

## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Catalyst Characterization

X-ray powder diffraction (XRD) was performed in a Rigaku X-Ray Diffractometer system (RINT-2200) with  $\text{CuK}\alpha$  radiation, in order to examine the crystalline phases and crystalline sizes of the sample. Information on the Au species was attained by UV-vis spectroscopy. The surface area was determined by the  $\text{N}_2$ -adsorption-BET method in a Autosorb-1 Gas Sorption System (Quantachrome Corporation). Temperature-programmed reduction (TPR) analysis was carried out to study the reduction behavior of the catalysts. The average particle size and the microstructure of the prepared catalyst were investigated by Transmission electron microscopy (TEM) analysis. Furthermore, Fourier Transform Infrared Spectroscopy (FTIR) was employed to identify the carbonate species presented in the catalysts.

##### 4.1.1 Surface Properties

Table 4.1 summarizes the actual gold loading, the mean crystallite size, the average size of gold particles as determined by TEM, and BET surface area for  $\text{Au/Fe}_2\text{O}_3\text{-TiO}_2$  catalysts at different Fe/Ti atomic ratios, different gold loadings, and different metal loading calcination temperatures. The actual gold loading was almost equal to the intended metal loading. For  $\text{Au/Fe}_2\text{O}_3\text{-TiO}_2$  catalysts, with increasing Fe/Ti atomic ratio the actual gold loading decreased. The  $\text{TiO}_2$  support has a specific surface area of  $58.5 \text{ m}^2/\text{g}$ . The surface areas of  $\text{Au/TiO}_2$  and  $\text{Au/Fe}_2\text{O}_3\text{-TiO}_2$  with different atomic ratios are very close to that of  $\text{TiO}_2$ . The surface area is not affected by the metal oxide support ( $\text{Fe}_2\text{O}_3$ ) added in  $\text{Au/TiO}_2$  catalysts. The slight decrease in the BET surface area by the  $\text{Fe}_2\text{O}_3$  addition is probably due to the blockage of some of the  $\text{TiO}_2$  pores (Chang *et al.*, 2006). Calcination temperature scarcely changed the BET surface area of the  $\text{Au/Fe}_2\text{O}_3\text{-TiO}_2$  catalyst. This can be concluded that the gold particles are stabilized against sintering during calcination in the presence of iron oxide in  $\text{Au/TiO}_2$  catalysts. On the other hand, with an increasing amount of gold in  $\text{Au/Fe}_2\text{O}_3\text{-TiO}_2$  resulted in a decrease in BET surface area, suggesting that agglomeration of gold particles might occur.

**Table 4.1** Physicochemical properties of the catalysts.

Catalyst	Calcine temp.	Au loading <sup>a</sup>	Crystallite size <sup>b</sup>	Au mean size <sup>c</sup>	BET surface
	(°C)	(wt%)	(nm)	(nm)	area (m <sup>2</sup> /g)
1% Au/TiO <sub>2</sub>	400	0.425	14.332	-	56.70
1% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:4)	200	0.934	10.237	4.12	56.20
1% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:4)	300	0.758	11.010	5.00	54.20
1% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:4)	400	0.994	14.518	4.58	54.20
1% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:1)	400	0.975	13.766	-	50.30
1% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (4:1)	400	0.580	14.507	-	50.50
3% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:4)	400	1.812	21.181	5.57	49.89
5% Au/Fe <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> (1:4)	400	3.724	21.273	5.45	49.64
1% Au/Fe <sub>2</sub> O <sub>3</sub>	400	0.936	-	-	81.16

<sup>a</sup>Gold contents were determined by XRF.

<sup>b</sup>Mean crystallite sizes were calculated from the average values of TiO<sub>2</sub> plane (101), (110), (200), (105), (211).

<sup>c</sup>Gold crystallite sizes were evaluated by TEM.

#### 4.1.2 UV Measurement

Normally, the DR/UV-vis spectroscopy can indicate the nature of Au species on the support. Many previous works, proposed that the absorption bands at <250 nm, 280–390 nm, and 500–700 nm could be represented the  $\text{Au}^{3+}$ , small gold clusters ( $\text{Au}_n, 1 < n < 10$ ), and gold Plasmon (or Au metallic,  $\text{Au}^0$ ) species, respectively (Escamilla-Perea *et al.*, 2010). The absorption band of bare  $\text{TiO}_2$  (Degussa-P25) nanoparticles suspension arises from several direct and indirect band gap transitions typical of the  $\text{TiO}_2$  semiconductor: a strong absorption contribution due to the  $\text{TiO}_2$  nanoparticles dominates the spectrum below 350 nm together with a smooth decay towards longer wavelengths (Fazio *et al.*, 2011). As a result, this technique has some limitations due to the difficulty in interpreting between the support and the resonance band of both  $\text{Au}^{3+}$  and gold clusters.

Figure 4.1 illustrates the diffuse reflectance UV-vis spectra of  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  supports with different Fe/Ti atomic ratios. The spectra showed an increase in the absorption band of  $\text{TiO}_2$  when the amount of  $\text{Fe}_2\text{O}_3$  was increased. Moreover, the spectra showed the absorption band shoulder-like peak at around 400 nm to 600 nm for the  $\text{Fe}_2\text{O}_3$  modified samples ( $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ ) which is assigned d-d transitions, as suggested by Zhan *et al.* (2011). Furthermore, the spectra of supported gold catalysts using chlorouric acid ( $\text{HAuCl}_4$ ) as a precursor, as shown in Figure 4.2, have a significant effect on UV-vis band features which appear small peak at around 500 nm to 600 nm for both 1%  $\text{Au}/\text{TiO}_2$  and 1%  $\text{Au}/\text{Fe}_2\text{O}_3$ . Besides, the 1%  $\text{Au}/\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  catalysts exhibited higher broadening peak and also shifted to higher wavelength when the Au was loaded ( $\text{Au}^0$  specie at around 550 nm). It can be concluded that the presence of  $\text{Au}^0$  related to the catalytic activities of 1%  $\text{Au}/\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  (1:4) catalysts because of it showed the broadening prominent peak in range of 500 nm to 700 nm (Wu and Chen, 2010). However, it is difficult to explain the catalytic activity of the catalysts with different Fe/Ti atomic ratios since the appearance of the band at around 500 nm in spectra of  $\text{Au}/\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  are not much different.

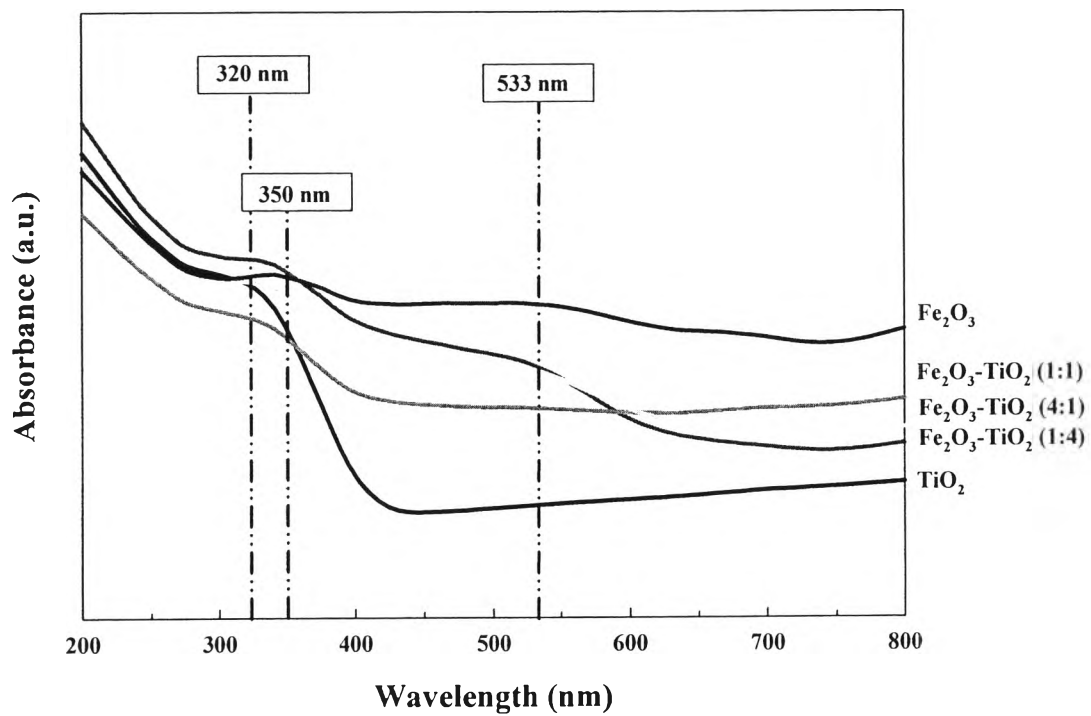


Figure 4.1 UV-vis DRS spectra of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> supports.

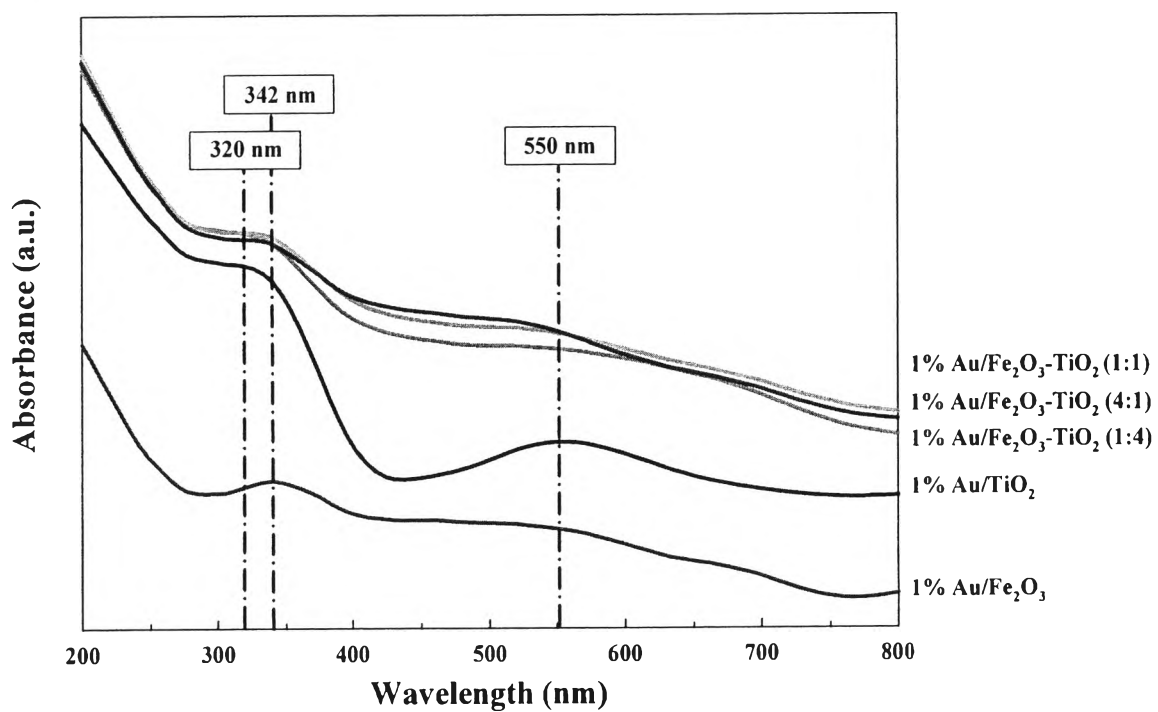
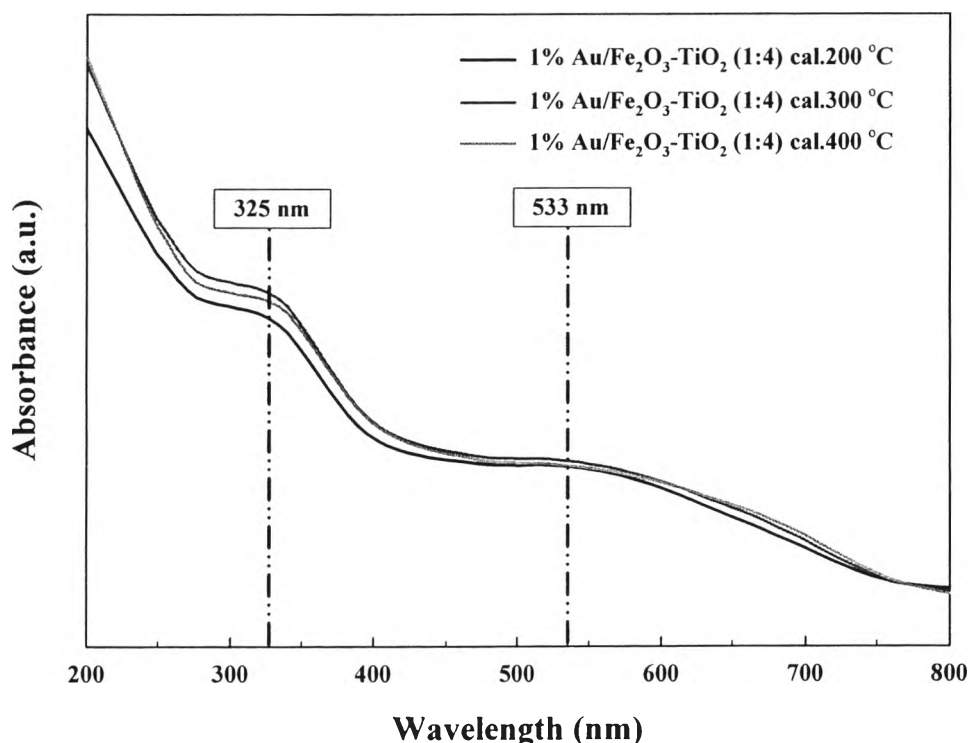


