



CHAPTER IV RESULTS AND DISCUSSION

4.1 Au/CeO₂, Au/Fe₂O₃-CeO₂, and Au/Fe₂O₃ Catalysts

In this part, Au/CeO₂, Au/Fe₂O₃ and Au/CeO₂-Fe₂O₃ catalysts were prepared by precipitation, co-precipitation and deposition-precipitation (DP) methods. The mixed supports were symbolized as CF(x), where x was the Ce/(Ce+Fe) atomic ratio. The prepared catalysts were tested in the oxidative steam reforming of methanol (OSRM). The impact of the support composition on the catalytic performance was studied by varying the Ce/(Ce+Fe) atomic ratio. Moreover, the effect of Au content, calcination temperature, steam/methanol molar ratio, oxygen/methanol molar ratio, and gas pretreatment on the catalytic pretreatment were studied in detail.

The catalytic activity tests were carried out in a vertical pyrex glass microreactor by packing with 100 mg catalyst of 80–120 mesh inside. The activity was investigated at varied temperature in the range of 200°C to 400°C under atmospheric pressure. The characterization results from several techniques, including TPR, XRD, TEM, UV-vis, FT-IR, TPO, and BET surface area of the prepared catalysts will be used to explain the catalytic activity and selectivity of the prepared catalysts in this part.

4.1.1 Effect of Type of Support on the Catalytic Performance of 1% Au Catalyst

To study effect of type of support on the catalytic performance of 1% Au, the Ce/(Ce+Fe) atomic ratios were varied (0, 0.25, 0.5, 0.75, and 1). The supports were prepared by precipitation and co-precipitation methods as the first step. After that, the 1 wt% Au metal was loaded on the prepared supports by deposition-precipitation (DP) method. All catalysts were calcined at 400 °C for 4 h. Figure 4.1 shows the methanol conversion and product concentration in the oxidative steam reforming of methanol reaction in the reaction temperature range of 200 °C to 400 °C.

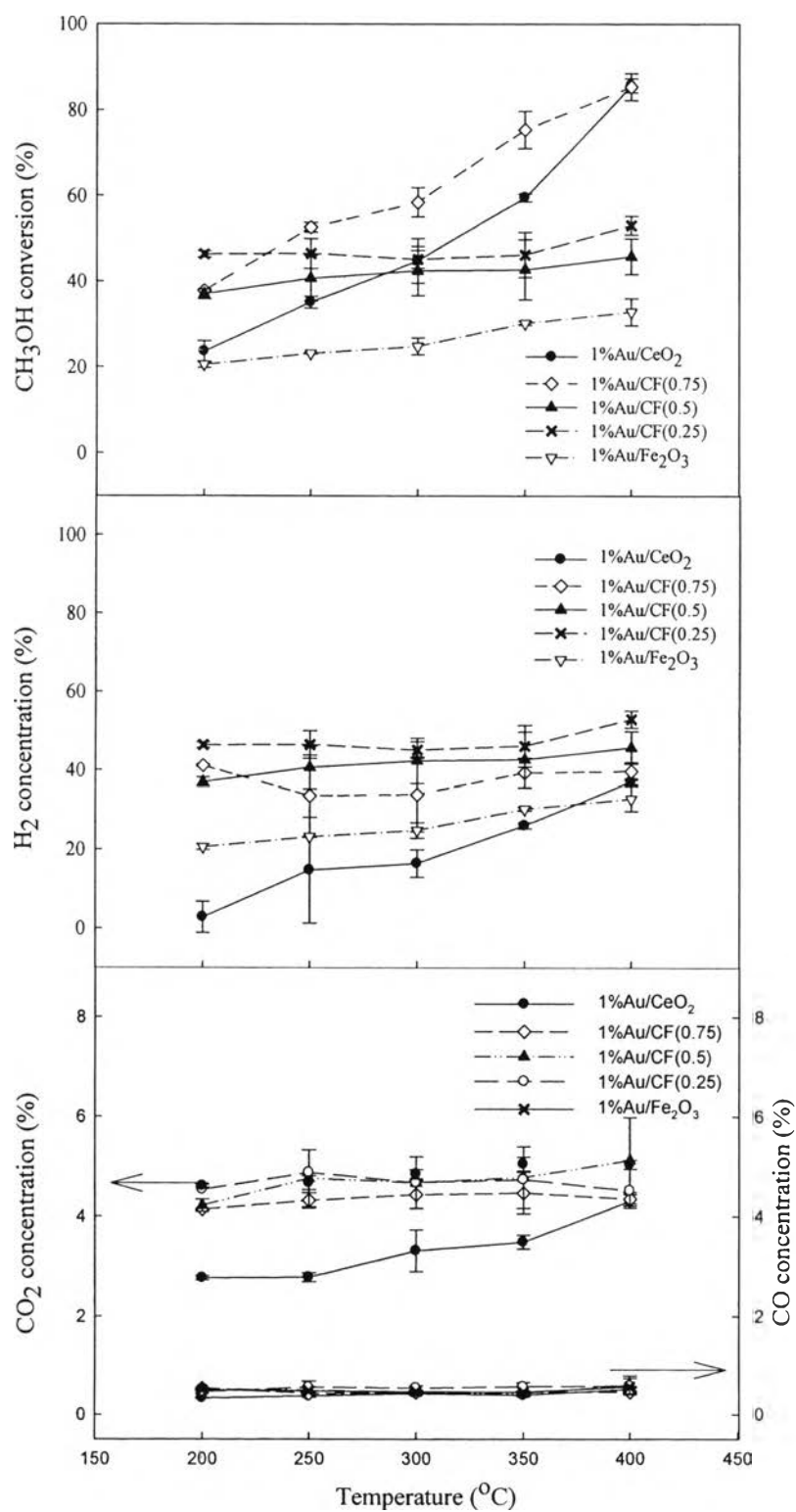


Figure 4.1 Effect of Ce/(Ce+Fe) atomic ratio on the methanol conversion, and concentration of H₂, CO, and CO₂ over 1 wt% of Au/CeO₂-Fe₂O₃ catalysts calcined at 400 °C. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)

It can be seen that the 1% Au/CF(0.25) exhibited the highest catalytic activity in the whole temperature study compared with other atomic ratios. The methanol conversion reached 91.4%, at 400 °C. The mixed supports showed higher methanol conversion and hydrogen concentration than pure support (1% Au/CeO₂, and 1% Au/Fe₂O₃). The product gases were H₂, CO₂, and CO, the catalyst had CO concentration in range of 0.3 % to 0.7 %, and CO₂ concentration around 3% to 5%. However no methane was observed. It has been reported that the addition of Fe into CeO₂ resulted in a remarkable increase in the catalytic performance (Hongyan *et al.*, 2008). In this work, the combination of CeO₂ and Fe₂O₃ can also enhance the OSRM reaction. Consequently, 1% Au/CF(0.25) was chosen as the optimal composition for further study.

4.1.1.1 X-ray Diffraction (XRD)

The XRD results of CeO₂, 1% Au/CeO₂, 1% Au/CF(0.25), 1% Au/CF(0.5), 1% Au/CF(0.75), 1% Au/Fe₂O₃, and Fe₂O₃ calcined at 400 °C are shown in Figure 4.2. The XRD diffractions of CeO₂ and 1% Au/CeO₂ present a very strong peak at $2\theta = 28.5^\circ$, which is characteristic of fluorite structure of CeO₂ (111). The other peaks at 33.08, 47.47, 56.33, 59.08, 69.40, 76.69, and 79.067 were corresponding to CeO₂ (200), CeO₂ (220), CeO₂ (311), CeO₂ (222), CeO₂ (400), CeO₂ (331), and CeO₂ (420) for CuK α (1.5406 Å) radiation, respectively (Kunming *et al.*, 2008). The XRD patterns result become broadening, or lower intensity when CeO₂ was mixed with higher amount of Fe₂O₃ as a support, resulting from the incorporation of small Fe ion in ceria crystal that mean the interaction of the mixed support (Lin *et al.*, 2008). The pure support (1% Au/CeO₂, and 1% Au/Fe₂O₃) has more csystallinity than the mixed supports, suggesting is that the combination of Ce and Fe oxide in the catalyst can reduce the Fe₂O₃ and CeO₂ crystallite sizes (Sirichaiprasert *et al.*, 2006). The position of pecks is shifted towards higher 2theta values as the Fe content in the solution. This suggests the formation of a Fe_xCe_{1-x}O₂ solid solution, with Fe₂O₃ entering in the fluorite structure of ceria, the lower ionic radius of Fe³⁺ (0.67 Å) compared to Ce⁴⁺ (0.97 Å) (Neri *et al.*, 2005). However, the Au peaks of the prepared catalysts cannot be observed due to low Au content as only 1 wt%, indicating either a high dispersion of gold or small Au particle size (Rui-hui

et al., 2010). The crystalline sizes of catalysts were calculated based on the Scherrer equation and the results are summarized in Table 4.1.

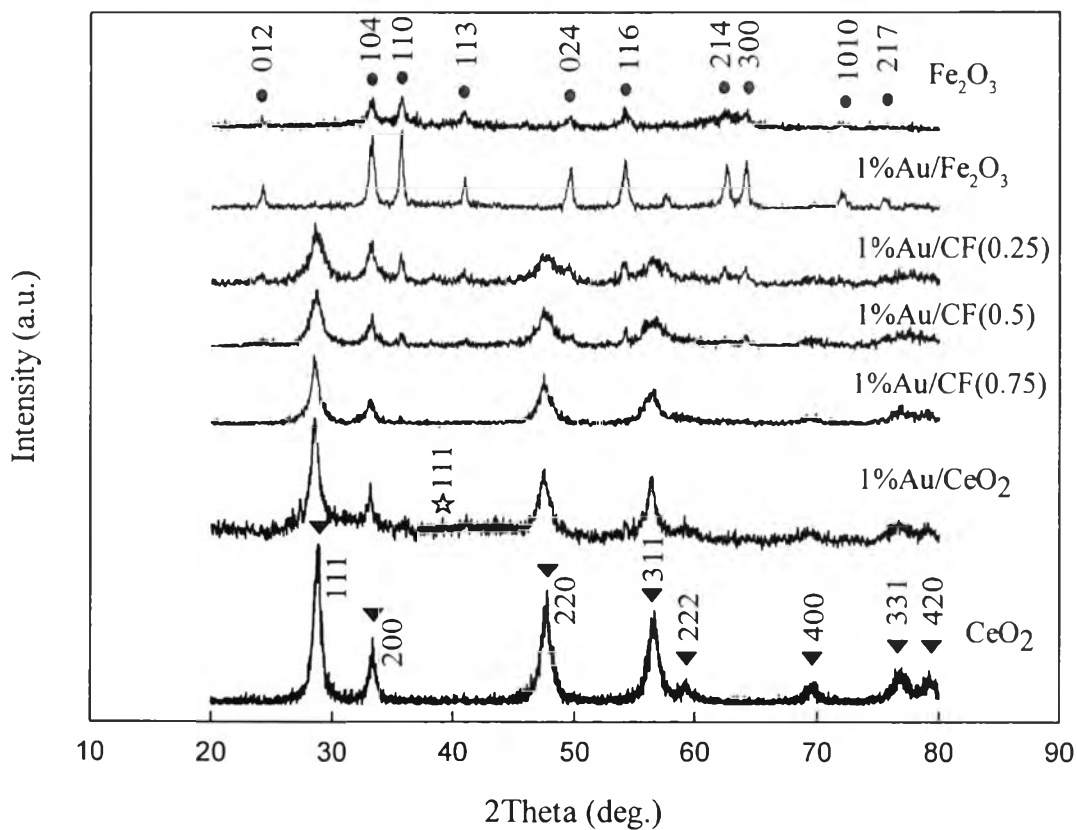


Figure 4.2 XRD patterns of supported Au catalysts: (▼) CeO₂; (●) Fe₂O₃; (☆) Au

Table 4.1 CeO₂ and Au crystallite sizes of the 1%Au catalysts over different supports.

