

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

The sol-gel process, which has a number of advantages: controlled pore size distribution, high purity, homogeneous dispersion and high surface area, was applied to prepare 5% nickel supported on alumina catalyst and alumina support. Then the effect of calcination temperature, reduction time and reaction temperature of 5% sol-gel Ni/Al₂O₃ were investigated. In addition, 5% nickel supported on commercial alumina and on sol-gel alumina, were also prepared by the impregnation technique to study the effects of alumina support and preparation technique.

Furthermore, the catalytic activity, stability, selectivity, activation energy and carbon deposition of all three 5% Ni/Al₂O₃ catalysts: sol-gel Ni/Al₂O₃, Ni/commercial Al₂O₃, and Ni/sol-gel Al₂O₃ were studied.

It is generally known that the structures of support and active phases on the catalyst greatly affect catalytic activity and stability. The surface areas of supports and catalysts were measured by nitrogen adsorption, based on BET model and the crystallite phases of the catalysts were identified by X-ray diffraction (XRD) in this study.

For the reforming of methane with carbon dioxide, nickel crystallite is the active site. After calcination in air at high temperatures, nickel nitrate decomposes to nickel oxide (NiO). Therefore, the catalyst has to be reduced by hydrogen to form metallic nickel crystallites, the active sites, for the reforming reaction. Catalyst reduction is a chemical reaction, in which it should be carried out at a high enough temperature for a certain time to achieve complete reduction of the catalyst. This temperature is an important

catalyst property, and it can be determined by temperature programmed reduction (TPR).

4.1.1 X-Ray Diffraction

The XRD patterns of fresh and used 5% sol-gel Ni/Al₂O₃, 5% Ni/commercial Al₂O₃, and 5% Ni/sol-gel Al₂O₃ are shown in Figures 4.1-4.3 and the crystallite phases found on the catalysts are shown in Table 4.1.

The XRD pattern of sol-gel Ni/Al₂O₃ shows that nickel in this catalyst is mainly in NiAl₂O₄ form. During calcination, nickel nitrate is decomposed to nickel oxide and then nickel oxide may react with γ -Al₂O₃, the support, to give nickel aluminate as shown in reaction (13) (Rostrup-Nielsen, 1984).



NiAl₂O₄ has a spinel lattice structure, and γ -Al₂O₃ has a lattice structure in which the oxygen atoms are arranged similarly to that in spinel. All the oxygen ions in a spinel structure are equivalent, forming a close-packed cubic arrangement. The oxygen ions are much larger than the cations fitted into two kinds of gaps, octahedral (surrounded by six atoms) and tetrahedral (surrounded by four atoms). Crystallographically, the atomic ratio of total metal to oxygen atoms is 3:4 for spinel but only 2:3 for γ -Al₂O₃. Hence, for γ -Al₂O₃, a portion of the metal gaps is vacant. This may be the reason for the greater solubility and compound formation between heavy metal cations and γ -Al₂O₃ (Satterfield, 1991).

For the Ni/commercial Al₂O₃ catalysts, after calcination at the same temperature (500 °C), nickel nitrate was decomposed to nickel oxide. NiO did not react with γ -Al₂O₃ as for sol-gel Ni/Al₂O₃ because NiAl₂O₄ was not found on this catalyst. However, it was reported that NiAl₂O₄ may form if the catalyst was calcined at high temperatures above 800 °C (Ho and Chou, 1995).

Table 4.1 The crystallite phases on 5% sol-gel Ni/Al₂O₃, fresh and used 5% Ni/sol-gel Al₂O₃ identified by XRD.

Catalyst	Crystallite phase
fresh 5% sol-gel Ni/Al ₂ O ₃	NiAl ₂ O ₄ , γ -Al ₂ O ₃
used 5% sol-gel Ni/Al ₂ O ₃	C, Ni, NiAl ₂ O ₄ , γ -Al ₂ O ₃
fresh 5% Ni/commercial Al ₂ O ₃	NiO, γ -Al ₂ O ₃
used 5% Ni/commercial Al ₂ O ₃	C, Ni, γ -Al ₂ O ₃
fresh 5% Ni/sol-gel Al ₂ O ₃	γ -Al ₂ O ₃
used 5% Ni/sol-gel Al ₂ O ₃	C, Ni, γ -Al ₂ O ₃

For the Ni/sol-gel Al₂O₃ catalysts, nickel compound was not found even though the catalyst had 5% Ni loading. The nickel compound on this catalyst may have very small crystallite sizes, less than 5 nm, since the XRD is sensitive to crystallite sizes in the range of about 5-50 nm (Satterfield, 1991).

Graphitic carbon and Ni crystallite were detected by XRD on all used catalysts at about two theta of 28 degrees and of 52 degrees, respectively. The minimum concentration detected by XRD is approximately 5% for compounds and 1% for elements. As the catalyst was reduced to metallic Ni crystallites, the carbon deposited on some of metallic nickel surface when used. However, Ni crystallite can be found on used catalysts due to the low concentration limit at 1% for metallic nickel.

4.1.2 Surface Area and the Reduction Temperature

The surface areas of catalysts and supports and reduction temperatures for the catalysts are shown in Table 4.2.

Table 4.2 The surface areas and the reduction temperatures (T_R) for the catalysts.

Catalyst and support	Surface area (m^2/g)	T_R ($^{\circ}C$)
5% sol-gel Ni/ Al_2O_3 (not calcined)	424.7	-
5% sol-gel Ni/ Al_2O_3 calcined at 500 $^{\circ}C$	367.8	785
5% sol-gel Ni/ Al_2O_3 calcined at 600 $^{\circ}C$	337.7	810
commercial alumina	183.8	-
sol-gel alumina calcined at 500 $^{\circ}C$	378.8	-
5% Ni/commercial Al_2O_3	158.9	573
5% Ni/sol-gel Al_2O_3	355.2	780

The surface area of 5% sol-gel Ni/ Al_2O_3 (367.8 m^2/g) is about those of sol-gel Al_2O_3 (378.8 m^2/g) and of Ni/sol-gel Al_2O_3 (355.2 m^2/g). It can be concluded that the addition of Ni by either sol-gel technique or impregnation technique had little effect on the surface area or the structure of catalysts.

Nickel compound on sol-gel Ni/ Al_2O_3 is $NiAl_2O_4$. It is inactive and can be reduced at a high temperature around 790 $^{\circ}C$ (Li and Chen, 1995). From TPR results shown in Table 4.2, sol-gel Ni/ Al_2O_3 was reduced at 785 $^{\circ}C$ which is close to that reported by Li and Chen (1995).

Nickel compound on Ni/commercial Al_2O_3 calcined at 500 $^{\circ}C$ is NiO and it can be reduced at 573 $^{\circ}C$ which is close to the temperature reported by Ho and Chou (1995) at 550 $^{\circ}C$.

The Ni/sol-gel Al_2O_3 catalyst was reduced at the reduction temperature for sol-gel Ni/ Al_2O_3 , but $NiAl_2O_4$ was not found on this catalyst.

