

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Catalyst Characterization

This section shows the catalyst characterization results of Au/TiO₂ with different preparation methods and metal loadings.

4.1.1 BET Surface Area

Surface area, total pore volume and average pore size results of prepared catalysts by deposition-precipitation method Degussa P-25 (DP1) are given in Table 4.1. The surface area was dependent on the initial surface area of support. Moreover, it also depended on the percentage of metal Au loading and calcination temperature. However, the variations were only 10%.

Table 4.1 Surface area of Au/TiO₂ catalysts prepared by DP1 method

Catalyst	Calcination Temperature (°C)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)
TiO ₂	–	61.95	20.75	0.32
0.5%Au	300	60.45	35.85	0.54
1.0%Au	300	59.40	39.17	0.58
3.0%Au	300	57.69	38.96	0.56
5.0%Au	300	57.74	36.38	0.53
0.5%Au	400	58.45	26.68	0.39
1.0%Au	400	59.12	38.49	0.56
3.0%Au	400	56.99	37.38	0.53
5.0%Au	400	55.38	36.44	0.54
1.0%Au +Mg citrate	400	59.29	36.44	0.54

As shown in Table 4.1, the BET surface area ranged from 55.38 to 61.95 m²/g. The BET surface area showed a slight decrease with increasing the percentages of Au loading. Moreover, the calcination temperature had a slight effect on the surface area. The BET surface area decreased with increasing in the calcination temperature. Total pore volume and average pore size changed slightly but there was no definite trend. The attempt to make Au more dispersed by adding Mg citrate into the catalyst preparation step was also not significant.

Table 4.2 presents the BET surface area, total pore volume and average pore size of prepared catalysts by deposition-precipitation method Sigma (DP2) showed the important role in initial surface area of support. The BET surface area remained the same with increasing in calcination temperature.

Table 4.2 Surface area of 1%Au/TiO₂ catalysts prepared by DP2 method

Catalyst	Calcination Temperature (°C)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)
TiO ₂	–	11.56	18.42	0.05
1.0%Au	300	11.42	20.26	0.08
1.0%Au	400	11.38	21.60	0.06

Table 4.3 lists the BET surface area, total pore volume and average pore size of prepared catalysts by ISG method as a function of calcination temperature. The BET surface area decreased while the average pore size increased with increasing in calcination temperature. This can be explained by sintering of at high temperature resulting in a decreased surface area. It is also possible that the agglomerated the Au crystallites blocked some of the pores of the support.

Table 4.3 Surface area of 1%Au/TiO₂ catalysts prepared by ISG method

Catalyst	Calcination temperature (°C)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)
TiO ₂ (SG)	400	109.00	5.61	0.153
1.0%Au	300	102.90	5.73	0.147
1.0%Au	400	86.62	6.70	0.145
1.0%Au	600	36.98	12.86	0.012

The BET surface area, total pore volume and average pore size of prepared catalysts by ISG method with different percentages of Au loading at the calcination temperature of 300°C are illustrated in Table 4.4. At higher Au loading, surface area showed a slight decrease.

Table 4.4 Surface area of Au/TiO₂ catalysts prepared by ISG method

Catalyst	Calcination temperature (°C)	Surface area (m ² /g)	Pore size (nm)	Pore volume (cc/g)
TiO ₂ (SG)	400	109.00	5.61	0.153
0.5%	300	105.90	5.75	0.152
1.0%	300	102.90	5.73	0.147
3.0%	300	102.00	5.38	0.137

4.1.2 X-ray Diffraction (XRD)

X-ray diffraction analysis was carried out for all catalysts. Figures 4.1 and 4.2 show the XRD patterns of Au/TiO₂ prepared by DP1 method at different percentages of Au loading at calcination temperatures of 300 and 400°C, respectively. Generally, there are three different forms of TiO₂ namely anatase, rutile and brookite. For the XRD patterns of TiO₂, the main peaks at $2\theta = 25.3^\circ$, 27.5° and 30.6° are for anatase, rutile and brookite, respectively. For the TiO₂ Degussa P-25, the peak ($2\theta=25.28^\circ$) of anatase and the peak ($2\theta=27.42^\circ$) of rutile phases were

observed (Farrell, 2001). The major phase is anatase and rutile exists as the minor phase. It was found that intensity of Au peaks increased with increasing percentage of Au loading.

Figure 4.3 presents the XRD patterns of 1%Au/TiO₂ prepared by DP1 method at calcination temperature of 300 and 400°C. The anatase and rutile forms of titania were observed. The position of XRD peaks 2θ of the both samples were almost the same but peak intensity of the sample was decreased with decreasing calcination temperature. It was observed that the calcination temperature increased, peak of titania becomes sharper and thinner because the sample has become more crystalline and had a larger crystallite size due to agglomeration at the higher temperature. There was no evidence of metallic Au on the titania surface, indicating that Au crystallite size was smaller than 5 nm and was well dispersed on the support.

Figure 4.4 shows the XRD patterns of 1%Au/TiO₂ prepared by DP1 catalyst with adding Mg citrate as a promoter at calcination temperature of 400°C. The anatase and rutile forms of titania were found. No metallic Au peak was observed. This was due to the fact that the amount Au loading was low.

The XRD patterns of 1%Au/TiO₂ prepared by DP2 method at calcination temperature of 300 and 400°C are given in Figure 4.5. The anatase form of titania was observed. It shows no evidence of metallic Au on the titania surface. It may be assumed that Au was well dispersed on the support.

The XRD patterns of 1%Au/TiO₂ prepared by ISG method at calcination temperature of 300, 400, and 600°C are shown in Figure 4.6. At calcination temperature of 400°C or lower, the same patterns that had only anatase form of titania were found. However, both the anatase and rutile forms were found at calcination temperature of 600°C. The evidence of Au in metallic form on catalyst surface was seen at calcination temperature of 300, 400, and 600°C.

Figure 4.7 exhibits the XRD patterns of Au/TiO₂ prepared by ISG method at different percentages of Au loading at calcination temperature of 300°C. For the XRD patterns of TiO₂, the main peak is anatase form. Furthermore, peaks of Au are observable for 1% and 3%Au loading because evidence that the crystallite size is larger than 5nm.

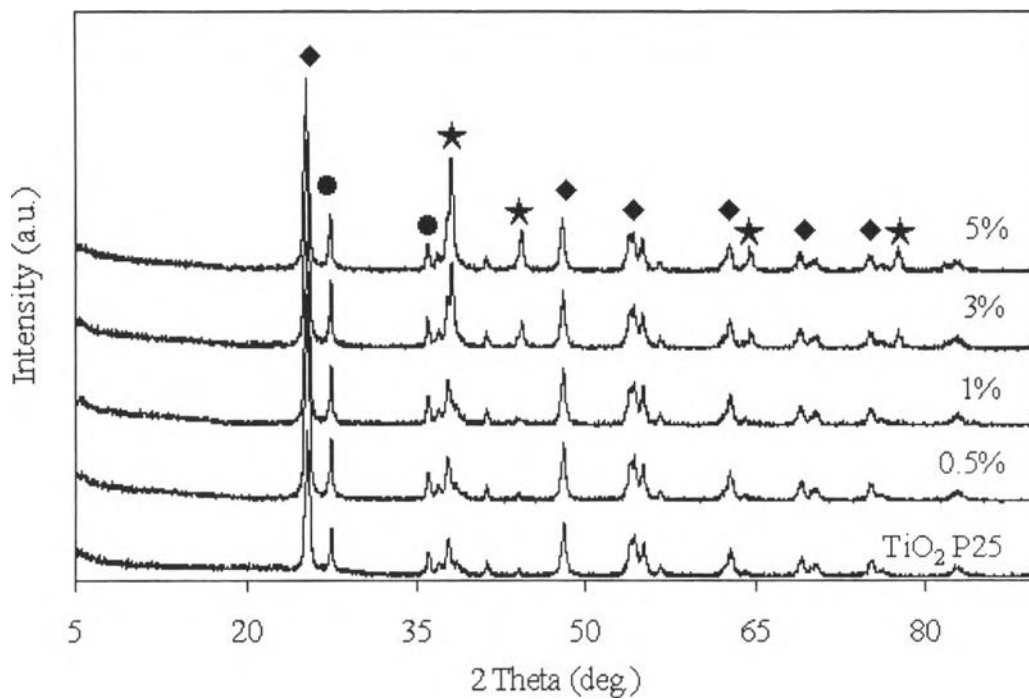


Figure 4.1 XRD patterns of Au/TiO₂ (DP1) catalysts with different Au loading calcined 300°C for 5 h; (◆), Anatase; (●), Rutile; (★), Au.

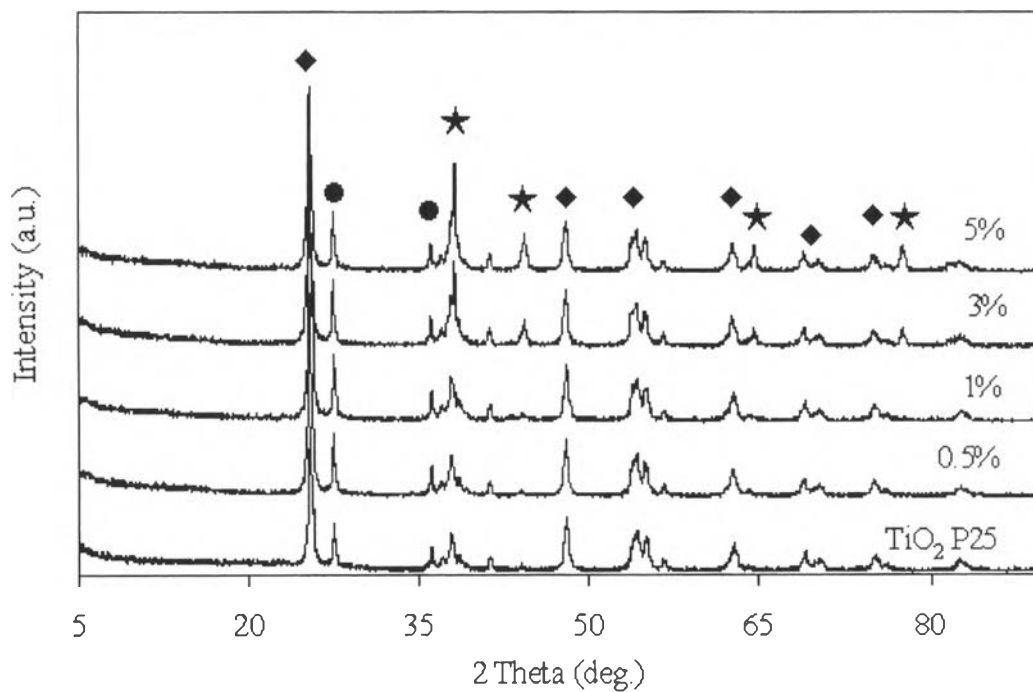


Figure 4.2 XRD patterns of Au/TiO₂ (DP1) catalysts with different Au loading calcined 400°C for 5 h; (◆), Anatase; (●), Rutile; (★), Au.

