



## CHAPTER IV

### RESULTS AND DISCUSSION

#### 4.1 Catalyst Characterization

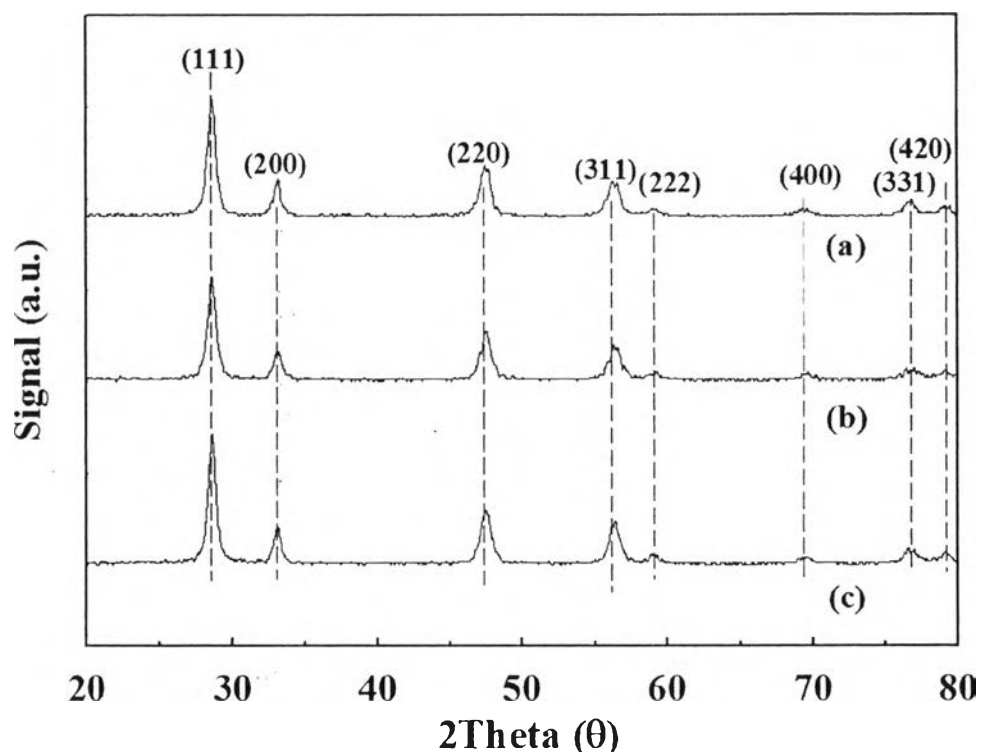
X-ray powder diffraction (XRD) was performed in a Rigaku X-Ray Diffractometer system (RINT-2200) with  $\text{CuK}_\alpha$  radiation, in order to examine the crystalline phases and crystalline sizes of the sample. Information on the Au species was attained by UV-vis spectroscopy. The surface area was 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 XRD Patterns

The X-ray patterns, in the angular range ( $20\text{--}80^\circ$ )  $2\theta$ , of as-prepared gold catalysts are presented in Figure 4.1. Patterns a, b, and c in Figure 4.1 showed the Au/La- $\text{CeO}_x$  catalysts in which the support were prepared by urea-gelation precipitation, step precipitation, and  $\text{NH}_4\text{OH}$  precipitation, respectively.

From Figure 4.1, it is clearly seen that there is no significant difference shown in the XRD result. In all three catalysts, no peak of metallic Au were observed at  $38.2$ ,  $44.4$ ,  $64.6$ , and  $77.7^\circ$ , which attributed to Au (111), Au (200), Au (220), and Au (311), respectively. This suggests that the Au particle is well dispersed on the surface of the catalyst or the particle size of Au is smaller in diameter than the detection limit of the diffractometer (5 nm) (Luengnaremitchai *et al.*, 2005). However, a very strong peak of crystalline features of  $\text{CeO}_2$  fluorite type-cubic structure were detected at XRD  $2\theta = 28.5^\circ$  (Arena *et al.*, 2006). In addition, the weaker peaks were also detected at  $33.08^\circ$ ,  $47.47^\circ$ ,  $56.33^\circ$ ,  $59.08^\circ$ ,  $69.40^\circ$ ,  $76.69^\circ$ , and  $79.07^\circ$ , which were corresponding to  $\text{CeO}_2$  (200),  $\text{CeO}_2$  (220),  $\text{CeO}_2$  (311),  $\text{CeO}_2$

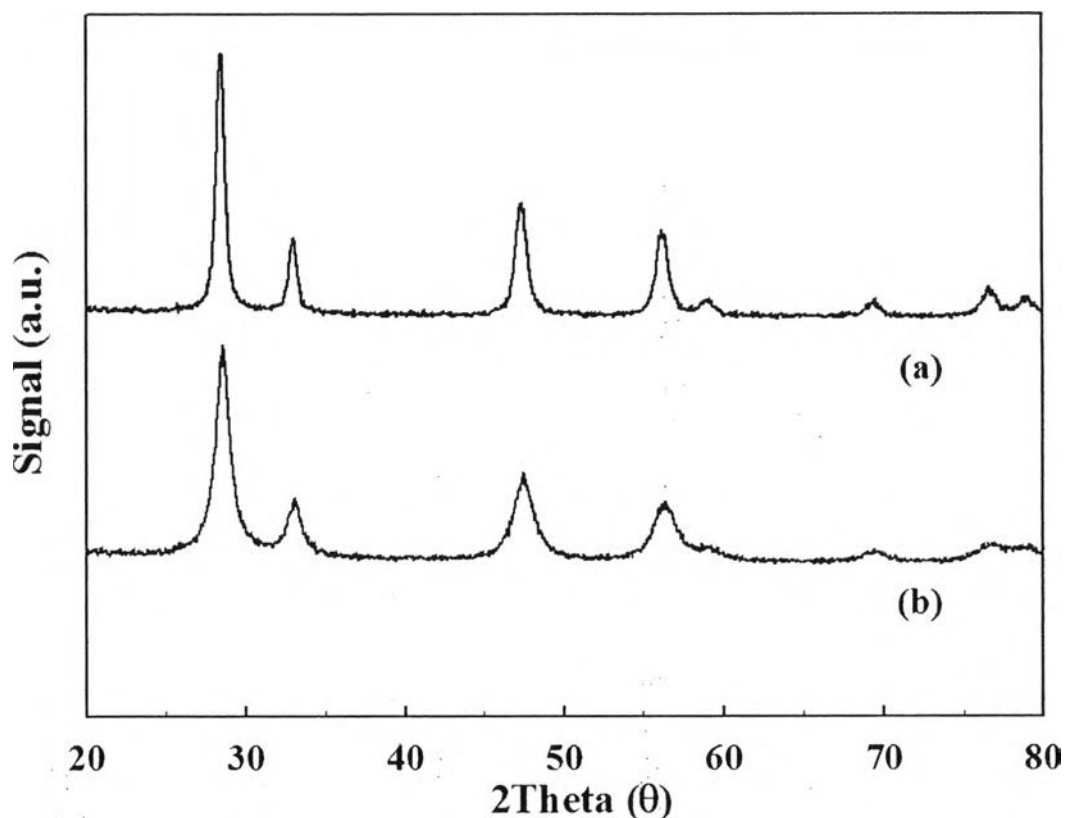
(222), CeO<sub>2</sub> (400), CeO<sub>2</sub> (331), and CeO<sub>2</sub> (420) for CuK $\alpha$  (1.5406 Å) radiation, respectively (Carabineiro *et al.*, 2010).



**Figure 4.1** X-Ray diffraction (XRD) patterns of gold supported catalysts in which the La-CeO<sub>x</sub> support were prepared in different methods : (a) Urea-gelation precipitation; (b) Step precipitation; (c) NH<sub>4</sub>OH precipitation; with 1%wt Au loading, dried by oven and calcined at 400°C for 4 hours.

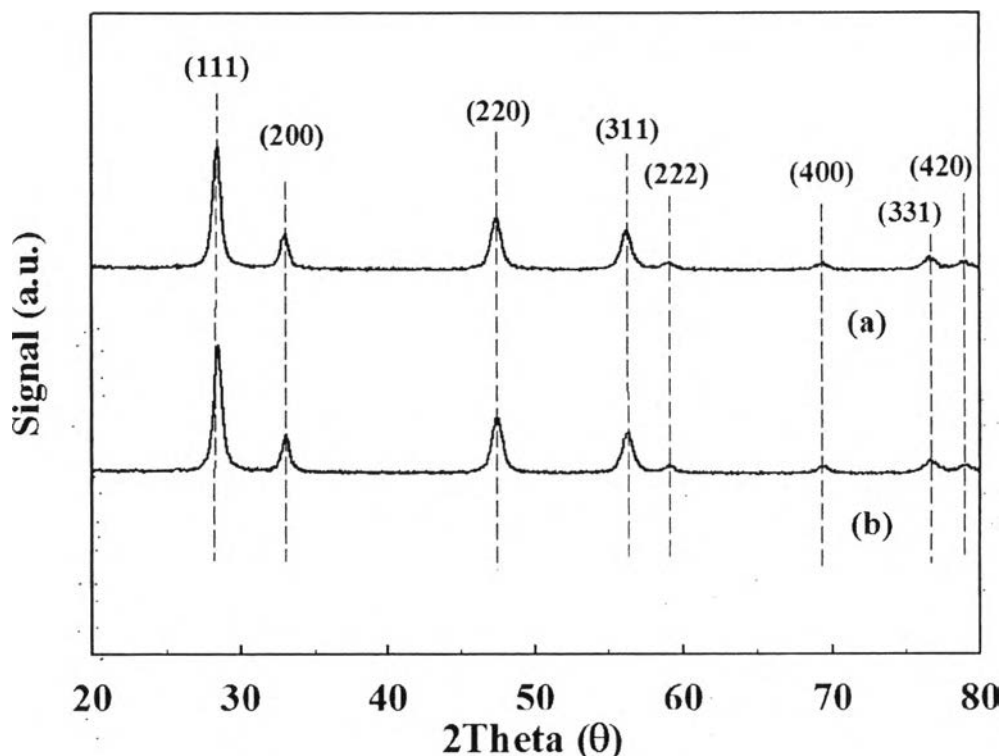
As can be seen, there were no peaks or no separate reflections of La<sub>2</sub>O<sub>3</sub> or La(OH)<sub>3</sub> can be observed in the above figure. However, Figure 4.2 showed a slight shift to lower angles, from 28.57° to 28.47°, as when La was added into CeO<sub>2</sub> support. Such shift is usually the result of the addition of promoters to the support, implying the incorporation of the La into the CeO<sub>2</sub> lattice. This idea was confirmed by the noticed of the increase in the lattice constant with the present of La dopant , as the radius of Ce<sup>4+</sup> and La<sup>3+</sup> is 0.097 and 0.116 nm, respectively. (Zhang *et al.*, 2010). Figure 4.2 illustrates the X-ray diffraction patterns of CeO<sub>2</sub> support and La-CeO<sub>x</sub> support, in which the pattern (a) showed La-CeO<sub>x</sub> support and pattern (b)

showed CeO<sub>2</sub> support. The intensity of the reflection of CeO<sub>2</sub> phase is higher with the addition of La.



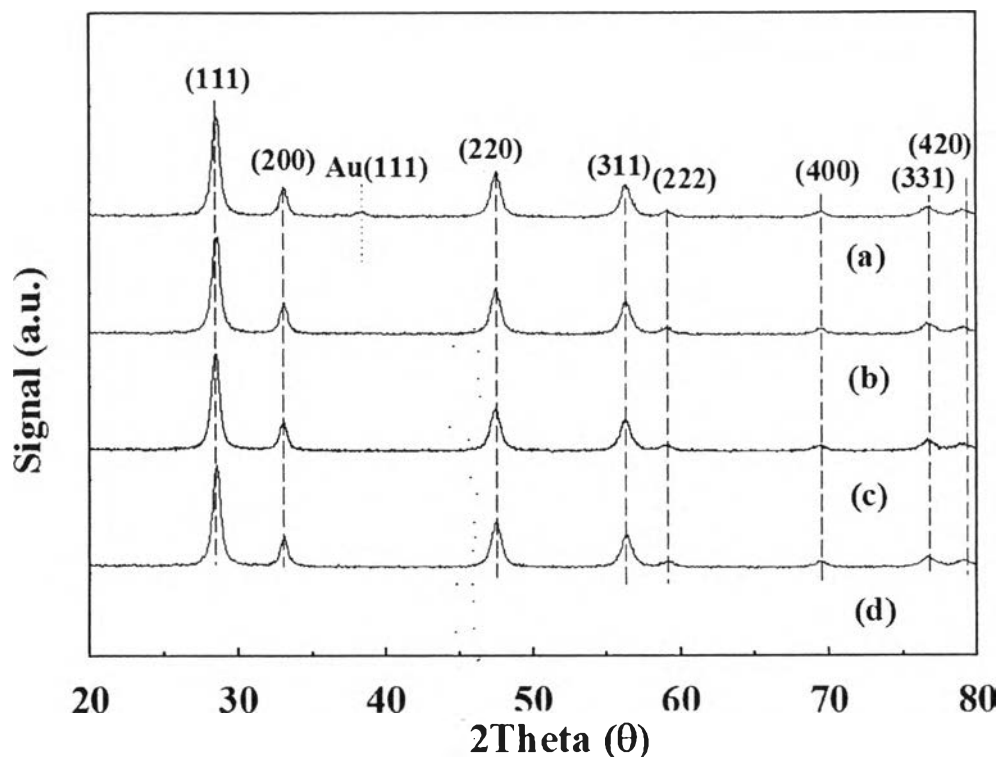
**Figure 4.2** X-Ray diffraction (XRD) patterns of two types of support: (a) La-CeO<sub>x</sub>; (b) CeO<sub>2</sub>

The diffraction peak attributed to La<sub>2</sub>O<sub>3</sub> (44.6°), LaOOH (29.4° and 31.1°), and LaO<sub>2</sub>CO<sub>3</sub> (22.3°) were not observed in this work, indicating that La species were highly dispersed into Ce species structure. The XRD patterns of 1%wt Au/La-CeO<sub>x</sub> catalysts, with two different drying techniques are illustrated in Figure 4.3. And from the Figure, the XRD patterns for oven dried and freeze dried catalysts are almost identical and still, no peaks of metallic gold can be identified. Both of the catalysts were calcined at 400°C and the supports were prepared by NH<sub>4</sub>OH precipitation method.