Catalysts	Crystallite size (nm)				
	CeO ₂ (111)	CeO ₂ (200)	CeO ₂ (220)	CeO ₂ (311)	Au(111)
CeO ₂	9.69	10.80	8.31	11.03	-
1% Au/CeO ₂	9.49	10.58	8.24	10.16	-
1% Au/CF(0.75)	8.94	9.26	7.03	7.14	-
1% Au/CF(0.5)	7.31	9.65	6.95	5.18	-
1% Au/CF(0.25)	6.52	10.05	6.78	4.14	-
1% Au/Fe ₂ O ₃	-	-	-	-	-
Fe ₂ O ₃	-	-	-	-	-

From Table 4.1, it showed that the mean CeO₂ crystallite size of CeO₂, 1% Au/CeO₂, 1% Au/CF(0.75), 1% Au/CF(0.5), 1% Au/CF(0.25) were 9.96, 9.62, 8.09, 7.27, and 6.87, respectively. It is clearly seen that the addition of Fe decreases the crystallinity of ceria as the incorporation of small Fe ion (0.67 Å) into the ceria crystal (Hongyan *et al.*, 2008).

4.1.1.2 X-ray Fluorescence (XRF)

In order to analyze the actual metal loading and composition of 1% Au/CeO₂, 1% Au/CF(0.75), 1% Au/CF(0.5), 1% Au/CF(0.25), and 1% Au/Fe₂O₃ calcined at 400 °C, XRF technique was used and the results are summarized in Table 4.2. The results showed that the actual Au and support composition Ce/(Ce+Fe) were similar to the expected results. In addition, the catalysts with low content of iron oxide (1% Au/CF(0.5) and 1% Au/CF(0.75)) gave the actual Au loading higher than 1% Au/ CeO₂ and 1% Au/Fe₂O₃, and the catalyst with high iron oxide content (1% Au/CF(0.25)).

Table 4.2 Au loading (wt%) and Ce/(Ce+Fe) ratio of supported Au catalysts

Catalysts	Actual Au loading (%)	Ce/(Ce+Fe)
1%Au/ CeO ₂	0.879	1
1%Au/CF(0.75)	1.106	0.70
1%Au/CF(0.5)	1.195	0.38
1%Au/CF(0.25)	0.803	0.20
1%Au/Fe ₂ O ₃	0.863	0

4.1.1.3 Surface Area Measurement (BET)

The surface areas of CeO₂, 1% Au/CeO₂, CF(0.75), 1% Au/CF(0.75), CF(0.5), 1% Au/CF(0.5), CF(0.25), 1% Au/CF(0.25), Fe₂O₃, and 1% Au/Fe₂O₃ are summarized in Table 4.3. The results showed that after loading Au on supports, the surface areas of all catalysts were decreased. It can be observed that the surface does not affect to the catalytic activity for this reaction.

Table 4.3 BET surface areas of catalysts

Catalysts	BET surface area (m ² /g)
CeO ₂	118.8
1%Au/ CeO ₂	100.8
CF(0.75)	111.0
1%Au/CF(0.75)	105.5
CF(0.5)	98.67
1%Au/CF(0.5)	92.69
CF(0.25)	160.2
1%Au/CF(0.25)	100.8
Fe ₂ O ₃	186.0
1%Au/Fe ₂ O ₃	81.16

4.1.2 Effect of Calcination Temperature on the Catalytic Performance

To study the effect of calcination temperature on the catalytic activity of 1% Au/CF(0.25), the supports were first prepared by a co-precipitation method, using calcination temperature at 400 °C and the 1%Au metal was loaded on the prepared supports by a deposition-precipitation (DP) method. The catalysts were annealed at three different calcination temperatures of 200, 300, and 400 °C for 4 h.

Many researchers reported that calcination temperature significantly affected on the catalytic activity (Chang *et al.*, 2008). Figure 4.3 shows the effect of calcination temperature on the methanol conversion and product concentration of 1% Au/CF(0.25) catalysts. The results showed that methanol conversion increased with increasing calcination temperature; however, when calcination temperature was increased from 300 °C to 400 °C, the methanol conversion and product concentration slightly decreased. It could be concluded that the appropriate calcination temperature was 300 °C. The calcination temperature had no significant effect much on the concentration of CO throughout the temperature range of 200 °C to 400 °C. However no methane was observed.

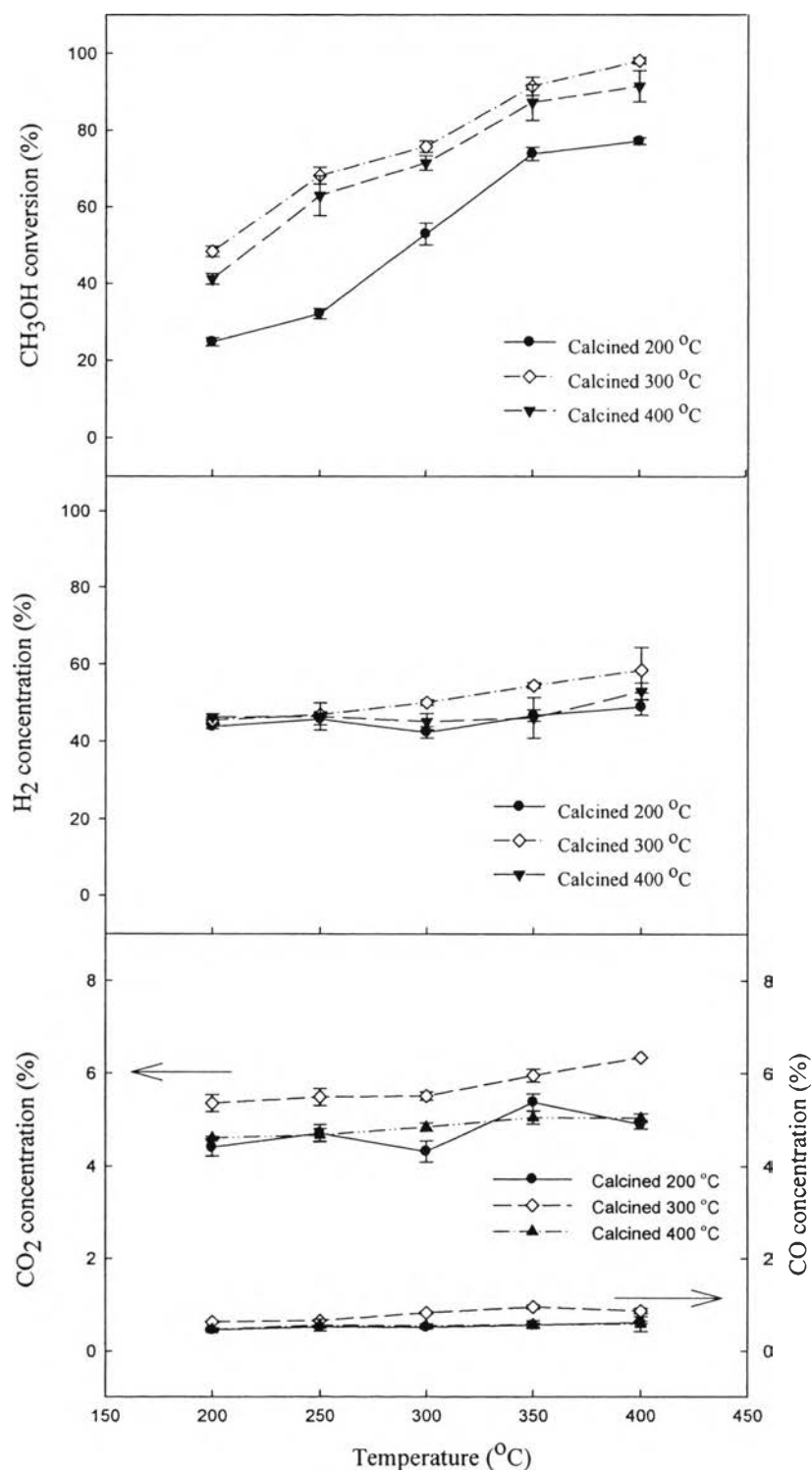


Figure 4.3 Effect of calcination temperature on the methanol conversion, and concentration of H₂, CO, and CO₂ over 1 wt% of Au/CF(0.25) catalysts. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)

4.1.2.1 Temperature-Programmed Reduction (TPR)

TPR technique was used to study the reduction profiles of the catalysts. Figure 4.4 shows the TPR profiles of 1% Au/CF(0.25) with various calcination temperatures. The low reduction temperature (100 °C to 200 °C) was attributed to the reduction of Au_xO_y species. The temperature reduction peak of 250 °C to 400 °C was attributed to the reduction of Fe_2O_3 to Fe_3O_4 (Venugopal *et al.*, 2003). The high temperature reduction peak of 600 °C to 650 °C was attributed to the reduction of Fe_3O_4 to FeO species (Venugopal *et al.*, 2003). In this study, the peak of the 1% Au/CF(0.25) calcined at 300 °C was shifted to lower temperature (147 °C) when compared with the catalysts calcined at 200 °C and calcined at 400 °C (156 °C and 152 °C, respectively). According to the reduction of Au_xO_y species peak, calcination temperature of 300 °C can reduce Au_xO_y species easier than other calcination temperatures. It can be conclusion that the catalysts calcined at 300 °C had the strong metal-metal interaction more than other calcination temperatures. When compare with TPR profiles of 1% Au/CF(0.25) and Fe_2O_3 support, the 1% Au/CF(0.25) was shifted to lower temperature of both the reduction of Fe_2O_3 to Fe_3O_4 , and the reduction of Fe_3O_4 to FeO species. In addition, the TPR profiles of 1% Au/CF(0.25) were no observed to the reduction peck of ceria because the TPR profiles of ceria exhibit a broad peak at high temperature around 800 °C that is referred to the bulk reduction from CeO_2 to Ce_2O_3 , and a broad peak situated close to 500 °C that is typically assigned to a surface reduction process (Jacobs *et al.*, 2005).

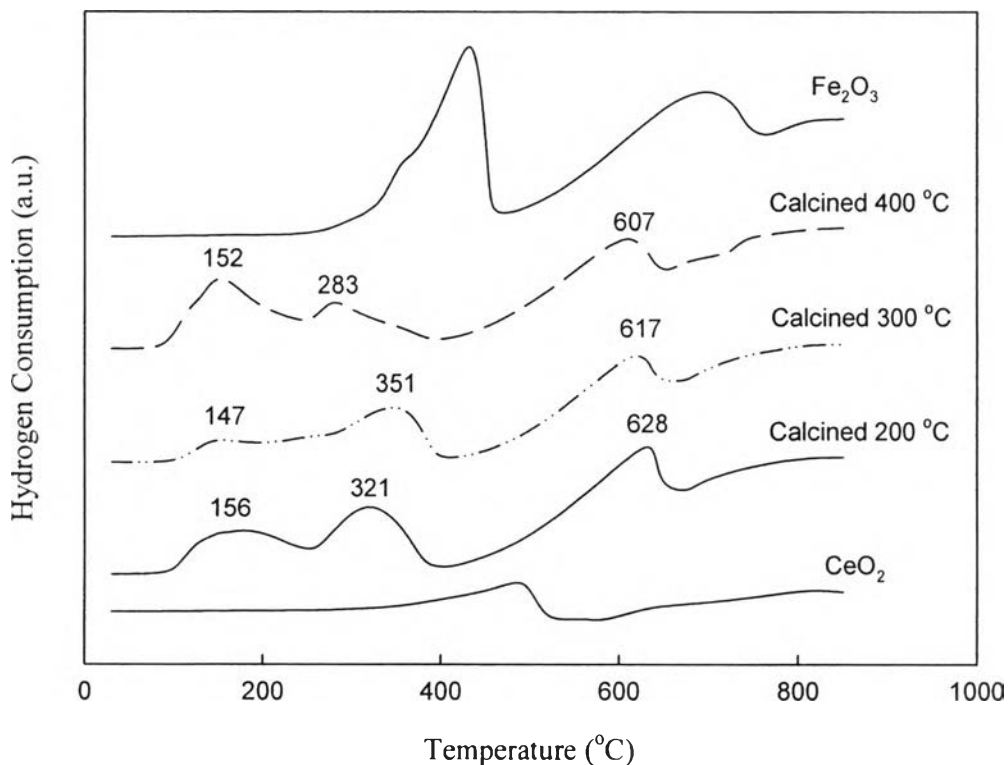


Figure 4.4 TPR profiles of 1 wt% Au/CF(0.25) with various calcination temperatures.