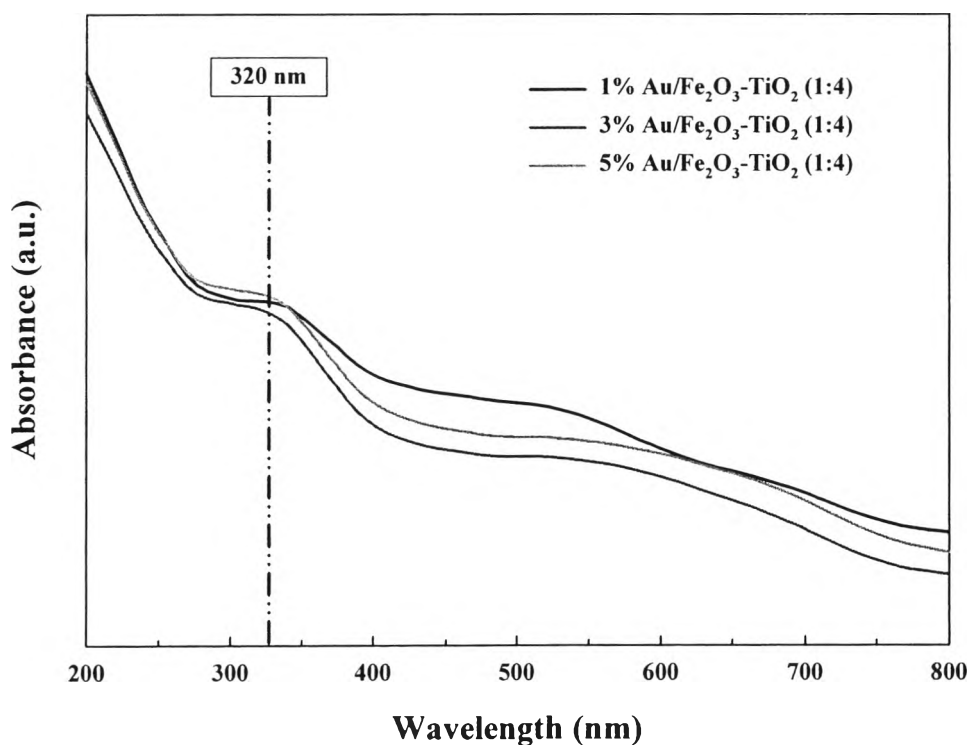
Figure 4.2 UV-vis DRS spectra of supported Au catalyst samples.

Figure 4.3 shows an absorption band of  $\text{TiO}_2$  at below 350 nm. The absorption band of gold metallic particles (plasmon band) was also observed at around 550 nm for 1%  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  calcined at different temperatures. However, it seems to be difficult to explain that how the catalytic activity related to calcination temperature from UV-vis spectroscopy. However, the higher calcination temperature the higher catalytic activity. The 1%  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  calcined at 400 °C showed the best catalytic performance. From UV-vis spectra, there is no significant difference among the samples with different calcination temperatures. On the other hand, from TPR result, the highest calcination temperature represented the greatest metal-metal interaction causing the formation of large Au metallic particles. However, the catalyst heat treatment is still important because of the  $\text{Au}^0$  cannot occur without heating (Bond and Thompson, 2000).



**Figure 4.3** UV-vis DRS spectra of 1%  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  (1:4) samples with different calcination temperatures.

Figure 4.4 shows the UV-vis spectra of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts calcined at 400 °C with different Au loadings: 1, 3, and 5 wt%. It can be seen that the absorption band in the region of gold metallic particles (plasmon band) was also observed at around 550 nm. This is no significant difference in absorption bands; however, when the amount of gold loading increased, the peak area of absorption band at 500 nm increased. It is interesting to note that the very broad bands for Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> with Au loading of 3-5 wt% shifted to higher wavelength in range of 500 nm to 700 nm which can be related to higher amount of Au<sup>0</sup>, resulting in higher catalytic activity. However, other characterization techniques are required to explain the catalytic activity because it might depend on other reasons such as type of interaction or amount of Au<sup>0</sup>.

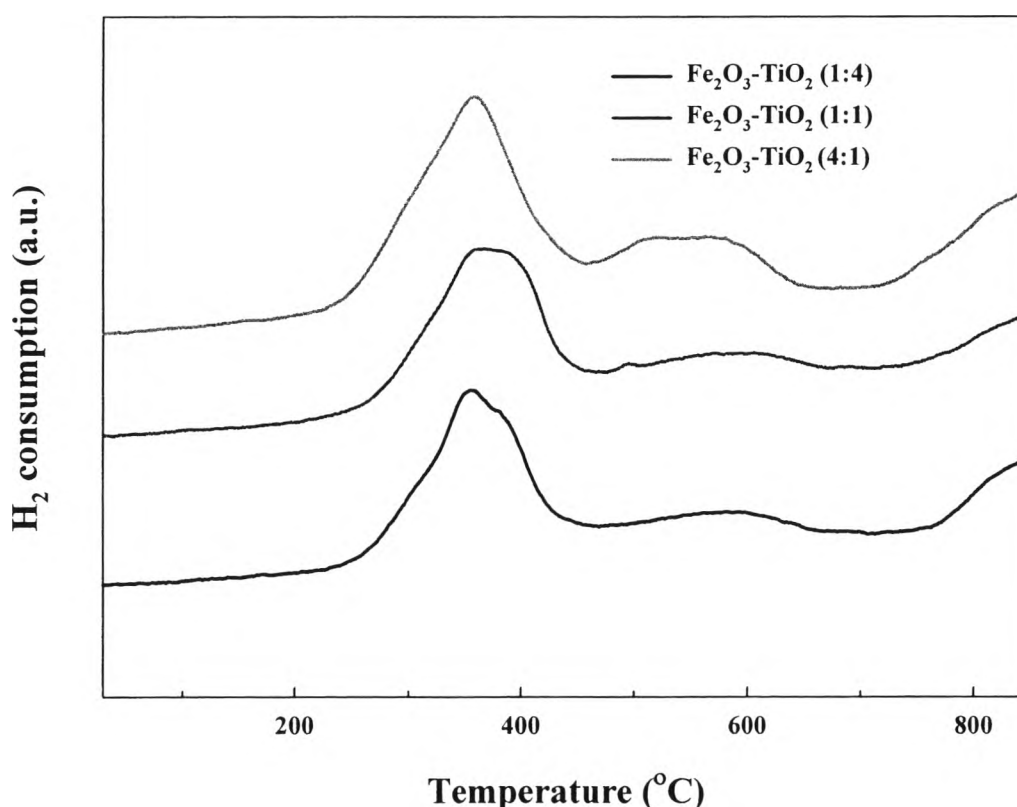


**Figure 4.4** UV-vis diffuse reflectance spectroscopy spectra of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) samples with different Au loadings.

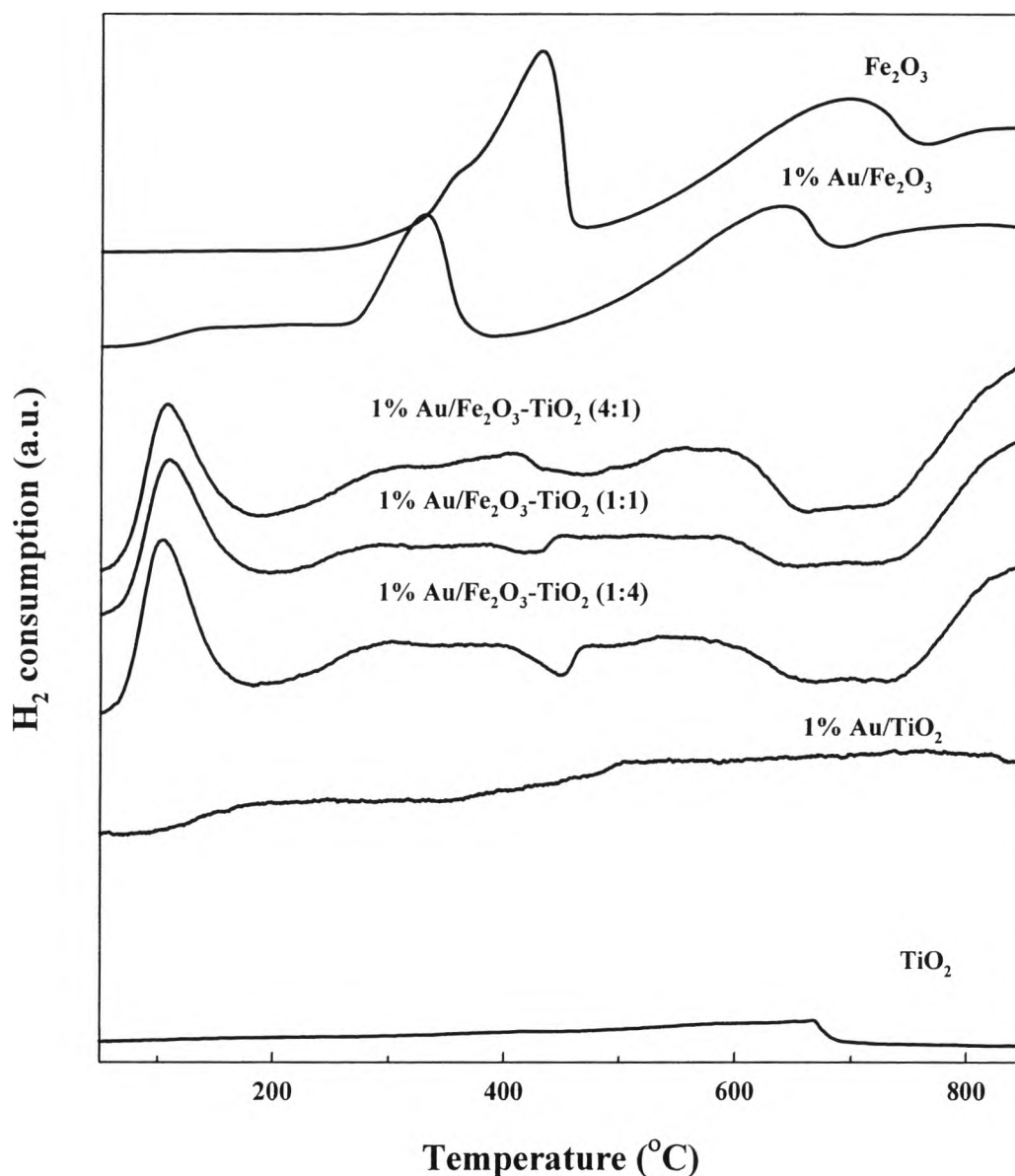
### 4.1.3 TPR Measurement

Temperature-programmed reduction (TPR) was used to characterize the characteristic of metal oxides, mixed metal oxides, metal oxides dispersed on a support including metal-metal and metal-support interaction of the prepared catalysts.