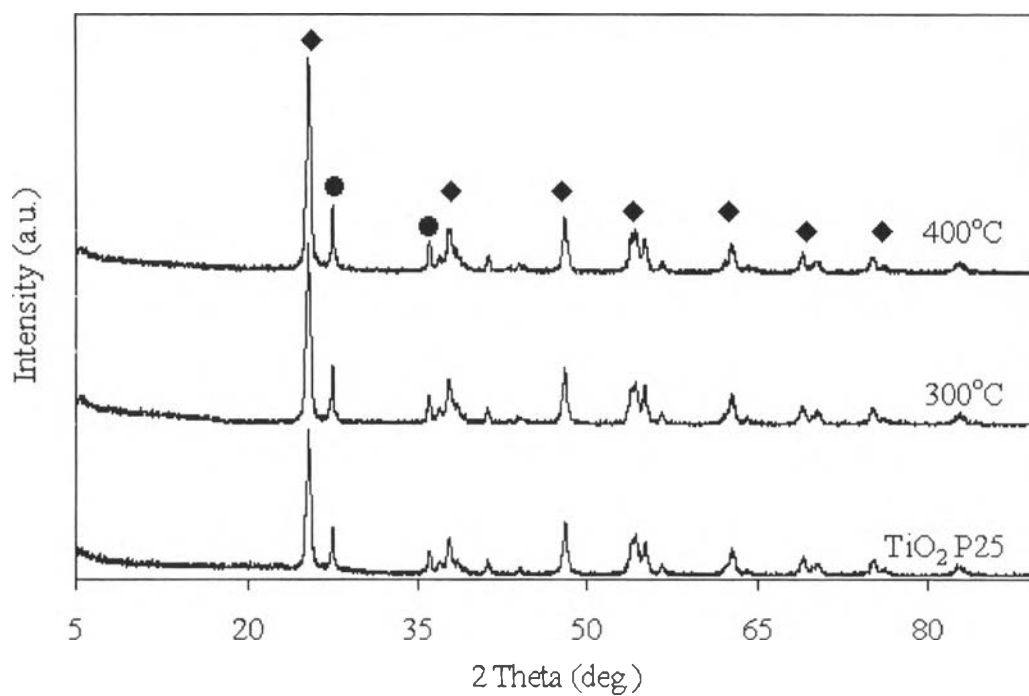


Figure 4.3 XRD patterns of 1%Au/TiO₂ (DP1) catalysts with different calcination temperatures (300 and 400°C for 5 h); (◆), Anatase; (●), Rutile.

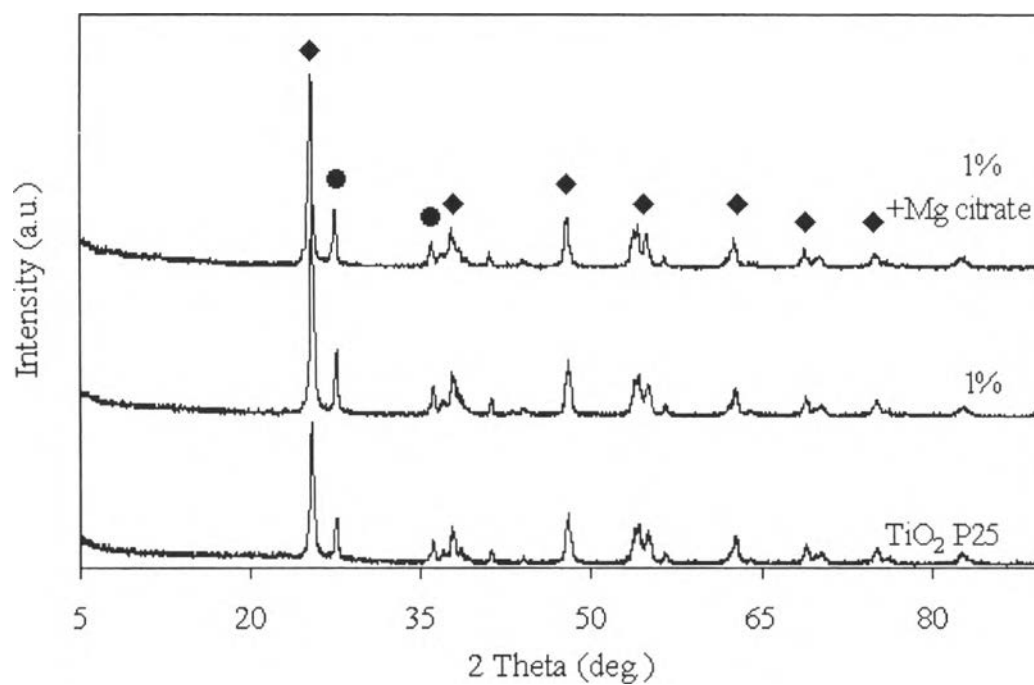


Figure 4.4 XRD patterns of 1%Au/TiO₂ (DP1) and 1%Au/TiO₂ (DP1) with Mg citrate calcined 400°C 5 h; (◆), Anatase; (●), Rutile.

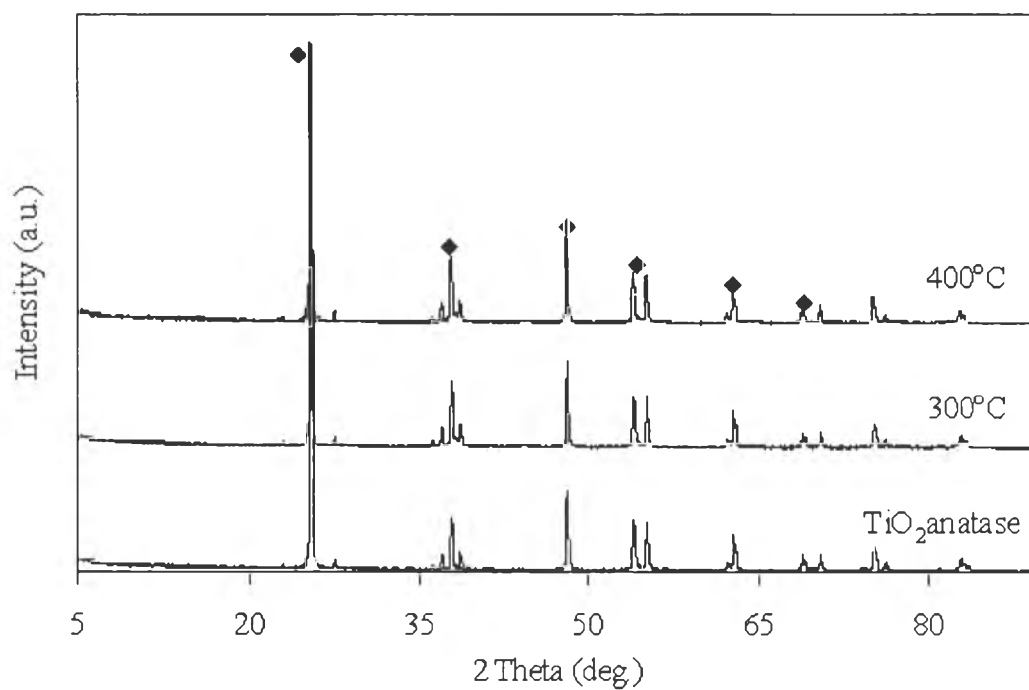


Figure 4.5 XRD patterns of 1%Au/TiO₂ (DP2) catalyst with different calcination temperatures (300 and 400°C for 5 h); (◆), Anatase.

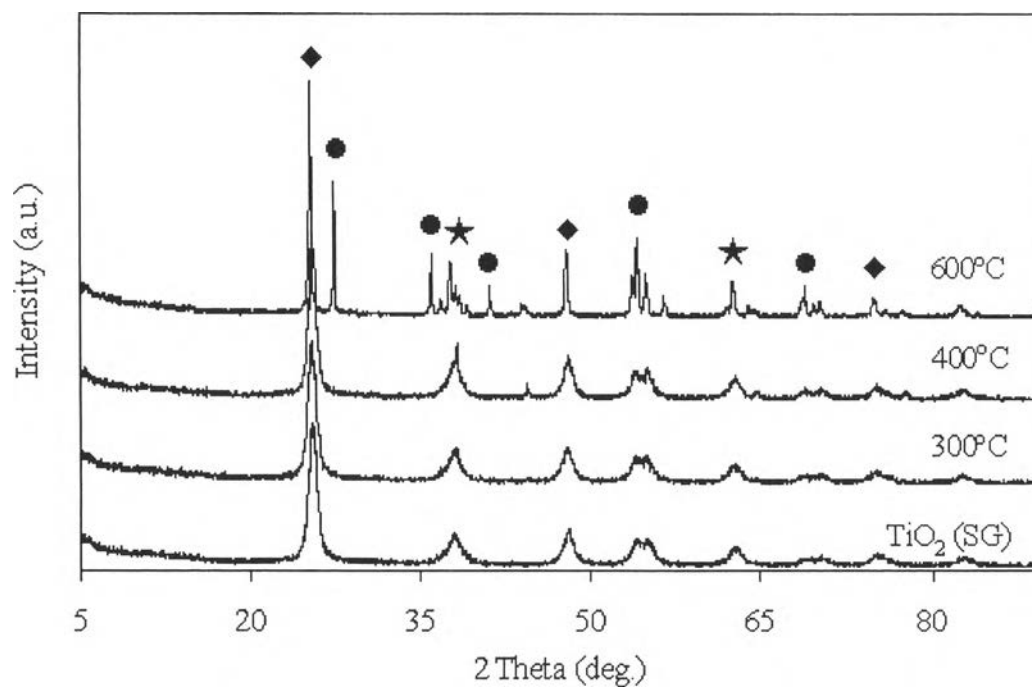


Figure 4.6 XRD patterns of 1%Au/TiO₂ (ISG) catalyst with different calcination temperatures (300, 400, and 600°C for 5 h); (◆), Anatase; (●), Rutile; (★), Au.

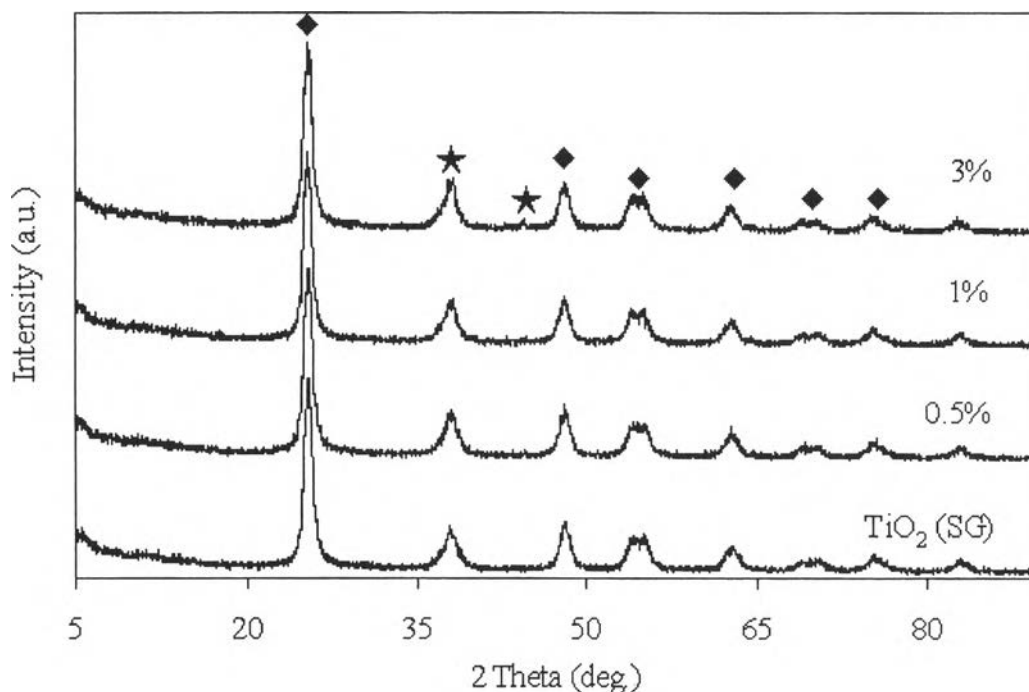


Figure 4.7 XRD patterns of Au/TiO₂ (ISG) catalysts with different Au loading calcined 300°C 5 h; (◆), Anatase; (★), Au.

