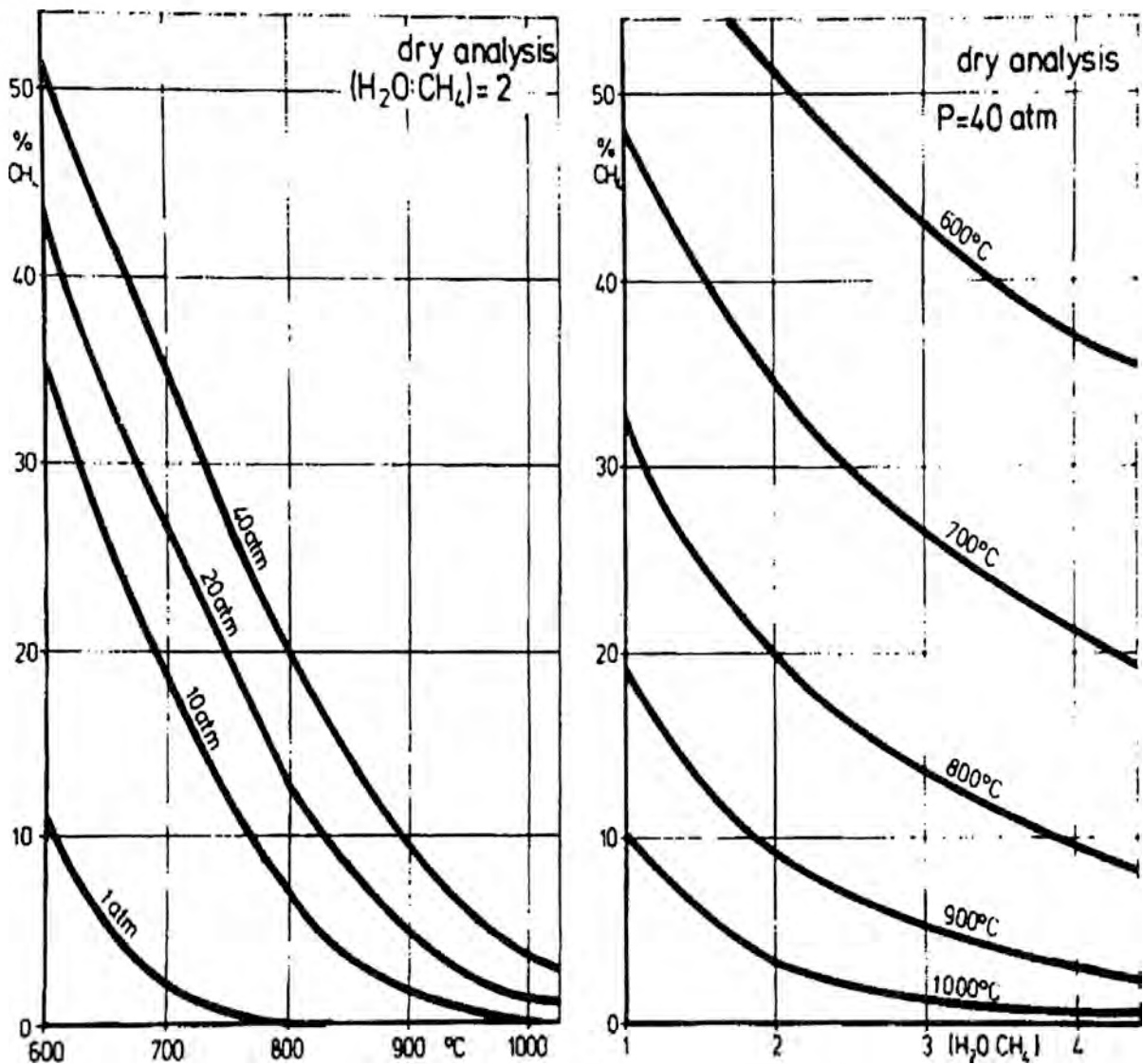


Figure 2.12: Methane content at chemical equilibrium [166]

According to Figure 2.12, the methane conversion decreases at higher pressure. The equilibrium was found to be in agreement with the study of methane steam reforming at high pressure by Lee et al. [67]. They found that high pressure has an opposite effect on the steam reforming of methane; it decreases the equilibrium conversion but it increases the permeation rate. Furthermore, it also was found that there is a significant increase in carbon deposition when increasing pressure. The effect of total pressure upon carbon formation from a mixture of methane and carbon dioxide is illustrated in Figure 2.13.

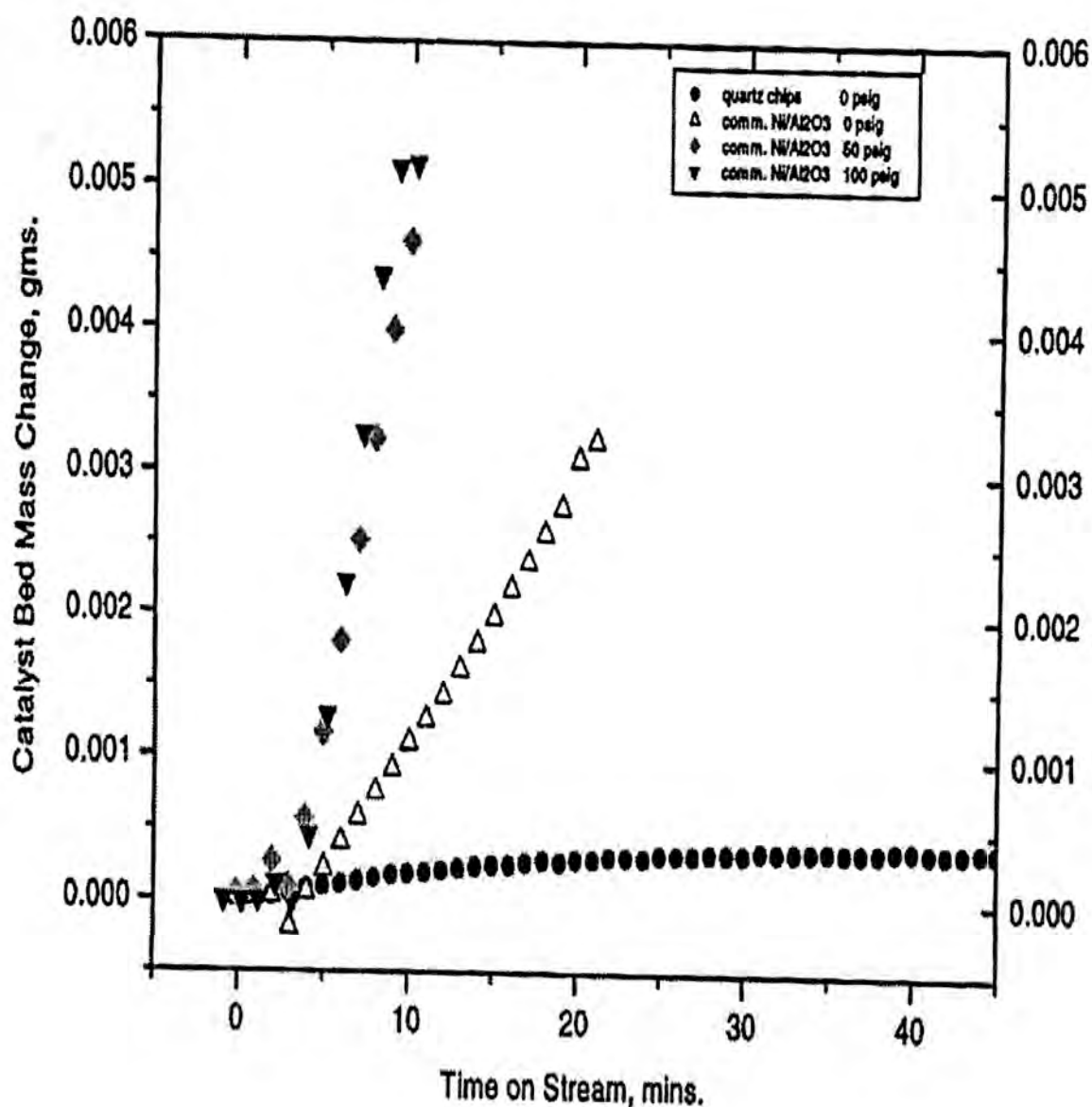


Figure 2.13: Effect of total pressure upon carbon deposition; conditions: 650°C, CO₂:CH₄ = 2:1, natural gas as CH₄, H₂, pre-reduction, 200mg sample holder (filled circles- quartz chips at 0 psig; inverted triangles- with increasing pressure at 100 psi) [67]

The maximum mass on the Ni catalyst profiles corresponds to where the feed flow was halted and a N₂ purge of the catalyst bed was initiated to prevent reactor rupture.

Armor et al [15] studied the carbon formation rate over NiO/MgO as a function of operation pressure during CO₂ reforming of CH₄. It was concluded that an increase in pressure resulted in a dramatic increase on carbon deposition rate [15].

Studies of methane steam reforming during 1981 and 2006 are summarized in Table 2.3.

Table 2.3: Summary of methane steam reforming studies (1981 – 2006)

Catalyst	T, °C	P, kPa	Orders CH ₄ (H ₂ O)	Ea, kJ /mol	Notes	Ref
Fe, Ni, Fe-Ni	700-900	101	1(0)	185	The decomposition of CH ₄ is r.d.s.	[64]
Alloys Ni/Al ₂ O ₃	550-675	505-1515	1(+)	a.364 b.317	Kinetics and diffusional influences study, a.CO production; b. CO ₂	[65]
Ni/ Al ₂ O ₃	740-915	101			Coke deposition study. Coke formation is r.d.s.	[33]
Ni/ Al ₂ O ₃	640-740	101	1	183	The dissociative adsorption of CH ₄ is r.d.s.	[68]
Ni/ NiAl ₂ O ₄ Spinel	450-525		0.24(0.28)	68.8	The reduced form of nickel-aluminate is highly active.	[69]
Ni/ Ni, Ca-Al ₂ O ₄	450-550		0.62(1.05)	90.4	Surface reaction is r.d.s.	[69]
Ni/ MgAl ₂ O ₄	500-575	303-505	1 1	a241.1 b243.9	A non monotonic dependence upon steam partial pressure a.CO production; b. CO ₂ production	[70]
Ni/ Al ₂ O ₄ + dopants	500-700	101		150	Carbon formation study over mono&bimetallic catalysts.	[71]
Ni/ Al ₂ O ₃	800	122	1(+)	B.45.2 N.45.1	Catalyst calcined at 1173 K showed less deactivation at 600h.	[72]
Ni/ CaAl ₂ O ₃	475-550	101-303	1	185	A nonmonotonic dependence upon steam partial pressure	[73]
Topsoe/ RKNR	350-400	101	1(-0.17)	59.6	Surface reaction is r.d.s.	[74]
Ni-wire	950				Confirmed the occurrence of gas-phase reactions	[75]
NiO/ MgO-Al ₂ O ₄	800	101			Protective layer of MgAl ₂ O ₄ spinel improved catalytic performance	[76]
NiO/ Al ₂ O ₃	500	101	0.91(-0.85)	284	H ₂ O and CO ₂ are major products of the methane steam reforming	[77]
Ni	$r = kP_{CH_4}$					[78]
Ni foil	$r = \frac{kP_{CH_4}}{1 + a[P_{H_2O} / P_{H_2}] + bP_{CO}}$					[79]
Ni/MgAl ₂ O ₄	$r = a / P_{CH_4}^{2.5} (P_{CH_4} P_{H_2O} - P_{CO} P_{H_2}^3 / b) / \alpha^2 + c / P_{CH_4}^{2.5} (P_{CH_4} P_{H_2O} - P_{CO} P_{H_2}^3 / d) / \alpha$					[80 and 81] ^a

^a $\alpha = 1 + K_{CO}P_{CO} + K_{H_2}P_{H_2} + K_{CH_4}P_{CH_4} + K_{H_2O}P_{H_2O} / P_{H_2}$

2.3 Experimental Technique

2.3.1 Materials

All gases used in the experimental work were supplied by Linde Gas, the purity and area of application are reported in Table 2.4.

Table 2.4 Gas Specifications

GAS	SPECIFICATION	USE
Hydrogen	Industrial dry, 99.9%	Catalyst Reduction
Helium	Ultra high purity, 99.999%	Carrier gas
Argon	High purity	Carrier gas
Nitrogen	Volumetric Std., 32.5 ± 0.25%	Carrier gas-single B.E.T and GC Standard
Methane	High purity, 99.9%	GC Standard

2.3.2 Chemicals

The purity, source and application of all chemicals used in the reaction study and details of the G.C. columns in the gas chromatography analysis are presented in Table 2.5 below.

Table 2.5 Chemical Specification

CHEMICAL	SPECIFICATIONS	USE
Nickel (II) Nitrate- Hexahydrate	FSE, Australia, 99.101%	Base-metal
Magnesium (II) Nitrate- Hexahydrate	Sigma, Aldrich, Australia Research Grade	Promoter
Monolite	Sigma, Aldrich, Australia 99.9%	Support
Molecular Sieve and Porapak mixture	CTR-1, 1.8 m length	GC column
Molecular Sieve	5-A, 1.8 m length	GC column

2.3.3 Catalyst Preparation

The preparation of catalyst is an integral part of catalytic reaction. There are two most common techniques for catalyst preparation. The first method involved impregnation of a metal salt in an aqueous solution onto a support material e.g. γ - Al_2O_3 . The other method of catalyst preparation is co – precipitation, in which solutions of metal salt are added together usually at constant ph, and precipitate into the desired product.

A general treatment after the synthesis is calcination (heating the sample in air, in order to ‘clean up and ‘stabilize’ the catalyst) and/or reduction (heating in a reducing atmosphere usually containing hydrogen, in order to activate the catalytic metal of the catalyst [20].

For the kinetic study of methane steam reforming in this thesis, wet co-impregnated MgO and Ni on a monolith was used. The preparation was divided into 2 steps.

The first step involved deposition of MgO on a ceramic monolith. A concentrated solution of $\text{Mg}(\text{NO}_3)_2$ was prepared by dissolving 160 g of $\text{Mg}(\text{NO}_3)_2(6\text{H}_2\text{O})$ in 100 g of deionised H_2O and stirred vigorously at room temperature until complete dissolution. The support monolith samples were cut into 1 cm X 1 cm X 1 cm cubes and dipped into the $\text{Mg}(\text{NO}_3)_2$ coating solution for 1 minute and then withdrawn slowly. The coated sample was blown with a jet of air in order to remove the extraneous material and dried at 120°C for 3 hours. Finally, the dried sample was calcined at 500°C in air for 3 hours. The amount of MgO deposited per coating was ca 3 wt%. Subsequently, the same procedure was repeated 4- 5 times. A coating load of 12 – 15% was achieved after 4 – 5 repeated coating as analysed by XRF.

The final step involved deposition of nickel on MgO coated ceramic monolith. Nickel was deposited on the MgO coated ceramic monolith by impregnation. In a typical preparation, a concentrated solution of $\text{Ni}(\text{NO}_3)_2(6\text{H}_2\text{O})$ in 15g of water was used. A dry MgO coated monolith sample was immersed in the $\text{Ni}(\text{NO}_3)_2$ solution for a short period of time and then removed from the solution quickly. The excess liquid was blown off with a jet of air. The $\text{Ni}(\text{NO}_3)_2$ impregnated sample was dried at 120°C for 3 hours and then calcined at 500°C for 4 hours. A nickel species (NiO) loading of 6- 8wt% was achieved by the above mentioned method (analysed by ICP).

2.3.4 B E T Surface Area Measurement

The determination of the BET surface areas by using the flow adsorption/desorption method using a calibrated gas mixture of 30% N₂/He was firstly described by Nelson and Eggersten [82]. The method has been suggested to give the best agreement with multipoint BET method [83]. Figure 2.14 showed the apparatus used in this particular measurement. The sample was weighed and loaded in the sample tube and degassed with pure nitrogen at 120°C for 1 hour, then cooled to room temperature. Injecting known volumes of nitrogen into the carrier gas was employed for the determination of the calibration curve of nitrogen. Two samples loops were used (a small loop of 0.5 ml and large loop of 5ml) so that the volume of nitrogen that evolved from a sample was between the loop volumes. Hence, a linear interpolation of the exact volume of nitrogen used could be obtained.

Subsequently, a flow of the H₂/He mixture was switched on to pass over the sample at liquid nitrogen temperature (-196°C). This resulted in adsorption of nitrogen from this onto the sample surface, as reflected in a negative peak on the chromatogram. After the baseline stabilized (ca 2-3 min), desorption of the nitrogen from the catalyst was achieved by replacing the liquid nitrogen with a water at ambient temperature. The amount of nitrogen desorbed was measured from the chromatogram.

Reproducible results could be obtained by repetition of the adsorption/desorption procedure described above

The following equation for calculation of the BET surface area is shows as [84]

$$S_{\text{BET}} = 4.35V_a(273/T)(1-XP_s/P_{\text{sat}})(760/P_{\text{atm}})/W_s$$

Where

S_{BET} = the BET surface area. m^2/g

V_a = the volume of the N_2 adsorbed/ desorbed, ml

T = room temperature

X = mole fraction of N_2 adsorbed/desorbed, ml

P_s = sample pressure. mmHg

P_{sat} = saturation pressure of N_2 , mmHg

P_{atm} = the atmosphere pressure, mmHg

W_s = the sample weight, g.

All calculations were based on desorption peaks as they were sharper in shape.

GC calibration were carried out to determine the response factors and retention times for H₂ CO₂ , N₂, CH₄ and CO by introducing available standard gases onto the column through the GC sample port inlet. Table 2.7 lists the response factors, the corresponding retention time for H₂, CO₂, N₂, CH₄ and CO.

Table 2.6 Operating conditions for GCs

Gas Chromatograph	Detector	Column	Carrier Gas	Flow Rate (ml/min)	Column Temp (°C)	Detector Temp (°C)	Current (mA)
GC-1 (Shimadzu 8A)	TCD	CTR-1	He	25	70	180	120
GC-2 (Shimadzu 8A)	TCD	Mol Sieve	Ar	28	40	180	70

Table 2.7 Response factors for GCs

Gas Chromatograph	Component	Retention time (min)	Response factor
GC-1 (Shimadzu 8A)	CO ₂	1.17	1.60
	N ₂	3.57	0.90
	CH ₄	5.89	1.0
	CO	7.85	0.89
GC-2 (Shimadzu 8A)	H ₂	0.67	0.091
	N ₂	1.68	1.0

2.3.6 An experiment for a kinetic study of steam reforming of methane at high pressure

The steam reforming rig was designed to operate at 600°C and 40 bars total pressure.(Figure 2.15) High pressure gases (CH_4 , N_2) were supplied from dedicated cylinders, while low pressure gases (H_2 , He, Ar) were supplied from the lab reticulation system. High pressure steam was produced by pumping water into a heater maintained at ~220°C which produced steam partial pressures up to 26bars. The catalyst was Ni/MgO deposited on a ceramic monolith support, held inside a stainless steel tube reactor.

After the catalyst was reduced at 600°C in a 30% H_2/N_2 mixture for 4 hours, methane and steam were introduced to the reactor. Products of the steam reforming reaction were H_2 , CO and CO_2 , all of which are analyzed along with unconverted CH_4 and N_2 downstream of the reactor. The reactor pressure could be accurately controlled using an electronic pressure controller immediately upstream of the GCs.

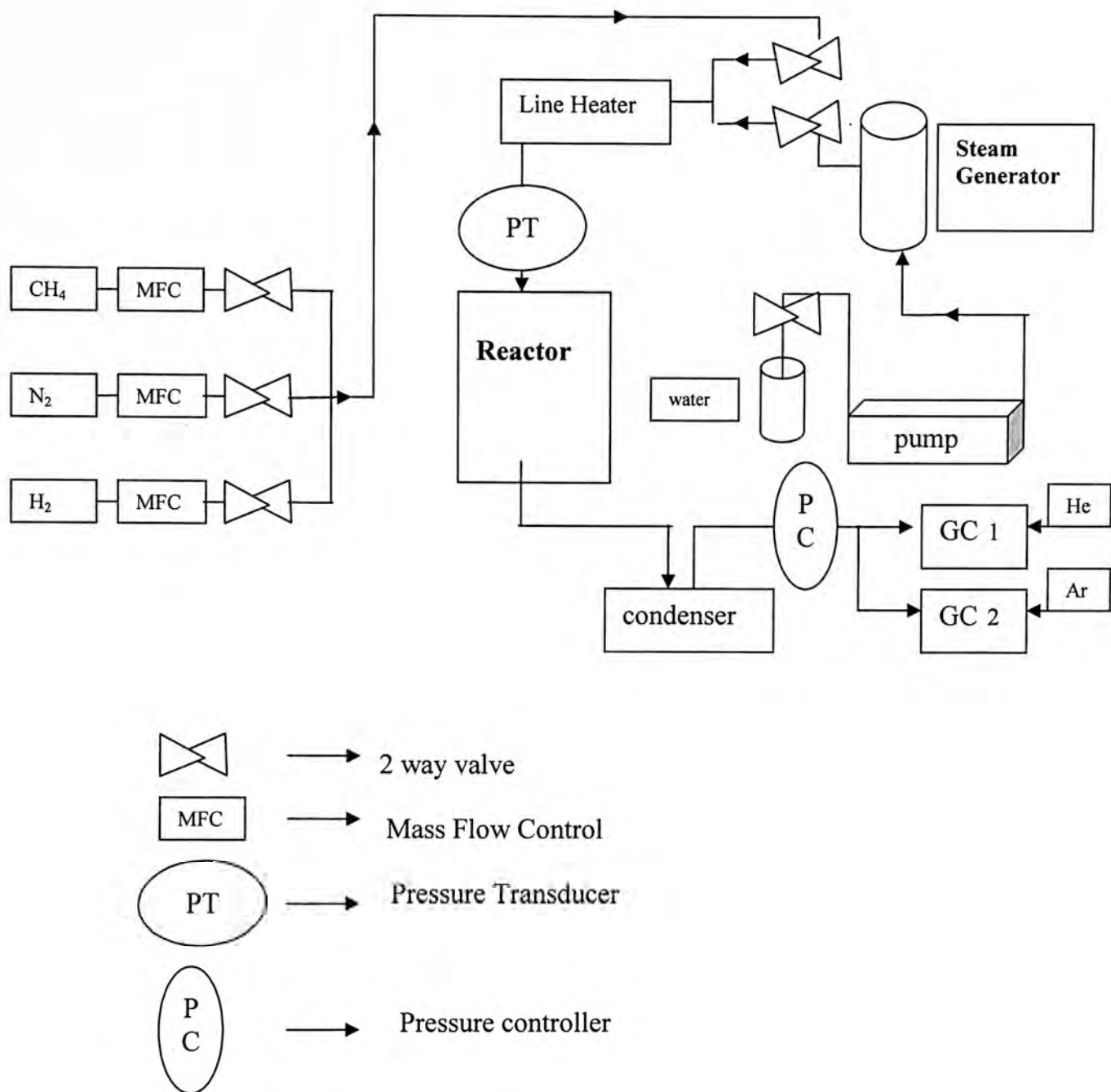


Figure 2.15: Flow diagram of experimental setup

2.4 Results and discussion

In order to study the kinetic of methane steam reforming at high pressure, The experimental runs described in Table 2.8 were conducted.

Table 2.8: Experimental conditions for kinetic measurements

Run	Temperature (°C)	CH ₄ (ml/min)	H ₂ O (ml/min)	N ₂ (ml/min)	$\frac{steam}{CH_4}$	P_{CH_4} bar	P_{H_2O} bar	P_{N_2} bar	Total flow (ml/min)
1	600	14.2	52.4	44.8	3.7	5.2	18.8	16.1	111.4
2	600	16.1	60.8	33.1	3.8	5.9	22	12.2	110
3	600	14.9	60.8	34.2	4.1	5.4	22	12.7	109.9
4	600	11.8	60.8	52	5.1	4.3	22	13.8	124.6
5	600	14.2	60.8	37.6	4.3	5.2	22	12.9	110.2
6	600	18.1	60.8	18.1	3.3	6.6	22	11.5	110
7	600	14.2	43.9	52	3.1	5.2	16.1	16	111.4
8	600	14.2	38.3	57.5	2.7	5.2	14	16.1	110
9	550	14.2	52.4	44.8	3.7	5.2	18.8	16.1	111.4
10	500	14.2	52.4	44.8	3.7	5.2	18.8	16.1	111.4
11	450	14.2	52.4	44.8	3.7	5.2	18.8	16.1	111.4

Catalyst characterization data for NiO/MgO is reported in Table 2.9

Table 2.9 Catalyst characterization data

Catalyst	wt%NiO loading	wt%MgO loading	Specific surface area (m ² /g)
Ni/MgO on monolith	6-8%	12–15%	1.1

The kinetic study of the reaction was divided into 5 parts

- 1) Determination of the kinetic orders of methane and the steam
- 2) Measurement of the energy of activation
- 3) The deactivation order of methane
- 4) The relationship between the steam methane ratio and the selectivity to carbon products (CO, CO₂ and C)
- 5) The constant parameter estimates of the different kinetic models.

2.4.1 The kinetics orders in methane and steam

Although a literature survey of methane steam reforming indicated that the reaction is first order with respect to methane, the role of steam on the reaction rate is in doubt. Several kinetic orders, which can be classified into 3 groups, have been observed by researchers. Negative order dependence of the rate of reaction upon steam partial pressure have been reported by Bodrov et al. [85], Ross and Steel [86], Al-Ubaid [87], Nikrich [88], and more recently Ma et .al [89]. Zero order dependence on steam was observed by Akers and Camp [90], Brodrov et al. [91 and 92], Münster and Grabke [93], and also by Sidjabadet [94]. Finally, positive orders have been reported by Atroshchenko et al. [95], Quach and Rouleau [96], Kopsel et al. [97] and De Deken et al. [98]. Nevertheless, it is interesting to note that alternative flexible rate expressions,

which could give both positive and negative order dependence (non-monotonic behavior) of the rate of reaction upon steam partial pressure, have been developed by Al-Ubaid [87], Xu and Fromet [99] and ,later, El-Nashaise et al. [100].

The relationship between the rate of reaction and the partial pressure of methane and steam is can be described by

$$R = k P_{CH_4}^m P_{H_2O}^n \tag{Eq. 2.17}$$

$$\log (\text{reaction rate}) = \log k + m \log P_{CH_4} + n \log P_{H_2O} \tag{Eq. 2.18}$$

where R is the rate of reaction, k is the rate constant, P_{CH₄} and P_{H₂O} are the partial pressure of methane and steam and m and n are kinetic order of methane and steam respectively.

The relationship between log of reaction rate based on mole consumption of methane and the partial pressure of methane is more useful in determining the kinetic order of methane. Similar arguments hold for the order in steam.

In order to determine the kinetic order with respect to methane, the reaction rate was based on the consumption rate of methane. The reaction rate can be defined as the rate of mole consumption of methane per one gram catalyst and one second. Reaction rates were measured by using different partial pressures of methane and constant partial pressure of steam (Table 2.10, Table 2.11, Table 2.12 and Figure 2.16). The calculation method is shown in APPENDIX A.

The kinetic order with respect to steam was based on the consumption rate of steam. The reaction rate is defined as the rate of mole consumption of steam per one gram catalyst and one second (Table 2.11, Table 2.12 , Table 2.13 and Figure 2.16). The calculation method s shown in APPENDIX A.

The kinetic order of methane can be measured from the slope of the relationship between $\log(\text{reaction rate})$ and $\log(\text{methane partial pressure})$ at constant steam partial pressure (Figure 2.16). In order to determine the kinetic order with respect to methane, five experiments were fed by different partial pressure of methane but at the same partial pressure of steam (22 bars). The result of reaction rate from the five experiments was shown in Table 2.10.

Table 2.10: The reaction rate at different partial pressure of methane feed but at the same partial pressure of steam (22 bars)

P_{CH_4} (bar)	Reaction Rate (mol g ⁻¹ s ⁻¹)		
	40bar	40 bar	40 bar
4.3	1.16 x 10 ⁻⁵	1.04 x 10 ⁻⁵	9.46 x 10 ⁻⁶
5.2	1.53 x 10 ⁻⁵	1.40 x 10 ⁻⁵	1.28 x 10 ⁻⁵
5.4	1.65 x 10 ⁻⁵	1.49 x 10 ⁻⁵	1.37 x 10 ⁻⁵
5.9	1.89 x 10 ⁻⁵	1.69 x 10 ⁻⁵	1.54 x 10 ⁻⁵
6.6	2.24 x 10 ⁻⁵	2.02 x 10 ⁻⁵	1.84 x 10 ⁻⁵

The calculated result of $\log(\text{reaction rate based on the decomposition of methane})$ and $\log(\text{partial pressure of methane})$ at constant steam partial pressure was used to plot the relationship between $\log(\text{reaction rate})$ and $\log(\text{partial pressure of methane})$ (in Figure 2.16) is shown in Table 2.11

Table 2.11 The relationship between log (reaction rate) and log (partial pressure of methane)

Log(P_{CH_4})	Log(Reaction Rate)		
	40bar	40 bar	40 bar
0.63	-4.93	-4.98	-5.02
0.72	-4.82	-4.85	-4.89
0.73	-4.78	-4.83	-4.86
0.77	-4.72	-4.77	-4.81
0.82	-4.65	-4.69	-4.73

Kinetic orders of methane were evaluated from the relationship between log (reaction rate) and log (partial pressure of methane) in Figure 2.16, and are shown in Table 2.12

Table 2.12 The kinetic orders of methane at different time and pressure

Duration time and pressure	Kinetic order
90 min(40bar)	0.82
120 min(40 bar)	0.82
150 min(40 bar)	0.82

The kinetic order of steam can be determined from a similar relationship (slope of the plot of $\log(P_{H_2O})$ vs. $\log(R)$ at constant P_{CH_4} (Figure 2.17). In order to determine the kinetic order in steam, five experiments were fed by different partial pressure of steam but at the same partial pressure of methane (5.2 bars). The result from the five experiments is shown in Table 2.13. A reaction rate in Table 2.13 is the mole of decomposed steam per one second and a gram of catalyst.

Table 2.13 The reaction rate at different partial pressures of steam and at the same partial pressure of methane (5.2 bars)

P_{H_2O} (bar)	Reaction Rate (mol g ⁻¹ s ⁻¹)		
	90 min(40 bar)	120 min(40 bar)	150 min(40 bar)
14	1.58 x 10 ⁻⁴	1.39 x 10 ⁻⁴	1.27 x 10 ⁻⁴
16	1.71 x 10 ⁻⁴	1.51 x 10 ⁻⁴	1.34 x 10 ⁻⁴
19	1.91 x 10 ⁻⁴	1.67 x 10 ⁻⁴	1.49 x 10 ⁻⁴
22	2.09 x 10 ⁻⁴	1.82 x 10 ⁻⁴	1.68 x 10 ⁻⁴

The calculated result of log(reaction rate based on the decomposition of steam) and log(steam partial pressure) at constant methane partial pressure, which was used to plot the relationship between log (reaction rate) and log (partial pressure of steam) in Figure 2.17, is shown in Table 2.14

Table 2.14 The calculation of log (reaction rate) and log (partial pressure of steam)

Log(P_{H_2O})	Log(Reaction Rate)		
	90 min(40bar)	120 min(40 bar)	150 min(40 bar)
1.15	-3.80	-3.86	-3.90
1.20	-3.78	-3.82	-3.87
1.28	-3.72	-3.78	-3.83
1.34	-3.68	-3.74	-3.77

Kinetic orders of steam were evaluated from the relationship between log (reaction rate) and log (partial pressure of steam) in Figure 2.17, are shown in Table 2.15.

Table 2.15 The kinetic orders of steam at different time and pressure

Duration time and pressure	Kinetic order
90 min(40bar)	0.619
120 min(40 bar)	0.611
150 min(40 bar)	0.615

The average kinetic order of methane and steam for methane steam reforming over the Ni/MgO/monolith at 600°C at 40 bar pressure were found to be 0.82 ± 0.002 and 0.62 ± 0.003 respectively. The methane kinetic order is quite close to previous literature, which reports that methane steam reforming is first order with respect to methane [90]. The steam order can be categorized as a positive order as reported by Atroshenko et al [95], Quach and Rouleau [96], Kopsel et al [97] and De Deken et al [98].

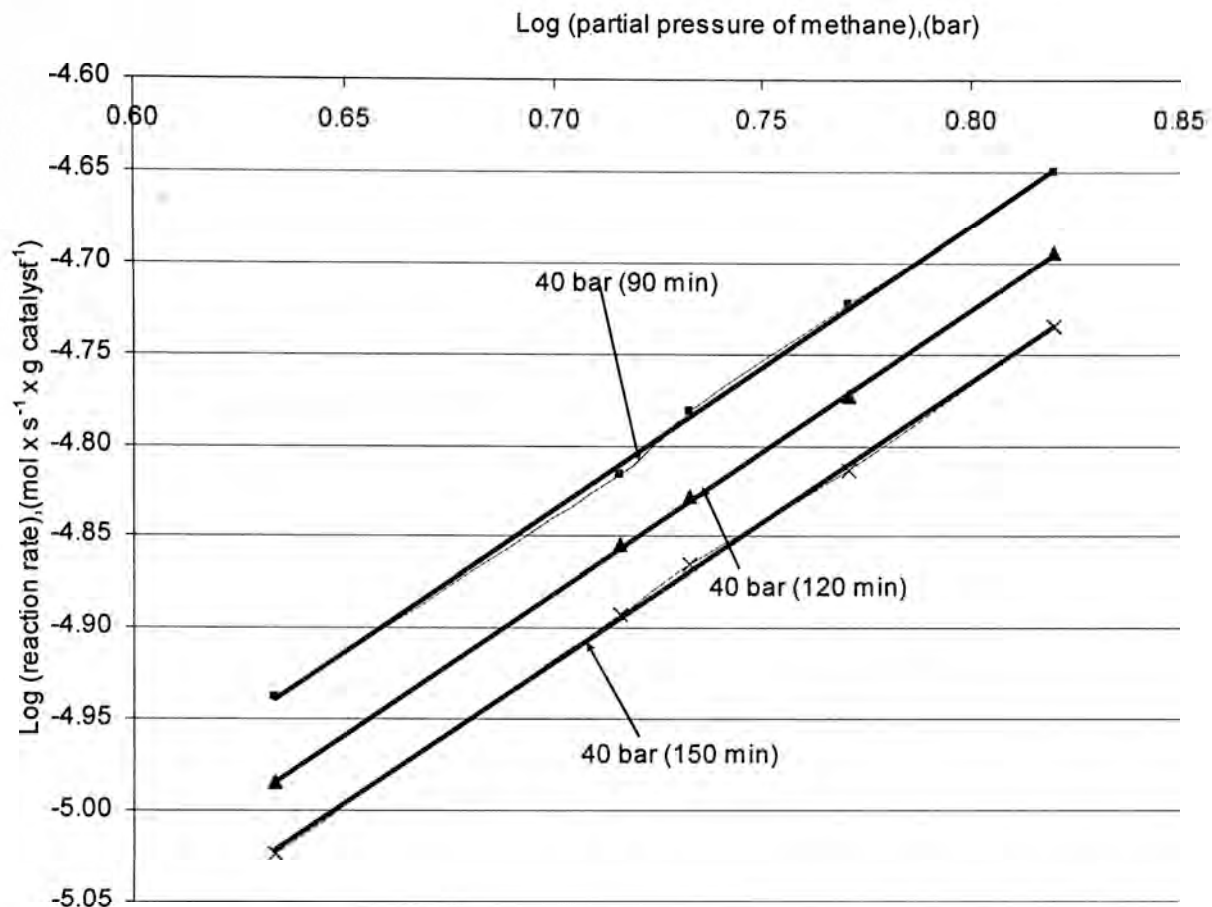


Figure 2.16: The relationship between log (reaction rate) and log (partial pressure of methane) for methane steam reforming over a Ni/MgO catalyst under 40 bar at $T = 600^\circ\text{C}$

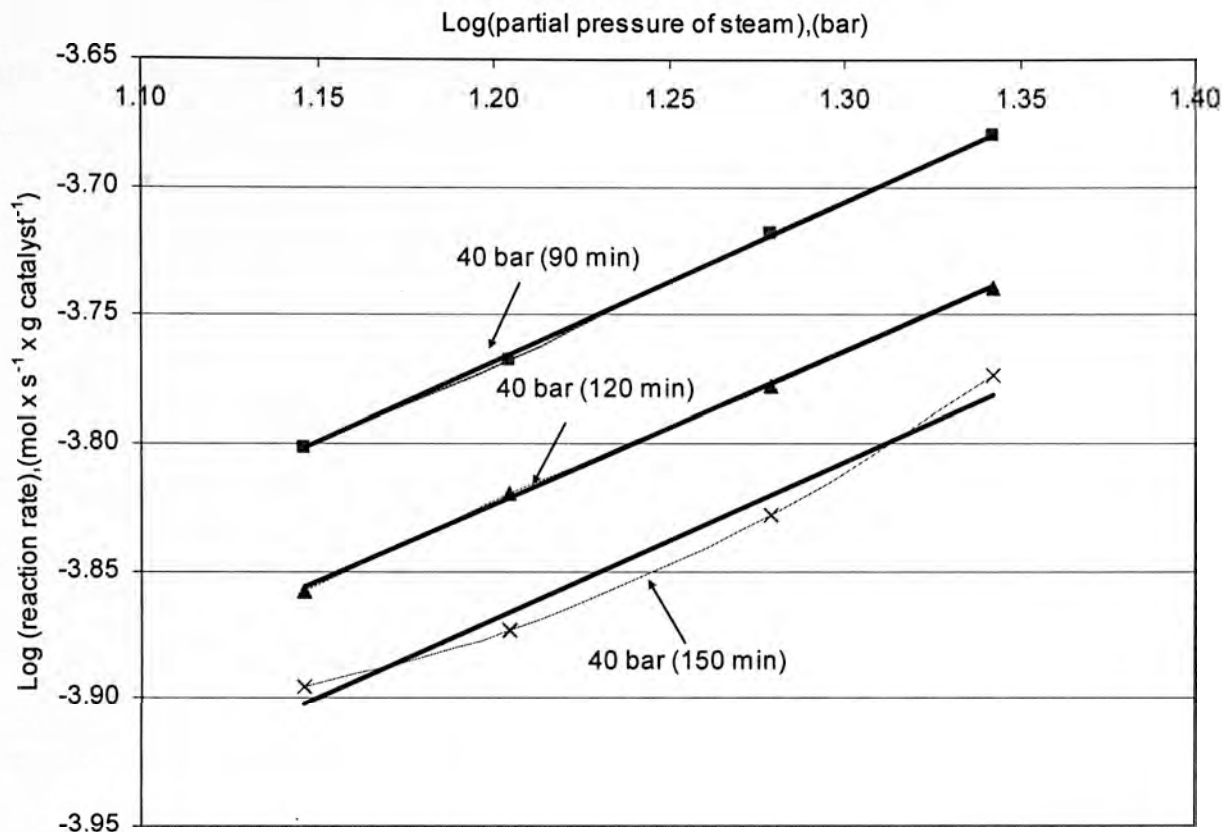


Figure 2.17: The relationship between log (reaction rate) and log (partial pressure of steam) for methane steam reforming over a Ni/MgO catalyst under 40 bar at T = 600 °C

2.4.2 Estimation of the activation energy

In order to estimate the energy of activation, four experimental runs at a methane partial pressure of 5.2bar and steam partial pressure of 18.8bar at different temperature (450°C to 600°C) were conducted. They are shown in Table 2.16.