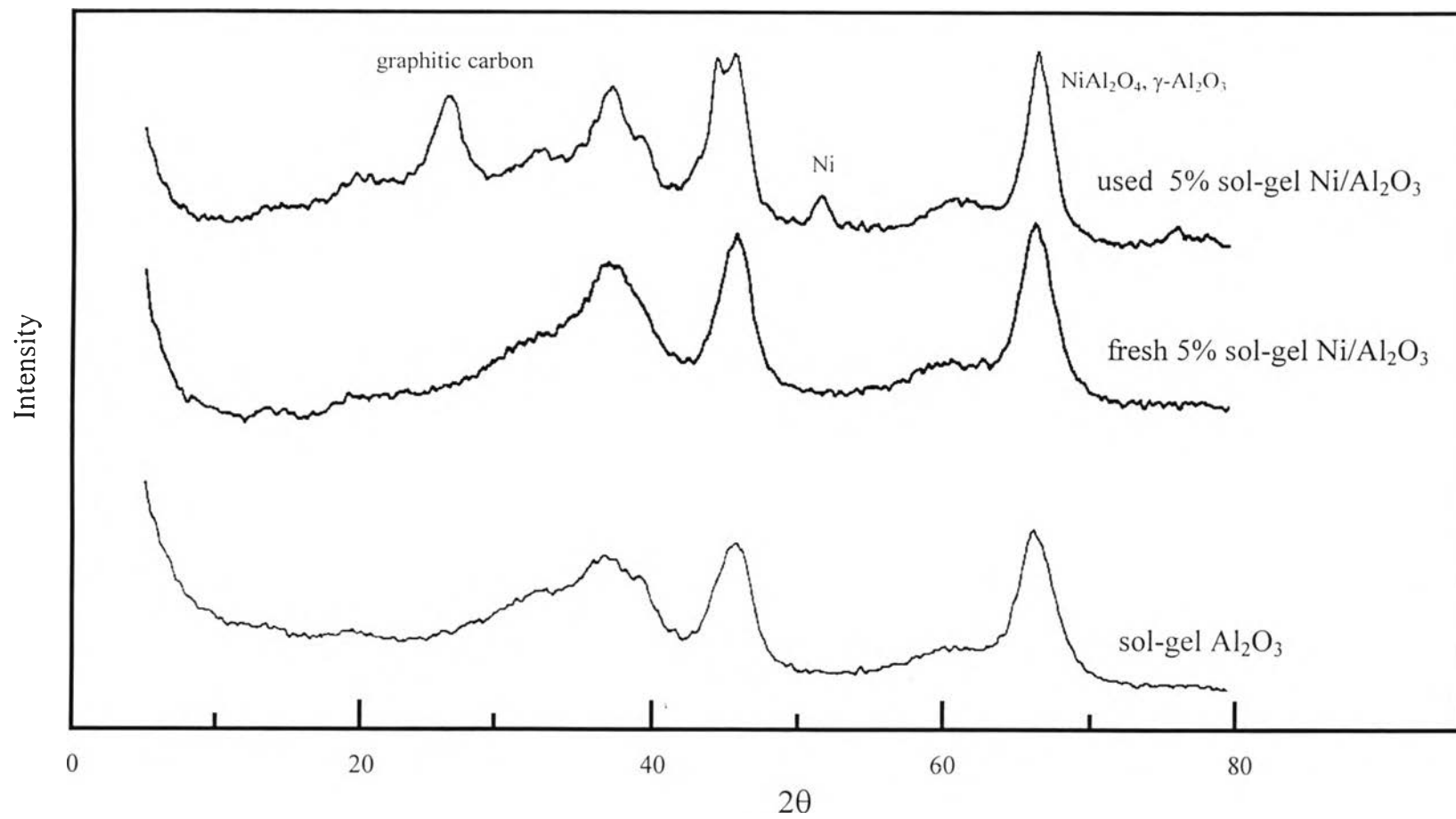


Figure 4.1 XRD patterns of sol-gel Al₂O₃, fresh and used 5% sol-gel Ni/Al₂O₃.

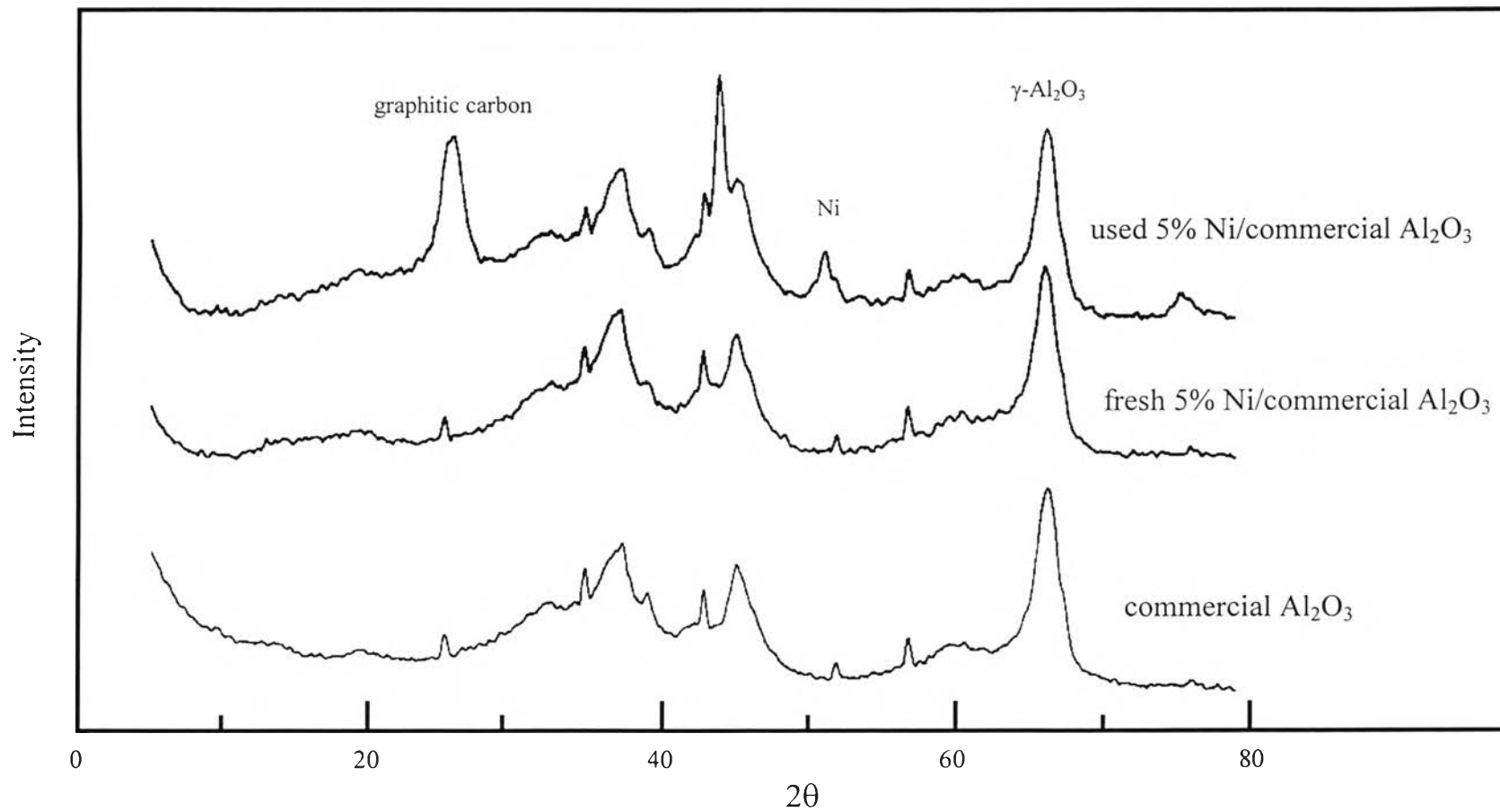


Figure 4.2 XRD patterns of commercial Al₂O₃, fresh and used 5% Ni/commercial Al₂O₃.