The XRD patterns were used to estimate the crystallite size of Au by line broadening of Au main peak at $2\theta = 38.2^\circ$ and use of Scherrer's Equation. The crystallite sizes of catalysts prepared by DP1 method are given in Table 4.5. There was no evidence of metallic Au on the titania surface when metal loading was smaller than 3%. This can be either due to the fact that the Au crystallite sizes were smaller than 5 nm or due to the weak signal resulting from the low metal content.

Table 4.6 presents the crystallite sizes of Au catalysts prepared by DP2 method at calcination temperature of 300 and 400°C. It was observed that the Au crystallite size was smaller than 5 nm by XRD characterization.

The crystallite sizes of Au catalysts prepared by ISG method at calcination temperatures of 300, 400, and 600°C are shown in Table 4.7. The crystallite sizes increased with increasing calcination temperature. No evidence of Au peak was obtained with 0.5%Au loading. This can be due to the weak signal of the low metal content and the small crystallite size.

Table 4.5 The crystallite size of Au catalysts prepared by DP1 method

Au loading (%)	Calcination temperature (°C)	Crystallite size of Au from XRD (nm)
0.5	300	Smaller than 5 nm
1.0	300	Smaller than 5 nm
3.0	300	30
5.0	300	33
0.5	400	Smaller than 5 nm
1.0	400	Smaller than 5 nm
3.0	400	31
5.0	400	35
1.0 + Mg citrate	400	Smaller than 5 nm

Table 4.6 The crystallite size of Au catalysts prepared by DP2 method

Au loading (%)	Calcination temperature (°C)	Crystallite size of Au from XRD (nm)
1.0	300	Smaller than 5 nm
1.0	400	Smaller than 5 nm

Table 4.7 The crystallite size of Au catalysts prepared by ISG method

Au loading (%)	Calcination temperature (°C)	Crystallite size of Au from XRD (nm)
0.5	300	Smaller than 5 nm
1.0	300	26
3.0	300	36
1.0	400	28
1.0	600	36

4.1.3 Atomic Absorption Spectroscopy (AAS)

The actual amounts of Au loading in all prepared catalysts were determined by AAS. Table 4.8 shows the comparison between the expected values and the actual values of Au contents in all Au catalysts prepared by DP1 method. Surprisingly, it was found that the actual values of Au contents were much lower than the expected values. The loss of Au metal might be due to the washing step.

Table 4.8 The measured percentages loading of Au/TiO₂ catalysts prepared by DP1 method

Calcination Temperature (°C)	Au loading (%)	Au loading (%) by AAS
300	0.5	0.44
300	1.0	0.91
300	3.0	2.77
300	5.0	4.71
400	0.5	0.42
400	1.0	0.81
400	3.0	2.86
400	5.0	4.33
400	1.0 + Mg citrate	0.95

The measured percentages loading of 1%Au/TiO₂ catalysts prepared by DP2 method with different calcination temperatures are given in Table 4.9. The measured percentages loading of 1%Au/TiO₂ were less than one.

Table 4.10 presents the measured percentages loading of Au/TiO₂ catalysts prepared by ISG method with different calcination temperatures and metal loadings. The measured percentages loading were lower than the required value. The discrepancy may be due to loss of Au metal during the preparation step.

Table 4.9 The measured percentages loading of 1%Au/TiO₂ catalysts prepared by DP2 method

Calcination Temperature (°C)	Au loading (%)	Actual Au loading (%) by AAS
300	1.0	0.89
400	1.0	0.88

Table 4.10 The measured percentages loading of Au/TiO₂ catalysts prepared by ISG method

Calcination Temperature (°C)	Au loading (%)	Actual Au loading (%) by AAS
300	0.5	0.41
300	1.0	0.82
300	3.0	2.30
400	1.0	0.78
600	1.0	0.76

4.1.4 Transmission Electron Microscope (TEM)

Figures 4.8 and 4.9 show TEM micrographs of 1%Au/TiO₂ (DP1) calcined at 300 and 400°C for 5 h, respectively. Au particles grew with increasing calcination temperature. The particle sizes of Au calcined at 300 and 400°C were 3.33 and 4.17 nm, respectively. Moreover, the particle sizes of Au calcined 400°C was observed to be hemispherical in shape. This shape was strongly attached to metal oxide supports at their flat planes and accordingly thermally more stable than spherical particles (Haruta, 1997).

TEM micrograph of 0.5%Au/TiO₂ (ISG) calcined 300°C for 5 h are given in Figure 4.10. The catalyst particles were mostly uniform. The particle size of Au was about 3.75 nm.

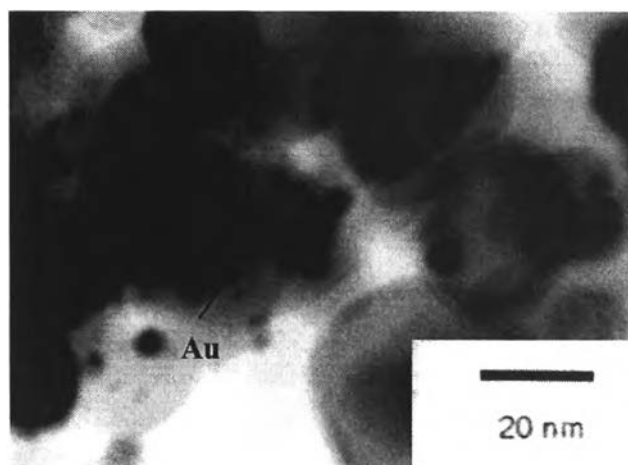


Figure 4.8 TEM micrograph of 1%Au/TiO₂ (DP1) calcined at 300°C for 5 h.

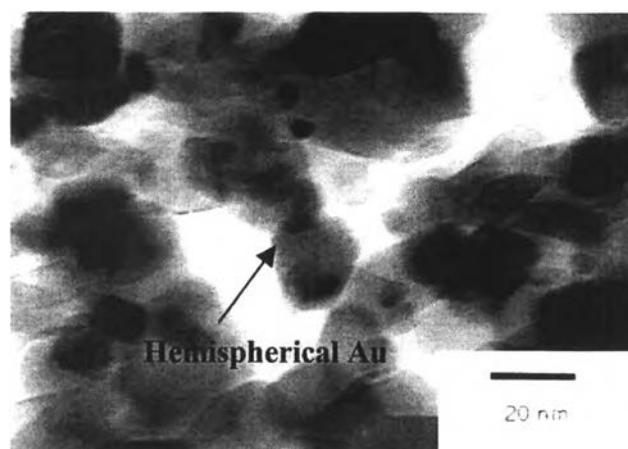


Figure 4.9 TEM micrograph of 1%Au/TiO₂ (DP1) calcined at 400°C for 5 h.

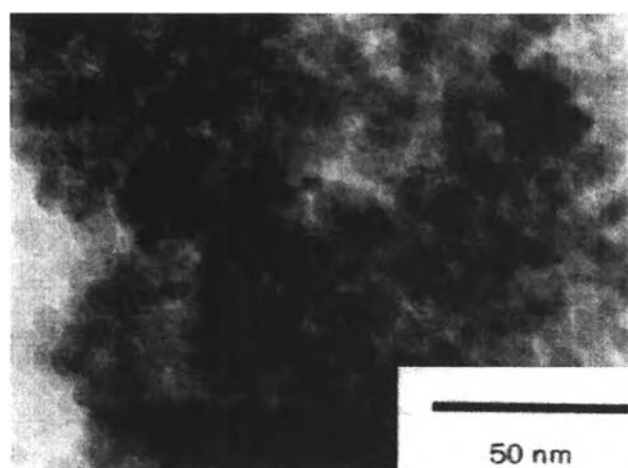


Figure 4.10 TEM micrograph of 0.5%Au/TiO₂ (ISG) calcined at 300°C for 5 h.

4.2 Catalyst Activity Testing

The catalytic activity tests were performed in the fixed bed reactor using 100 mg catalyst at 80-120 mesh in size. The reactant gas contained 1%CO, 1%O₂, 2%CO₂, 2.6%H₂O, and 40% H₂ balance in He at the total flow rate of 50 ml/min (SV=30,000 mlg⁻¹h⁻¹) and at atmospheric pressure.

4.2.1 Effect of Catalyst Pretreatment

The relationship between CO conversion and selectivity versus temperature of 1%Au/TiO₂ catalysts prepared by DP1 method calcined at 400°C for 5 h, tested under different pretreatment procedures (pure O₂, pure H₂, and pure He at 200°C for 2 h) are given in Figures 4.11 (a) and (b). It can be observed that O₂ pretreatment gave higher activity than He and H₂ pretreatment. O₂ pretreatment caused the Au catalyst surface to be O₂ rich as well as stabilizing the oxide bonds to the support. This is in agreement with the findings of Park and Lee (1999).

At low temperature, CO conversion was low because strong adsorption of CO and covered the catalyst surfaces. High coverage of CO, inhibited the dissociative O₂ adsorption and limited the rate of reaction. When the rate of desorption increased with an increase in temperature, CO conversion increased until CO conversion reached maximum. Further increase in temperature decreased CO conversion because rate of H₂ adsorption increased. The selectivity was maximum at low temperature and then slowly decreased with increasing temperature. After this part, pure O₂ pretreatment at 200°C for 2 h was selected as the appropriate pretreatment condition for this method. An interesting observation is that the most active catalyst was also the most selective.

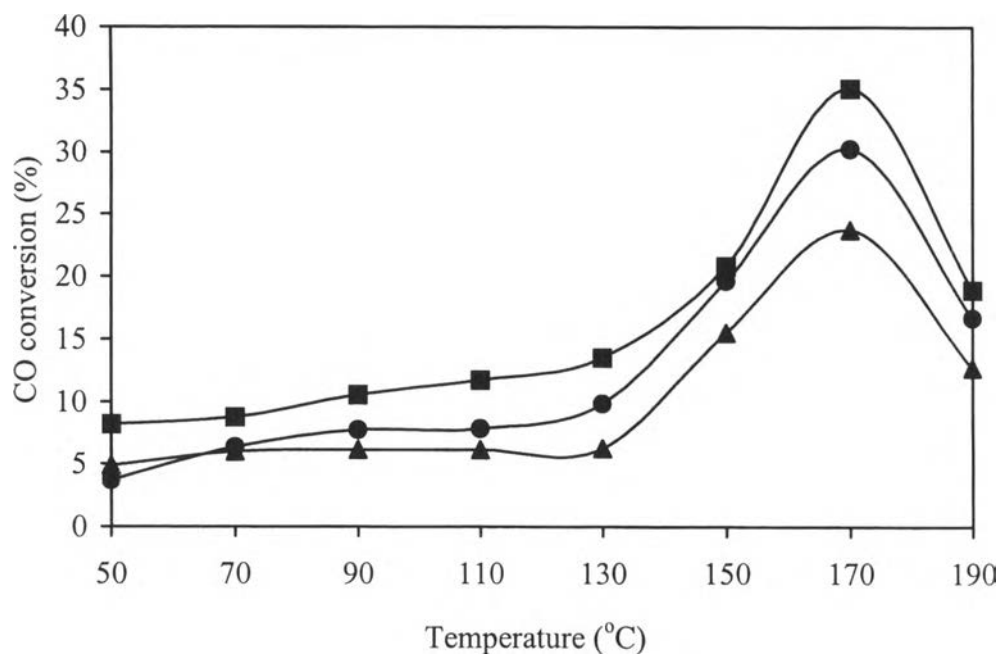


Figure 4.11 (a) Effect of pretreatment method on CO conversion of 1%Au/TiO₂ (DP1) catalyst calcined at 400°C for 5 h; (■), pure O₂ at 200°C for 2 h; (●), pure He at 200°C for 2 h; (▲), pure H₂ at 200°C for 2 h.