Table 2.16: The reaction rate at a methane partial pressure of 5.2bar and steam partial pressure of 18.8bar at different temperatures (400°C to 600°C)

T (°C)	Rate Reaction(mol g ⁻¹ s ⁻¹)		
	90 min	120 min	150 min
600	1.95 x 10 ⁻⁵	1.68 x 10 ⁻⁵	1.60 x 10 ⁻⁵
550	8.05 x 10 ⁻⁶	6.92 x 10 ⁻⁶	6.58 x 10 ⁻⁶
500	3.28 x 10 ⁻⁶	2.84 x 10 ⁻⁶	2.71 x 10 ⁻⁶
450	1.37 x 10 ⁻⁶	1.16 x 10 ⁻⁶	1.12 x 10 ⁻⁶
400	6.42 x 10 ⁻⁷	4.89 x 10 ⁻⁷	4.63 x 10 ⁻⁷

The calculation results of rate coefficient (k) at different temperature, based on the results of rate of reaction at different temperatures are shown in Table 2.17.

Table 2.17: The results of rate coefficient (k) at different temperature (400°C to 600°C)

T (°C)	k (constant rate of reaction)		
	90 min	120 min	150 min
600	1.11 x 10 ⁻⁹	9.54 x 10 ⁻¹⁰	9.07 x 10 ⁻¹⁰
550	4.57 x 10 ⁻¹⁰	3.93 x 10 ⁻¹⁰	3.74 x 10 ⁻¹⁰
500	1.87 x 10 ⁻¹⁰	1.61 x 10 ⁻¹⁰	1.54 x 10 ⁻¹⁰
450	7.77 x 10 ⁻¹¹	6.63 x 10 ⁻¹¹	6.34 x 10 ⁻¹¹
400	3.21 x 10 ⁻¹¹	2.78 x 10 ⁻¹¹	2.63 x 10 ⁻¹¹

The energy of activation was evaluated from Arrhenius equation.

$$\ln k = \ln A - E_a/RT$$

(Eq. 2.19)

where k is the rate coefficient, A is frequency factor, E_a is the energy of activation and

R is the gas constant equal to 8.314J/mol. The calculated result of ln (the rate coefficient) and 1 / T(K) at different time are shown in Table 2.18.

Table 2.18 The calculated result of ln (the rate coefficient) and 1/T(K) at different time

1/T (K ⁻¹)	ln(k)		
	90 min	120 min	150 min
0.00114	-20.62	-20.77	-20.82
0.00122	-21.51	-21.66	-21.71
0.00129	-22.40	-22.55	-22.59
0.00138	-23.28	-23.43	-23.48
0.00149	-24.16	-24.31	-24.36

Consequently, E_a can be determined from the slope of the relationship between ln(k) and 1/T divided by R (Figure. 2.18).

Average slope of Figure 2.18 = 12718.6807

E_a = 12718.68 x 0.008314 kJ/mol

E_a = 106 ± 0.2 kJ /mol

This result is close to the energy of activation result (102 kJ/mol) for methane steam reforming over Ni on MgO at 450 – 750°C and atmospheric pressure [101].

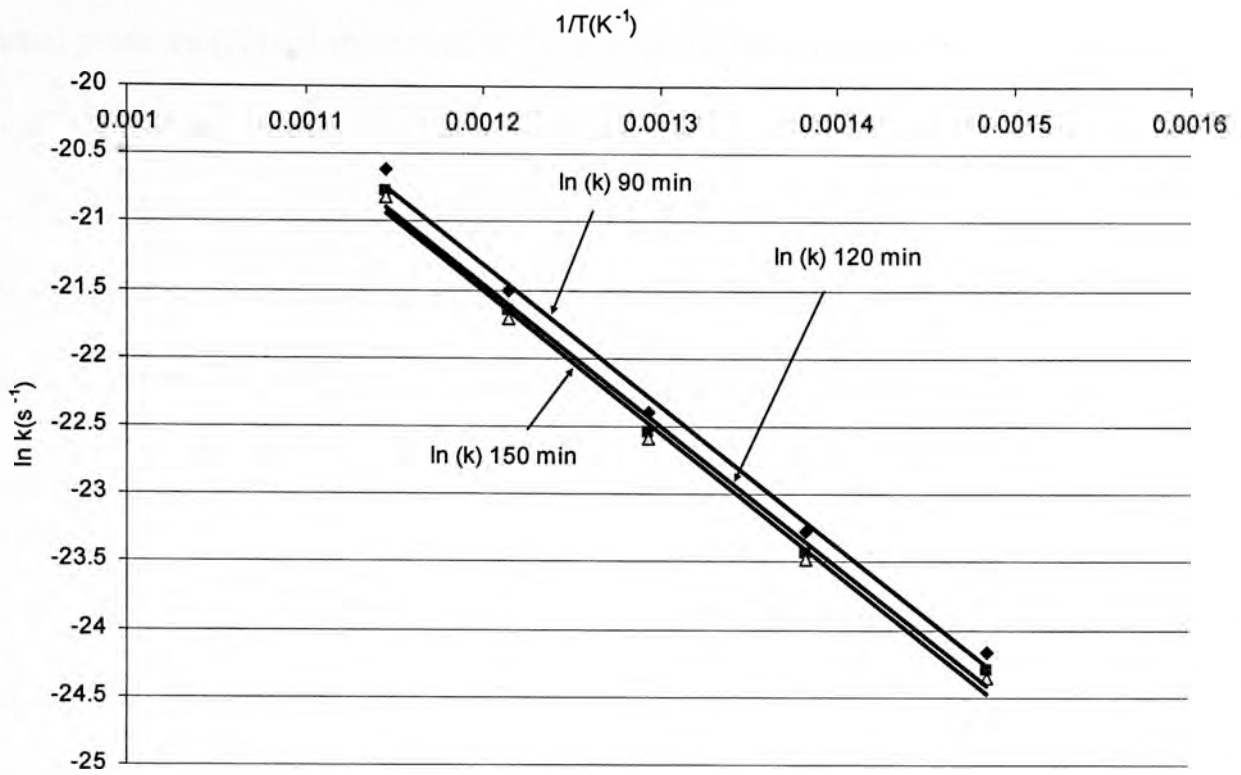


Figure 2.18: The Arrhenius plot of methane steam reforming over a Ni/MgO catalyst under 40 bar in the temperature range from 400°C to 600°C

2.4.3 The deactivation order

The generalized power rate equation has been used to examine the role of methane and steam on the deactivation rate.

$$\frac{-dc}{dt} = k \cdot A_s [\text{reactants}, \text{products}]^d \cdot \eta \quad (\text{Eq. 2.20})$$

where k = the rate constant for the deactivation, A_s = the surface area, d = the order of deactivation and η = the effectiveness factor [105].

The deactivation order of methane is determined from the slope of the plot between $\log$ (deactivation rate) and $\log$ (partial pressure of methane).

Five experimental runs at different methane partial pressure feed and constant steam partial pressure (22bar) were used to determine the deactivation order of methane based on different partial pressure of methane feed. The log of partial pressures of methane feed was used to plot with the log of deactivation rate. Finally, the deactivation order based on the partial pressures of methane feed was evaluated from the slop of the plot between the log of partial pressures of methane feed and the log of deactivation rate. The deactivation rate can be evaluated from $\frac{\Delta \text{ reaction rate}}{\Delta \text{ time}}$.

Table 2.19: The deactivation rate at different methane partial pressure and constant steam partial pressure (22bar)

The partial pressure of methane (bar)	Deactivation rate during 90-120 mins(mol g ⁻¹ s ⁻¹)	Deactivation rate during 120-150 mins(mol g ⁻¹ s ⁻¹)
4.3	3.99 x 10 ⁻⁸	2.98 x 10 ⁻⁸
5.2	4.30 x 10 ⁻⁸	3.21 x 10 ⁻⁸
5.4	5.57 x 10 ⁻⁸	4.00 x 10 ⁻⁸
5.9	6.92 x 10 ⁻⁸	4.97 x 10 ⁻⁸
6.6	7.34 x 10 ⁻⁸	5.96 x 10 ⁻⁸

In order to evaluate the deactivation order in methane, the calculated results of log of deactivation rate and log of partial pressure of methane feed are shown in Table 2.20 and plotted in Figure 2.19.

Table 2.20: The calculated results of log of deactivation rate and log of partial pressure of consumed methane feed

Log (Partial pressure of methane)	Log(deactivation rate during 90-120 mins)	Log (deactivation rate during 120-150 mins)
063	-7.40	-7.53
0.72	-7.37	-7.49
0.73	-7.25	-7.40
0.77	-7.16	-7.30
0.82	-7.13	-7.22

According to Figure 2.19, the deactivation order (slope of the relationship between log (deactivation rate) and log (feed partial pressure of methane) is shown in Table 2.21.

Table 2.21: The deactivation order of methane based on different partial pressure of methane feed

Duration time and pressure	Deactivation order
90 - 120 min(40bar)	0.974
120 – 150 min(40 bar)	0.991

The deactivation orders of methane during 90–120 minute and 120–150 minute were found to be 0.974 and 0.991 respectively. In conclusion, the average deactivation order in the second case was found to be 0.98 ± 0.01 .

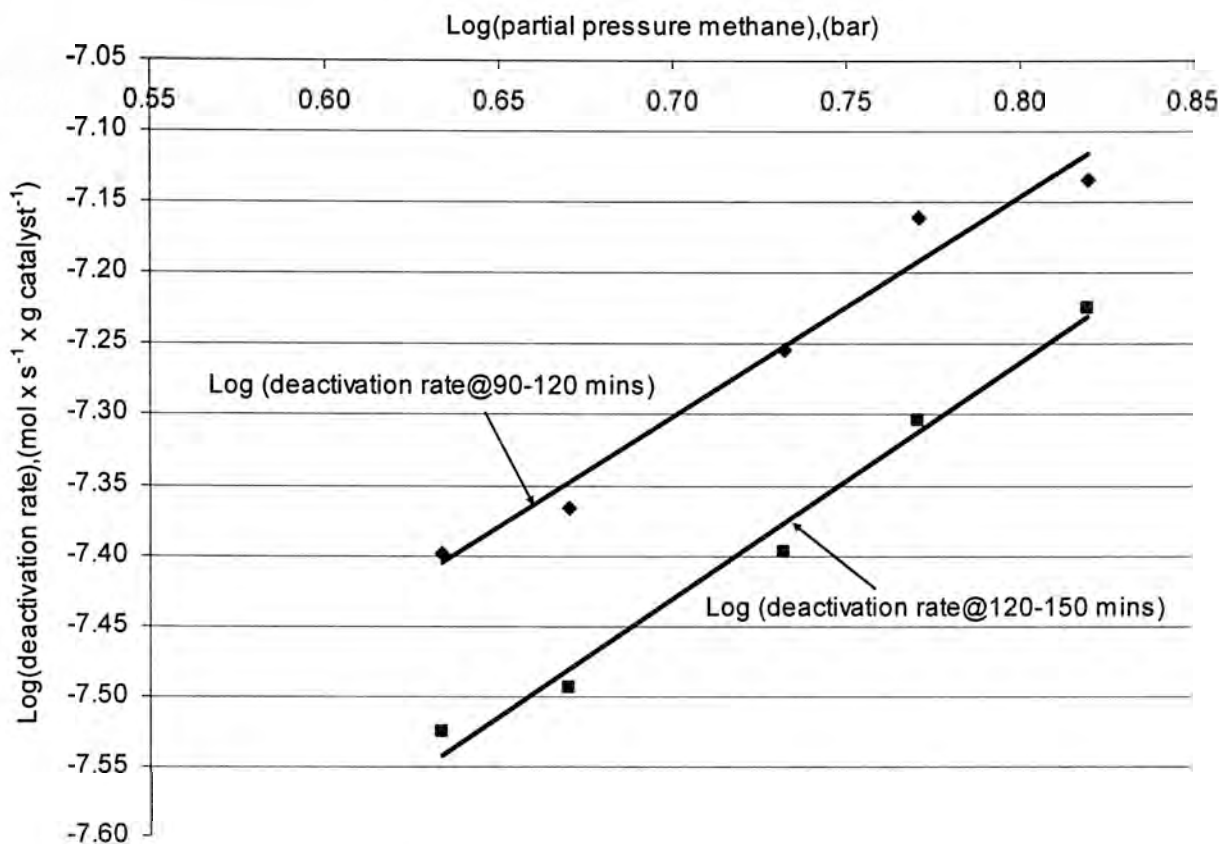


Figure 2.19 The relationship between log(partial pressure of methane) and log(deactivation rate) for methane steam reforming over a Ni/MgO catalyst under 40bar at $T = 600^{\circ}\text{C}$

2.4.4 The relationship between steam methane ratio and selectivity for carbon products (CO, CO₂ and C)

The selectivity to carbon products measured at different steam:methane ratios is given in Table 2.22. The selectivity to carbon products is defined as the proportion of carbon products (CO, CO₂ and C) formation from methane steam reforming over a Ni/MgO catalyst, in which the overall selectivity to three main carbon products, CO, CO₂ and C, is 1. The calculation method for carbon products (CO, CO₂ and C) is shown in APPENDIX A.

Table 2.22 The selectivity to carbon products measured at different steam methane ratio

Steam methane ratio	pressure = 1 bar			pressure = 40 bar		
	%Coke	%CO	%CO ₂	%Coke	%CO	%CO ₂
5.1	62	15	23	65	10	25
4.3	65	14	21	69	8	22
4.1	70	12	18	71	9	19
3.8	80	11	9	77	6	16
3.3	88	9	5	80	7	13

Figure 2.20 shows the relationship between steam: methane ratio and the selectivity to carbon products.

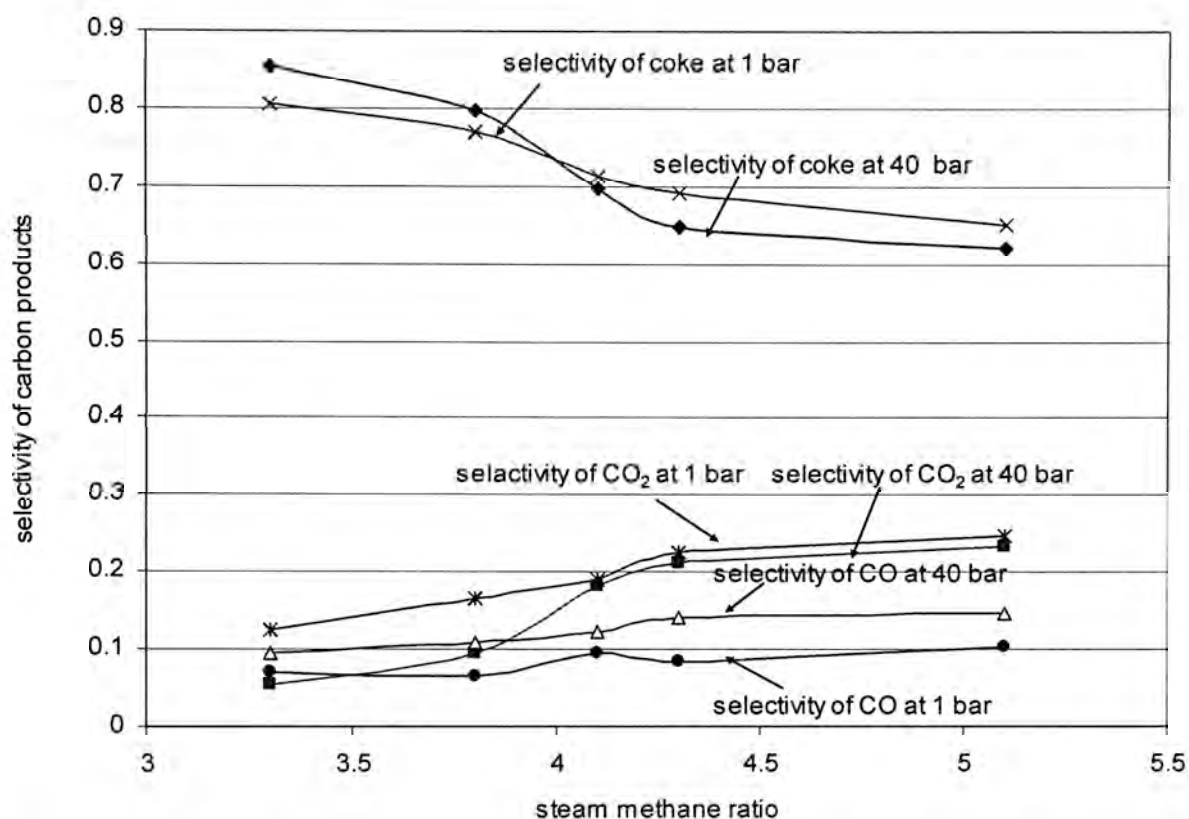


Figure 2.20: The relationship between steam:methane ratio and the selectivity of carbon products for methane steam reforming over a Ni/MgO catalyst under 40bar and 1bar

According to Figure 2.20, when the steam: methane ratio increased, the selectivity to carbon monoxide and carbon dioxide increased and the selectivity to coke decreased.

The reduction in coke formation with increasing steam ratio can be expressed by the simplified mechanism of carbon formation on a nickel catalyst



According to Equation 2.23, coke formation can be reduced by increasing the steam: methane ratio. The selectivity to coke was much higher than other carbon products.

The result was in agreement with the thermodynamic equilibrium in which coke formation reaction is more highly favorable than methane steam reforming and water gas shift reaction [106].

Sidjabat [94] also demonstrates that, at 500°C, carbon was formed during the steam reforming of methane over Ni/MgO-H₂O with a C/H₂O ratio as 4.5atoms/mole. He also states that, below 500°C, no carbon formation was observed.

Doppler et al [107] harnessed X – ray photoelectron spectroscopy (XPS) to detect various carbon species on Ni/MgO. It was found that only surface carbon was on MgO whereas carbidic carbon existed only on the Ni⁰ surface.

The high selectivity to carbon at high pressure was explained by Chirstensen et al [106]. They stated that the size of whisker carbon formed on Ni metal particle under high pressure is much larger than the size of whisker carbon formation on Ni metal particle at atmospheric pressure [106].

In conclusion, the ratio C: CO₂: CO was 4.85:1.52 :1 when the steam: methane ratio varied from 4 to 5 whereas C:CO₂:CO was 8.23:0.73:1 when the steam: methane ratio varied from 3 to 4. The result is in reasonable agreement with the study of simulation of steam reforming of methane to syngas over NiO/MgO/SA-5205(prepared by depositing NiO on MgO precoated SA-5205 support) by Choudhary et al [108]. They concluded that the CO selectivity was lower and the CO₂ selectivity was higher when the ratio of steam was increased because of the increase in the rate of the water – gas shift reaction. This conclusion was supported by the study of Dong et al [109] that showed CO was the primary product from methane steam reforming on Ni-MgO.

Consequently, increasing the steam ratio, relative to an increase in oxygen, can convert CO as the primary product into CO₂ by the water gas shift reaction.



According to the results, if syngas (H₂ – CO) is the desirable product, a high steam ratio is a more favored than a low steam ratio.

2.4.5 The constant parameter estimates of different kinetic models

In this study, the kinetics of methane steam reforming was investigated for three reaction temperatures and the data were correlated with a power law as well as with Langmuir-Hinshelwood-Hougen-Watson (LHHW) models [110].

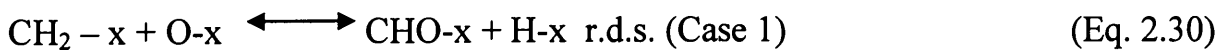
There are seven fundamental steps for the interaction between gas and solid phases during catalysis in heterogeneous systems

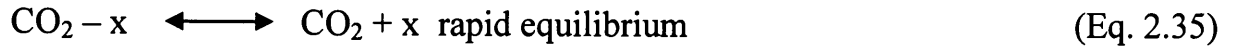
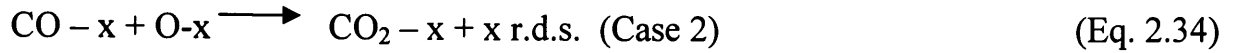
1. Reactants transport from the bulk to the external surface of the solid catalyst particle
2. Movement of reactants from the external surface to the pore interior by a diffusional process
3. Adsorption of reactants on internal catalyst surface
4. Surface reaction in the adsorbed state
5. Product desorption
6. Transport of products by a diffusion process through pores to the external surface
7. Mass transfer of products from external surface to bulk fluid

Elementary steps, including simultaneous chemisorption of methane and water, could clearly be a combination of several routes to yield the observed products.

Subsequently, such mechanisms can be applied as fundamental to the derivation of Langmuir-Hinshelwood kinetic models. In addition to this class of rate equations, Eley-Rideal type rate expression may also be formulated, since data from other workers also suggest either that gas and steam may react with adsorbed species [110] or that methane may attack chemisorbed species [110]. True catalytic reactions preclude the possibility of both species reacting in the gas phase. Consequently, the following mechanisms are identifiable:

A. Langmuir-Hinshelwood mechanism





Case 1: Assumed that a surface reaction between $\text{CH}_2\text{-x}$ and O-x species is rate determining (r.d.s.). The following rate expression can be obtained [111]

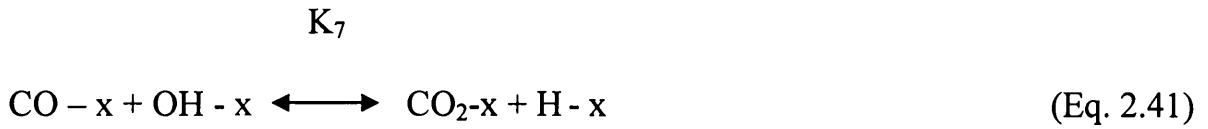
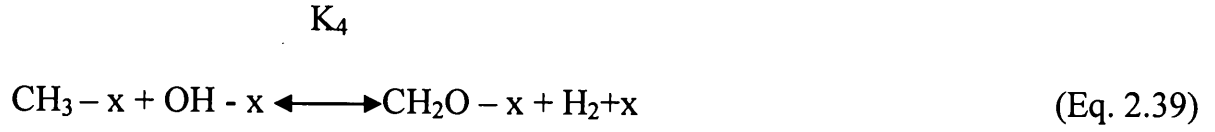
$$-\text{r} = \frac{kP_{\text{CH}_4}P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \left[\frac{2K_1P_{\text{CH}_4}}{P_{\text{H}_2}} + \frac{2K_2P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right]^2} \quad (\text{Eq. 2.36})$$

Case 2: Reaction (Eq. 2.34) is the r.d.s as has been proposed by Soliman et al. [112]

$$-\text{r} = \frac{kP_{\text{CH}_4}P_{\text{H}_2\text{O}}}{P_{\text{H}_2} 2 \left[1 + \frac{K_1P_{\text{CH}_4}}{P_{\text{H}_2}^3} + K_2(P_{\text{H}_2})^{0.5} + \frac{K_2P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right]^2} \quad (\text{Eq. 2.37})$$

2. Consideration of less acidic supports and assuming the existence of competitive adsorption between methane and steam on nickel active sites, Ma [113] has proposed five different mechanisms of which one scheme survived statistical scrutiny when fitted to the kinetic data of the catalyst. This scheme involved



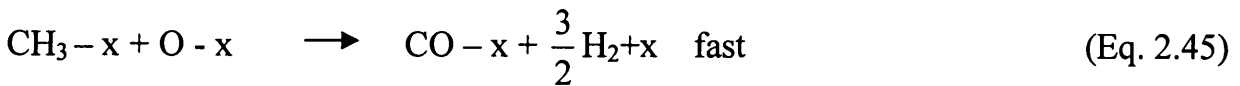


Assuming that the reaction (Eq. 2.39) is the r.d.s., then

$$-r = \frac{kP_{CH_4}}{\left[1 + K_1P_{CH_4} + \frac{K_2P_{H_2O}}{(P_{H_2})^{0.5}}\right]^2} \quad (\text{Eq. 2.43})$$

where $k = K_3 K_1$; and $K_2 = K_4 K_8^{1/2}$

3. The following scheme is also possible, since dissociative chemisorption of methane as r.d.s. has previously been reported [82].



It was reported by Rostrup-Nielsen [11] that the systems could be regarded as irreversible if the reaction is sufficiently far from equilibrium. Consequently, Leach et al. [114] and Chahar et al [115] report that the hydrogen stripping of methane from $CH_2 - *$ has not been chosen since exchange studies have not supported the existence of this species.

The rate expression based on equation 2.44, then becomes

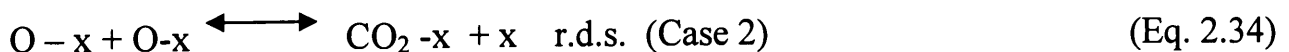
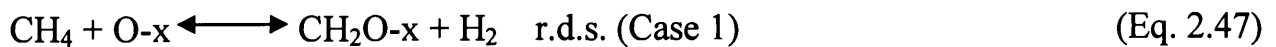
$$-r = \frac{kP_{CH_4}}{\left[1 + K_1(P_{H_2})^{0.5} + \frac{K_2 P_{H_2O}}{P_{H_2}}\right]^2} \quad (\text{Eq. 2.46})$$

where $K_1 = K_H^{-1/2}$; and $K_2 = K_w$

Equation 2.42 is similar to Rostrup-Nielsen's model [11] although it has been derived from a different mechanism. However this model has different parameter meanings in K_1 .

B. Eley-Rideal mechanisms

These involve reaction between gas phase molecules and adsorbed species:





Case 1: The reaction (Eq. 2.47) is r.d.s. and

$$-r = \frac{kP_{H_2O}P_{CH_4}}{P_{H_2} \left[1 + K_1(P_{H_2})^{0.5} + \frac{K_2P_{H_2O}}{(P_{H_2})} \right]} \quad (\text{Eq. 2.49})$$

where K_1 and K_2 represent $K_H^{-1/2}$ and K_w respectively.

Case 2: if reaction (Eq. 2.34) is assumed as the r.d.s., then

$$-r = \frac{kP_{H_2O}P_{CH_4}}{P_{H_2}^3 \left[1 + K_1(P_{H_2})^{0.5} + \frac{K_2P_{CH_4}P_{H_2O}}{(P_{H_2})^3} \right]} \quad (\text{Eq. 2.50})$$

Where $-r$ is rate of methane disappearance, $\text{mol g}^{-1}\text{s}^{-1}$,

k is rate constant

p_{CH_4} is partial pressure of methane, kPa

p_{H_2O} is partial pressure of steam, kPa

p_{H_2} is partial pressure of hydrogen, kPa

K_1 , K_2 and K_3 are adsorption equilibrium constants.

Four experiments were selected to determine rate constants and adsorption equilibrium constants in each model by using trial and error methods from an excel program (based on the closest calculated rate reaction).

The detail of the four experiments is shown in Table 2.23.

Table 2.23: The reaction rate at different partial pressure of methane, steam and hydrogen and steam methane ratio

H₂O:CH₄	<i>P</i>_{CH₄} kPa	<i>P</i>_{H₂O} kPa	<i>P</i>_{H₂} kPa	Reaction rate (mol g⁻¹ s⁻¹)
4.3	520	2200	799	1.40 x 10 ⁻⁵
4.1	540	2200	1593	1.50 x 10 ⁻⁵
3.8	590	2200	2276	1.71 x 10 ⁻⁵
3.3	660	2200	1041	2.03 x 10 ⁻⁵

The estimation of parameter for each model is reported Table 2.24.

Table 2.24: Parameter estimates of the models

Model	Constant	600 °C
A 1, Case 1	k	2.67×10^{-4}
	K ₁	- 0.295
	K ₂	-2.06
A 1, Case 2	k	1.75×10^{-5}
	K ₁	7.87
	K ₂	-0.38
	K ₃	0.6
A 2	k	9.566×10^{-8}
	K ₁	0.02
	K ₂	0.01
A 3	k	6.33×10^{-6}
	K ₁	0.72
	K ₂	0.08
B, Case 1	k	5.08×10^{-4}
	K ₁	-0.18
	K ₂	-0.12
B, Case 2	k	1.095
	K ₁	-0.12
	K ₂	0.1

The experimental reaction rate and calculated reaction rate in each model is show in Table 2.25.

Table 2.25: The experimental reaction rate and calculated reaction rate in each model

Experimental Reaction rate (mol g ⁻¹ s ⁻¹)	Model A1 case1 Reaction rate (mol g ⁻¹ s ⁻¹)	Model A 1 case 2 Reaction rate (mol g ⁻¹ s ¹)	Model A 2 Reaction rate (mol g ⁻¹ s ¹)	Model A 3 Reaction rate (mol g ⁻¹ s ¹)	Model B case 1 Reaction rate (mol g ⁻¹ s ¹)	Model B case 2 Reaction rate (mol g ⁻¹ s ¹)
1.40 x 10 ⁻⁵	1.63 x 10 ⁻⁵	9.92 x 10 ⁻³	1.40 x 10 ⁻⁵	2.14 x 10 ⁻⁵	2.56 x 10 ⁻⁵	1.64 x 10 ⁻⁵
1.50 x 10 ⁻⁵	1.51 x 10 ⁻⁵	1.17 x 10 ⁻⁴	1.75 x 10 ⁻⁵	8.85 x 10 ⁻⁶	6.34 x 10 ⁻⁶	8.18 x 10 ⁻⁶
1.71 x 10 ⁻⁵	1.71 x 10 ⁻⁵	1.71 x 10 ⁻⁵	2.16 x 10 ⁻⁵	6.25 x 10 ⁻⁶	3.28 x 10 ⁻⁶	1.70 x 10 ⁻⁵
2.03 x 10 ⁻⁵	2.03 x 10 ⁻⁵	2.09 x 10 ⁻³	2.03 x 10 ⁻⁵	2.03 x 10 ⁻⁵	2.03 x 10 ⁻⁵	4.06 x 10 ⁻⁶

The relationship between experimental reaction rate and steam: methane ratio is compared with the relationship between other model reaction rate and steam: methane ratio as shown in Figure 2.21.

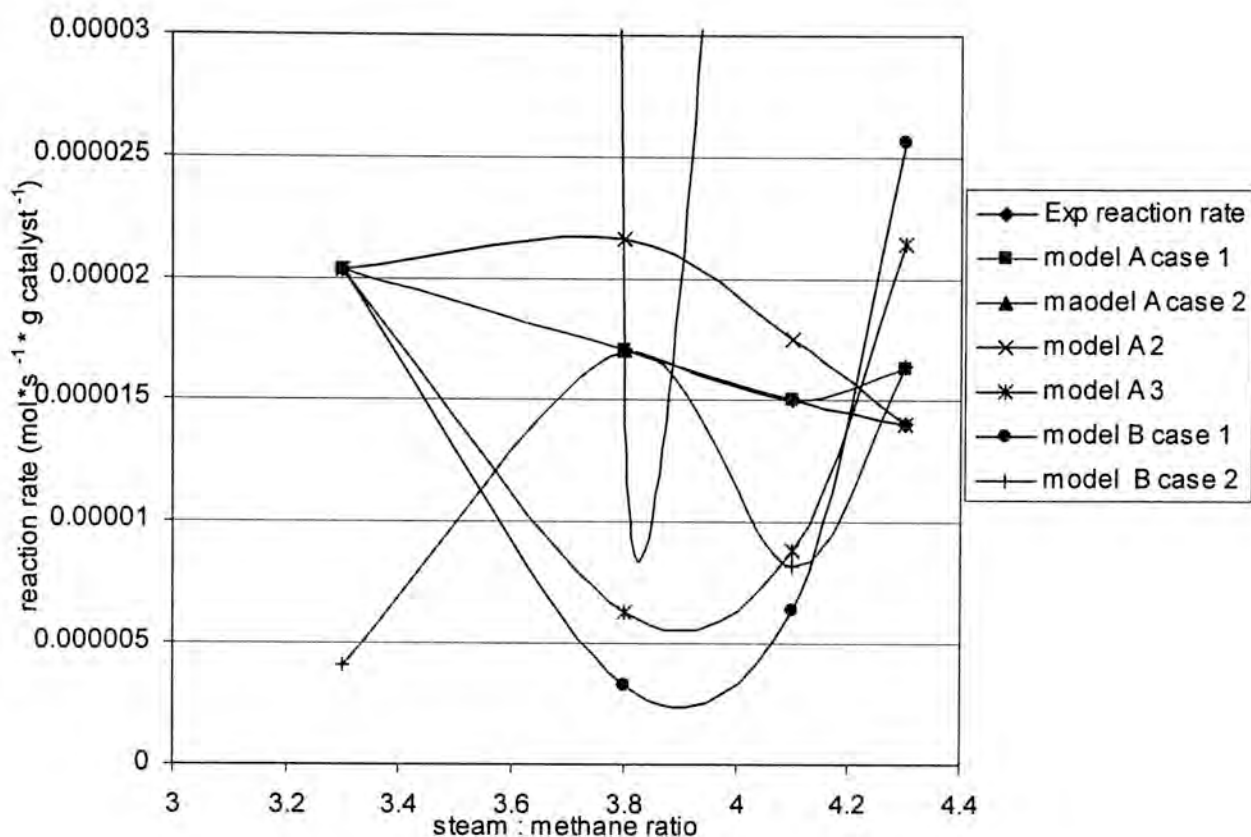


Figure 2.21: The relationship between experimental reaction rate and steam: methane ratio compared with the relationship between other model reaction rate and steam: methane ratio for methane steam reforming over a Ni/MgO catalyst under 40 bar.

