CHAPTER IV
RESULTS AND DISCUSSION

4.1 Catalyst Characterization

Co-precipitation method was chosen to prepare gold catalysts in this work because this method can give small particles of gold on metal oxide supports. Small gold particles are a crucial factor for high activity in gold catalysts as described by several researchers. Furthermore, in order to compare the characterization results with Rattanachatchai's work (2000), 0.5% gold loading on two metal oxide types was prepared by co-precipritation method at same conditions used in Rattanachatchai's work as described in Chapter III.

4.1.1 Actual Gold Loadings of Prepared Catalysts

The actual amounts of gold loading in all prepared catalysts were determined by Atomic Absorption Spectroscopy. Table 4.1 shows the

Table 4.1 The actual amounts of gold loading in all prepared catalysts.

Support	Calcination temperature ($^{\circ}$C)	Wt.% of gold content		
		Prepared value	Actual value	Rattanachatchai's value
NiO	500	0.5	0.12	0.12
Y_2O_3	300	0.5	0.12	0.18
	400	0.5	0.12	0.19
	500	0.5	0.12	0.18
	600	0.5	0.12	-

comparison between the expected values and the actual values of gold contents in all gold catalysts with different supports prepared by co-precipitation method.

Surprisingly, it was found that the actual values of gold contents were much lower than the prepared values. Similar results were also found in Rattanachatchai's work (2000). In this study, the actual values of gold loadings were approximately the same at ~0.12 %. All studied catalysts had the actual values of gold content lower than the expected value because of the hygroscopic property of hydrogen tetrachloroaurate trihydrate, the precursor of gold catalysts. During the weighing step, hydrogen tetrachloroaurate trihydrate adsorbed water molecules rapidly from the atmosphere. So the original values from weighing were higher than the actual values. In addition, the washing step also contributed to a considerable loss of gold. An amount of gold was washed out by hot distilled water for several times.

4.1.2 The BET Surface Areas of Prepared Catalysts

The BET surface areas of the gold-doped oxide catalysts prepared at different calcination temperatures using co-precipitation method and two types of supports are shown in Table 4.2. The results obviously indicated that the BET surface areas of NiO and Y_2O_3 calcined at $500^{\circ}C$ decreased substantially when gold (0.12%) was added to the catalysts. A possible explanation for the decrease in the total surface area when adding gold to metal oxide was that the loaded gold covered some surface of the supports, hence resulting in the decrease of the total BET surface areas.

Table 4.2 The BET surface areas of NiO, Y_2O_3, 0.12% Au/NiO and 0.12% Au/Y_2O_3 catalysts prepared by co-precipitation method.

Sample	BET surface areas of catalysts at different calcination temperatures (m^2/g)			
	300°C	400°C	500°C	600°C
NiO	-	-	34.28	-
Au/NiO	-	-	27.02	-
Y_2O_3	-	-	80.17	-
Au/Y_2O_3	66.47	43.59	57.75	82.6

As shown in Figure 4.1, the BET surface area of 0.12% Au/Y_2O_3 decreased when calcination temperature increased from 300°C to 400°C. On the other hand, when calcination temperature increased from 400°C to 500°C and 600°C, the BET surface area increased. The reason of this unusual phenomenon will be explained later with the results of the phase transfer obtained from XRD and TGA studies.
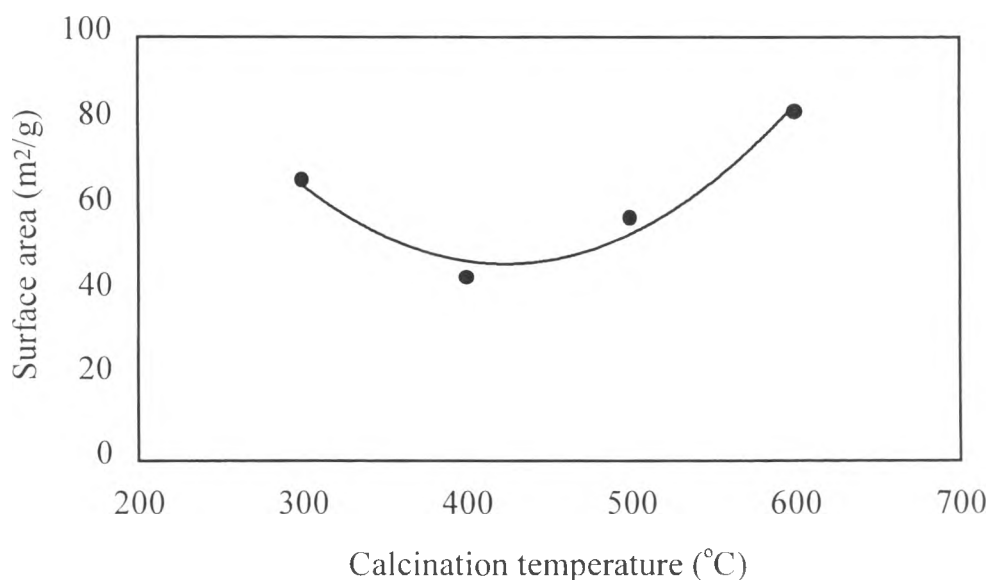

Figure 4.1 BET surface areas of 0.12% Au/Y_2O_3 at different calcination temperatures.