Figure 4.5 displays the reduction peak of  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  support at different Fe/Ti atomic ratios. The  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  samples showed low temperature reduction peak between 240 °C to 430 °C with a broad peak between 480 °C to 680 °C. Compared with the reduction peak of pure  $\text{TiO}_2$  and  $\text{Fe}_2\text{O}_3$ , the low temperature reduction peak should be assigned to the reduction of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ , while the broad peak at higher temperature should be mentioned to the reduction of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  and bulk  $\text{TiO}_2$ . Besides, the higher temperature than 780 °C should be ascribed to the reduction of  $\text{FeO}$  to  $\text{Fe}$  which more difficult to reduce compared with the pure  $\text{Fe}_2\text{O}_3$ .



**Figure 4.5**  $\text{H}_2$ -TPR profiles of  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  supports with different atomic ratios.



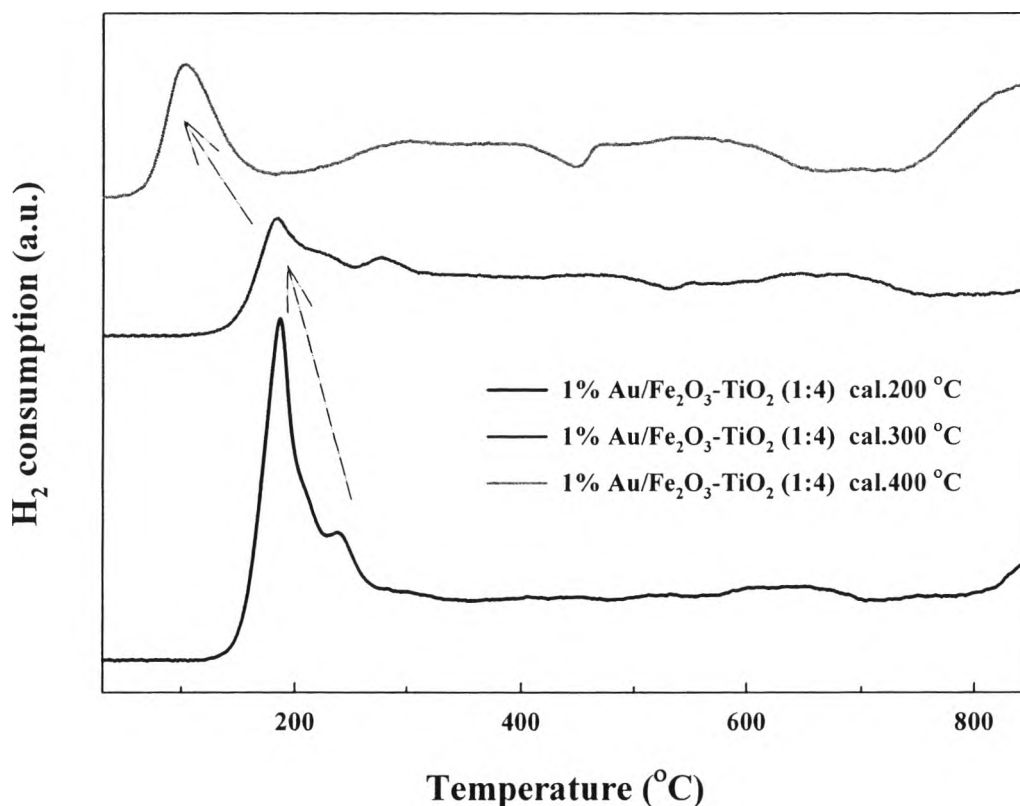
**Figure 4.6** H<sub>2</sub>-TPR profiles of all samples with 1% gold loading.

The reduction peak of Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and 1% Au catalysts are shown in Figure 4.6. The reduction peak of pure TiO<sub>2</sub> sample showed a poorly identified peak at 640 °C. However, 1% Au/TiO<sub>2</sub> was observed two small broad peaks at low temperature (200 °C) and at high temperature (500 °C). These suggested that Au<sub>x</sub>O<sub>y</sub> in 1% Au/TiO<sub>2</sub> can be partially reduced by H<sub>2</sub> at low temperature (Zhu *et al.*, 2004) and the reduction peak at high temperature can be assigned to reduction of bulk TiO<sub>2</sub>. In addition, the reduction of pure Fe<sub>2</sub>O<sub>3</sub> are consisted of one low temperature peak between 300 °C and 430 °C and a broad peak at between 510 °C and 730 °C. The low



temperature corresponds to the reduction peak of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ . The broad reduction peak correspond to reduction of  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$  and at temperature higher than  $750\text{ }^\circ\text{C}$  correspond to reduction peak of  $\text{FeO}$  to  $\text{Fe}$  (Chang *et al.*, 2009). The reduction peak of 1%  $\text{Au}/\text{Fe}_2\text{O}_3$  showed smaller peak than pure  $\text{Fe}_2\text{O}_3$  and also shifted toward lower temperature at between  $280\text{ }^\circ\text{C}$  and  $360\text{ }^\circ\text{C}$ , between  $500\text{ }^\circ\text{C}$  and  $680\text{ }^\circ\text{C}$  and at higher  $680\text{ }^\circ\text{C}$  that can be ascribed to the reduction peak of  $\text{Fe}_2\text{O}_3$  to its corresponding metallic phase. However, no reduction of  $\text{Au}_x\text{O}_y$  was observed. These suggested that  $\text{Au}_x\text{O}_y$  in 1%  $\text{Au}/\text{Fe}_2\text{O}_3$  can be fully reduced by  $\text{H}_2$  at ambient temperature. It can be implied that the addition of  $\text{Au}$  helped the reducibility of support by shifting peak toward lower temperature.

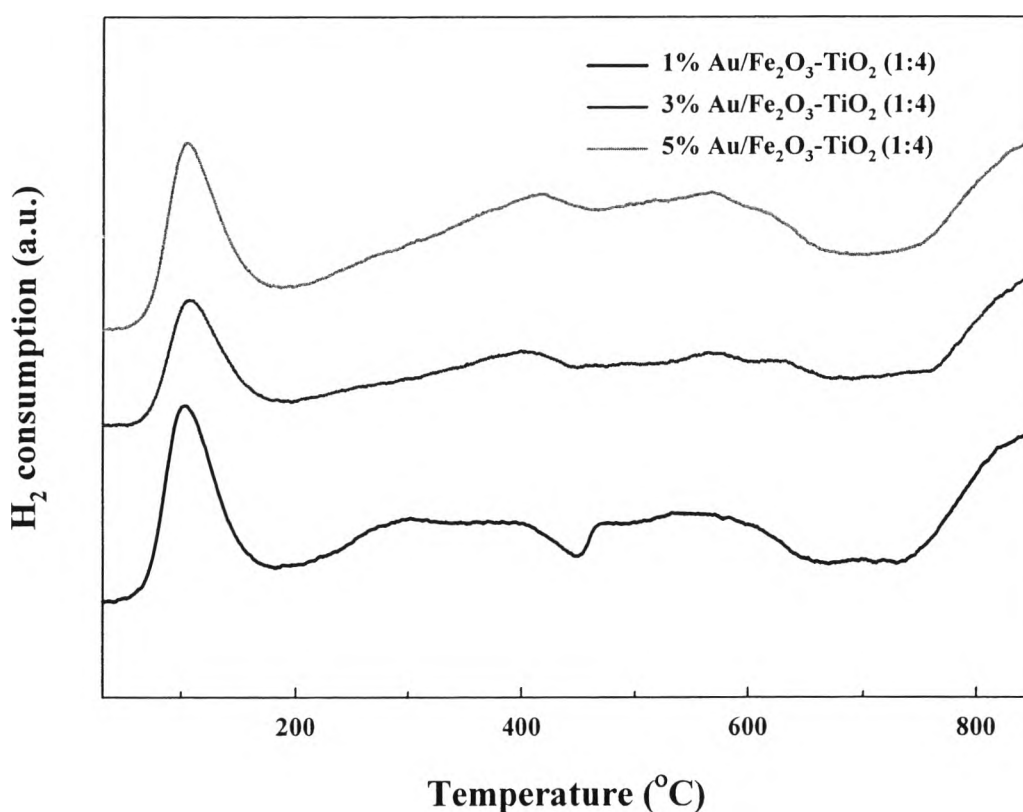
For 1%  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  (Figure 4.6), the sharp reduction peak at about  $165\text{ }^\circ\text{C}$ , which assigned to the reduction of both gold oxide ( $\text{Au}_x\text{O}_y$ ) to metallic gold ( $\text{Au}^0$ ) and  $\text{Au-Fe-O}$  in  $\text{Fe}_2\text{O}_3\text{-TiO}_2$ , was observed, resulting in the specific reduction peak of  $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  exhibited lower  $\text{H}_2$  consumption compared with the reduction peak ( $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$ ) of  $\text{Fe}_2\text{O}_3\text{-TiO}_2$  supports. Nevertheless, the two stage reduction peaks ( $\text{Fe}_2\text{O}_3$  to  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_3\text{O}_4$  to  $\text{FeO}$ ) can be clearly seen at the presence of  $\text{Fe}$  content which the specific reduction peaks shifted to lower temperature for all  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  catalysts compared to bulk  $\text{Fe}_2\text{O}_3$ . The enhancement of reducibility of  $\text{Fe}_2\text{O}_3$  is due to the effect of the hydrogen spillover from metallic phase to support (Chang *et al.*, 2009). In addition, at higher amount of  $\text{Fe}$ , these peaks were shifted to higher temperature because excess amount of  $\text{Fe}$  may not involved in interaction with  $\text{Au}$  specie. The amount of  $\text{H}_2$  consumption was dependent on the  $\text{Fe}$  contents in the reduction region of iron oxide. It is plausible that more  $\text{Fe}$  contents in catalysts more  $\text{H}_2$  consumption in TPR process. On the other hand, the increasing of reduction temperature of gold oxide led to an increase the interaction between gold and  $\text{TiO}_2$  species.



**Figure 4.7** H<sub>2</sub>-TPR profiles for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts with different calcination temperatures.

The reduction peak of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst at different calcination temperatures are presented in Figure 4.7. The profiles indicated two reduction peaks along with broad peak at high temperatures. These peaks are cited to the reduction peak of Au and Fe oxides to its corresponding metallic species. The sample calcined at 200 °C showed a reduction peak at 200 °C with a small shoulder peak at 240 °C, which could be assigned to the reduction peak of both Au<sub>x</sub>O<sub>y</sub> and Au-Fe interaction in 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalyst. When increasing calcination temperature, the result showed a decrease in the reduction peak and the reduction peak also was shifted to lower temperature. It can be explained that the increasing of calcination temperature can improve the metal-metal interaction of the catalyst. The lower reduction temperature indicated the decrease crystallite size of gold oxide (Au<sub>x</sub>O<sub>y</sub>) with increasing calcination temperature and also improved metal dispersion of gold metal on the support that related to the TEM result (Chang *et al.*, 2009). At the reduction peak of Fe<sub>2</sub>O<sub>3</sub> to Fe<sub>3</sub>O<sub>4</sub> and Fe<sub>3</sub>O<sub>4</sub> to FeO, there is no obvious

difference of the reduction temperature of these species with increasing calcination temperature. However, it was noticed that lower  $H_2$  consumption of iron oxide region which Au could have a strong interaction with Fe and resulted to decrease  $H_2$  consumed. These due to the amount of  $H_2$  consumption was dependent on the Fe contents in the reduction region of iron oxide as mentioned above. It could be concluded that high calcination temperature have an effect on the catalytic activity with Au metallic species and metal-metal interaction.