4.1.2.2 UV-visible Spectroscopy

There are many research works studied the presence of small Au metal by UV-vis spectroscopy to identify the gold species on support. The gold metallic (Au^0) peak is known to be located between 520–570 nm for gold particle on metal oxides and gold clusters (Au_n , $1 < n < 10$) can be observed at 280–380 nm (Park *et al.*, 2006). Figure 4.5 shows that the catalyst calcined at 300 °C had more gold metallic (Au^0) than other calcination temperatures the catalysts calcined at 300 °C had larger peak area between 500–600 nm than the catalyst calcined at 200 °C and 400 °C. The absorption band < 250 nm can be assigned to cationic gold species (Au^{3+}) (Zanella *et al.*, 2004), it can be noticed that at this point, 1 wt% Au/CF(0.25) catalysts had stronger absorption band than CF(0.25) support, indicating that there were Au^{3+} species on the prepared catalyst. However, the investigation of Au^{3+} by UV-vis was still unclear because of the overlap of mixed support, according to the stacking of ceria oxide and Au^{3+} band, show in the range of

200–350 nm and < 250 nm (Zanella *et al.*, 2004). In addition, Smolentseva E. and coworkers found that the increasing of calcination temperature can contribute to the gold nanoparticles or Au^0 species (Smolentseva *et al.*, 2006) while this testing did not show the same trend, according to the catalyst calcined at 300 °C had the most gold metallic (Au^0).

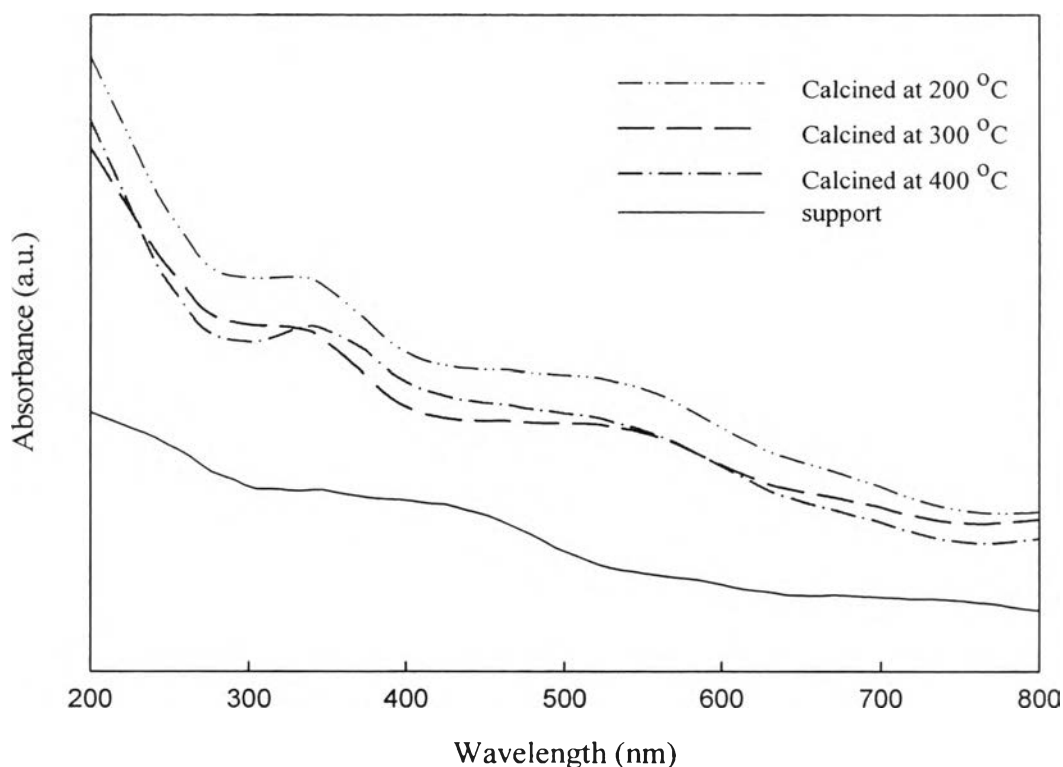
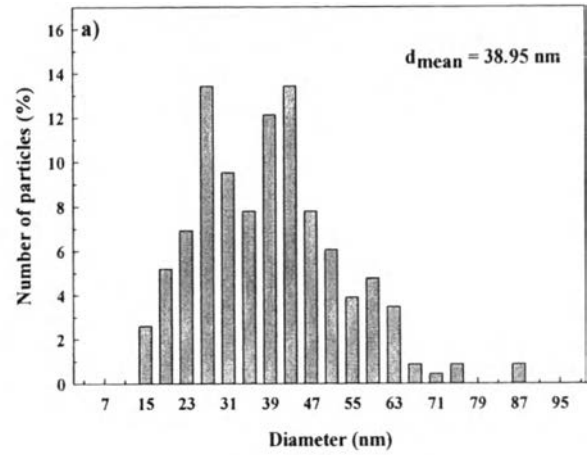
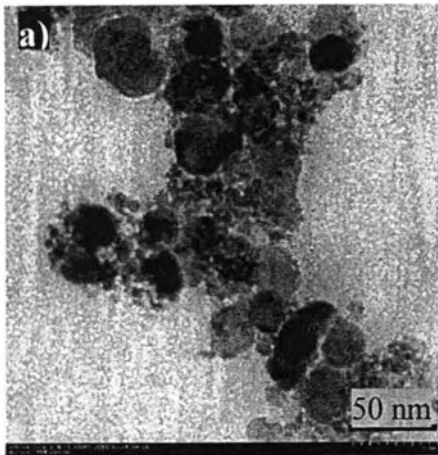


Figure 4.5 Diffuse reflectance UV-vis spectra of 1% Au/CF(0.25) various calcination temperatures.

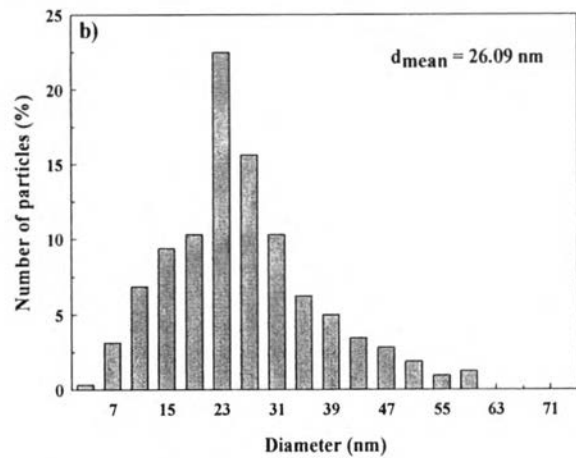
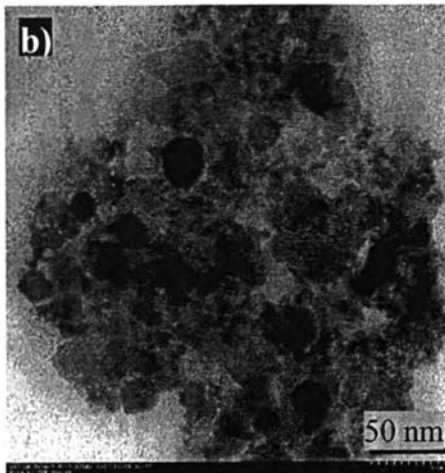
4.1.2.3 Transmission Electron Micrograph (TEM)

Figure 4.6 shows the TEM images of the 1 wt% Au/CF(0.25) with different calcination temperatures for measure the dispersion of mixed support. The mean crystalline size of mixed support with various calcination temperatures of 200 °C, 300 °C, 400 °C were 38.95, 26.09, and 44.25 nm, respectively. TEM technique cannot measure the Au crystalline size because of the overlap between Au and mixed support that XRD technique also cannot detect to the peak of Au. So that used SEM technique to mapping the dispersion and used SEM-

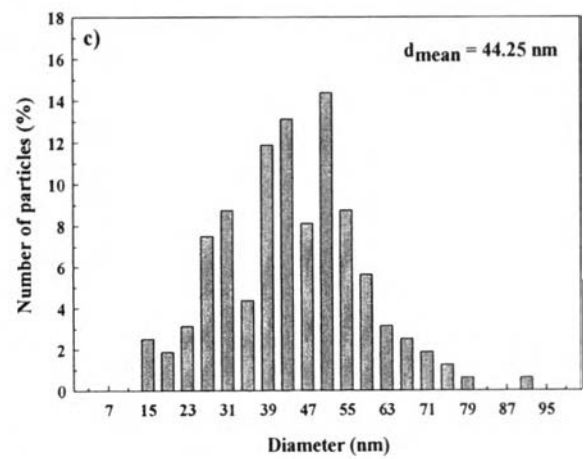
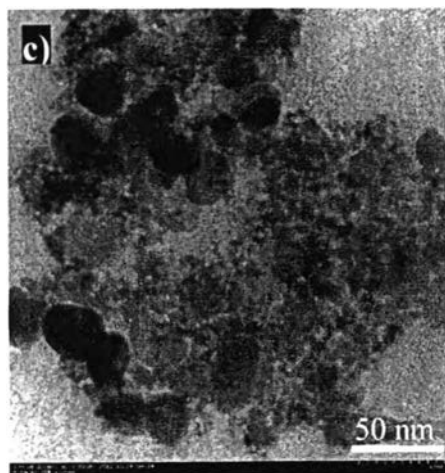
eds to analyst composition as shown in Appendix B that agreed with XRF result. Calcination temperature at 300 °C had the highest dispersion when compare with other calcination temperatures. This phenomenon corresponds to the highest activity testing of calcination temperature at 300 °C. It can be conclude that the suitable calcination temperature was 300 °C for the OSRM reaction.



a) Calcined at 200 °C



b) Calcined at 300 °C



c) Calcined at 400 °C

Figure 4.6 TEM images of 1% Au/CF(0.25) with various calcination temperatures.

4.1.2.4 X-ray Diffraction (XRD)

The XRD results of 1% Au/CF(0.25) with various calcination temperatures are shown in Figure 4.7.

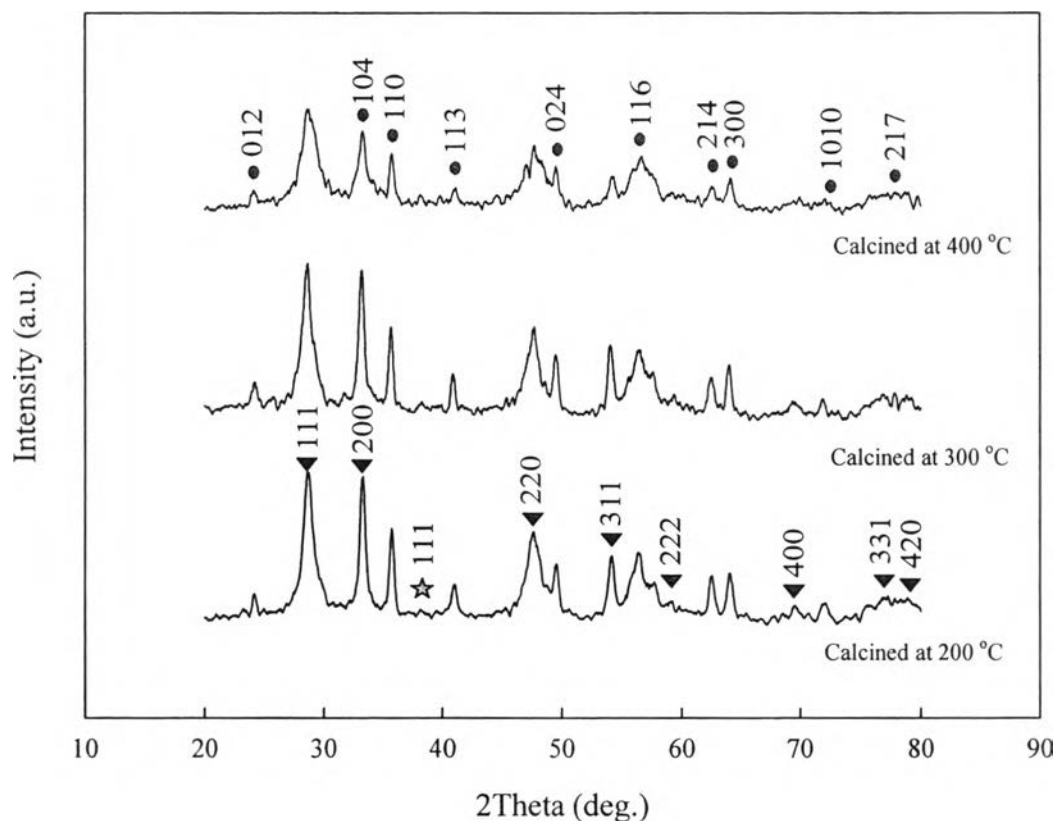


Figure 4.7 XRD patterns of supported Au catalysts: (▼) CeO₂; (●) Fe₂O₃; (☆) Au.