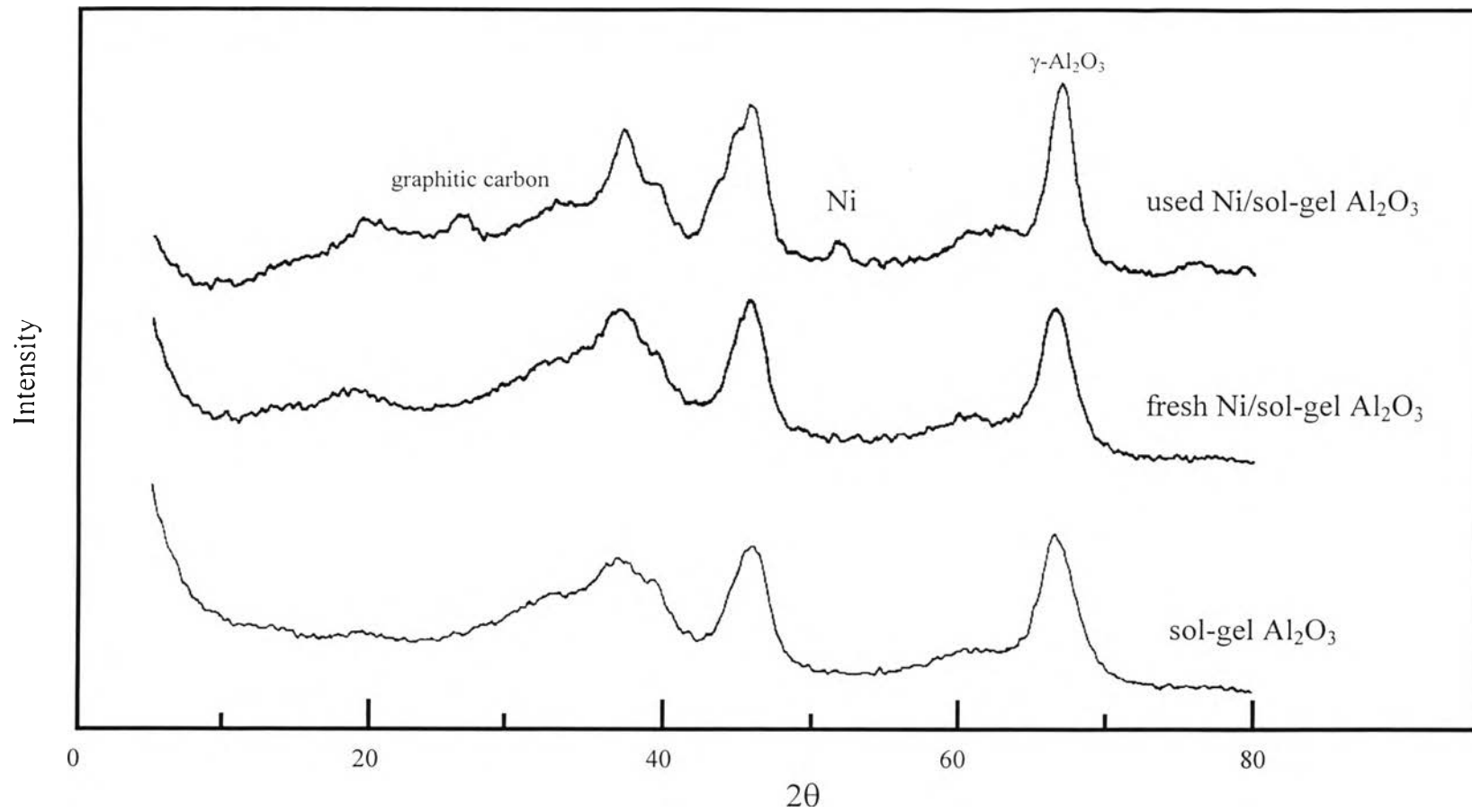


Figure 4.3 XRD patterns of sol-gel Al₂O₃, fresh and used 5% Ni/sol-gel Al₂O₃.

From XRD results, nickel compounds on Ni/sol-gel Al₂O₃ had very small crystallite sizes, and as a result is reducible at high temperatures.

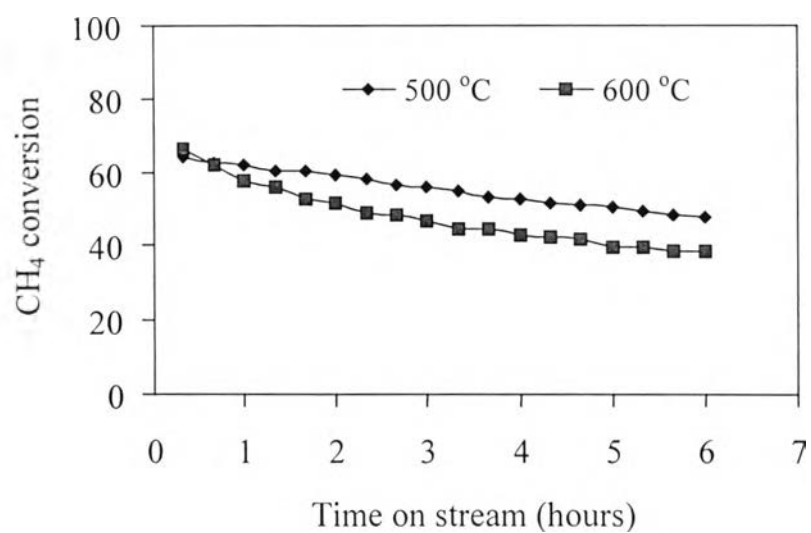
4.2 The Effect of Calcination Temperature

Since a minimum calcination temperature for the catalysts must be above 400 °C in order to decompose nickel nitrate to NiO (Ho and Chou, 1995) and to get rid of the organic impurities left in the catalysts. The temperature of 500 °C or higher was therefore chosen as calcination temperature in this study.

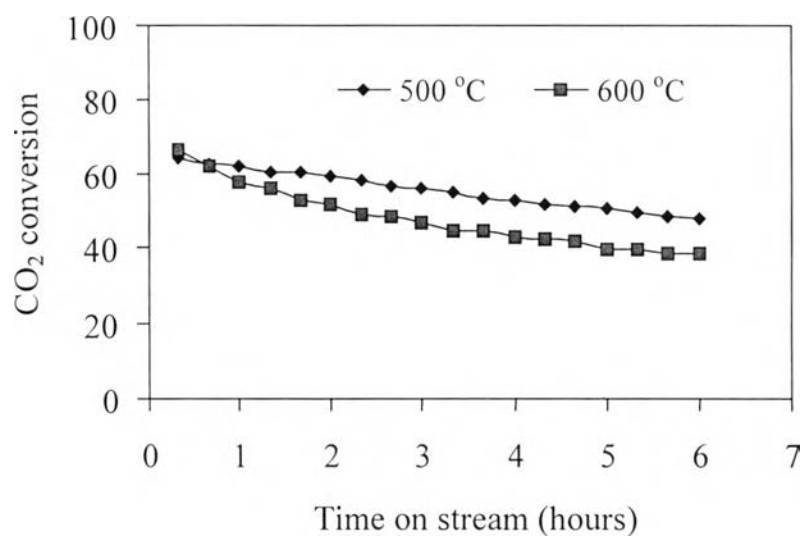
The 5% sol-gel Ni/Al₂O₃ catalysts calcined in air at 500 and 600 °C and reduced at 785 and 810 °C, respectively for 4 hours, were tested at 700 °C and their catalytic activities are shown in Figure 4.4. The catalyst calcined at 600 °C tended to deactivate faster than one calcined at 500 °C probably because of catalyst sintering during reduction as well as calcination. The XRD pattern of sol-gel Ni/Al₂O₃ shows the presence of NiAl₂O₄ in the catalyst. NiAl₂O₄ was reduced to Ni crystallite by the reaction (14).



Metallic Ni crystallites may aggregate to form larger crystallites, a more stable state, by surface diffusion in case of the reduction at high temperatures. It was expected to observe the sintering of nickel at the temperature above 600 °C (Zhang and Verykios, 1994). Therefore, the catalyst reduced at the higher temperature has more sintering and may have larger nickel crystallites after the reduction for the same period of time. Carbon can quickly form on a larger Ni crystallite, so the catalyst calcined at 600 °C and reduced at higher temperature tended to deactivate faster than one calcined at 500 °C. The catalyst calcined at higher temperature had stronger metal-support interaction, so it may be more difficult to reduced, needing a high temperature reduction.



(a)



(b)

Figure 4.4 Catalytic activity of 5% sol-gel Ni/Al₂O₃ calcined at 500 °C and 600 °C when tested at 700 °C: (a) CH₄ conversion (b) CO₂ conversion.

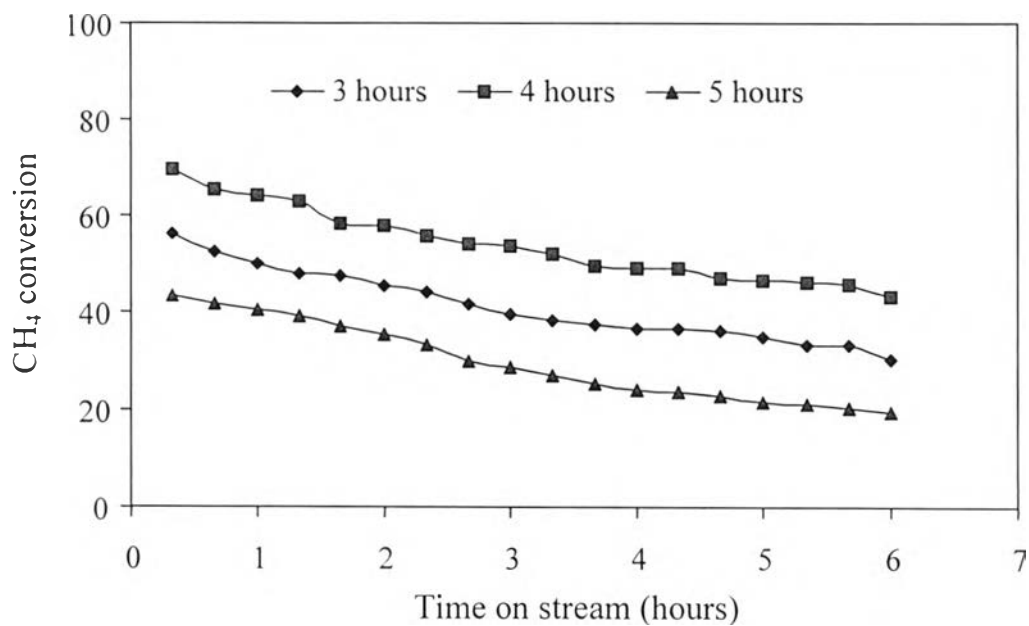
The catalyst calcined at 500 °C has surface area of 367.8 m²/g, whereas the one calcined at 600 °C has surface area of 331.1 m²/g. This is most likely due to closing of some of the narrow pores in the alumina support.