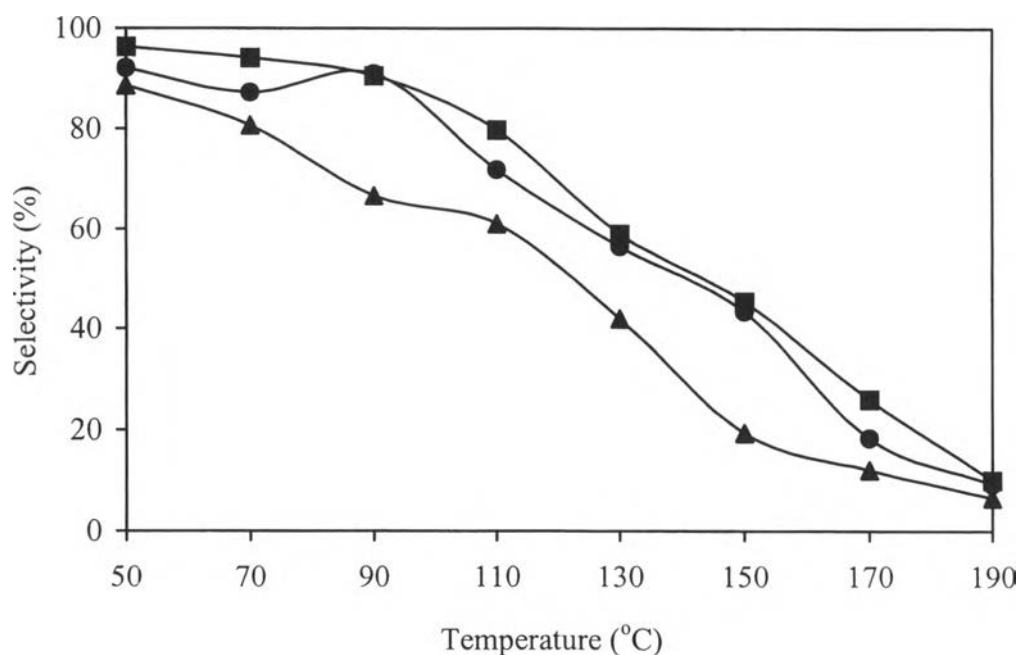


Figure 4.11 (b) Effect of pretreatment method on selectivity of 1%Au/TiO₂ (DP1) catalyst calcined at 400°C for 5 h; (■), pure O₂ at 200°C for 2 h; (●) pure He at 200°C for 2 h; (▲), pure H₂ at 200°C for 2 h.

Figures 4.12 (a) and (b) show the relationship between CO conversion and selectivity versus temperature of 1%Au/TiO₂ prepared by ISG method calcined at 400°C for 5 h, which were investigated under different pretreatment procedures (pure O₂, pure H₂, and pure He at 200°C for 2 h). It can be found that pretreatment in the reducing condition gave higher activity than He and O₂ pretreatment. The improvement in catalytic activity was accompanied by decreasing in the residual and the particle size of Au. Furthermore, H₂ pretreatment resulted in the formation of water on the catalyst surface, which gave the hydroxyl group making pretreatment better. The reducing condition was observed the best pretreatment for preparing by ISG method in order to improve activity. From this point, H₂ pretreatment was chosen for next experiment.

4.2.2 Effect of Calcination Temperature

Figures 4.13 (a) and (b) present the effect of calcination temperature on the activity of 1%Au/TiO₂ prepared by DP1 method calcined at 300 and 400°C for 5 h. Catalyst calcined at 400°C gave higher activity than calcined at 300°C. As the calcination temperature was increased, the catalyst gained activity, in spite of the thermal coagulation resulting in the larger particle size of Au. TEM observations revealed not only the changes in particle size but also those in particle shape from spherical shape to hemispherical shape. This indicated that the close contact between gold particles and the support surface was the most important for the reaction (Tsubota *et al.*, 1995). The size of Au particle gradually increased with increasing temperatures for calcination. The catalytic activity for CO oxidation appears when DP precursors are calcined at temperatures of 573 K and above (Okumura *et al.*, 1998). One possibility was that the catalyst calcined at 400°C might eliminate more carbonate than calcined 300°C. So the catalyst surface was more open for oxygen adsorption. After this part, the temperature at 400°C for 5 h was chosen as the best calcination temperature for this method. The BET surface area of both catalysts (Table 4.1) was not significant. The phase from XRD was observed to be the same but intensity of XRD pattern was decreased with decreasing in temperature as shown in Figure 4.3.

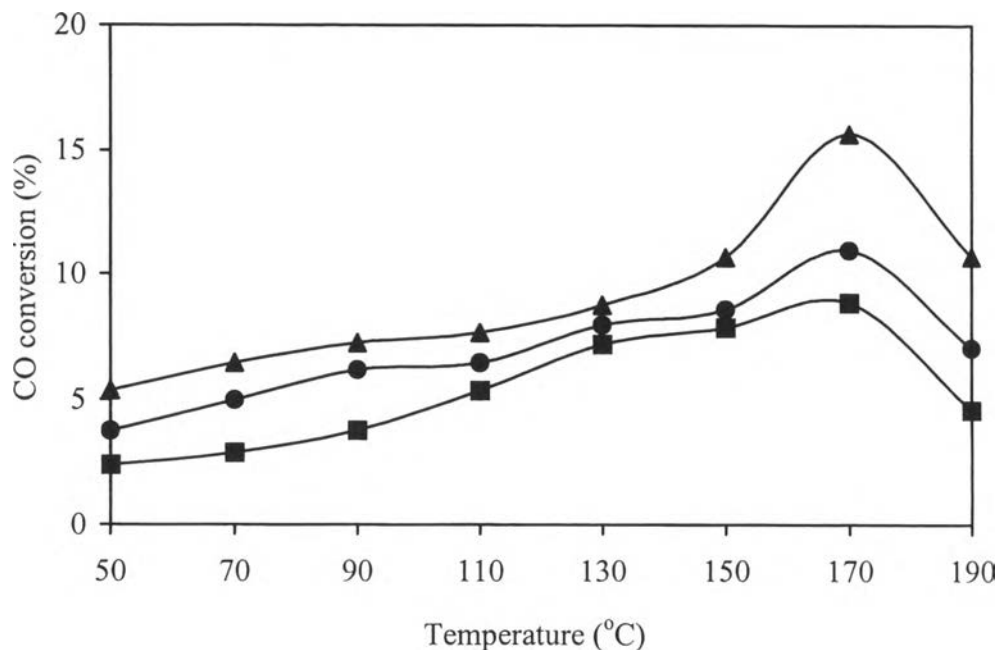


Figure 4.12 (a) Effect of pretreatment method on CO conversion of 1%Au/TiO₂ (ISG) catalyst calcined at 400°C for 5 h; (■), pure O₂ at 200°C for 2 h; (●), pure He at 200°C for 2 h; (▲), pure H₂ at 200°C for 2 h.

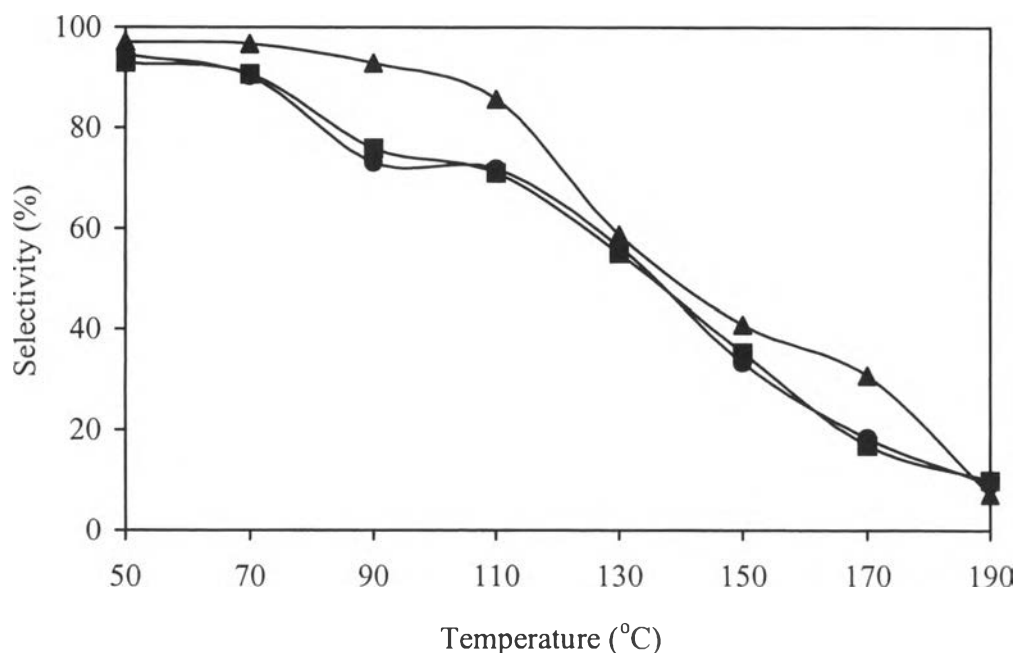


Figure 4.12 (b) Effect of pretreatment method on selectivity of 1%Au/TiO₂ (ISG) catalyst calcined at 400°C for 5 h; (■), pure O₂ at 200°C for 2 h; (●), pure He at 200°C for 3 h; (▲), pure H₂ at 200°C for 2 h.

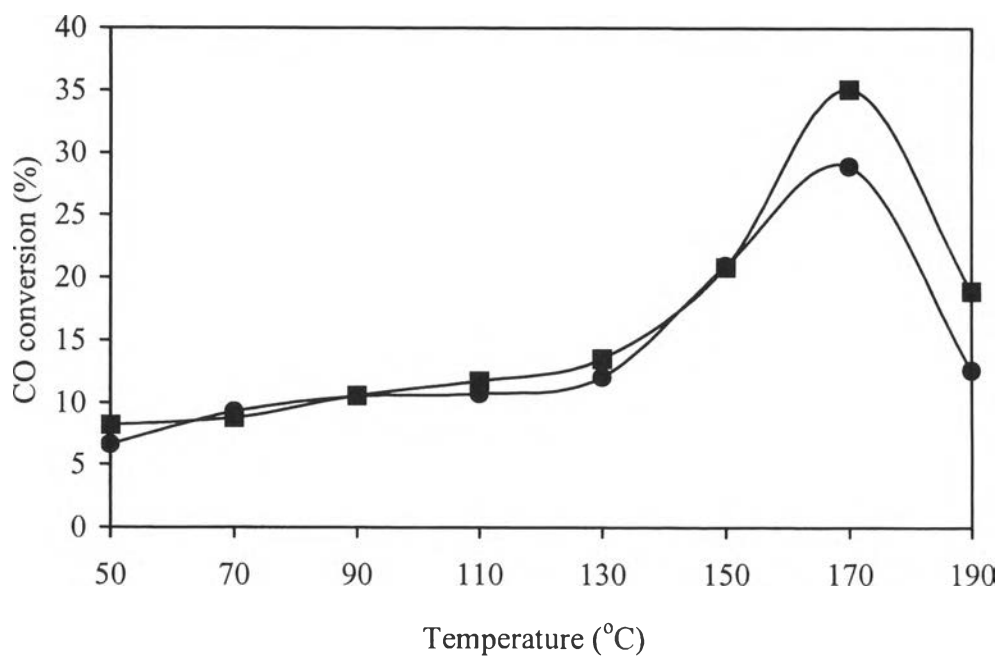


Figure 4.13 (a) Effect of calcination temperature on CO conversion of 1%Au/TiO₂ (DP1) catalyst; (●), 300°C; (■), 400°C.