Table 4.4 CeO₂ and Au crystallite sizes of the 1% Au/CF(0.25) with different calcination temperatures

Catalysts	Crystallite size (nm)				
	CeO ₂ (111)	CeO ₂ (200)	CeO ₂ (220)	CeO ₂ (311)	Au(111)
Calcined at 200 °C	8.26	10.41	7.90	4.62	-
Calcined at 300 °C	6.52	10.05	6.78	4.14	-
Calcined at 400 °C	7.95	10.84	6.12	3.62	-

From Table 4.4, it showed that the mean CeO_2 crystallite sizes of 1% Au/CF(0.25) calcined at 200 °C, 300 °C, and 400 °C were 7.80, 6.87, and 7.13, respectively. It can be noticed that calcination temperature does not affect much to crystallite size of catalyst.

4.1.2.5 X-ray Fluorescence (XRF)

In order to analyze the actual metal loading, and composition of 1% Au/CF(0.25) with various calcination temperatures, XRF technique was used and the result are summarized in Table 4.5. The result showed that calcination temperature did not affect much on the actual Au loading and Ce/(Ce+Fe) ratio

Table 4.5 Actual Au loading and Ce/(Ce+Fe) of 1%Au/CF(0.25) with various calcination temperatures

Catalysts	Actual Au loading (%)	Ce/(Ce+Fe)
Calcined 200 °C	0.840	0.20
Calcined 300 °C	0.894	0.20
Calcined 400 °C	0.803	0.20

4.1.2.6 Surface Area Measurement (BET)

The surface areas of 1 wt% Au/CF(0.25) with various calcination temperatures were summarized in Table 4.6. The result shown that the surface area did no significant affect on the catalytic activity.

Table 4.6 BET surface areas of 1% Au/CF(0.25) with various calcination temperatures

Catalysts	BET surface area (m^2/g)
Calcined 200 °C	105.27
Calcined 300 °C	99.75
Calcined 400 °C	100.8

4.1.3 Effect of Au Content on the Catalytic Performance

The Au/CF(0.25) were prepared by a deposition-precipitation technique with various Au contents of 1 wt%, 3 wt%, and 5 wt%. All catalysts were calcined at 300°C for 4 hours.

It is well known that small Au particle size is highly active for many reactions (water-gas shift reaction, selective oxidation of CO in hydrogen rich stream, and etc.) (Haruta *et al.*, 2001). However, in this study, the result showed that the catalytic activity increased with increasing Au content from 1 wt% to 3 wt% and while the Au content was increased from 3 wt% to 5 wt%, the methanol conversion and concentration of H₂, and CO₂ slightly dropped, as shown in Figure 4.8. The 3% Au content exhibited the highest performance among the catalyst studied. In addition, The comparison of with and without metal loading for OSRM reaction was investigated, the catalytic behavior of loading Au can much improve for both methanol conversion and hydrogen concentration all the temperature reaction than without Au loading. It can be concluded that the Au catalyst plays an important role for hydrogen production from the OSRM reaction. In addition, the Au content had no significant effect on the concentration of CO throughout the temperature range of 200 °C to 400 °C. However no methane was observed.

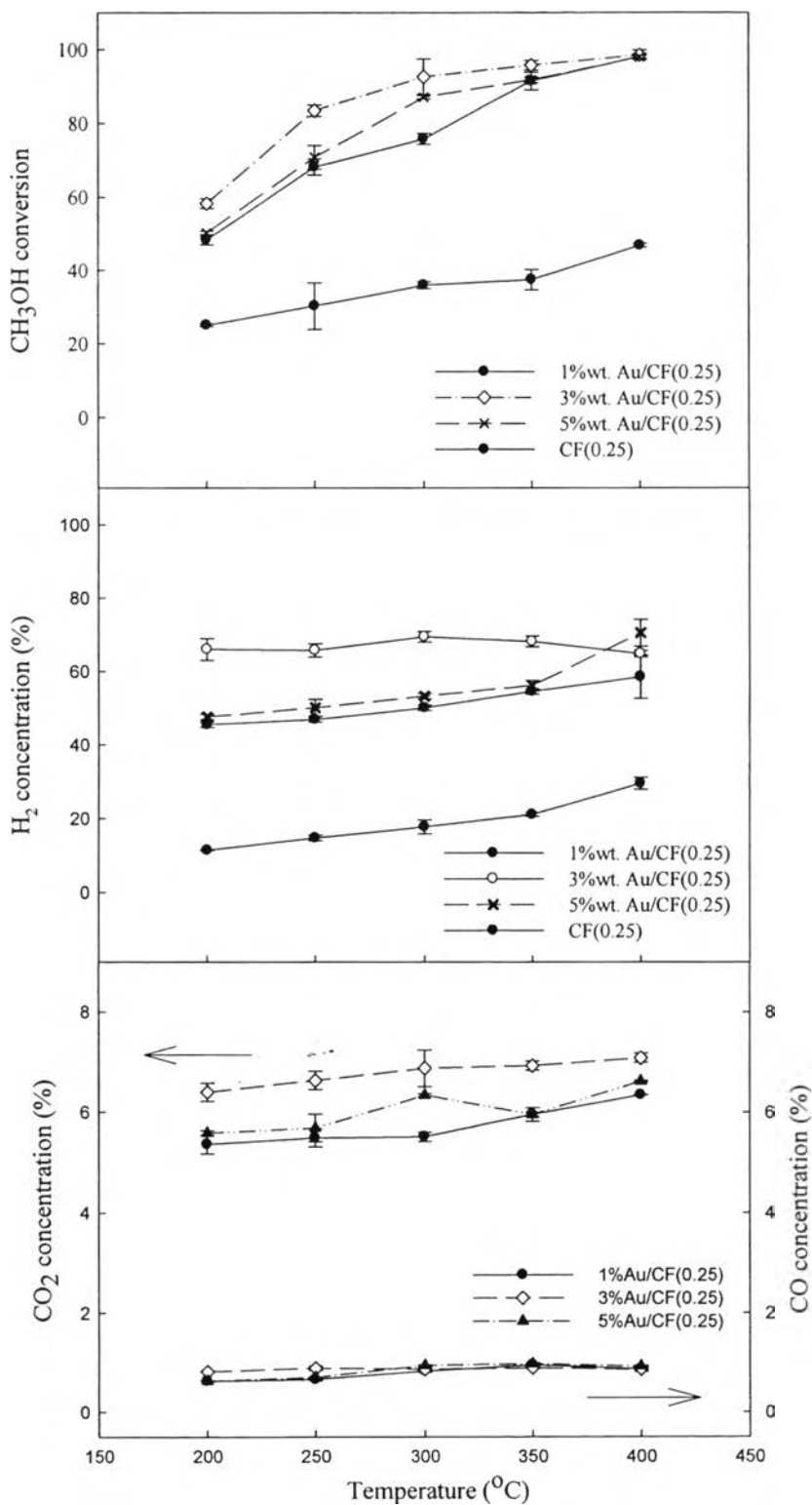


Figure 4.8 Effect of Au content on methanol conversion, and concentration of H₂, CO₂, and CO over Au/CF(0.25) catalysts. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)

4.1.3.1 Temperature-Programmed Reduction (TPR)

Figure 4.9 shows the TPR patterns of the 1% Au/CF(0.25), 3% Au/CF(0.25), and 5% Au/CF(0.25). The low temperature reduction peak of 100 °C to 150 °C could be ascribed to the reduction of O₂ species adsorbed on small gold particle, and reduction of ceria surface sites located around gold particle (Tabakova *et al.*, 2011). At this position, the peak of the 3% Au/CF(0.25) was shifted to lower temperature (122 °C) as when compared with 1% Au/CF(0.25) and 5% Au/CF(0.25) (148 °C and 132 °C, respectively). The high temperature reduction peak of 300 °C to 400 °C was attributed to the reduction of Fe₂O₃ to Fe₃O₄, the peak of 3% Au/CF(0.25) was slightly decreased to 312 °C, which indicates that Au exerts a positive influence on the ease of Fe₂O₃ reduction the occurs at lower temperature (Chang *et al.*, 2008). The strong metal-metal and metal-support interaction in the prepared catalysts, leading to enhanced ability to reduce O₂ from iron oxide. The high temperature reduction peak (600 °C to 650 °C) was attributed to the reduction of Fe₃O₄ to FeO species. The reduction of Fe₃O₄ was much less affected by the presence of gold. When compare with TPR profiles of 1% Au/CF(0.25) and Fe₂O₃ support, the 1% Au/CF(0.25) was shifted to lower temperature of both the reduction of Fe₂O₃ to Fe₃O₄, and the reduction of Fe₃O₄ to FeO species. In addition, the TPR profiles of 1% Au/CF(0.25) were no observed to the reduction peck of ceria.

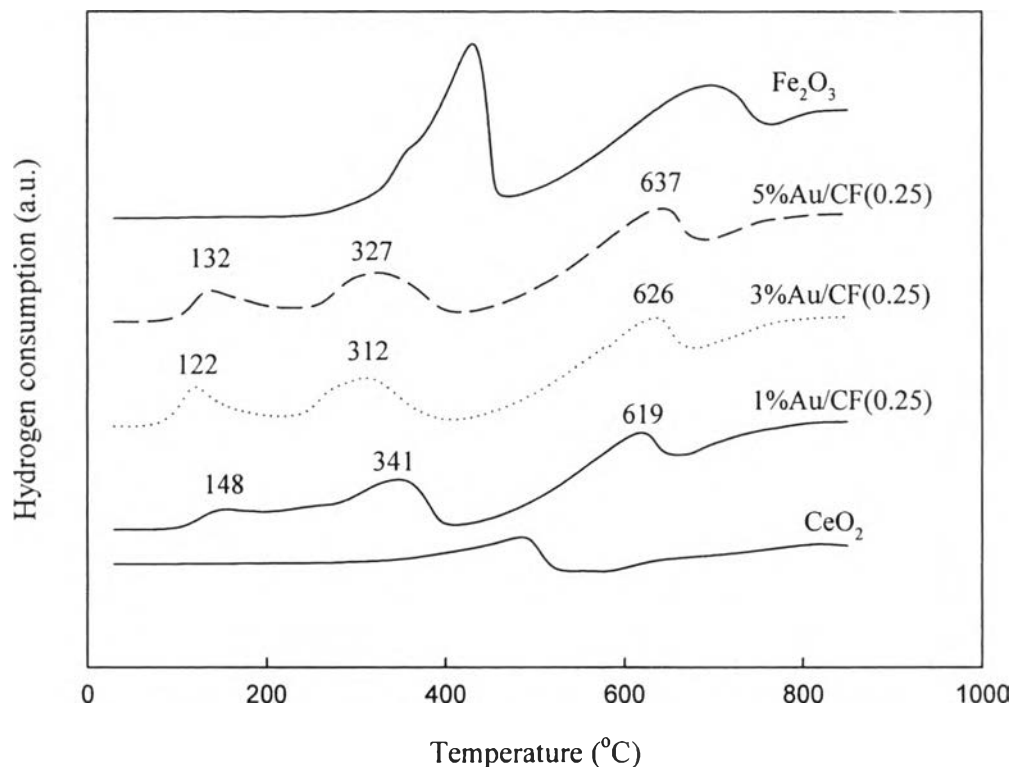


Figure 4.9 TPR profiles of Au/CF(0.25) calcined at 300 °C with different Au loadings.