4.3 The Effect of Reduction Time

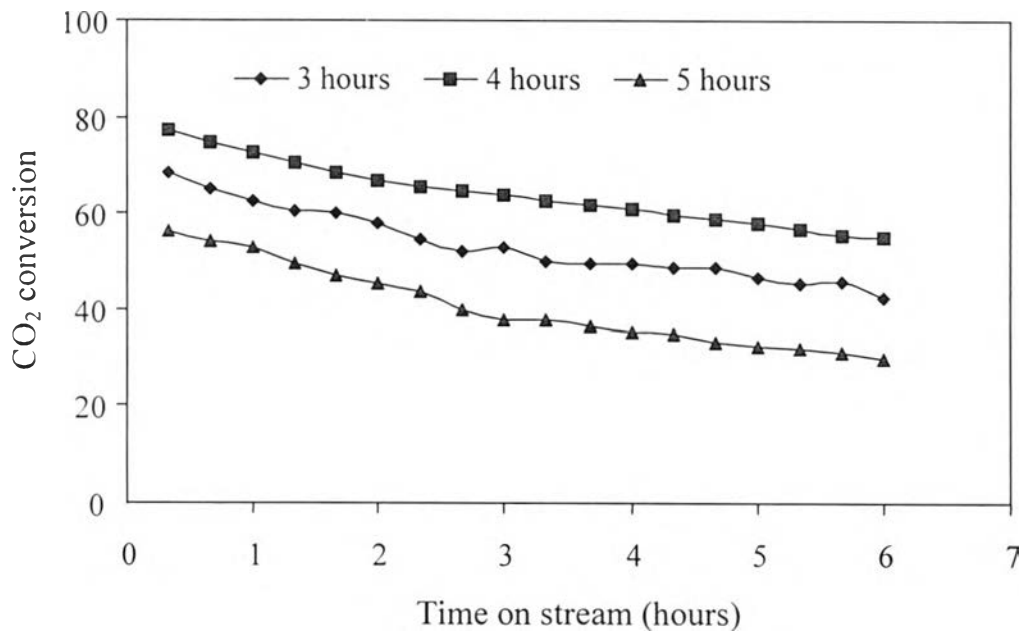
The 5% sol-gel Ni/Al₂O₃ catalysts calcined at 500 °C in air, and reduced at 785 °C for 3, 4, 5 hours were tested at 700 °C and their activities are shown in Figure 4.5. It was found that the catalyst reduced for 4 hours had higher catalytic activity over the ones reduced for 3 and 5 hours. Catalyst reduction is a chemical reaction, thus it should be carried out at high enough temperature for enough time for completion. The reduction temperature is obtained from temperature programmed reduction (TPR), so the catalysts are certainly reduced at high enough temperature. However, TPR shows the reduction temperature but not the time for reduction.

For the case that the catalysts are reduced above Tamman temperature, which is about 600 °C for nickel (Zhang and Verykios, 1994), a suitable time for catalyst reduction should be determined to prevent extensive sintering. From the catalytic activities shown in Figure 4.5, it is clear that the reduction for 3 hours may not be long enough to reduce the catalyst completely, whereas the reduction for 5 hours was too long and may have caused serious catalyst sintering during the reduction. After the catalyst was reduced to nickel crystallites completely, it can aggregate to form larger particles resulting in lower surface areas and lower activities.

The catalytic activity of the catalyst is proportional to the total active surface area effectively exposed to reactants. Therefore, the catalyst reduced for 5 hours, which had lower active surface area, had lower catalytic activity compared to one reduced for 4 hours.



(a)



(b)

Figure 4.5 Catalytic activity of 5% sol-gel Ni/Al₂O₃ calcined at 500 °C reduced for 3,4 and 5 hours when tested at 700 °C: (a) CH₄ conversion (b) CO₂ conversion.

4.4 The Effect of Reaction Temperature

The 5% sol-gel Ni/Al₂O₃ catalysts calcined at 500 °C in air, and reduced at 785 °C for 4 hours were tested at 600, 650, 700 and 750 °C. Their catalytic activities at various temperatures are shown in Figure 4.6 and the average of CO, H₂ selectivity, CO:H₂ ratio and water formation rate at varied temperatures over 6 hours are shown in Table 4.3.

The reforming of methane with carbon dioxide is a highly endothermic reaction; as a result, higher methane and carbon dioxide conversions are observed at higher temperatures. The catalysts tested at four different temperatures deactivate with time on stream due to carbon deposition on the catalyst. The catalyst tested at 750 °C deactivated quickly compared to one tested at lower temperature (700, 650 and 600 °C). At high temperatures, the nickel crystallites can aggregate to form larger particles with time on stream and carbon can quickly deposit on the large nickel crystallites resulting in fastest deactivation with time compared to ones tested at lower temperatures.

The product distribution of methane reforming reaction is controlled by the reverse water gas shift reaction:



It uses CO₂ and H₂ to produce CO and H₂O, which is an undesirable by-product, so CO₂ conversion is higher than CH₄ conversion as shown in Figure 4.6 and CO selectivity is higher than H₂ selectivity as shown in Table 4.3.

For the same catalyst, CO, H₂ selectivity and CO:H₂ changed with temperature because the rate of each secondary reaction: reaction (4)-(7) was different at various temperatures. The water is produced by the reverse water gas shift which is endothermic reaction, so the water formation rate increased with increasing temperature as shown in Table 4.3.

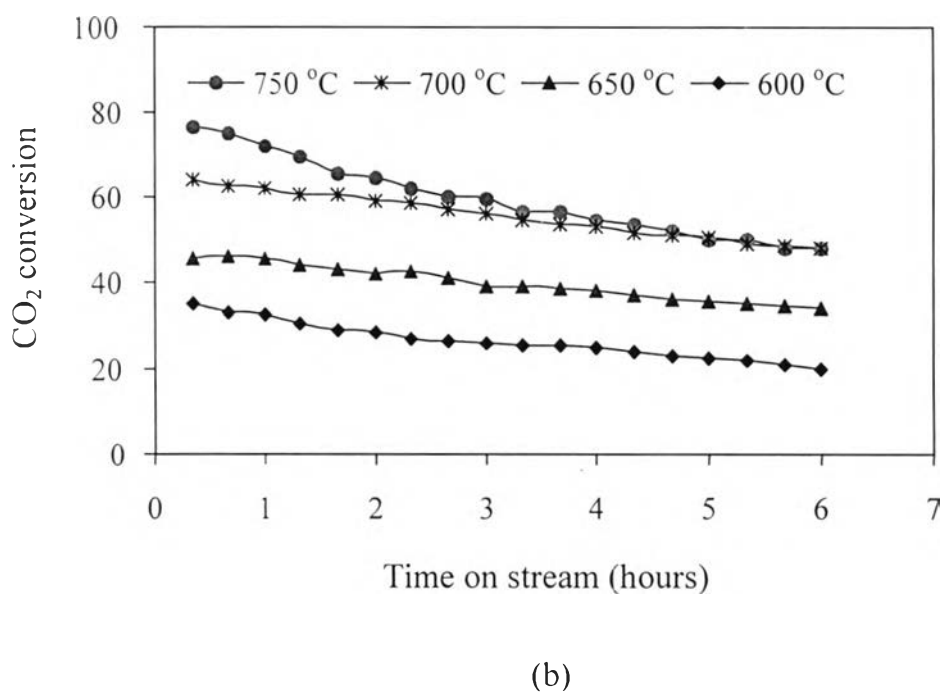
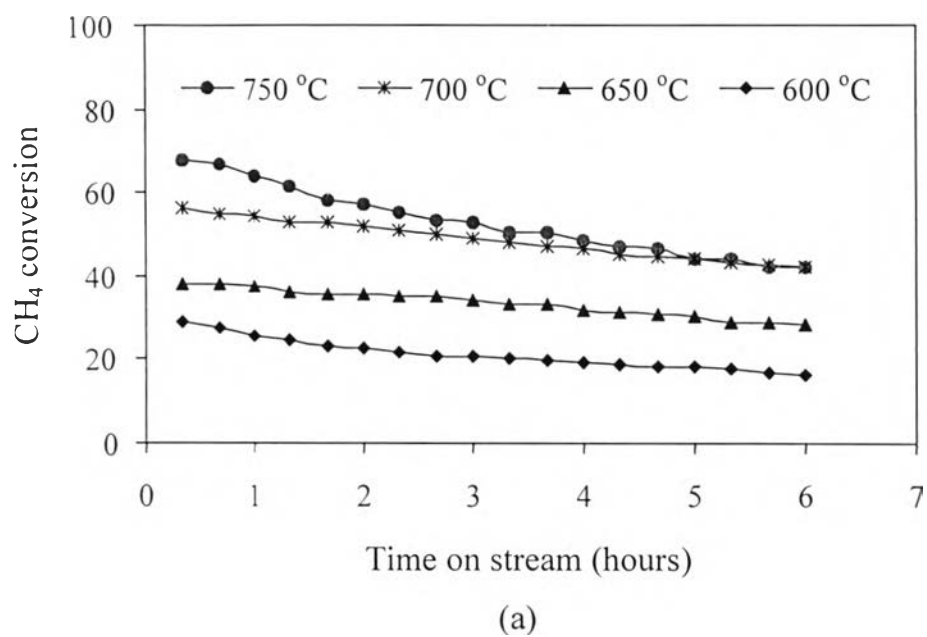