As has been shown in Figure 2.21, experimental reaction rates gave the best fit of the model A 1 (Langmuir-Hinshelwood mechanism case 1) when compared with other models. The result can be supported by the closest data between the experimental reaction rates and the calculated reaction rates of the model A 1 (Langmuir-Hinshelwood mechanism case 1) in Table 2.25.

In conclusion, the reaction rate data were also explained by Langmuir – Hinshelwood – Hougen – Wastson models and the result suggested that a surface reaction between $\text{CH}_2 - x$ and $\text{O} - x$ was rate determining step.

2.5 Conclusions

The main finding of the present studies may be highlighted as follow

1. The kinetic orders of methane and steam at a pressure of 40 bar were found to be 0.82 and 0.62 respectively.
2. The estimation of energy of activation was found to be 106 kJ/mol.
3. Deactivation orders of methane were studied. The deactivation order of methane was based on feeding various partial pressure of methane and was found to be to 0.99. Carbon formation is probably a major cause of catalyst deactivation.
4. Coke is the largest product. An increase in steam:methane ratio led to increased selectivity to CO₂ and decreased selectivity to CO because of an increase in the rate of the water-gas shift reaction.
5. The experimental result gave the closest agreement to a Langmuir–Hinshelwood mechanism case 1, in which reaction occurred between adsorbed methane–species and adsorbed steam derived species. The rate reaction can be described as

$$-r = \frac{kP_{CH_4}P_{H_2O}}{P_{H_2} \left[\frac{2K_1P_{CH_4}}{P_{H_2}} + \frac{2K_2P_{H_2O}}{P_{H_2}} \right]^2}.$$

2.6 Recommendation

The above finding and conclusion may lead to the necessity of further investigation including:

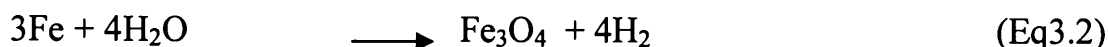
1. The use of other high pressures for the kinetic study in order to evaluate the relationship between the pressure and other factors such as the coke formation and energy of activation,
2. The study of other promoters such as Al_2O_3 or (CeO) compared with MgO ,
3. The use of higher hydrocarbon for the kinetic study,
4. To investigate whether catalyst deactivation is caused by sintering of the metal and/or the support,
5. Detailed studies of catalyst deactivation due to carbon deposition.

Chapter 3

The study of the steam - iron process

3.1 Introduction

A study of the steam – iron process using different reductants was conducted and is described in the second section of the thesis. The steam-iron process is an interesting option to convert hydrocarbons to hydrogen. There are two main steps for this reaction. The original technology is based on a periodic reduction/ re-oxidation cycle of iron (Eq. 3.1 – Eq. 3.2) [116].



Fundamentally, there are five significant advantages for the two – step process [116]:

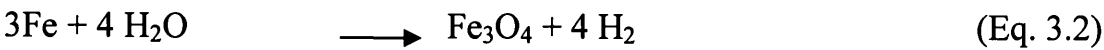
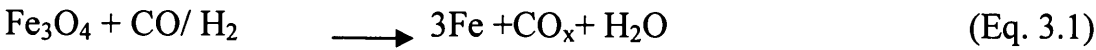
- (i) a reduction in investment cost for units by periodic operation of one single reactor;
- (ii) a reduction in investment and operational costs due to the use of a cheap material (iron oxides);
- (iii) the good quality of hydrogen product
- (iv) avoidance of separation of CO and H₂
- (v) more than one life cycle is possible as the redox proceeds.

Due to these five advantages, the steam iron process is closely examined in the thesis in order to improve understanding and to develop the steam iron process for industrial application in the future.

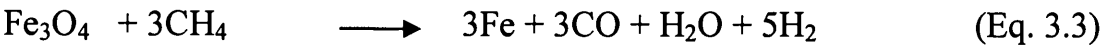
3.2 Literature survey

3.2.1 The steam iron process

The original steam iron process is a combination of two reactions. The first step is to reduce iron oxide with gas derived by gasification of coal or natural gas such as hydrogen, carbon monoxide and methane. The second step involves the oxidation of reduced iron metal with water vapor. The two reaction steps can be shown as [116]:



An alternative reduction stage involving methane has been developed in recent years [116].



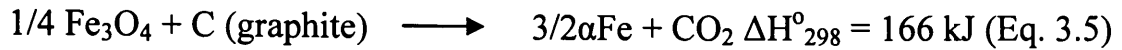
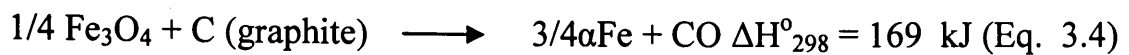
According to thermodynamic equilibrium the steam-iron process is favorable at $> 727^\circ\text{C}$. It was reported by Galvita and Sundmacher [116] that the reduction of iron with methane is the slower process or control step. Consequently, the kinetic studies of iron oxide reduction with different reductants have been carried out.

3.2.2 Kinetic studies of iron oxide reduction

The reduction of Fe_2O_3 and Fe_3O_4 to Fe using several reductants has been demonstrated.

3.2.2.1 Traditional process

Due to the availability and low price of coke, the application of coke as a reactant is favorable as a reductant. Coke gasification to produce CO and H_2 is highly endothermic and relies strongly on high temperatures. As a result, direct reaction is favored:



It was reported by Tamaura et al [117] that although Fe_3O_4 could be thermodynamically reduced direct to α Fe at temperatures over 1200°C , α Fe was not formed in the short time of reaction. Following that report, Fe_3O_4 was found to be readily reduced to FeO for the first step of reduction and the reduction of FeO into Fe was the second and rate - determining step [117].

In contrast, the main drawback of using coke as reductant is the accumulation of ash. Approximately 30% decrease in the coal conversion led to the accumulation of ash and obstructed intimate contact between metal oxide and the carbon component in coal.

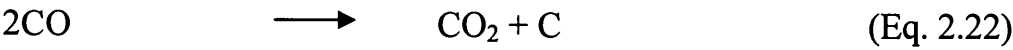
3.2.2.2 Modified process

In order to minimize ash accumulation and pollution gases emissions from the steam-iron process, other gases such as natural gas (methane containing ethane and propane), hydrogen and carbon monoxide have been proposed as reductants for the first step of the steam iron process (Eq 3.1) [116]. Currently, there are three favored reductants, H_2 , CO and methane for the reduction of iron oxide.

In order to understand the kinetics of the reduction of iron oxide as the controlling step and due to an absence of a data on the kinetics of iron oxide reduction with methane, the kinetics of the reduction of iron oxide with hydrogen and CO should be considered.

3.2.2.2.1 Kinetic studies of iron oxide reduction with carbon monoxide

Generally, it was expected that the decomposition of CO by the inverse of the Boudouard reaction (Eq. 2.22) took place simultaneously. According to the thermodynamic equilibrium, carbon deposition on metallic iron is favorable at temperature lower than 1000 °C and high CO concentrations. Increasing temperature and CO concentration results in reduction of iron oxides.



The reduction of Fe₂O₃ and Fe₃O₄ to Fe has been demonstrated in several studies [117,118,119,120, 121, 122 and 123]. These results vary depending on experimental conditions such as particle sizes and temperature. Wimmers et al [118] stated that larger particle sizes reduce coke formation though a phase boundary mechanism whereas the reduction of smaller particle sizes involves the formation and growth of nuclei especially at low temperature. Furthermore, it was reported that, at 570°C, Fe₂O₃ was reduced through Fe₃O₄ as an intermediate before completely reducing to Fe [118]. This result was in agreement with a study by Tiernan et al [119] who found that the energy activation of the first reduction (Fe₂O₃ $\longrightarrow$ Fe₃O₄) was 96 kJ/mol. It was also found that the energy of activation of the second reduction reduced from 69 to 59 kJ/mol as the process continued.

In addition, several controlling mechanisms for the reduction of oxide and of ores containing iron oxide have been proposed by various researchers. Shimokawabe [120] proposed a random nucleation mechanism for the reduction of Fe₂O₃ whilst Sastri et al [121] suggested a phase boundary mechanism. It was concluded by Tiernan et al [119] that Fe₂O₃ was reduced to Fe₃O₄ via the boundary phase mechanism whereas Fe₃O₄ was reduced to Fe via random nucleation. Moreover, the reduction of Fe₃O₄ to FeO

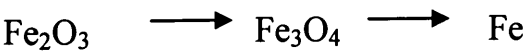
between 900 and 1200 °C was studied by El-Geassy [122]. As a result, a mixed reaction mechanism in the early stages of reduction followed by interfacial chemical reactions was proposed as a controlling mechanism for the reduction of Fe₃O₄ to FeO, whereas the controlling mechanism for the reduction of FeO to Fe in fluidized bed reactor was studied by Harbermann et al [123], who found two controlling steps for the reduction. Mass transport in the gas phase was the primary controlling mechanism whereas the second step was the internal reduction of small iron particles.

3.2.2.2.2 The kinetic studies of iron oxide reduction with hydrogen

The steam iron process using hydrogen as reductant is the basic model for the steam iron process using methane as reductant. Most research groups for the steam iron process used storage and supply of hydrogen by the redox of iron oxides as the reference for the production of pure hydrogen from methane mediated by the redox of iron oxide [124, 125 and 126].

The reducibility of bulk iron oxide with hydrogen has been investigated by many research groups, using TPR (the Temperature- programmed reduction method) which has been widely applied to characterize solid materials [124].

Unmult et al [125] showed that there were two peaks in the reduction profile of 5%Fe/SiO₂ by TPR; at 307 °C and 447 °C. The two peaks were recognized to be due to following processes:



The reduction profile of both α- Fe₂O₃ and Au/α- Fe₂O₃ reported by Munteanu et al [126], also involved two peaks at 280 and 427 °C.

Some kinetic studies of Fe₂O₃ with hydrogen were concluded as shown in Table 3.1.

Table 3.1 Summary of measured apparent activation energies of hematite reduction by hydrogen (kJ/mol)

Parameter	Temperature range (°C)	Activation energy kJ/mol	Material and experimental conditions	Ref.
Raw material	460-500	56.8	Pure Fe ₂ O ₃	[127]
	460-500	72.3	Pure Fe ₂ O ₃ heated to 850°C	[127]
	460-500	89.4	Heamatite ore	[127]
	450-700	246.0	Fe ₂ O ₃ $\longrightarrow$ Fe ₃ O ₄ , The precursor of Fe ₂ O ₃ was FeOOH	[128]
	450-700	93.0	Fe ₃ O ₄ $\longrightarrow$ Fe, precursor of Fe ₂ O ₃ was FeOOH	[128]
	450-700	162.2	Fe ₂ O ₃ $\longrightarrow$ Fe ₃ O ₄ , precursor of Fe ₂ O ₃ was ferrihydrite	[128]
	450-700	104.0	Fe ₃ O ₄ $\longrightarrow$ Fe, precursor of Fe ₂ O ₃ was ferrihydrite	[128]
Pellets	700-925	109.9	Iron ore: 80% Fe ₂ O ₃ , 18% FeO, globular pellets	[129]
	1000-1150	18.0	Iron ore: 80% Fe ₂ O ₃ , 18% FeO, globular pellets	[129]
	< 500	30.1 and 56.4	Ferric oxide pellets, degree of reduction (Fe ₂ O ₃ $\longrightarrow$ Fe ₃ O ₄) < 0.001, electrical conductivity	[130]

Parameter	Temperature range (°C)	Activation energy kJ/mol	Material and experimental conditions	Ref.
Step $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$	290-480	124.0	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, 67% H_2 (H_2 -Ar), $\approx 3\%$ H_2O	[131]
	250-450	139.2	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, hydrogen-argon mixture (10% H_2)	[126]
	450-700	246.0	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, precursor of Fe_2O_3 was FeOOH	[128]
	450-700	162.0	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, precursor of Fe_2O_3 was ferrihydrite	[128]
	250-610	106.0	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, 5% H_2 in He	[132]
	300-900	89.1	$\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4$, 5% H_2 in N_2	[133]
Step $\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$	290-480	172.0	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}^0$, 67% H_2 (H_2 -Ar), $\approx 3\%$ H_2O	[131]
	450-700	93.0	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, the precursor of Fe_2O_3 was FeOOH	[128]
	450-700	104.0	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, the precursor of Fe_2O_3 was ferrihydrite	[128]
	250-610	54.0	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, 5% H_2 in He	[132]
	300-900	70.4	$\text{Fe}_3\text{O}_4 \rightarrow \text{Fe}$, 5% H_2 in N_2	[133]
	250-450	77.3	$\text{Fe}_3\text{O}_4 \rightarrow \text{FeO}$, hydrogen-argon mixture (10% H_2)	[126]

Parameter	Temperature range (°C)	Activation energy kJ/mol	Material and experimental conditions	Ref.
$\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$	250-450	85.7	$\text{FeO} \longrightarrow \text{Fe}$, hydrogen-argon mixture (10% H_2)	[126]
	580 and 720	72.0	Wüstite $\longrightarrow$ Fe	[134]
Presence of water vapor in the reducing gas mixture	465, 485 and 505	52.7	Pure Fe_2O_3 with 4% water vapor (w.v.)	[135]
	465, 485 and 505	55.2	Pure Fe_2O_3 with 7.5% w.v.	[135]
	465, 485 and 505	58.9	Pure Fe_2O_3 with 2% w.v.	[135]
	465, 485 and 505	53.1	Pure Fe_2O_3 with 5% w.v.	[135]
	290-480	124.0	$\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4$, 67% H_2 (H_2 -Ar), $\approx$ 3% H_2O	[131]
	290-480	172.0	$\text{Fe}_3\text{O}_4 \longrightarrow$ Fe metal, 67% H_2 (H_2 -Ar), $\approx$ 3% H_2O	[131]
Impurities	460-500	109.9	Fe_2O_3 and MgO	[127]
	460-500	107.8	Fe_2O_3 and Al_2O_3 or In_2O_3 or Li_2O_3	[127]
	460-500	129.2	Fe_2O_3 and TiO_2	[127]

Some controlling mechanisms of the iron oxide reduction were concluded as shown in Table 3.2.

Table 3.2 Controlling mechanism of the iron oxide reduction

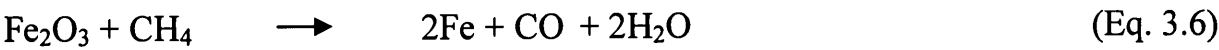
Gas	Solid	Temperature range (°C)	Kinetics controlling mechanism	Ref.
H ₂	Pure Fe ₂ O ₃	460-500	Topochemical reaction at the interface gas/solid: $kt = 1 - (1-x)^{1/3}$	[127]
	Pure Fe ₂ O ₃ with 2.5-7.5% water vapor	460-500	Increased rate of reduction attributed to a hydrogen spill-over effect: the chemisorbed hydrogen atoms activate the surface migration	[127]
	Pure Fe ₂ O ₃ + foreign metal oxides (Al ₂ O ₃ ...) or hematic ore	460-500	Retardation of the reduction kinetics due to structure factor: topochemical reaction and different mechanism involving the mixed oxide (FeAl ₂ O ₄ ...) formed at the surface of Fe ₂ O ₃	[127]
	Pure Fe ₂ O ₃ + fresh metal powders	460-500	Increased rate of reduction	[127]
	Pure Fe ₂ O ₃ with water vapor	465, 485 and 505	The rate increased with water vapor content between 2.5 and 7.5%: this is attributed to H spill-over. The rate determining step is identified to be the desorption of H ₂ O	[131]

Gas	Solid	Temperature range (°C)	Kinetics controlling mechanism	Ref.
H ₂	α-Fe ₂ O ₃ (Merck, pro analysis) Addition of 3%H ₂ O to the reducing gas	290-480	Self-catalyzed nucleation (autocatalysis): nuclei catalyze further nuclei formation, due to branching of nuclei or to the assists during the acceleration by assuring fast hydrogen spill-over	[131]
5% H ₂ /He	Fe ₂ O ₃ (99.98%, Aldrich)	250-610	The prereduction step (Fe ₂ O ₃ to Fe ₃ O ₄) was described by an “nth-order” expression	[132]
	Fe ₂ O ₃ (99.98%, Aldrich) or Fe ₃ O ₄ (99.997%, Alfa Chemicals)	250-610	The reduction of Fe ₃ O ₄ followed a nucleation or autocatalytic mechanism. Metal nuclei formed are believed to dissociate and activate dihydrogen molecules leading to autocatalytic reacher.	[132]
5% H ₂ /N ₂	Iron oxide prepared by precipitation of Fe(NO ₃)O ₃ . 9 H ₂ O	300-900	Fe ₂ O ₃ $\longrightarrow$ Fe ₃ O ₄ , unimolecular model [a first order reaction:	[133]
		300-900	Fe ₃ O ₄ $\longrightarrow$ Fe two-dimensional nucleation according to Avrami-Erofeyev model	[134]

Gas	Solid	Temperature range (°C)	Kinetics controlling mechanism	Ref.
H ₂	Ferric oxide pellet	<500	For degree of reduction =x<0.01: thin layer at the pellet surface has been reduced: chemisorption of H ₂ on the oxygen vacancies	[130]
CO,H ₂	Iron ore: 80% Fe ₂ O ₃ , 18% FeO-globular pellets	700-1150	Chemical reaction: the advance of reaction front during reduction : $kt = 1 - (1-x)^{1/3}$	[129]

3.2.2.2.3 The production of pure hydrogen from methane mediated by the redox of iron oxide

The study of the effect of steam on the iron produced by using methane as reductant is the main part of the last section of the thesis. Consequently, the production of pure hydrogen from methane mediated by the redox of iron oxide is strongly analyzed.



Steinfeld et al [136] revealed that the thermodynamic equilibrium at 1 atm over 1027°C for the Fe₃O₄ + CH₄ system composes of metallic iron in the solid phase and a mixture of 67% H₂ and 33% CO in the gaseous phase. However, their experimental result, when conducted at 1 atm and temperatures ranging from 900 °C to 1000 °C, showed that the reaction did not reach chemical equilibrium.

3.2.2.2.3.1 Equilibrium comparison analysis of the CH₄ and Fe₂O₃ system

Due to the incomplete reduction of CH₄ into CO₂ and H₂O at high temperature, in which some of the CH₄ may be oxidized to CO or decomposed to C and H₂, the analysis of the equilibrium composition of CH₄ and Fe₂O₃ is essential for the steam iron process using CH₄ as the reducing agent. The equilibrium composition of CH₄ and Fe₂O₃ at different molar ratio of CH₄ /Fe₂O₃ and different temperatures was calculated by Xin et al [137] by using the criteria of minimizing the Gibbs free energy (Figure 3.1)

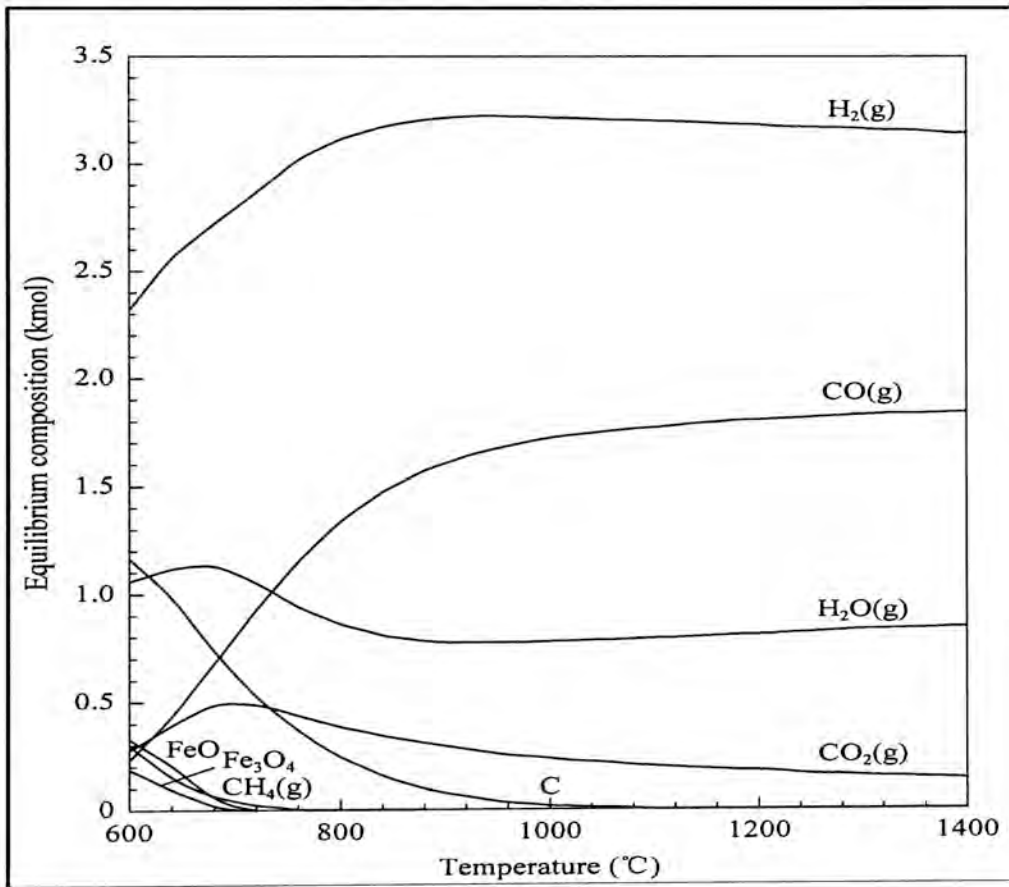


Figure 3.1: Equilibrium composition at various temperatures at Fe₂O₃/ CH₄ ratio of 1:2 [137]

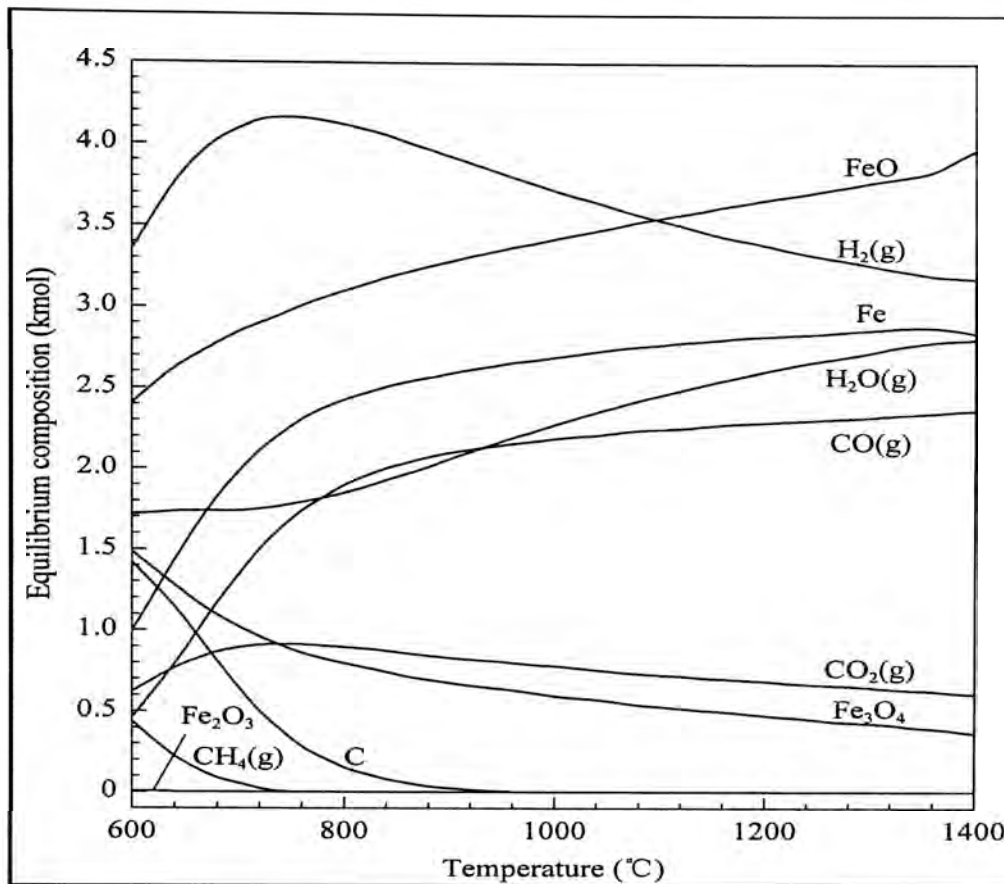


Figure 3.2: Equilibrium composition at various temperatures at $\text{Fe}_2\text{O}_3/\text{CH}_4$ ratio of 4:3 [137]

Figure 3.2 shows that, when the molar ratio of $\text{CH}_4/\text{Fe}_2\text{O}_3$ is 4:3 (which is the theoretical ratio of the reaction between CH_4 and Fe_2O_3 to generate CO_2 , H_2O and metallic Fe), carbon is formed below 950°C . The carbon deposition depends on the amount of oxygen carrier. The concentration of H_2 increases to reach a peak at 750°C , and decreases at temperature lower than 750°C [137].

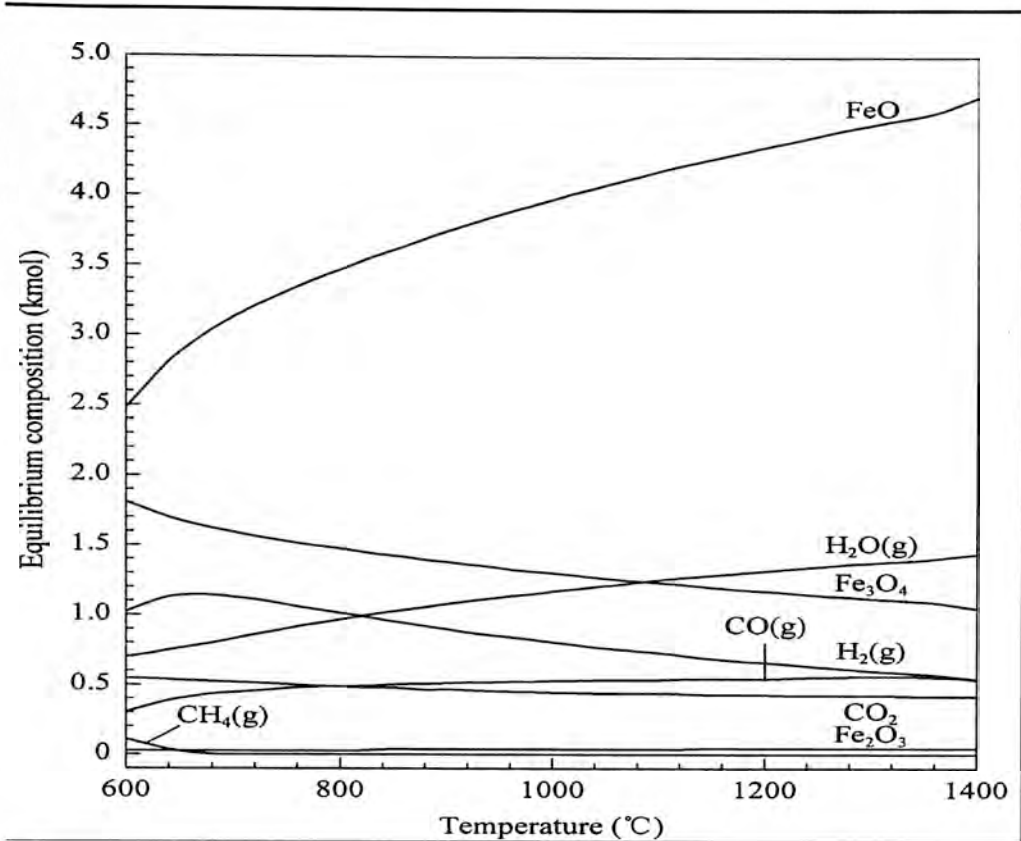


Figure 3.3: Equilibrium composition at various temperatures at $\text{Fe}_2\text{O}_3/\text{CH}_4$ water ratio of 4:1 [137]

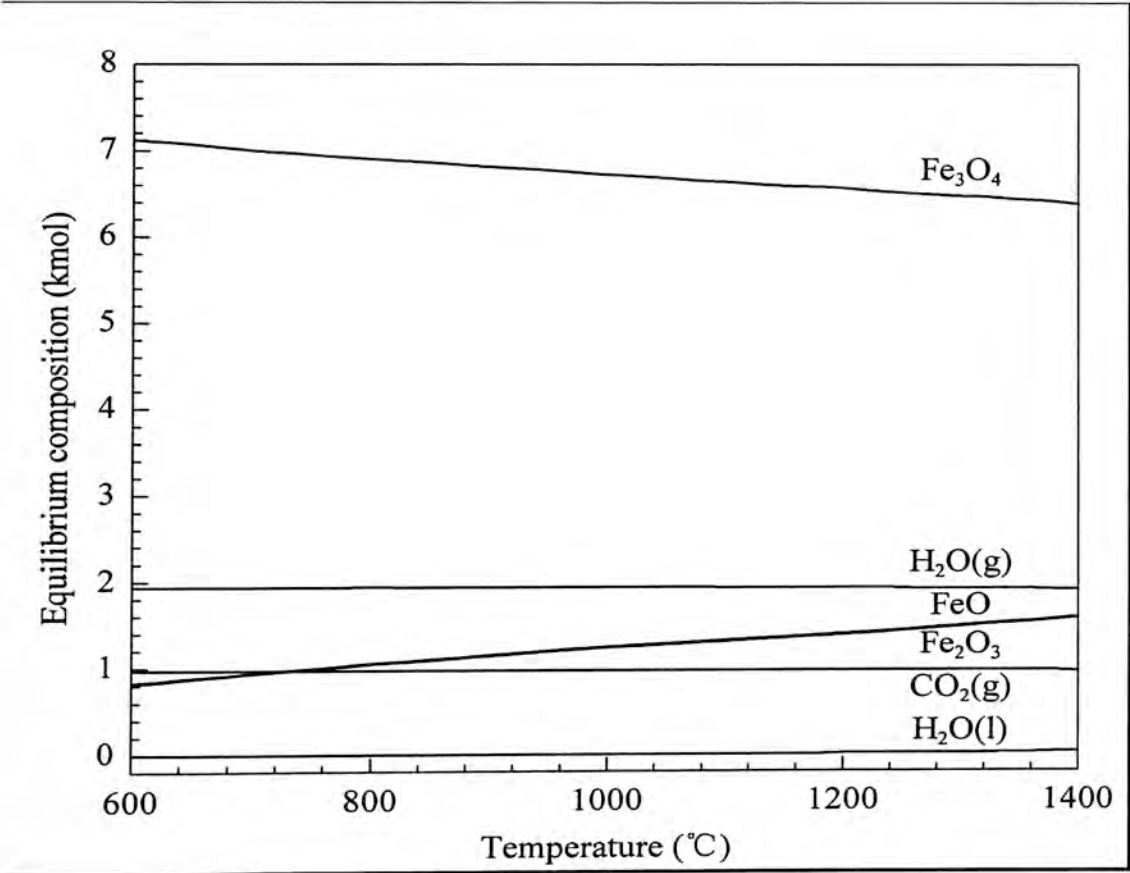


Figure 3.4: Equilibrium composition at various temperatures at $\text{Fe}_2\text{O}_3/\text{CH}_4$ molar ratio of 12:1 [137]

When the $\text{Fe}_2\text{O}_3/\text{CH}_4$ ratio is high (Figure 3.3 and Figure 3.4), no carbon is formed.

By comparison of Figure 3.3 and Figure 3.4, the products from the completed reduction of Fe_2O_3 with CH_4 (such as CO_2 and H_2O) when the molar ratio of $\text{Fe}_2\text{O}_3/\text{CH}_4$ is 12:1, are seen to be higher than the products formed when the molar ratio of $\text{Fe}_2\text{O}_3/\text{CH}_4$ is 4:1. Moreover, H_2 and CO is not generated when the molar ratio of $\text{Fe}_2\text{O}_3/\text{CH}_4$ is 12:1 [137].

It is expected that some reactive Fe_2O_3 is likely to be reduced to other lower forms of iron oxide such as Fe_3O_4 and FeO . The amount of FeO and Fe_3O_4 increase at higher temperature because FeO and Fe_3O_4 can be produced by decomposition of Fe_2O_3 [137].

It is shown in Figure 3.1 that the quantity of Fe_2O_3 is not enough for the completion of CH_4 reduction when the molar ratio of $\text{Fe}_2\text{O}_3/\text{CH}_4$ is 1:2. Consequently, only a little CO_2 and H_2O is formed, whereas much CO and H_2 are formed [137].

3.2.2.2.3.2 Kinetic studies of iron oxide reduction with methane

Dorokhovitch et al [138] have studied the reduction of pure iron oxide with 2-2.5% CH_4 . It was found that iron oxide starts to be reduced at 400°C and then was completely reduced at a temperature range from 550°C to 600°C . The activation energy of the process was found to be 113.04 kJ/mole.

The chemical equilibrium component of the system $\text{Fe}_3\text{O}_4 - \text{CH}_4$ at 1027°C and 1 atm was studied by Stienfeld et al [137]. They state that the chemical equilibrium component of the system corresponds to metallic Fe and a 2:1 gas mixture of H_2 and CO . Moreover, it also was found that there were two stages for the reduction; Fe_3O_4

was reduced to FeO and then FeO was finally reduced to Fe. The overall reaction rate, including CH₄ conversion and the yield of hydrogen, increases following increasing temperature. Carbon was also observed, resulting from the cracking of CH₄ when temperature was increased. The apparent activation energy was found to reach a peak at 30% reduction and the apparent activation energy decreased when increasing the percentage of reaction until the completion of reduction. To compare with other reducing agents such as CO and H₂, the reduction of Fe₃O₄ with CH₄ is significantly more successful over 1100 °C.

The reaction kinetics of iron oxide with CH₄ was also studied by Nekrasov et al [139]. They reveal that the first stage of reduction (Fe₂O₃ → Fe₃O₄) was observed for the temperature range from 400°C to 600°C, whereas the second stage of reduction (Fe₃O₄ → FeO) occurred over 800°C. Shortly after the appearance of the second stage, the final stage of reduction (FeO → Fe) began.

3.2.2.2.3.3 A comparison of reducing iron oxide with methane and hydrogen at different temperatures

The total oxygen conversion during the reduction of Fe₂O₃ using methane or hydrogen and at different operating temperatures is given in Table 3.3

Table 3.3 Total oxygen conversion during the reduction of Fe₂O₃ and promoted Fe₂O₃ using methane or hydrogen at different operating temperatures [116].