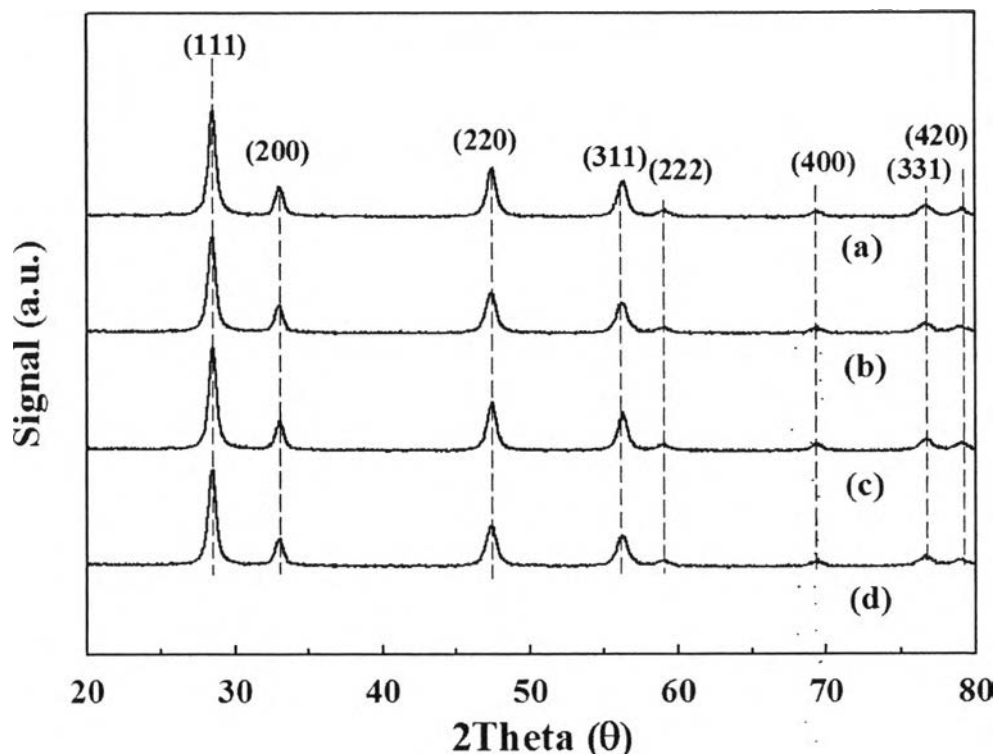
**Figure 4.3** X-Ray diffraction (XRD) of 1%wt Au/La-CeO<sub>x</sub> catalysts, using different drying methods: (a) Freeze dried; (b) Oven dried; calcined at 400°C, and the support was prepared by NH<sub>4</sub>OH precipitation.

Figure 4.4 reveals the X-ray diffraction data of pure La-CeO<sub>x</sub> support and Au/La-CeO<sub>x</sub> catalysts, calcined at 400°C, with different Au loadings. The XRD of 1%wt Au/La-CeO<sub>x</sub> and 3%wt Au/La-CeO<sub>x</sub> samples still showed no peaks of metallic gold species, as in previous cases. However, a barely visible peak of metallic Au(111) at 38.2° can be detected for 5%wt Au/La-CeO<sub>x</sub>, this signifying the presence of sufficiently large metal gold particles. These results agree with those obtained from DR/UV-vis spectroscopy and TPR results.



**Figure 4.4** X-Ray diffraction (XRD) of Au/La-CeO<sub>x</sub> catalysts, with different gold loading: (a) 5%wt Au/La-CeO<sub>x</sub> catalysts; (b) 3%wt Au/La-CeO<sub>x</sub> catalysts; (c) 1%wt Au/La-CeO<sub>x</sub> catalysts; (d) Pure La-CeO<sub>x</sub> support; using freeze dry technique, and the support was prepared by NH<sub>4</sub>OH precipitation.

The X-ray diffraction data were collected for 1%wt Au/La-CeO<sub>x</sub> catalysts with different calcination temperatures in Figure 4.5. XRD pattern (d) showed the crystalline phase of uncalcined 1%wt Au/La-CeO<sub>x</sub> catalysts. Whereas XRD patterns (a), (b), and (c) demonstrated the crystalline phase of 1%wt Au/La-CeO<sub>x</sub> catalysts at the calcination temperature of 500°C, 400°C, and 300°C, respectively. And by studying the XRD analysis, no appreciable difference between the uncalcined and calcined catalysts were noted.

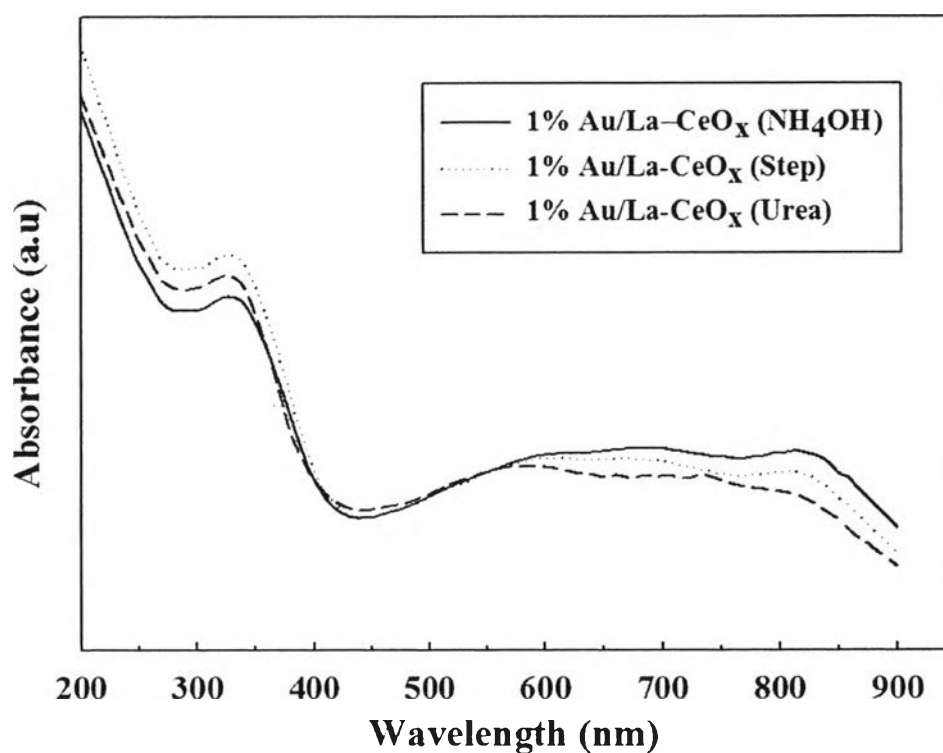


**Figure 4.5** X-Ray diffraction (XRD) of 1%wt Au/La-CeO<sub>x</sub> catalysts, with different calcination temperature: (a) 500°C; (b) 400°C; (c) 300°C; (d) uncalcined; using freeze dry technique, and the support was prepared by NH<sub>4</sub>OH precipitation.

#### 4.1.2 UV Measurement

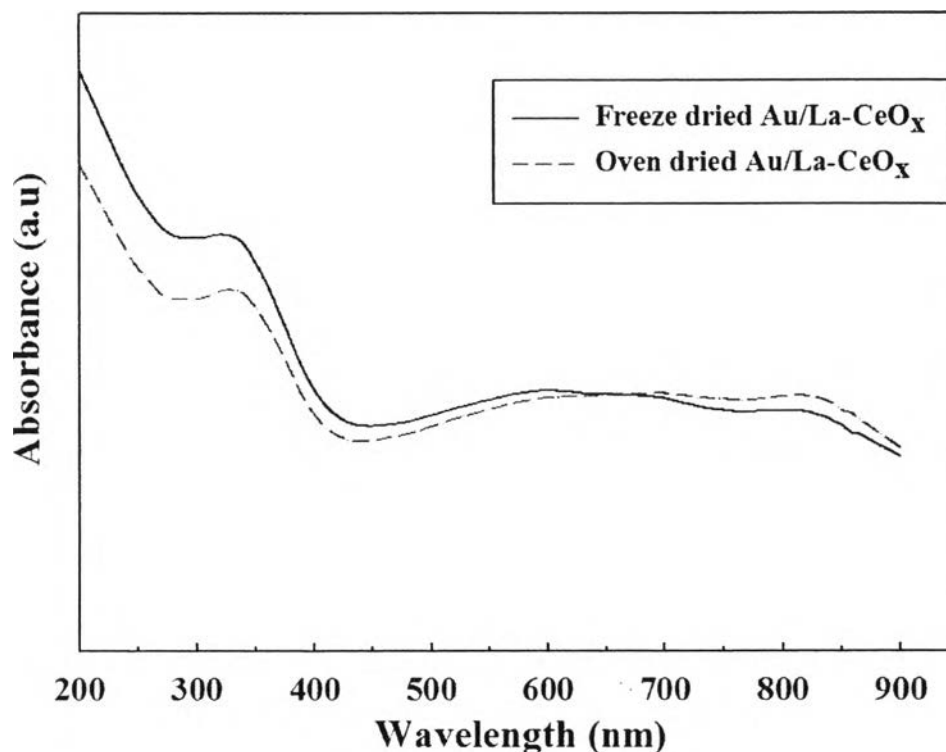
The DR/UV-vis spectroscopy is used to study the existence of Au metal on the support and also to analyze Au species. From the literature review, the absorptions at < 250 nm, 280–390 nm, and 500–600 nm represent Au<sup>3+</sup> species, small gold clusters (Au<sub>n</sub>, 1 < n < 10), and gold nanoparticles (Plasmon or Au metallic species, Au<sup>0</sup>), respectively (Escamilla-Perea *et al.*, 2010). However, the cerium oxide also exhibits bands in the range of 230–400 nm (Tu *et al.*, 2009). As a result, this technique has some limitations due to the difficulty in interpreting between the support and the resonance band of both Au<sup>3+</sup> and gold clusters. Figures 4.6–4.9 represent the diffuse reflectance UV-vis spectra of all prepared Au/La-CeO<sub>x</sub> catalysts.

Figure 4.6 illustrates the diffuse reflectance UV-vis spectra of all 1%wt Au/La-CeO<sub>x</sub> samples, in which the La-CeO<sub>x</sub> support were prepared by NH<sub>4</sub>OH precipitation, step precipitation, and urea-gelation precipitation. The bands of cerium oxide and gold plasmon can be observed at 230–400 nm and 500–600 nm, respectively.



**Figure 4.6** UV-vis DRS spectra of 1%wt Au/La-CeO<sub>x</sub> samples with different support preparation methods; using oven dry technique and calcined at 400°C.

The comparison of the UV-vis spectra of freeze dried and oven dried 1%wt Au/La-CeO<sub>x</sub> is shown in Figure 4.7. It can be seen that the drying method have an insignificant effect on the dispersion of the gold particles on the support.

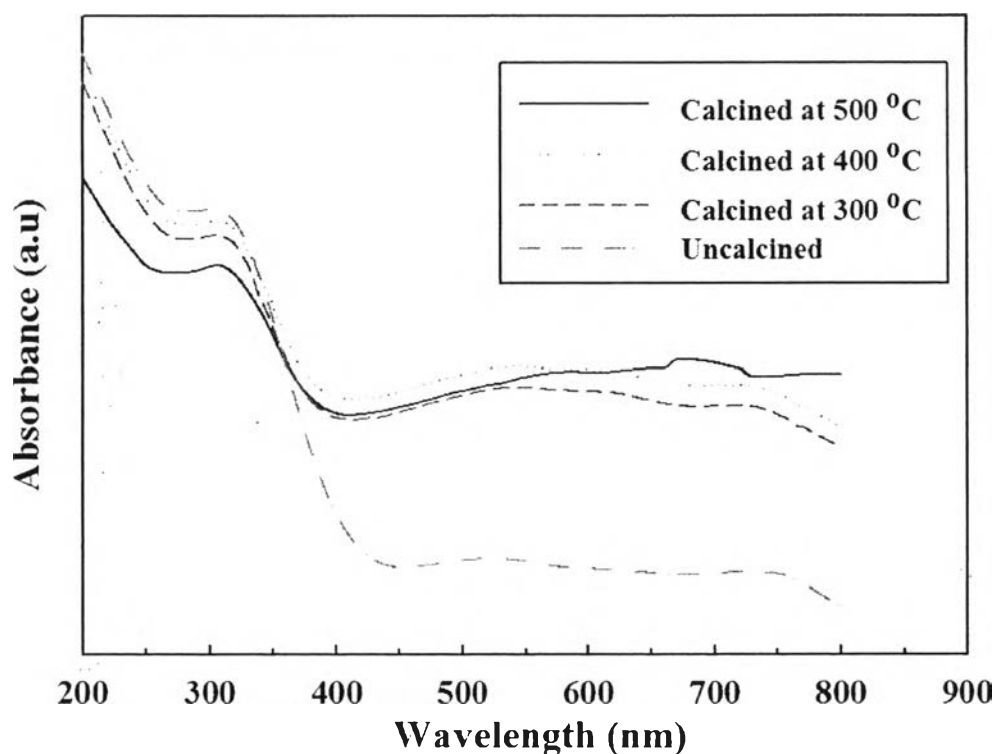


**Figure 4.7** UV-vis DRS spectra of 1%wt Au/La-CeO<sub>x</sub> samples with different drying techniques; calcined at 400°C and the support was prepared by NH<sub>4</sub>OH precipitation.

Figure 4.8 shows the different in the UV-vis spectra of 1%wt Au/La-CeO<sub>x</sub> at different calcination temperatures. All the samples demonstrated the absorption band in the 500–600 nm region, which is characteristic reflectance of metallic gold. According to the Figure, the spectra of uncalcined catalyst showed a reduced amount of Au<sup>0</sup> specie or metallic gold absorption band when compared to the calcined catalysts, which implied that Au<sup>0</sup> specie or metallic gold were formed after the catalyst went through the calcination process. This result is supported by those reported in the literature. Bond *et al.* (2006) suggested that the main advantage of heat treatment is to reduce the Au<sup>3+</sup> specie to Au<sup>0</sup> specie or metallic gold, for being the active sites. In addition, we can also see that the Au plasmon band of the catalyst calcined at 300°C is lesser than that of the catalysts calcined at 400°C and 500°C. Similarly, in the study of Eun and coworkers, it was mentioned that the higher the calcination temperature, the higher amount of metallic Au or Au<sup>0</sup> specie

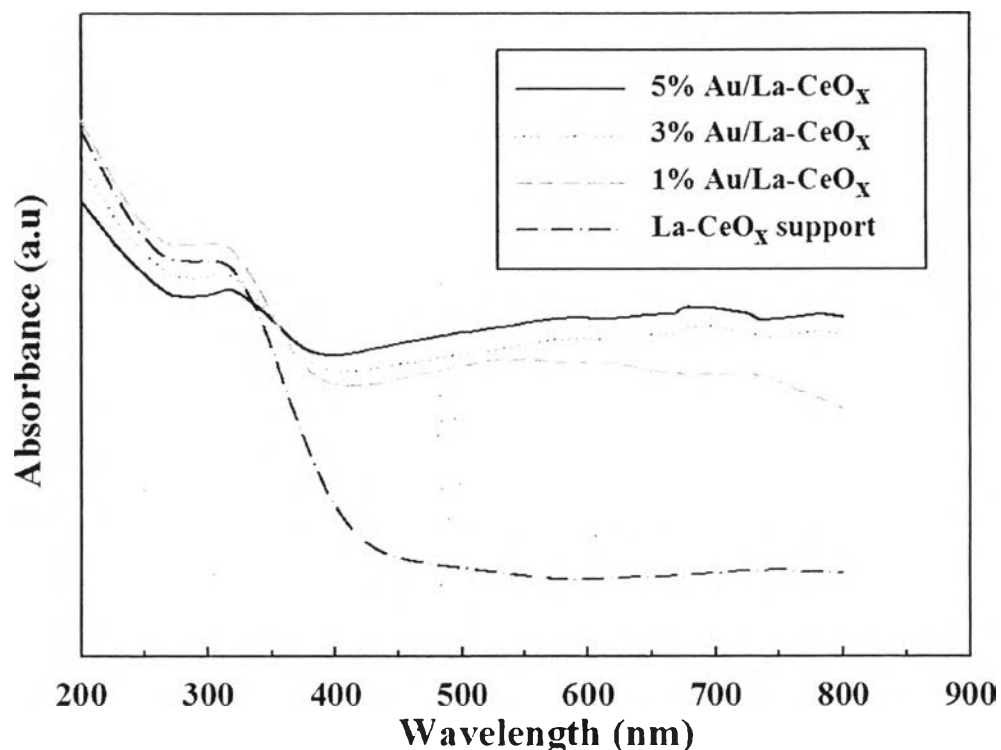


was formed from the reduction of  $\text{Au}^{3+}$  to  $\text{Au}^0$ . In conclusion, the alteration of calcination temperature affects the gold species formed on the catalyst.