Figure 4.6 Catalytic activity of 5% sol-gel Ni/Al₂O₃ calcined at 500 °C when tested at 600, 650, 700, 750 °C: (a) CH₄ conversion (b) CO₂ conversion.

Table 4.3 The average of CO, H₂ selectivity, CO:H₂ ratio and water formation rate of 5% sol-gel Ni/Al₂O₃ at various temperatures over 6 hours on stream.

Temperature (°C)	S _{CO} (%)	S _{H₂} (%)	CO:H ₂ ratio	r _{H₂O} (micromole/sec)
750	66.07	56.19	1.24	19.26
700	69.68	63.59	1.17	16.58
650	72.48	56.25	1.40	11.79
600	68.34	45.14	1.68	9.35

4.5 Catalytic Activity, Stability and Selectivity

Three of 5% Ni/Al₂O₃ catalysts: sol-gel Ni/Al₂O₃, Ni/commercial Al₂O₃, and Ni/sol-gel Al₂O₃ were tested at 700 °C, and their catalytic activities are shown in Figure 4.7. It was found that all three catalysts had almost the same initial CH₄ and CO₂ conversions and then deactivated quickly with time on stream due to carbon deposition. From the XRD result, Ni/sol-gel Al₂O₃ had smallest crystallite size which probably smaller than 5 nm or it had highest Ni dispersion. Because carbon slowly deposited on small Ni crystallite, this catalyst therefore showed longer stability over the other catalysts.

For all three catalysts, the product distribution is controlled by the reverse water gas shift reaction as CO₂ conversion is higher than CH₄ conversion as shown in Figure 4.7 and CO selectivity is higher than H₂ selectivity as shown in Table 4.4.

Water formation rate of sol-gel Ni/Al₂O₃, is about that of Ni/sol-gel Al₂O₃. This implies that the effect of the reverse water gas shift reaction on these two catalysts are around the same.

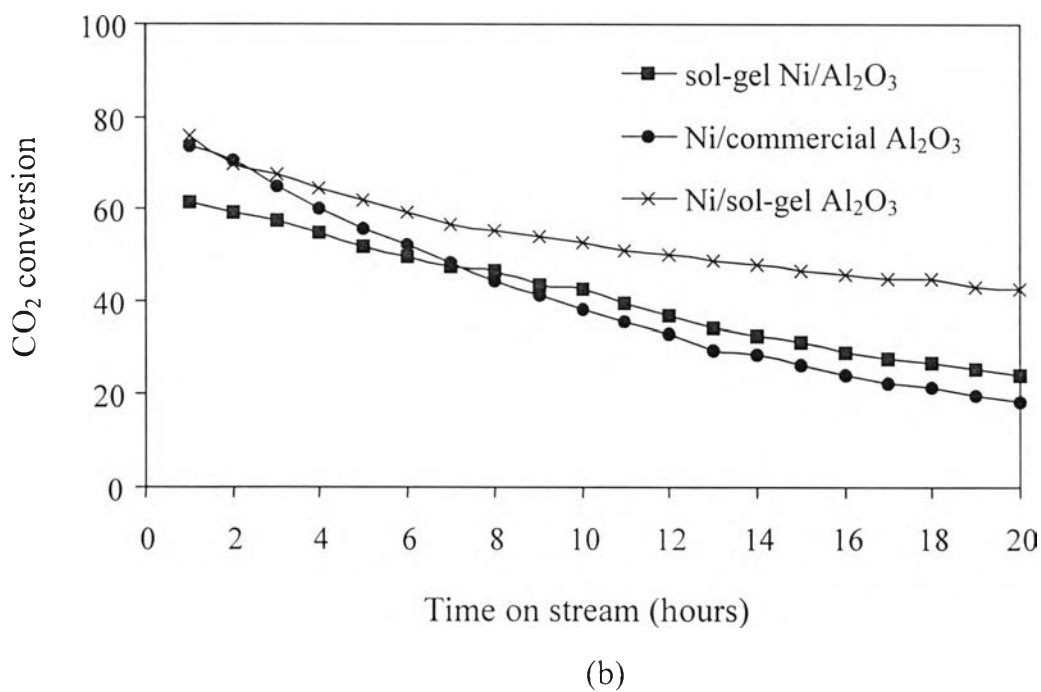
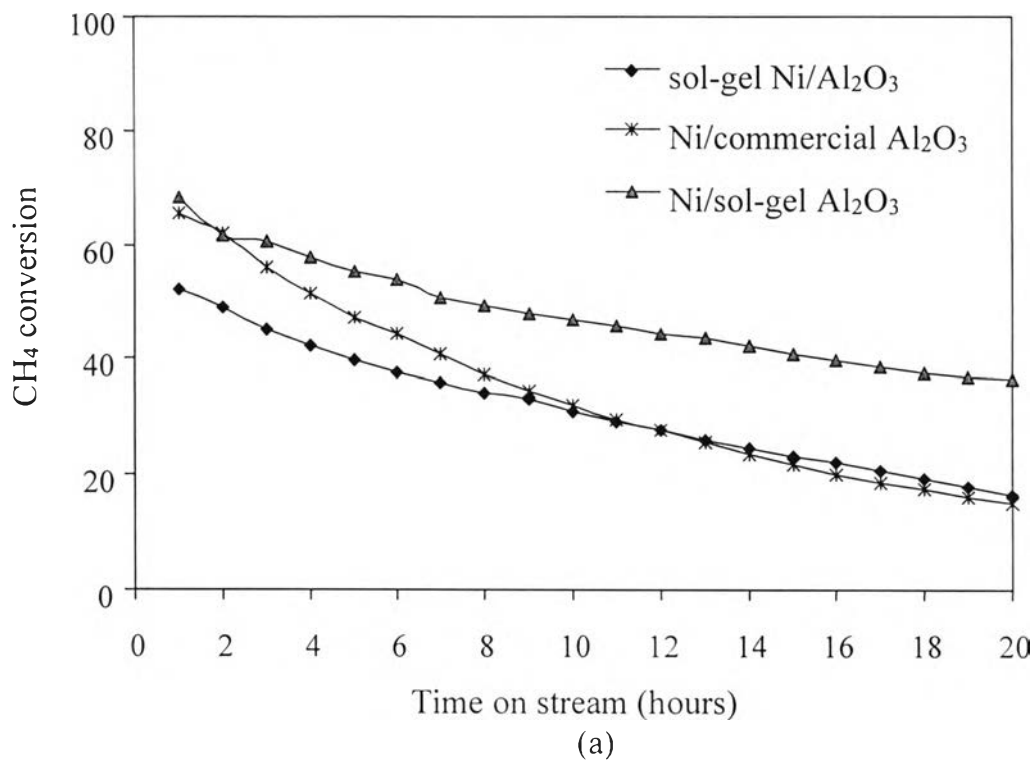


Figure 4.7 Catalytic activity of 5% sol-gel Ni/Al₂O₃, 5% Ni/commercial Al₂O₃ and Ni/sol-gel Al₂O₃ when tested at 700 °C: (a) CH₄ conversion, (b) CO₂ conversion.

Table 4.4 The average of CO, H₂ selectivity, CO:H₂ ratio and water formation rate of all three catalysts over 20 hours on stream.