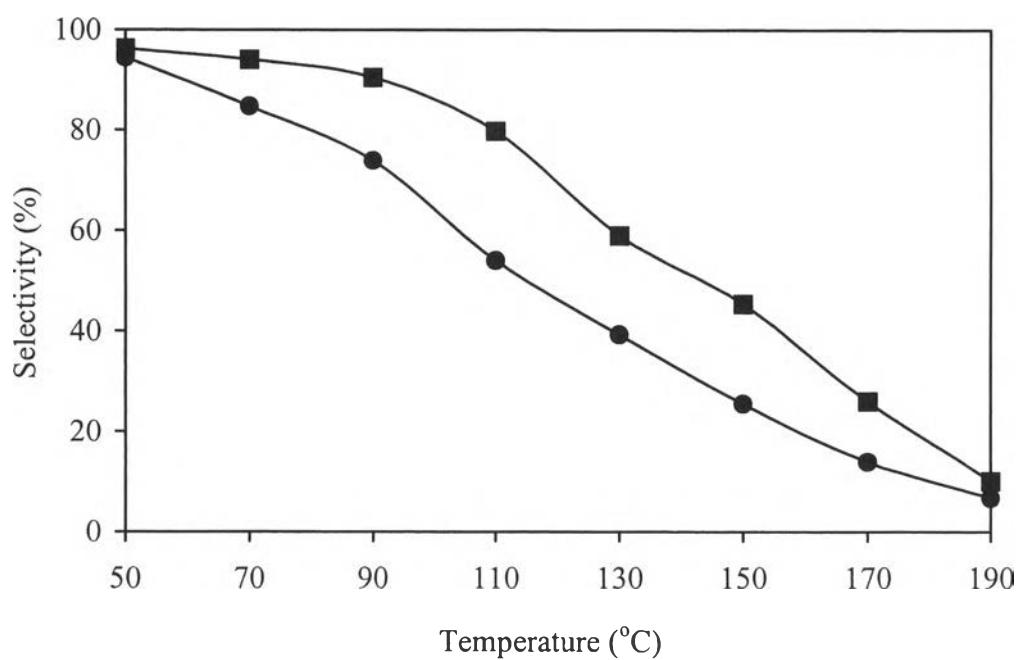


Figure 4.13 (b) Effect of calcination temperature on selectivity of 1%Au/TiO₂ (DP1) catalyst; (●), 300°C; (■), 400°C.

The effect of calcination temperature on the activity of 1%Au/TiO₂ prepared by DP2 method calcined at 300 and 400°C for 5 h are illustrated in Figures 4.14 (a) and (b). The activity of catalyst calcined 400°C showed slightly higher than calcined 300°C. It can be explained in the same as catalyst prepared by DP1.

Figures 4.15 (a) and (b) exhibit the effect of calcination temperature on the activity of 1%Au/TiO₂ prepared by ISG method. The higher activity was in the order of 300, 400, and 600°C, respectively. This result can be confirmed by the BET characterization. The BET surface area of these samples decreased with increasing the calcination temperature as shown in Table 4.3.

4.2.3 Effect of Metal Loading

Figures 4.16 (a) and (b) show the effect of Au loading (0.5%, 1%, 3%, and 5%) on TiO₂ catalysts prepared by DP1 method calcined at 400°C for 5 h. The 1%Au/TiO₂ gave the higher catalytic activity than 0.5%, 3%, and 5%Au/TiO₂, respectively. This result can be explained by BET surface area measurement (Table 4.1) and particle size of Au. The 1%Au/TiO₂ had the highest surface area and particle size of Au was less than 5 nm. There appeared to be an optimal average Au particle size of about 5-10 nm for best activity and selectivity (Bethke and Kung, 2000). Haruta (1997) found that a physical mixture of TiO₂ powder with Au particles of diameter around 5 nm calcined in air at different temperatures indicates that the contact structure of Au particles which yields the longest distance of perimeter interface is important for the genesis of high activity at low temperatures. The activity increased with decreasing particle size of Au due to the increased Au/support interface present with smaller particles, where CO oxidation took place. Although the particle size of 0.5%Au loading was less than 5 nm, its catalytic activity showed lower than 1%Au loading. The 1%Au/TiO₂ obtained more Au than 0.5%Au/TiO₂. So there were much more interface of Au and support in order to occur reaction. After this finding, 1%Au loading was optimum value for this study.

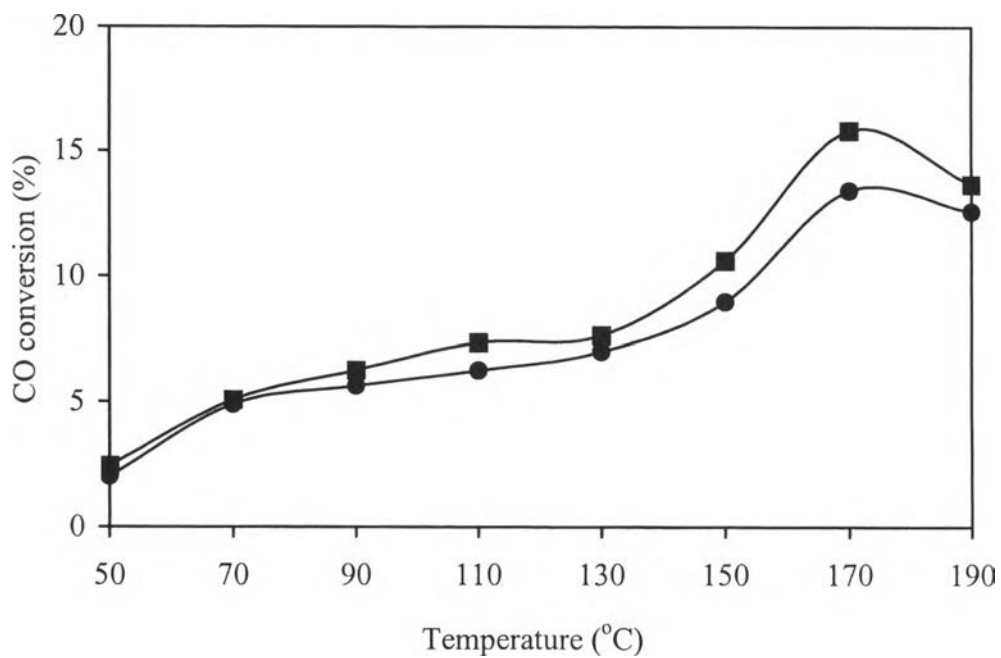


Figure 4.14 (a) Effect of calcination temperature on CO conversion of 1%Au/TiO₂ (DP2) catalyst; (●), 300°C; (■), 400°C.

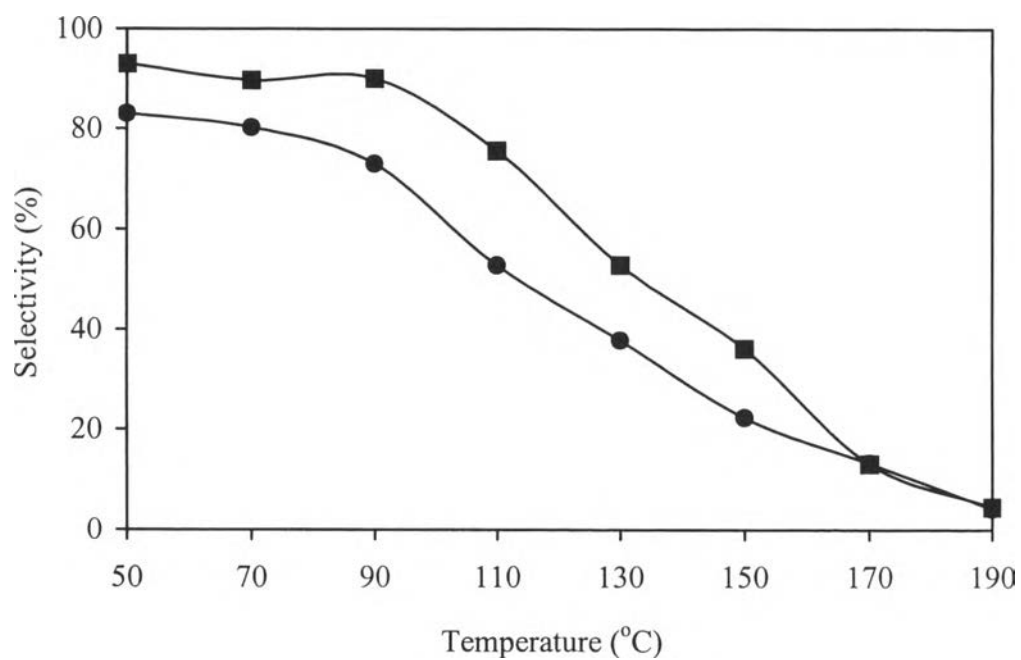


Figure 4.14 (b) Effect of calcination temperature on selectivity of 1%Au/TiO₂ (DP2) catalyst; (●), 300°C; (■), 400°C.

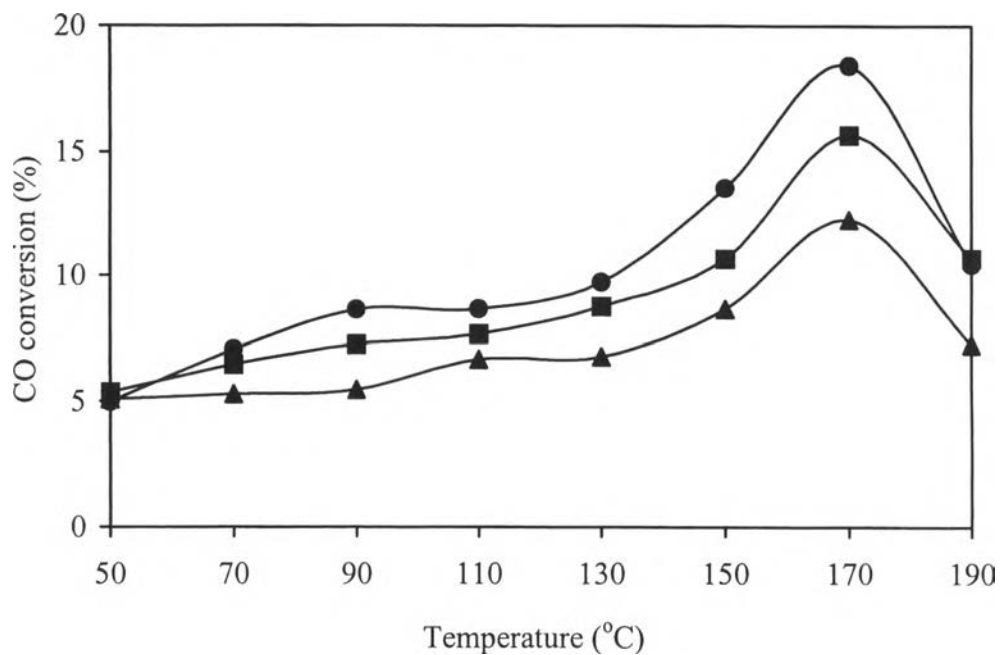


Figure 4.15 (a) Effect of calcination temperature on CO conversion of 1%Au/TiO₂ (ISG) catalyst; (●), 300°C; (■), 400°C; (▲), 600°C.