4.1.3 X-ray Diffraction Patterns

X-ray diffraction analysis was carried out for 0.12% Au/Y$_2$O$_3$ calcined at different temperatures in order to study the phase transfer of yttrium oxide compounds. The XRD patterns of the catalysts with different calcination temperatures are illustrated in Figure 4.2. It was noticed that Au/Y$_2$O$_3$ catalyst calcined at 300 and 400°C had broader peaks and noisier signals than those calcined at 500 and 600°C. It can be implied that yttrium oxide crystals calcined at 300 and 400°C were smaller than those calcined at 500 and 600°C because the crystalline size is inversely proportional to the peak width. In other words, the noisier peak is the result of the smaller crystal size.
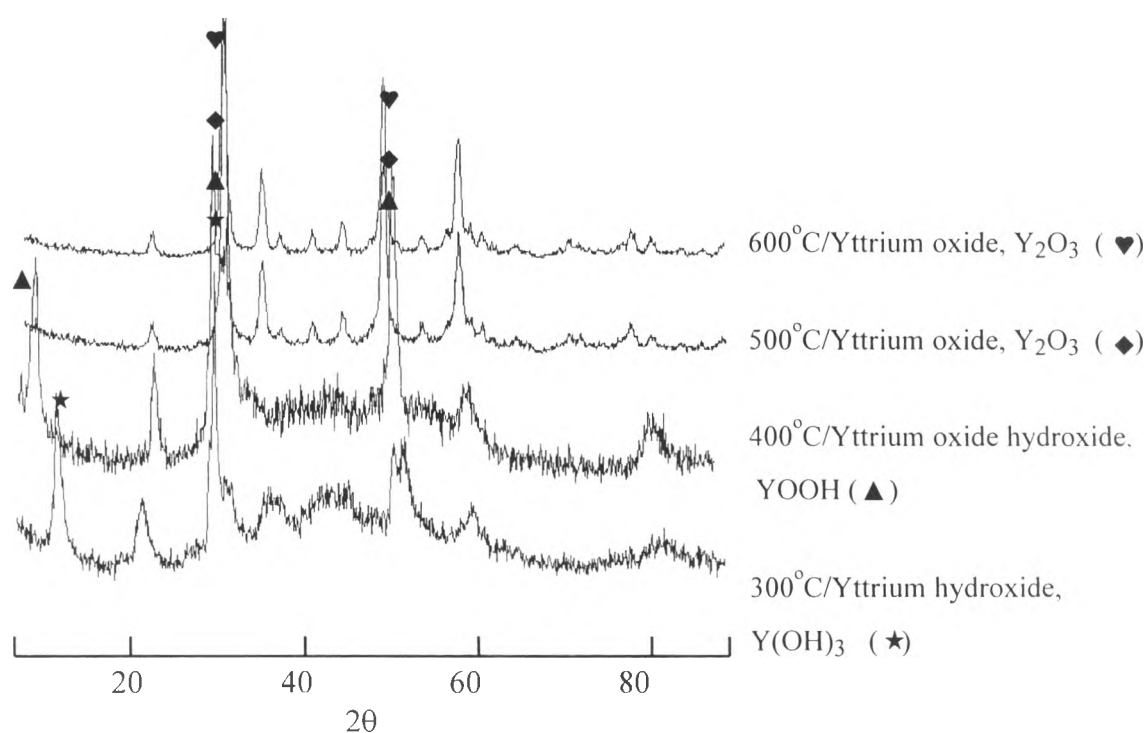

Figure 4.2 XRD patterns of a series of 0.12% Au/ Y$_2$O$_3$ having different calcination temperatures.

To confirm this assumption, crystalline sizes of yttrium compounds at different calcination temperatures calculated by Debye-Scherrer equation are shown in Figure 4.3. When comparing Figure 4.3

with Figure 4.1, the plots of crystalline sizes and surface areas gave the same trends. The crystalline sizes decreased from 0.31 nm to 0.19 nm when calcination temperatures increased from 300°C to 400°C. In addition, when calcination temperatures increased from 400°C to 600°C, the crystalline sizes increased from 0.19 nm to 0.24 nm.