**Figure 4.8** UV-vis DRS spectra of 1%wt Au/La-CeO<sub>x</sub> samples at different calcination temperatures; using freeze dry technique and the support was prepared by NH<sub>4</sub>OH precipitation.

Figure 4.9 compared the UV-vis spectra of freeze dried Au/La-CeO<sub>x</sub> catalysts, with different gold loading. According to the Figure, the Au plasmon band was more pronounced when the Au loading was increased to 5%wt. This proved that, higher gold content was loaded on the catalysts. Therefore, this is one of the evidence that can support the XRD result, which the peak of Au(111) or metallic gold can be spotted at higher 5%wt Au loading.



**Figure 4.9** UV-vis DRS spectra of freeze dried Au/La-CeO<sub>x</sub> samples with different gold loadings; calcined at 400°C and the support was prepared by NH<sub>4</sub>OH precipitation.

#### 4.1.3 TPR Measurement

The temperature-programmed reduction (TPR) analyses were performed to obtain information on the reducibility of a series of catalysts. Figures 4.10, 4.11, 4.12, 4.13 represent the TPR profiles of Au/La-CeO<sub>x</sub> catalysts with different support preparation method, drying technique, gold loading, and calcination temperature, respectively.

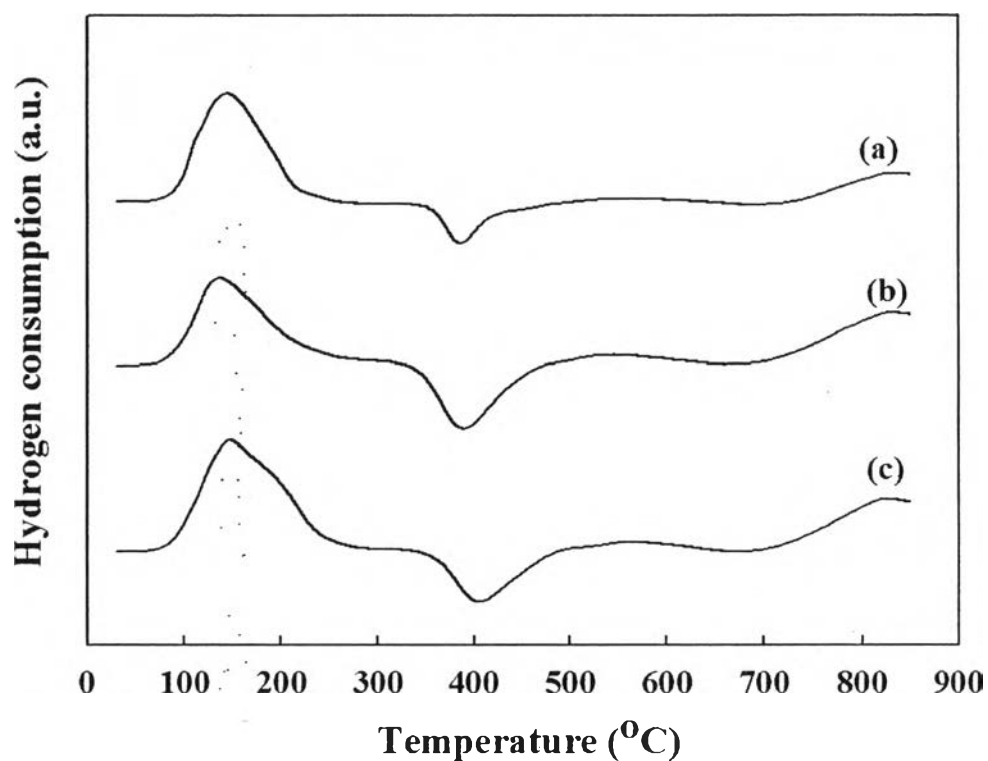
According to Andreeva *et al.* (2006), two major reduction peaks of TPR spectra are registered for pure ceria samples. The first peak (500–600°C) corresponds to the lower temperature ceria surface shell reduction (or reduction of surface oxygen species). And the second peak, the high-temperature peak at about 800–900°C is assigned to the reduction of bulk oxygen and the formation of lower oxides of cerium. However, when gold is introduced as the active sites on the surface

of ceria, the surface shell reduction is facilitated whereas there is little effect, if any, on the bulk oxygen of ceria. The lower temperature reduction peak showed a downward shift to the lower temperature at (100–200°C) and the high-temperature peak remains the same (Carabineiro *et al.*, 2010). It has been proposed that the presence of gold improves the reducibility of the surface oxygen on CeO<sub>2</sub>, or in other words, it weakens the adjacent surface Ce-O bond which helps in the oxygen transfer across the solid–gas interface during reaction (Venezia *et al.*, 2005). Furthermore, there are more cases of other metals, such as Pt, Ni and Cu, which showed the same effect on the TPR peak when added on ceria support (Jacobs *et al.*, 2004).

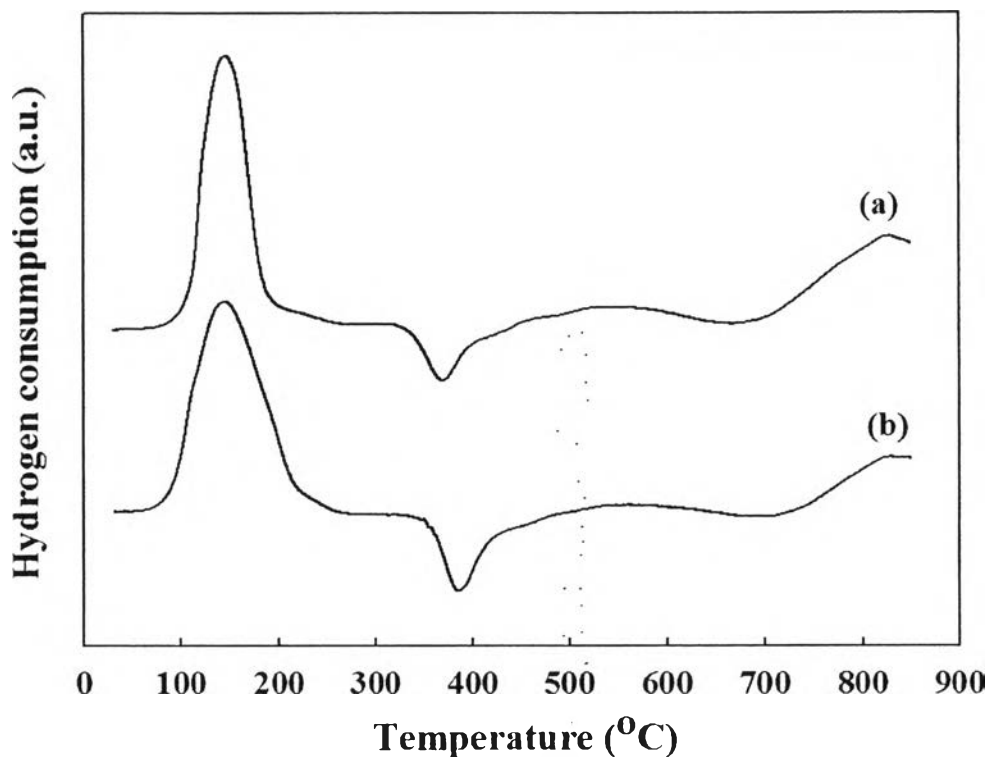
From Figures 4.10–4.13, all samples apart from pure support show the low temperature peak at 100–200°C and the high temperature peak at 800–900°C, which is similar to those reported in the literature (Scire *et al.*, 2003). However, there are also the occurrences of the negative peak in the TPR profiles in the temperature range of 320–400°C. No strong evidence is found on this unusual behavior of Au supported catalyst. But such behavior has been found palladium and copper supported catalysts. Ding *et al.* (2008) have studied the one step preparation of silica supported Pd/Sr and Pd/Ba catalysts via organometallic precursors: application in hydrogenation and hydrochlorination and they have reported a negative peak at around 98°C of Pd/SiO<sub>2</sub> samples. They suggested that a negative peak represents the release of H<sub>2</sub> from the decomposition of the palladium hydride phase ( $\beta$ -phase), which can be formed from metallic palladium already produced in the catalyst preparation or during the initial flushing with hydrogen at room temperature. This idea is also support by Lieske *et al.* (1985). While Labaki *et al.* (2004) have reported a negative TPR peak of copper–zirconium compound at 440°C. They explained the phenomenon as the hydrogen trapping or the release of hydrogen trapped in the solid.

Figures 4.10 and 4.11 represent the TPR spectra of 1%wt Au/La-CeO<sub>x</sub> samples, with different support preparation technique and different drying techniques, respectively. Notably, no remarkable different is observed for the reduction peaks in for different support preparation methods. Whereas, the TPR spectra for different in drying method shows a notable difference. The peak for freeze dried catalyst is taller and narrower than the peak for oven dried catalyst. This

shows that by using freeze dried, the catalyst is well dispersed when compared to that of the oven dried catalyst.

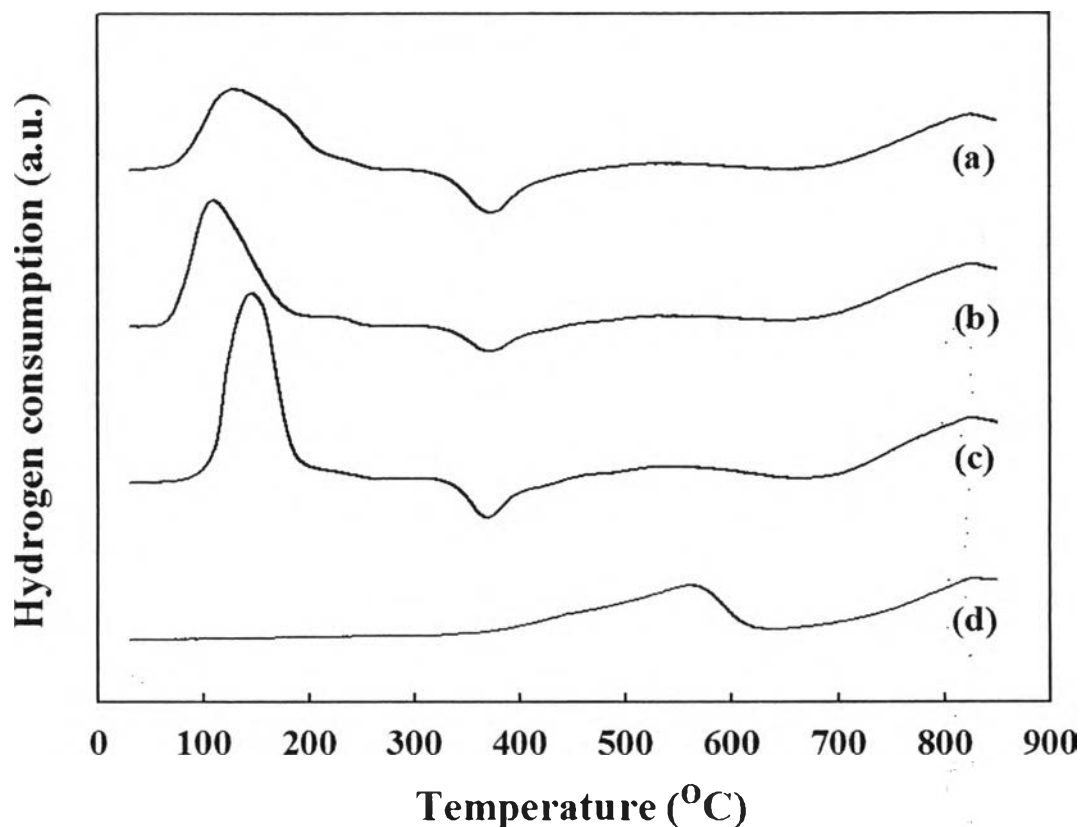


**Figure 4.10** TPR curves for 1%wt Au/La-CeO<sub>x</sub> catalysts using different support preparation techniques: (a) NH<sub>4</sub>OH precipitation; (b) Step precipitation; (c) Urea-gelation precipitation; using oven dry and calcined at 400°C for 4 hours.



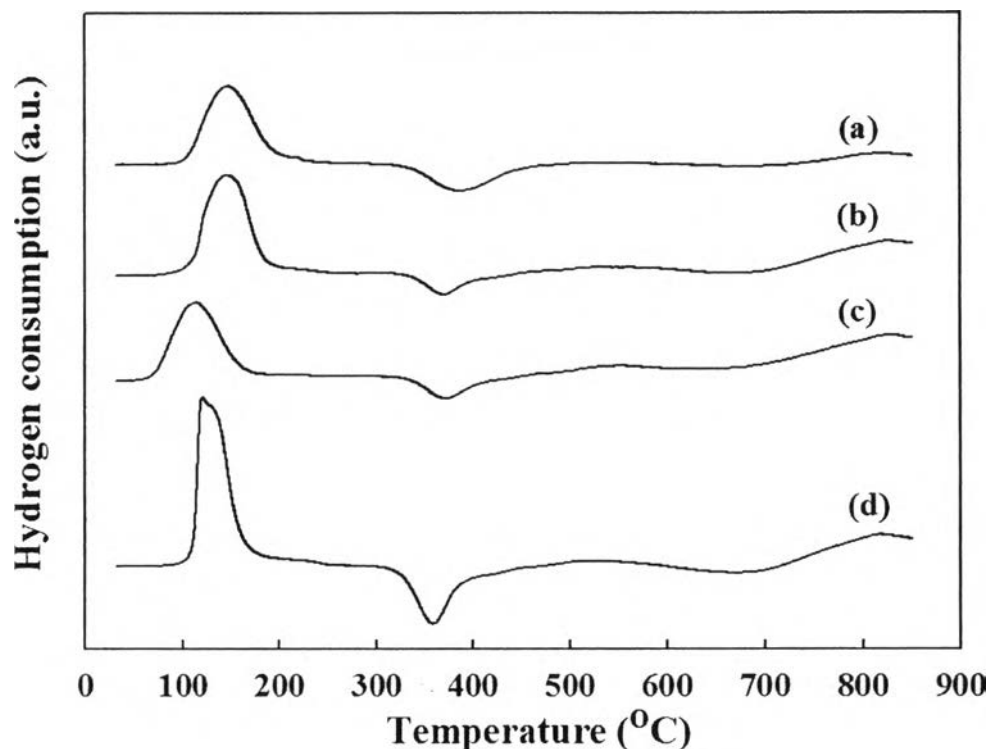
**Figure 4.11** TPR curves for Au/La-CeO<sub>x</sub> catalysts, using different drying methods: (a) Freeze dried; (b) Oven dried; with 1%wt Au loading, and the support was prepared by NH<sub>4</sub>OH precipitation.