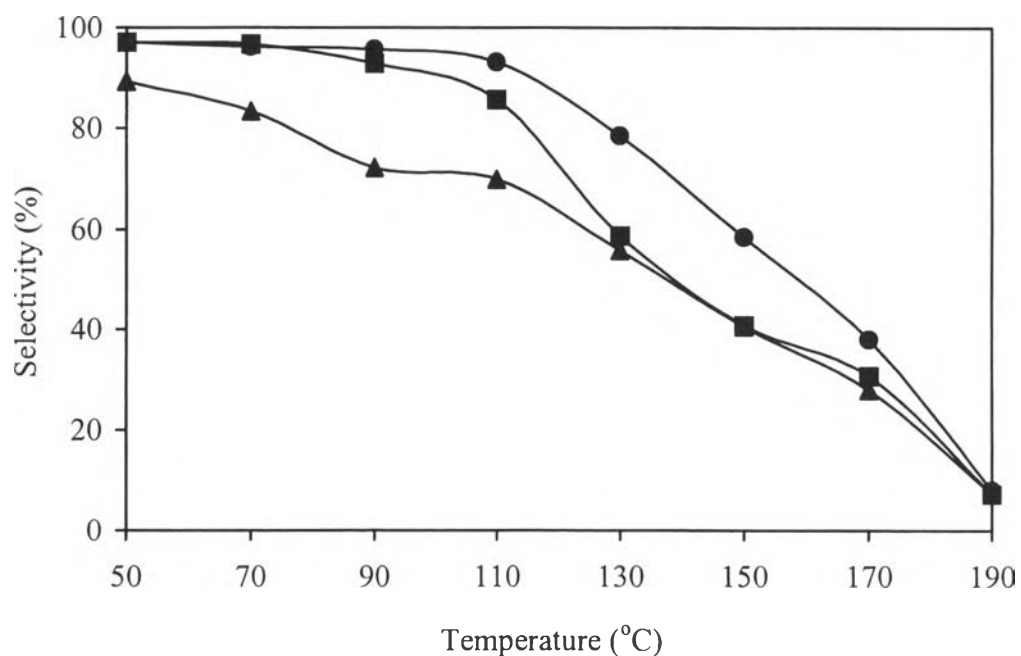


Figure 4.15 (b) Effect of calcination temperature on selectivity of 1%Au/TiO₂ (ISG) catalyst; (●), 300°C; (■), 400°C; (▲), 600°C.

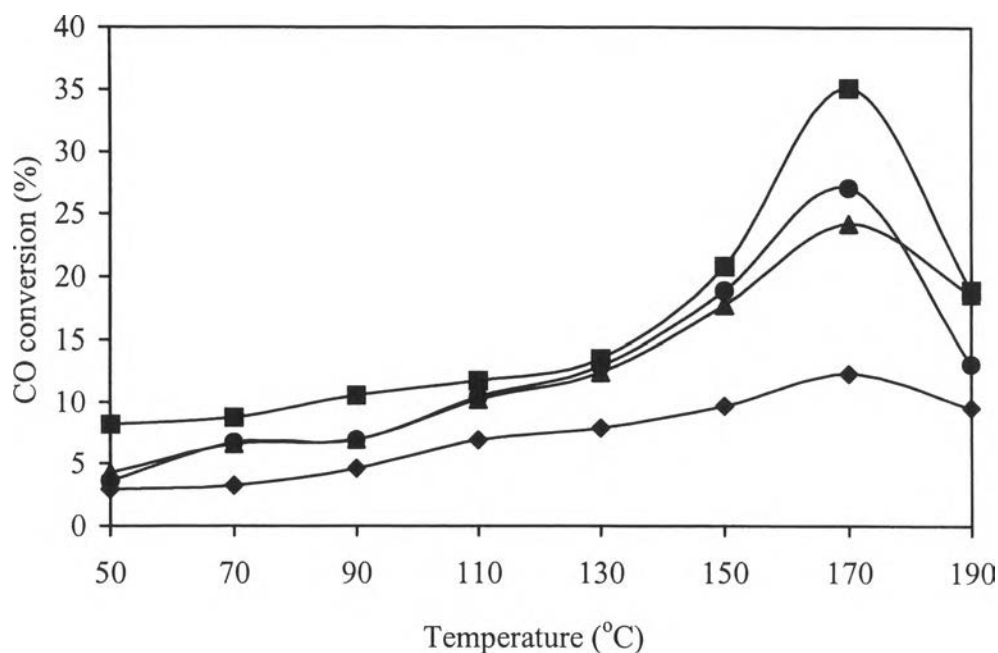


Figure 4.16 (a) Effect of Au loading on CO conversion of Au/TiO₂ (DP1); (●), 0.5%Au; (■), 1%Au; (▲), 3%Au; (◆), 5%Au.

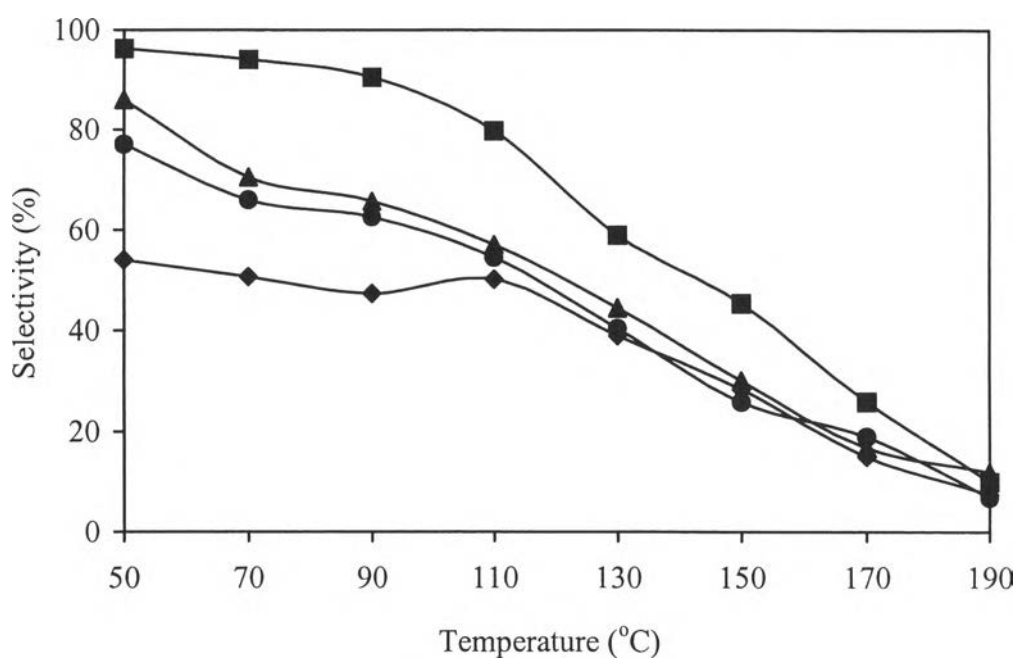


Figure 4.16 (b) Effect of Au loading on selectivity of Au/TiO₂ (DP1); (●), 0.5%Au; (■), 1%Au; (▲), 3%Au; (◆), 5%Au.

Figures 4.17 (a) and (b) show the effect of Au loading (0.5%, 1%, and 3%) on TiO₂ catalysts prepared by ISG method calcined at 300°C for 5 h. The 0.5%Au/TiO₂ gave the highest catalytic activity. This result can be explained by BET surface area measurement (Table 4.4) and particle size of Au from TEM result. The 0.5%Au loading had the highest surface area and the smallest Au particle size.

4.2.4 Effect of Catalyst Preparation

Figures 4.18 (a) and (b) exhibit the CO conversion and selectivity of Au/TiO₂ catalyst with different preparation methods. The 1%Au/TiO₂ DP1 catalyst with adding Mg citrate as promoter had the best performance among the four types of catalyst preparation. Normally, Mg citrate plays an important role in the preparation of highly dispersed Au catalyst with TiO₂ as support. The unique role of Mg citrate might be, firstly, to prevent coagulation during calcination due to blockage by citrate anions sticking on TiO₂ surface. The second role can be assumed to suppress earthquake effect caused by crystallization of Ti(OH)₄ to TiO₂ because Mg²⁺ ion was found to retard the crystallization of amorphous TiO₂, and finally, it can be effected to reduce the particle size of Au for preparation of Au/TiO₂ (Sakurai and Haruta, 1996).

It can be seen that the activity of DP1 catalyst was higher than DP2 and ISG catalysts. This result which was compared between samples prepared by DP1 and DP2 method can be described by the data obtained from BET surface area measurement and phase of TiO₂ from XRD. Higher activities correlate with the higher surface area. A mixture of anatase and rutile phases obtained higher activity than only anatase phase. While the result compared between samples prepared by DP1 and ISG can be explained by effect of phase support from XRD measurement. In addition, DP method has more strong interaction between the support and the metal than ISG method. The DP catalyst support is much more crystalline and probably Au particles are stabilized at the grain boundaries where they can interact strongly with support. It can be concluded that the reaction proceeds mainly on the perimeter interface of Au particles. For impregnation method, the metal solution is physically loaded into the pores of support, so the Au metal may not go uniformly to the pore of support. It can be supported by the AAS characterization. The ISG

method had the lower percent Au loading than DP method. Haruta (1997) reported that the impregnation methods can hardly lead to high dispersion of Au except for a few cases of very low metal loadings because of the lower melting point of Au and partly because the catalyst precursors are often calcined at low temperatures where chlorine still remains in the metal oxide supports.

4.2.5 Effect of CO₂

Figures 4.19 (a) and (b) present the effect of CO₂ addition to the feed stream on the activities of 1%Au/TiO₂ prepared by DP1 method calcined at 400°C for 5 h. Decreasing the CO₂ concentration from 10% to 2% and to 0% slightly increased the conversion of catalyst but the selectivity was not significantly different by the presence of CO₂ in reactant gas. The retention of CO₂ led to increase coverage of the surface by the bicarbonate intermediate species and decay of catalytic activity. Furthermore, higher CO₂ partial pressures above these catalysts may shift the equilibrium toward retention of CO₂ (Hoflund *et al.*, 1995).

4.2.6 Effect of H₂O

The effect of the presence of water vapor of 1%Au/TiO₂ prepared by DP1 method calcined at 400°C for 5 h are shown in Figures 4.20 (a) and (b). Generally, the catalytic activity of catalyst is depressed in the presence of water vapor. The catalytic performance was tested by feeding 10% and 2.6% H₂O in the feed. As the result, the activity became significantly higher than no water vapor. It was considered that H₂O adsorbed on the catalyst surface might effectively activate O₂ on the surface.

For gold there is a theory that the active site is one which is either hydroxylated or is neighboring a gold hydroxyl. Hemispherical shape and good contact are also important in that the active sites including the hydroxylated. They are not on the surface of gold crystallites but at the interfaces and this means that water vapor had positive effect on the activity of CO oxidation.