XRD also provided the data of the crystalline structure of yttrium oxide compounds from the library software of XRD equipment. Yttrium oxide compounds calcined at 300°C had more amorphous phase and were referred to as yttrium hydroxide, $Y(OH)_3$, in the simple hexagonal form. When increasing calcination temperature to 400°C, yttrium hydroxide, $Y(OH)_3$, changed the crystalline structure to yttrium oxide hydroxide, YOOH, which is in a simple monoclinic form. From 400 to 500°C, yttrium oxide hydroxide, YOOH, was converted to yttrium oxide, Y_2O_3, with the body-centered cubic form.
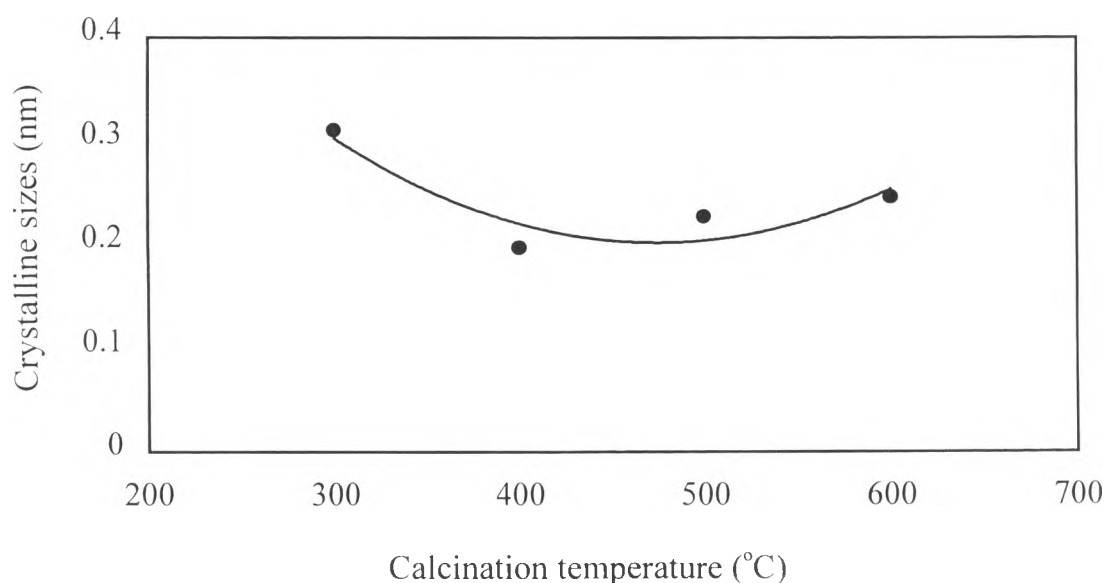

Figure 4.3 Crystalline sizes of 0.12% Au/Y_2O_3 at different calcination temperatures.

In addition, no peak of gold was detected. It was believed that the crystal size of gold might be too small to be detected by XRD.

4.1.4 Results of Thermalgravimetric Analysis (TGA)

In order to determine the phase transfer of yttrium oxide, TGA technique was employed to measure the weight loss with increasing temperature. Figure 4.4 illustrated the TGA profile of 0.12% gold loaded onto yttrium precipitate before calcination. Three main temperature domains could be distinguished: ambient temperature to 200°C, 200-300°C, and 300-600°C. The first peak of the weight loss observed up to 200°C should be due to the removal of the water adsorbed on yttrium precipitate. Between 200 and 300°C, the removal of nitrate and water from yttrium nitrate hydroxide hydrate ($Y_6(NO_3)_8O(OH)_8 \cdot 16H_2O$), which was the precursor of the yttrium oxide determined by XRD, to yttrium hydroxide ($Y(OH)_3$) took place. According to XRD results described before, the phase transfer occurred during 300-600°C as shown by the water release from yttrium compounds.
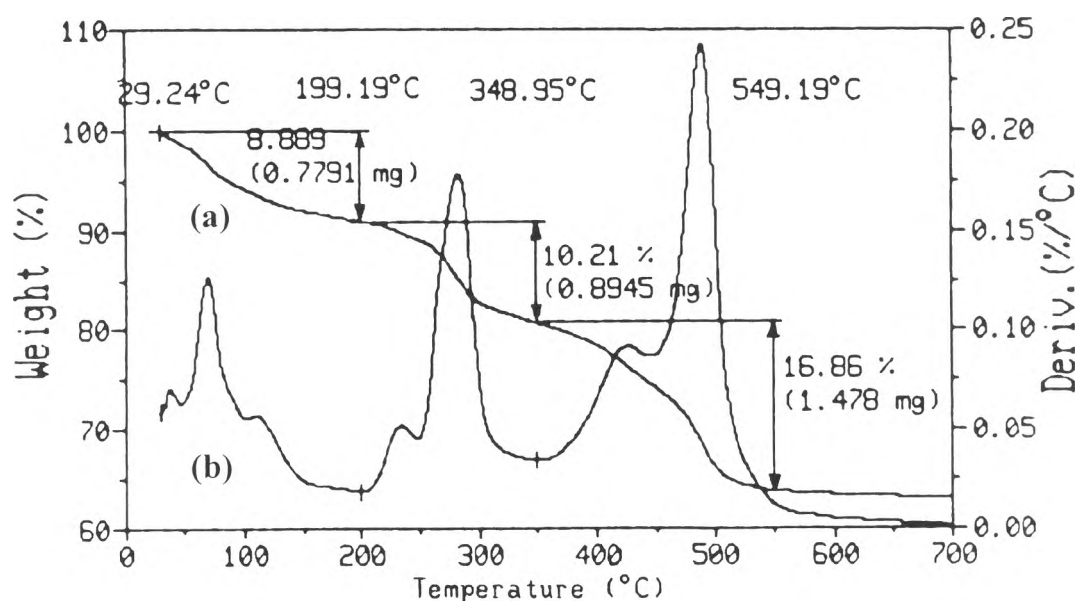

Figure 4.4 TGA profile of the 0.12% Au/Y_2O_3; (a) weight loss, and (b) differential weight loss.

Above 300°C, yttrium hydroxide was firstly converted to yttrium oxide hydroxide (YOOH) as shown in a little peak. The highest peak of the weight loss was at 500°C which was resulted from the water loss from the transformation of yttrium oxide hydroxide (YOOH) to yttrium oxide (Y_2O_3).

In conclusion, this phase transfer supports the explanation of the unusual change of the surface area upon increasing calcination temperatures from 300 to 600°C.