Catalyst	S _{CO} (%)	S _{H₂} (%)	CO:H ₂ ratio	r _{H₂O} (micromole/sec)
5% sol-gel Ni/Al ₂ O ₃	60.68	54.21	1.27	21.61
5% Ni/commercial Al ₂ O ₃	68.62	61.37	1.21	19.13
5% Ni/sol-gel Al ₂ O ₃	64.81	56.59	1.21	21.66

4.6 Activation Energy

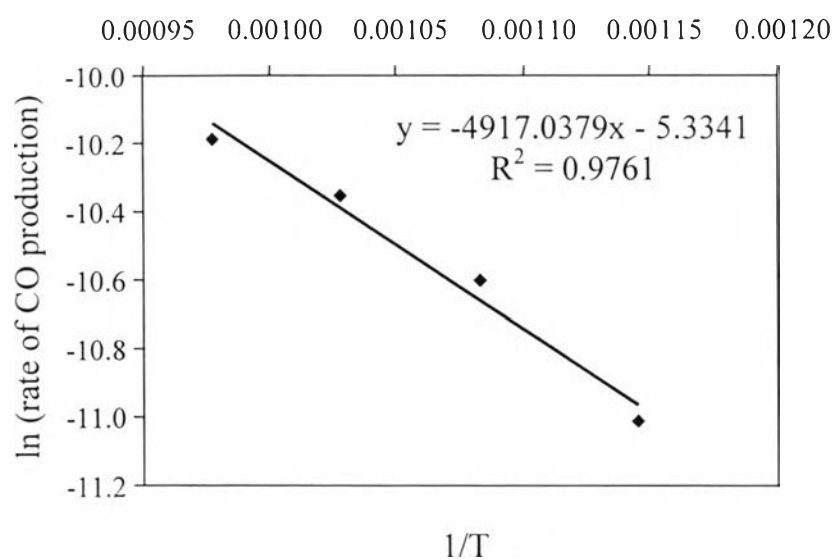
Catalysts provide a faster path for chemical reactions by lowering the activation energy. Lower activation energy leads to higher rates of reaction. However, in a reversible reaction, the catalysts speed up both forward and reverse reactions. Therefore the equilibrium is not changed, but it can be reached quicker.

Three of 5% Ni/Al₂O₃ catalysts (sol-gel Ni/Al₂O₃, Ni/commercial Al₂O₃, and Ni/sol-gel Al₂O₃) were tested at 600, 650, 700 and 750 °C. The activation energies based on the CO and H₂ formation rate are obtained from Arrhenius equation by plotting the logarithm of reaction rates: CO and H₂ formation rate at different temperatures versus the reciprocal of temperature (1/T). The slope of Arrhenius plot is $-E_a/R$ and the activation energy is equal to the slope multiplied by $-R$, where R is the gas constant.

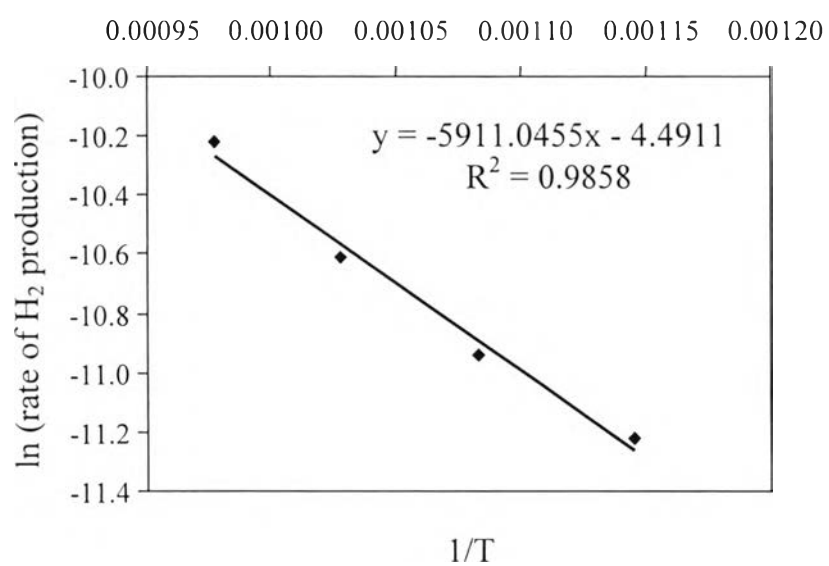
Arrhenius equation:

$$\ln(\text{rate of reaction}) = \ln A - \frac{E_a}{RT} \quad (15)$$

The Arrhenius plots of three prepared 5% Ni/Al₂O₃ based on CO and H₂ formation rate are shown in Figures 8-10 and the activation energies of the three catalysts based on CO and H₂ are shown in Table 4.5.

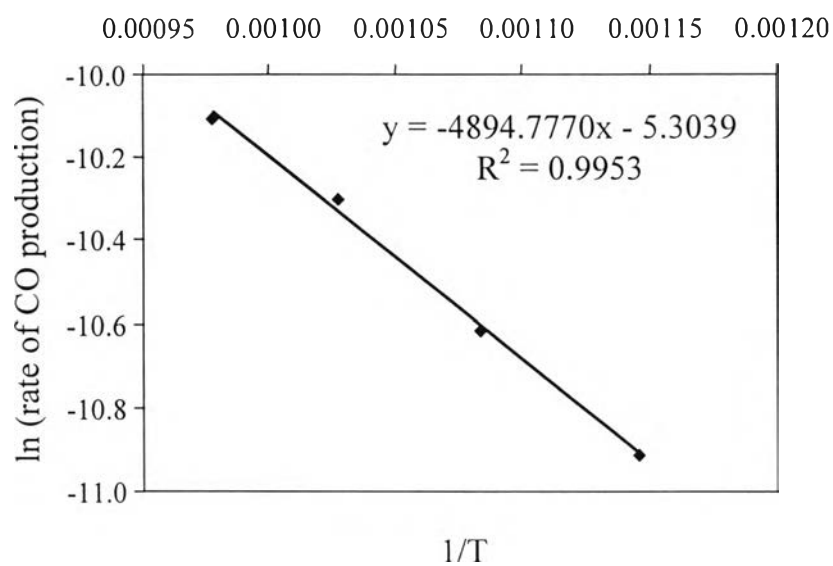


(a)

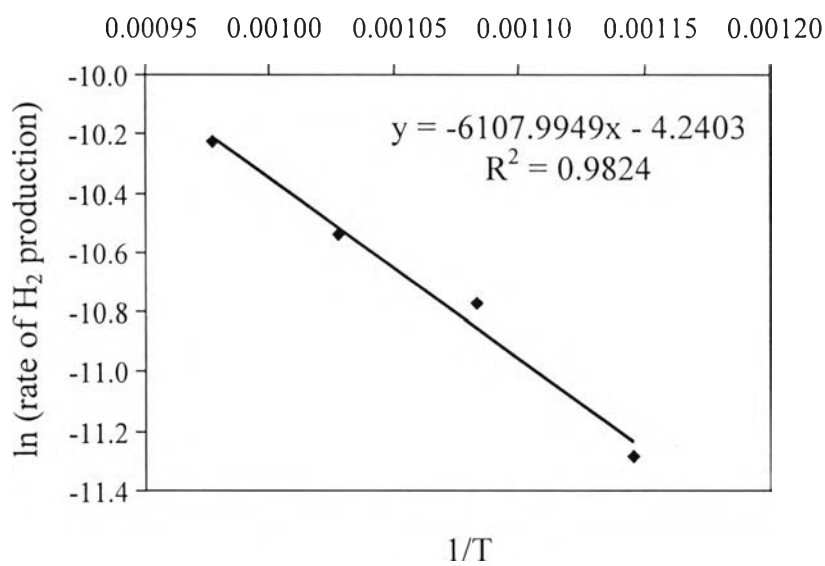


(b)

Figure 4.8 Arrhenius plots of 5% sol-gel Ni/Al₂O₃: (a) based on CO formation rate (b) based on H₂ formation rate.