Catalytic materials	Oxygen conversion (%)			
	Reduction by CH ₄		Reduction by H ₂	
	700 °C	800°C	700 °C	800°C
Fe ₂ O ₃	0.6	6.8	34.7	46.3
50wt% Fe ₂ O ₃ – Ce _{0.5} Zr _{0.5} O ₂	1.6	13.0	53.5	60.0
30wt% Fe ₂ O ₃ – Ce _{0.5} Zr _{0.5} O ₂	3.0	20.9	73.2	76.0

The oxygen conversion for the reduction of Fe₂O₃ based catalyst with H₂ and CH₄ at 700 °C and 800 °C is shown in Table 3.3[116]. The calculation of the oxygen conversion was based on the removal of oxygen moles in the reactants and storage of oxygen moles in the gas products [116].

$$X_{O_2} = \frac{(H_2O + 2CO_2 + CO)}{(3Fe_2O_3 + 2CeO_2)} \times 100\% \tag{Eq. 3.7}$$

According to the Table 3.3, the reduction of pure iron oxide by methane (0.6%) was almost 60 times slower than the reduction by hydrogen (34.7%) at 700 °C, whereas the oxidation of methane (6.8%) was only 6 times slower than the oxidation of hydrogen (46.3%) at 800 °C. It is interesting to observe that the addition of Ce_{0.5}Zr_{0.5}O₂ to iron oxide, using both hydrogen and methane as reducing agents, significantly increased the oxidation rate when compared with pure iron oxide. For 50%wt.% Fe₂O₃- Ce_{0.5}Zr_{0.5}O₂ and 30%wt% Fe₂O₃-Ce_{0.5}Zr_{0.5}O₂, the oxidation

conversion increased from 1.6% and 3% at 700 °C to 13% and 20.9% at 800 °C respectively, whereas the oxidation conversion increased from 53.5% at 700 °C and 60% to 73.2% and 76.0% at 800 °C respectively for reduction with hydrogen. In conclusion, the addition of $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ can enhance the reduction rate but the efficiency of reducing Fe_2O_3 based catalyst with methane was low compared to reducing with hydrogen [116].

3.2.2.2.3.4 Comparison of Fe_2O_3 with other metal candidates

There is also the possibility that other metal oxide – metal combinations could mimic these reactions. Possible systems are listed below and the corresponding thermodynamics are shown in Figure 3.5.

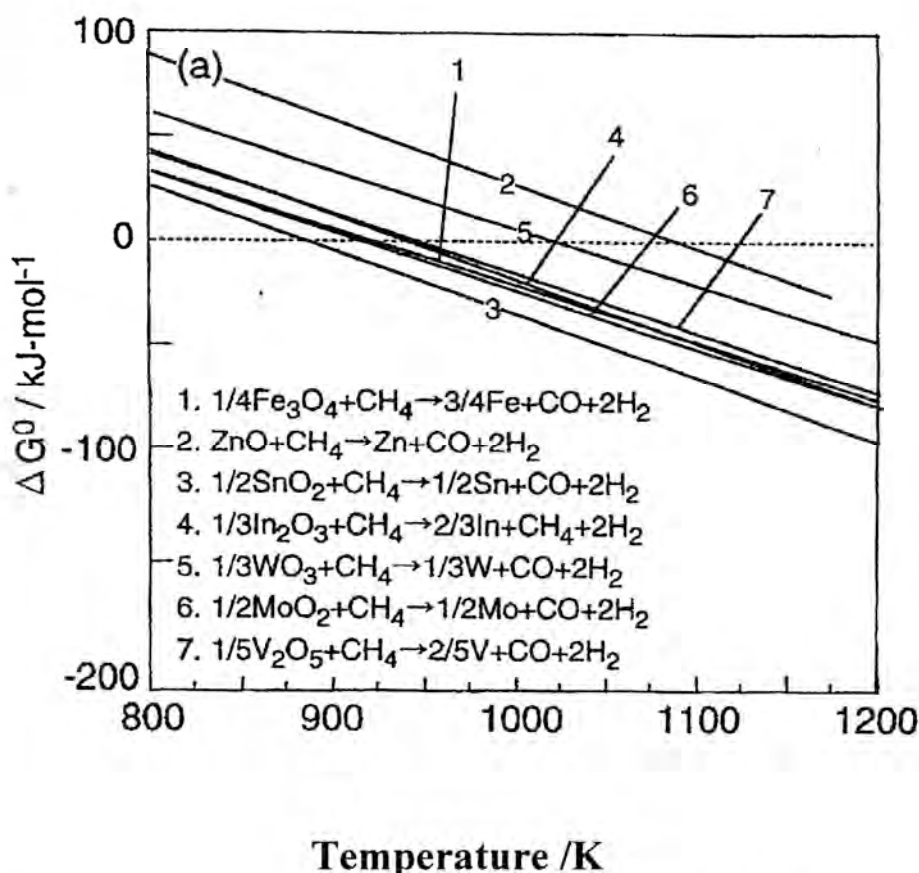


Figure 3.5: Variations in ΔG^0 for the reactions (a) $1/yM_xO_y + CH_4 \longrightarrow CO + 2H_2 + x/yM$ with temperature(K) for the metal oxide, redox pair candidates[144]

1. $1/4Fe_3O_4 + CH_4 \longrightarrow 3/4Fe + CO + 2H_2$	$\Delta H^0_{298K} = 244 \text{ kJ}$
2. $ZnO + CH_4 \longrightarrow Zn + CO + 2H_2$	$\Delta H^0_{298K} = 313 \text{ kJ}$
3. $1/2SnO_2 + CH_4 \longrightarrow 1/2Sn + CO + 2H_2$	$\Delta H^0_{298K} = 253 \text{ kJ}$
4. $1/2In_2O_3 + CH_4 \longrightarrow 2/3 In + CO + 2H_2$	$\Delta H^0_{298K} = 273 \text{ kJ}$
5. $1/2WO_3 + CH_4 \longrightarrow 1/3 W + CO + 2H_2$	$\Delta H^0_{298K} = 245 \text{ kJ}$
6. $1/3MoO_2 + CH_4 \longrightarrow 1/2 Mo + CO + 2H_2$	$\Delta H^0_{298K} = 259 \text{ kJ}$
7. $1/5V_2O_5 + CH_4 \longrightarrow 2/5 V + CO + 2H_2$	$\Delta H^0_{298K} = 274 \text{ kJ}$

According to the Figure 3.5, the reduction of Fe_3O_4 with methane does not become spontaneous until well over about 647 °C and is the third lowest temperature where reduction with methane occurs (higher than SnO_2 , MoO_2 but somewhat lower than V_2O_5 [140].

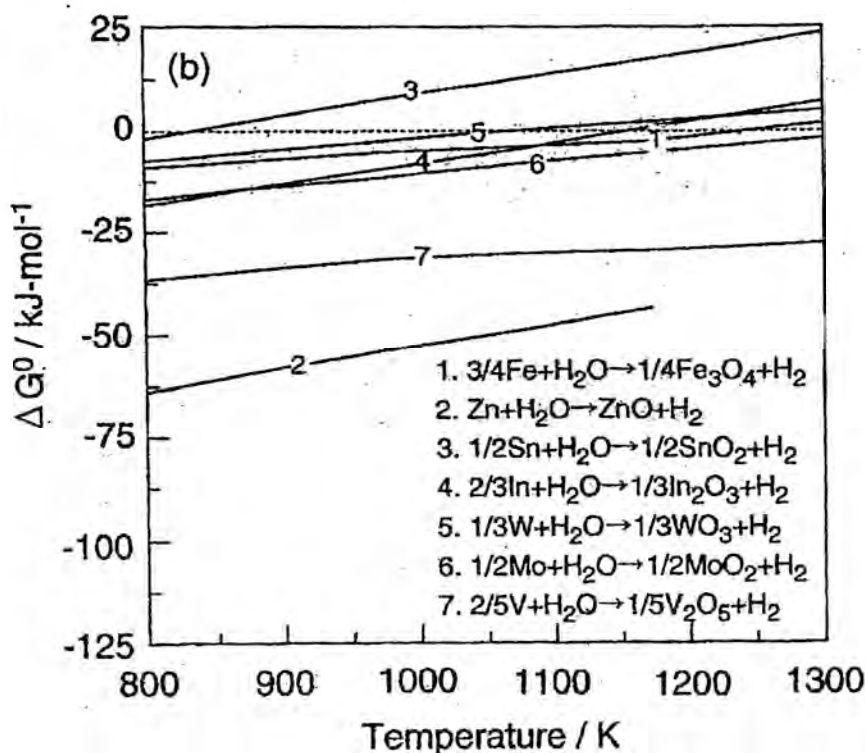


Figure 3.6: The relationship between ΔG and different temperature(K) for the oxidation of a variety of metal candidates with water [140]

This relationship can demonstrate the possibilities of water decomposition over different metal candidates. As shown in Figure 3.6, the oxidation of Fe with water vapor can occur spontaneously up to a temperature of 977°C. Fe is the fifth favorable catalyst at lower than 827°C, whereas it is the fourth favorite at temperature over 827°C. Table 3.4 shows yield and selectivity of gaseous carbon products for methane reforming using a variety of metal oxides oxidants at 900 °C for 60 minutes. A low ratio between H_2 and CO demonstrates efficient oxidation by the metal oxide. Iron oxide produces the fifth lowest H_2/CO but produces a similar H_2/CO ratio to SnO_2 [140].

Table 3.4 Yields and selectivity of gaseous carbon products from the methane reaction^a using metal oxide as oxidants at 900 °C for 60 min [140]

Metal oxide ^b	Yield of product %		Selectivity of product%		H ₂ /CO
	CO	CO ₂	CO	CO ₂	
Fe ₃ O ₄	9.4	5.6	62.7	37.3	1.86
ZnO	6.7	0.7	90.5	9.5	2.65
SnO ₂	6.0	15.8	27.5	72.5	1.84
In ₂ O ₃	8.4	5.2	61.8	38.2	2.11
WO ₃	17.3	1.6	91.5	8.5	1.20
MoO ₂	10.4	2.1	83.2	16.8	2.63
V ₂ O ₅	25.9	5.1	83.5	16.5	2.68

^a A 50% mixture of CH₄-N₂ was fed at a flow rate of 12cm³ min⁻¹

^b 0.63- 1.60 g of metal oxide was used for the reaction: the amounts of the oxide in the metal oxides packed in the reactor were fixed to be 17.3 mmol

It also was reported that, although Fe₃O₄ is less reactive than other thermodynamic candidates such as ZnO and WO₃ [141], Ni(II)- ferrite powder has much higher activity and selectivity than candidates such as ZnO and WO₃ [141 and 142].

There are also two main issues to be solved in this technology [143].

- 1) Accelerating the reaction rate, especially the reduction rate (Eq 3.1), which is reported to be the rate controlling rate.
- 2) Preventing the sintering of Fe and Fe₃O₄ which causes in a decrease in the reactivity of Fe in the regeneration process.

3.2.2.2.3.5 The acceleration of the rate of reduction

An increase in the reaction rate in the steam/iron process not only maximizes hydrogen production but also minimizes the deactivation of catalyst. It was claimed by Fukuse and Suzuka [144] that the suppression of deactivation in the steam/iron process resulted from either accelerating the reduction rate or reducing the rate of oxidation. Furthermore, it was found that the balance of the stoichiometry of reduction and oxidation reaction for the prevention of catalyst deactivation is essential. Hence, the addition of promoter for the enhancement of rate has been examined by several researchers.

Firstly, it was found by Urasaki et al [145] that the reduction rate and oxidation rate were enhanced by the addition of a tiny amount (0.23 mol %) of both palladium and zirconia onto the ferric oxide. Both the reduction rate and the oxidation rate were significantly increased by palladium whereas only the oxidation rate was accelerated by zirconia.

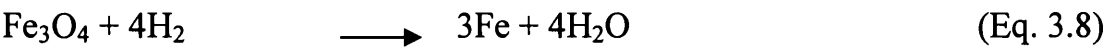
Cu was another effective promoter for the enhancement of both reduction and oxidation in the steam-iron process, but the addition of Cu causes a fast sintering of iron [146]. Similarly, the addition of Ni to iron oxide enriched the reduction rate with methane in the steam iron process and lowered the temperature of oxidation reaction with steam but was highly favorable for iron sintering [147].

Moreover, the application of $\text{Pt} - \text{Fe}_2\text{O}_3 - \text{Ce}_{0.5}\text{Zn}_{0.5}\text{O}_2$ resulted in a remarkable improvement of methane oxidation rate for the steam-iron process when compared to iron oxide without support. This improvement directly led to a reduction in

temperature of operation. For this process, Ce species were used as key promoters to prevent iron sintering [148]. However, the additional Rh and Ir on the iron oxides also enhanced both the reduction rate and the oxidation rate.

3.2.2.2.6 The prevention of sintering of iron

The sintering of iron oxide has a significant adverse effect on the steam – iron process. This sintering results in bad reproduction of the process, especially the repeatability of water splitting in the oxidation reaction (Eq 3.2). In order to avoid iron sintering, Takenaka et al. [149] suggested that the reduction of pure iron oxide has to be performed below at least 750 °C.



A method for minimizing sintering during repeated redox cycles as well as improving the reactivity of the iron oxide would increase the feasibility of producing hydrogen by the steam – iron reaction in comparison with other technologies such as the steam reforming or partial oxidation of methane [150 and 151].

Sintering of iron oxide in the residual oil cracking process with the generation of hydrogen through the steam – iron process at 510 °C was found to be caused by the accumulation of wustite (FeO) [144]. Otsuka et al [152] also stated that, at 400 °C, the sintering of iron oxide appeared during repeating redox cycle. Moreover, they stated that sintering was suppressed by the co – precipitation of iron oxide with 3mol% of a foreign element and also stated that the reduction and oxidation rate could be enriched by this added foreign element [152 and 153]. Iron sintering was also suppressed by the addition of Al, V, Cr, Ga and Mo [152].

In addition, due to the longer cycling time of the steam iron process over the temperature range 800 – 900 °C compared with non-supported Ni(II) ferrite, iron sintering could be suppressed and the reactivity of the steam-iron process could be enriched by using ZrO₂ supported Ni(II)- ferrite (Ni_{0.39} Fe_{2.61} O₄/ ZrO₂). In contrast, it was found that only 33 % of Ni_{0.39}Fe_{2.61}O₄/ZrO₂ reacted in the process due to the parasitic property of ZrO₂ [154].

According to Takenaka et al [147], the addition of Cr to Cu (II) or Ni (II) ferrite prevented iron sintering promoted by Ni and Cu species. A longer life for the steam/iron promoter and a rich yield of hydrogen production were also facilitated by using Ba promoted iron oxide. Further study of Ba promoted iron oxide showed that the addition of Ba to ferric oxide by co precipitation gave greater hydrogen yield and stability than addition by co-impregnation [155].

3.2.2.3 Carbon formation

Carbon formation is the one of main issues of the steam - iron process. Carbon formation in the literature survey is discussed in three sections. The first sector discusses formation of filamentous carbons over supported Fe catalysts through methane decomposition. The other two sectors discuss carbon formation on NiO and carbon deposition during the steam -iron process using methane as reductant.

3.2.2.3.1 Formation of filamentous carbons over supported Fe catalysts through methane decomposition

Although methane is the simplest hydrocarbon, the formation of filamentous carbon at high temperature is highly favorable.

There are several studies of the formation of filamentous carbon formation from methane over Fe-based catalyst [156,157,158,159 and 160]. These studies indicate that methane, which was diluted with hydrogen, decomposed on catalysts at temperatures over 1000 °C. It was shown that the filamentous carbons grew from iron species in the liquid state, which were saturated with carbon. The transformation to saturation of iron species took place at over 1000 °C. Deactivation of Fe-based catalysts resulted from the coverage of the catalytically active iron species with graphite, which caused the iron species to fail to contact with methane. It was suggested that, in order to minimize the deactivation of Fe based catalysts, hydrogen should be fed at temperature less than 800 °C. However, the most recent research showed that methane decomposition on Fe based catalyst can occur without cofeeding hydrogen at temperature less than 800 °C.

The effect of different promoters such as SiO₂, Al₂O₃, TiO₂ and ZrO₂ added to iron oxide was analyzed by Ermakova et al [161]. The results showed that the addition of SiO₂ to iron oxide led to a high yield of filamentous carbons for the methane decomposition over the temperature range 680 °C to 800 °C. They concluded that the fluid iron species were favorable for the formation of filamentous carbon at temperature lower than 800 °C. Further, Takenaka et al [162] examined the effect of SiO₂ and Al₂O₃ with Fe₂O₃ for methane decomposition at 800 °C. It was found that the addition of Al₂O₃ to iron oxide had a higher catalytic activity than the addition of SiO₂. The particle sizes of catalytically active species were also found to have a very strong influence on the catalytic activity. Smaller size particles of Fe₂O₃ were transformed during reaction into Fe₃C (cementite), whereas the larger particles were transmuted into Fe saturated with carbon (austentite). Finally, the characteristics of

filamentous carbons from methane decomposition over Fe₂O₃/SiO₂ were found to consist of many spherical carbon units, in addition to chain-like carbon fibers.

3.2.2.3.2 Carbon deposition during the steam iron process using methane as reductant

It was found by Takenaka et al [149] that products such as CO and CO₂ were formed in the oxidation of Fe with water vapor (Eq. 3.9) as a result of undesirable oxidation of carbon deposited on Fe based catalyst. Consequently, one main objective during the production of pure hydrogen from methane mediated by iron oxide is to minimize carbon deposition. However, CO and CO₂ were not formed during the oxidation reaction of Ni-Cr-FeO_x with water vapor at temperatures lower than 487°C [149].



Table 3.5: Total amounts of hydrogen, CO and CO₂ formed in the oxidation of the reduced iron oxide samples with water vapor [149]

Sample	H ₂ /Fe	CO/Fe	CO ₂ /Fe	*H ₂ /Fe
CO-Cr-FeO _x	1.7	0.02	0.04	1.4
Ni-Cr-FeO _x	1.7	0.05	0.18	1.3
Cu-Cr-FeO _x	1.8	0.01	0.08	1.6
Rh-Cr-FeO _x	1.3	<0.01	0.01	1.3
Pd-Cr-FeO _x	1.5	0.01	0.03	1.4
Ir-Cr-FeO _x	1.4	<0.01	0.02	1.4
Pt-Cr-FeO _x	1.4	<0.01	<0.01	1.4

*H₂/Fe = Excess amounts of hydrogen formed though the deposited carbon with water vapor

According to Table 3.5, CO and CO₂ formed by the oxidation of Pt-Cr- FeO_x, Rh-Cr-FeO_x and Ir-Cr- FeO_x with water vapor were very small as compared to the oxidation of other reduced iron oxide samples. Moreover, the addition of Pt, Rh and Ir to Cr-FeO_x lowered the temperature of oxidation. However, the cost of these additives is very expensive.

Galvita et al [116] studied carbon formation on Fe₂O₃- Ce0.5Zr0.2O₂ after reduction with methane by passing 10% O₂ flow (60 cm³/min) over the solid. The amount of carbon deposition was determined by calculation of generated CO and CO₂ from oxidation with oxygen. They found that coking was not observed at a degree of reduction lower than 60%, whereas coke was increasingly formed at reduction above

60%. The degree of reduction (DR) was calculated from initial Fe_2O_3 and the hydrogen consumed in reduction and formed in reoxidation [116].

$$\text{DR} = \frac{(3[\text{Fe}_2\text{O}_3] - \sum \{H_{2\text{consumed}}\} - [H_{2\text{formed}}])}{(3 \times [\text{Fe}_2\text{O}_3])} \tag{Eq. 3.10}$$

Coefficient = 3 is from the three steps of reduction ($\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4 \longrightarrow \text{FeO}$ or Fe)

3.3 Experimental Techniques

3.3.1 Materials

All gases used in the experimental work were supplied by Linde Gas purity and area of application are reported in Table 3.6.

Table 3.6 Gas Specifications

GAS	SPECIFICATION	USE
Hydrogen	Industrial dry, 99.9%	Reactant and reducing gas
Carbon monoxide	High purity, 99.9%	Reactant and reducing gas
Carbon dioxide	High purity, 99.9%	Reactant and reducing gas
Methane	High purity, 99.9%	Reactant and reducing gas
Argon / Helium	1%Argon /Helium	Reference and diluent gas for MS
Argon/ Nitrogen	0.55%Argon/ Nitrogen	Reference and diluent gas for MS
Nitrogen	Volumetric Std., 32.5 ± 0.25%	Carrier gas-single B.E.T and balance gas

3.3.2 Chemicals

The purity, source and application of all chemicals used in the reaction study are presented in Table 3.7 below.

Table 3.7 Chemical Specification

CHEMICAL	SPECIFICATIONS	USE
Nickel (II) Nitrate- Hexahydrate	FSE, Australia, 99.101%	Base-metal
Chromium(II) Nitrate- Hexahydrate	Sigma, Aldrich, Australia Research Grade	Promoter
Urea	Sigma, Aldrich, Australia 99.9%	
Ferric nitrate	Sigma, Aldrich, Australia 99.9%	
Silicon oxide	Sigma, Aldrich, Australia 99.9%	Support

3.3.3 Catalyst preparation

3.3.3.1 Co – precipitation of iron oxide with promoter

The iron oxide (initial state Fe₂O₃) sample used was prepared by means of precipitation of an aqueous Fe(NO₃)₃9H₂O with urea at 80⁰C. The sample with various metal additives was prepared from an aqueous solution of Fe(NO₃)₃ and a solution of foreign metal nitrates, such as by co precipitation of Fe(NO₃)₃9H₂O and Cr(NO₃)₃9H₂O.

The co precipitation was continued until the pH of solution remained at 7. The precipitates were filtered, washed and dried at 120 °C for 10 hours. Subsequently, the calcination of dried samples was performed at 500 °C for 10 hours under air. The additive amount of each species of foreign metal was adjusted to be 5% weight of total metal oxide weight. The weight ratio was $W_{Cr_2O_3} / (W_{Cr_2O_3} + W_{Fe_2O_3}) = 0.05$.

3.3.3.2 The wet impregnation of 5% NiO on SiO₂

The support (SiO₂) was washed for 8 – 10 hours with demineralized water and dried at 120 °C for 4 hours before impregnation with the nickel nitrate solution. Prior to impregnation, the nickel nitrate solution was prepared by dissolving the required mass of nickel nitrate salt in a few mls of demineralized water, based on the mass of the support (SiO₂). After preparation, the catalyst was oven – dried for 12 hours at 120 °C and then calcined at 500 °C for 10 hours.

3.3.4 Catalyst Characterization

3.3.4.1 Surface Area Measurement- BET Surface Area (S_{BET})

The total surface area measurement was determined using the BET approach and was carried out using a ASAP 2000 Micromeritics surface area analyser. A sample of ca. 0.1 gram was loaded in the sample tube, dried and degassed at 120°C under helium for about four hours and then cooled to liquid nitrogen temperature (-196 °C) by immersing the sample tube into a liquid nitrogen container. The analyzer automatically measured, recorded and calculated nitrogen adsorption at various pressures.

In principle, the amount of adsorbate (nitrogen gas) required to form a monolayer of molecules on the catalyst surface was determined from the following BET expression equation [163]:

$$\frac{P}{V_a(P_0 - P)} = \frac{1}{V_m C} + \frac{(C - 1)}{V_m C} \frac{P}{P_0} \quad (\text{Eq. 3.11})$$

Where, V_a is the volume of gas adsorbed at pressure P ;

P_0 is the gas saturation pressure;

V_m is the volume necessary to cover the entire adsorbing surface by a monomolecular layer;

C is a constant involved with energy of adsorption.

A plot of $P/(V_a(P_0 - P))$ versus relative pressure of P/P_0 in the range of 0.05 to 0.3 gave a straight line with the intercept of $1/(V_m C)$ and a slope of $(C - 1)/(V_m C)$ respectively. The volume of gas required to form an adsorbed monolayer of V_m and the surface area per gram of catalyst sample of S was determined by:

$$S = \frac{V_m A_m N_a}{W V_0} \quad (\text{Eq. 3.12})$$

where, S is the specific surface area of the sample in m^2g^{-1} ;

N_a is the Avogadro's number, 6.023×10^{23} molecules / mol

A_m is the area of an adsorbed molecule, m^2 ;

V_0 is 22414 ml / mol; and

W is the sample weight, g.

3.3.4.2 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a very useful tool for the identification of crystalline compounds and determination of the crystalline size. This technique is based on the fact that each XRD pattern is unique for each crystalline substance. It is normally used for metal crystallites with size of 300 ~ 5000 nm [164].

The relationship between the known wavelength (λ) and the angle of incidence of X-ray radiation obeys the Bragg equation [164]:

$$n\lambda = 2d\sin\theta \quad (\text{Eq. 3.13})$$

where, n is an integer, $n=1, 2, 3, \dots$

λ is the wavelength of incident radiation;

d is the crystal plane distance, or “ d spacing”, and

θ is the angle of incidence.

The determination of “ d spacing”, together with the relative intensities of the diffraction lines, constitutes the diffraction pattern of a given crystal.

The XRD patterns were determined by a Phillip’s X’Pert System with a 3710 controller and 1830 generator using Ni-filtered $\text{CuK}\alpha$ ($\lambda = 15.42 \text{ nm}$) radiation at 40 kV and 30mA.

3.3.4.3 Mass Spectrometer (MS)

During thermal characterization, a Balzer ThermoStar Quadrupole Mass Spectrometer (MS) was used to detect all species of inlet and outlet gases.

The MS separates components based on their mass to charge ratios (m/e ratios). Each species has a characteristic spectrum of m/e ratios. Under the influence of an electromagnetic field, the gases entering an evacuated chamber are separated, resolved onto a detection plate and the resultant electrical signals are amplified. These amplified analogue signals are converted into digital signals by A/D converters contained within the MS before being recorded by a Personal Computer (PC) [165].

The interesting gases, such as CO_2 , CO , H_2 , H_2O , O_2 , Ar and He were monitored at mass number (m/e) of 44, 12(28), 2, 18(17), 32(16), 40 and 4 by MS respectively. Ar (ca.1% Ar/He) was used as the reference gas. All spectra have been corrected by subtracting corresponding background signals in the mass spectra.

3.3.5 Description of Experimental Setup

In order to illustrate the experimental procedure, the steam - iron process is described by using methane as the reductant. Iron oxide samples were packed in a quartz tube reactor (ID 80 mm x 50 cm long). The sample was supported on quartz wool to prevent the sample falling out of reactor: 0.242 grams of 4% Cr_2O_3 – 96% Fe_2O_3 (400-600 μm) was used as the catalyst sample for the reduction with methane. Initially 30ml/min of methane passed through the system and then 70 % CH_4 and 30% of 1 % Ar in He mixture were passed. Temperature programming was used for the reduction, which was induced by increasing temperature from 200 °C to 650 °C at 5 °C per

minute. The process continued until the total time for the reduction was approximately 100 minutes. Subsequently, the reduced sample was oxidized with approximately 2.3% vapor water in nitrogen at 650 °C. The final experimental step was the estimation of carbon deposition on the iron oxide. 10%O₂ was passed to the reactor held at 650 °C in order to evaluate the approximate amount of carbon deposited by measuring the carbon dioxide produced.

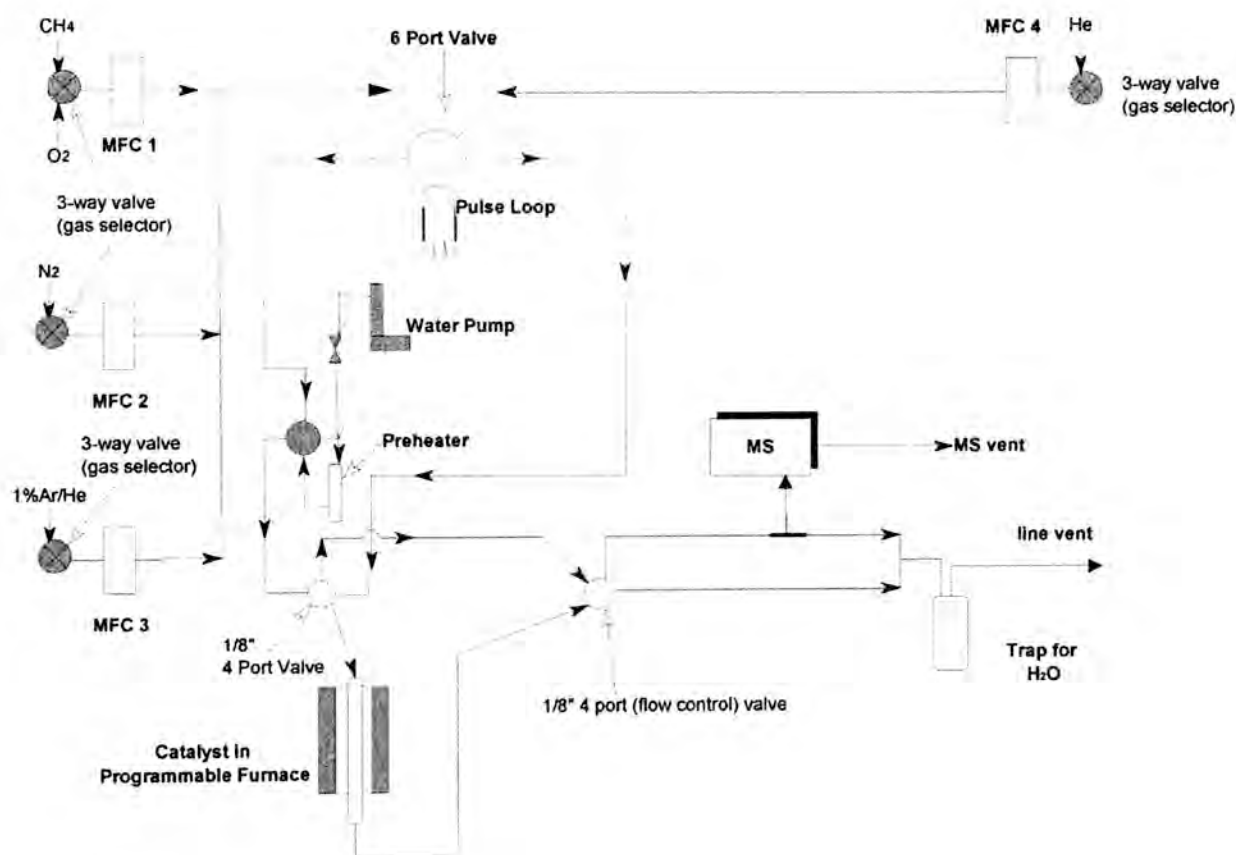


Figure 3.7: Flow diagram of experimental setup

According to the figure 3.7, there were 2 initial lines of gases. He used to stabilize mass spectrometer when no reactant gasses were passed to mass spectrometer and reactant mixture gases, were passed to 6 port valve. The 6 port valve was used to select 2 inlet gas lines to pass 3 out lines. One outlet line flows to mix with water steam. Another outlet line flows to pulse loop before mixing with water steam same

as the first line. The last outlet line flows without mixing water steam. After that, the two outlet lines, one mixed with steam and another one without steam were selected by the 4 port valve before the reactor. The 4 port valve was used to select the gas line to pass to reactor or direct to the last 4 port valve before the mass spectrometer. Finally, the last 4 port valve before the mass spectrometer was used to select the gas line to flow to the mass spectrometer or to vent.

3.4 Results and discussions

The study of the steam - iron process was divided into four parts, which were categorized by the reductant.

- 1) the steam - iron process using H₂ as reductant
- 2) the steam - iron process using H₂ /CO mixture as reductant
- 3) the steam - iron process using CH₄ as reductant
- 4) the steam - iron process using CH₄ /CO₂ mixture as reductant

Three samples were analyzed by B E T Surface Area Measurement before the experiment and after the first redox cycle of steam iron process.

Table 3.8: Specific surface areas of, Ni-FeO_x, and Ni-Cr-FeO_x before the experiment and after the first redox cycle of steam iron process

Sample	Specific surface area (m ² g ⁻¹)	
	Before the redox	After the first cycle ^a
4%Cr ₂ O ₃ – 96% Fe ₂ O ₃	48	18 ^a
5%NiO - 5%Cr ₂ O ₃ – 90% Fe ₂ O ₃	40	8 ^a
5%NiO - 5%Cr ₂ O ₃ – 90%Fe ₂ O ₃	40	14 ^b

a = the steam iron cycle using CH₄ as reductant

b = the steam iron cycle using 10% CO₂ and 70% CH₄ mixture as reductant

3.4.1 The steam - iron process using H₂ as a reductant

To start the experimental work for the steam – iron process, the accuracy and the reliability of the experimental system (setup) was primarily examined. Storage and supply of hydrogen by the redox of the iron oxides was applied for checking reliability and accuracy of the experimental system.

The first cycle based on the reduction of hematite (Fe₂O₃) into Fe metal [166].



Subsequently, the iron metal is oxidized by steam into magnetite (Fe₃O₄) to generate hydrogen.



The further redox cycle based on the reduction of magnetite (Fe₃O₄) into Fe metal and the oxidation of Fe metal into magnetite (Fe₃O₄) is used because Fe metal can not easily be oxidized back to hematite (Fe₂O₃) [166].



The redox reaction was repeated over several cycles. The application of this redox cycle can theoretically supply and store 1.33 mole of hydrogen per 1 mol of iron metal based on equation (Eq.3.8). However, the iron oxide without other metal does not give repetitive result as a result of sintering of iron and of heavy deactivation.

Consequently, Cr – FeO_x, which can be efficiently used repeatedly, was suggested for the formation of pure hydrogen [166]. Takenaka et al [166] also demonstrate that the ferrites Cr_xFe₃₋₄O₄ were highly stable during the redox cycle because of the inhibition

of contacts between iron metal particles during the redox. Hence, the sintering of iron species in the sample was mitigated. It is interesting to note that the use of Cr – FeO_x allows repetition of the redox cycle more than 10 times [166]. As a result, Cr – FeO_x was selected to be used as the modified iron oxide for checking the reliability and accuracy of the experimental system.

3.4.1.1 Initial testing

3.4.1.1.1 Accuracy and reliability of the experimental setup

0.104 gram of 4%Cr₂O₃ – 96% Fe₂O₃ (0.624 mmol Fe₂O₃) was packed into the reactor and then 14% H₂/ 76 %N₂ / 10% of 1 % Ar in He mixture were passed to the reactor. TPR was used for the first reduction by increasing the temperature from 25 °C to 150°C (5 °C per a minute) and then 150 °C to 550 °C (3 °C per a minute) the reduction was then continued at 550 °C until no water was observed. Subsequently, the reduced sample was oxidized with approximately 2.3% vapor water at 550 °C. Further reductions were performed at 550 °C (isothermal temperature) and the re-oxidations were performed at the same temperature.

The first reduction of 4%Cr₂O₃-Fe₂O₃

The literature survey suggest that there are three oxides during the reduction of iron oxide with hydrogen; hematite (Fe₂O₃), magnetite (Fe₃O₄) and wusitite(FeO) [167]. However, the last one (FeO) is unstable below 570 °C when it decomposes to Fe and Fe₃O₄ [167].

It was confirmed that the reduction of Fe₂O₃ to Fe metal under Temperature Program Reduction proceeds in two steps via the Fe₃O₄ intermediate. The experimental result

for the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with hydrogen showed two peaks of reduction (Figure 3.8), which was in agreement with previous literature [118, 119 and 168].