4.2 Catalytic Activity of Prepared Gold Catalysts

4.2.1 Carbon Monoxide Oxidation

4.2.1.1 The effect of Calcination Temperature

The catalytic activity of 0.12% Au on yttrium oxides for carbon monoxide oxidation at 300°C was studied under a range of calcination temperatures. Four calcination temperatures of 300, 400, 500 and 600°C, were studied. The results of the catalytic activity are presented in Table 4.3, in which the data from XRD and BET surface area results are also included. The catalyst calcined at 300°C gave carbon monoxide conversion of 94.97%. As explained before, yttrium hydroxide was formed at this calcination temperature. Carbon monoxide conversion reached a maximum of ~100% when the catalyst was calcined at 400°C (yttrium oxide hydroxide form) and at 500°C (mixture of yttrium oxide hydroxide and yttrium oxide). For the catalyst calcined at 600°C (yttrium oxide form), the conversion of carbon monoxide obviously decreased to 67.27%. The results showed a significant of crystalline structure with different calcination temperatures on the catalytic activity. It can be concluded that yttrium oxide hydroxide gave very high catalytic activity of carbon monoxide oxidation. On the other hand, yttrium oxide, calcined at 600°C, gave the lowest conversion. From the TGA data shown in Figure 4.4, it can be seen that yttrium oxide compounds was continuously losing water from

yttrium oxide hydroxide to become yttrium oxide in a temperature range between 400 and 600°C. In the phase transition of yttrium oxide compounds at 500°C, the compound structure should be a mixture between yttrium oxide hydroxide and yttrium oxide. The mixture of these two forms of yttrium compounds still kept the high conversion of carbon monoxide. Furthermore, the relationship between the BET surface area and the catalytic activity indicated that carbon monoxide conversion increased with decreasing surface area.

Table 4.3 The effect of calcination temperatures of 0.12% Au/Y_2O_3 on carbon monoxide oxidation at 1%CO in air with SV = 2.1×10^4 ml/h g_{cat}.

Calcination temperature (°C)	Crystalline structure of yttrium[a]	BET surface area (m^2/g)	Carbon monoxide conversion (%)
300	Yttrium hydroxide ($Y(OH)_3$)	66.47	94.97
400	Yttrium oxide hydroxide (YOOH)	43.59	100.00
500	Yttrium oxide hydroxide and yttrium oxide (YOOH and Y_2O_3)	57.75	99.98
600	Yttrium oxide (Y_2O_3)	82.60	67.27

[a] XRD results.

4.2.1.2 Effect of Gold Loading on CO Oxidation

Au/NiO and Au/Y_2O_3 with a range of gold loading ~0.1-0.2%, calcined at 500°C, were investigated for the oxidation of carbon monoxide at 200 and 300°C respectively. The reaction temperatures for each

gold catalyst were varied in order to determine the optimum temperature that gave the highest conversion. From Table 4.4, an addition of gold onto NiO resulted in increasing CO conversion from 37.76 to 80.60%. However, an increase in the gold loading from 0.12 to 0.26% led to a decrease in CO conversion. Surprisingly, in the case of Y_2O_3, CO conversion increased extremely from 0 to 100% when adding gold onto yttrium oxide with the gold loading in the range 0.12% to 0.23%. When comparing the catalytic activity of the two metal oxides of gold catalysts, interesting result was found.

Table 4.4 The effect of gold loading on NiO and Y_2O_3, calcined at 500°C on carbon monoxide oxidation at 1%CO in air with SV = 2.1×10^4 ml/h g_{cat}.

Metal oxide	Au (wt.%)	Surface area (m²/g)	Carbon monoxide conversion (%)
NiO[a]	0.00	34.28	37.76
	0.12	27.02	80.60
	0.26[c]	35.18	63.02
Y_2O_3[b]	0.00	80.17	0.00
	0.12	57.88	100.00
	0.23[c]	38.46	100.00

[a] 200°C, 1%CO in air.

[b] 300°C, 1%CO in air.

[c] gold catalysts from Rattanachatchai (2000).

The result was that pure NiO had a very low conversion of 37.76% for CO oxidation while pure Y_2O_3 was absolutely inactive for CO oxidation. Loading gold onto NiO with 0.12% did not increase the CO conversion as much as the case of the same gold loading onto Y_2O_3. When adding gold onto NiO, conversion increased from 37.76 to 80.60%. However, adding gold onto Y_2O_3 gave a dramatic effect on the catalytic activity as demonstrated in the conversion of carbon monoxide from 0 to 100%. At higher gold loadings, when the gold loading was increased to 0.26% in NiO, CO conversion decreased to 63.02%. On the other hand, Y_2O_3 was still active to give 100% CO conversion when the gold loading was increased to 0.23%.

When taking the BET surface area values into account, a higher gold loading in Y_2O_3 led to a general decrease in the surface area and an increase in the activity. In fact, no correlation had been found in gold content, surface area and carbon monoxide conversion of NiO. However, the results indicated that 0.12% gold loading for both supports was the optimum loading for carbon monoxide oxidation in a range of low gold loadings.