The different TPR curves of freeze dried Au/La-CeO<sub>x</sub> samples with different gold loadings are depicted in Figure 4.12. For the plain support peak, the peaks of mixture of ceria lanthanum oxide and bulk oxygen are observed at 500–600°C and 800–900°C, respectively. And the shift of low temperature peak is noted when gold is added in to the support. Furthermore, in the profiles of gold loaded catalysts, the low temperature peak is happened to be broader when the content of gold is higher. This could be explained by that the particle size of gold is becoming bigger with the increase of gold content.



**Figure 4.12** TPR curves of Au/La-CeO<sub>x</sub> catalysts, with different gold loadings: (a) 5%wt Au/La-CeO<sub>x</sub> catalysts; (b) 3%wt Au/La-CeO<sub>x</sub> catalysts; (c) 1%wt Au/La-CeO<sub>x</sub> catalysts; (d) Pure La-CeO<sub>x</sub> support; using freeze dry technique, and the support was prepared by NH<sub>4</sub>OH precipitation.

Figure 4.13 contrasted the calcination temperature of the 1%wt Au/La-CeO<sub>x</sub> freeze dried samples. It can be observed that the TPR peak of uncalcined catalyst is the narrowest, indicating that uncalcined catalyst has the smallest Au particles. Whereas, the TPR peak of the catalyst calcined at 500°C is wide in size, indicating the presence bigger Au particles.



**Figure 4.13** TPR curves for 1%wt Au/La-CeO<sub>x</sub> with different calcination temperatures: (a) Calcined at 500°C; (b) Calcined at 400°C; (c) Calcined at 300°C; (d) Uncalcined; using freeze drying and the support was prepared by NH<sub>4</sub>OH precipitation technique.

#### 4.1.4 BET Surface Area Measurement

Table 4.1 summarized the BET surface area characterisation results of the Au/La-CeO<sub>x</sub> catalysts obtained physical adsorption of N<sub>2</sub> at -196°C. The BET surface area of 1%wt Au/LaCeO<sub>x</sub>, in which the supports were prepared by urea-gelation precipitation, step-precipitation, and NH<sub>4</sub>OH precipitation are 17.82, 26.37, and 38.15m<sup>2</sup>/g, respectively. The findings are in agreement with the activity of the catalysts. The 1%wt Au/La-CeO<sub>x</sub> (NH<sub>4</sub>OH precipitation) confirms the higher CO conversion than the 1%wt Au/La-CeO<sub>x</sub> (step precipitation and urea-gelation precipitation). However, this result disagrees with the results from other literature. Li

*et al.* (2000) found out that urea-gelation precipitation method provide ceria-based samples a higher surface area than conventional co-precipitation method.

Whereas, for freeze dried and oven dried Au/La-CeO<sub>x</sub> catalysts, there is no much difference in the surface area.

**Table 4.1** Surface area of Au/La-CeO<sub>x</sub> catalysts

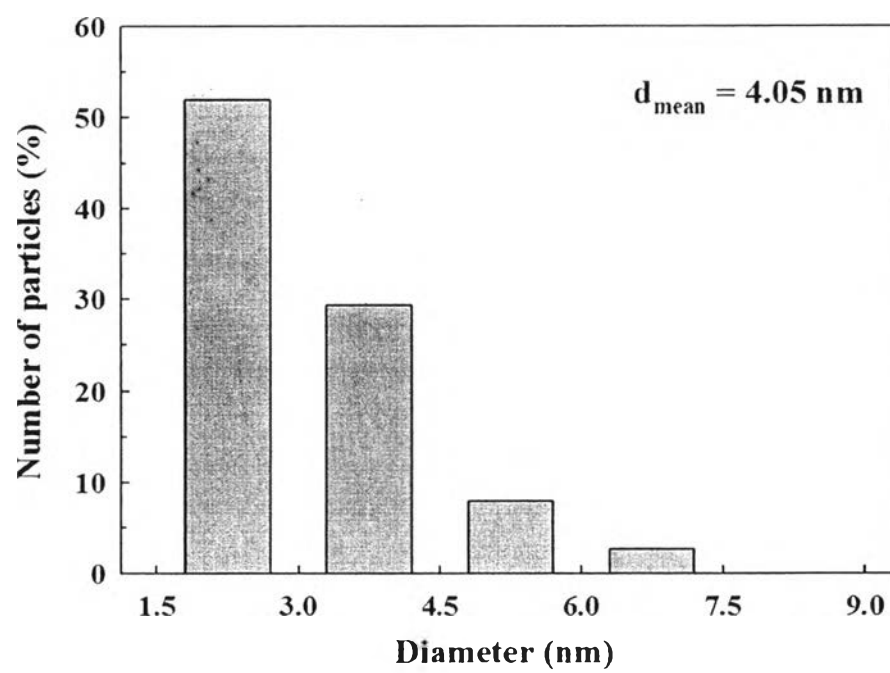
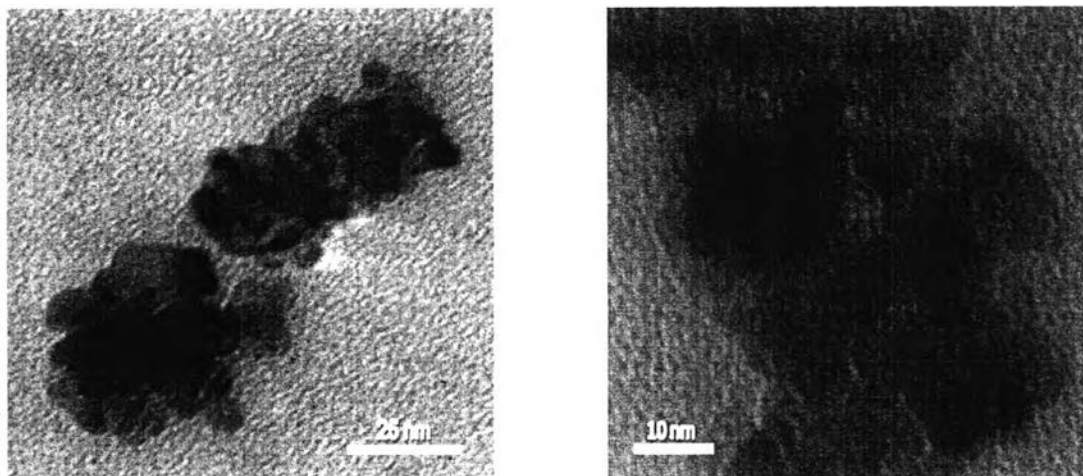
<b>Support Preparation Technique</b>	<b>Drying Method</b>	<b>Gold Loading (%)</b>	<b>Calcination temperature (°C)</b>	<b>BET surface area (m<sup>2</sup>/g)</b>
Urea-gelation precipitation	Oven	1	400	17.82
Step precipitation	Oven	1	400	26.37
NH <sub>4</sub> OH precipitation	Oven	1	400	38.07
NH <sub>4</sub> OH precipitation	Freeze	1	400	42.12

#### 4.1.5 TEM Result

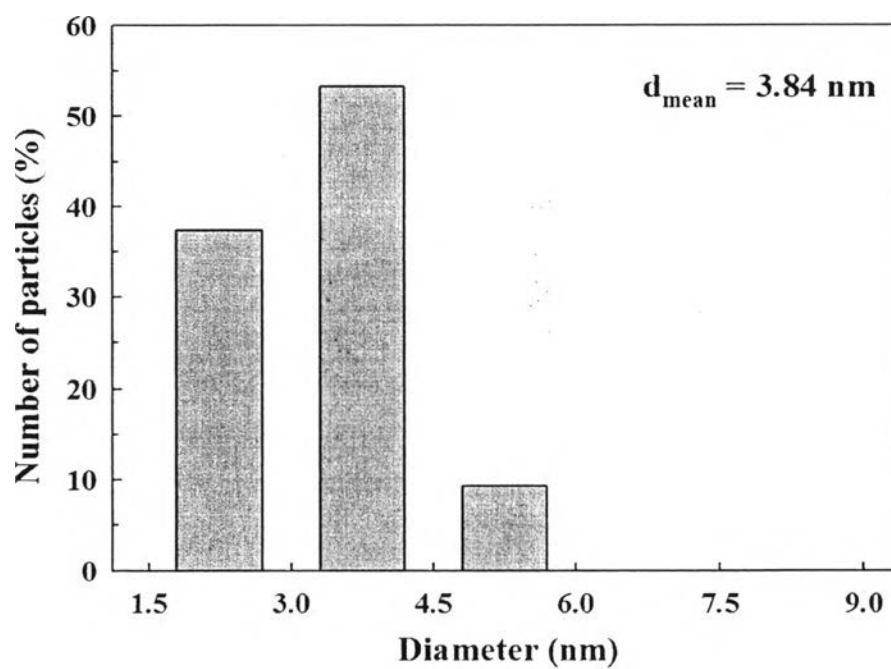
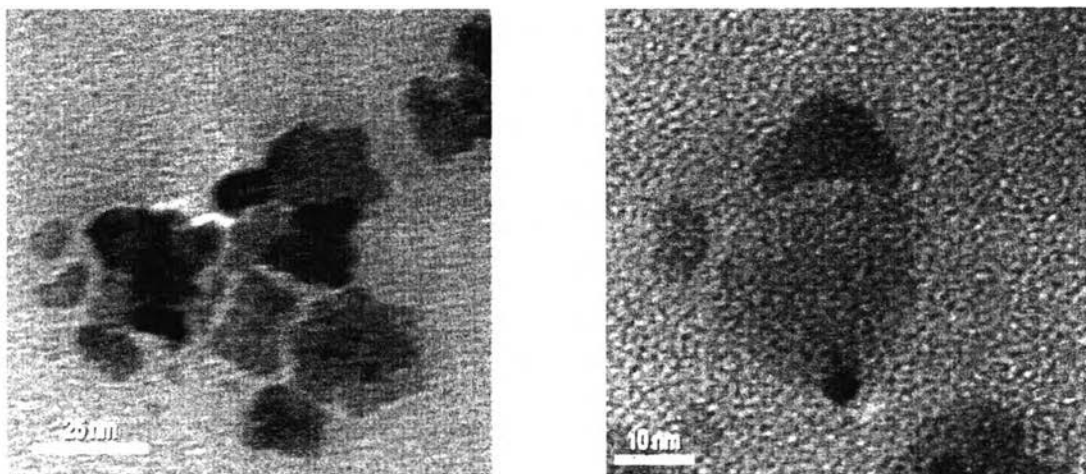
Representative Transmission Electron Microscope (TEM) images and the particle size distribution bar graphs of the supported gold catalysts, with different drying methods, are shown in Figure 4.14. The dark spots signify the Au particles on the supports. The mean particle size of Au of freeze dried and oven dried catalysts were 3.84 and 4.05 nm, respectively

The difference in the dispersion of gold between freeze dried and oven dried samples can be clearly seen from the distribution bar graph. This result agrees with the TPR result showing that the freeze dried sample demonstrates a better gold dispersion when compare to that oven dried sample. Additionally, the trends of gold dispersion were consistent with the TPR result.





a) Oven dried Au/La-CeO<sub>x</sub>

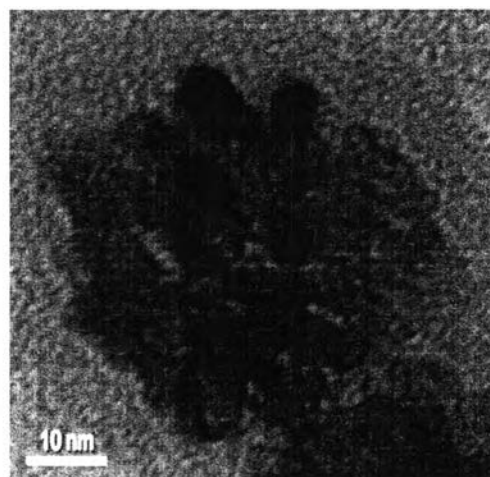
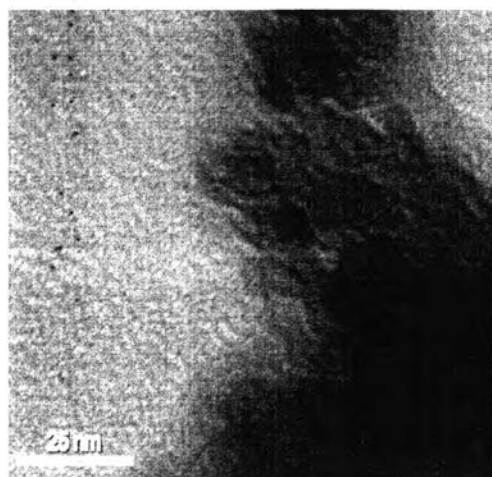