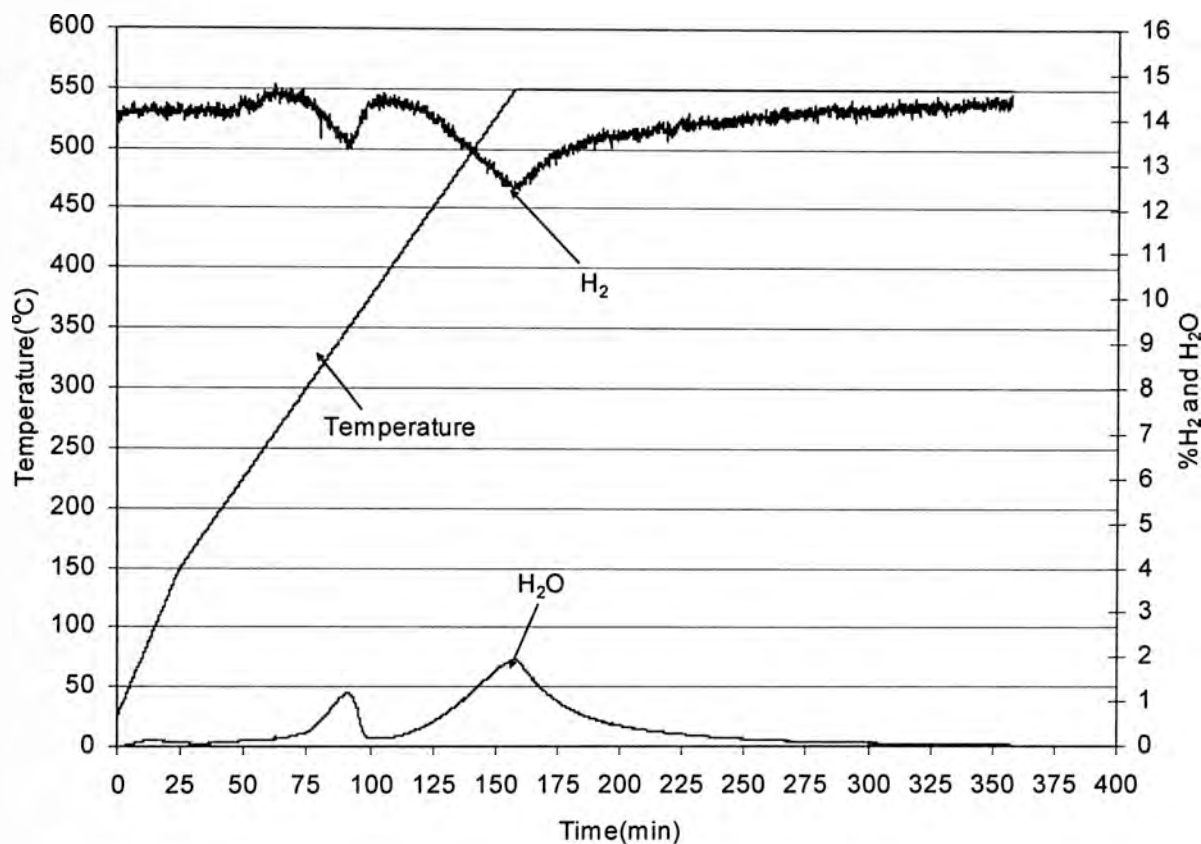
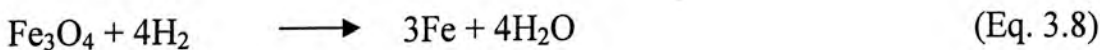
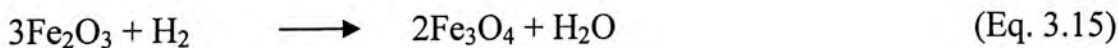


Figure 3.8: TPR profile during the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂

The first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂ is the composition of two step reduction.



The further reduction of oxidised catalyst

Figure 3.9 shows the further five reduction of 4% Cr₂O₃ - Fe₂O₃ with hydrogen

The equilibrium constant for the reduction of Fe₃O₄ with hydrogen (Eq. 3.8) at a temperature at 550°C is 0.25. Consequently, the percentage of H₂O and H₂ in the equilibrium should be 2.7% and 10.8% when feeding 13.5% H₂ into the system [166].

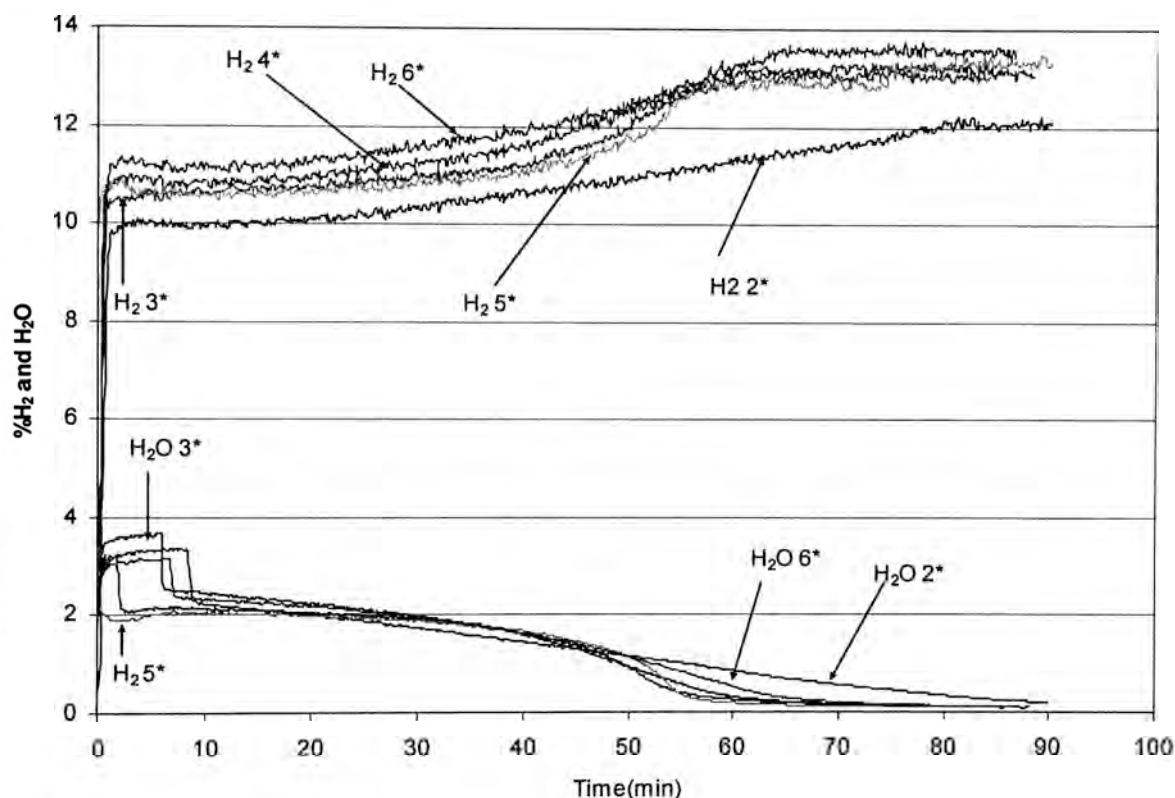
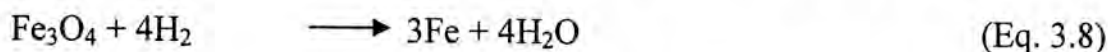


Figure 3.9: The percentage of gases during the further five reduction cycles with H₂ after passing H₂O (2.3%) over first reduced 4%Cr₂O₃ – 96% Fe₂O₃ at 550°C

2* = the second reduction, 3* = the third reduction 4* = the fourth reduction,

5* = the fifth reduction, 6* = the sixth reduction

According to Figure 3.9, at equilibriums, the average amount of H₂O was 2.7% and H₂ was 10.8%. As a result, the experimental results were found to be in agreement

with the thermodynamic equilibrium for the reduction of Fe_3O_4 with hydrogen (Eq. 3.8).

The oxidation of reduced 4% Cr_2O_3 - Fe_2O_3

The further redox cycle based on the reduction of magnetite (Fe_3O_4) into Fe metal and the oxidation of Fe metal into magnetite (Fe_3O_4) was used because Fe metal can not easily be oxidized back to hematite (Fe_2O_3).

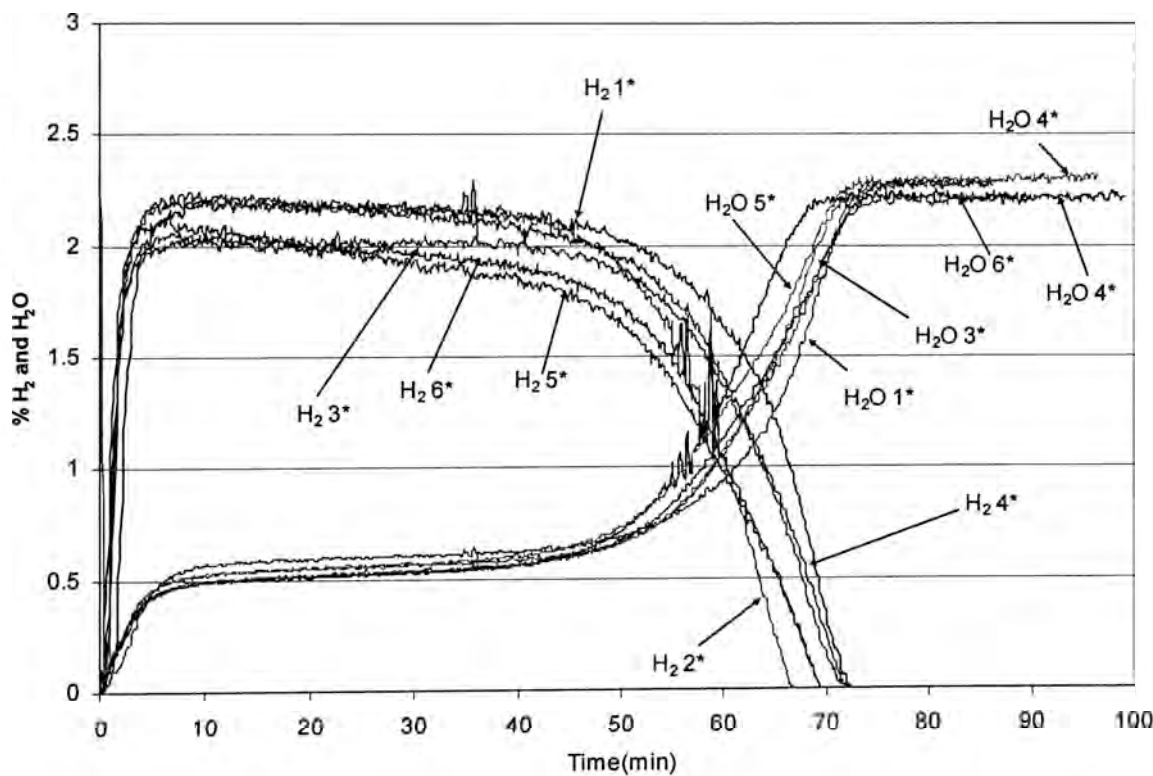


Figure 3.10: The percentage of H_2 formed and H_2O consumed during oxidation of reduced 4% Cr_2O_3 – 96% Fe_2O_3 with H_2O (2.3%) at 550°C

1* = the first oxidation, 2* = the second oxidation, 3* = the third oxidation

4* = the fourth oxidation, 5* = the fifth oxidation, 6* = the sixth oxidation

The comparison between the experimental results and the expected results is summarised below.

Reduction

Table 3.9: The comparison between the experimental results of hydrogen consumed from the reduction and their expected results as based on equations 3.15 and 3.8.

The calculation method is shown in APPENDIX B.

Cycle	Result H ₂ (mmol)	ExpectedH ₂ (mmol)	Ratio (result/expect)
1	1.85	1.872	0.99
2	1.68	1.664	1.01
3	1.61	1.664	0.97
4	1.66	1.664	1.00
5	1.59	1.664	0.96
6	1.62	1.664	0.97

Table 3.10: The comparison between the experimental results of water generated from the reduction and the expected results

The calculation method of experimental result is shown in APPENDIX B.

Cycle	Result H ₂ O (mmol)	Expected H ₂ O (mmol)	Ratio (result/expect)
1	1.85	1.872	0.99
2	1.65	1.664	0.99
3	1.69	1.664	1.02
4	1.64	1.664	0.98
5	1.69	1.664	1.02
6	1.70	1.664	1.02

Oxidation

Table 3.11: The comparison between the experimental results of hydrogen generated from the oxidation and the expected results

The calculation method of experimental result is shown in APPENDIX B.

Cycle	Result H ₂ (mmol)	Expected H ₂ (mmol)	Ratio (result/expect)
1	1.49	1.664	0.89
2	1.50	1.664	0.90
3	1.55	1.664	0.90
4	1.55	1.664	0.93
5	1.55	1.664	0.93
6	1.55	1.664	0.93

Table 3.12: The comparison between the experimental results of water consumed during the oxidation and the expectable results

The calculation method for the experimental result is shown in APPENDIX B.

Cycle	Result H ₂ O (mmol)	Expected H ₂ O (mmol)	Ratio (result/expect)
1	1.75	1.664	1.05
2	1.67	1.664	1.00
3	1.69	1.664	1.01
4	1.68	1.664	1.01
5	1.61	1.664	0.97
6	1.55	1.664	0.93

The slightly lower ratio in Table 3.11 when compared with other tables probably resulted from errors of measurement from the Mass Spectrometer. As has been shown, higher ratios were observed when the cycle time was extended. However the mass spectrometer focuses on short residence times. Consequently, a subsequent oxidation process would be extended in order to make sure that the hydrogen product from oxidation of iron with steam was measured.

In conclusion, the calculation results from the experiments were 90% or better of the expected results. In conclusion, the experimental setup was assessed to be accurate and reliable.

3.4.1.2 The Mechanism and kinetics of the reduction with hydrogen

The temperature – programmed reduction (TPR) method has been widely applied to characterise solid materials [169, 170, 171, 172, 173, 174, 175, 176, 177 and 178].

The TPR method was developed by Kissinger for the demonstration of the effect of varying reaction conditions from differential thermal analysis (DTA) patterns. Kissinger's approach was adapted by Wimmers et al [173] to calculate TPR patterns using kinetic expressions.

The reducibility of bulk iron oxides by TPR has been studied by several researchers. It was reported by Brown et al [176] that there is a remarkable difference between the reducibility of Fe_2O_3 measured by TPR and the reducibility of Fe_3O_4 measured by TPR. They also insist that the reduction of Fe_2O_3 to Fe_3O_4 is the first step in the reduction of iron oxide with hydrogen, resulting in a low - temperature peak in the profile of Fe_3O_4 reduction corresponding to this reaction.

Furthermore, Unmuth et al [179] harnessed the TPR technique to study the reduction of iron oxide with hydrogen. The catalysts were prepared by loading metal on silica gel and calcined in air at 200 °C. It was found that the reduction profile for 5% FeO/95% SiO_2 consisted of two peaks, (at 307 °C and 447 °C), which corresponded to the following process: $\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$

Munteanu et al [180] also studied TPR data for $\alpha - \text{Fe}_2\text{O}_3$ and Au/ $\alpha - \text{Fe}_2\text{O}_3$ systems. It was found that the TPR profiles for $\alpha - \text{Fe}_2\text{O}_3$ also consisted of two peaks, at 280°C and 427 °C.

It must be emphasized that the literature data diverges to a large extent, since different oxides exist (Fe_2O_3 , Fe_3O_4 and FeO) and different samples can contain impurities or dopants. There are huge differences in the previous literature resulting from several

factors such as the selection of reduction temperature, the particle/crystallite size and the reducing agent.

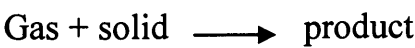
Temperature – programmed reduction

Temperature – programmed reduction studies were performed by passing 14% H₂/ 76 %N₂ / 10% of 1 % Ar in He to the reactor in which 0.104 gram of 4% Cr₂O₃ – 96%Fe₂O₃ (0.624 mmol) was packed. The first temperature – programmed reduction experiment involved a temperature ramp of 3°C from room temperature to 550 °C and was used to check the accuracy and the reliability of the system, as a reference.

The other two temperatures – programmed reduction experiments used a temperature ramp of 5 °C and 8 °C from room temperature to 750 °C for determining the maximum temperature (*T_{max}*) for two peaks of the reduction.

Theoretical approach

Consider a reaction



The reaction can be described by Equation 3.16 [173]:

$$\text{rate} = \frac{-[gas]}{dt} = k(T) [gas]^n \quad \text{s.a.} \tag{Eq. 3.16}$$

where [gas] is gas concentration, *n* the order of reaction and, *k* the rate constant given by the Arrhenius equation, where *T* the Kelvin temperature, *R* the gas constant and *E* is the activation energy. s.a. is the surface area of the solid.

$$k(T) = A e^{-E/RT} \tag{Eq. 3.17}$$

Let α be the fraction reacted of solid reactant, and *n* be the reaction order. A simplified mathematical form of the reaction kinetics can be described as

$f(\alpha) = (1 - \alpha)^n$ This assumes that the order is the same as the order used to describe the order in gas.

And the reaction rate can be written as

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (\text{Eq. 3.18})$$

Integration (3.18), yields

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = g(\alpha) = k(T)t$$

In the TPR process, temperature is also a function of time, thus:

$$\psi = \frac{dT}{dt} \quad (\text{Eq. 3.19})$$

where ψ is the constant heating rate in the TPR experiment.

Thus $g(\alpha)$ indicates the function related only on fraction conversion α , and the temperature T .

The concepts are found suitable for obtaining kinetic processes under different conditions. However, this form of $f(\alpha)$ can not describe the kinetics of nucleation or diffusion process. Four types of $f(\alpha)$ [173 and 181] are given in Table 3.13 which summarises some gas-solid reaction kinetic models: The Avrami-Erofeev model is concerned with the nucleation process from the statistical probability treatment [182 and 183]; the unimolecular model is expected to be a first order reaction, and the three-dimensional diffusion model [184] is according to the Jander equation which assumes the reaction to proceed equally in all faces of the particles, with the reaction rate is diminishing as a consequence of increasing thickness of the barrier layer. The $f(\alpha)$ and $g(\alpha)$ function of different reduction models are reported in Table 3.13.

Table 3.13: The $f(\alpha)$ and $g(\alpha)$ function of different reduction models

Reduction model	$f(\alpha)$	$g(\alpha)$
Three-dimensional nucleation according to Avrami- Erofeev [190 and 191]	$(1-\alpha)(-\ln(1-\alpha))^{2/3}$	$(-3\ln(1-\alpha))^{1/3}$
Two-dimensional nucleation according to Avrami- Erofeev [190 and 191]	$(1-\alpha)(-2\ln(1-\alpha))^{1/2}$	$(-2\ln(1-\alpha))^{1/2}$
Unimolecular decay	$(1-\alpha)$	$(-\ln(1-\alpha))$
Three-dimensional diffusion according to Jander ^{a,b} [192]	$3/2(1-\alpha)^{1/3}((1-\alpha)^{-1/3}-1)^{-1}$	$(1-(1-\alpha)^{1/3})^2$

^a This model is geometrically defined as a shrinking/unreacted core or contraction sphere models, with reaction proceeding topochemically.

^b Gas diffusion through the product layer as the rate-determining step

^c
$$g(\alpha) = \int_0^\alpha \frac{d\alpha}{f(\alpha)}$$

Combination of Eqs (3.18)-(3.19) leads to:

$$\frac{d\alpha}{dT} = \frac{1}{\psi} k(T) f(\alpha) = \frac{A}{\psi} e^{-E/RT} f(\alpha) \tag{Eq. 3.20}$$

where

$$k(T) = A e^{-E/RT}$$

Thus TPR patterns da/dT versus T can be calculated by integrating Eq. (3.20):

$$\int_0^\alpha \frac{d\alpha}{f(\alpha)} = \frac{A}{\psi} \int_{T_0}^T e^{-E/RT} dT = g(\alpha) \tag{Eq. 3.21}$$

Combining Equations (3.20) and (3.21), the integration can be solved [185 and 186]:

$$g(\alpha) = \frac{AE}{R\psi} P(x) \tag{Eq. 3.22}$$

where

$$x = \frac{E}{RT}$$

Doyle [186] has tabulated the most commonly found values of $P(x)$

$$P(x) = \int_x^\infty \frac{e^{-u}}{u^2} du = \frac{e^{-x}}{x} - Ei(-x) \quad (\text{Eq. 3.23})$$

$$Ei(-x) = - \int_x^\infty e^{-u} du \quad (\text{Eq. 3.24})$$

And for computing purposes, $P(x)$ can be approached by the following simplification:

$$P(x) = \frac{e^{-x}}{x} \left(\frac{674.567 + 57.421x - 6.055x^2 - x^3}{1699.066 + 841.655x + 49.313x^2 - 8.02x^3 - x^4} \right) \quad (\text{Eq. 3.25})$$

The equation 3.25 is based on the equation 3.23 and 3.24.

The integration approaching equation can be used for $9 \leq x \leq 174$ [183]. Thus functions of $g(\alpha(T))$ and $f(\alpha(T))$ are given, and combining Eqs. (3.22) and (3.23) can give a simulation TPR pattern:

$$\frac{d\alpha}{dT} = \frac{A}{\psi} e^{-E/RT} f(\alpha) = \frac{A}{\psi} e^{-E/RT} f(\alpha(T)) \quad (\text{Eq. 3.26})$$

where A and E were calculated by experimental data.

Since the maximum reaction rate occurs at a TPR peak,

$$\left[\frac{d}{dT} \left(\frac{d\alpha}{dT} \right) \right]_{T=T_{\max}} = 0 \quad (\text{Eq. 3.27})$$

Then,

$$\frac{d}{dT} \left[\frac{A}{\psi} e^{-E/RT} f(\alpha) \right]_{T=T_{\max}} = \frac{e}{RT_{\max}^2} \frac{A}{\psi} e^{-E/RT_{\max}} f(\alpha) + \frac{A}{\psi} e^{-E/RT_{\max}} x \left(\frac{df(\alpha)}{d\alpha} \right)_{T=T_{\max}} \left(\frac{d\alpha}{dT} \right)_{T_{\max}} = 0 \quad (\text{Eq. 3.28})$$

From Eq. (3.26), $f(\alpha) = (d\alpha/dT)(\psi/A)(e^{E/RT})$ the equation becomes:

$$\left(\frac{d\alpha}{dT} \right)_{T=T_{\max}} x \left[\frac{E}{RT_{\max}^2} + \frac{A}{\psi} e^{-E/RT} \left(\frac{df(\alpha)}{d\alpha} \right)_{T=T_{\max}} \right] = 0 \quad (\text{Eq. 3.29})$$

Since $(d\alpha/dT)_{T=T_{\max}} \neq 0$, Eq. (3.29) can be reduced to

$$\left[\frac{E}{RT_{\max}^2} + \frac{A}{\psi} e^{-E/RT_{\max}} \left(\frac{df(\alpha)}{d\alpha} \right)_{T=T_{\max}} \right] = 0 \quad (\text{Eq. 3.30})$$

Thus A can be calculated by:

$$A = \frac{-E}{RT_{\max}^2} x \frac{\psi e^{E/RT_{\max}}}{(df(\alpha)/d\alpha)_{T=T_{\max}}} \quad (\text{Eq. 3.31})$$

From Eq. (3.31) one has:

$$\ln \left(\frac{\psi}{T_{\max}^2} \right) = \frac{-E}{RT_{\max}} - \ln \left(\frac{E}{AR} \right) + C \quad (\text{Eq. 3.32})$$

where $(df(\alpha)/d\alpha)_{T=T_{\max}}$ is assumed as a constant C, since the reduction mechanism at the TPR peak did not change with heating rate.

Plotting $\ln(\psi/T_{\max}^2)$ leads to a temperature-programmed Arrhenius plot, in which the slope is equal to $-E/R$

Results

Under all linear heating rates employed, the reduction of Fe₂O₃ showed two overlapping peaks indicating a two – step reduction process. The temperatures of the maximum peaks for different temperature ramps are shown in Table 3.14.

Table 3.14: Variation of T_{max} with Linear Heating Rate (β) for Fe₂O₃ Reduction

ψ (°C/ min)	T_{max} (°C) Peak [1]	T_{max} (°C) Peak [2]
3	346	548
5	372	597
8	392	648

According to Eq 3.32

$$In\left(\frac{\psi}{T_{max}^2}\right)=\frac{-E}{RT_{max}}-In\left(\frac{E}{AR}\right)+C$$

(Eq. 3.32)

In order to determine the energy of activation, the calculated results of 1/ T_{max} rate and $ln(\psi / T_{max}^2)$ are shown in Table 3.15.

Table3.15: The calculated results of $1/ T_{max}$ rate and $\ln(\psi / T^2_{max})$

ramp of Temp (K/min)	1st peak		2nd peak	
	$1/ T_{max}$ (10^{-4} ,1/K)	$\ln(\psi / T^2_{max})$ (1/K)	$1/ T_{max}$ (10^{-4} ,1/K)	$\ln(\psi / T^2_{max})$ (1/K)
3	16.15	-11.76	12.18	-12.32
5	15.50	-11.33	11.50	-11.93
8	15.03	-10.92	10.86	-11.57

Temperature – programmed Arrhenius plots for the two – step reduction are shown in Figure 3.11

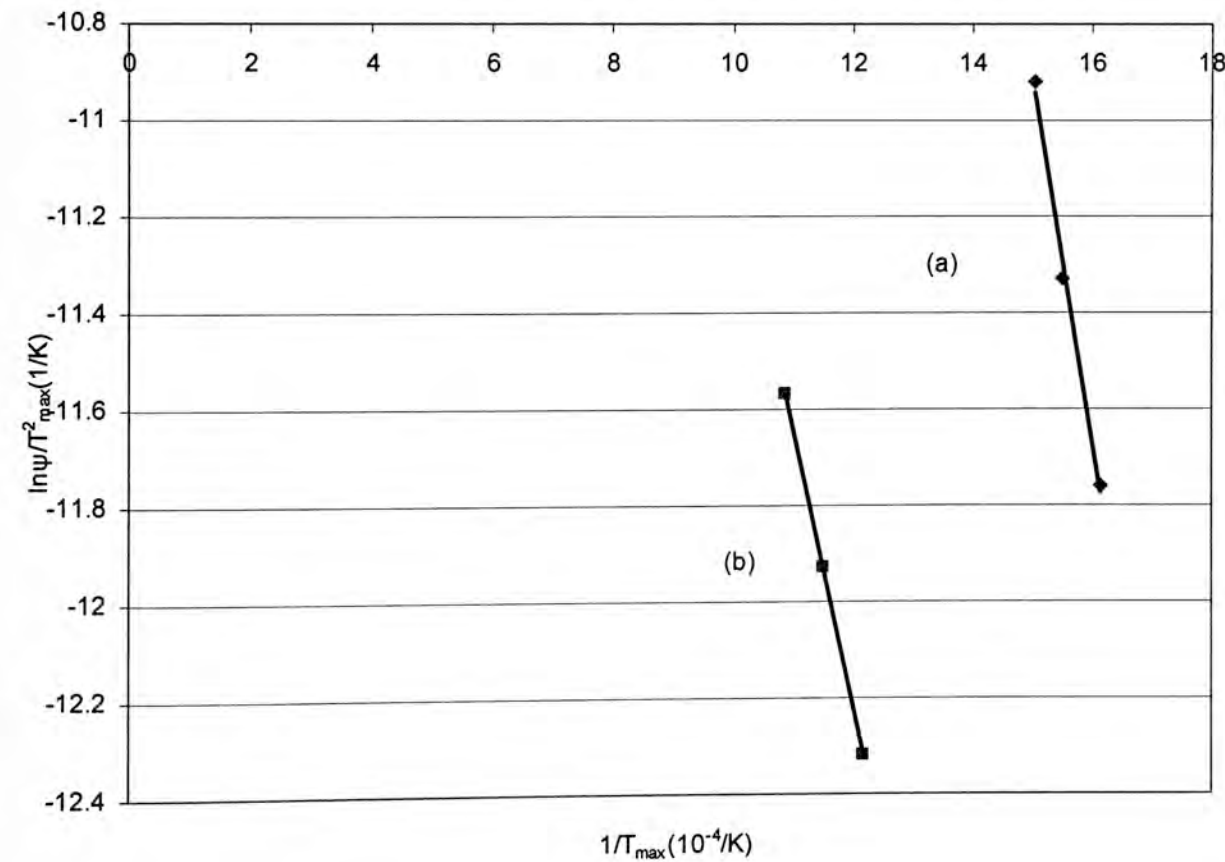


Figure 3.11: Temperature – programmed Arrhenius plots for the two – step reduction. (a) $Fe_2O_3 \rightarrow Fe_3O_4$, (b) $Fe_3O_4 \rightarrow Fe$ [173]

The relationships between $1/T_{\max}$ rate and $\ln(\psi / T_{\max}^2)$ for the two peaks of reduction were plotted in order to determine slope of the relationships, which is $-E_a/R$

The slope of first peak of the reduction ($\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4$) was -0.77.

$$-0.77 \text{ (slope)} = -E_a/R \text{ ; } R = 0.008314 \text{ kJ/mol}$$

$$E_a = 0.77 \times 0.008314$$

$$E_a = 92.4 \text{ kJ/mol}$$

The slope of second peak of the reduction ($\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$) was -0.57.

$$-0.57 \text{ (slope)} = -E_a/R \text{ ; } R = 0.008314 \text{ kJ/mol}$$

$$E_a = 0.57 \times 0.00831$$

$$E_a = 68.2 \text{ kJ/mol}$$

The $\frac{df(\alpha)}{d\alpha}$ function of 4 different reduction models are calculated and reported in

Table 3.16.

Table 3.16: The $\frac{df(\alpha)}{d\alpha}$ function of different reduction models

Reduction model	$\frac{df(\alpha)}{d\alpha}$
Three-dimensional nucleation according to Avrami- Erofeev (model 1)	$(1-\alpha)((-2/3\ln(1-\alpha))^{1/3})(1-\alpha)^{-1}-$ $(-\ln(1-\alpha))^{2/3}$
Two-dimensional nucleation according to Avrami- Erofeev (model 2)	$(1-\alpha)(-\ln(1-\alpha))^{1/2}(1-\alpha)^{-1}-$ $(-2\ln(1-\alpha))^{1/2}$
Unimolecular decay (model 3)	-1
Three-dimensional diffusion according to Jander ^{a,b} (model 4)	$-1/2(1-\alpha)^{2/3}((1-\alpha)^{1/3}-1)^{-1}-$ $(-1/3(1-\alpha)^{-4/3})^{-2}$

The evaluation of A values of two-reaction steps for different model are reported in Table 3.17.

Table 3.17: A values of two-reaction steps calculated by using $Ea= 92.4$ (kJ/mol), $T_{max}= 346$ °C for the first reduction step $Fe_2O_3 \longrightarrow Fe_3O_4$, $Ea= 68.2$ (kJ /mol), $T_{max}= 548$ °C for the second reduction step $Fe_3O_4 \longrightarrow Fe$, and $\psi = 3$ °C /min
As calculated from Eq. 3.33

$$A = \frac{-Ea}{RT_{max}^2} \times \frac{\psi e^{Ea/RT_{max}}}{(df(\alpha)/d\alpha)_{T=T_{max}}} \tag{Eq. 3.33}$$

Reduction model	A, s^{-1} for $Fe_2O_3 \longrightarrow Fe_3O_4$	A, s^{-1} for $Fe_3O_4 \longrightarrow Fe$
Three-dimensional nucleation according to Avrami- Erofeev	3.28×10^7	271
Two-dimensional nucleation according to Avrami- Erofeev	1.16×10^7	86.6
Unimolecular decay	5.39×10^6	803
Three-dimensional diffusion according to Jander	4.02×10^4	5.99

$\frac{d(\alpha)}{dT}$ for different model can be calculated

$$\frac{d\alpha}{dT} = \frac{1}{\psi} k(T) f(\alpha) = \frac{A}{\psi} e^{-E/RT} f(\alpha) \tag{Eq. 3.34}$$

The TPR patterns for $\psi = 3\text{ }^{\circ}\text{C/min}$ as calculated using the different reduction models listed in Table 3.17 and the experimental results of the TPR pattern of $3\text{ }^{\circ}\text{C/min}$ for the first peak ($\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4$) are shown in Figure 3.12.

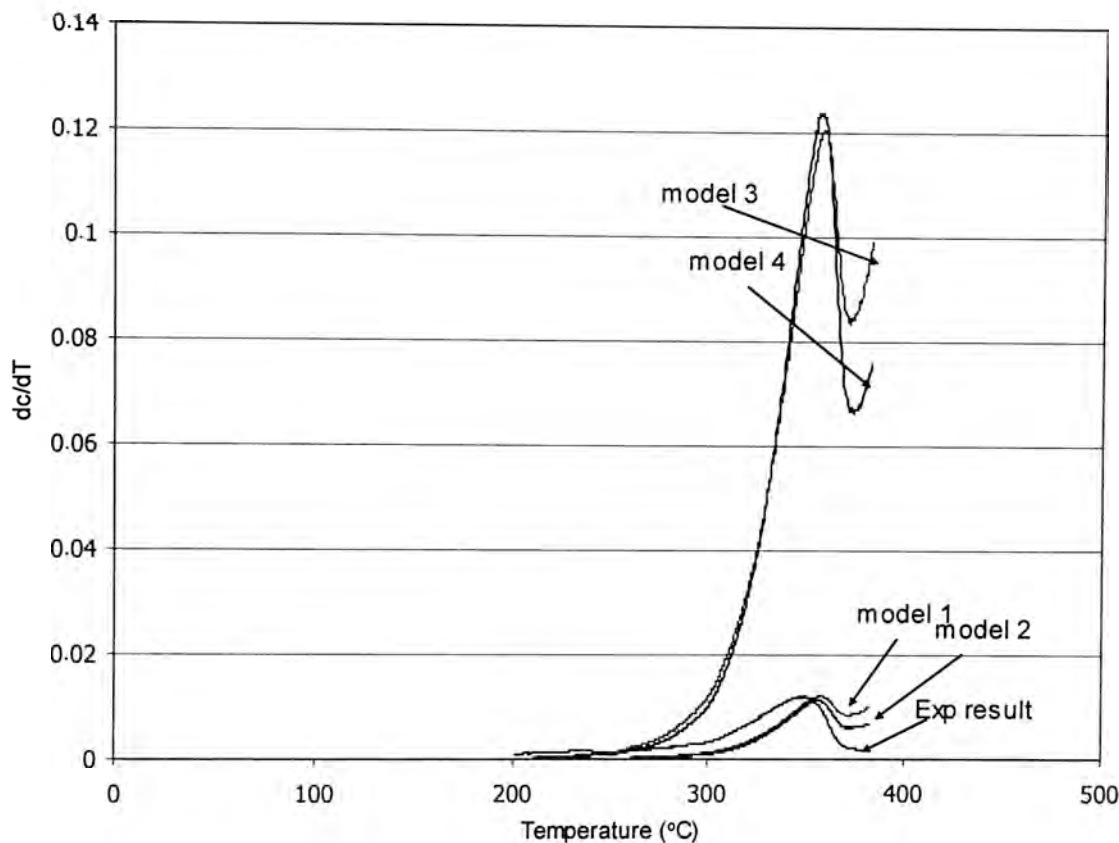


Figure 3.12: TPR patterns of different heating rates compared with experimental data for $\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4$ (model 1 = Three-dimensional nucleation according to Avrami- Erofeev , model 2 = Two-dimensional nucleation according to Avrami- Erofeev, model 3 = Unimolecular decay and model 4 = Three-dimensional diffusion according to Jander)

The TPR pattern for the second peak and $\psi = 3\text{ }^{\circ}\text{C /min}$ calculated by the different reduction models listed in Table 3.17 and the experimental results of TPR pattern of $3\text{ }^{\circ}\text{C /min}$ for the second peak ($\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$) are shown in Figure 3.13.