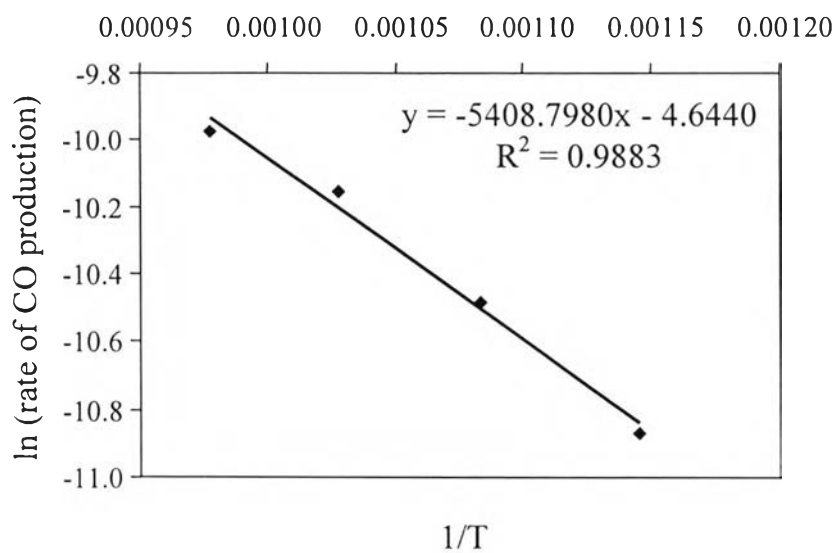


(a)

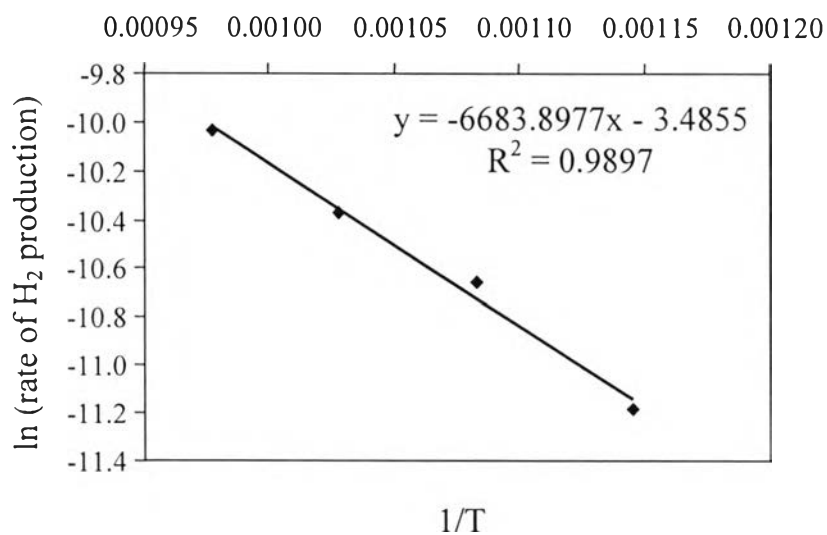


(b)

Figure 4.9 Arrhenius plots of 5% Ni/commercial Al₂O₃: (a) based on CO formation rate (b) based on H₂ formation rate.



(a)



(b)

Figure 4.10 Arrhenius plots of 5% Ni/sol-gel Al₂O₃: (a) based on CO formation rate (b) based on H₂ formation rate.

Table 4.5 The activation energies of 5% sol-gel Ni/Al₂O₃, 5% Ni/commercial Al₂O₃ and 5% Ni/sol-gel Al₂O₃ based on CO and H₂ formation rate.

Catalyst	Activation energy (kJ/mol)	
	Based on r _{CO}	Based on r _{H₂}
5% sol-gel Ni/Al ₂ O ₃	40.88	49.14
5% Ni/commercial Al ₂ O ₃	40.69	50.78
5% Ni/sol-gel Al ₂ O ₃	44.97	55.57

The Arrhenius equation is only strictly valid for an elementary reaction. If a reaction is accompanied by parallel or consecutive side reactions, deviations from the straight line in Arrhenius plot may be experienced for overall rate (Froment and Bischoff, 1990). The reforming of methane with carbon dioxide involves many possible reactions. Consequently, the Arrhenius plot may deviate from straight line and the activation energy based on CO formation rate may be different from that based on H₂ formation rate.

The activation energy of sol-gel Ni/Al₂O₃ is around that of Ni/commercial Al₂O₃ but the activation energy of Ni/sol-gel Al₂O₃ based on both CO and H₂ formation rate is higher. This implies that the reaction mechanism of Ni/sol-gel Al₂O₃ is probably different from that of the sol-gel Ni/Al₂O₃ and Ni/commercial Al₂O₃.

4.7 Carbon Deposition Studies

Temperature programmed oxidation (TPO) for three 5% Ni/Al₂O₃ catalysts tested for 20 hours were conducted on a thermogravimetric analyzer (TGA). When carbon is oxidized, the catalyst weight decreases will be recorded by TGA as a function of temperature and time. The amount of carbon

is total catalyst weight loss and the oxidation temperature for carbon is the temperature at the peak of the catalyst-weight versus temperature curve. The oxidation temperatures for carbon and % carbon are shown in Table 4.6.

As shown in Figure 4.11, the carbon deposited on sol-gel Ni/Al₂O₃ and on Ni/commercial Al₂O₃ were oxidized at the temperature around 690 °C, whereas the carbon on Ni/sol-gel Al₂O₃ is oxidized at the lower temperature of 675 °C. This implies that the type of carbon on Ni/sol-gel Al₂O₃ may be slightly different from that on the other two catalysts.

All of the TPO profiles for the catalysts used for 20 hours shown in Figure 4.12 are not symmetric, so there are at least two types of carbon formed on each catalyst. % carbon on three catalysts are in the following order: sol-gel Ni/Al₂O₃ > Ni/commercial Al₂O₃ ~ Ni/sol-gel Al₂O₃. However, the intensity of graphitic carbon shown in Figures 4.1-4.3 were in the following order: Ni/commercial Al₂O₃ > sol-gel Ni/Al₂O₃ > Ni/sol-gel Al₂O₃. Ni/commercial Al₂O₃ and Ni/sol-gel Al₂O₃ had almost the same % carbon but intensity of graphitic carbon for Ni/commercial Al₂O₃ is much higher than that of Ni/sol-gel Al₂O₃. Therefore, there must be more amorphous carbon on Ni/sol-gel Al₂O₃. Compared to Ni/commercial Al₂O₃, sol-gel Ni/Al₂O₃ had higher % carbon but lower intensity of graphitic carbon. Therefore, there are more amorphous carbon on sol-gel Ni/Al₂O₃.

Table 4.6 The oxidation temperatures for carbon and % carbon on all three catalysts used for 20 hours.

Catalyst	T _{oxidation} (°C)	% Carbon
5% sol-gel Ni/Al ₂ O ₃	693	25.15
5% Ni/commercial Al ₂ O ₃	690	17.89
5% Ni/sol-gel Al ₂ O ₃	675	17.61

Wang and Lu (1998b) reported that two types of carbon (amorphous and graphitic carbon) formed on used catalysts and the carbon situated on the metal particles or in their close vicinity will exhibit higher gasification activity which lead to slow deactivation or better catalyst stability. The amorphous carbon could be eliminated by CO_2 , but the graphitic carbon could not be eliminated by CO_2 due to its longer filament and the distance from the nickel particle. In case that the carbon deposited on catalyst was dominated by graphitic carbon, the entire Ni surface was blocked leading to the total loss of catalytic activity.

Ni/commercial Al_2O_3 and Ni/sol-gel Al_2O_3 had almost the same % carbon, but Ni/commercial Al_2O_3 had higher intensity of graphitic carbon. This may be the reason for faster deactivation for Ni/commercial Al_2O_3 . In addition, Ni/sol-gel Al_2O_3 had lowest intensity of graphitic carbon; hence, it had the best stability.

In summary, the catalyst deactivation caused by carbon deposition depends on the amount, type, and location of the carbon formed.