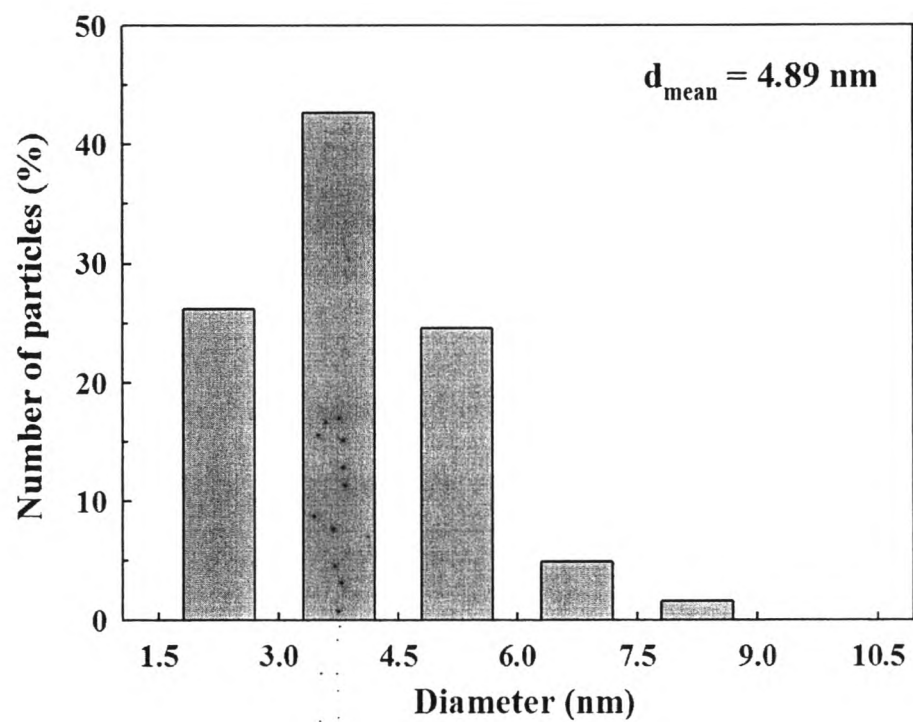
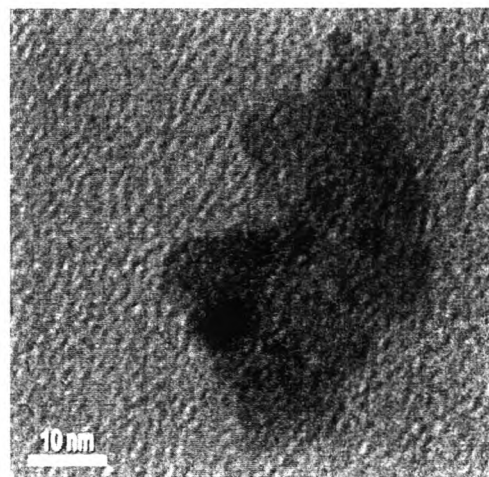
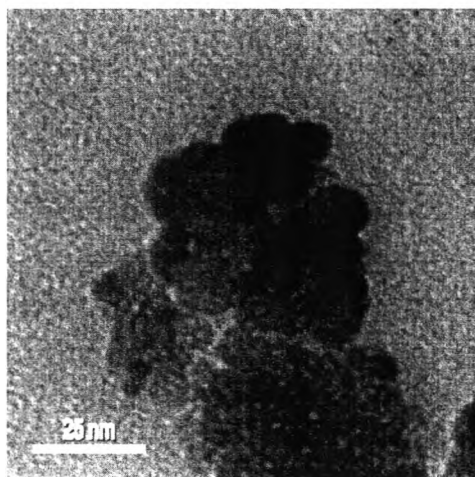
b) Freeze dried Au/La-CeO<sub>x</sub>

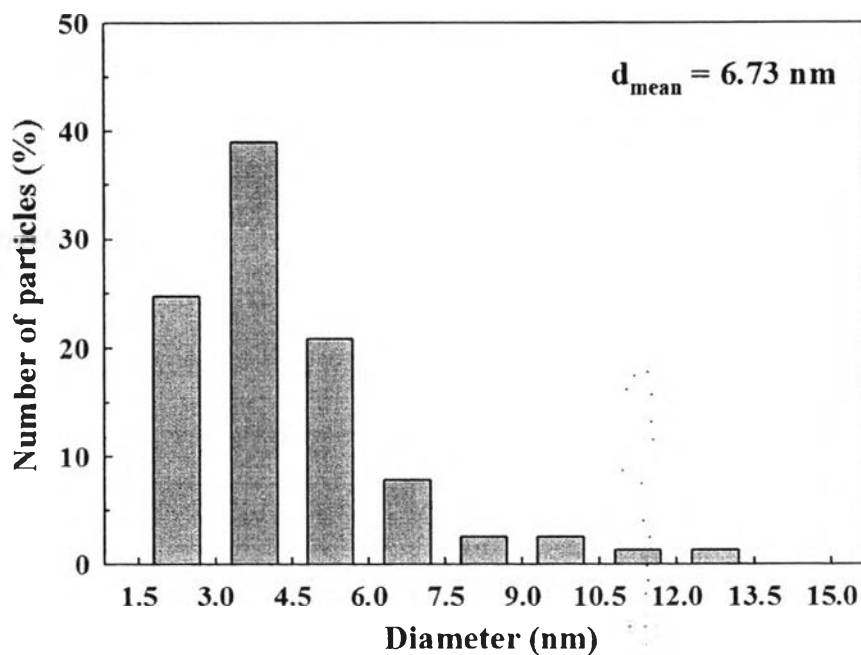
**Figure 4.14** TEM images and the particle size distribution bar graph of freeze dried and oven dried 1%wt Au/La-CeO<sub>x</sub> catalysts; calcined at 400°C and the support is prepared by NH<sub>4</sub>OH precipitation technique.

Figure 4.15 illustrates the TEM microphotographs and the particle size distribution bar graph of the freeze dried Au/La-CeO<sub>x</sub>, with gold loading of 3%wt and 5%wt. The mean Au particle of 3%wt and 5%wt Au/La-CeO<sub>x</sub> were 4.89 and 6.73 nm, respectively.

By comparing Figure 4.15 both (a) and (b) with Figure 4.14 (b), it is clearly seen that the mean Au particle sizes increases when percentage of gold loading increases. The 1%wt Au/La-CeO<sub>x</sub> has the smallest Au particle sizes of 3.69 nm, while the 5%wt Au/La-CeO<sub>x</sub> has the largest Au particle sizes. Moreover, these findings were in agreement with the previous characterization results (XRD and TPR).



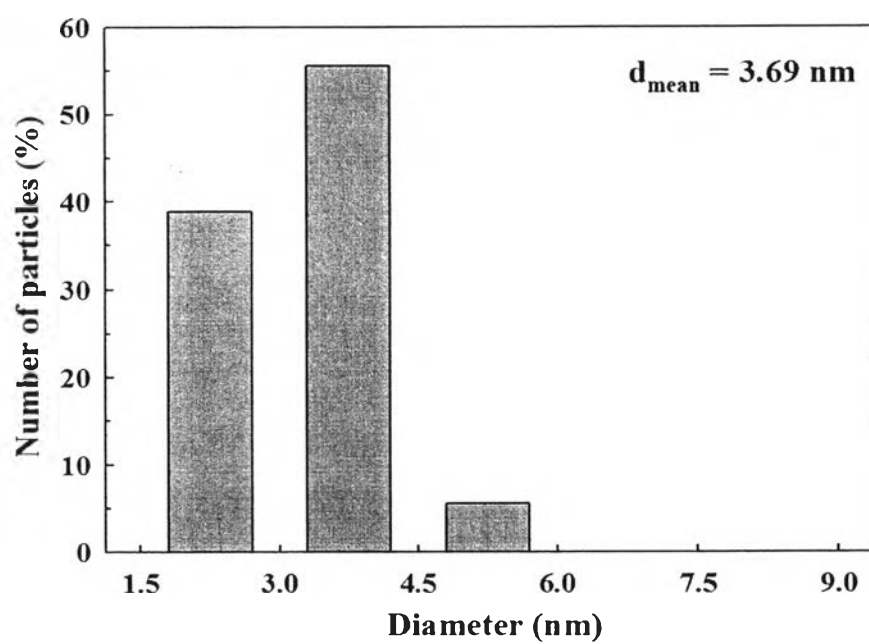
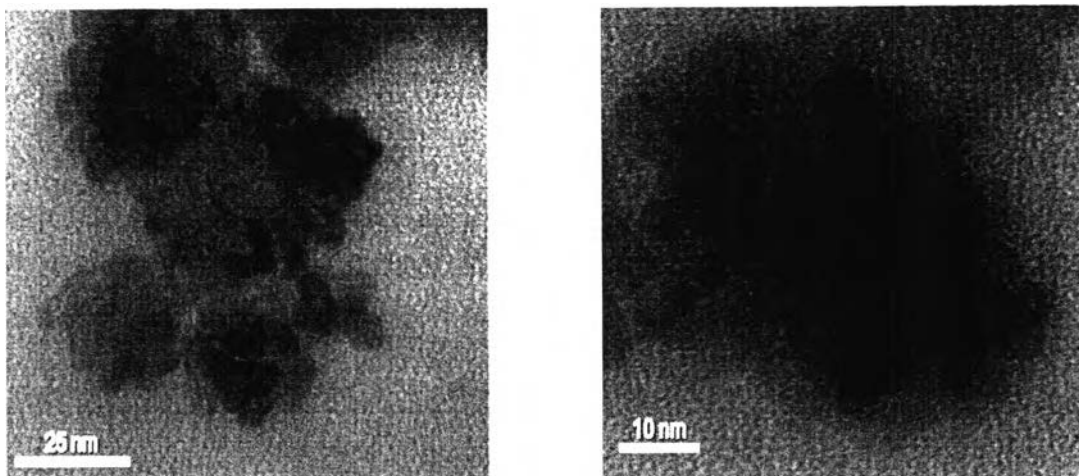
a) 3%wt Au/La-CeO<sub>x</sub>



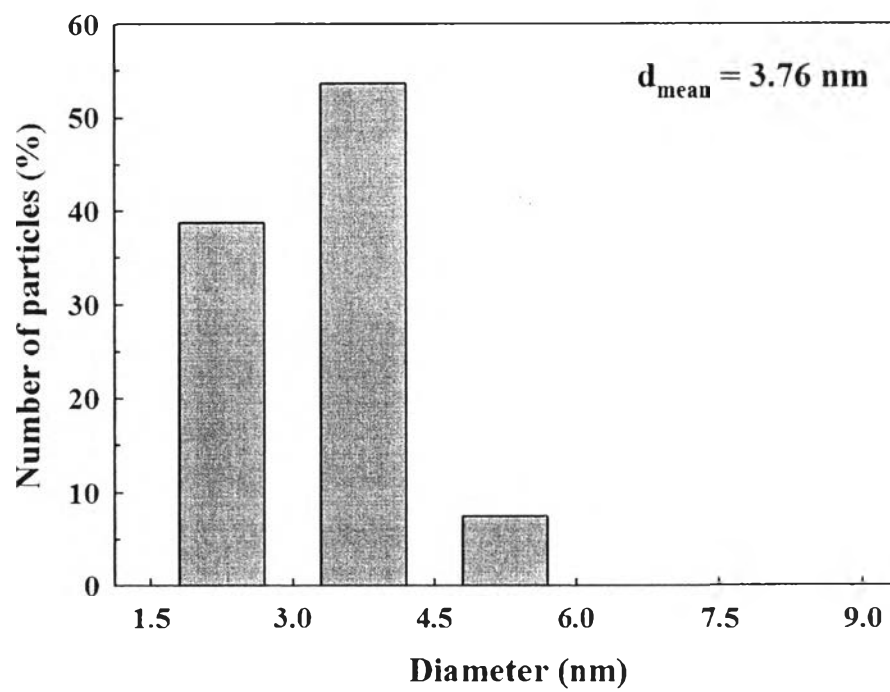
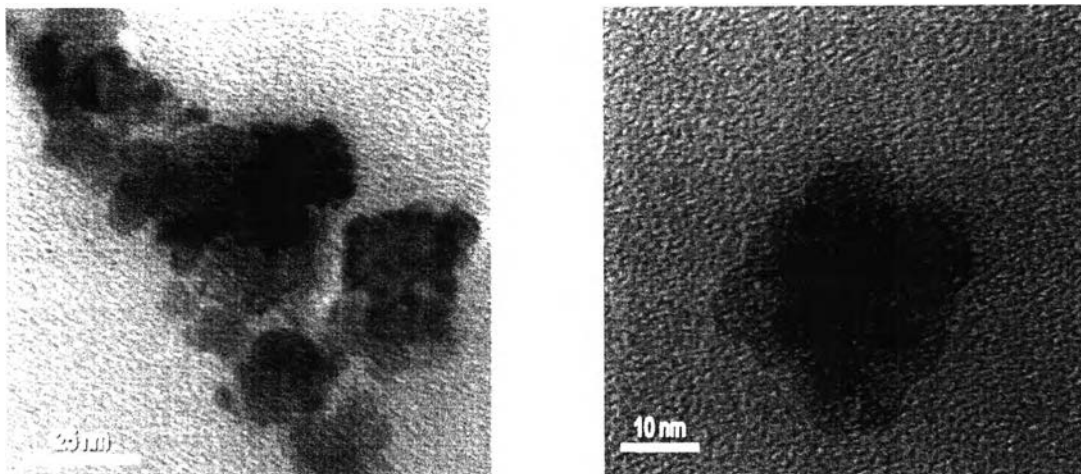
b) 5%wt Au/La-CeO<sub>x</sub>

**Figure 4.15** TEM images of freeze dried Au/La-CeO<sub>x</sub> catalysts with different Au loadings; calcined at 400°C and the support is prepared by NH<sub>4</sub>OH precipitation technique.

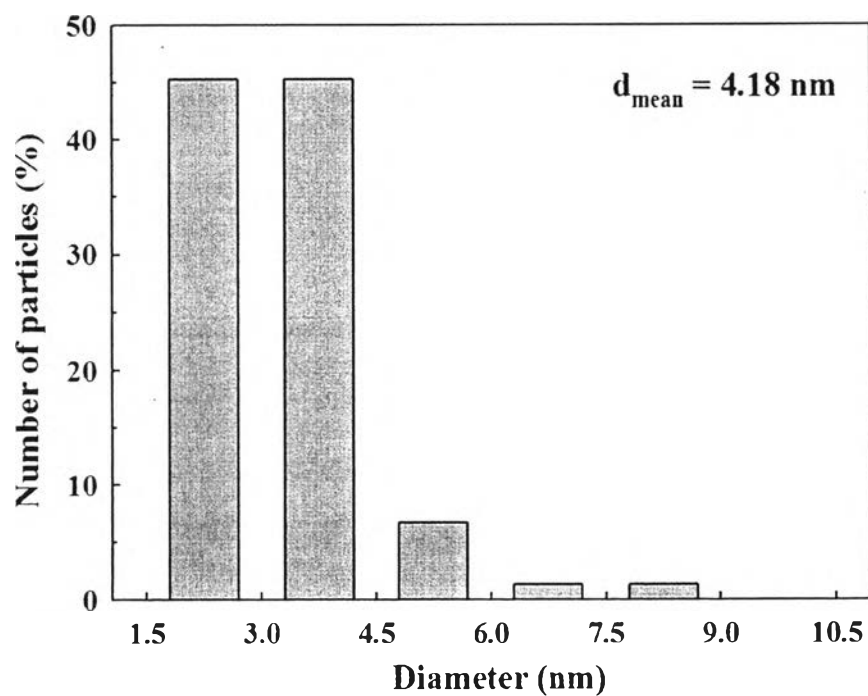
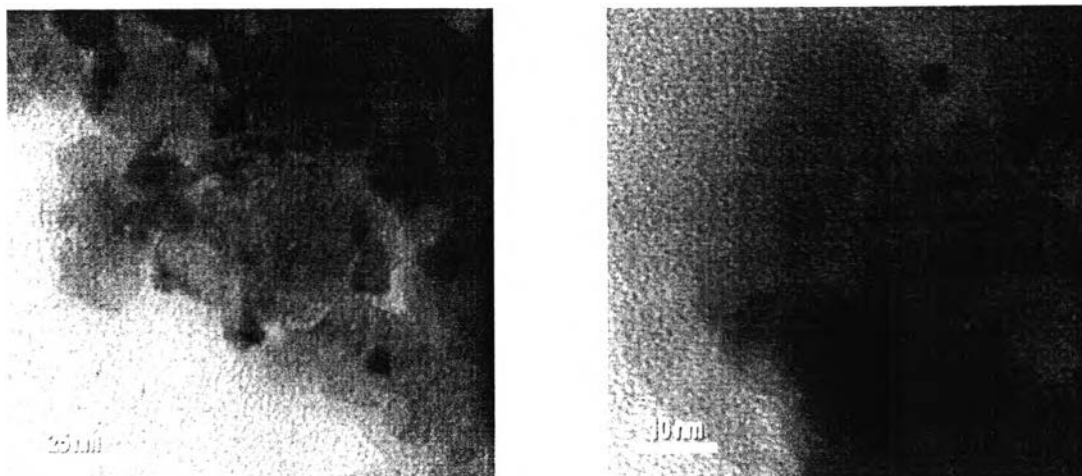
Figure 4.16 shows the TEM images of freeze dried 1%wt Au/La-CeO<sub>x</sub> with different calcination temperatures: uncalcined, 300°C, and 500°C. The mean Au particle sizes of uncalcined, 3%, and 5%wt Au/La-CeO<sub>x</sub> were 3.69, 3.76, and 4.18 nm, respectively. From Figure 4.16 and Figure 4.14 (b), it can be noticed that the size of the Au particles increased with the increase in calcinations temperature.