4.2.1.3 The Effect of Reaction Temperature on CO Oxidation

In order to study the effect of metal oxides on gold catalysts, which was demonstrated by comparing their light-off temperatures, a low gold loading range was chosen to prevent the interference from the gold loading effect. Gold content at 0.12% was selected for both metal oxide types since this gold loading was the optimum point of carbon monoxide conversion in both NiO and Y_2O_3. From the XRD result, the calcination temperature of 500°C was selected to assure that nickel and yttrium were in the structure of metal oxides. Yttrium, in particular, was changed from metal hydroxide to metal oxide at around 500°C. Nickel and yttrium were prepared in the same manner to compare the effect of metal oxide type on the catalytic activity.
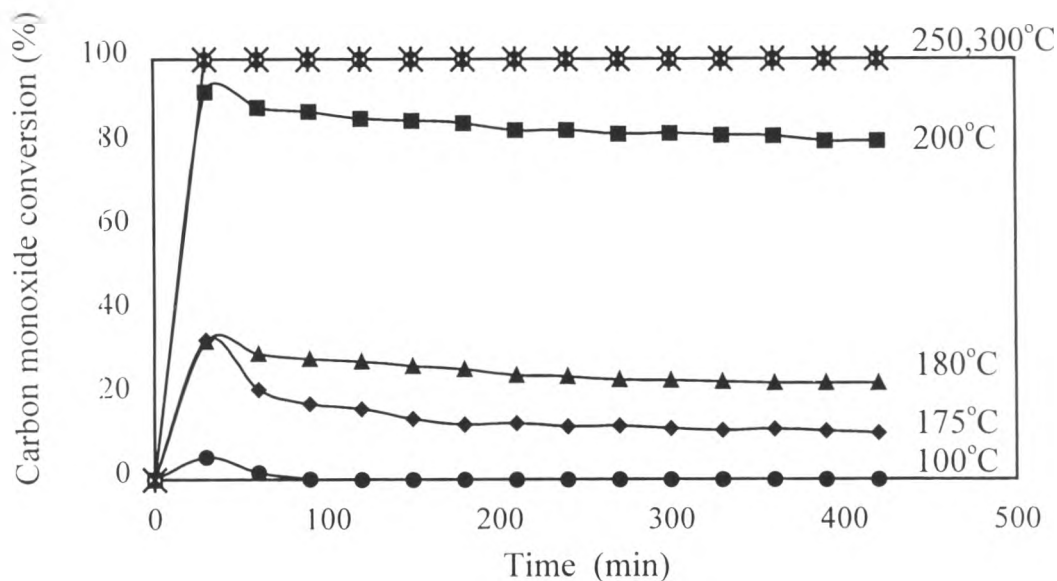
Figure 4.5 Carbon monoxide conversion as a function of time on 0.12% Au/NiO at different oxidation temperatures, using 1%CO in air with SV = 2.1×10⁴ ml/h g_cat.
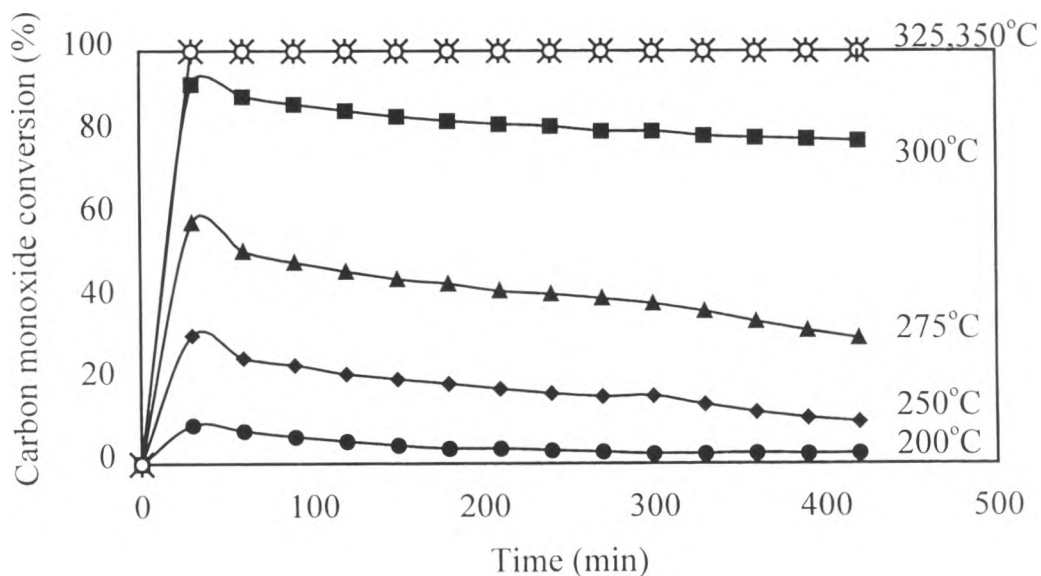

Figure 4.6 Carbon monoxide conversion as a function of time on 0.12% Au/Y₂O₃ at different oxidation temperatures, using 1%CO in air with SV = 2.1×10⁴ ml/h g_cat.