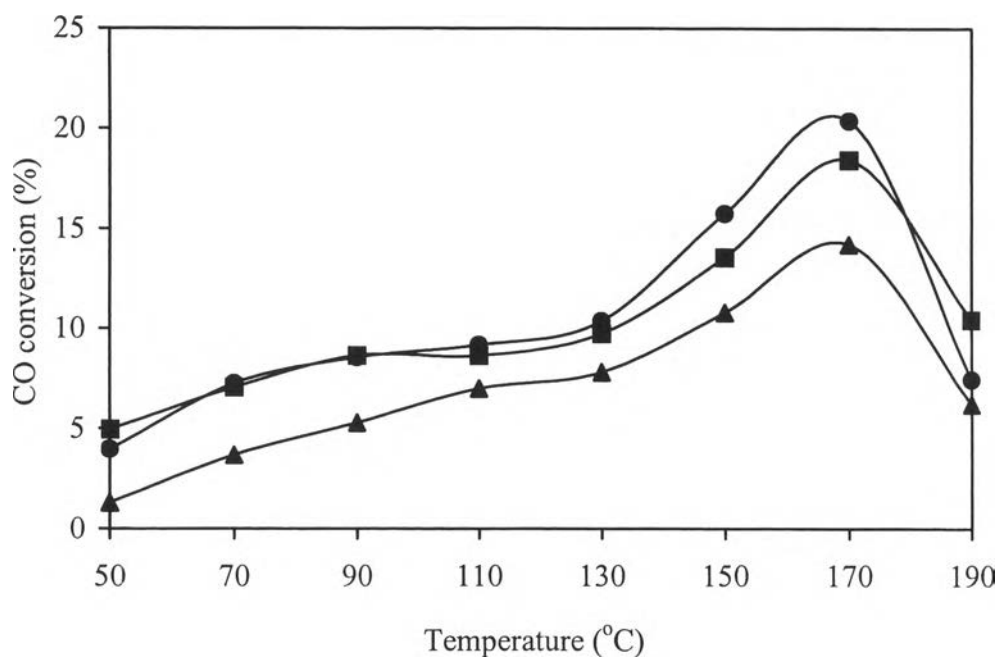


Figure 4.17 (a) Effect of Au loading on CO conversion of Au/TiO₂ (ISG); (●), 0.5%Au; (■), 1%Au; (▲), 3%Au.

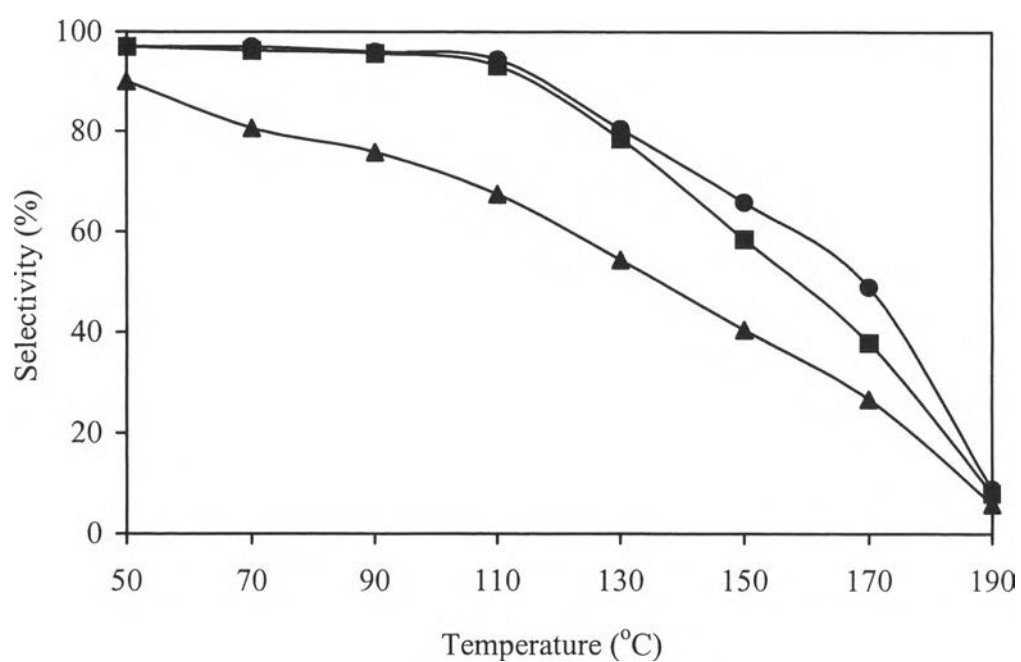


Figure 4.17 (b) Effect of Au loading on selectivity of Au/TiO₂ (ISG); (●), 0.5%Au; (■), 1%Au; (▲), 3%Au.

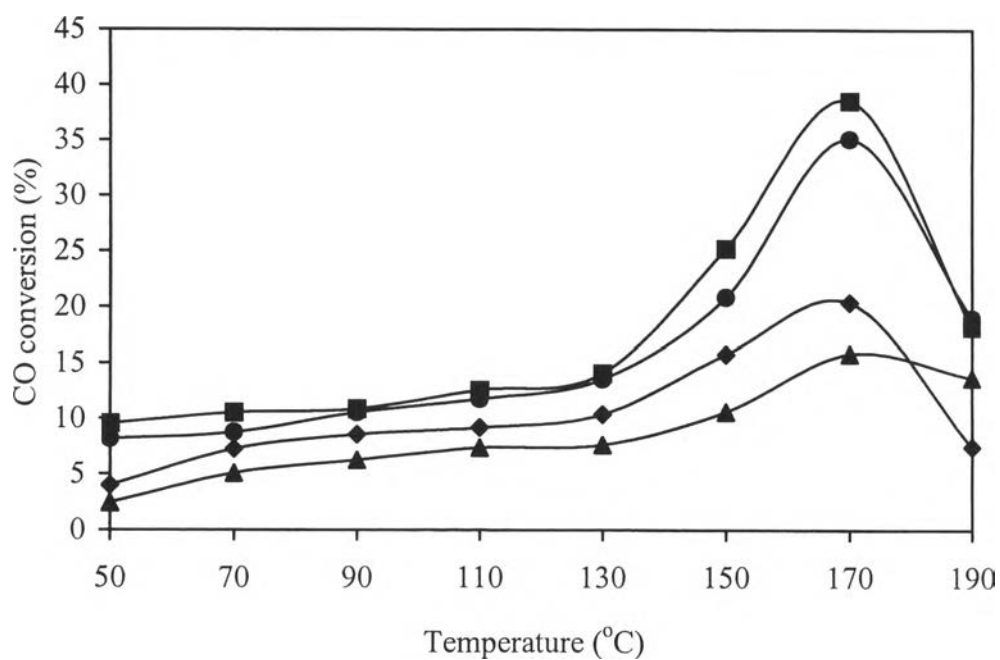


Figure 4.18 (a) Effect of catalyst preparation on CO conversion of Au/TiO₂ catalyst; (●), DP1; (■), DP1 with Mg citrate; (▲), DP2; (◆), ISG.

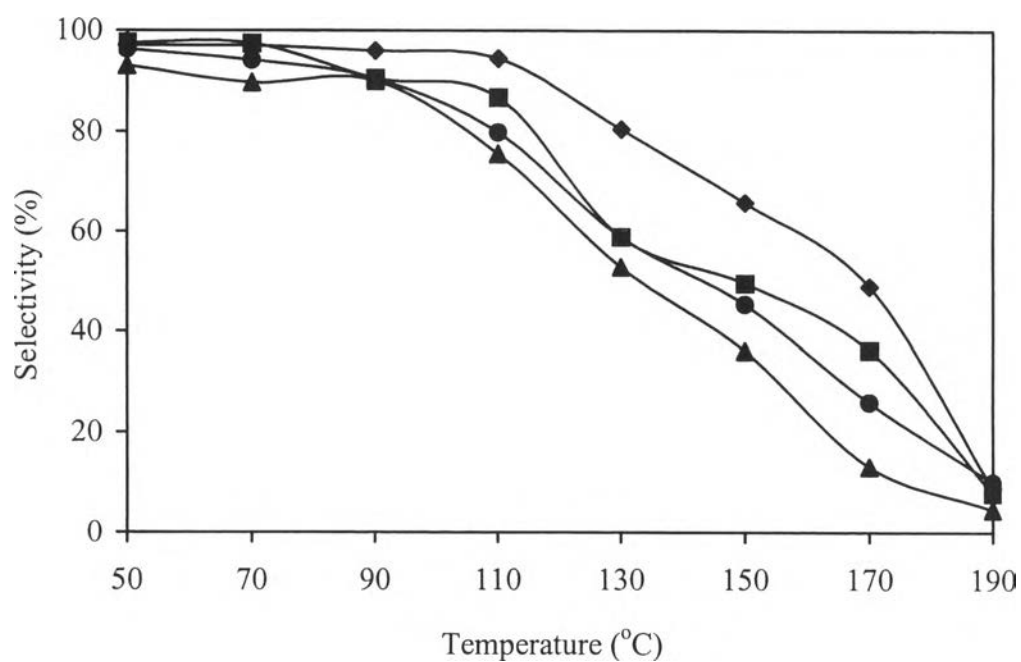


Figure 4.18 (b) Effect of catalyst preparation on selectivity of Au/TiO₂ catalyst; (●), DP1; (■), DP1 with Mg citrate; (▲), DP2; (◆), ISG.

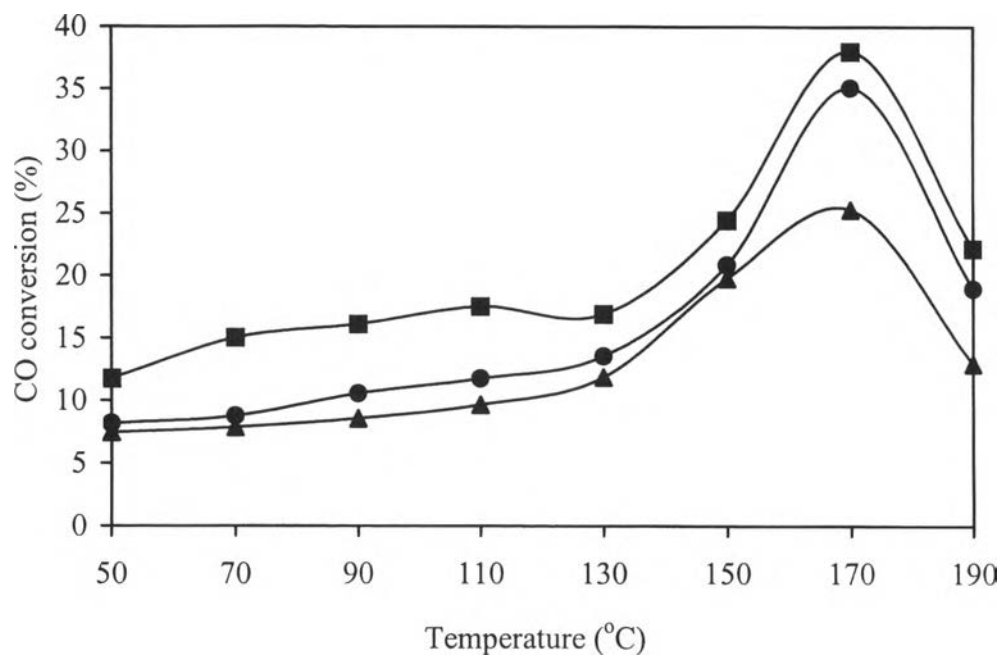


Figure 4.19 (a) Effect of CO₂ concentration on CO conversion of 1%Au/TiO₂ (DP1) catalyst;(▲), 10%CO₂; (●), 2%CO₂; (■), 0%CO₂.