**Figure 4.8**  $H_2$ -TPR profiles of  $Au/Fe_2O_3-TiO_2$  (1:4) catalysts with different Au loadings.

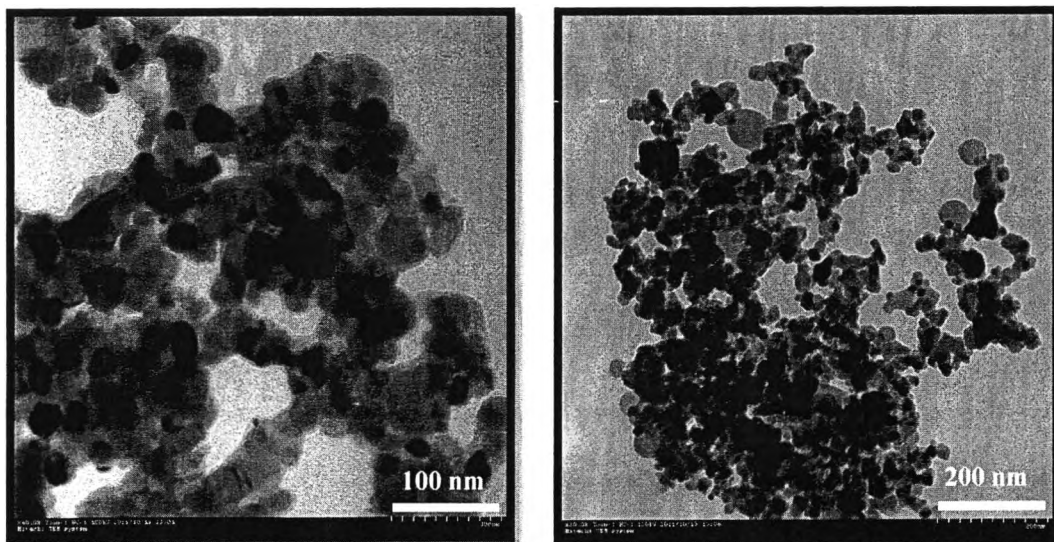
As shown in Figure 4.8, it can be observed that the increasing of Au loading does not seem to improve metal-metal interaction in  $Au/Fe_2O_3-TiO_2$  catalyst since there is no significant difference in reduction peak between 70 °C to 180 °C, (reduction peak of  $Au_xO_y$ ). Similarly to previous section, the reduction temperature between 260 °C to 650 °C is assigned to iron oxide to its corresponding metallic

species. However, the result showed that the reduction peak in iron oxide region shifted to higher reduction temperature with increasing amount of gold loading. It can be explained that higher gold content affect to excess Fe interact with gold species very less which could be enhanced metal-metal interaction and also enhance metal dispersion (Chang *et al.*, 2009).

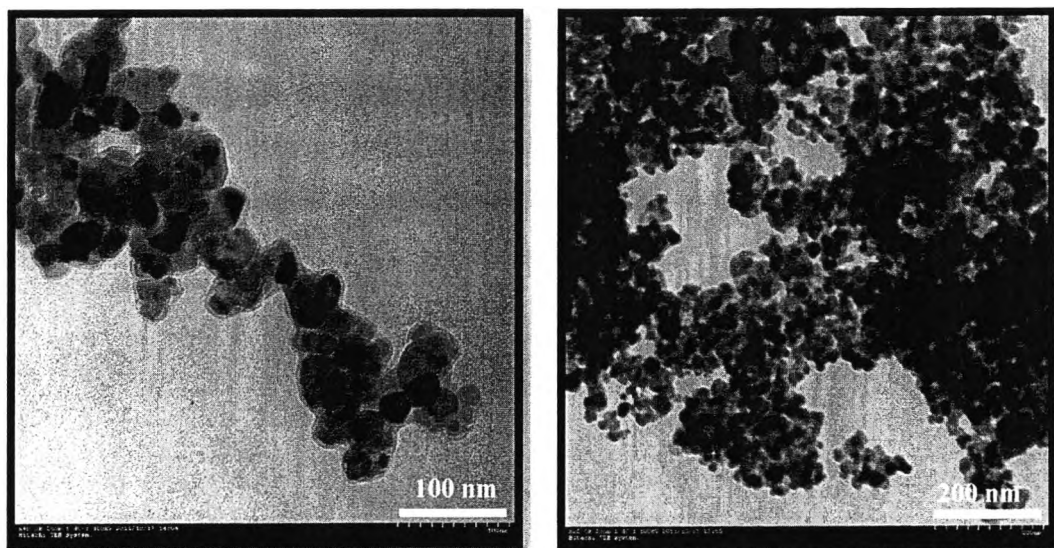
#### 4.1.4 TEM Result

The catalytic activity of supported Au catalysts firmly depends on the Au particle size. The Au particle size on the support can be handle by suitable composite support of the catalyst and suitable calcination temperature as well as the optimum Au content. Accordingly, it is necessary to study the Au particle size and size distribution in more detail for the prepared catalysts with different support compositions, different calcination temperatures and different Au loadings by TEM analysis.

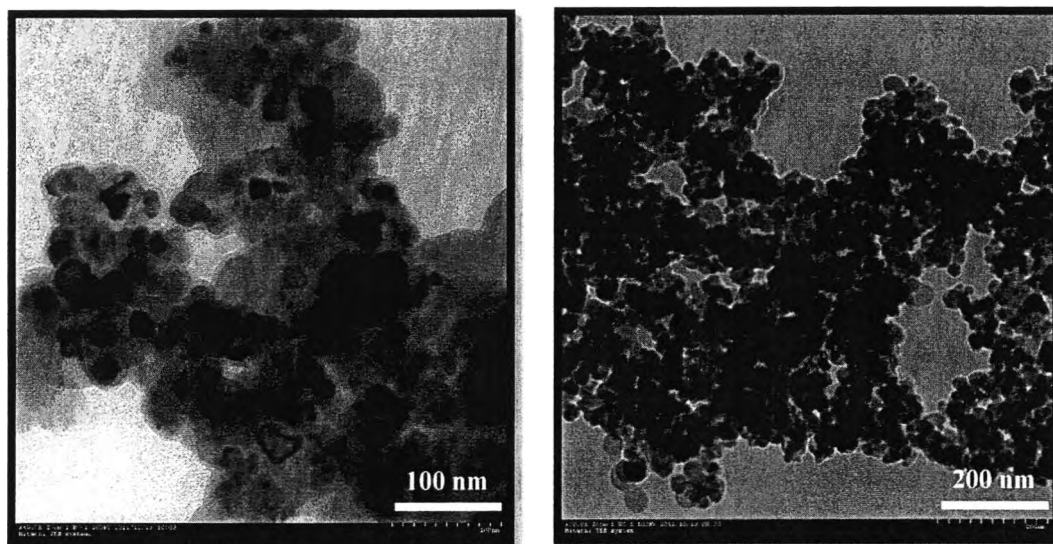
Representative Transmission Electron Microscope (TEM) images and the particle size distribution bar graphs of the support (shown in Appendix C), with different calcination temperatures are shown in Figure 4.9. The dark spots indicated the Au particles on the supports. The mean particle size of Au with different calcination temperatures at 200, 300, and 400 °C were 4.12, 5, and 4.58 nm, respectively. As a result, the mean particle size tended to increase with increasing calcination temperature. This result agrees with the TPR result, showed that when increasing calcination temperature the metal-metal interaction was increased. Therefore, it can be concluded that 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C represents the highest catalytic activity due to high metal-metal interaction which have an significant effect on PROX reaction. Moreover, the trends of metal dispersion were consistent with the TPR result.



a) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 200 °C



b) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 300 °C



c) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C

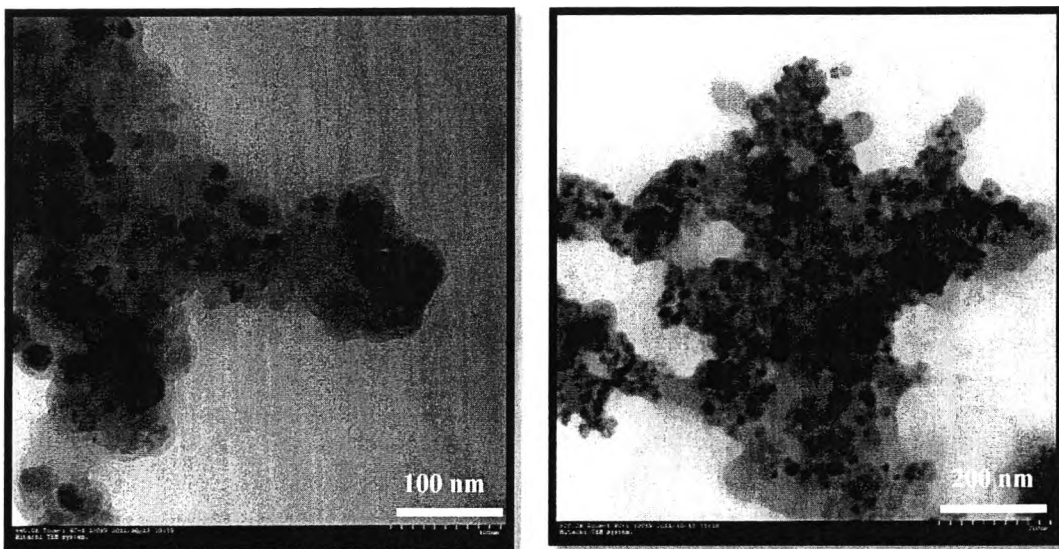
**Figure 4.9** TEM images of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts; a) calcined at 200 °C, b) calcined at 300 °C, and c) calcined at 400 °C.

Figure 4.9 c) and Figure 4.10 illustrates the TEM microphotographs of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts calcined at 400 °C. The catalysts with gold loading of 1%, 3%, and 5 wt% have the mean Au particle size of 4.58, 5.57, and 5.45 nm, respectively.

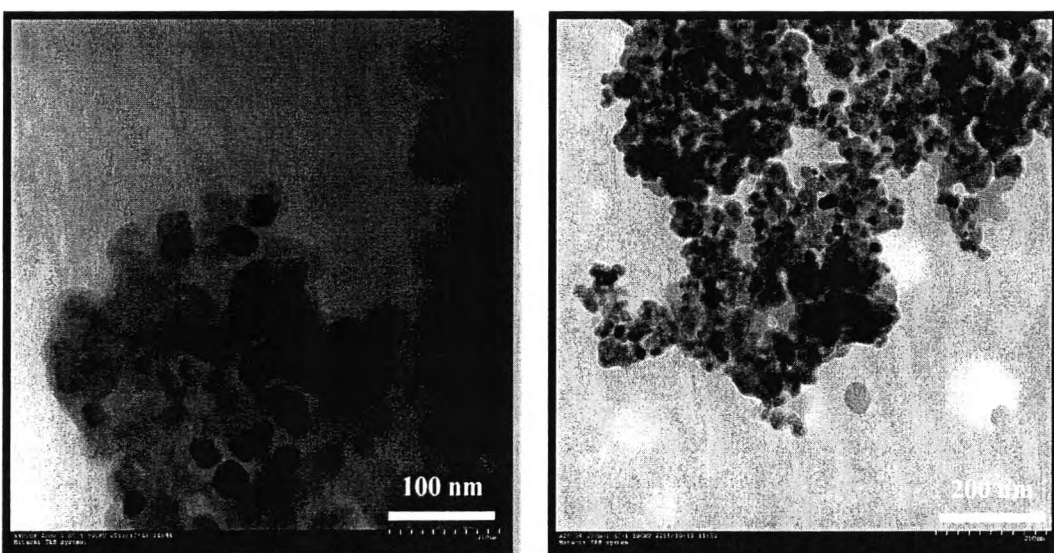
From Figure 4.9 c) Figure 4.10 a–b, it is clearly seen that the mean Au particle sizes slightly increase with increasing the gold loading. Therefore, in this experiment the Au loading seem to have no affect to the Au particle size. The highest catalytic activity could be obtained at 5 wt% Au loading. According the TPR profiles, it should be noted that the decrease in interval of reduction temperature of gold oxide when higher Au loadings (3 to 5 wt%) could be referred to the dispersion improvement. This kind of observation has also been reported in another type of catalyst such as Ni/CeO<sub>2</sub>-ZrO<sub>2</sub> (Pérez-Hernández *et al.*, 2011).