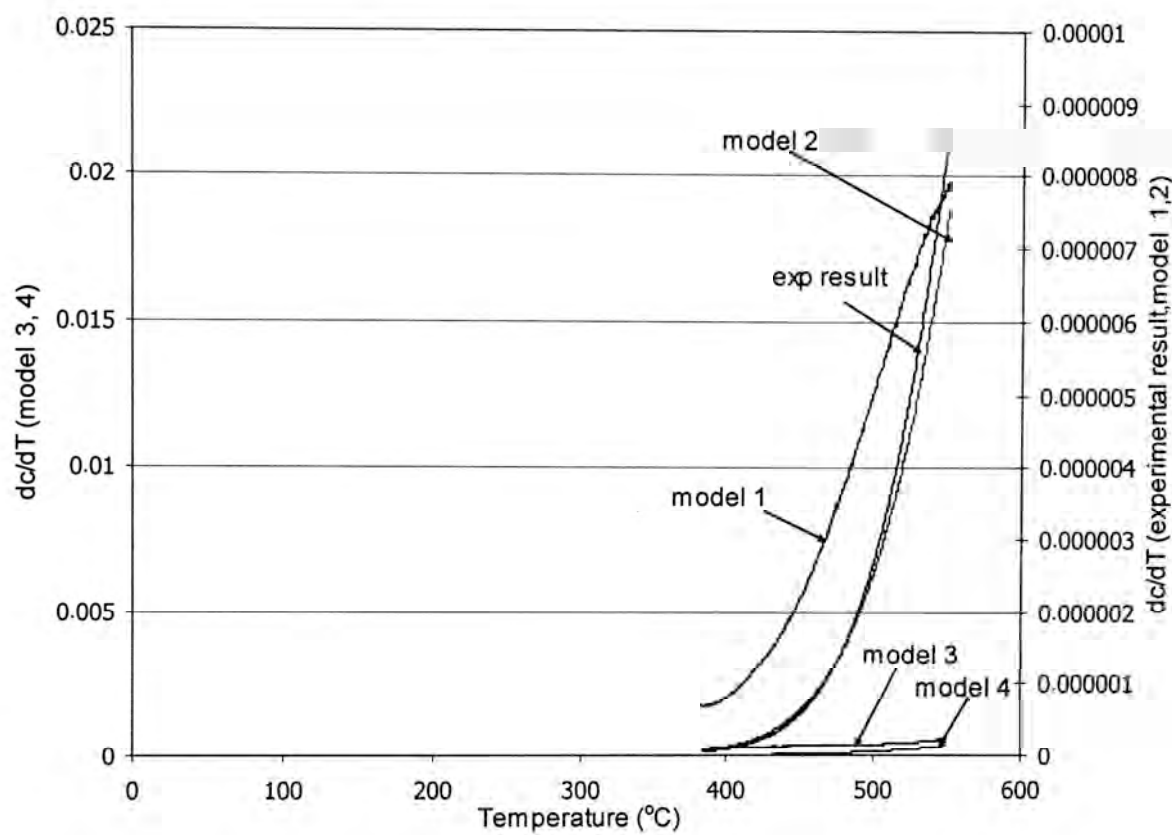


Figure 3.13: TPR patterns of different heating rates compared with experimental data for $\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$ (model 1 = Three-dimensional nucleation according to Avrami- Erofeev , model 2 = Two-dimensional nucleation according to Avrami- Erofeev, model 3 = Unimolecular decay and model 4 = Three-dimensional diffusion according to Jander)

It was observed that the first peak of $\text{Fe}_2\text{O}_3 \longrightarrow \text{Fe}_3\text{O}_4$ was the closest fit to the prediction of three-dimensional nucleation according to Avrami- Erofeev and the second peak of $\text{Fe}_3\text{O}_4 \longrightarrow \text{Fe}$ also was the closest fit to the prediction of three-dimensional nucleation according to Avrami- Erofeev.

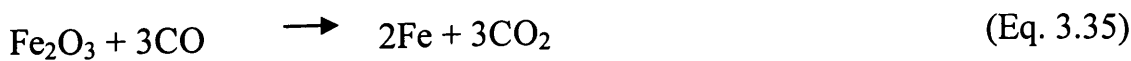
A list of models were calculated in this work but did not fit with the experimental results, as shown (These calculated models are from Table 3.2):

- i Topochemical reaction at the interface gas/solid: $r = 1 - (1-x)^{1/3}$ [127]
- ii Topochemical reaction and different mechanism involving the mixed oxide (FeAl₂O₄...) formed at the surface of Fe₂O₃ [127]
- iii Chemical reaction: the advance of reaction front during reduction in: $r = 1 - (1-x)^{1/3}$ [129]
- iv Thin layer at the pellet surface has been reduced: chemisorption of H₂ on the oxygen vacancies and Self-catalyzed nucleation [130]
- v Autocatalysis nuclei catalyze further nuclei formation, due to branching of nuclei or to the assists during the acceleration by assuring fast hydrogen spill-over [131]

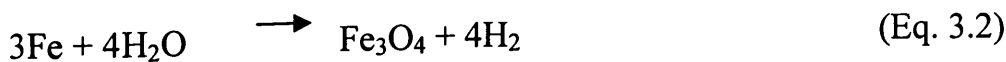
3.4.2 The steam - iron process using H₂ /CO mixture as a reductant

Another promising steam iron process for high – purity hydrogen production is the application of a gas mixture of H₂ and CO as the reductant. There are two main overall reactions of the reduction of iron oxide but the process may involve the production of FeO [187 and 188].

The two reactions in the first step of the steam iron process are shown in Eq. 3.35 and Eq. 3.14.



The oxidation in the second step of the steam iron process was shown in Eq. 3.2.



It is interesting to note that the excess water produced during the reduction step (Eq. 3.14) can result in oxidizing Fe back to Fe_3O_4 and losing surface area of catalyst due to the temperature produced during oxidation by water [189].

3.4.2.1 Results and discussion

0.243 gram of 4% Cr_2O_3 – 96% Fe_2O_3 (1.46 mmol Fe_2O_3) was packed into the reactor and a 10 % CO: 30 % H_2 mixture was admitted. TPR was used for the first and second reduction by increasing temperature from 25 °C to 400 °C (10 °C per min) and then from 400 °C to 650 °C (5 °C per min). The reduction was continued at 650 °C and stopped when the amount of product water decreased and the amount of hydrogen increased (Figure 3.14 and 3.15). Water reacts with CO, to form hydrogen via the water gas shift reaction. It can be assumed that no further CO reacts with iron oxide after the water gas shift reaction has been established. Subsequently, the reduced sample was oxidized with approximately 2.3% vapor water vapor at 650 °C.

Reduction of iron oxide with syngas as studied by TPR

TPR profiles during the first reduction and the second reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with 10 % CO and 30 % H₂ mixture are shown in Figure 3.14 and Figure 3.15.

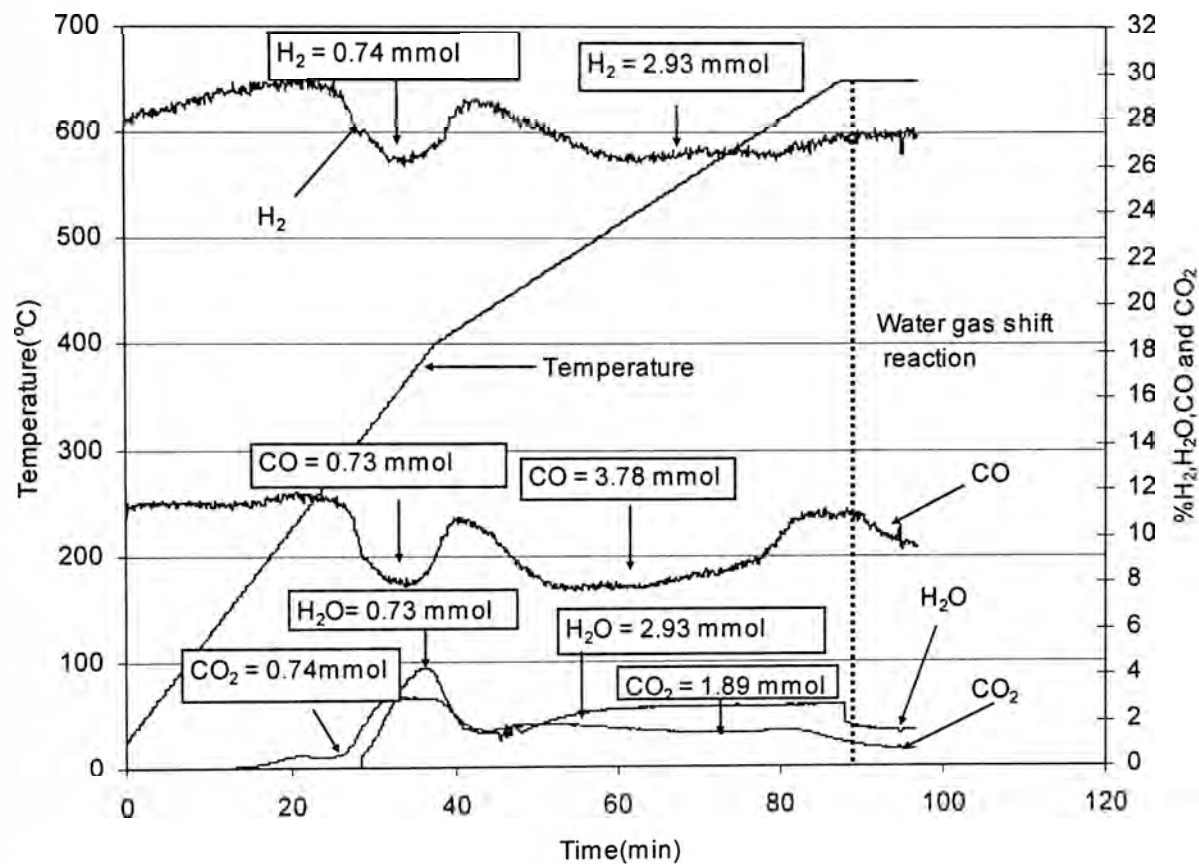


Figure 3.14: TPR profile during the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with 10 % CO and 30 % H₂ mixture

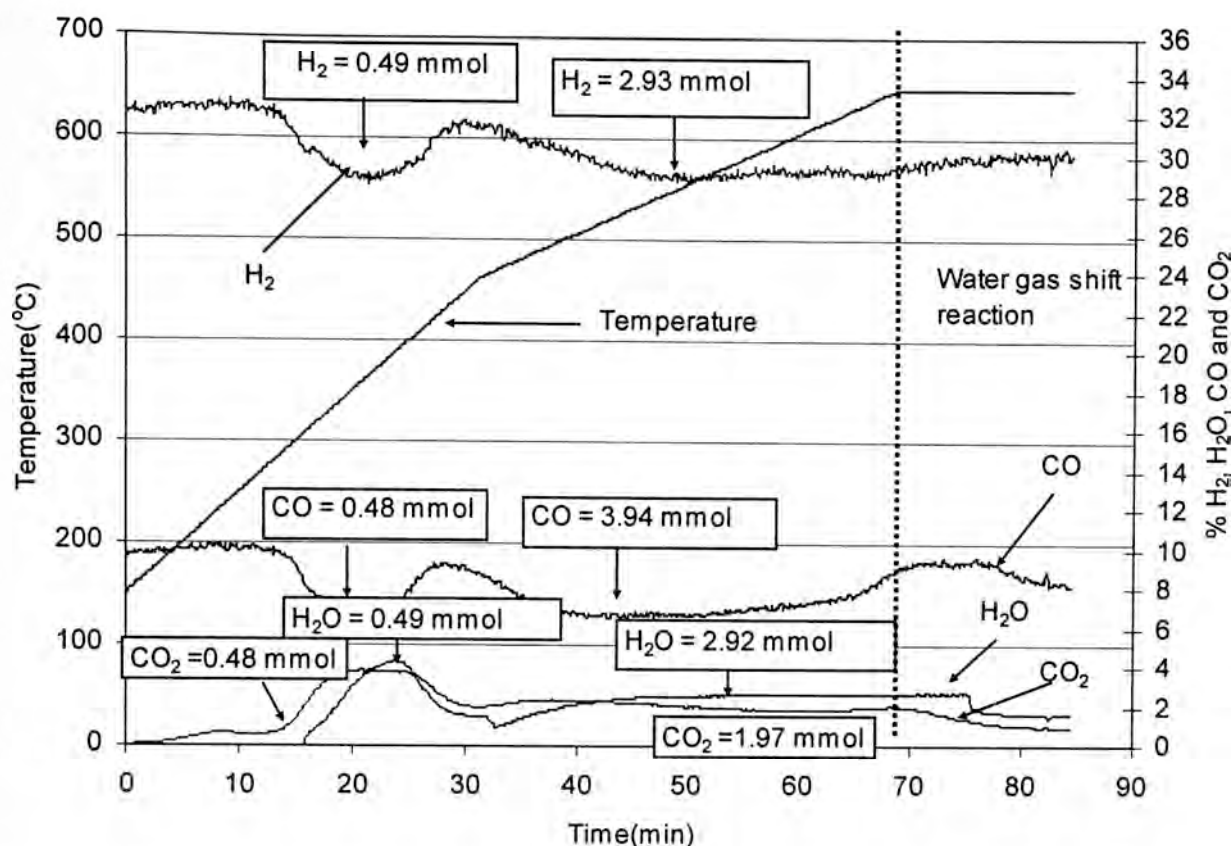
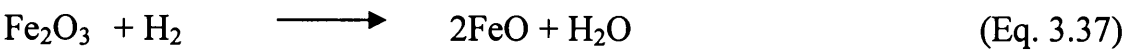
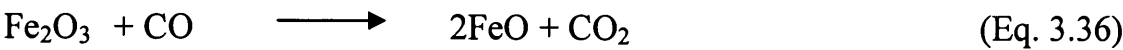


Figure 3.15: TPR profile during the second reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with a 10 % CO and 30 % H₂ mixture after passing H₂O (2.3%) over first reduced 4%Cr₂O₃ – 96% Fe₂O₃ sample at 550°C

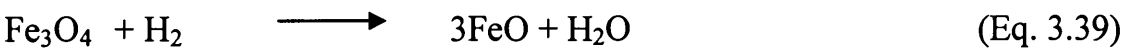
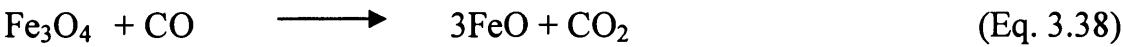
The reduction of ferric oxide by syngas (H₂ and CO) is assumed to take place via a series pathway in which the products of the reaction are FeO, Fe and Fe₃C. Evidence from previous literature indicates that Fe₃C is found among the products of the reaction. Various iron carbides being formed in such reducing atmospheres (and in the presence of carbon) have been identified [187, 190, 191 and 120]. It is also confirmed that the supported catalyst based on iron oxide transformed easily into iron carbide when it was reduced with syngas (H₂ and CO) [192]. Consequently, after reduction of iron oxide to iron carbide, no further CO reacts with iron oxide after the water gas shift reaction has been established. The Boudouard reaction (Eq. 2.21) is included in

considerations to demonstrate the formation of carbon and the production of carbon dioxide.

According to the Figure 3.14 – Figure 3.15, the system can be divided into 3 parts. The first part involves the temperature range from 245 – 427 °C. The expected chemical reaction for the first reduction in the first stage was proposed[192].



Furthermore, the expected chemical reaction for the second reduction in the first stage was proposed.



The consumption of reductant and the production of CO₂ and H₂O during the first stage of the reduction step of the first redox cycle were calculated on the basis of equations (Eq. 3.36 and Eq. 3.37) and are compared with the experimental results in Table.3.18.

Table 3.18: The calculated consumption of reductant and the production of CO₂ and H₂O in the first stage of the reduction step of first redox cycle and comparison with the experimental results

The calculation method of experimental result is shown in APPENDIX B.

Component	Experimental Result (mmol)	Expected result based on equation (Eq. 3.36, Eq. 3.37) (mmol)	Ratio (result/expect)
CO consumed	0.73	0.73	1.00
H ₂ consumed	0.74	0.73	1.01
CO ₂ formed	0.74	0.73	1.01
H ₂ O formed	0.73	0.73	1.00

Expected result based on equation (Eq. 3.36 and Eq. 3.37)



Total mole of formed FeO = 2.92 mmol

The consumption of reductant and the production of CO₂ and H₂O in the first stage of the reduction step of the second redox cycle were calculated on the basis of equations (Eq. 3.38 and Eq. 3.39) and are compared with the experimental results in Table.3.19.

Table 3.19: The consumption of reductant and the production of CO₂ and H₂O in the first stage of the reduction step of second redox cycle were calculated and are compared with the experimental results

The calculation method of experimental result is shown in APPENDIX B.

Component	Experimental Result (mmol)	Expected reaction based on equation (Eq. 3.38, Eq. 3.39) (mmol)	Ratio (result/expect)
CO consumed	0.48	0.486	0.99
H ₂ consumed	0.49	0.486	1.00
CO ₂ formed	0.48	0.486	0.99
H ₂ O formed	0.49	0.486	1.00

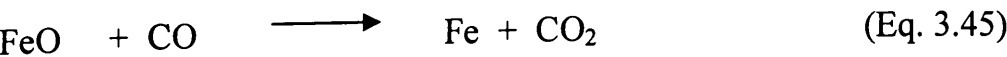
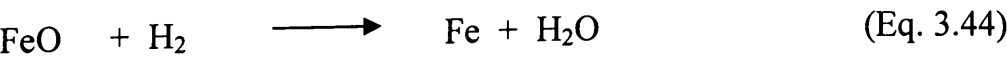
Expected result based on equation (Eq. 3.38, Eq. 3.39), (unit = mmol)

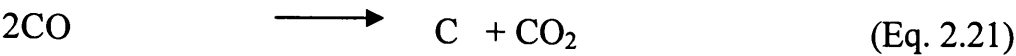
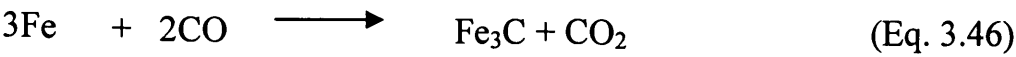


$$\text{Total mole of formed FeO} = 2.92 \text{ mmol}$$

In conclusion, the close agreement of the experimental result with the expected value indicated that FeO is an intermediate product for the reduction of iron oxide with syngas.

The second stage involved the temperature range from 427 °C to 650 °C. The expected chemical reactions are;





It was reported that the reduction of the iron – based catalyst sample with hydrogen leads to the metallic state and that CO or syngas reduction leads to a metallic state and to a small amount of iron carbide or carbon formation [172]. It was expected that FeO can be fully reduced to Fe by H₂ and CO and excess CO can further reduce Fe to Fe_xC or carbon formed on iron metal.

The calculation results for the second stage of the first and second reductions of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂ and CO mixture based on equations (Eq. 3.44, Eq. 3.45, Eq. 3.46 and Eq. 2.21) are shown in Table 3.20.

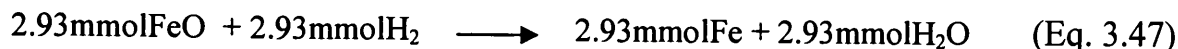
Table 3.20: The calculation results of the second stage of the first and second reductions of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂ and CO mixture based on equation
The calculation method of experimental result is shown in APPENDIX B.

Component	The experimental result of First reduction (mmol)	The experimental result of second reduction (mmol)
CO consumed	3.78	3.94
H ₂ consumed	2.93	2.93
CO ₂ formed	1.89	1.97
H ₂ O formed	2.93	2.92

According to Table 3.20, the calculated amounts of hydrogen consumption were in agreement with the expected amounts of hydrogen for the completion reduction of FeO to Fe (2.93 mmol for both the first reduction and the second reduction) . This

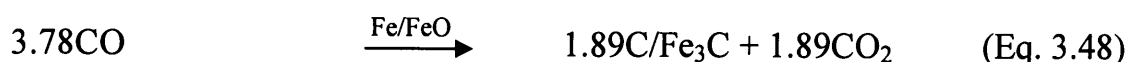
calculated amount of consumed hydrogen was in agreement with the calculated amount of formed water.

The first reduction and the second reduction for the second stage

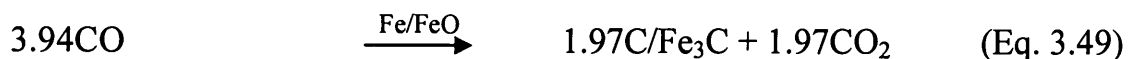


It can be concluded that FeO was only reduced by H₂ into Fe rather than reduced by both CO and H₂. Under such circumstance, CO in the second part was mainly consumed to form carbon or iron carbide. This could involve:

The first reduction (unit = mmol)

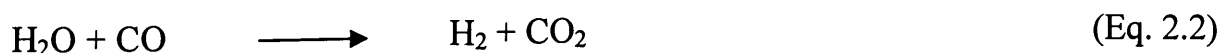


The second reduction after the first re – oxidation (unit = mmol).



The amounts of carbon formation or iron carbide from the first and the second reduction of iron oxide, (1.89 mmolC/Fe₃C and 1.97 mmolC/Fe₃C respectively), were in agreement with that expected from the experimental amount of CO formed (1.89 mmol and 1.97 mmol respectively) from the oxidation with steam after the reduction as shown in Eq.3.50 and Eq 3.52.

During the third stage of the reduction after FeO was fully reduced with hydrogen to iron metal, the amount of water and CO used was significantly decreased and the amount of H₂ was increased. As a result, the water gas shift reaction is the main reaction in the third stage of the reduction.



In order to prevent the loss of surface area of Fe based catalyst resulting from the oxidation of iron metal with steam, the reduction reaction was stopped and the system was switched to the oxidation step.

The chemical reactions of the oxidation of iron metal and of carbon formed on iron metal with water vapor are shown in Eq 3.2 and Eq. 2.22.



The amount of CO_2 formed in both two oxidation cycles was very small. The experimental result of two oxidation cycles is shown in Figure 3.16.

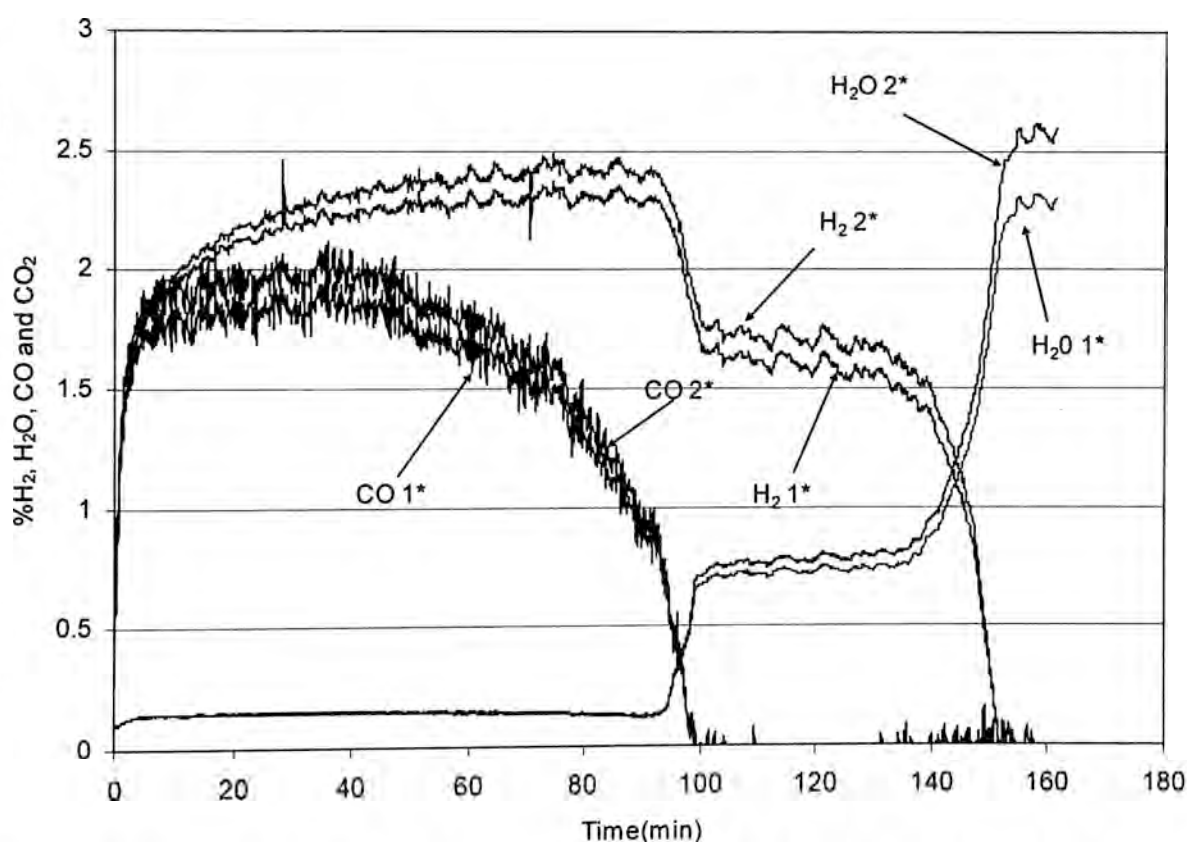


Figure 3.16: TPR profile during the first and second oxidation with H_2O (2.3%) at 650°C after the reduction of $4\%\text{Cr}_2\text{O}_3 - 96\%\text{Fe}_2\text{O}_3$ with 10 % CO and 30 % H_2 mixture

1* = the first oxidation, 2* = the second oxidation

The calculation results of the first and second oxidation after the reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂ and CO mixture are shown in Table 3.21.

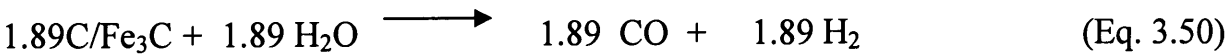
Table 3.21: The calculation results of the first and second oxidation after the reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂ and CO mixture

The calculation method of experimental result is shown in APPENDIX B.

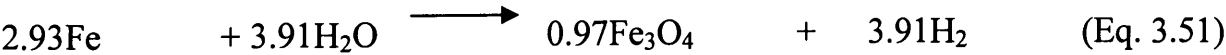
Component	The experimental result of the first oxidation (mmol)	The experimental result of the second oxidation (mmol)
H ₂ O consumed	5.8	5.88
H ₂ formed	5.8	5.88
CO formed	1.89	1.97

The calculation of the consumption of C/Fe₃C and Fe for the first oxidation after the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ were based on Eq 2.22 and Eq. 3.2.

The consumption of C/Fe₃C (unit = mmol), (mmol CO formed = 1.89 mmol)

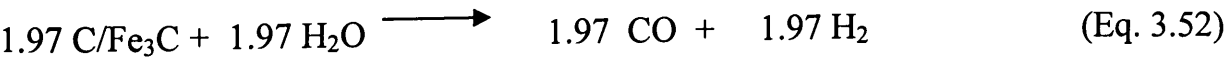


The consumption of Fe(unit = mmol), (mmol H₂ consumed = 5.8 – 1.89 = 3.91 mmol)

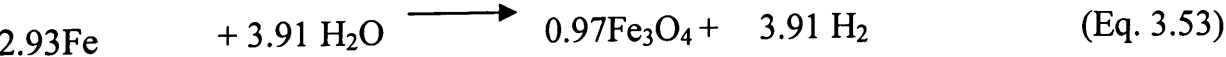


The calculation of the consumption of C/Fe₃C and Fe for the second oxidation after the second reduction of 4%Cr₂O₃ – 96% Fe₂O₃ were based on Eq 2.22 and Eq. 3.2.

The consumption of C/Fe₃C (unit = mmol), (mmol CO formed = 1.97 mmol)



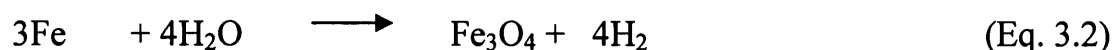
The consumption of Fe(unit = mmol) (mmol H₂ consumed = 5.88 – 1.97 = 3.91 mmol)



In conclusion, Fe was fully oxidized into Fe_3O_4 and carbon or iron carbide was formed during reduction but was completely oxidized with vapor water in the oxidation step.

3.4.3 The steam iron process using CH_4 as the reductant

Methane is expected to be as alternative reductant for the steam iron process. The formation of methane based on the reduction of hematite (Fe_2O_3) with methane and the subsequent oxidation of iron with water vapor are described by Eq 3.6 and Eq. 3.2.



However, it was found from the previous literature that there are two important issues in using methane as reductant in the steam iron process.

The first problem is the poor reducibility of the methane reduction. It was demonstrated that, in order to complete the reduction of Fe_3O_4 by methane and the subsequent oxidation of iron metal with water vapor, the process must be performed at $> 727^\circ\text{C}$ [143]. To compare with the two previous experimental results, the complete reduction of Fe_3O_4 with hydrogen to Fe can be performed at 550°C whereas the complete reduction of Fe_3O_4 with syn-gas mixture to Fe can be performed at 650°C . Thus methane has a remarkably lower reducibility than hydrogen or a syngas mixture.

The second problem arises from carbon formation during the reduction of iron oxide with methane. It is generally accepted that iron metal catalyses methane decomposition into hydrogen and carbon ($\text{CH}_4 \longrightarrow \text{C} + 2\text{H}_2$), which may lead to

blockage of gases in the reactor [143]. In order to avoid any blockage, the quartz tube reactor was set in a horizontal dimension and the catalyst sample was packed in such a way that gas flow could continue.

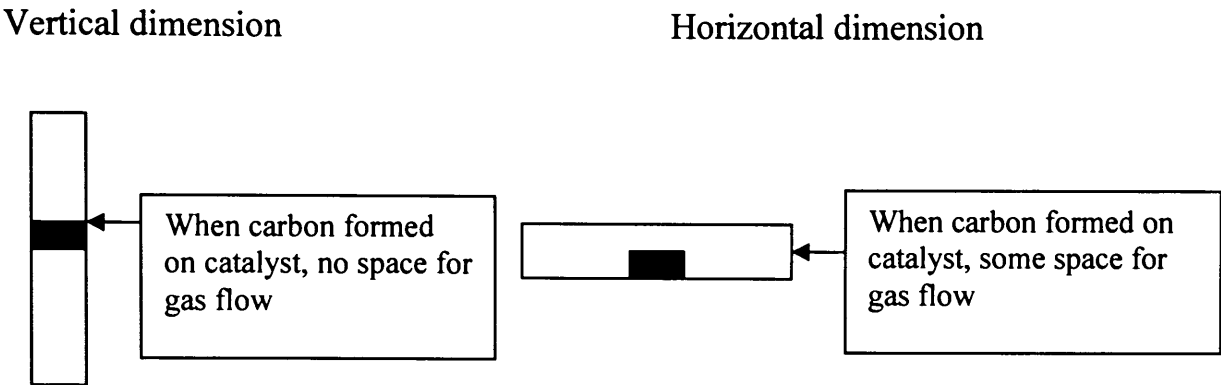


Figure 3.17: The catalyst loading pattern in a vertical reactor and in a horizontal reactor

Two experimental results using a vertical reactor and a horizontal reactor are shown in Figure 3.18 and Figure 3.19 respectively. The two experimental processes were performed at the same condition, the only difference being the dimension of the reactor. Approximately 0.104 gram of 5%NiO – 5%Cr₂O₃ - 90 %Fe₂O₃ was packed into the center of the reactor and then 90 % CH₄/ 10% of 1 % Ar in He mixture was passed. TPR was conducted by increasing the temperature from 200 °C to 650 °C by 5 °C per minute. The two experimental results were used to show the effect of the blockage of gas flow on the experimental process and the effectiveness of a change in the dimension of the reactor from vertical into horizontal.

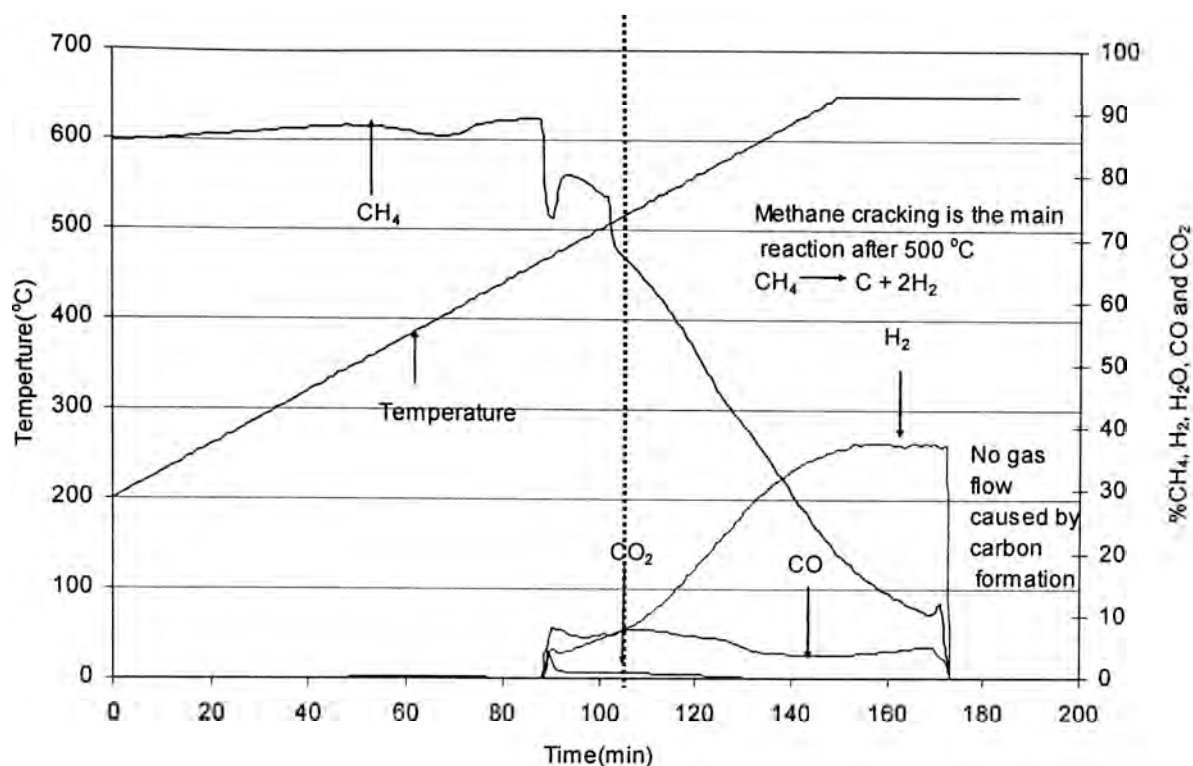


Figure 3.18: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 90 %CH₄ / 10% of 1 % Ar in He mixture using the vertical reactor

According to Figure 3.18, methane cracking ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) was the main reaction above 500 °C. Carbon deposited on the catalyst sample caused a blockage of gas flow.

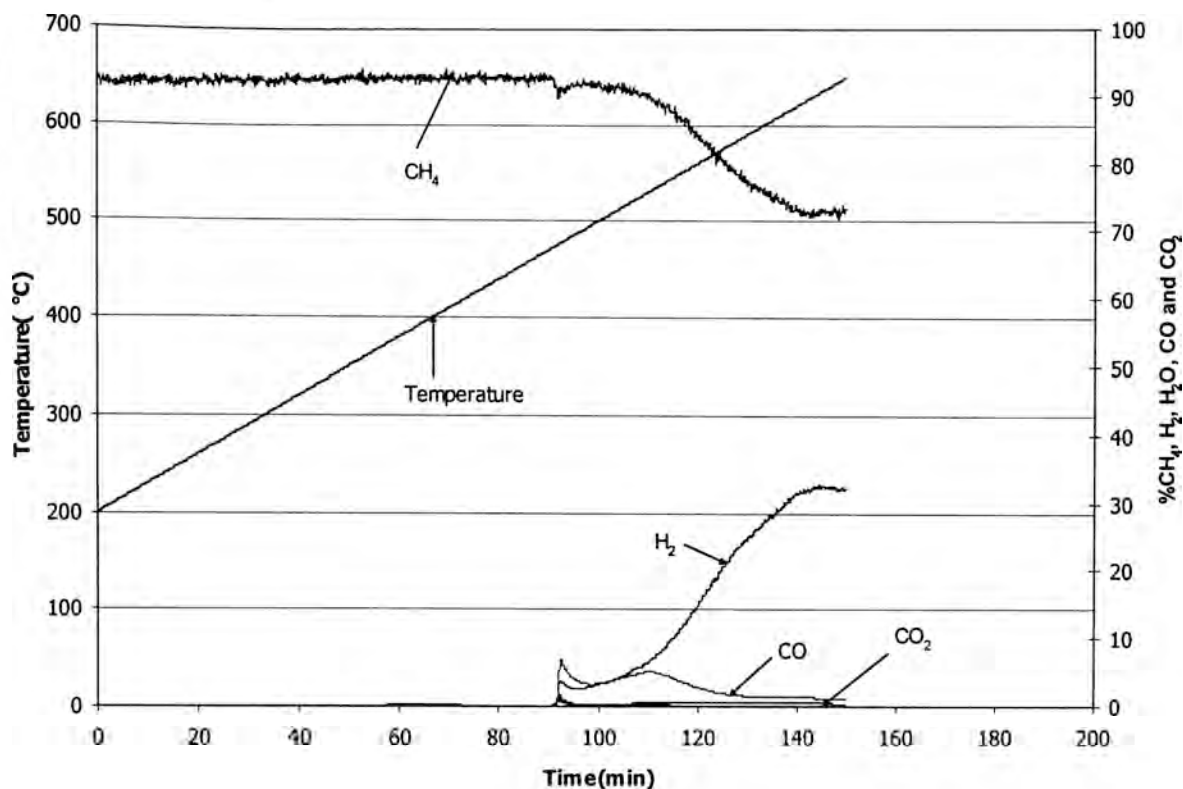


Figure 3.19: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 90 %CH₄ / 10% of 1 % Ar in He mixture using the horizontal reactor

According to Figure 3.19, although methane cracking ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$) was the main reaction above 500 °C, no significant issues of a gas block from carbon deposition was observed. It should be noted, however, that some by-passing can occur. The calculated amount of H₂ formation (20.33 mmol) was approximately 2 times the calculated amount of CH₄ consumption (10.16 mmol). The calculated ratio result was in agreement with the stoichiometric equation of methane cracking.