a) Uncalcined Au/La-CeO<sub>x</sub>



b) Au/La-CeO<sub>x</sub> calcined at 300°C



c) Au/La-CeO<sub>x</sub> calcined at 300°C

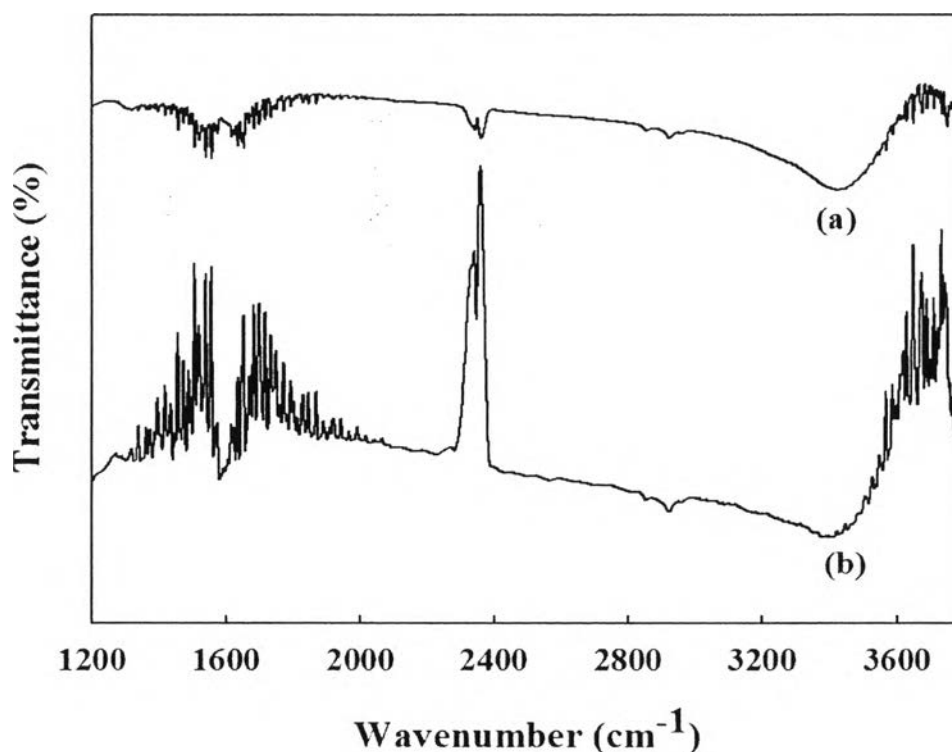
**Figure 4.16** TEM images of 1%wt Au/La-CeO<sub>x</sub> with different calcination temperatures; freeze dried and the support is prepared by NH<sub>4</sub>OH precipitation technique.



#### 4.1.5 FT-IR Measurement

Fourier transform infrared spectroscopy (FT-IR) was utilized to examine the surface of the catalyst before and after the on-line deactivation test for 28 hours. The results from the FT-IR spectroscopy are shown in Figure 4.17.

From the Figure, in OH region, a broad transmission negative band was observed in the range of 3200–3600  $\text{cm}^{-1}$  for both fresh and spent catalysts, owing to the OH stretching mode of  $\text{H}_2\text{O}$  molecules (El-Moemen *et al.*, 2009). There were also the appearance of two strong bands at 2343 and 2362  $\text{cm}^{-1}$ , which represent the molecular adsorbed  $\text{CO}_2$  interacting with surface cations or the support. Moreover, for the spent catalyst, the bands of formate species on  $\text{Ce}^{3+}$  (1585 and 2853  $\text{cm}^{-1}$ ) and the bands of formate species on  $\text{Ce}^{4+}$  (2924 and 2955  $\text{cm}^{-1}$ ) were more pronounced when compared to the fresh catalyst (Tabakova *et al.*, 2003).



**Figure 4.17** FTIR spectra of 1%wt Au/La-CeO<sub>x</sub> catalysts: (a) Fresh catalyst; (b) After stability test; using freeze drying, calcined at 400°C and the support is prepared by  $\text{NH}_4\text{OH}$  precipitation technique.

## 4.2 Activity Measurement

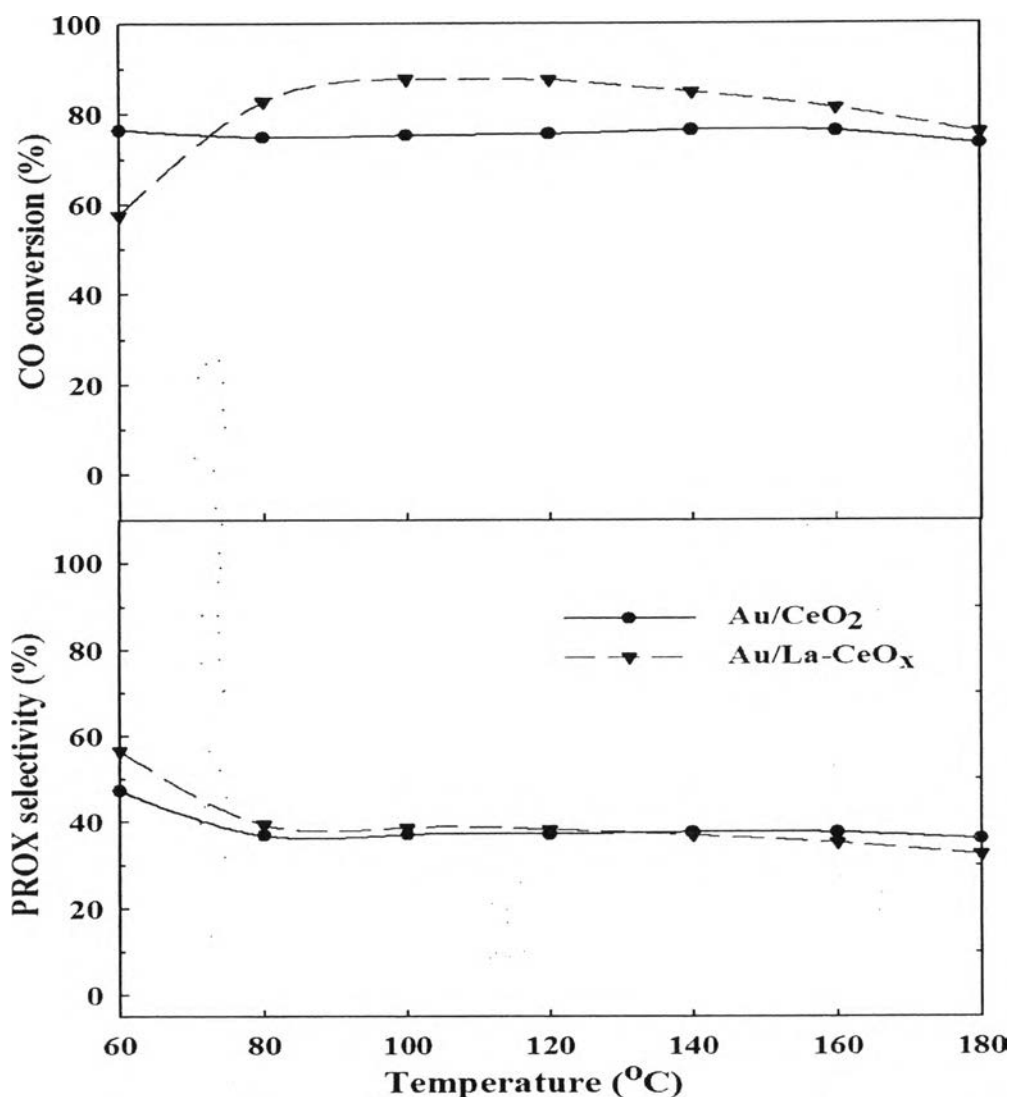
This section shows the catalytic activity results of the prepared catalysts. The catalytic activity measurement was performed in a fixed-bed catalytic micro-reactor under atmospheric pressure, with 80–120 mesh in size of 100 mg catalyst. The activity was observed at various temperatures over the range of 60–180°C under gas mixture conditions of 1% CO, 1% O<sub>2</sub>, and 40% H<sub>2</sub> balanced in He at the total flow rate of 50 ml min<sup>-1</sup>.

### 4.2.1 Effect of Adding La to the CeO<sub>2</sub> Support

The deposition-precipitation technique was used to load gold on both the CeO<sub>2</sub> support and La-CeO<sub>x</sub> support. Then, the 1%wt Au/CeO<sub>2</sub> and 1%wt Au/La-CeO<sub>x</sub> was dried by oven overnight and calcined at 400°C for 4 hours.

As it has been known that CeO<sub>2</sub> support was an attractive support for noble metal catalysts in various reactions (the water gas shift reaction, the catalytic combustion of VOC, and the low-temperature oxidation of CO), besides it also had been reported that the addition of rare earth metals as a promoter can improve the properties of the catalysts by stabilizing ceria and modifying its morphology (Zhang *et al.*, 2007). Consequently, the effect of the present of rare earth additive, La, in the CeO<sub>2</sub> support was studied, in which the result is shown in Figure 4.18.

From the result, it can be seen that activity of 1%wt Au/La-CeO<sub>x</sub> was visibly higher than the activity of 1%wt Au/CeO<sub>2</sub>. The CO conversion of 1%wt Au/La-CeO<sub>x</sub> almost reached 90%, while the CO conversion of 1%wt Au/CeO<sub>2</sub> was highest at 75.5%. Hence, it can be concluded that the doping of La improves the activity of Au-ceria catalyst, which is also in agreement with the result of Zhang *et al.* (2007).

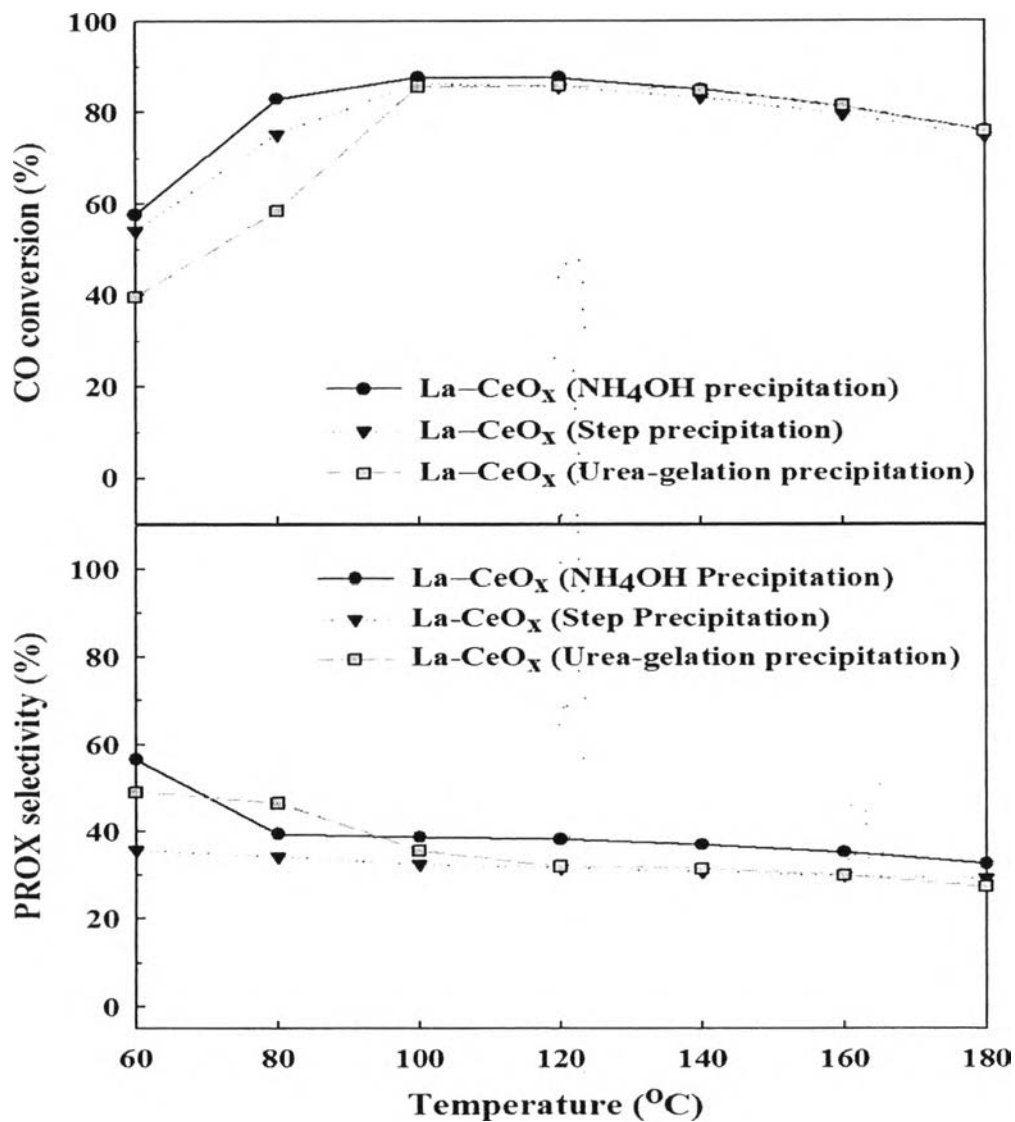


**Figure 4.18** CO conversion and selectivity as a function of reaction temperature for PROX reaction over 1%wt Au/CeO<sub>2</sub> and 1%wt Au/La-CeO<sub>x</sub>

#### 4.2.2 Effect of Support Preparation Method on the Catalytic Activity

The La-CeO<sub>x</sub> supports were prepared by three different ways, which were NH<sub>4</sub>OH precipitation, step precipitation, and urea-gelation precipitation. The prepared supports were then used in preparing catalysts by deposition-precipitation technique, dried by oven overnight and calcined at 400°C for 4 hours. Subsequently, the prepared 1%wt Au/La-CeO<sub>x</sub> catalysts were studied with various operating

temperatures. Figure 4.19 illustrates the catalytic activity in terms of CO conversion and PROX selectivity with different support preparation methods.



**Figure 4.19** CO conversion and selectivity as a function of reaction temperature for PROX reaction over 1%wt Au/La-CeO<sub>x</sub> with different support preparation techniques.