Figure 4.11 shows the TEM images of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C, with O<sub>2</sub> pretreatment for 2 h. The mean Au particle sizes increased to 6.37 nm compared to 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C

without O<sub>2</sub> pretreatment (4.58 nm). These findings were in agreement with the previous TPR characterization results.

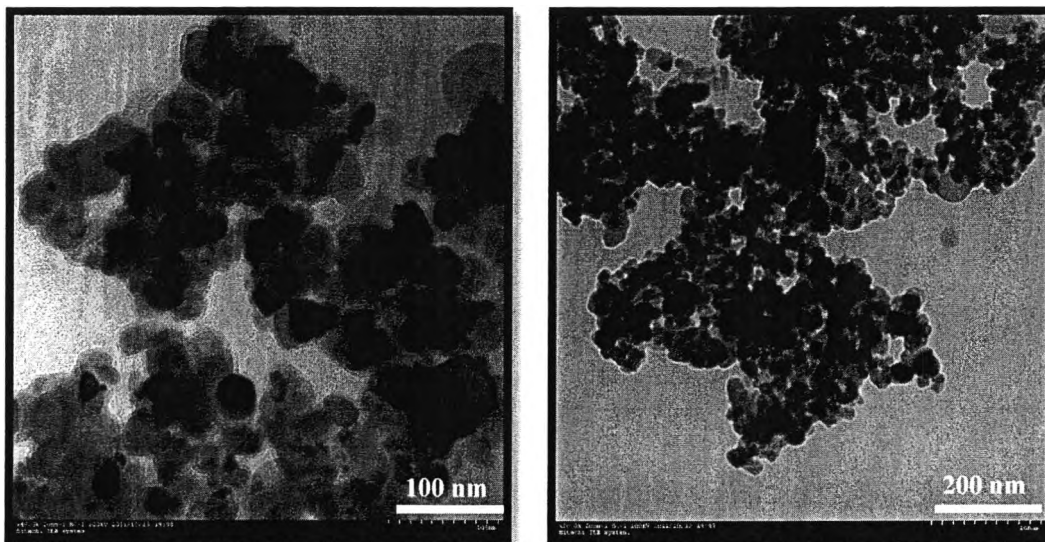


a) 3% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C



b) 5% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C

**Figure 4.10** TEM images of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C with different gold loadings; a) 3%, and b) 5 wt%.



a) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C with O<sub>2</sub> pretreatment

**Figure 4.11** TEM images of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) calcined at 400 °C with O<sub>2</sub> pretreatment at 200 °C for 2 h.

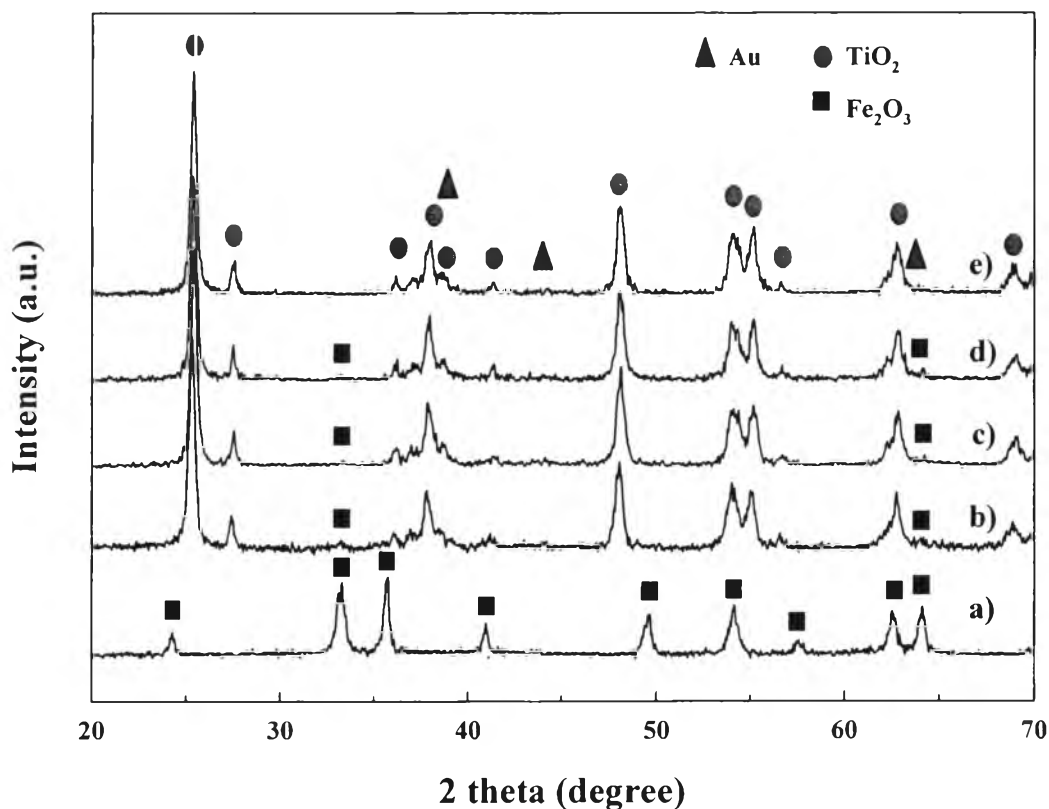
#### 4.1.5 XRD Patterns

The X-ray diffraction patterns, in the angular range (20–70°) 2θ, of as-prepared gold catalysts are presented in Figure 4.12. Patterns a, b, c, d, and e in Figure 4.12 showed the 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts with various atomic ratios of Fe/Ti.

It is clearly seen that there is a significant difference shown in the XRD result. In all samples, no peak of metallic gold (2θ = 38.2°, 44.4°, and 64.5°) or gold oxide (2θ = 25.5° and 49.8°) were observed, which suggests that the fine dispersion of gold particles on support surface and fewer amount of gold species that is out of the detected limitation of XRD (Ou *et al.*, 2008). However, a very strong peak of crystalline features of TiO<sub>2</sub> were detected at 2θ = 25.3° (Yang *et al.*, 2009). Moreover, the weaker peaks were also detected at 36.10, 48.10, 55.1, 63.00, and 69.00° which were corresponding to anatase TiO<sub>2</sub>; TiO<sub>2</sub> (110), TiO<sub>2</sub> (101), TiO<sub>2</sub> (200), TiO<sub>2</sub> (211), TiO<sub>2</sub> (204), and TiO<sub>2</sub> (116) for CuKα (1.5406 Å) radiation, respectively (Chang *et al.*, 2008). In Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub>, Fe existed as Fe<sub>2</sub>O<sub>3</sub> (hematite) and Fe<sub>3</sub>O<sub>4</sub> (magnetite). Diffraction peaks which contribute from Fe<sub>2</sub>O<sub>3</sub> were found at 2θ



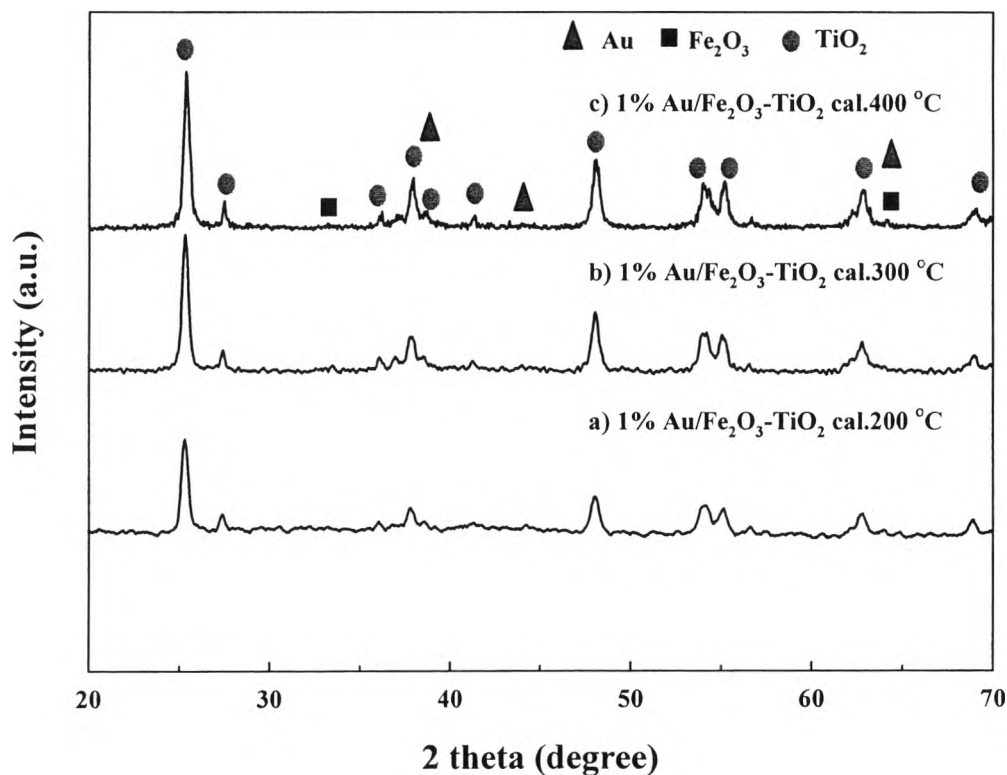
= 33.20° and 64.00° with increasing Fe content in the mixed support (Chang *et al.*, 2009). Additionally, the crystallite sizes of TiO<sub>2</sub> were calculated, using the Scherrer equation and the results are summarized in Table 4.1.



**Figure 4.12** X-Ray diffraction (XRD) patterns of: (a) 1% Au/Fe<sub>2</sub>O<sub>3</sub>; (b) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (4:1); (c) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:1); (d) 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4); (e) 1% Au/TiO<sub>2</sub>.