To compare with the previous reductants, (H₂ and syn gas), 0.242 gram of 4%Cr₂O₃ – 96% Fe₂O₃ was used as the catalyst sample for reduction with methane.

Approximately 0.242 gram of 4%Cr₂O₃ – 96% Fe₂O₃ was packed into the center of the reactor and 70 % CH₄ and 30% of 1 % Ar in He mixture were passed into the

reactor. The temperature was increased from 200 °C to 650 °C at 5 °C per minute. The total time for the reduction was approximately 100 minutes. Subsequently, the reduced sample was oxidized with approximately 2.3% vapor water at 650 °C. The experimental result is shown in Figure 3.20.

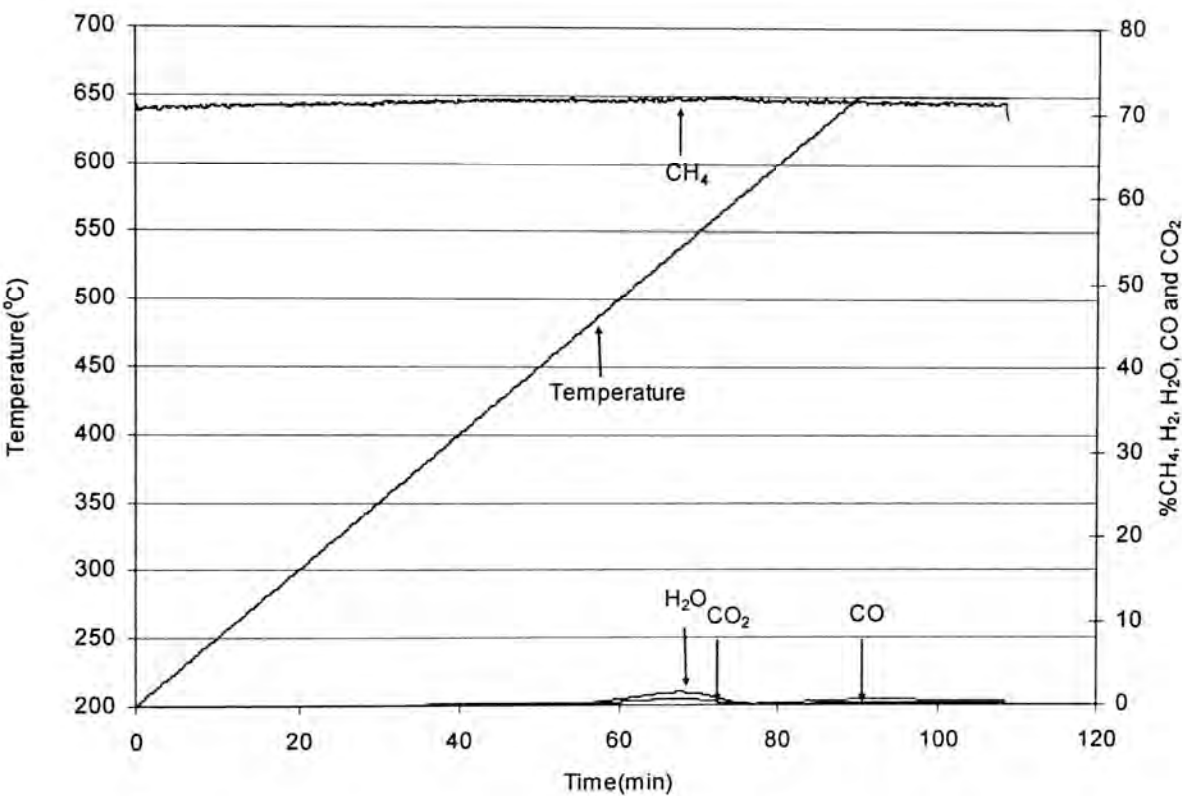


Figure 3.20: TPR profile during the first reduction of 4%Cr₂O₃ – 90% Fe₂O₃ with CH₄ (70%)

Figure 3.20 shows that little methane consumption or gas product formation was observed from the reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with methane. Hence, the reduction of 4%Cr₂O₃ – 96% Fe₂O₃ was very low. Subsequently, no hydrogen was formed when water vapor was passed in the oxidation step. It can be concluded that the iron oxide sample (Fe₂O₃) was not significantly reduced into other forms of iron oxide (Fe₃O₄, FeO) or iron metal (Fe). The experimental result was in agreement with

the Takenaka et al study [149], who found that the reduction of iron oxide containing only Cr cations with methane is very slow at temperatures, lower than 750 °C. They also recommend that Ni was the best promoter to add to Cr – FeO_x for the enhancement of the redox reaction at low temperature [149].

The addition of 5%NiO to 5%Cr₂O₃ – 95% Fe₂O₃ was examined for the reduction with methane and the oxidation of the reduced sample with 2.3 % water vapor. The experimental process was performed under the same conditions as the previous experiment. TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄ and increased temperature rate 5°C /min is shown in Figure 3.21.

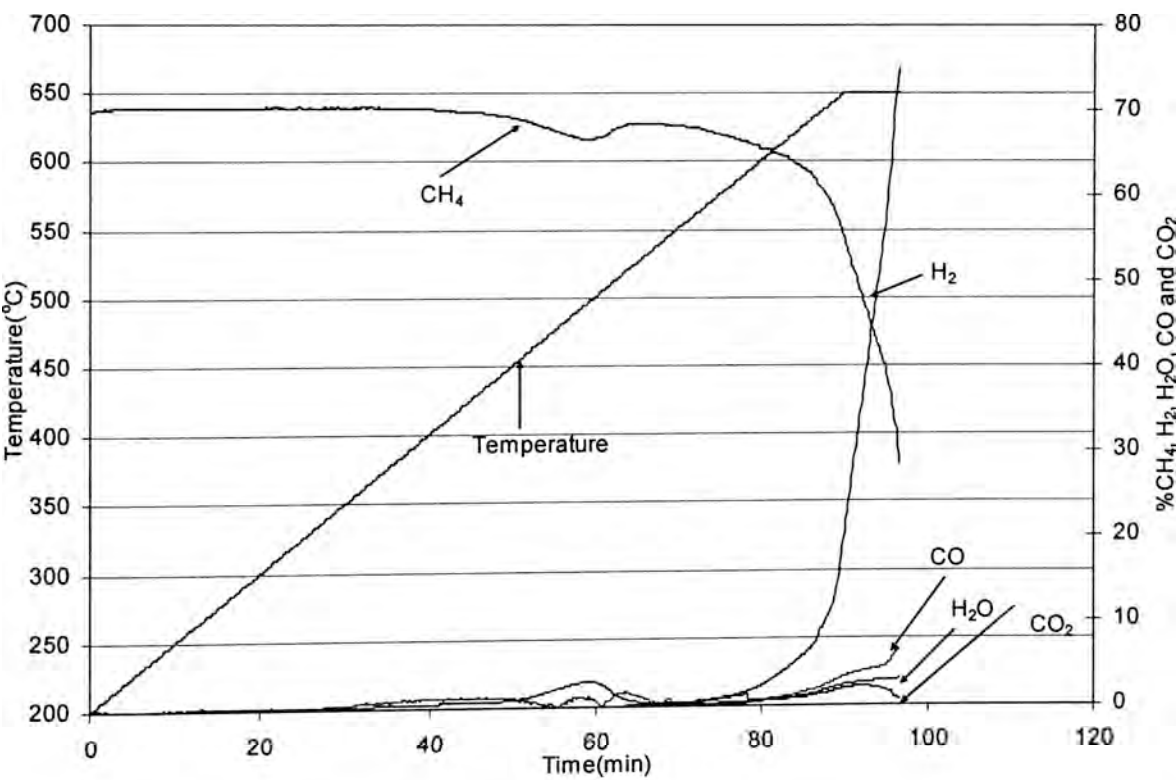


Figure 3.21: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄ and increased temperature rate 5°C /min

According to Figure 3.21, the addition of NiO into $\text{Cr}_2\text{O}_3 - \text{Fe}_2\text{O}_3$ improved the activity of the reduction, but Ni was highly favorable for carbon formation ($\text{CH}_4 \rightarrow \text{C} + 2\text{H}_2$). The extensive carbon deposition on the catalyst resulted in the substantial loss of surface area. The surface area loss was found to be 85 % after the first redox, and the surface area sharply reduced from $40 \text{ m}^2/\text{g}$ to $6 \text{ m}^2/\text{g}$. The XRD result of reduced 5%NiO - 5% $\text{Cr}_2\text{O}_3 - 90\% \text{Fe}_2\text{O}_3$ after its reduction with pure CH_4 (70%) is shown in Figure 3.22.

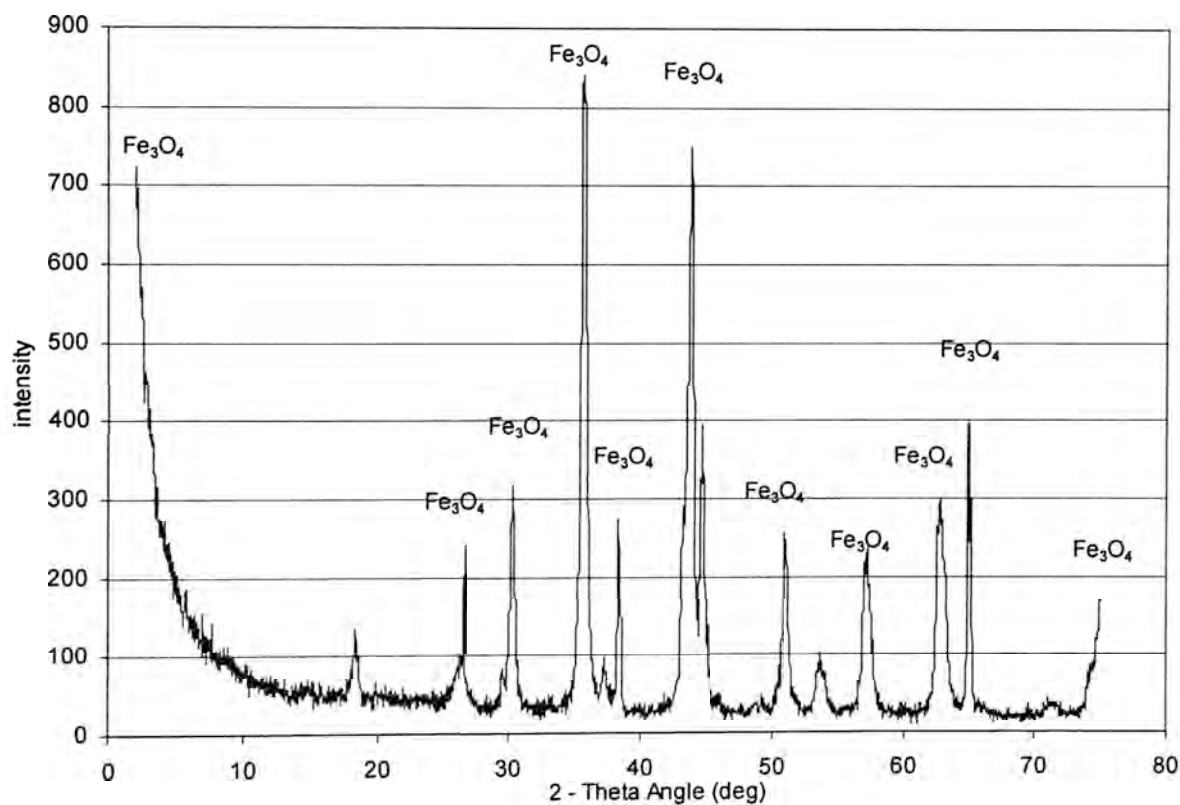
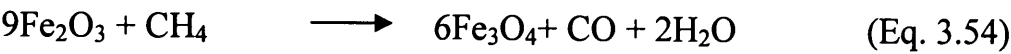


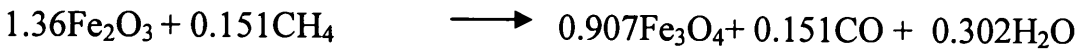
Figure 3.22: XRD result of reduced 5%NiO - 5% $\text{Cr}_2\text{O}_3 - 90\% \text{Fe}_2\text{O}_3$ after its reduction with CH_4 (70%)

When compared with the previous experiment (temperature ramping rate from of 3°C per minute), carbon formation during ramping at 5°C per minute was much higher. According to the XRD result (Figure 3.22), the majority of Fe_2O_3 was reduced only to

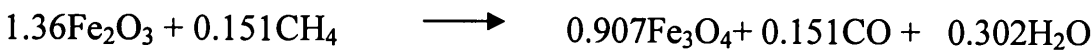
Fe₃O₄. The temperature for the reduction of Fe₂O₃ with methane into Fe₃O₄ was observed to occur between 382 °C and 567 °C.



The expectation from calculation was shown in Table 3.21. (unit = mmol)



Expected result (unit = mmol)



The calculation result was in agreement with the expected reaction.

The experimental result was in agreement with the study of iron oxide reduction with CH₄ as reported by Nekrasov et al [139]. They reveal that the first stage of reduction (Fe₂O₃ → Fe₃O₄) was observed for the temperature range from 400°C to 600°C.

According to them, at temperatures lower than 650 °C, Fe₂O₃ was not reduced into FeO and Fe metal. However, it was found that carbon formation was a serious problem when using methane as reductant at temperatures higher than 567°C.

Methane cracking is the main reaction above this temperature.

Subsequently, the reduced sample was oxidized with 2.3% vapor water and the result is shown in Figure 3.23.

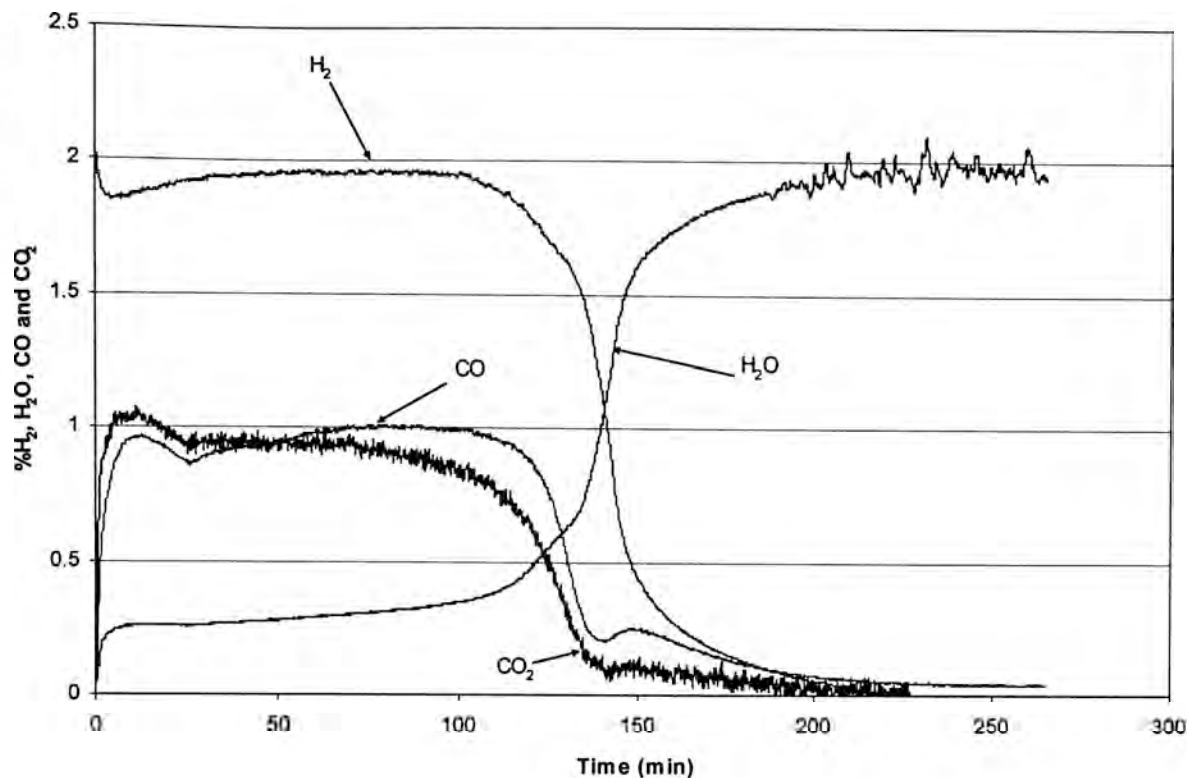


Figure 3.23: TPR profile during the oxidation by water vapor after the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄ at 650 °C

The calculation results of the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄ is shown in Table 3.22 and the oxidation after the reduction is shown in Table 3.23.

Table 3.22: The calculation results of the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄

The calculation method of experimental result is shown in APPENDIX B.

Component	The first part of reduction (mmol) (382 °C - 567 °C)	The second part of reduction (mmol) (567 °C - 650 °C, remain at 650 °C for 20 mins)
CH ₄ consumed	0.151	4.92
CO formed	0.151	0.83
H ₂ formed	0	7.2
CO ₂ formed	0	0.49
H ₂ O formed	0.302	0.5
C formed	0	3.6 (H ₂ /2=7.2/2)

Table 3.23: The calculation results of the oxidation by water vapor after the first reduction of %NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure CH₄ at 650 °C

The calculation method of experimental result is shown in APPENDIX B.

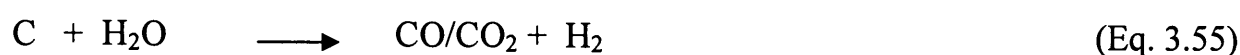
Component	Oxidation (mmol) (650 °C)
CO formed	1.83
H ₂ formed	3.6
CO ₂ formed	1.77
H ₂ O consumed	3.62

According to the calculated carbon mole balance between the second part of reduction (Table 3.22), and the oxidation (Table 3.23), the carbon formed on catalyst sample can be completely oxidized by vapor water.

The second part of reduction

$$\begin{aligned}\text{Carbon formed} &= 0.83 \text{ CO} + 0.49\text{CO}_2 + 3.6 \text{ C}(\text{CH}_4 \longrightarrow \text{C} + 2\text{H}_2) \text{ (Eq. 2.20)} \\ &= 4.92 \text{ mmol}\end{aligned}$$

The subsequent oxidation step



$$\begin{aligned}\text{Carbon consumed} &= 1.83 \text{ CO} + 1.77\text{CO}_2 \\ &= 3.6 \text{ mmol}\end{aligned}$$

In order to estimate the residual carbon deposited on the catalyst, 10% oxygen plus 90% Ar in He was passed to the reactor at 650 °C. It was observed that no oxygen was consumed and no carbon dioxide and carbon monoxide were formed. As a result, it was established that the carbon formed on the catalyst sample may be completely oxidized by vapor water.

However the significant difference between carbon deposited during reduction and that removed during oxidation infers that some form of unreactive carbon is deposited. Iron carbide is an obvious candidate.

In order to confirm that carbon formed on the Ni, a sample of 5% NiO – 95% SiO₂ prepared by wet – impregnation and examined using the same experimental conditions and compared with a blank run. The experimental results are shown in Figure 3.24 and Figure 3.25.

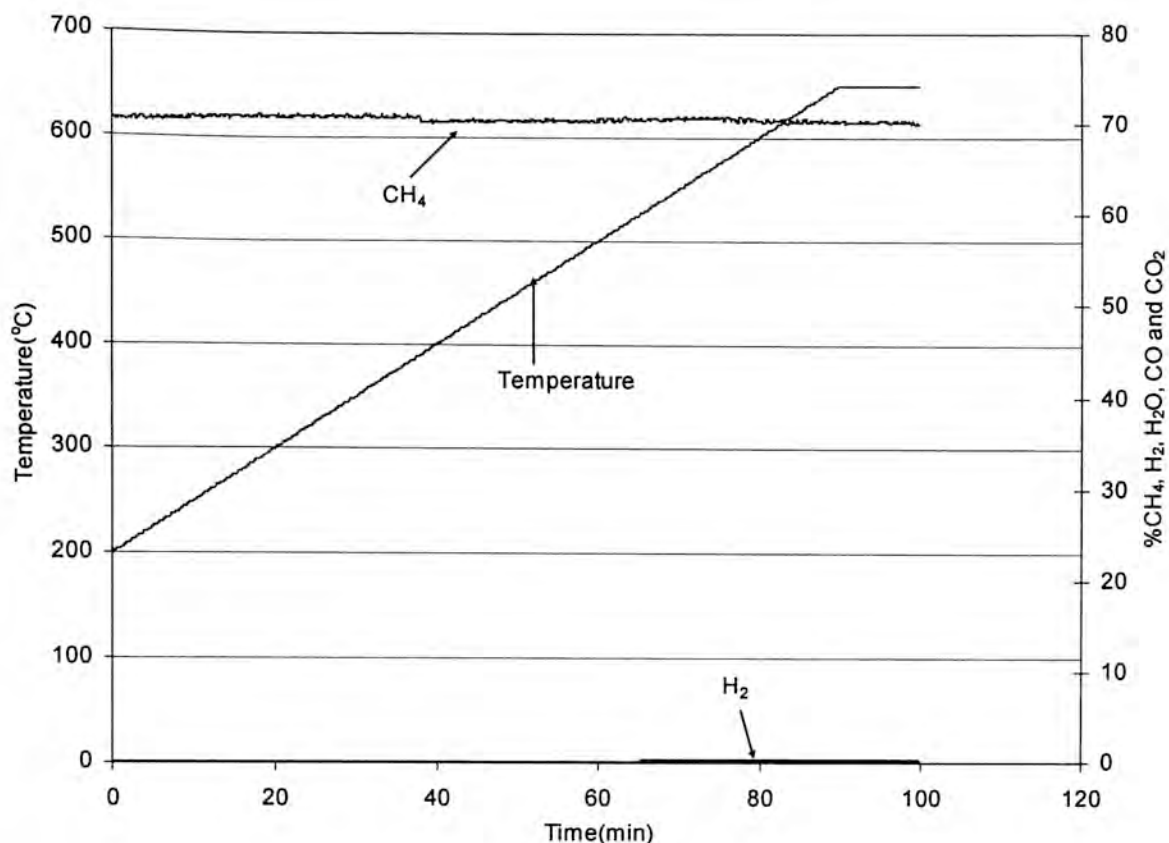


Figure 3.24: TPR profile during the blank test by passing pure CH₄ through an empty reactor and increased temperature rate of 5°C/min

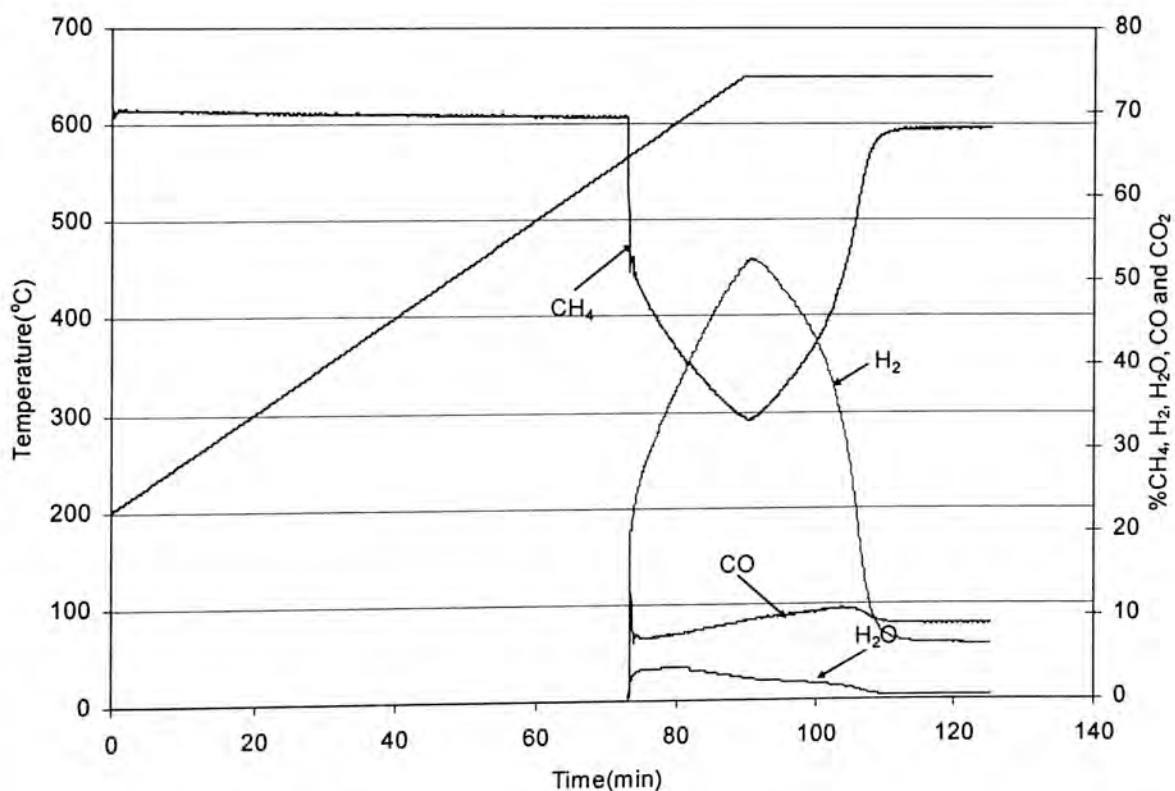


Figure 3.25: TPR profile during the first reduction of 5% NiO – 95% SiO₂ with pure CH₄ (70%) and increased temperature rate 5°C/min

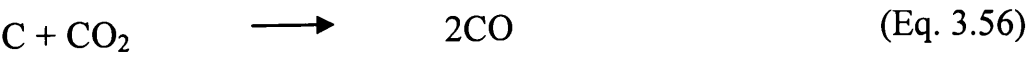
It was found that only 0.04 mmol of hydrogen was formed from methane cracking for the blank test whereas 22.94 mmol of hydrogen was formed from methane cracking when passing pure methane over 5% NiO – 95% SiO₂. Substantial carbon was formed above 567 °C. The experimental result of significant carbon formation above 567 °C when passing pure methane over 5% NiO – 95% SiO₂ was similar to the experimental result for 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ reduction with pure methane.

In conclusion, due to the similar results from the reduction of both 5% NiO – 95% SiO₂ and 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with pure methane, substantial amounts of carbon were formed from methane cracking on NiO above 567 °C.

The high carbon deposition on NiO is in agreement with several studies, which demonstrate that Ni has a higher tendency to be deactivated than noble metals, principally by the deposition of carbon [201-203].

3.4.4 The effect of using CH₄ and CO₂ mixtures as reductant

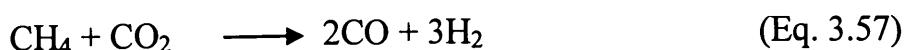
In order to minimize carbon deposition on 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃, CO₂ was introduced in a mix with CH₄. The concept was to use CO₂ for the oxidization of carbon deposited on NiO.



Three feed gases containing 10%, 15% and 20% CO₂ plus 70 % CH₄ were used respectively. 0.242 grams of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ were packed in the center of the reactor. The temperature was increased from 200 °C to 650 °C at 5 °C per minute. The reduction process took approximately 100 minutes. Subsequently, the

reduced sample was oxidized with approximately 2.3% vapor water at 650 °C. The reason to let the reaction proceed only for approximately 100 minutes was that the excess amount of water formed from the reverse of the water gas shift reaction during the reduction process started to oxidize the catalyst. Furthermore, the excess water resulted in oxidizing Fe back to Fe₃O₄ and to loss of surface area. Consequently, hydrogen formation during the oxidation process failed to occur [189]. In order to maximize the H₂O formation without possibly affecting the hydrogen yield, an optimal CH₄ and CO₂ ratio was used.

No hydrogen was formed when passing 2.3% vapor water after the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with a 20% CO₂ and 70% CH₄ mixture, whereas a small amount of hydrogen was formed when passing 2.3% vapor water after the reduction of the catalyst with 15% CO₂ and 70% CH₄ mixture. The oxidation of the sample with 2.3% water was successful after the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10% CO₂ and 70% CH₄ mixtures. An increase in the percentage of percent CO₂ mixed with CH₄ resulted in an increase in the forward reaction of methane reforming rather than the reduction of iron oxide with methane and methane cracking.



Results

The calculation results of the first reduction and first oxidation of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with three feed gases: 10%, 15% and 20% CO₂ plus 70 % CH₄ are shown in Table 3.24.

Table 3.24: The calculation results of the first reduction of 5% NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with three feeding gases :10%, 15% and 20% CO₂ plus 70 % CH₄

The calculation method of experimental result was shown in APPENDIX B.

% CO ₂ in mixture	reduction(mmol)				
	CH ₄	CO	H ₂	CO ₂	H ₂ O
10%	-10.90	+6.60	+20.00	-3.83	+1.51
15%	-8.33	+5.78	+3.44	-2.43	+1.22
20%	-0.151	+2.07	+0.32	-2.1	+0.89

+ = formed amount (mmol), - = consumed amount (mmol)

The experimental result of TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture, 15% CO₂ and 70% CH₄ mixture and 10% CO₂ and 70% CH₄ mixture are shown in Figure 3.26 , Figure 3.27 and Figure 3.28 respectively.