For all catalysts, it was found that the CO conversion increased when the temperature increased from 60°C to 100°C. However, when the temperature reached 100°C, the CO conversion started to be almost steady (at 85–88 %CO conversion) and eventually the CO conversion dropped when the temperature

increased to 160°C. In addition, it can also be seen that the different support preparation methods did not exhibit a significant impact on the CO conversion in the optimum condition for PEMFC application (~100–140°C). Nevertheless, the La-CeO<sub>x</sub> support prepared by NH<sub>4</sub>OH precipitation method showed better selectivity when compared to the other two support preparation methods (step precipitation and urea-gelation precipitation). Consequently, NH<sub>4</sub>OH precipitation method was the technique chosen for preparing catalysts.

Accordingly, the surface area of 1%wt Au/La-CeO<sub>x</sub> (NH<sub>4</sub>OH precipitation) was found to be the highest among the other two catalysts (step precipitation and urea-gelation precipitation). Therefore, in this work, the highest activities for 1%wt Au/La-CeO<sub>x</sub> (NH<sub>4</sub>OH precipitation) could be attributed to the highest in surface area (Table 4.1).

#### 4.2.3 Effect of Drying Method on the Catalytic Activity

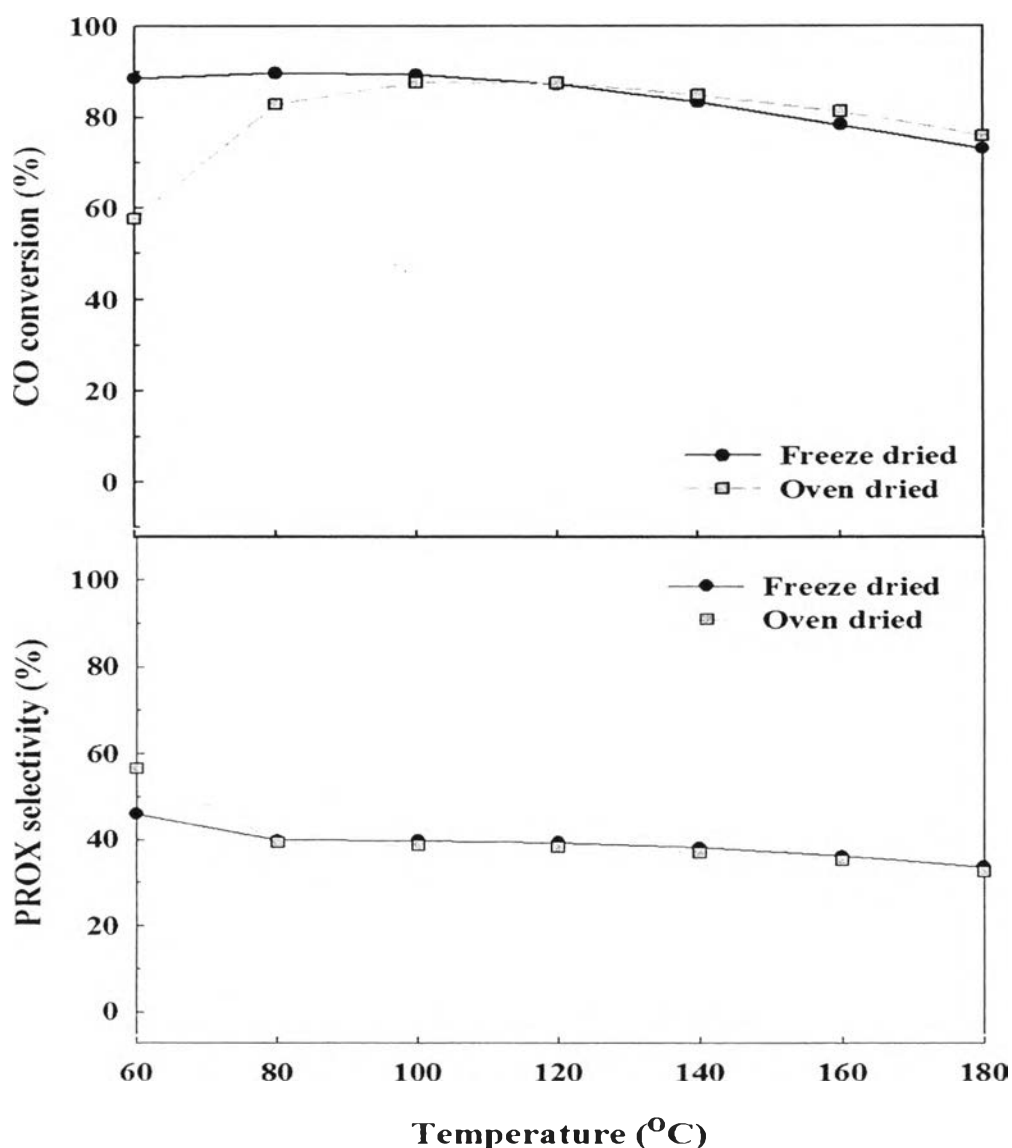
The influences of drying methods of 1%wt Au/La-CeO<sub>x</sub> catalysts on the catalytic performance were investigated. The catalysts were prepared by deposition-precipitation technique, while keeping the finest method, NH<sub>4</sub>OH precipitation, to prepare the La-CeO<sub>x</sub> supports. The prepared catalysts were then dried by oven or by freeze dry, followed by calcination at 400°C for 4 hours.

The catalytic activity in terms of CO conversion and PROX selectivity with two ways of drying methods is shown in Figure 4.20. For this case, it is seen that there was a slight difference in catalytic activity observed in the realistic temperature range (~100–140°C). The freeze dried 1%wt Au/La-CeO<sub>x</sub> catalyst shows a better CO conversion of 90.9% and PROX selectivity of 40.8%, which are higher than that of the oven dried 1%wt Au/La-CeO<sub>x</sub> catalyst.

Goguet *et al.* (2007) proposed that the technique used to remove the water retained on the catalyst after the washing step, has an influence on the catalyst's activity and stability. The rate at which water is eliminated and the gold ensemble mobility determines the metal-support interaction and the final gold dispersion on the support. The removal of water is possible at both low temperature and high temperature. At low temperature, the removal of water is achievable when pressure is reduced. Under reduced pressure, the mobility of gold is also low. This

leads to the better gold dispersion, ensuring the minimal coalescence. In contrast, the water removal can be done under ambient pressure at higher temperature ( $>70$  °C). At higher temperature, the gold hydroxide mobility is increased and, consequently, reduced the gold dispersion which is unfavorable to the catalytic activity.

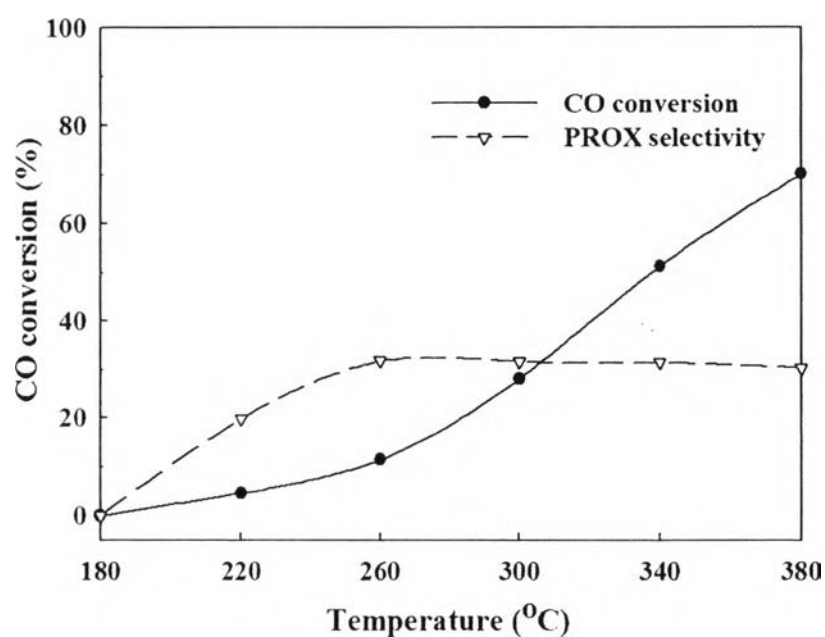
Therefore, we can say that the difference in the activities of both catalysts corresponds to the difference in the gold dispersion on the support. As previously mentioned, the freeze dried 1%wt Au/La-CeO<sub>x</sub> shows a better dispersion than the oven dried 1%wt Au/La-CeO<sub>x</sub>, as confirmed by the TPR characterization.



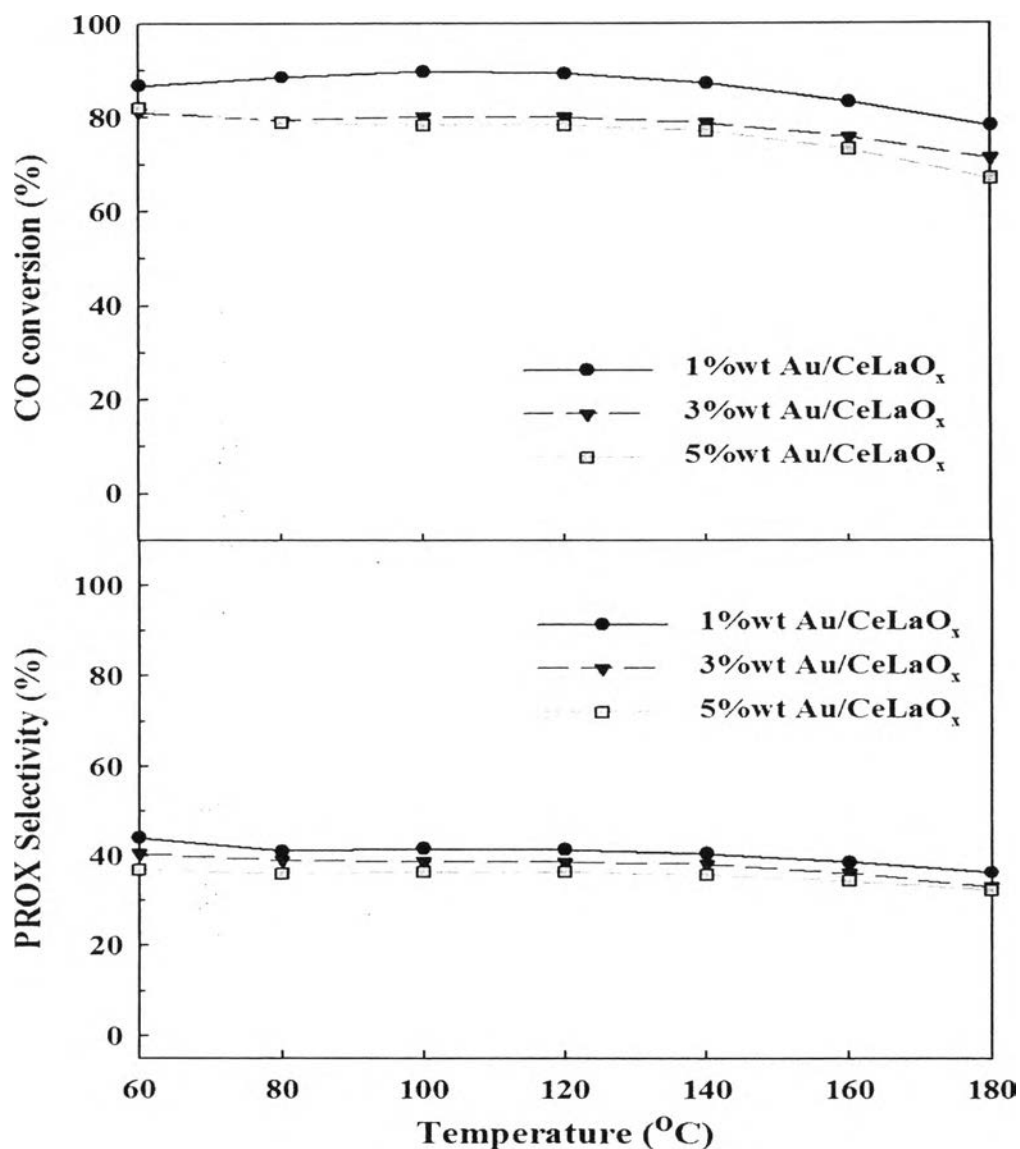
**Figure 4.20** Effect of drying method on CO conversion and PROX selectivity over 1%wt Au/La-CeO<sub>x</sub> catalysts.

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

Figure 4.21 shows the CO conversion and the PROX selectivity of the plain La-CeO<sub>x</sub> support with no Au loading prepared by NH<sub>4</sub>OH precipitation. While the CO conversion and PROX selectivity versus temperature curves obtained over Au/La-CeO<sub>x</sub> catalysts with different gold loadings are shown in Figure 4.22. The amounts of gold loading were varied at 1%wt, 3%wt, and 5%wt. The catalysts were prepared by deposition-precipitation, dried by freeze drying and calcined at 400°C.



**Figure 4.21** Catalytic activity of La-CeO<sub>x</sub> plain support(prepared by NH<sub>4</sub>OH precipitation technique)



**Figure 4.22** Effect of gold loading on CO conversion and PROX selectivity over freeze dried Au/La-CeO<sub>x</sub> catalysts.

It can be seen that when no Au is present, the La-CeO<sub>x</sub> support was inactive until the temperature reached 180°C. Then, the activity of the La-CeO<sub>x</sub> support increased with the increase in temperature. The CO conversion of the La-CeO<sub>x</sub> support reached the maximum at 70.09% (at the temperature of 380°C), and tend to increase further if the temperature go beyond 380°C. While, the PROX selectivity of the La-CeO<sub>x</sub> support seemed to be unwavering at 30–32% (at the temperature of 260–380°C). However, when gold was introduced into the La-CeO<sub>x</sub>



support, the catalyst became active for PROX reaction even the temperature is as low as 60°C. This phenomenon is in agreement with the prediction of the improvement in the reducibility of the surface oxygen on CeO<sub>2</sub> when metallic gold is present, as shown in the TPR characterization result (Figure 4.12).

For Figure 4.22, the CO conversion along with PROX selectivity decreased when the amount of gold loading increased. The catalytic activity of 1%wt Au/La-CeO<sub>x</sub> was the highest, followed with that of the 3%wt Au/La-CeO<sub>x</sub>, and the catalytic activity of 5%wt Au/La-CeO<sub>x</sub> was the least. The explanation could be that at low gold loading, gold nano-particles could be well dispersed and the crystallite size of gold becomes small. This assumption is also supported by the results of XRD, TPR, and TEM characterizations. The XRD peak of Au(111) can only be detected at 38.5°, when gold content is 5%wt. The TPR result proved that the peak becomes broader when more amount of gold is loaded on the support. Plus, TEM showed that the more metal content in the catalysts, the larger the Au particle sizes.