4.1.3.2 UV-visible Spectroscopy

Figure 4.10 shows the gold species on support, it was found that when Au content was increased from 1 wt% to 5 wt%, there was no significant effect to the gold species. According to the intensity of gold metallic (Au^0) at 500–600 nm, cationic gold species (Au^{3+}) at < 250 nm, and gold clusters (Au_n , $1 < n < 10$) at 280–380 nm (Park *et al.*, 2006), had quite the same trend. However, it can be seen that the Au^0 and Au^{3+} species were detected. Bond and coworker found that the combination with Au^0 and Au^{3+} is necessary to obtain the activity (Bond *et al.*, 2006). In contrast, there are many researches about gold species as Chang and coworker reported that the active catalysts always contain metallic Au particle (Chang *et al.*, 2008), whereas Jacobs and coworker proposed that the active non-metallic species are responsible for high activity in WGS reaction (Jacobs *et al.*, 2005). Nevertheless, the state of the active gold catalysts is still unclear.

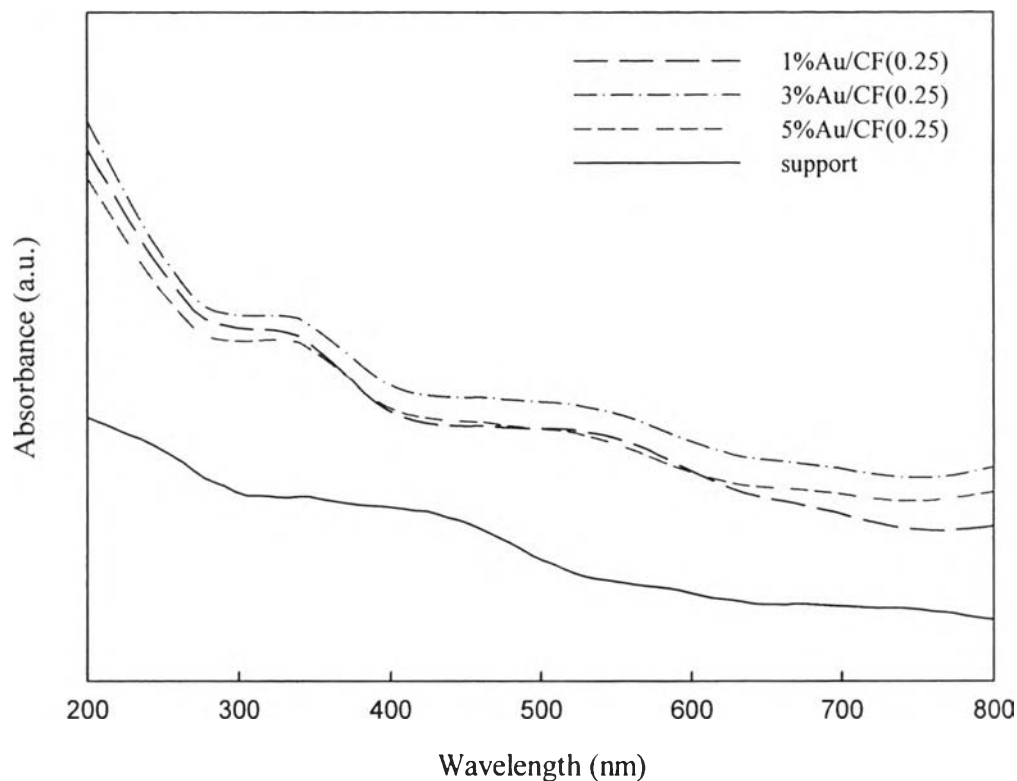
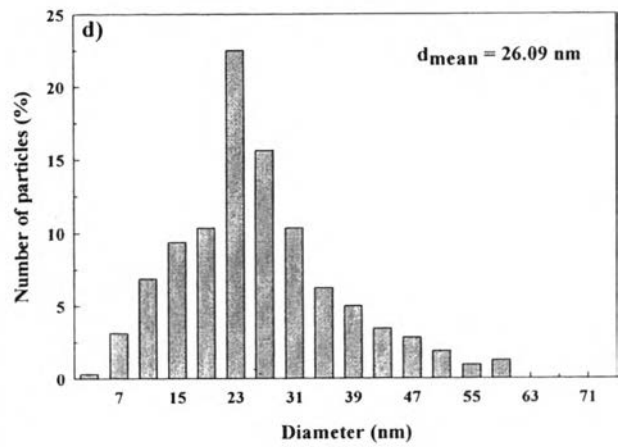
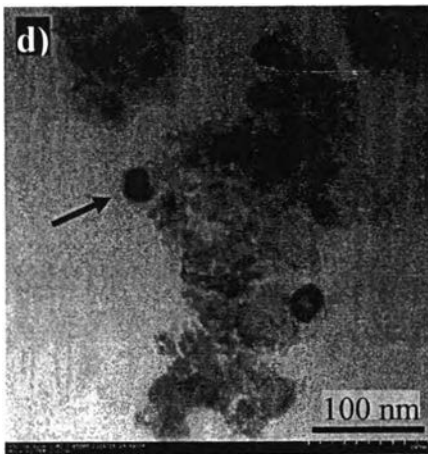


Figure 4.10 Diffuse reflectance UV-vis spectra of Au/CF(0.25) calcined at 300 °C with different Au loadings.

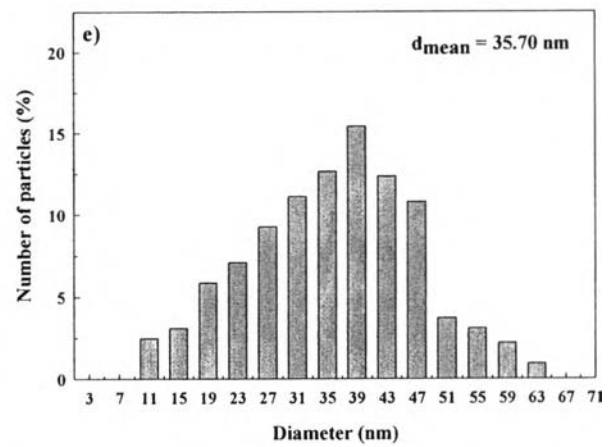
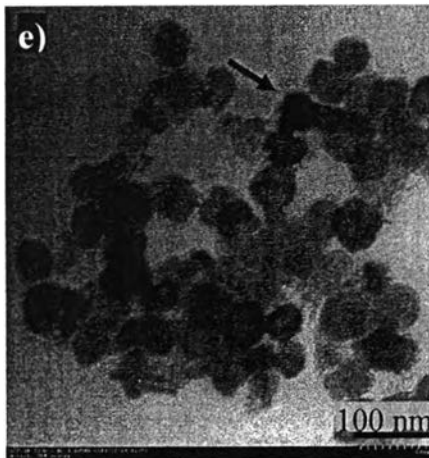
4.1.3.3 Transmission Electron Micrograph (TEM)

TEM images of the Au/CF(0.25) catalysts with various Au contents are shown in Figure 4.11. The mean crystalline size of mixed support with varying Au contents of 1 wt%, 3 wt%, 5 wt% were 26.09, 35.70, 39.44 nm, respectively. According to result, increase Au loading effect to larger of mixed support crystalline size. TEM technique cannot measure the Au crystalline size because of the overlap between Au and mixed support that XRD technique also cannot detect to the peak of Au, suggesting that Au crystalline size was lower than 5 nm. So that used SEM technique to mapping the dispersion and used SEM-eds to analyst composition as shown in Appendix B that agreed with XRF result. According to the results, when increasing of the Au content from 1 wt% to 3 wt% the methanol conversion and hydrogen yield was increased. In contrast, when increased the Au content from 3 wt% to 5 wt% the methanol conversion and hydrogen yield was

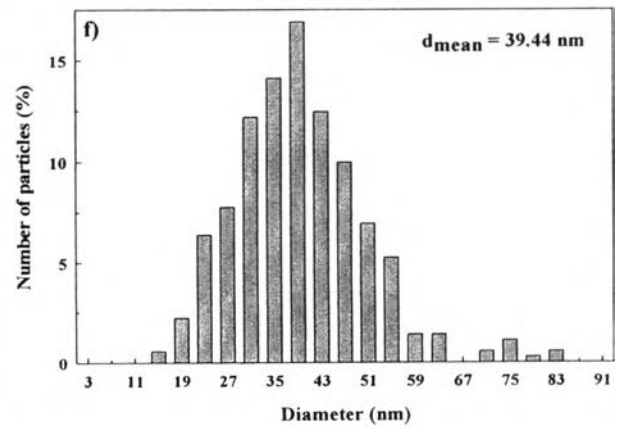
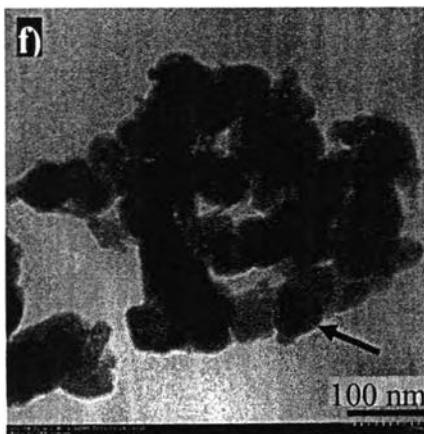
decreased but higher than 1 wt%. Therefore, it can be concluded that a large crystalline size of mixed support on the Au/CF(0.25) was no significant effect to the catalytic activity.



d) 1 wt% Au/CF(0.25)



e) 3 wt% Au/CF(0.25)



f) 5 wt% Au/CF(0.25)

Figure 4.11 TEM images of Au/CF(0.25) calcined at 300 °C with different Au loadings.

4.1.3.4 X-ray Diffraction (XRD)

The XRD results of Au/CF(0.25) calcined at 300 °C with different Au loadings are shown in Figure 4.12.

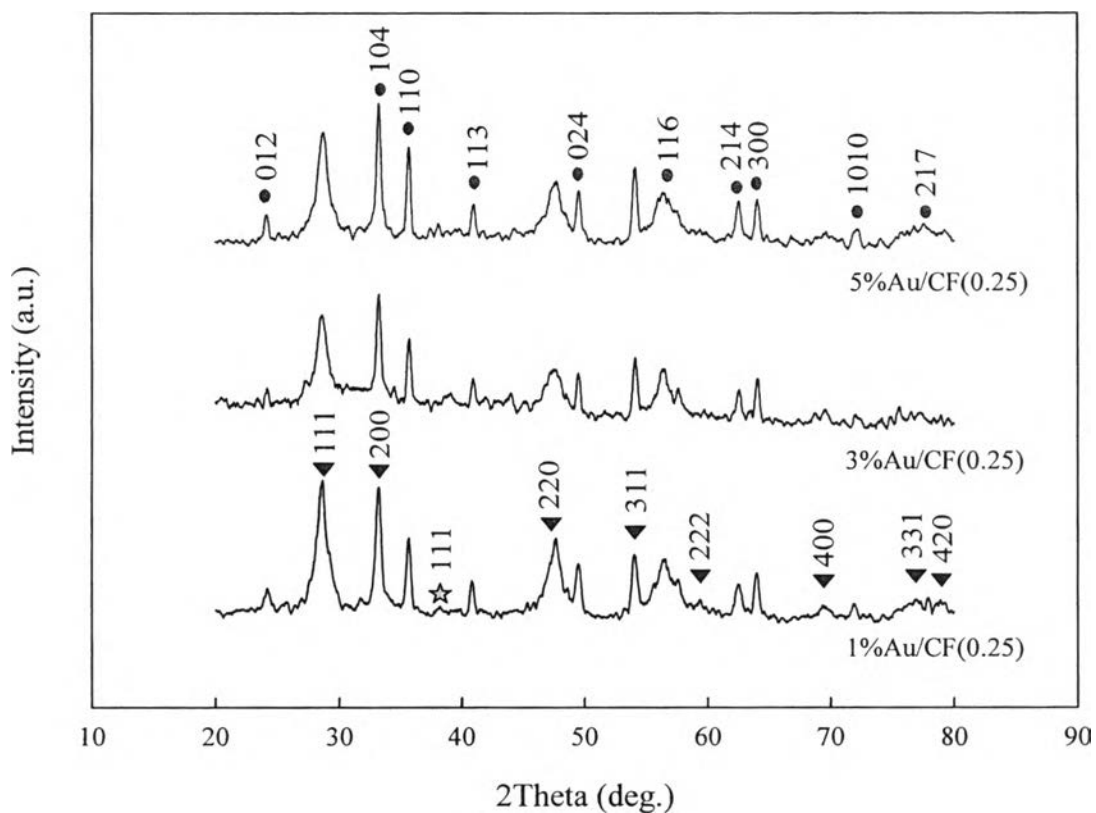


Figure 4.12 XRD patterns of supported Au catalysts: (▼) CeO₂; (●) Fe₂O₃; (☆) Au

Table 4.7 CeO₂ and Au crystallite sizes of the Au/CF(0.25) calcined at 300 °C with different Au loadings.