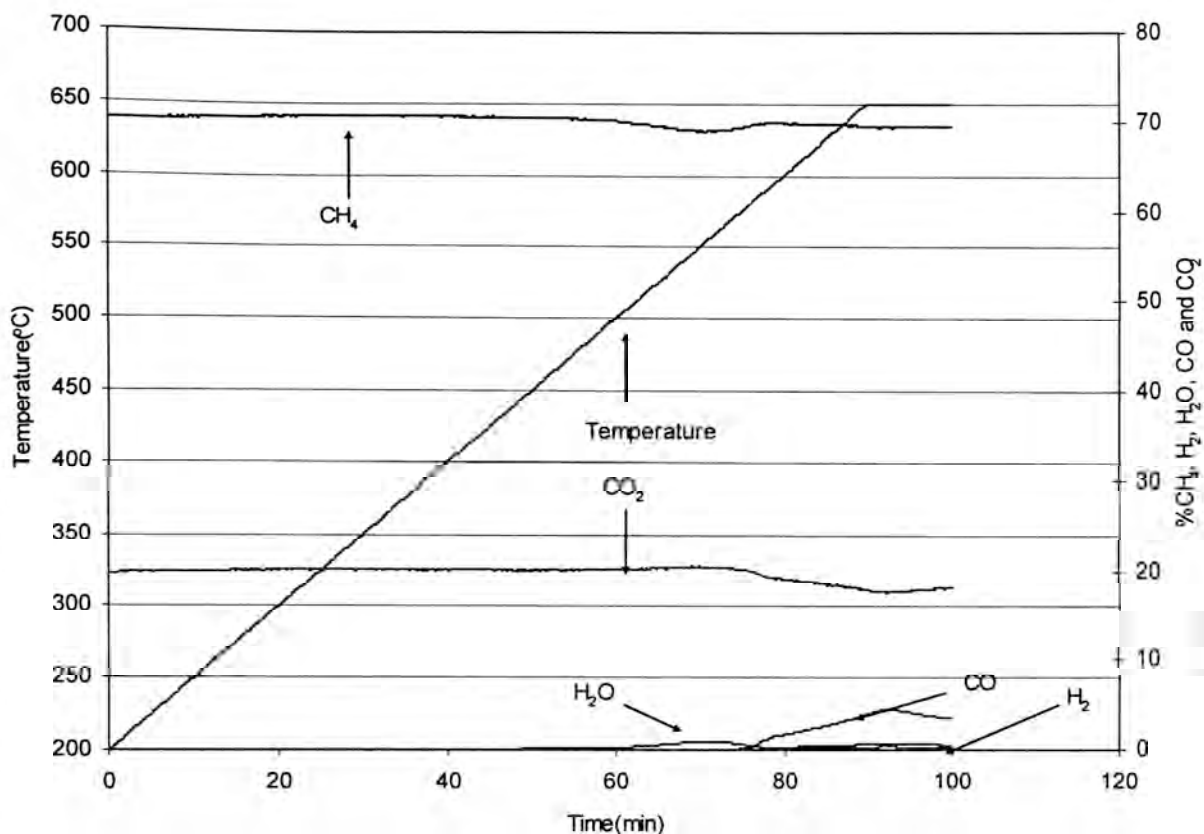


Figure 3.26: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture

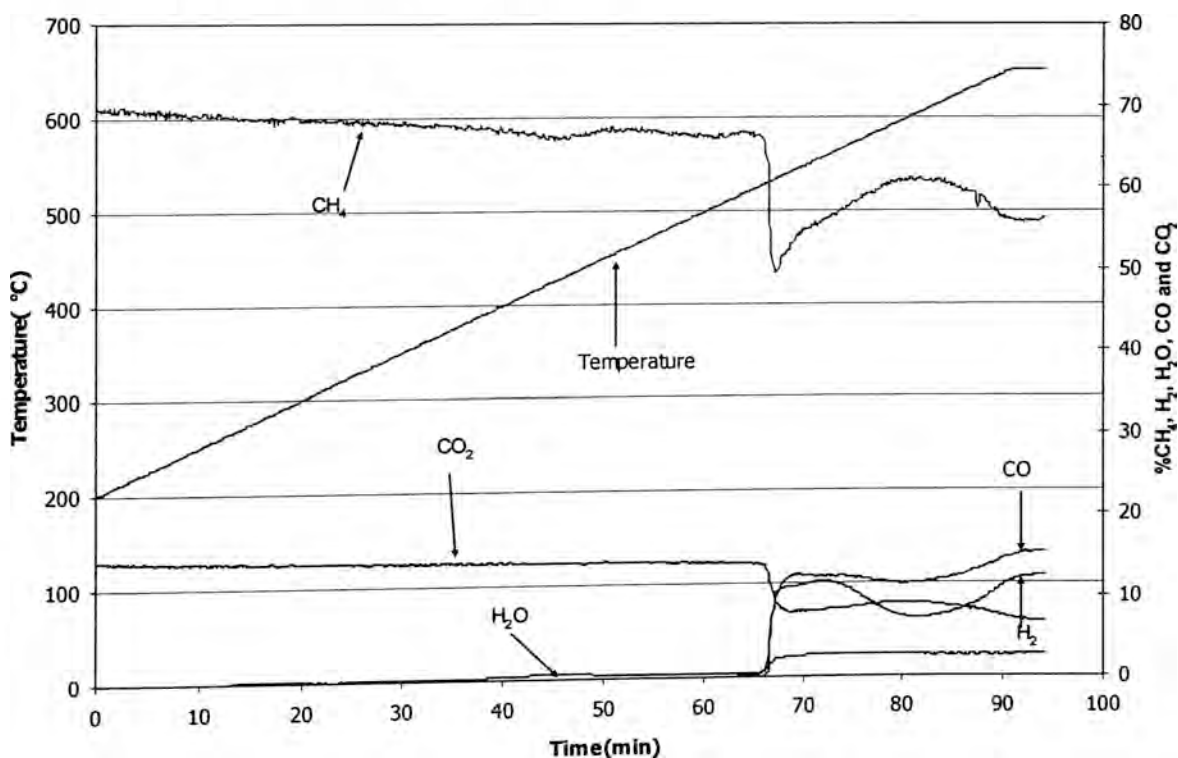


Figure 3.27: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 15% CO₂ and 70% CH₄ mixture

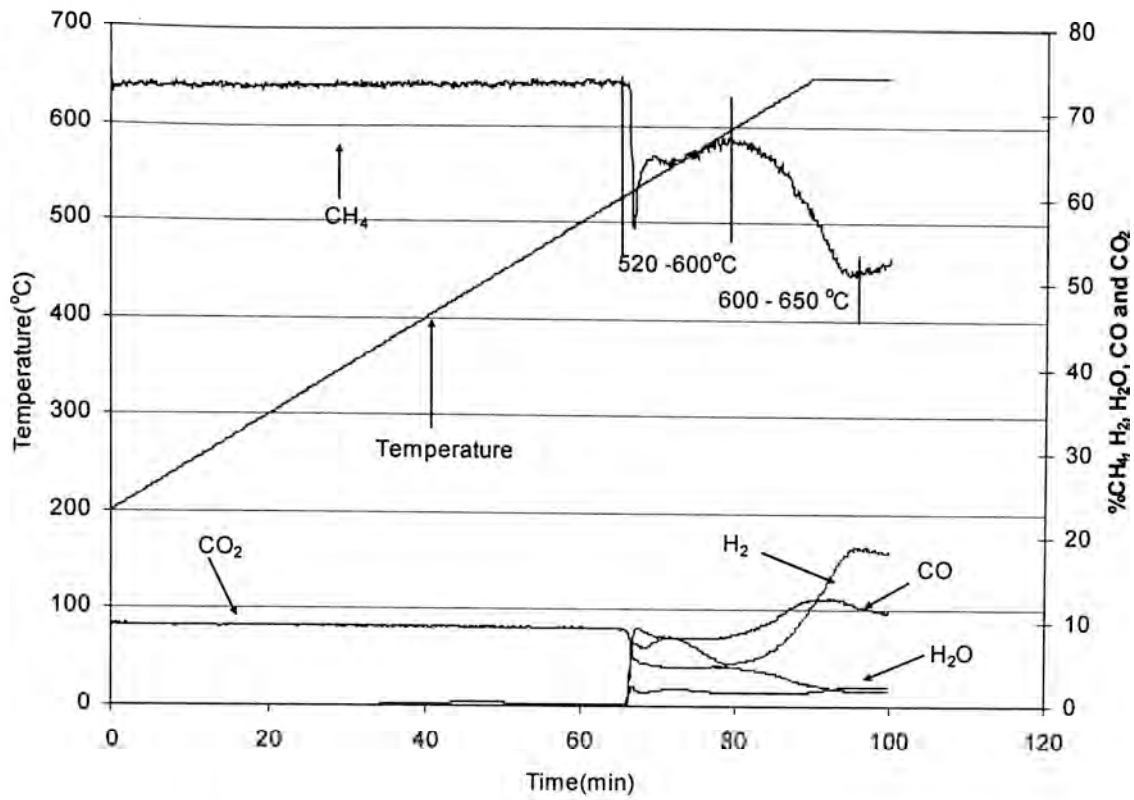
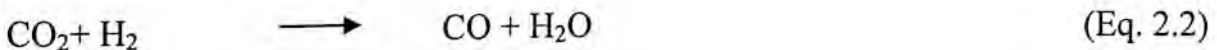
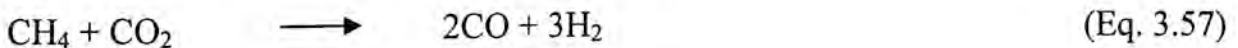
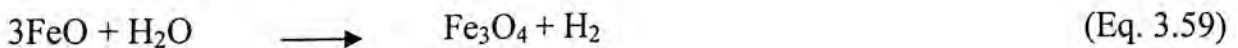
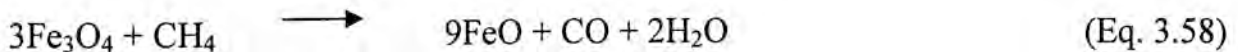
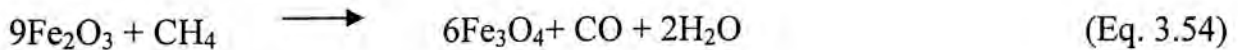


Figure 3.28: TPR profile during the first reduction of 5%NiO - 5%Cr₂O₃ - 90% Fe₂O₃ with 10% CO₂ and 70% CH₄ mixture

The possible reactions of the first reduction of 5%NiO - 5%Cr₂O₃ - 90% Fe₂O₃ are as follows:



Inspecting the reduction of 5%NiO - 5%Cr₂O₃ - 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture, it is seen that only a small amount of methane was consumed during the

reduction. To compare the result for 15 % CO₂ and 20% CO₂ at a temperature range from 600 – 650 °C, the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture formed more CO but less H₂. It is concluded that the water gas shift reaction is more favorable for the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 15% CO₂ and 70% CH₄ mixture, whereas methane cracking was more favorable for the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10% CO₂ and 70% CH₄ mixture.

According to the XRD result, Fe₂O₃ was only reduced into Fe₃O₄. It implies that Fe₂O₃ was reduced to FeO but that FeO was oxidized by product water back into Fe₃O₄. The XRD result is shown in Figure 3.29.

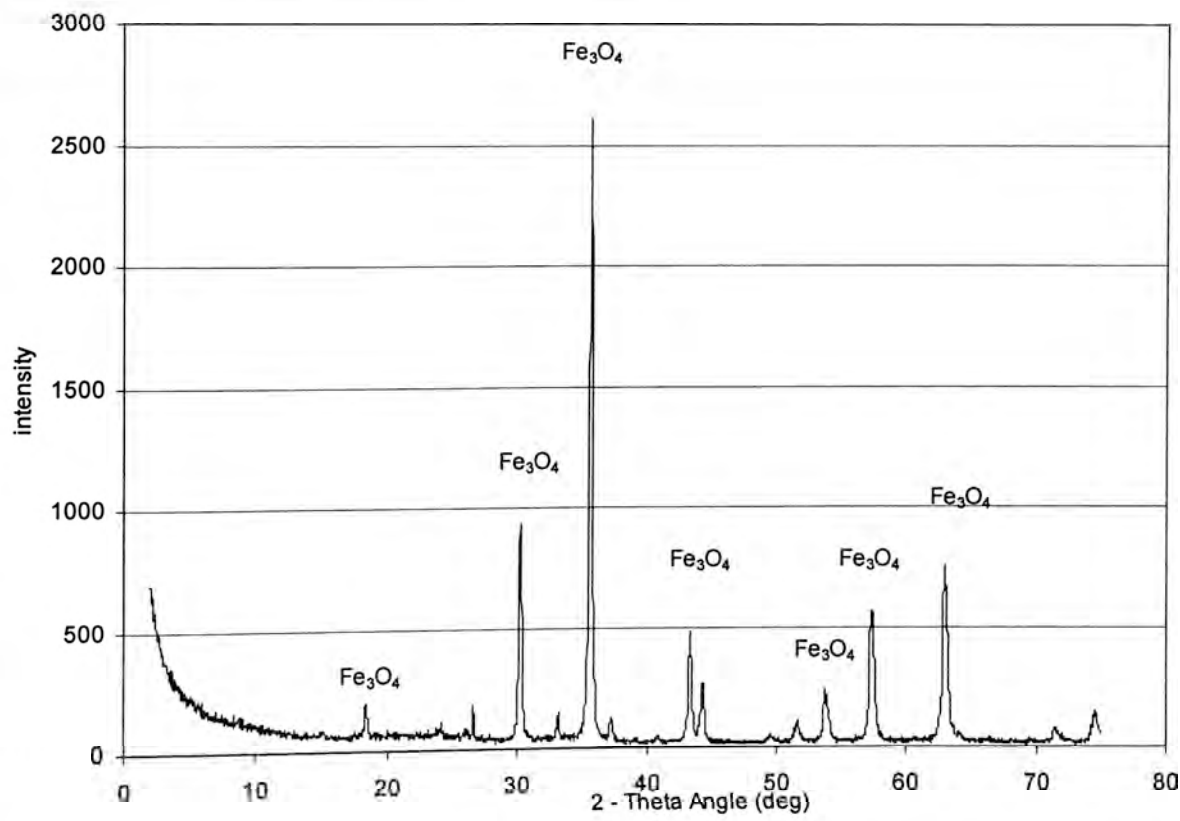


Figure 3.29: XRD result of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ after its reduction with 10% CO₂ and 70% CH₄

The experimental result was in agreement with the study of iron oxide reduction with CH₄ by Nekrasov et al [139]. They reveal that the first stage of reduction (Fe₂O₃ Fe₃O₄) was observed over the temperature range 400°C to 600°C.

The oxidation process

The calculation results of the first oxidation of reduced 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ in three feed gases with 10%, 15% and 20% CO₂ plus 70 % CH₄ is shown in Table 3.25.

Table 3.25: The calculation results of the first oxidation of reduced 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ in three feed gases with 10%, 15% and 20% CO₂ plus 70 % CH₄

The calculation method is shown in APPENDIX B.

% CO ₂ mixture	oxidation(mmol)			
	H ₂ O	H ₂	CO	CO ₂
10%	-4.56	+4.58	+3.41	+1.14
15%	-0.68	+0.64	+0.63	0
20%	0	0	0	0

+ = formed amount (mmol), - = consumed amount (mmol)

TPR profile during the oxidation with 2.3 % water vapor at 650 °C after the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10%, 15% and 20%,CO₂ and 70% CH₄ mixture is shown in Figure 3.30.

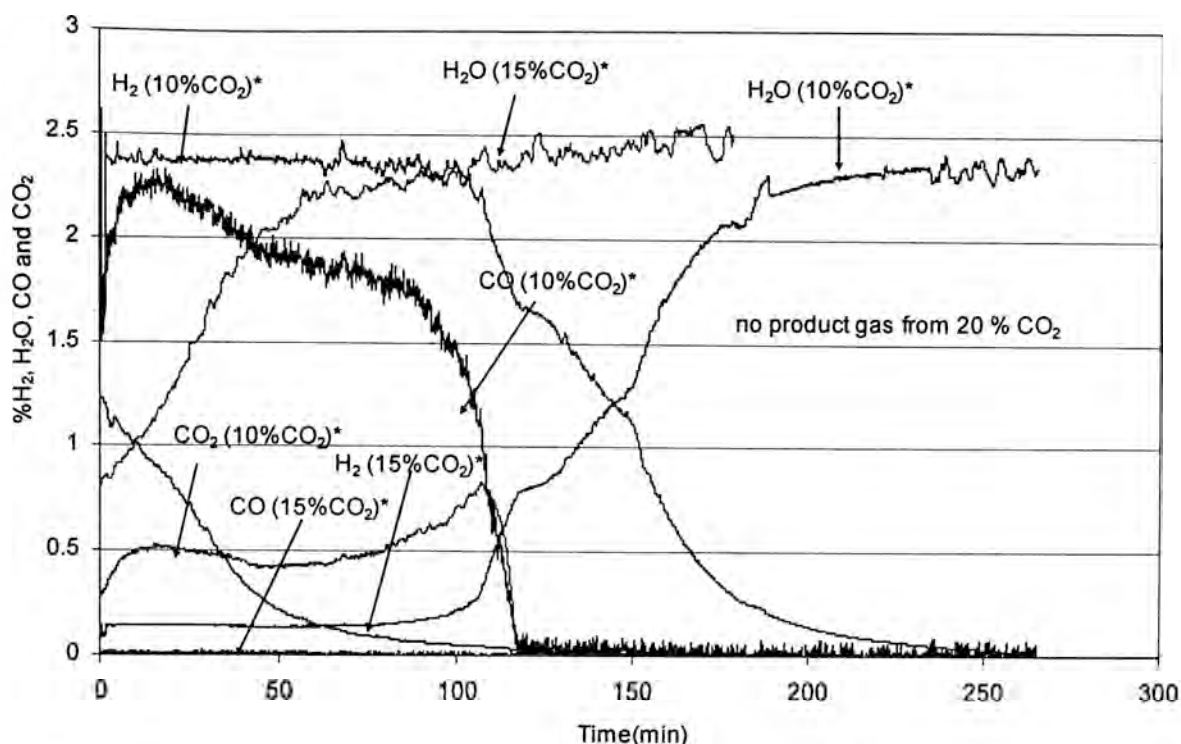
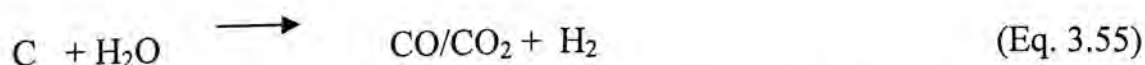


Figure 3.30: TPR profile during the oxidation with 2.3 % water vapor at 650 °C after the first reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10%, 15% and 20%,CO₂ and 70% CH₄ mixture

According to Figure 3.30, no hydrogen was formed during the oxidation process after the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture. In addition a small amount of hydrogen was formed during the oxidation process after the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 15% CO₂ and 70% CH₄ mixture. Finally, the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10% CO₂ and 70% CH₄ mixture was the most successful for the formation of hydrogen during the oxidation reaction.



It can be confirmed by both results (the reduction process and the oxidation process) that no hydrogen was formed during the oxidation process after the reduction of

5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture because no carbon formation from methane cracking was observed during the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture.



Similarly, carbon formation during the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 10% CO₂ and 70% CH₄ mixture is much more favorable than formation during the reduction with 15% CO₂ and 70% CH₄ mixture.

This is clear from the oxidation process after reduction using the 10% CO₂ and 70% CH₄ mixture that much more hydrogen was formed than after the reduction with 15% CO₂ and 70% CH₄ mixtures. Furthermore, Davis et al [190] reported that the excess amount of formed water from the reverse water gas shift reaction (which was a highly favorable reaction for both the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 20% CO₂ and 70% CH₄ mixture and the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with 15% CO₂ and 70% CH₄ mixture) starts to reduce the surface area. Furthermore, the excess water can result in the oxidation of Fe back to Fe₃O₄ and to loss of surface area of catalyst

In conclusion, it was found that the percentage of CO₂ fed into the reduction process has an effect on the hydrogen formation in the oxidation step. An increase in the percentage of CO₂ mixed with CH₄ resulted in an increase in the forward reaction of methane dry reforming rather than the reduction of iron oxide with methane and methane cracking. As a result, only reduction by 10 % CO₂ mixed with CH₄ was successful for hydrogen formation during the subsequent oxidation of the reduced sample with vapor water.

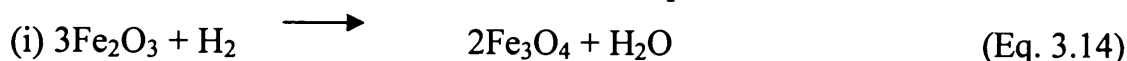
3.5 Conclusions

The study of the steam iron process was divided into 4 parts, which were categorized by the kind of reductant used in processes.

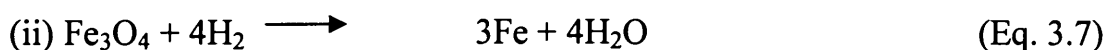
- 1) The steam iron process using H_2 as reductant.
- 2) The steam iron process using H_2 /CO mixture as reductant
- 3) The steam iron process using CH_4 as reductant
- 4) The steam iron process using CH_4 /CO₂ mixture as reductant

- 1) The steam iron using H_2 as reductant (using 4%Cr₂O₃ – 96% Fe₂O₃ as catalyst)

The first reduction is the composition of a two step reduction;



The energy of activation of the process was found to be about 92.4 kJ/mol and it was observed that the first experimental peak observed from the experimental result was the closest fit to be a three-dimensional nucleation model developed by Avrami-Erofeev



The energy of activation was found to be about 68.2 kJ/mol and it was observed that the second peak of $Fe_3O_4 \longrightarrow Fe$ from experimental result was not explained by any other model.

- 2) The steam iron process using 30% H_2 / 10%CO mixture as reductant (using 4%Cr₂O₃ – 96% Fe₂O₃ as catalyst)

It was found that FeO was the intermediate for the reduction of Fe₂O₃ with H_2 /CO mixture to Fe metal. The Fe₂O₃ can be completely reduced to Fe at 650 °C. In addition, carbon or iron carbide was formed during reduction but was completely oxidized with vapor water in the oxidation step.

3) The steam iron process using CH₄ as reductant

3.1) The steam iron process using CH₄ as reductant (using 4%Cr₂O₃ – 96% Fe₂O₃ as catalyst)

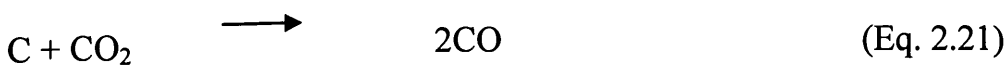
The reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with methane was very slow under 650 °C and no hydrogen formation was observed from the subsequent oxidation with water vapor at 650 °C. As a result, methane was the worst reductant when compared with H₂ and H₂ /CO.

3.2) The steam iron process using CH₄ as reductant (using 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ as catalyst)

NiO was added to increase the activity of the reduction of iron oxide with methane. However, Fe₂O₃ also was reduced into only Fe₃O₄ for the temperature range from 382 °C to 567 °C. After 567 °C, it was found that carbon formation on NiO is a serious problem which was found to be due to methane cracking over 5% NiO – 95% SiO₂. For both 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ and 5% NiO – 95% SiO₂, methane cracking was the main reaction above 567 °C. The carbon formed on %NiO - 5%Cr₂O₃ – 90% Fe₂O₃ could be oxidized with vapor water in the oxidation step.

4) The steam iron process using CH₄ /CO₂ mixture as reductant (using 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ as catalyst)

The introduction of CO₂ was applied to oxidize formed carbon during the reduction of 5%NiO - 5%Cr₂O₃ – 90% Fe₂O₃ with methane.



It was found that the percentage CO₂ feed into the reduction process has an effect on the hydrogen formation in the oxidation step. An increase in a percentage of percent CO₂ mixed with CH₄ results in an increase in the forward reaction of methane dry

reforming rather than the reduction of iron oxide with methane and methane cracking. As a result, only 10 % CO_2 mixed with CH_4 was successful in increasing the hydrogen formation from the subsequent oxidation of the reduced sample with vapor water.

Although the introduction of CO_2 can suppress carbon formation, the strong oxidization of reduced iron oxide with formed water during the reduction process and the higher favorable water gas shift reaction adversely affects the complete reduction of iron oxide into iron metal.

3.6 Recommendation

The above finding and conclusion may lead to the necessity of further investigation including

1. The use of higher temperature for the reduction of iron oxide based catalyst with methane in order to obtain complete reduction into iron metal,
2. The study of other promoters such as Pt, Pd and Cu compared with Ni,
3. The use of the alkaline earth metal oxides, such as MgO, CaO and BaO as support for %NiO - 5%Cr₂O₃ – 90% Fe₂O₃ in order to suppress carbon formation during reduction,
4. The study of other thermodynamic favorable candidates such as WO₃, MnO₂ and ZnO₂ compared with Fe₂O₃,
5. To investigate the cause of catalyst deactivation by sintering of the metal and / or the support,
6. Detailed studies of catalyst deactivation due to carbon deposition as well as poisoning by sulphur.

Chapter 4

Conclusion and recommendation

The overall aim of this thesis was to develop the production of hydrogen from methane by using catalysts. This thesis focused on two sectors of study.

- 1) A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure
- 2) The study of the steam iron process over promoted Fe-oxide based catalyst.

4.1 A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure.

The first sector is a kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure. Although Ni catalyst is well known for methane steam reforming, carbon formation is also a serious issue for methane steam reforming over Ni catalyst. This thesis has studied the use of magnesia, MgO to suppress carbon formation.

A kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure was carried out. The first part of the present study was to determine the kinetic orders of methane and the steam, which were found to be 0.82 and 0.62 respectively at 40 bars and 600 °C.

A second study was to measure the energy of activation. The estimation of energy of activation also was found to be 106 kJ/mol. The dynamics of methane decomposition was suggested to be dependent on only the rate constants for C-H bond elementary

steps on Ni surface because the estimated energy of activation was close to the energy of activation for the C-H bond elementary step on Ni surface.

A third study was to evaluate the deactivation orders of methane, which was based on feeding various partial pressure of methane. The deactivation order of methane was found to be to 0.99.

A fourth study was to investigate the relationship between the steam to methane ratio and the selectivity to carbon products (CO, CO₂ and C). The selectivity to coke was highest when compared with other carbon products: carbon monoxide and carbon dioxide. Carbon formation is probably a major cause of catalyst deactivation. An increase in steam: methane ratio led to increased selectivity to CO₂ and decreased selectivity to CO because of an increase in the rate of water - gas shift reaction.

A final study was to determine the constant parameter estimates of the different kinetic models. Experimental reaction rates gave the best fit to a model Langmuir-Hinshelwood mechanism case 1, where reaction occurred between adsorbed methane – species and adsorbed steam derived species. The rate reaction can be explained as –

$$r = \frac{kP_{CH_4}P_{H_2O}}{P_{H_2}^2 \left[\frac{K_1P_{CH_4}}{P_{H_2}} + \frac{K_2P_{H_2O}}{P_{H_2}} \right]^2} .$$

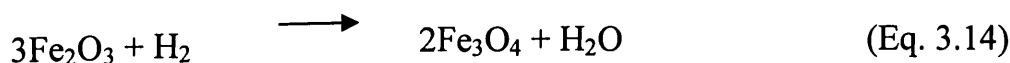
Five recommendations are suggested for the further investigation of a kinetic study of methane steam reforming over a Ni/MgO catalyst at high pressure

1. The use of other high pressures for the kinetic study order to evaluate the relationship between the pressure and other factors such as the coke formation and energy of activation,
2. The study of other promoters such as Al₂O₃ or (CeO) compared with MgO,
3. The use of higher hydrocarbon for the kinetic study,
4. To investigate whether catalyst deactivation is caused by sintering of the metal and / or the support,
5. Detailed studies of catalyst deactivation due to carbon deposition.

4.2 A study of the steam – iron process

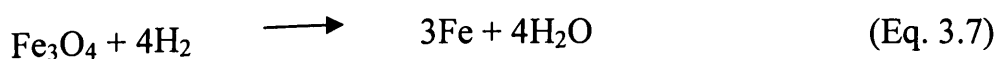
A study of the steam – iron process using four different reductants (H₂, H₂ /CO mixture, CH₄ and CH₄ /CO₂ mixture), was conducted and is described in the second section of the thesis.

A study of the steam iron using H₂ as reductant over 4%Cr₂O₃ – 96% Fe₂O₃ focused on the first reduction of 4%Cr₂O₃ – 96% Fe₂O₃ with H₂. The first stage reduction was shown as:



The estimation of energy of activation for the first stage reduction was found to be 92.36 kJ/mol and the experimental result was explained in terms of a three-dimensional nucleation model according to Avrami- Erofeev.

The second stage reduction was shown as:



The estimation of energy of activation for the second stage reduction was found to be 68.2 kJ/mol and the experimental result was not explained by any other models.

A study of the steam iron using H_2 /CO mixture as reductant over 4% Cr_2O_3 – 96% Fe_2O_3 was carried out. Firstly, FeO was found to be the intermediate for the reduction of Fe_2O_3 with H_2 /CO mixture to Fe metal. Secondly, the complete reduction of Fe_2O_3 into Fe was observed at 650 °C. Finally, carbon or iron carbide formation was observed during the reduction and carbon or iron carbide was found to be completely oxidized with steam in the oxidation step.

A study of the steam iron using CH_4 as reductant over 4% Cr_2O_3 – 96% Fe_2O_3 showed that CH_4 was the worst reductant as compared with two previous reductants.

Consequently, the addition of NiO was applied for an increase in the activity of the reduction of iron oxide with methane. Although the reduction of Fe_2O_3 into Fe_3O_4 was successful for the range 382 °C to 567 °C for the steam iron using CH_4 as reductant over %NiO - 5% Cr_2O_3 – 90% Fe_2O_3 , carbon formation on NiO was highly favorable over 567 °C. This result was confirmed by methane cracking over 5% NiO – 95% SiO_2 . For both 5%NiO - 5% Cr_2O_3 – 90% Fe_2O_3 and 5% NiO – 95% SiO_2 , methane cracking was the main reaction after above 567 °C. The carbon formed on 5%NiO - 5% Cr_2O_3 – 90% Fe_2O_3 could be completely oxidized with steam in the oxidation step.

Due to a serious issue of carbon formation on NiO during the reduction of 5%NiO - 5% Cr_2O_3 – 90% Fe_2O_3 with methane, the introduction of CO_2 mixed with CH_4 was used to suppress formed carbon on NiO. Although CO_2 oxidized formed carbon during the reduction, the strong oxidation of reduced iron oxide with formed water

formed during the reduction process, and the higher favorable reaction of the resultant water gas shift reaction adversely affected on the complete reduction of iron oxide into iron metal.

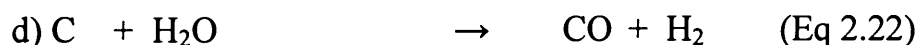
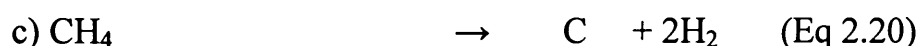
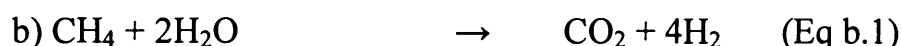
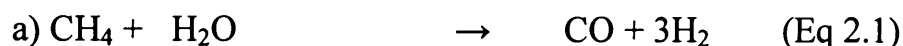
It was suggested six recommendations for the further investigation of a study of the steam – iron process can be made.

1. The use of higher temperature for the reduction of iron oxide based catalyst with methane in order to obtain complete reduction into iron metal,
2. The study of other promoters such as Pt, Pd and Cu compared with Ni,
3. The use of the alkaline earth metal oxides, such as MgO, CaO and BaO as support for %NiO - 5%Cr₂O₃ – 90% Fe₂O₃ in order to suppress carbon formation during reduction,
4. The study of other thermodynamic favorable candidates such as WO₃, MnO₂ and ZnO₂ compared with Fe₂O₃,
5. The investigation of the cause of catalyst deactivation by sintering of the metal and / or the support
6. Detailed studies of catalyst deactivation due to carbon deposition as well as poisoning by sulphur.

APPENDIX A Calculation of reaction rate for the kinetic study of methane steam reforming by using Ni/MgO at high pressure

1. Establishment of a Material Balance

The combined steam reforming of methane involves a complex set of chemical reactions. As the consumed steam could not be directly determined, the areas of CH₄, CO and CO₂ from GC1, the areas of hydrogen from GC2, and the stoichiometry of these complex chemical reactions were employed for this issue. Four reactions are considered for the calculation of consumed steam in which two major reactions lead to the decomposition of methane by steam into two different products; CO and CO₂, the other minor reactions are coke formation and carbon gasification.



$$\text{Reaction rate of CH}_4 \text{ consumed} = a + b + c$$

$$\text{Reaction rate of H}_2\text{O consumed} = a + 2b + d$$

$$\text{Reaction rate of H}_2 \text{ formed} = 3a + 4b + 2c + d$$

$$\text{Reaction rate of Coke formed} = c$$

$$\text{Reaction rate of Coke consumed} = d$$

$$\text{Reaction rate of CO formed} = a + d$$

$$\text{Reaction rate of CO}_2 = \text{b}$$

$$\text{a} = \frac{(S_{co} \times \%CH_4\text{conversion} \times CH_4\text{feed})}{(1000 \times 22.4 \times W_{catalyst})}$$

$$\text{b} = \frac{(S_{co_2} \times \%CH_4\text{conversion} \times CH_4\text{feed})}{(1000 \times 22.4 \times W_{catalyst})}$$

$$\text{c} = \frac{(S_{coke} \times \%CH_4\text{conversion} \times CH_4\text{feed})}{(1000 \times 22.4 \times W_{catalyst})}$$

G.C. 1 calculation

$$S_{co} = \frac{(A_{co})}{(RF_{CO} \times A_{CH_4\text{feed}})}$$

$$S_{co_2} = \frac{(A_{co_2})}{(RF_{CO_2} \times A_{CH_4\text{feed}})}$$

$$S_{coke} = (1 - (1 - \%CH_4\text{conversion}) - S_{co} - S_{co_2})$$

G.C. 2 calculation

$$\text{H}_2 \text{ formed (molg}^{-1}\text{s}^{-1}) = \frac{\frac{(A_{N_2\text{bypass}})}{(A_{N_2})} \times A_{H_2} \times Q_{N_2}}{(1000 \times 22.4 \times W_{catalyst} \times RF_{H_2} \times \text{Corrected } A_{N_2})}$$

Where % conversion of methane was calculated from the change of area of methane

% conversion of methane $= 1 - \left[\frac{(A_{CH_4})}{(A_{N_2})} \right] \times \left[\frac{(A_{N_2\ bypass})}{(A_{CH_4\ bypass})} \right]$

Reaction rate of methane $= \frac{[\%CH_4\ conversion \times CH_4\ feed]}{[W_{catalyst}]}$

Definitions

Sco = The selectivity of carbon monoxide

Sco2 = The selectivity of carbon dioxide

Scoke = The selectivity of coke

CH4feed = The flow rate of methane (ml/s)

%CH4conversion = % conversion of methane

A_{CH₄} = Area of methane measured by G.C.
as a result of reaction

A_{CH₄ bypass} = Area of methane measured by G.C.
When methane by pass

A_{N₂} = Area of nitrogen measured by G.C.
as a result of reaction

A_{N₂ bypass} = Area of nitrogen measured by G.C.
When on nitrogen by pass

Aco = Area of carbon monoxide measured by
G.C. as a result of reaction

A_{CO_2}	=	Area of carbon dioxide measured by G.C. as a result of reaction
A_{H_2}	=	Area of hydrogen measured by G.C. as a result of reaction
RF_{CO}	=	Response factor of carbon monoxide
RF_{CO_2}	=	Response factor of carbon monoxide
RF_{H_2}	=	Response factor of hydrogen
Q_{N_2}	=	The flow rate of nitrogen (ml/s)
$W_{catalyst}$	=	weight of catalyst (g)
Correct A_{N_2}	=	The ratio between area of nitrogen during reaction and area of nitrogen by- pass

APPENDIX B Calculation of the formation and consumption of gases

via the mass spectrometer

1) The current of gases from mass spectrometer was converted to the percentage of gases.

To convert ion current to percentage, a conversion factor was determined for a bypass condition.

For example, the average of the ion current of hydrogen for 20 cycles was 1.88×10^{-12} when 14.36% of hydrogen was fed during bypass.

$$\begin{aligned}\text{Consequently, conversion factor} &= 14.36\% / 1.88 \times 10^{-12} \\ &= 7.62 \times 10^{12}\end{aligned}$$

The percentage of gases involved during reaction was determined by multiplying the ion current of gases during reaction and conversion factor.

For example, the ion current of hydrogen at 30 minutes during reaction was 1.78×10^{-12} .

$$\begin{aligned}\text{the percentage of hydrogen} &= 1.78 \times 10^{-12} \times 7.62 \times 10^{12} \\ &= 13.54 \%\end{aligned}$$

2) The percentage of gases from mass spectrometer was converted to the mole of gases

The area between the percentage of formation and consumption of gases and time was integrated by the Excel program shown Fig B.1

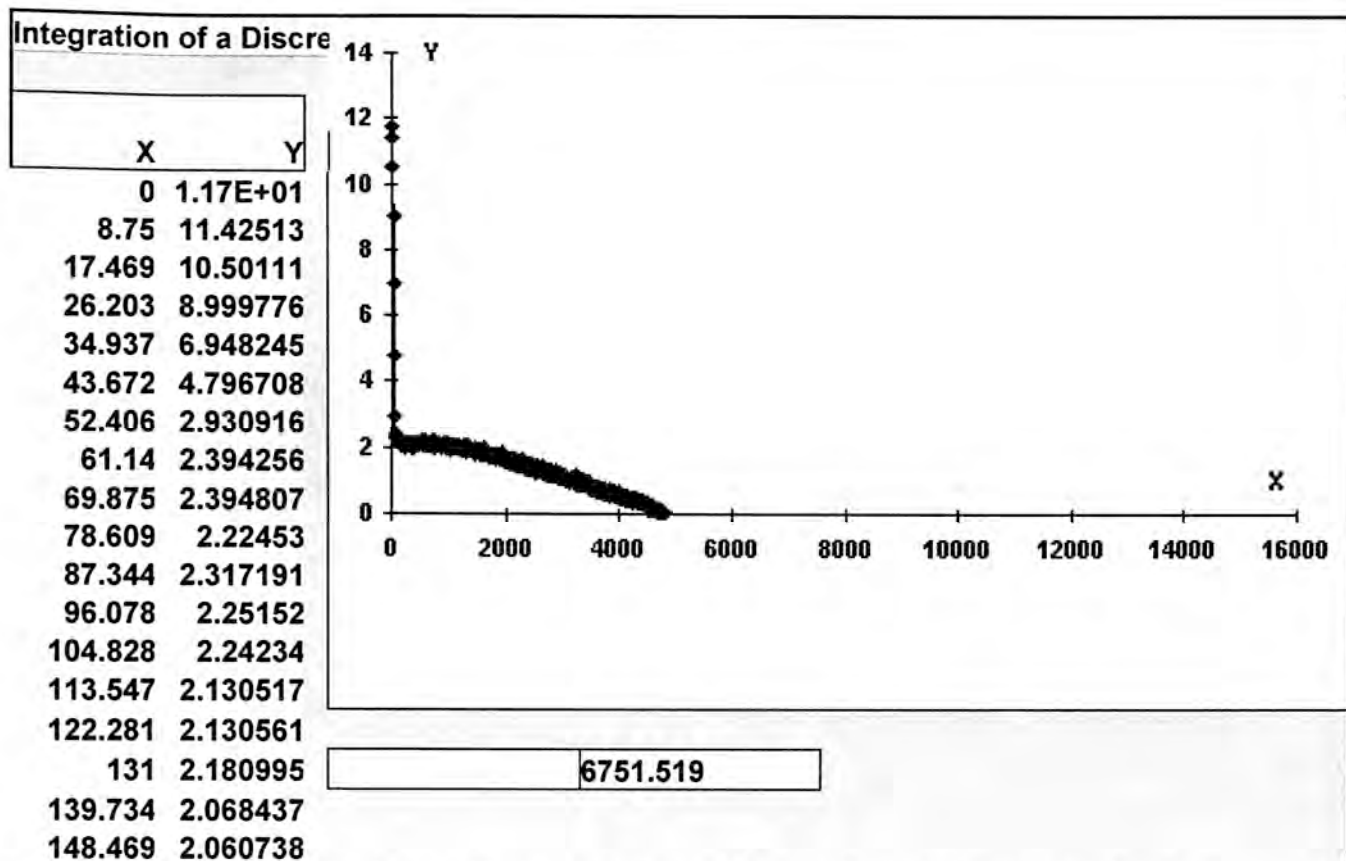


Figure B.1 The area between the percentage of formation and consumption of gases and time was integrated by the Excel program

Subsequently, the area was converted to the mole of gas.

The mole of gas =
$$\frac{\text{(the total of integrated area x total flow rate x correct STP gas)}}{(60 \times 22414 \times 100)}$$

correct STP gas = the ratio between STP temperature (K) and room temperature (K)

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