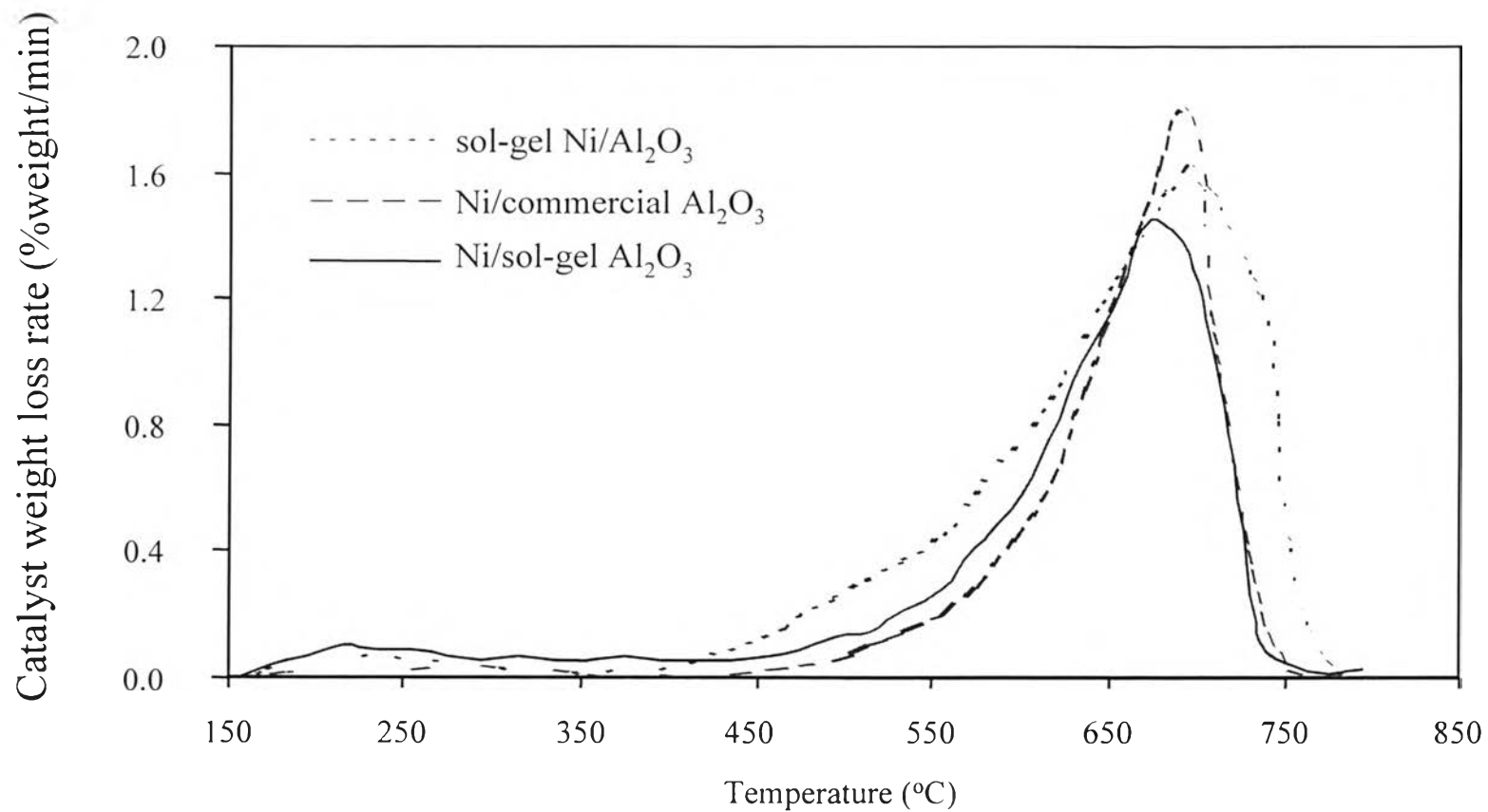
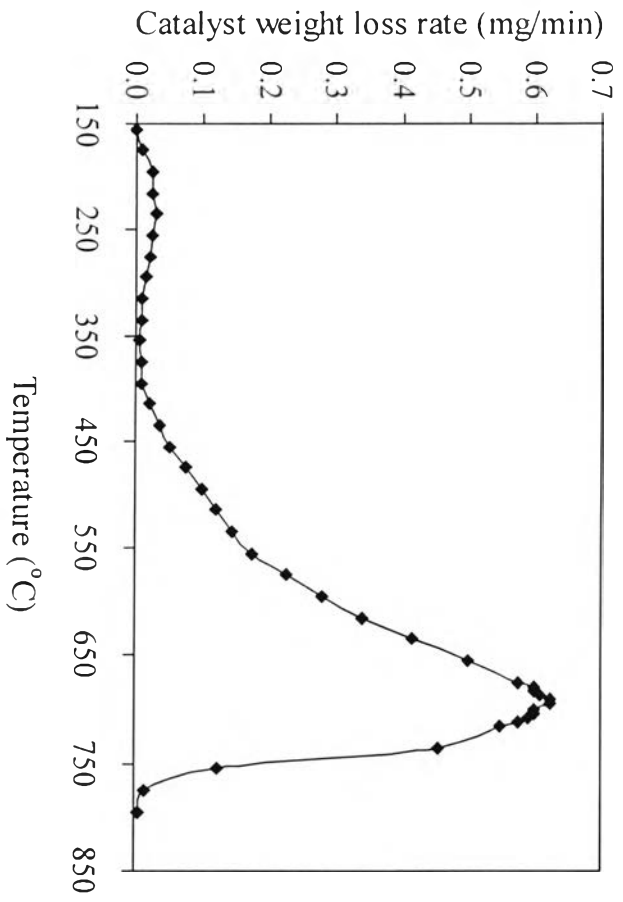
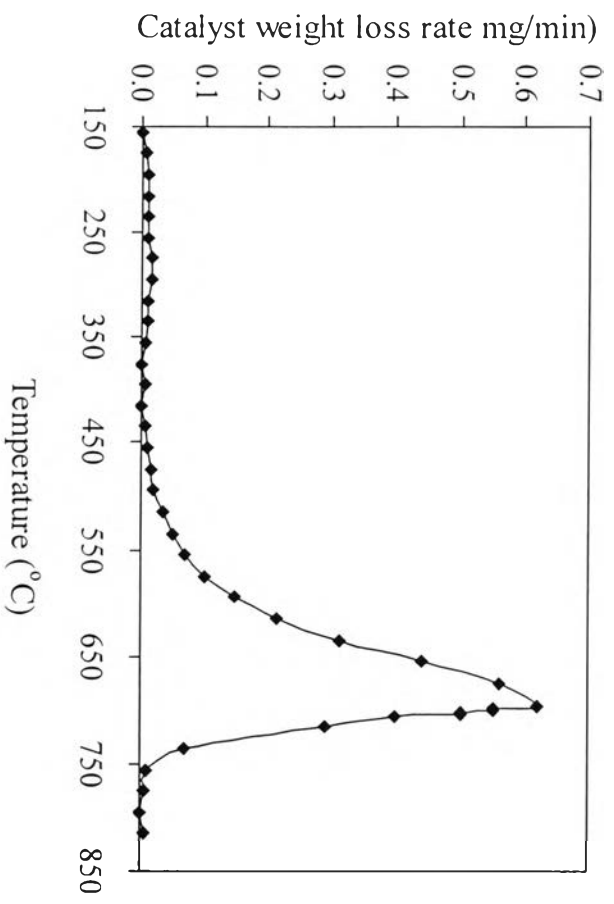


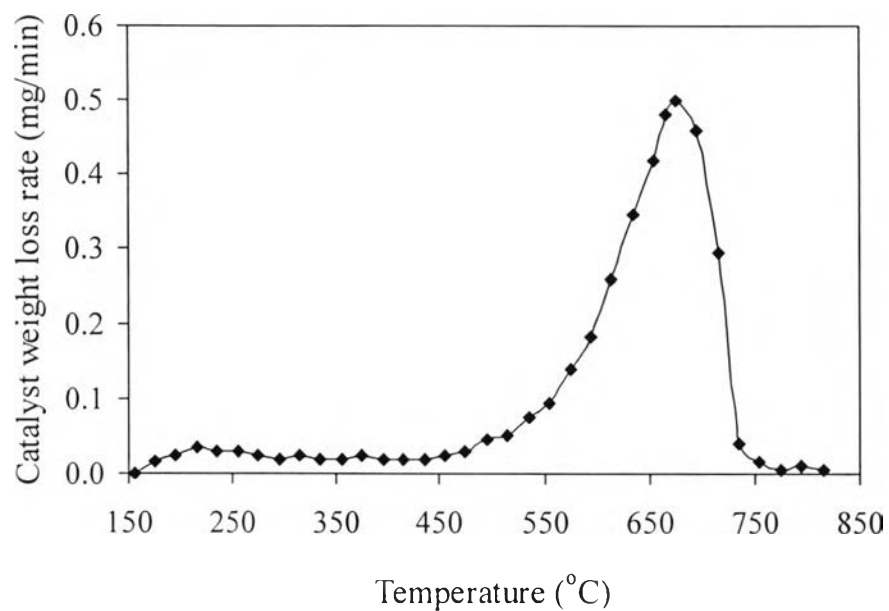
Figure 4.11 Temperature programmed oxidation (TPO) profiles of all three catalysts when tested for 20 hours.



(a)



(b)



(c)

Figure 4.12 Temperature programmed oxidation (TPO) profiles of the catalysts when tested for 20 hours: (a) 5% sol-gel Ni/Al₂O₃, (b) 5% Ni/commercial Al₂O₃, (c) 5% Ni/sol-gel Al₂O₃.