Carbon monoxide conversions of 0.12% Au/NiO and 0.12% Au/Y_2O_3, calcined at 500°C, at different oxidation temperatures with respect to time are shown comparatively in Figures 4.5-4.6. Carbon monoxide conversion of 0.12% Au/NiO at 100-200°C initially increased and then decreased until it reached the steady state at approximately 200 min. Initially carbon monoxide conversion increased until reaching a maximum because the catalysts were still fresh. At low temperatures, CO oxidation showed low conversion at steady state because the chemical kinetic dominated to the reaction. For the reaction temperature higher than 250°C, the complete conversion of CO oxidation was achieved after ten minutes of reaction time and the high activity maintained throughout the study time. A similar result of Au/Y_2O_3 was found except for the reaction temperatures ranging from 200-300°C where the continuous decay of carbon monoxide conversion was found when time increased. The constant decrease in carbon monoxide conversion may be resulted from carbon monoxide acting as a poison by blocking the active sites of Au/Y_2O_3. At higher reaction temperatures, 250-300°C for Au/NiO and 325-350°C for Au/Y_2O_3, the effect of heat transfer and pore diffusion were so important during the initial period that it gave a steep line of the increasing carbon monoxide conversion. At reaction temperatures greater than 325°C, Au/Y_2O_3 did not show a decline of carbon monoxide conversion since the heat transfer and the pore diffusion overcame the effect of carbon monoxide poisoning on the material.

Figure 4.7 illustrates the carbon monoxide conversion at different oxidation temperatures on Au/NiO and Au/Y_2O_3. The results showed the relationship between carbon monoxide conversion at steady state and the reaction temperature. The reaction temperature at the conversion of 50 % is called the light-off temperature. Carbon monoxide oxidation occurred when the reaction temperature exceeded 100°C on Au/NiO and 200°C on Au/Y_2O_3. The effect of pore diffusion was found in the temperature

range of $180\text{-}200^{\circ}C$ on Au/NiO and $275\text{-}300^{\circ}C$ on Au/Y_2O_3. The range of the reaction temperatures of $200\text{-}300^{\circ}C$ on Au/NiO and $300\text{-}350^{\circ}C$ on Au/Y_2O_3 was the mass transfer limit. The light-off temperature of Au/NiO, $185^{\circ}C$, was significantly lower than that of Au/Y_2O_3, $265^{\circ}C$. The temperatures for 100% carbon monoxide conversion were $250^{\circ}C$ for Au/NiO and $325^{\circ}C$ for Au/Y_2O_3. For CO oxidation, the result indicated that NiO was a much better support than Y_2O_3.

Figure 4.8 illustrates the Arrhenius plots of the oxidation of carbon monoxide by Au/NiO and Au/Y_2O_3. The reaction rates were measured at the carbon monoxide conversion less than 15%, at which the bulk mass transfer resistance was found negligible. The reaction rates were calculated under the conditions of a fixed-bed reactor in the presence of excess oxygen and on the assumption that the reaction rate was independent of the concentrations of carbon monoxide and oxygen (Haruta *et al.*, 1993). From Fig.4.8, the activation energy of 7.241 kCal/mole for Au/NiO, was lower than that of 15.852 kCal/mole for Au/Y_2O_3. The lower activation energy of Au/NiO agreed with the lower light-off temperature when compared to those of Au/Y_2O_3.

4.2.2 Methanol Oxidation

The relationship between methanol conversion and time at different oxidation temperatures are shown in Figures 4.9 and 4.10 for gold supported on NiO and Y_2O_3 respectively. For both catalysts, the times required to achieve the steady state were about 200 min when the reaction temperatures did not exceed $250^{\circ}C$. At low temperatures, methanol conversion firstly increased and then decreased until it reached the steady state. This was because at low temperatures, only the chemical kinetic effect dominated. The catalyst was fresh initially, so the conversion was slightly higher than that at the steady state when some fraction of the catalyst's surface was covered permanently by methanol.
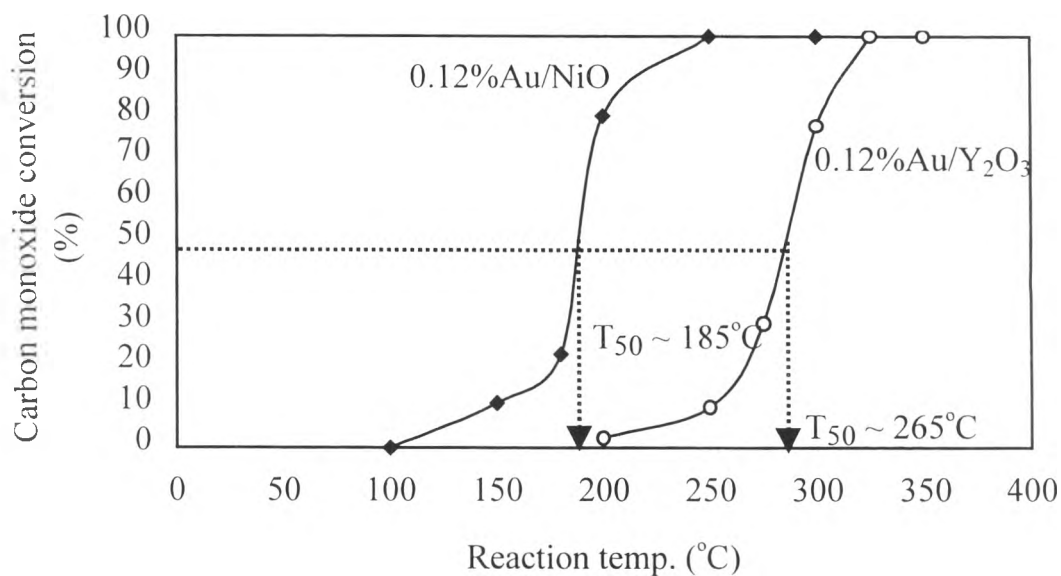
Figure 4.7 Carbon monoxide conversion as a function of reaction temperature on 0.12% Au/NiO and 0.12% Au/Y_2O_3 using 1%CO in air with SV = 2.1×10^4 ml/h g_{cat}.
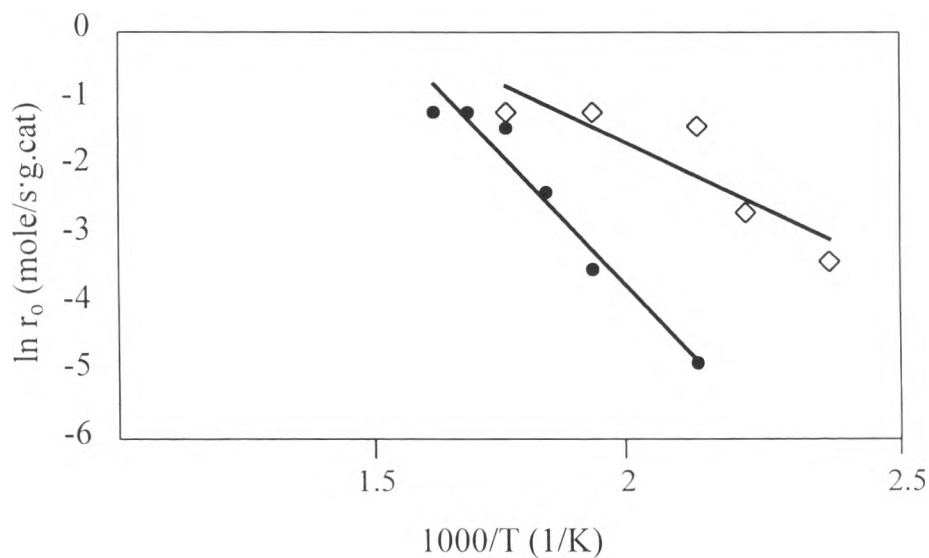