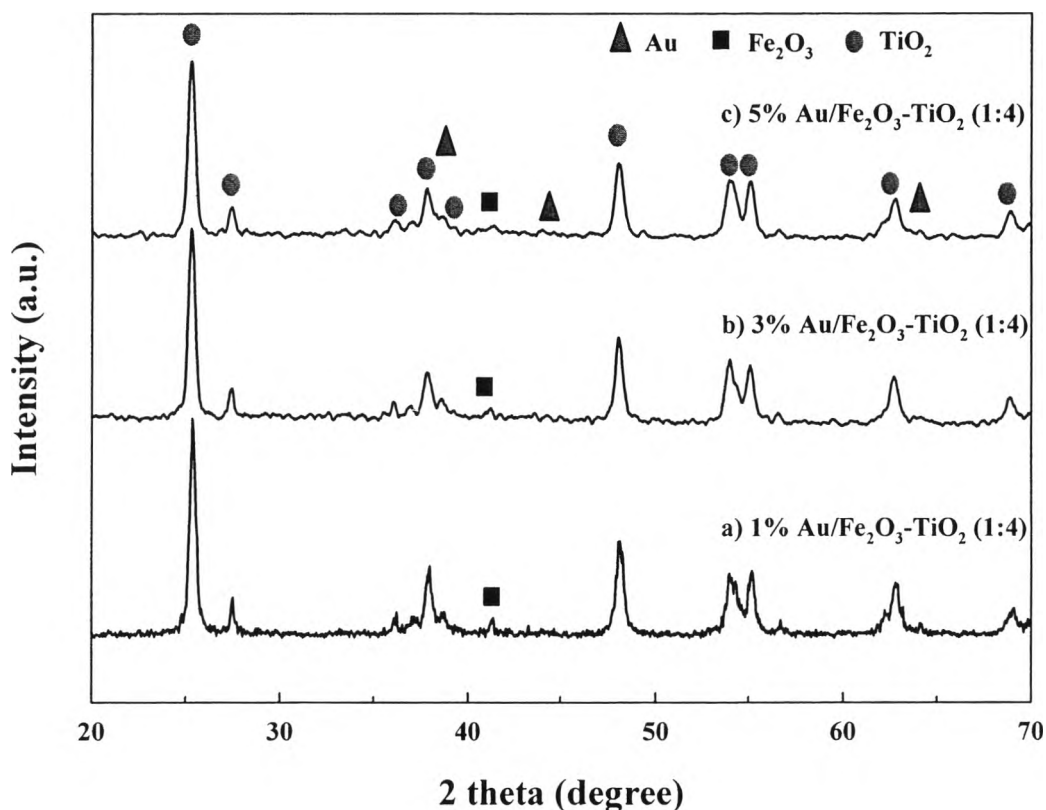
The XRD patterns of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts with different calcination temperatures are illustrated in Figure 4.13. The changes induced by thermal treatment on the mixed support and the metal were observed. The XRD patterns for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst calcined at 200 °C showed that the sample has a structure with a low crystallinity in the presence of some Fe<sub>2</sub>O<sub>3</sub> phase. It was supposed that the most part of titania oxide is presented as amorphous. However, the crystallinity of titania oxide (TiO<sub>2</sub>) increased with increasing

calcination temperature. In addition, all of samples are almost identical and still no peaks of metallic gold can be identified.



**Figure 4.13** XRD patterns of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts with different calcination temperatures: (a) calcined at 200 °C; (b) calcined at 300 °C; (c) calcined at 400 °C.

Figure 4.14 revealed the XRD patterns, of Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts, calcined at 400 °C, with different Au loadings. The XRD of the samples still showed no peaks of metallic gold species. Moreover, there is no significant difference in term of crystallinity for all catalysts. These results agreed with those obtained from catalytic activity data that the samples had almost the same catalytic activity.



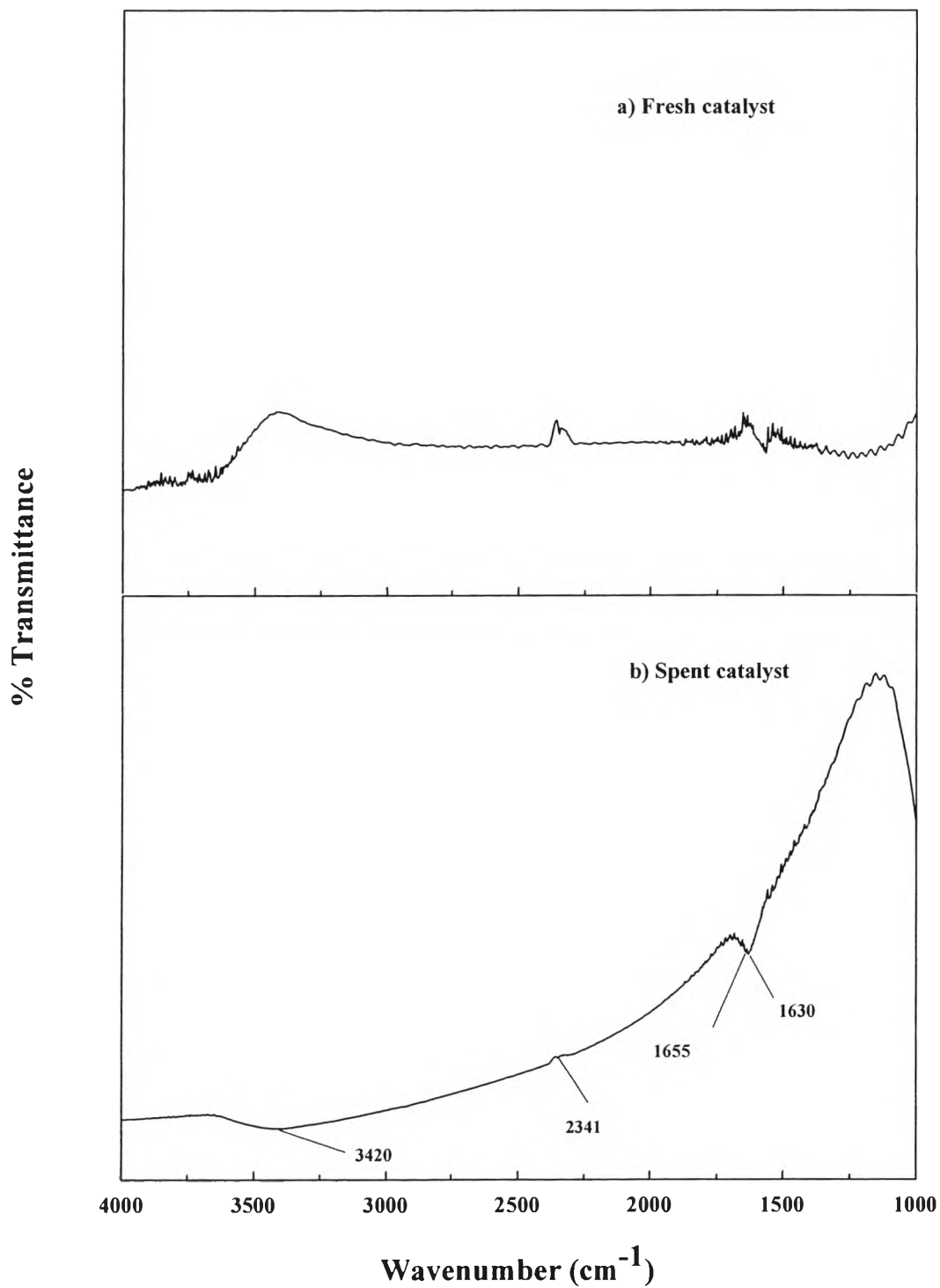
**Figure 4.14** XRD patterns of  $\text{Au}/\text{Fe}_2\text{O}_3\text{-TiO}_2$  (1:4) catalysts with different gold loadings: (a) 1 wt%; (b) 3 wt%; (c) 5 wt%.

#### 4.1.6 FT-IR Measurement

Fourier transform infrared spectroscopy (FT-IR) was utilized to examine the catalyst surface before and after deactivation test for 16 h. The results from the FT-IR spectroscopy are shown in Figure 4.15.

A broad transmission band was observed in the range of  $3200\text{--}3600\text{ cm}^{-1}$  for fresh catalyst, owing to the O-H stretching mode of  $\text{H}_2\text{O}$  molecules (Daté *et al.*, 2001). After the sample was exposed to the reactant with CO and with  $\text{CO}_2$  led to marked changes in the IR spectra in O-H stretching region, including a decrease in intensity to negative band in this range (O-H stretching mode, already assigned to bicarbonates). These result suggested the interactions between adsorbed carbonate-like species and surface hydroxyl groups through hydrogen bonding. The appearance of IR band at  $1800\text{--}900\text{ cm}^{-1}$  region which are contributed to carbonate-like species formed on the support and on gold were observed. The intensities of these bands are correlated inversely with the conversion of CO to  $\text{CO}_2$ , consistent with inference that

carbonate-like species formed on gold clusters block the active sites and caused the deactivation (Hao *et al.*, 2009).



**Figure 4.15** FTIR spectra of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts: (a) fresh catalyst; (b) spent catalyst.

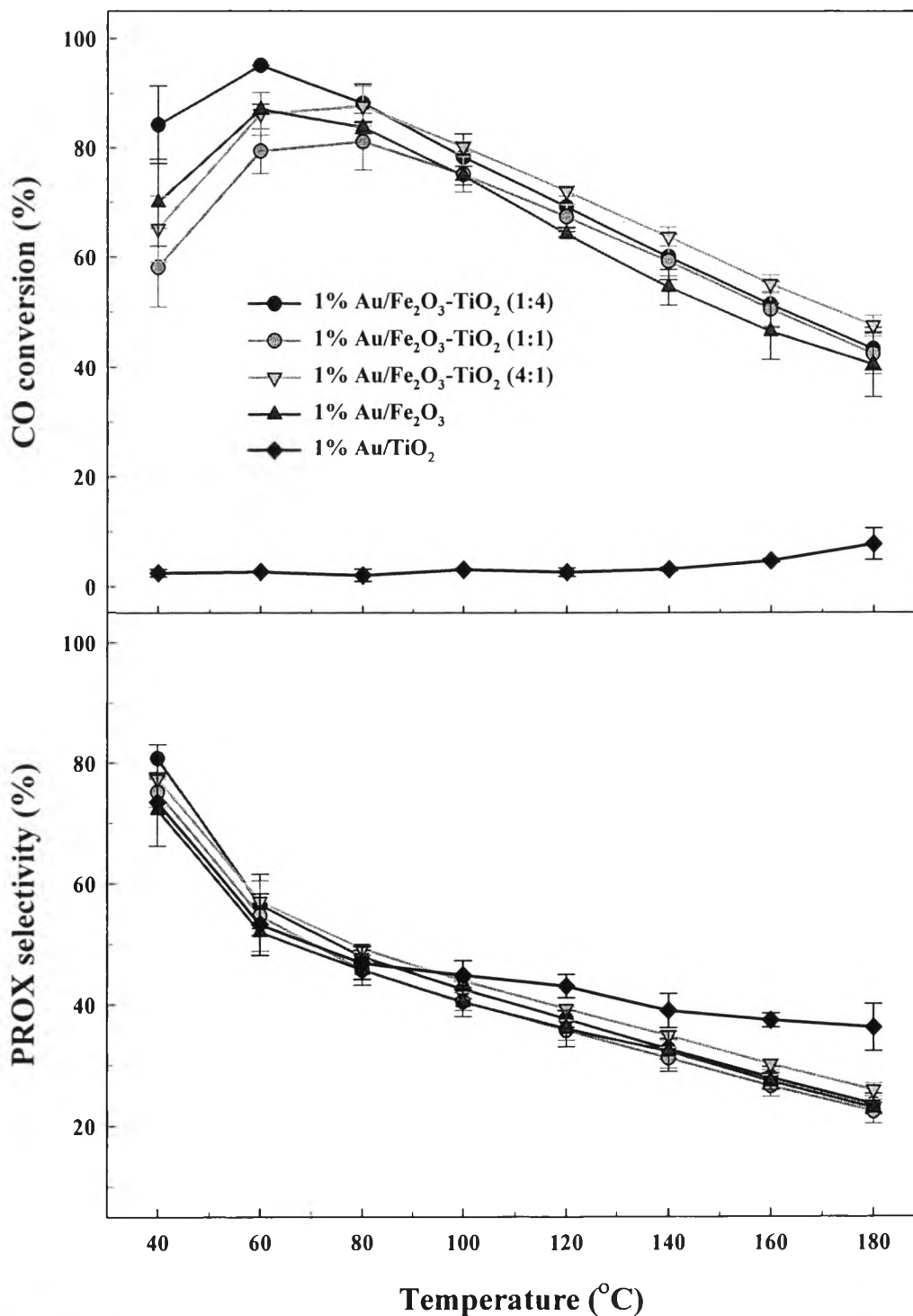
## 4.2 Activity Measurement

In this part, the catalytic activity of the prepared catalysts were investigated. The catalytic activity measurement was carried out under atmospheric pressure in a fixed-bed catalytic micro-reactor. A 100 mg catalyst of 80–120 mesh in size was loaded into the quartz reactor. The reactant flow consisted of 1% CO, 1% O<sub>2</sub>, and 40% H<sub>2</sub> balanced in He passing through the catalyst bed at the total flow rate of 50 ml/min (GHSV = 30000 mlg<sup>-1</sup>h<sup>-1</sup>) and the activity was observed at various temperatures in the range of 40 to 180 °C.