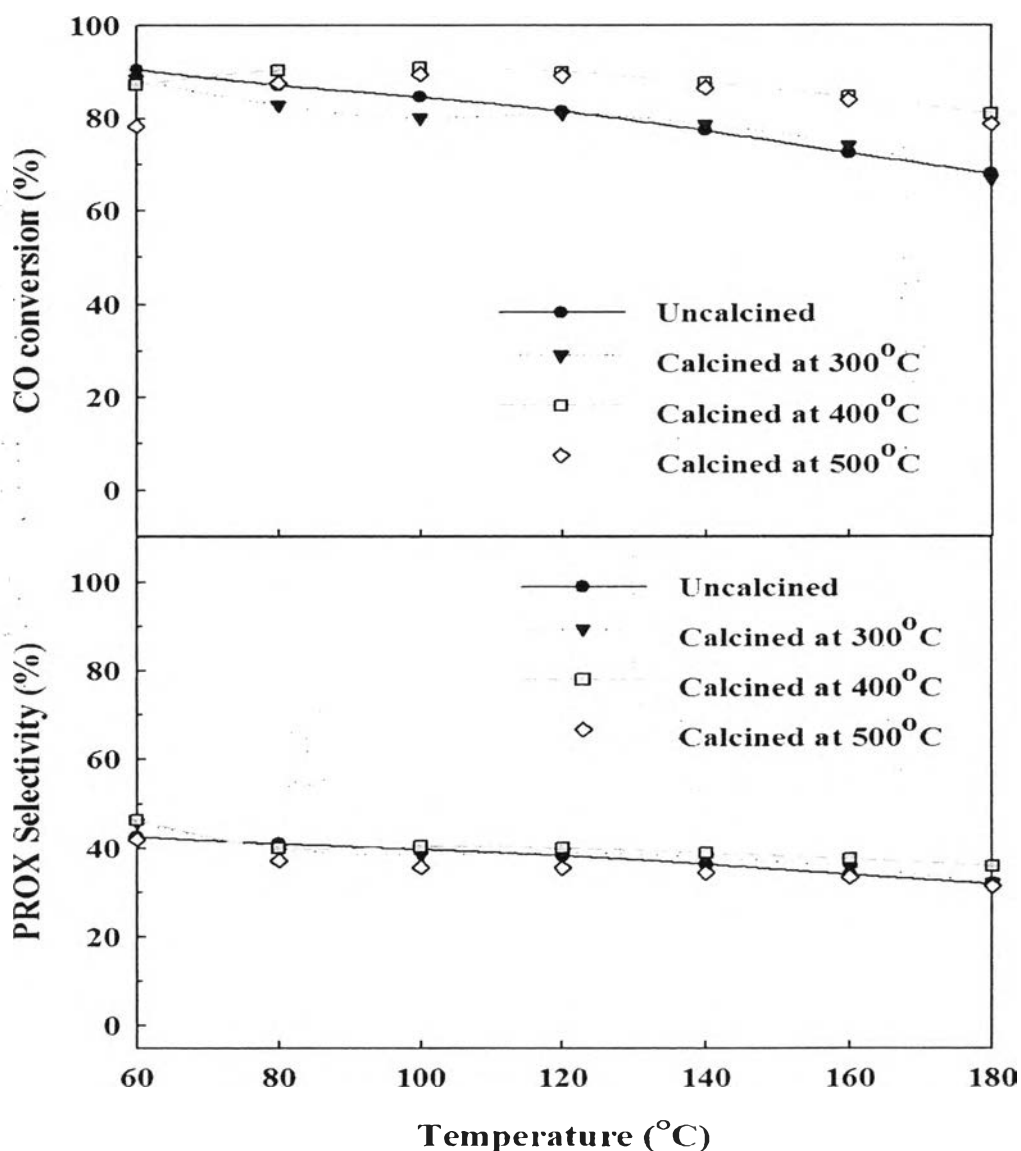
Hence, it can be concluded the small gold particles sizes play a significant role in the PROX reaction. And for that reason, the Au loading of 1%wt was selected as the optimum concentration of gold for Au/La-CeO<sub>x</sub> catalyst.

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

PROX of CO reaction was carried out in the temperature range of 60 to 180°C, over a series of Au/La-CeO<sub>x</sub> catalysts with different calcination temperatures. The La-CeO<sub>x</sub> support was prepared by NH<sub>4</sub>OH precipitation technique and the Au/La-CeO<sub>x</sub> catalysts were prepared by deposition-precipitation technique. The catalysts were freeze dried and the Au content was 1%wt.

Figure 4.23 performs the catalytic behaviors of uncalcined Au/La-CeO<sub>x</sub> catalyst and Au/La-CeO<sub>x</sub> catalysts with different calcination temperatures of 300, 400, and 500°C. Two trends can be observed for in the CO conversion of the catalysts. The uncalcined and the catalyst calcined at 300°C gave the highest CO conversion at 60 °C and CO conversion of the two catalysts decrease with the increase in temperature. Unlike the CO conversion of the catalysts calcined at 400°C and 500°C, which increased when the temperature increased to from 60–100°C. The catalysts calcined at 400°C and 500°C showed the maximum CO conversion of

90.9% and 89.4% (at 100°C), respectively. Yet, the catalytic activity of both the catalysts calcined at 400°C and 500°C started to decrease after the reaction temperature went beyond 100°C, as shown in Figure 4.23.



**Figure 4.23** Effect of calcination temperature on CO conversion and PROX selectivity over freeze dried Au/La-CeO<sub>x</sub> catalysts.

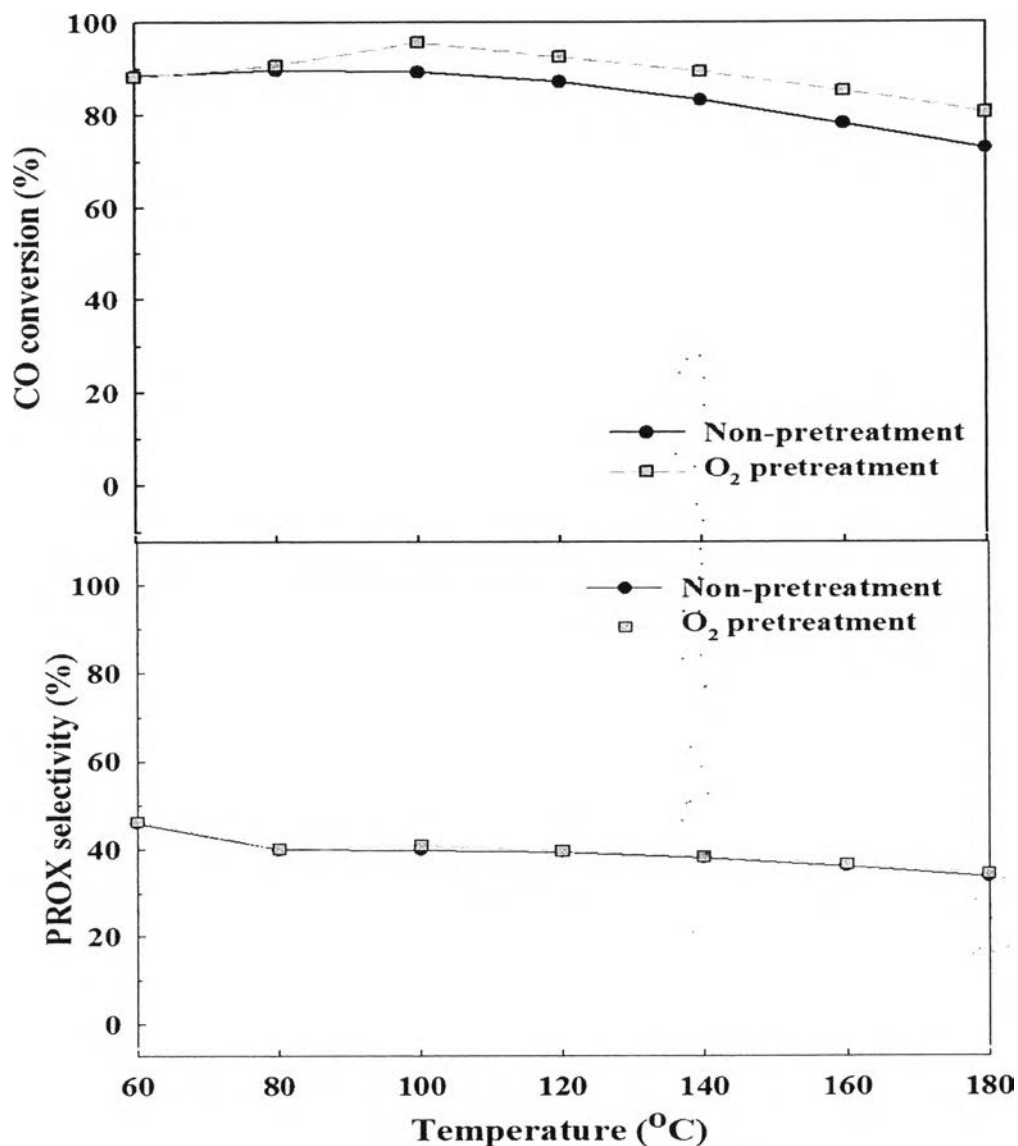
The catalytic performances of uncalcined catalyst and the catalyst calcined at 300°C could be related to the amount of Au<sup>0</sup> specie or Au metallic particle presence in the catalysts. The uncalcined catalyst and the catalyst calcined at 300°C contained lesser amount of Au<sup>0</sup> specie as confirmed in the UV-vis

characterization result (Figure 4.8). Eun *et al.* (1999) suggested that the higher the calcination temperature, the higher amount of metallic Au or Au<sup>0</sup> specie was formed from the reduction of Au<sup>3+</sup> to Au<sup>0</sup>. Bera and Hegde (2002) have also reported that the catalytic activities of Au/CeO<sub>2</sub> catalysts in the CO oxidation decreased with the increasing in the concentration of Au<sup>3+</sup> species.

However, for the catalytic activities of the catalysts calcined at 400°C and 500°C. The proposition of this effect is that the increase in calcination temperature caused the Au particles to increase in their size, or in other words, to undergo a small phenomenon of sintering. This proposition can be confirmed by the TEM result (Figure 4.16).

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

The oxygen pretreatment of the catalyst was marked to be one of the influence parameters on the activity of the catalyst. Therefore, the oxygen pretreatment was carried out on the 1%wt Au/La-CeO<sub>x</sub> catalyst (freeze dried, calcined at 400°C) at the temperature of 120°C for 30 minutes. After that, the catalyst was experienced the activity test (PROX reaction) with 1% CO, 1% O<sub>2</sub>, and 40% H<sub>2</sub> balanced in He at the temperature range of 60–180°C. The catalyst activity, in terms of CO conversion and PROX selectivity, of oxygen pretreated catalyst is shown in Figure 4.24.



**Figure 4.24** CO conversion and PROX selectivity as a function of reaction temperature for PROX reaction over oxygen pretreated 1%wt Au/La-CeO<sub>x</sub> catalyst; using freeze dry technique, calcined at 400°C, and the support was prepared by NH<sub>4</sub>OH precipitation.

The CO conversion and PROX selectivity, after oxygen pretreatment of catalyst, increased to 95.6% and 40.8%, respectively. The reason behind this phenomenon is that the oxygen pretreatment at low temperatures causes surface oxygen species adsorbs on active site's surface (Qua *et al.*, 2005). Consequently, the

oxygen pretreatment was further used for investigating the deactivation test of the prepared catalysts in PROX reaction.

#### 4.2.7 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 stage 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 and O<sub>2</sub> to the active sites (Raphulu, 2004).

Thus, the catalyst deactivation evaluation is vital to enable practical catalyst designs and also, to develop better understanding of the catalyst's activity. In the present work, catalyst deactivation evaluation was taken at a temperature of 100°C in order to study the stability of the prepared catalyst in simulated reformed gas mixtures containing 1% CO, 1% O<sub>2</sub>, and 40% H<sub>2</sub> balanced in He, under atmospheric pressure.

Figure 4.25 shows the stability test of oxygen pretreated 1%wt Au/La-CeO<sub>x</sub> catalyst; using freeze dry technique, calcined at 400°C, and the support was prepared by NH<sub>4</sub>OH precipitation. It is clearly seen that the prepared catalyst presented a fine stable properties and its activity kept constant for 19 hours.

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

It is reported that the addition of water up to 10% in the PROX reaction was found to slightly reduce the catalytic activity, at the reaction temperature of 110°C (Date *et al.*, 2001). 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). But fortunately, 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 4.25.

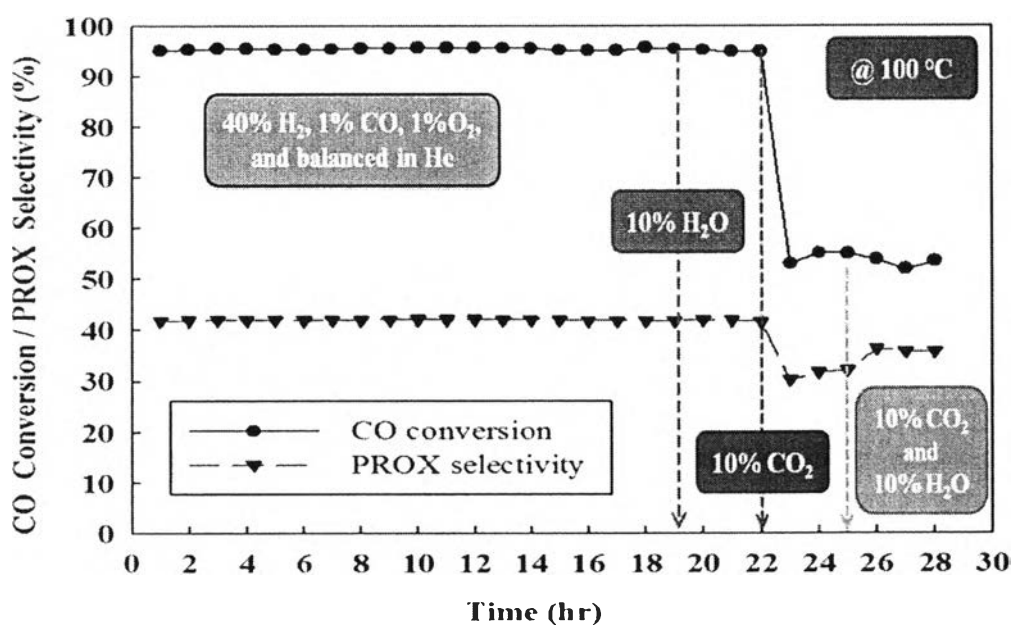
##### 4.2.7.2 *Effect of CO<sub>2</sub> in the Feed Stream*

Figure 4.25 also illustrates the change 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 (Srinivas *et al.*, 1996) and the CO<sub>2</sub> absorption on the catalyst (as confirmed in Figure 4.17) which prevented O<sub>2</sub> adsorption and splitting on support. The CO conversion and PROX selectivity decreased significantly to around 53% and 30% respectively.

#### 4.2.7.3 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, and 40% H<sub>2</sub> 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 Au/La-CeO<sub>x</sub> catalyst is shown in Figure 4.25. From the Figure, the presence of CO<sub>2</sub> and H<sub>2</sub>O in feed stream increased the PROX selectivity, while the CO conversion decreased slightly. The outcome was similar to the result of Schubert *et al.* (2004) 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.



**Figure 4.25** Deactivation test of oxygen pretreated 1%wt Au/La-CeO<sub>x</sub> catalyst; using freeze dry technique, calcined at 400°C, and the support was prepared by NH<sub>4</sub>OH precipitation.