Figure 4.8 Arrhenius plots for 0.12% Au/NiO and 0.12% Au/Y_2O_3 using 1%CO in air with SV = 2.1×10^4 ml/h g_{cat}.
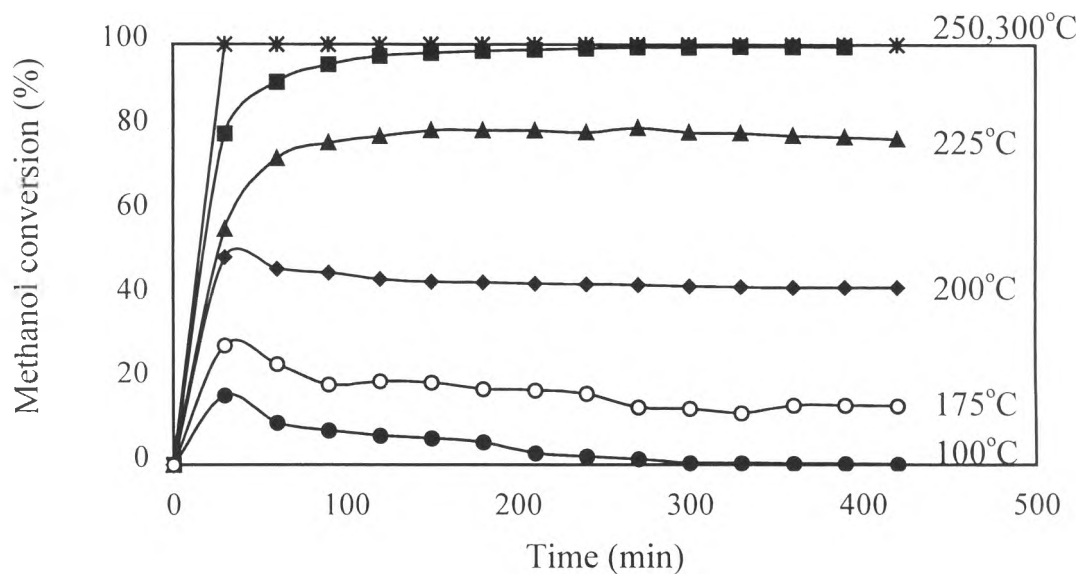
Figure 4.9 Methanol conversion as a function of time on 0.12% Au/NiO at different oxidation temperatures using 5,000 ppm of methanol with SV = 2.1×10⁴ ml/h g_{cat}.
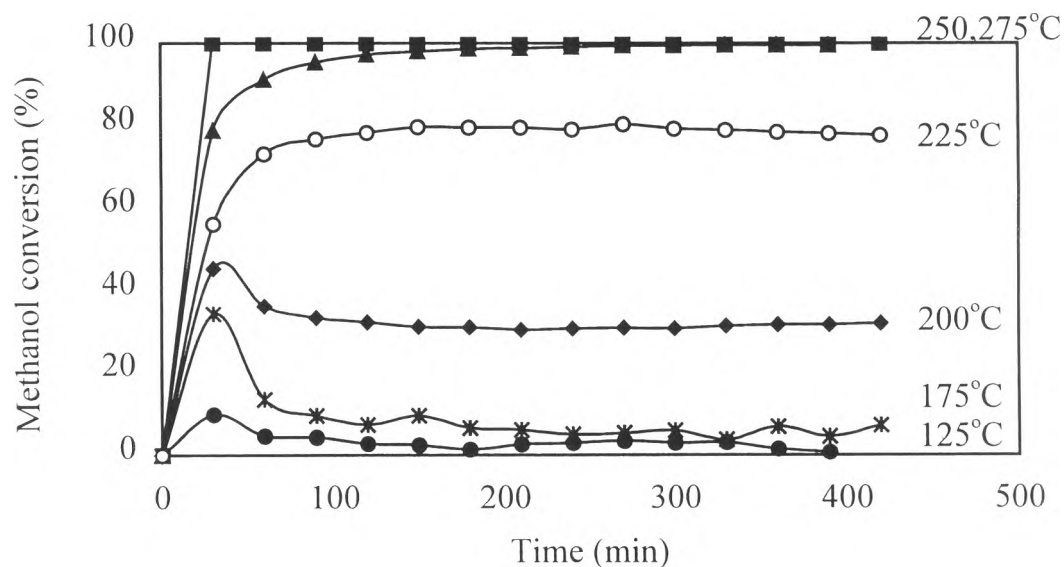