Catalysts	Crystallite size (nm)				
	CeO ₂ (111)	CeO ₂ (200)	CeO ₂ (220)	CeO ₂ (311)	Au(111)
1 wt% Au/CF(0.25)	6.52	10.05	6.78	4.14	-
3 wt% Au/CF(0.25)	6.03	9.87	5.47	4.26	-
5 wt% Au/CF(0.25)	6.11	10.21	5.52	4.63	-

From Table 4.7, it showed that the mean CeO₂ crystallite size of Au/CF(0.25) calcined at 300 °C with 1 wt%, 3 wt%, and 5 wt% were 6.87, 6.41, and 6.62, respectively. It can be noticed that Au loading had no significant effect on the crystallite size of catalyst.

4.1.3.5 X-ray Fluorescence (XRF)

In order to analyze the actual metal loading, and composition of Au/CF(0.25) calcined at 300 °C with different Au loadings, XRF technique was used and the result are summarized in Table 4.8. It can be noticed that catalyst of 1 wt%, 3 wt%, and 5 wt% had actual Au loading 0.894, 2.499, and 3.838, respectively that nearly by calculation. In addition, Au loading was no significant effect to the support composition and gave Ce/(Ce+Fe) ratio similar to the expected results.

Table 4.8 XRF results of Au/CF(0.25) calcined at 300 °C with different Au content

Catalysts	Actual Au loading (%)	Ce/(Ce+Fe)
1% Au/CF(0.25)	0.894	0.20
3% Au/CF(0.25)	2.599	0.19
5% Au/CF(0.25)	3.838	0.20

4.1.3.6 Surface Area Measurement (BET)

The surface areas of Au/CF(0.25) calcined at 300 °C with different Au content were summarized in Table 4.9. The results shown that the surface area was increased with an increasing Au loading.

Table 4.9 BET surface areas of Au/CF(0.25) calcined at 300 °C with different Au content

Catalysts	BET surface area (m ² /g)
1% Au/CF(0.25)	99.75
3% Au/CF(0.25)	87.36
5% Au/CF(0.25)	84.61

4.1.4 Effect of Catalyst Pretreatment

The gas pretreatment of catalyst is important for many chemical reactions such as CH₄ conversion, Dinh Lam and coworker found that O₂ pretreatment improve catalytic activity (CH₄ conversion has reached 90% instead of 80%), and the oxygen presence in the feed seems to inhibit in a significant manner the deactivation of catalyst (Dinh *et al.*, 2009). The different pretreatments will provide different characteristic of the catalysts that Zhenping and coworker found that the Ag-SiO₂ mixture was treated with oxygen at 300 °C, silver particles were dispersed on the SiO₂ support whereas untreated had very few silver particle were attached on the support, and the silver particles were separated from each other (Zhenping *et al.*, 2004). It is interesting to investigate the effect of gas pretreatment, which is O₂ oxidation at 200 °C for 2 hour on the activity of 3 wt% Au/CF(0.25) catalysts (calcined at 300 °C). The effect of catalyst pretreatment on the activity of 3 wt% Au/CF(0.25) catalyst are shown in Figure 4.13. The activity of 3 wt% Au/CF(0.25) increased with an increase in reaction temperature and methanol conversion reached almost 100% at 400 °C. The pretreated catalyst exhibited same trend as unpretreated in terms of methanol conversion and hydrogen concentration while the O₂ pretreated catalyst had higher CO₂ concentration than unpretreated catalyst according to CO was oxidized to CO₂ (Velu *et al.*, 2001). The pretreated catalyst had no significant effect on the concentration of CO₂, and CO throughout the temperature range of 200 °C to 400 °C. However no methane was observed.

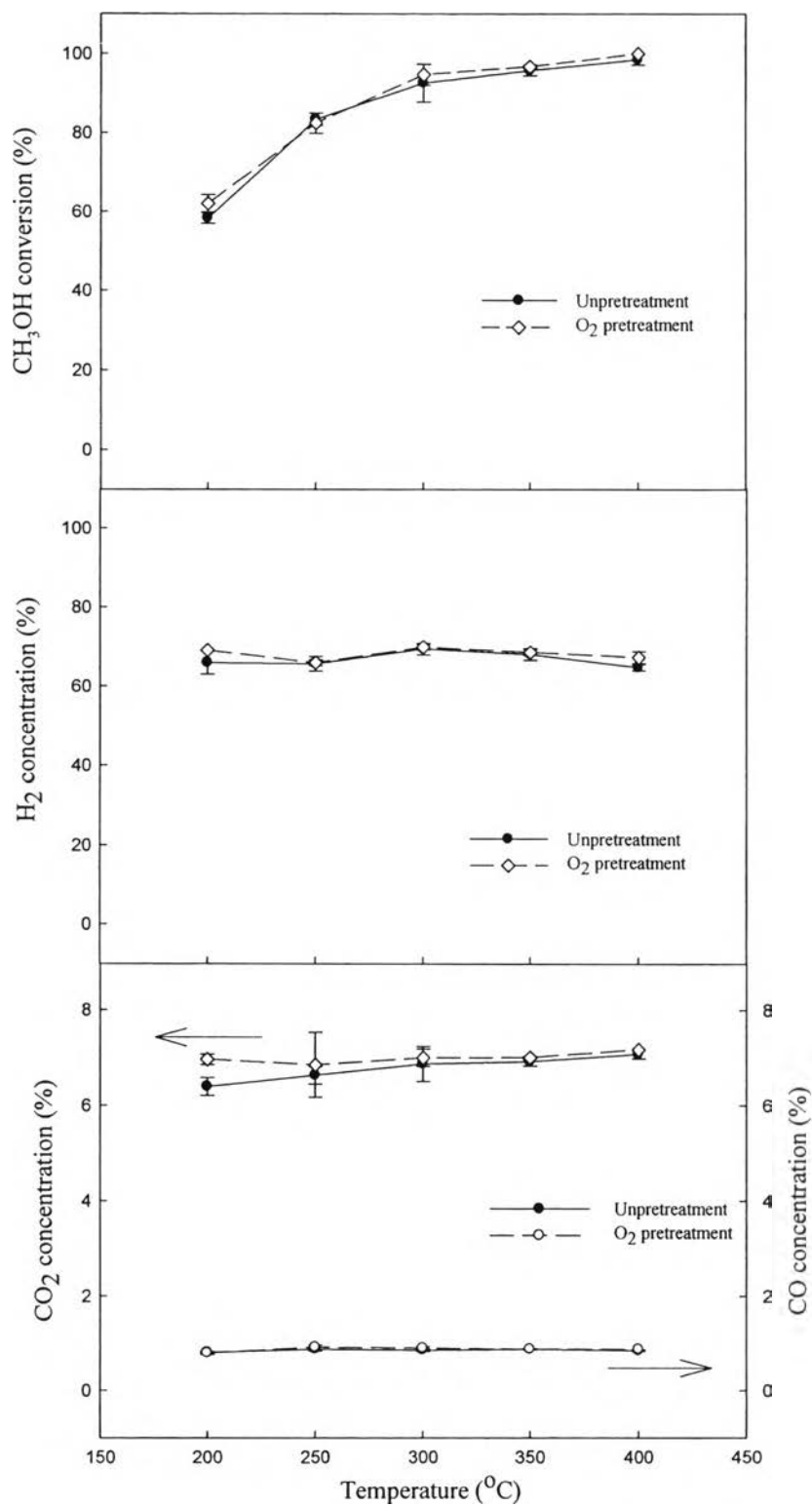


Figure 4.13 Effect of O₂ pretreatment on the methanol conversion, and concentration of H₂, CO₂, and CO over 3 wt% Au/CF(0.25) catalysts. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)

4.1.5 Effect of H₂O/CH₃OH Molar Ratio on the Catalytic Performance

The effect of H₂O/CH₃OH molar ratio on the activity and selectivity of 3 wt% Au/CF(0.25) prepared by a deposition-precipitation technique calcined at 300 °C for 4 h. were studied. The catalysts were tested on various H₂O/CH₃OH molar ratios at 1, 2, 3, 4, respectively, by using reaction temperature from 200 °C to 400 °C. Figure 4.18 displays that the methanol conversion increase along with reaction temperature of all H₂O/CH₃OH molar ratios. Generally, the addition of steam leads to SRM reaction, resulting in, endothermic reaction (Bichon *et al.*, 2006). The H₂O/CH₃OH molar ratio of 2 exhibited the highest methanol conversion, H₂ concentration and CO₂ concentration of all reaction temperature testing. It can be noticed that when H₂O/CH₃OH molar ratio was increased from 1 to 2, the catalytic activity was slightly increased, but further increasing H₂O/CH₃OH molar ratio from 2 to 3, the catalytic activity was gradually decreased. Moreover, when H₂O/CH₃OH molar ratio was increased from 3 to 4, the catalytic activity was obviously dropped. These phenomena were explained by using FT-IR technique that the formation of hydroxyl groups and carbonate species which blocked the active sites of catalysts during reaction (Houteit *et al.*, 2006). It could be concluded that the appropriate of H₂O/CH₃OH molar ratio was 2 corresponding to El-Moemen and coworker, they explained that appropriate steam can decompose the carbonate species (El-Moemen *et al.*, 2009). In addition, the difference of H₂O/CH₃OH molar ratio did not significant effect to CO concentration and no methane was observed.

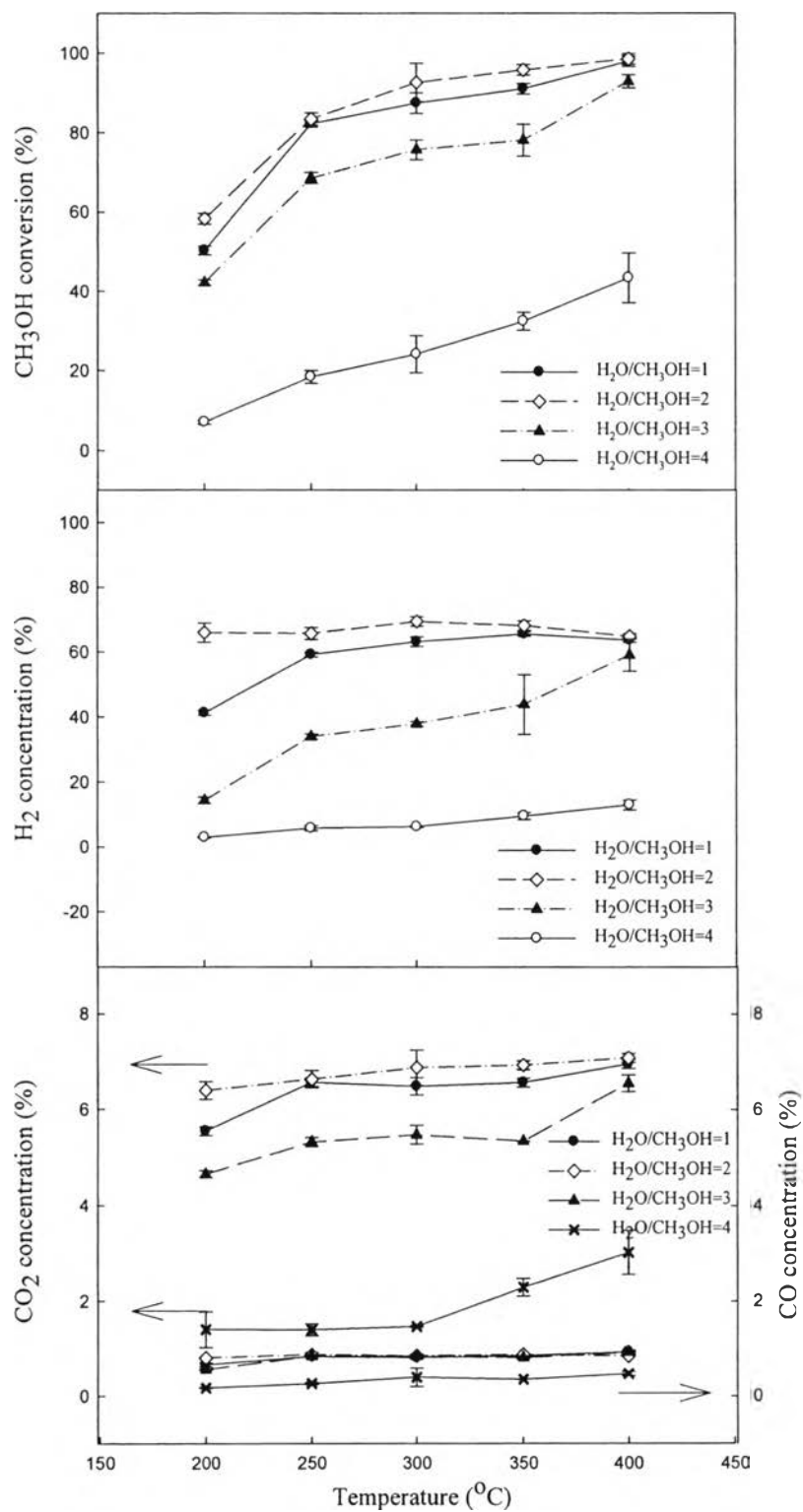


Figure 4.14 Effect of H₂O/CH₃OH molar ratio on the methanol conversion, and concentration of H₂, CO₂, and CO over 3 wt% Au/CF(0.25) catalysts calcined at 300 °C.