### 4.2.1 Effect of Support Atomic Ratio on the Catalytic Activity

The Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (0:1, 1:1, 1:4, 4:1, and 1:0) supports were prepared by incipient wetness impregnation. The prepared supports were then used in preparing a catalyst by deposition-precipitation technique, dried at 110 °C overnight and calcined at 400 °C for 4 h. Subsequently, the prepared 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts were studied with various operating temperatures (40 to 180 °C). Figure 4.16 illustrates the catalytic activity in terms of CO conversion and PROX selectivity of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts with various atomic ratios of Fe/Ti.

From Figure 4.16, it was found that the CO conversion increased with increasing temperature reaching a maximum, which were 7.64% for 1% Au/TiO<sub>2</sub> at 180 °C, 94.99% for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) at 60 °C, 81.03% for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:1) at 80 °C, 87.56% for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (4:1) at 80 °C, 86.95% for 1% Au/Fe<sub>2</sub>O<sub>3</sub> at 60 °C, and then the CO conversion decreased at higher temperature. In addition, for selectivity data can also be seen that for each catalyst selectivity is strongly decreased when temperature increased. Therefore, the different support atomic ratio have a significant effect on the CO conversion in the order: 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) > 1% Au/ Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (4:1) > 1% Au/Fe<sub>2</sub>O<sub>3</sub> > 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:1) > for 1% Au/TiO<sub>2</sub>. Consequently, in this work, the highest activities for 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) could be attributed to the TPR profile that showed high metal-metal interaction and the better gold dispersion.



**Figure 4.16** CO conversion and selectivity as a function of reaction temperature over 1% Au/ $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  catalysts with various atomic ratios of Fe/Ti.

#### 4.2.2 Effect of Calcination Temperature on the Catalytic Activity

Figure 4.17 displayed the CO conversion of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts calcined at different temperatures as a function of temperature, the calcination temperature played an important role in providing good catalytic performance for CO oxidation. The catalyst sample calcined at 400 °C showed the best performance and lower temperature required for CO conversion (in the range of 40 to 100 °C). In addition, with increasing reaction temperature, significant decreases in CO conversion and selectivity could be observed. The low catalytic activity of the catalysts calcined at 200 °C and 300 °C could be due to the poor interaction between gold nanoparticles that related to TPR. The lower amount of metallic Au or Au<sup>0</sup> specie was formed, as shown in the UV-vis characterization. Nevertheless, when higher calcination temperature could lead to a significance decrease in gold nanoparticles and support grain which resulted in an increase in catalytic activity.

#### 4.2.3 Effect of Gold Loading on the Catalytic Activity

Figure 4.18 shows the effect of different gold loadings on CO conversion and the PROX selectivity versus temperature curves obtained over Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts. The amounts of gold loading were varied at 1%, 3%, and 5 wt%. The catalysts were prepared by deposition-precipitation, dried, and calcined at 400 °C.

In general, the increase in Au loading could increase the activity of the catalyst significantly (Lui *et al.*, 2010). As illustrated in Figure 4.18, with increasing Au loading, the catalytic activity for PROX slightly increased. However, it seem to be no significant difference. In this case, it can be concluded that Au loading has no significant effect on CO conversion and the PROX selectivity. In the present work, a proper Au loading was proposed to be at 1 wt% when both catalytic activity and cost of catalyst were taken into consideration. However, a slightly increase in catalytic activity was observed when increasing Au loading resulting in high the dispersion and better metal-metal interaction, as mentioned in TPR result.

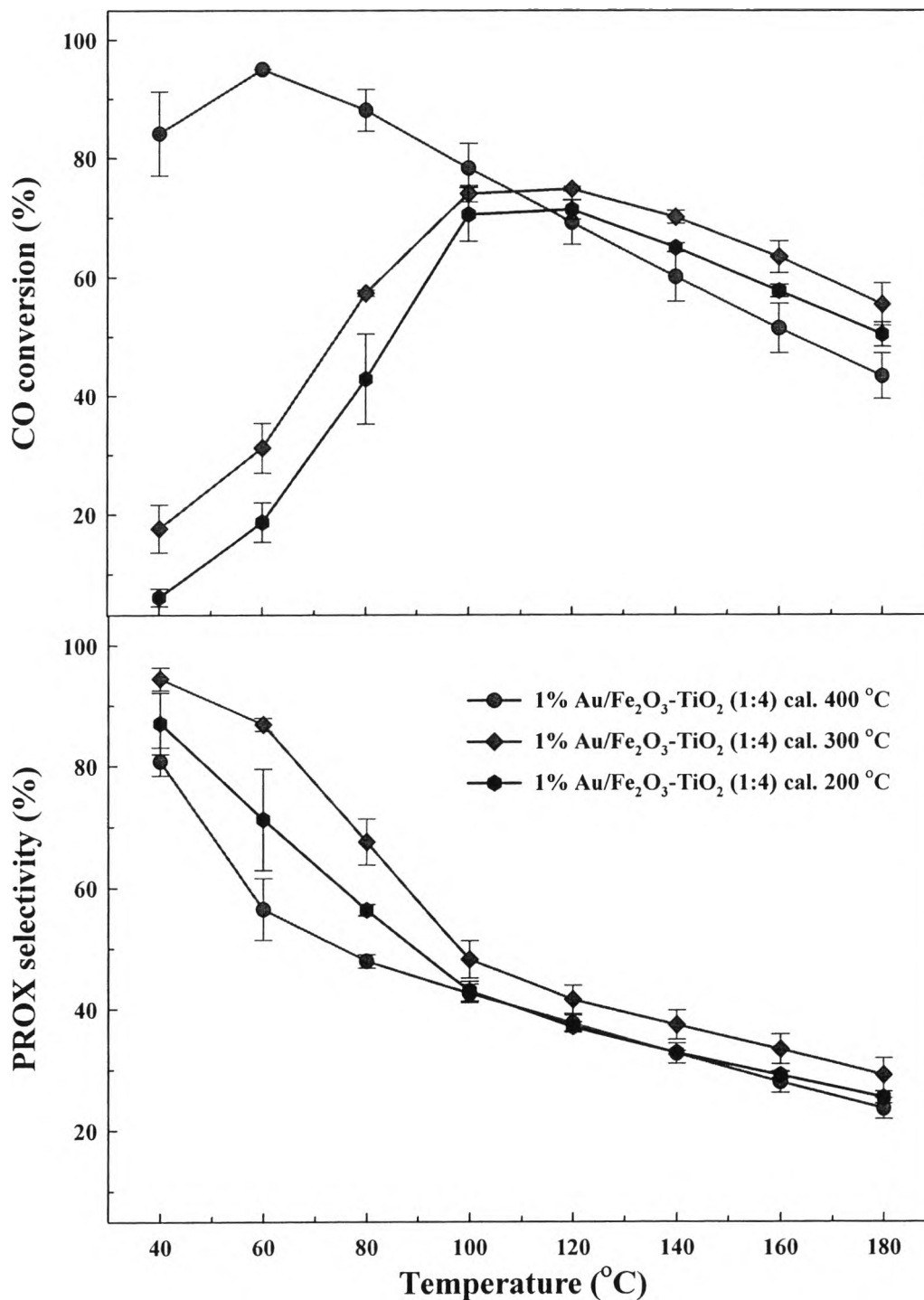
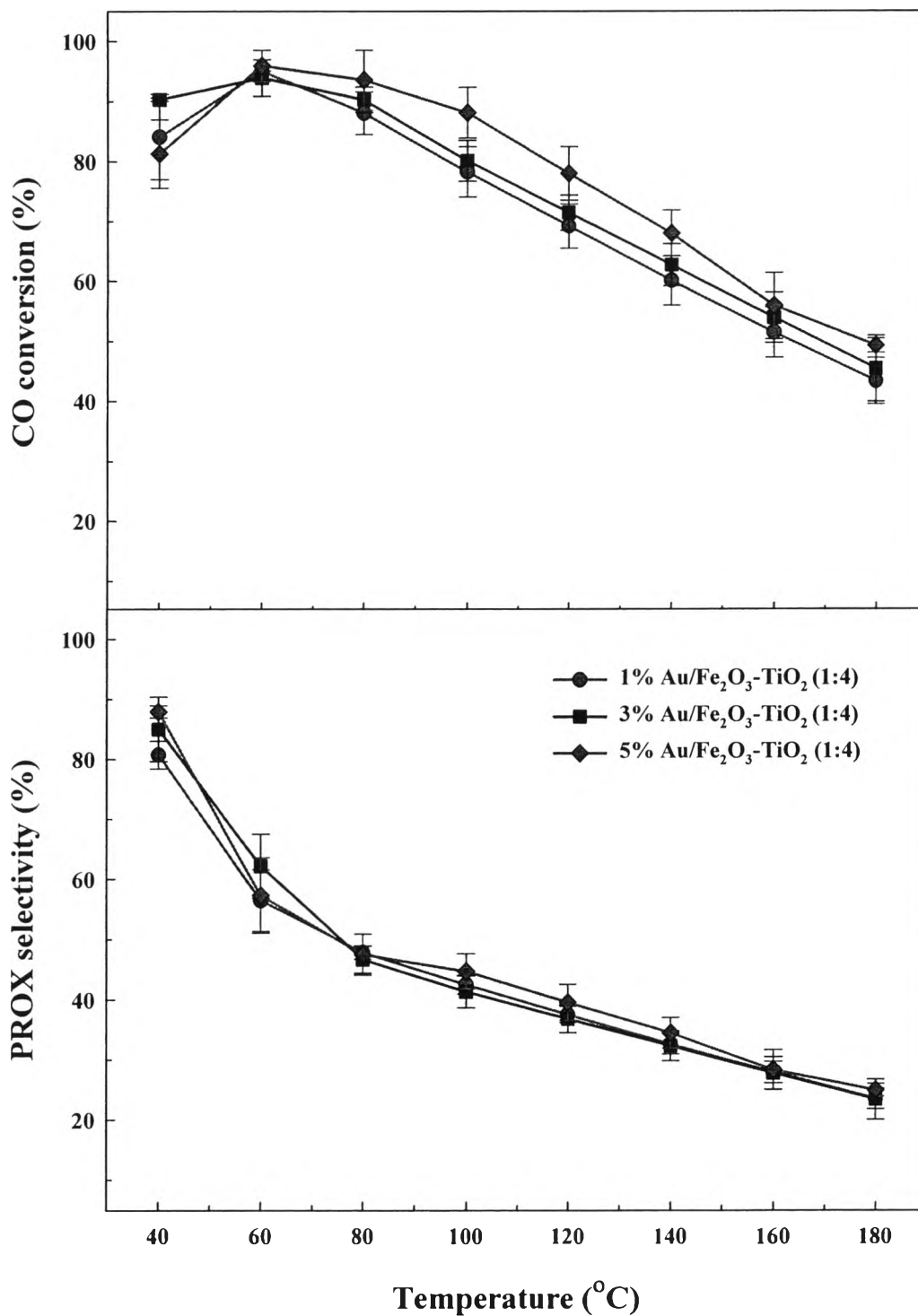


Figure 4.17 Effect of calcination temperature on CO conversion and PROX selectivity over 1% Au/ Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> catalysts.