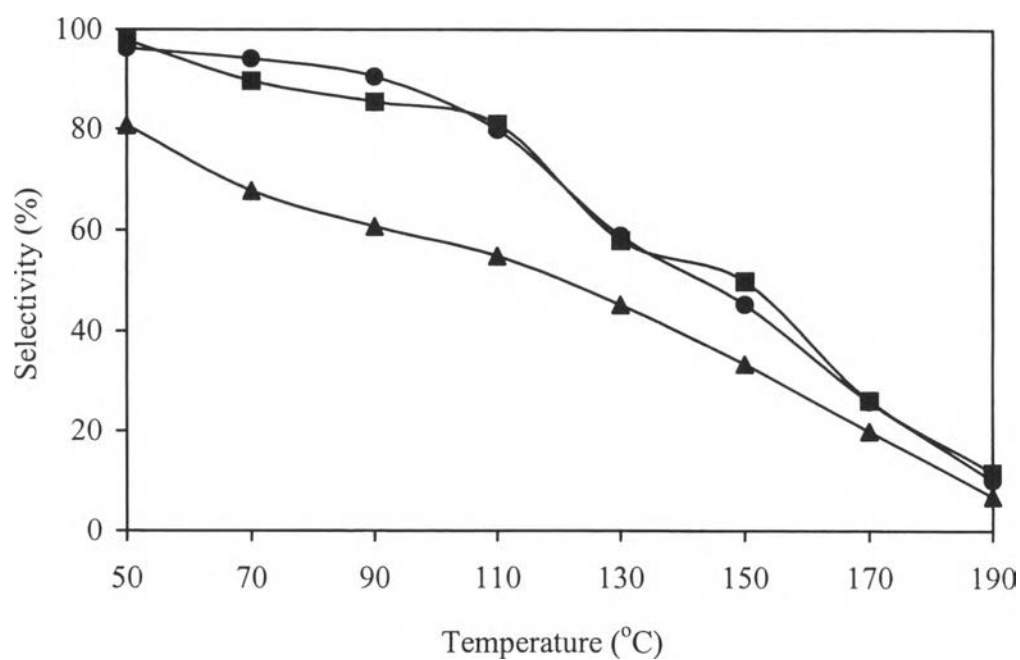


Figure 4.19 (b) Effect of CO₂ concentration on selectivity of 1%Au/TiO₂ (DP1) catalyst;(▲), 10%CO₂; (●), 2%CO₂; (■), 0%CO₂.

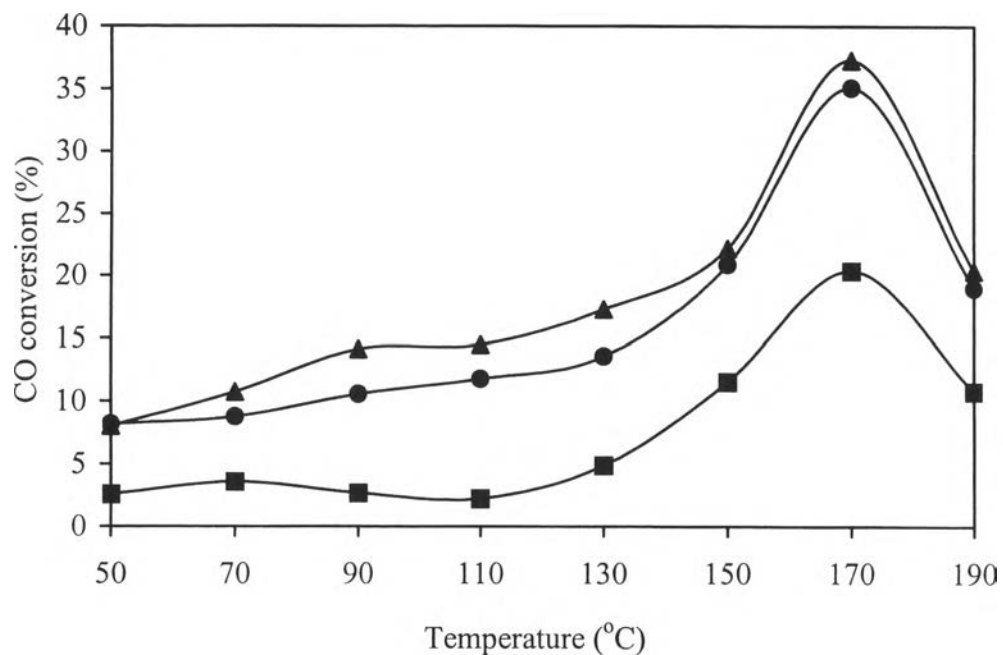


Figure 4.20 (a) Effect of water vapor on CO conversion of 1%Au/TiO₂ (DP1) catalyst; (▲), 10%H₂O; (●), 2.6%H₂O; (■), 0%H₂O.

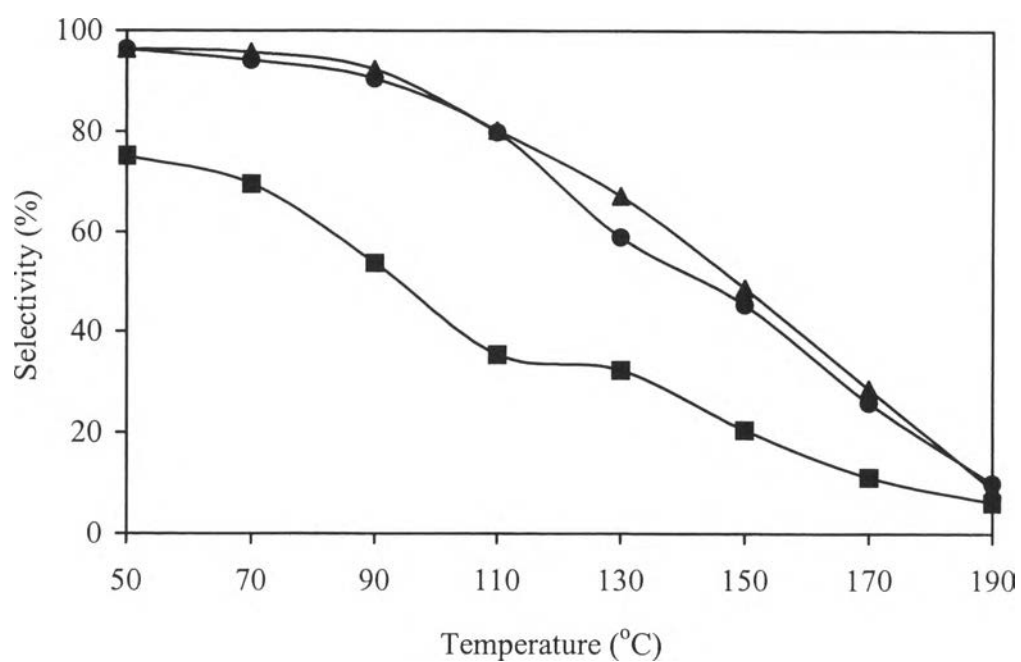


Figure 4.20 (b) Effect of water vapor on selectivity of 1%Au/TiO₂ (DP1) catalyst; (▲), 10%H₂O; (●), 2%H₂O; (■), 0%H₂O.

4.2.7 Deactivation Test

Figure 4.21 shows deactivation test of 1%Au/TiO₂ prepared by DP1 method calcined at 400°C for 5 h. The stability of catalyst was tested for 48 h under reaction condition for selective CO oxidation at 170°C. From the result, the catalyst showed good stability in activity during the tested time.

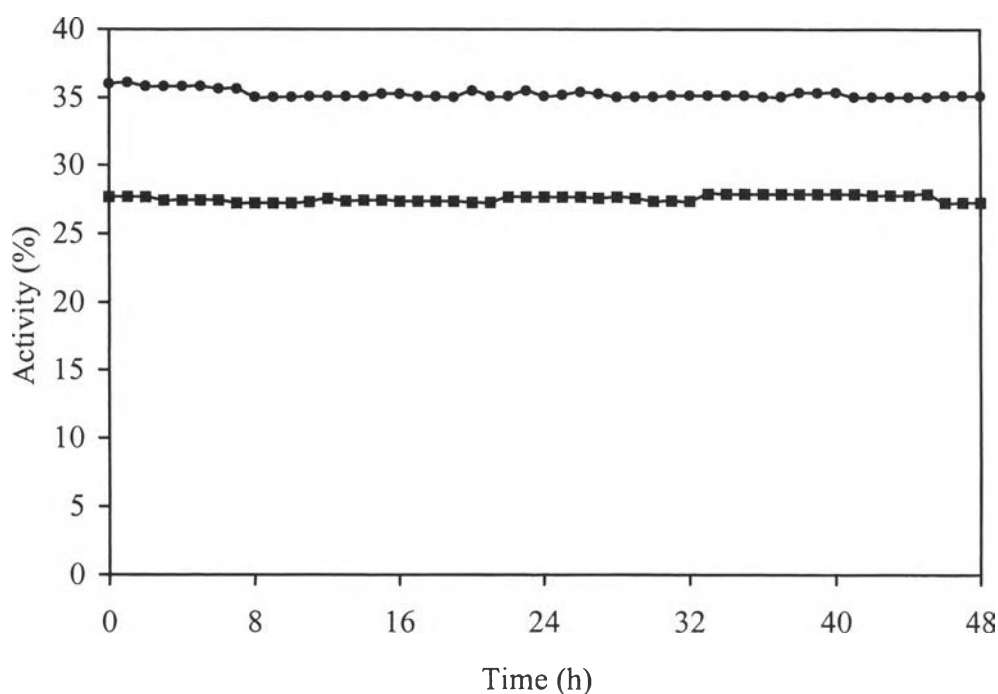


Figure 4.21 Deactivation test of 1%Au/TiO₂ (DP1) catalyst calcined at 400°C for 5 h; (●), conversion; (■), selectivity.

4.2.8 Comparison of Activity with Literature

Table 4.11 compares the activity between this work for Au/TiO₂ prepared by DP1 method with adding Mg citrate (Mg/Au ratio=18) and Bethke and Kung (2000)'s work for Au/ γ -Al₂O₃ prepared by DP with adding Mg citrate (Mg/Au ratio=1.55). The experiments were performed at similar operating condition.

The Au/TiO₂ catalyst showed higher %CO conversion than Au/ γ -Al₂O₃ catalyst but this catalyst had its maximum conversion at a higher temperature. The selectivity of Au/TiO₂ catalyst was lower than Au/ γ -Al₂O₃ catalyst.

Table 4.11 Comparison with reported results from the literature

	This work	Bethke and Kung(2000)
Catalysts	Au/TiO ₂	Au/ γ -Al ₂ O ₃
Preparation method	DP with Mg citrate	DP with Mg citrate
Calcination temperature(°C)	400	350
Calcination time (h)	5	4
Surface area (m ² /g)	59	240
Reactant gas	1%CO, 1%O ₂ , 2%CO ₂ , 2.6%H ₂ O, and 40% H ₂ balance in He	1%CO,0.5%O ₂ , 48%H ₂ , and 50.5%He
Total flow rate(ml/min)	50	90
Reaction temperature (°C)	170	100
CO conversion (%)	39	35
Selectivity (%)	36.	45