4.1.5.1 Fourier Transform Spectroscopy (FT-IR)

The FT-IR spectra of spent 3%wt Au/CF(0.25) catalysts with different H₂O/CH₃OH molar ratios are shown in Figures 4.15 for hydroxyl groups and carbonate species were formed during the reaction. Hydroxyl group can be formed in the range of 3200-3600 cm⁻¹ (El-Moemen *et al.*, 2008), it can be seen that at a H₂O/CH₃OH molar ratio of 2, the FT-IR spectrum of the spent catalyst showed the lowest negative band in this range. In contrast, at a H₂O/CH₃OH molar ratio of 4, the band of OH group with the strong signal of transmittance was observed, corresponding to the lowest catalytic activity. The carbonate species were detected in many positions in the range of 800–1800 cm⁻¹ and 2500–3000 cm⁻¹ (El-Moemen *et al.*, 2008). The different positions of each peak indicated type of carbonate and formate species are shown in Table 4.10. The strong bands appeared at 853, 1070–1045, and 1340 cm⁻¹ indicated the carbonate species on ceria, 1370, 2921, and 2949 indicated the formate species on Ce⁴⁺, and 1370, and 2848 indicated the formate species on Ce³⁺ (Tabakova *et al.*, 2003). It can be noticed that a H₂O/CH₃OH molar ratio of 4, the strongest peak of both formate species and carbonate species were observed, inferior that the molar ratio at 3, 1, and 2, respectively. From FT-IR results, it can be concluded that the catalytic activity depends on the amount of remaining carbonate and formate species on the active site (Costello *et al.*, 2003).

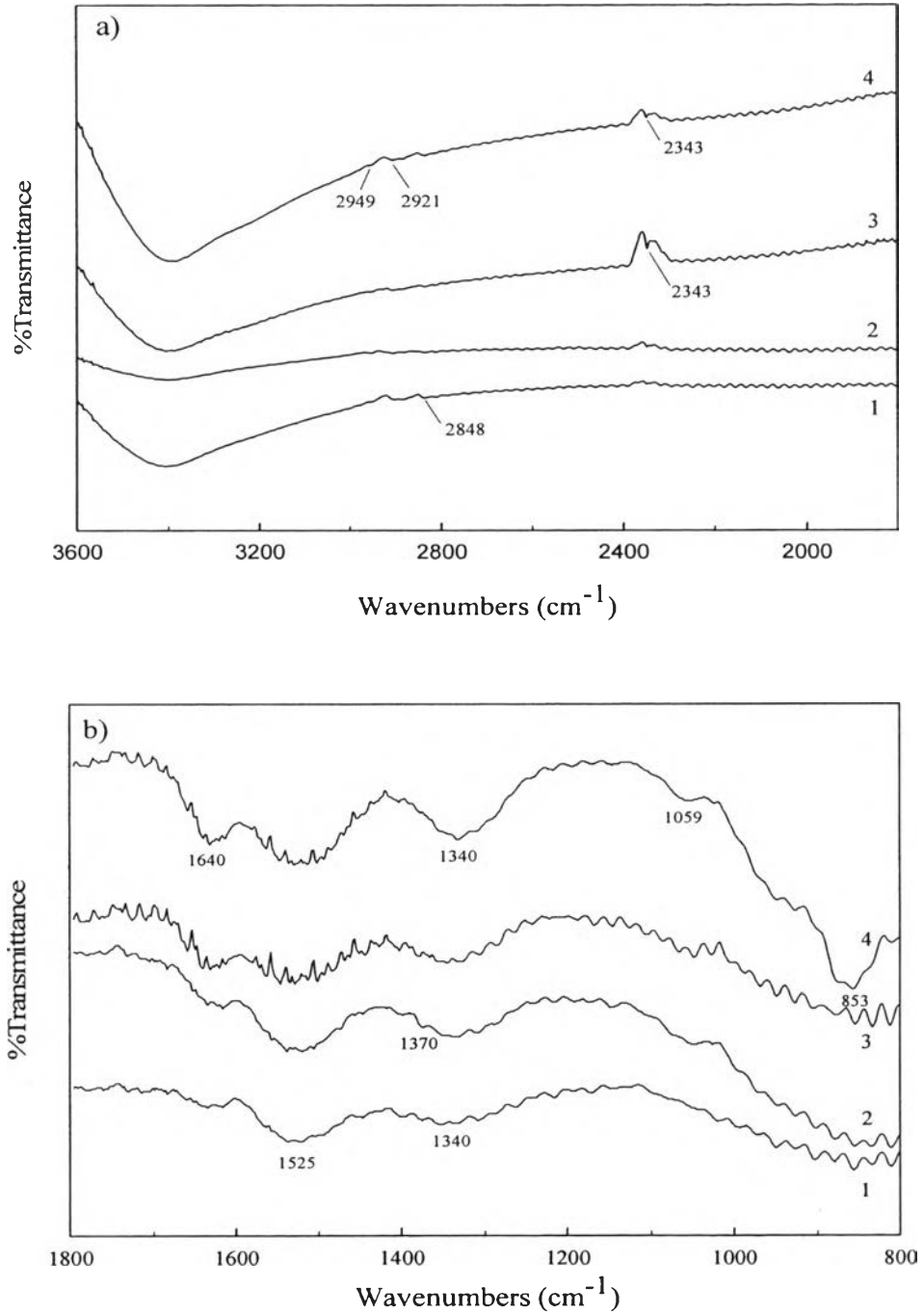


Figure 4.15 FTIR spectra of 3 wt% Au/CF(0.25) catalysts calcined at 300 °C after reaction. (a) and (b) (1) H₂O/CH₃OH molar ratio of 1; (2) H₂O/CH₃OH molar ratio of 2; (3) H₂O/CH₃OH molar ratio of 3; (4) H₂O/CH₃OH molar ratio of 4.

Table 4.10 Frequency and assignment of carbonate, formate, and intermediate bands of spent 3 wt% Au/CF(0.25) calcined at 300 °C (Tabakova *et al.*, 2003)

Wavenumber (cm ⁻¹)	Assignment
1370, 2848	Formate species on Ce ³⁺
1370, 2921, 2949	Formate species on Ce ⁴⁺
853, 1070–1045, 1340	Carbonate species on Ceria
1525	Bicarbonate species on Ceria
1640	Bending mode of undissociated H ₂ O
2343	Linear CO ₂ weakly interacting with ceria

4.1.6 Effect of O₂/CH₃OH Molar Ratio on the Catalytic Performance

To study the effect of O₂/CH₃OH molar ratio on the activity and selectivity of 3 wt% Au/CF(0.25) prepared by deposition-precipitation technique calcined at 300°C for 4 h. The catalysts were tested on various O₂/CH₃OH molar ratios of 0, 0.4, 0.6, 0.8, and 1.2 and a H₂O/CH₃OH molar ratio of 2 was kept at reaction temperature range of 200 °C to 400 °C. Figure 4.16 shows, the methanol conversion and product concentration with different O₂/CH₃OH molar ratios, when oxygen was added in the feed can enhance the catalytic activity in low range temperature (200 °C – 300 °C) and the catalytic activity exhibited higher H₂ production when compare with SRM reaction (Hong *et al.*, 2008) that the addition of oxygen is simultaneous POM and SRM processes that can enhance H₂ production rate in lower temperature (Velu *et al.*, 2001). Moreover, at a O₂/CH₃OH molar ratio of 0.6, gave the highest catalytic activity was observed, it reached more than 90% and 70% for methanol conversion and hydrogen concentration, respectively, at 300 °C. In contrast, when O₂/CH₃OH molar ratio was added from 0.6 to 0.8, the result showed that hydrogen production was decreased resulting in, hydrogen consumption via hydrogen oxidation (Patel *et al.*, 2007). Generally, the SRM has higher hydrogen concentration more than OSRM, and POM reaction because the addition of oxygen, hydrogen is oxidized to H₂O that against this testing. In addition, the presence oxygen in the feed had higher CO₂ concentration than absence oxygen because CO was oxidized to CO₂ (Velu *et al.*, 2001) and the difference of O₂/CH₃OH molar ratio did not affect much to the CO concentration. However, methane was not detected in this experiment. In conclusion, the concentration of the mixture oxygen, steam, and methanol was appropriated resulting in high activity in OSRM in low temperature range.

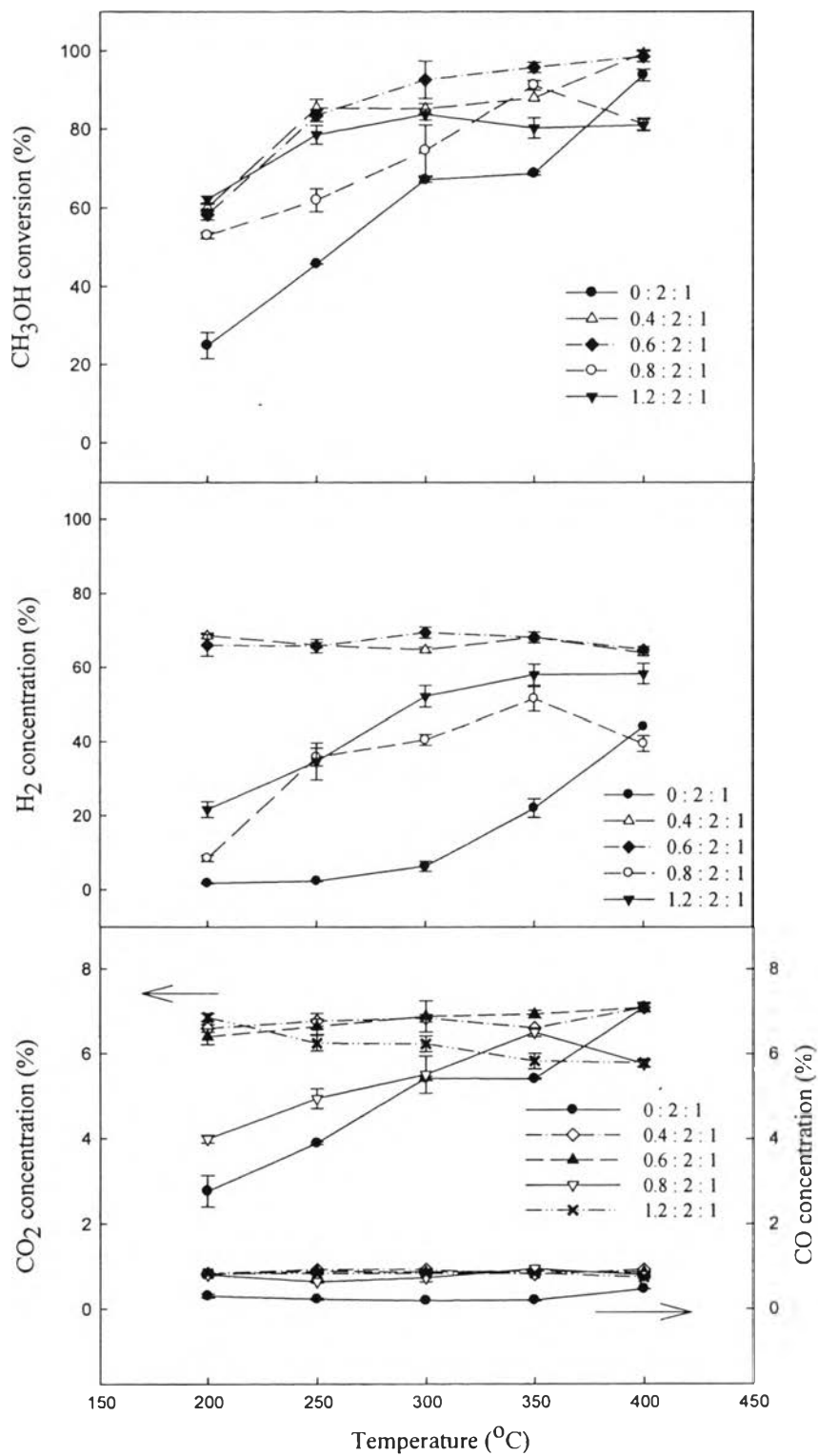


Figure 4.16 Effect of O₂/H₂O/CH₃OH molar ratio on methanol conversion, and concentration of H₂, CO₂, and CO over 3 wt% Au/CF(0.25) catalysts calcined at 300 °C.