Figure 4.10 Methanol conversion as a function of time on 0.12% Au/Y₂O₃ at the different oxidation temperatures using 5,000 ppm of methanol with SV = 2.1×10⁴ ml/h g_{cat}.

In contrast, at high temperatures greater than 225°C, methanol conversion initially increased as a function of time and then leveled off. At high temperatures, the reaction reached the appropriate condition and the effects of heat transfer and pore diffusion were so significant that it resulted in a higher conversion of methanol. The freshness of catalyst was not important in comparison with the mass and heat transfer or pore diffusion effect at high temperatures. As a consequence, the conversion did not decrease with time at steady state at higher temperatures.

Figure 4.11 illustrates methanol conversion as a function of reaction temperature on Au/NiO and Au/Y$_2$O$_3$. It showed a similar trend of the relationship between methanol conversion at steady state and the reaction temperature for both catalysts. The light-off temperature of 206°C for Au/NiO was slightly lower than that of 211°C for Au/Y$_2$O$_3$. Although at low temperatures, Au/NiO gave slightly higher methanol conversion than that found in Au/Y$_2$O$_3$, however, when the temperature was greater than 225°C, methanol conversions of both catalysts were the same.
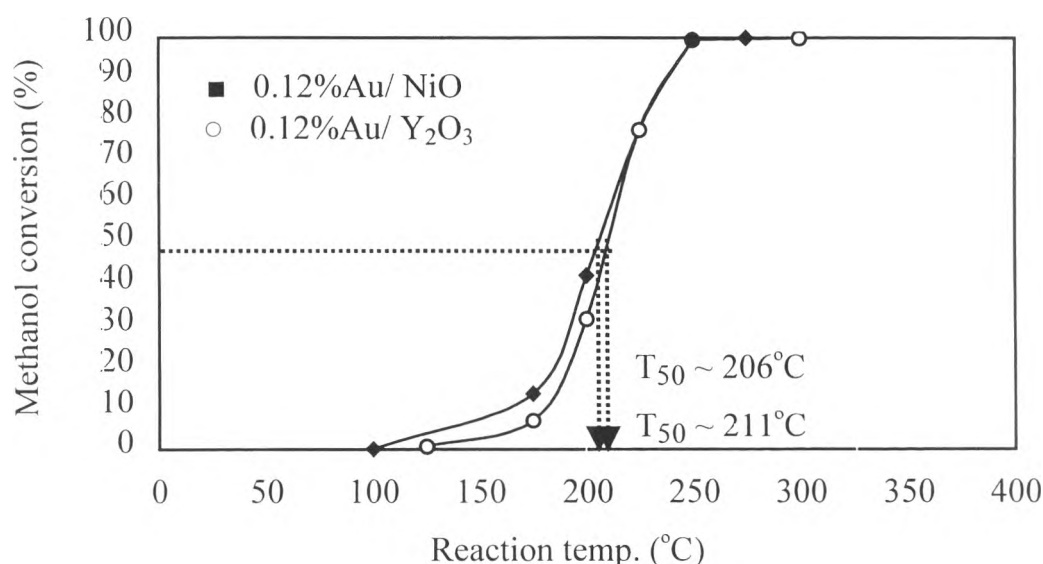

Figure 4.11 Methanol conversion on as a function of reaction temperature 0.12% Au/NiO and 0.12% Au/Y$_2$O$_3$ using 5,000 ppm of methanol with SV = 2.1×10^4 ml/h g$_{cat}$.

At low temperatures of methanol oxidation, an unknown by-product was observed from signal of gas chromatography (GC) by FID detector. From checking standard substances by GC to find the unknown by-product, it was neither formaldehyde (HCOH) nor formic acid (HCOOH). Few possible by-products, which were reported in literature of methanol oxidation, may be methyl formate (HCOOCH$_3$) (Sukjit, 1999) or dimethyl ether (CH$_3$OCH$_3$) (Li *et al.*, 2000) as shown in Equations 4.1 and 4.2, respectively.

$$2CH_3OH + O_2 \longrightarrow HCOOCH_3 + 2H_2O \qquad (4.1)$$

$$2CH_3OH \longrightarrow CH_3OCH_3 + H_2O \qquad (4.2)$$

Since no by-product was detected at high temperatures, the reaction should be a complete combustion as follows (Equation 4.3).

$$2CH_3OH + 3O_2 \longrightarrow CO_2 + 2H_2O \qquad (4.3)$$