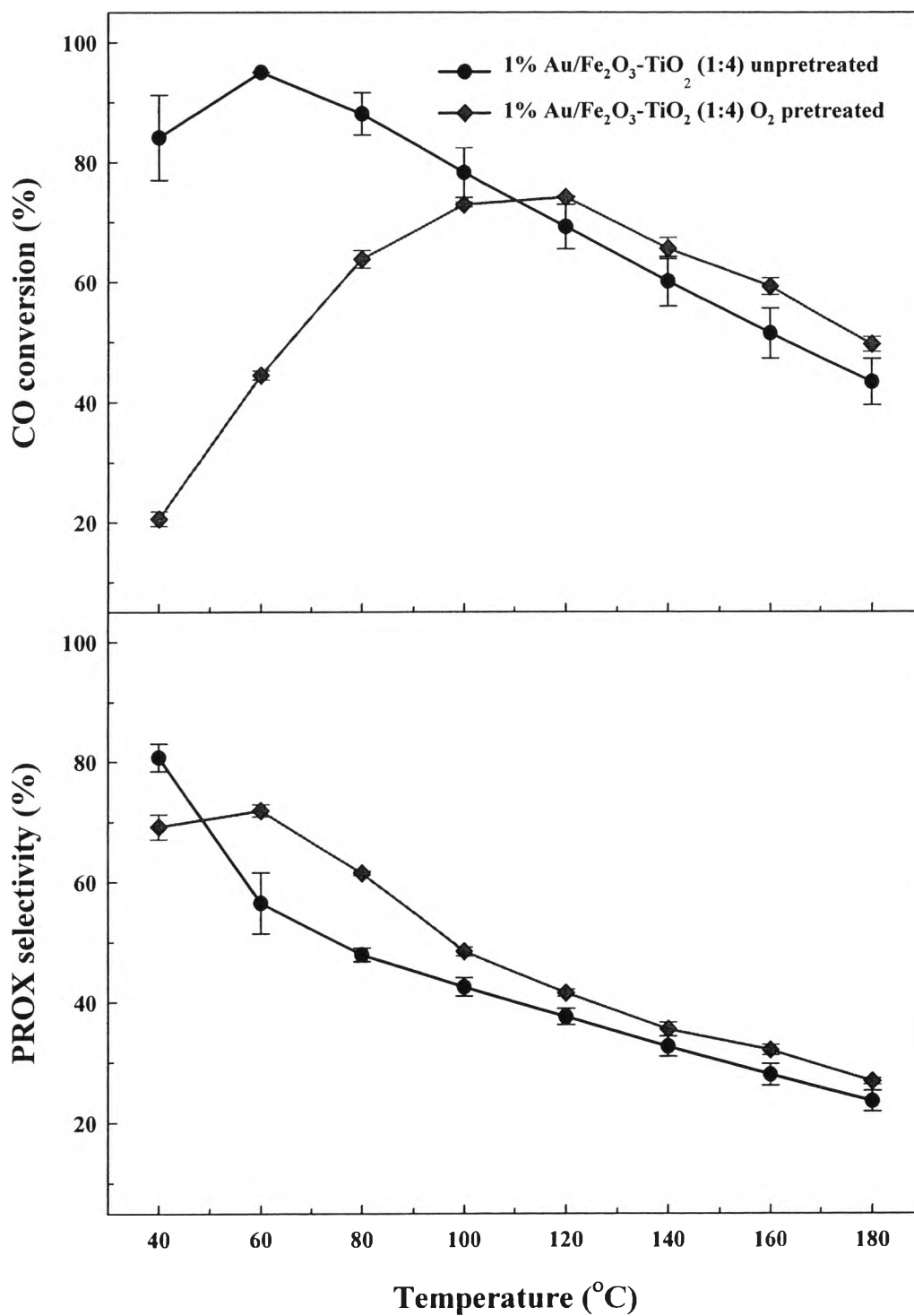


**Figure 4.18** Effect of gold loading on CO conversion and PROX selectivity over Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalysts.

#### 4.2.4 Effect of O<sub>2</sub> Pretreatment on the Catalytic Activity

The oxygen pretreatment of the catalyst was marked to be one of the important parameters on the activity of the catalyst. Therefore, the 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst calcined at 400 °C was pretreated with oxygen at 200 °C for 2 h. After that, the catalyst was experienced the activity test (PROX reaction) with 1% CO, 1% O<sub>2</sub>, 40% H<sub>2</sub>, and balanced in He at the temperature range of 60 °C to 180 °C. The catalyst activity, in terms of CO conversion and PROX selectivity, of oxygen pretreated catalyst is shown in Figure 4.19.

The CO conversion, after oxygen pretreatment of catalyst decreased from 94.99% to 44.47% at 60 °C. The reason behind this phenomenon is that the surface oxygen species are formed on gold surface after the catalyst is treated with oxygen at low temperatures the reaction activity was decreased (Qu *et al.*, 2005). From the above experiments, it can be concluded that the activity of Au catalysts for PROX reaction are related with the surface oxygen species on gold, and the interaction of oxygen species with gold. As we known, the reaction of CO with O<sub>2</sub> requires both CO and O<sub>2</sub> be adsorbed on the catalyst surface, the reaction temperature for CO oxidation here is lower (40 °C to 100 °C). Then the surface oxygen species adsorbed on gold surface are not desorbed under these temperatures, and they are occupying reactive sites. Thus the strongly adsorbed surface oxygen species block the adsorption and diffusion of weak adsorbed surface oxygen result to a decrease in the catalytic activity of the catalyst. Moreover, the O<sub>2</sub> pretreated catalyst had a lower metal-metal interaction as supported by TPR result (not shown here). The reduction peak of pretreated catalyst is smaller than that of untreated catalyst and also combined with the support, which can be implied that oxygen pretreatment led to increase metal-support interaction and may cause the gold particles aggregate to larger ones (related with TEM result) then decrease metal dispersion of catalyst (Chang *et al.*, 2009), resulting in low catalytic activity for PROX reaction.



**Figure 4.19** CO conversion and PROX selectivity as a function of reaction temperature for PROX reaction over 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst pretreated with oxygen.

#### 4.2.5 Deactivation Test

Catalyst deactivation is one of the major problems for practical PROX catalysts. It is mainly due to some modification in the surface structure and the chemical composition of the catalyst, which is believed to take place at some stages in the reaction process. For gold-based catalyst in PROX reaction, the catalyst deactivation may be caused by phase transitions such as the formation of carbonates species and/or blocking the access of CO<sub>2</sub> and H<sub>2</sub>O at a catalytic the active sites (Sirichaiprasert *et al.*, 2008).

Thus, the catalyst deactivation evaluation is vital to enable practical catalyst designs and also to develop better understanding of the catalyst activity. In the present work, catalyst deactivation evaluation was taken at a temperature of 60 °C. The stability of the prepared catalyst was tested in simulated reformed gas mixtures containing 1% CO, 1% O<sub>2</sub>, 40% H<sub>2</sub>, and balanced in He, under atmospheric pressure.

Figure 4.20 shows the stability test of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst calcined at 400 °C. It is clearly seen that the prepared catalyst presented a fine stable properties and its activity kept constant for 16 h.

##### 4.2.5.1 Effect of H<sub>2</sub>O in the Feed Stream

In general, it is believed that the catalytic activity of the catalyst is liable to be suppressed in the presence of water vapor (Luengnaruemitchai *et al.*, 2004). On contrary, the presence of water on the reaction stream was found to be favorable to the catalytic activity for CO oxidation reaction (Buccozzi *et al.*, 2001). In the present work, the prepared catalyst showed a stable catalytic activity, even though the H<sub>2</sub>O concentration was as high as 10% in the feed stream, as shown in Figure 4.20. Daté and coworkers suggested that the presence of OH<sup>-</sup> group extends the lifetime of the catalyst and prevents the deactivation by carbonate-like species accumulation.

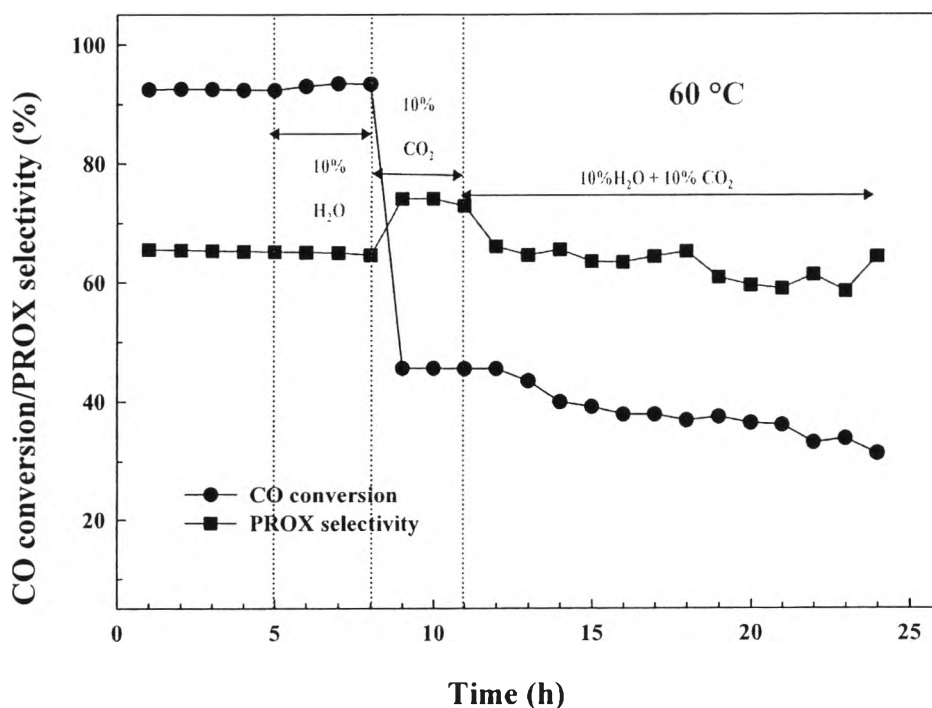
##### 4.2.5.2 Effect of CO<sub>2</sub> in the Feed Stream

Figure 4.20 also illustrates the changes in the activity of the catalyst when CO<sub>2</sub> was added to the feed stream. It can be clearly seen that the presence of CO<sub>2</sub> showed depressing effect on the catalytic activity owing to both the build-up of carbonates species on the catalyst's surface (Schubert *et al.*, 2001) and

the CO<sub>2</sub> adsorption on the catalyst (as confirmed in Figure 4.15) which surface carbonate-like species reduces the supply of oxygen required for CO oxidation reactions. The CO conversion decreased significantly from 95% to around 43%.

#### 4.2.5.3 Effect of Combination of CO<sub>2</sub> and H<sub>2</sub>O in the Feed Stream

The simulating practical fuel gas mixtures containing 1% CO, 1% O<sub>2</sub>, 10% CO<sub>2</sub>, 10% H<sub>2</sub>O, 40% H<sub>2</sub>, and balanced in He was used in order to examine the stability of the prepared catalyst. The effect of CO<sub>2</sub> and H<sub>2</sub>O on the catalytic performance of the prepared 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst calcined at 400 °C was investigated at a constant temperature (60 °C). From Figure 4.20, the presence of CO<sub>2</sub> and H<sub>2</sub>O in feed stream slightly decreased the CO conversion and the PROX selectivity. From the result, it was similar to the result of Naknam *et al.* (2009) who studied the influence of CO<sub>2</sub> and H<sub>2</sub>O on the PROX activities over a Au/ $\alpha$ -Fe<sub>2</sub>O<sub>3</sub> catalyst. They explained that the accumulation of carbonate-like species on the catalyst surface. This in turn then blocks the active sites for the PROX reaction. In addition, when adding CO<sub>2</sub> and H<sub>2</sub>O in feed may cause some blocking on at a the active sites, as mentioned above (Sirichaiprasert *et al.*, 2008).



**Figure 4.20** Deactivation test of 1% Au/Fe<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> (1:4) catalyst calcined at 400 °C.