4.1.7 Comparison of Stability between Unpretreated Catalyst and Pretreatment Catalyst

The stability of unpretreated and O₂ pretreated catalysts for 720 minutes, 12 hours, was tested at 350 °C, as shown in Figure 4.17. The activity of unpretreated was slightly decreased from 95.7 to 91 for methanol conversion and from 85.87 to 82 for hydrogen yield. The activity of pretreated catalyst also was slightly decreased from 96.75 to 93 for methanol conversion and from 86.76 to 84.5 for hydrogen yield. The activity of O₂ pretreated catalyst showed a little bit higher than unpretreated catalyst.

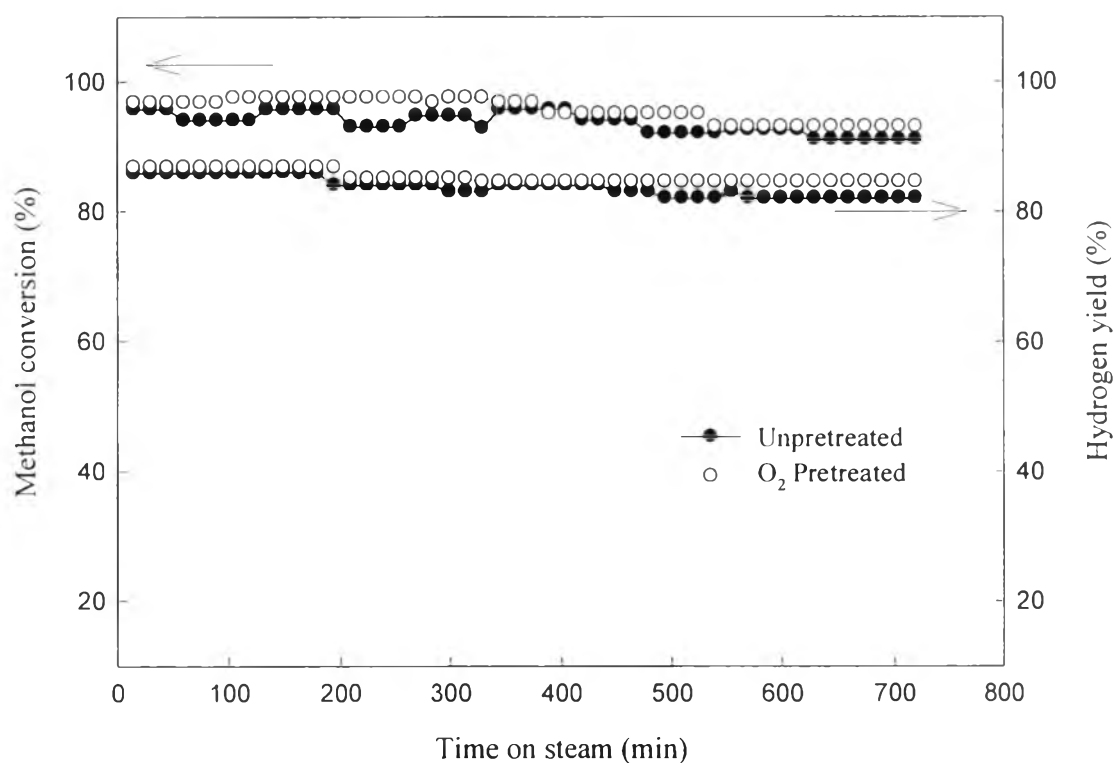


Figure 4.17 Stability testing of the 3 wt% Au/CF(0.25) at reaction temperature of 350 °C. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)

4.1.7.1 X-ray Diffraction (XRD)

Figure 4.18 shows the XRD patterns of spent unpretreated and O₂ pretreated catalysts and compared with 3 wt% Au/CF(0.25) fresh catalyst. The spent catalyst was test for 720 minutes, 12 hours. The magnetite phase can be observed at crystallographic plane of 220, 110, 113, and 116. The hematite phase can be observed at crystallographic plane of 104, and 024 (Salvatore *et al.*, 2008), it can be noticed that the spent catalysts had higher magnetite phase and lower hematite phase than fresh catalyst resulting in, the activity of catalyst was decreased according to, Salvatore and coworker reported that the hematite phase was active phase for catalytic activity (Salvatore *et al.*, 2008). When compare between spent unpretreated and O₂ pretreated catalysts, there are no phase changing when catalyst are treated with O₂. Suggesting that, the O₂ pretreatment did not significantly affect the morphology of support.

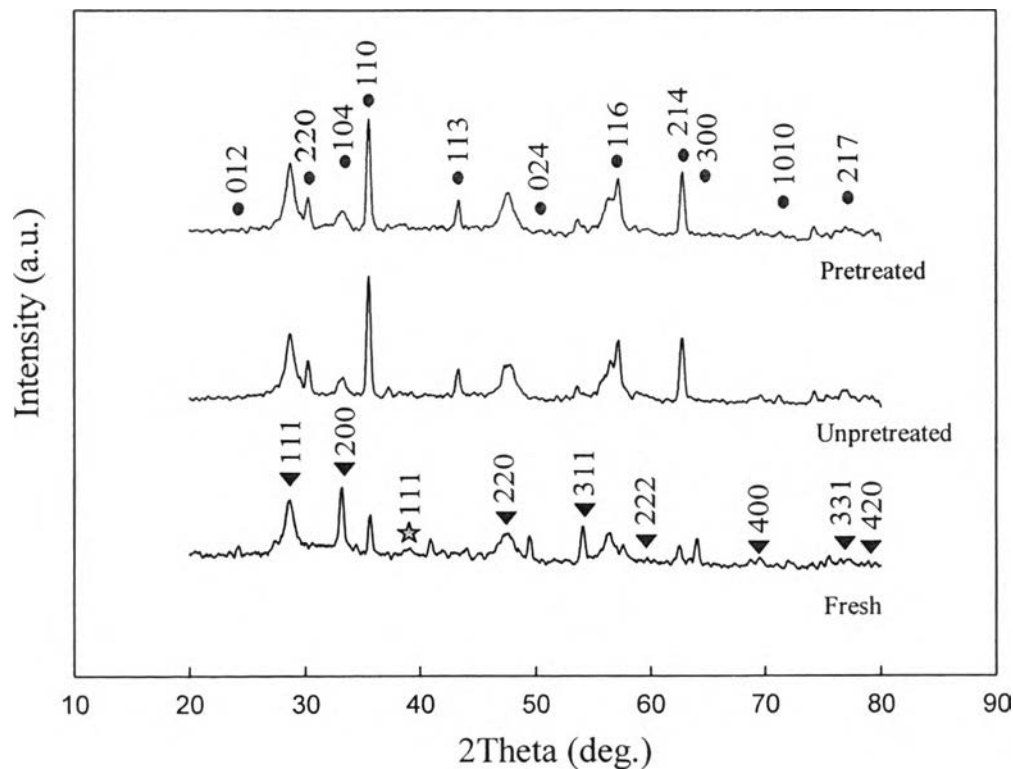


Figure 4.18 XRD patterns of supported Au catalysts: (▼) CeO₂; (●) Fe₂O₃; (☆) Au

4.1.7.2 Temperature-Programmed Oxidation (TPO)

The TPO experiments were investigated on the spent catalyst and the amount of carbon deposition (coke formation) was measured on untreated and pretreated of 3 wt% Au/CF(0.25) catalyst. The catalysts were carried out at 350°C for 12 hours. The untreated catalyst was found peak with high intensity from 150 °C to 400 °C, the O₂ pretreated catalyst was found obvious peak at 84.5 °C implying that different carbonaceous species were formed. According to the low temperature (<200 °C), the coke deposited was not polyaromatic type could be assigned to the oxidation of the weakly polymerized coke deposited on the metal particles. At high temperature (>350 °C), the coke components were polyaromatic type represented the high polymerized coke deposited near the metal-support interphase (Luengnaruemitchai *et al.*, 2008). In addition, low temperature peak of O₂ pretreated catalyst at 84.5 °C was indicated carbonaceous deposition that intermediate to coke formation (Guisnet *et al.*, 2001). It was found that the amount of carbon deposition for untreated catalysts was 0.629 wt% and O₂ pretreated catalyst was found very low carbon deposition as 0.0526 wt% agree with the result, O₂ pretreated catalyst gave higher activity than untreated catalyst. However, the little amount of coke formation does not affect much to the catalytic activity of the catalyst corresponding to, Armor and coworker reported that the coke formation does not affect dramatically the catalytic activity of the catalyst (Armor *et al.*, 2008).

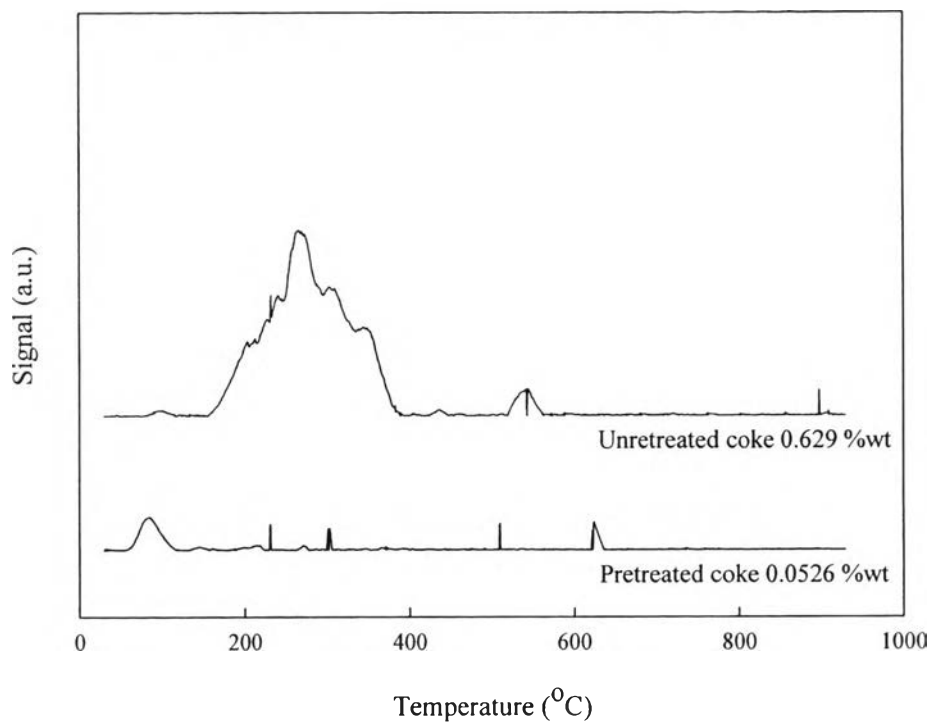


Figure 4.19 TPO profiles of spent 3 wt% Au/CF(0.25) after reaction temperature 300 °C, and time on stream 12 hour. (Reaction conditions: O₂/H₂O/CH₃OH molar ratio = 0.6:2:1)