



## CHAPTER IV

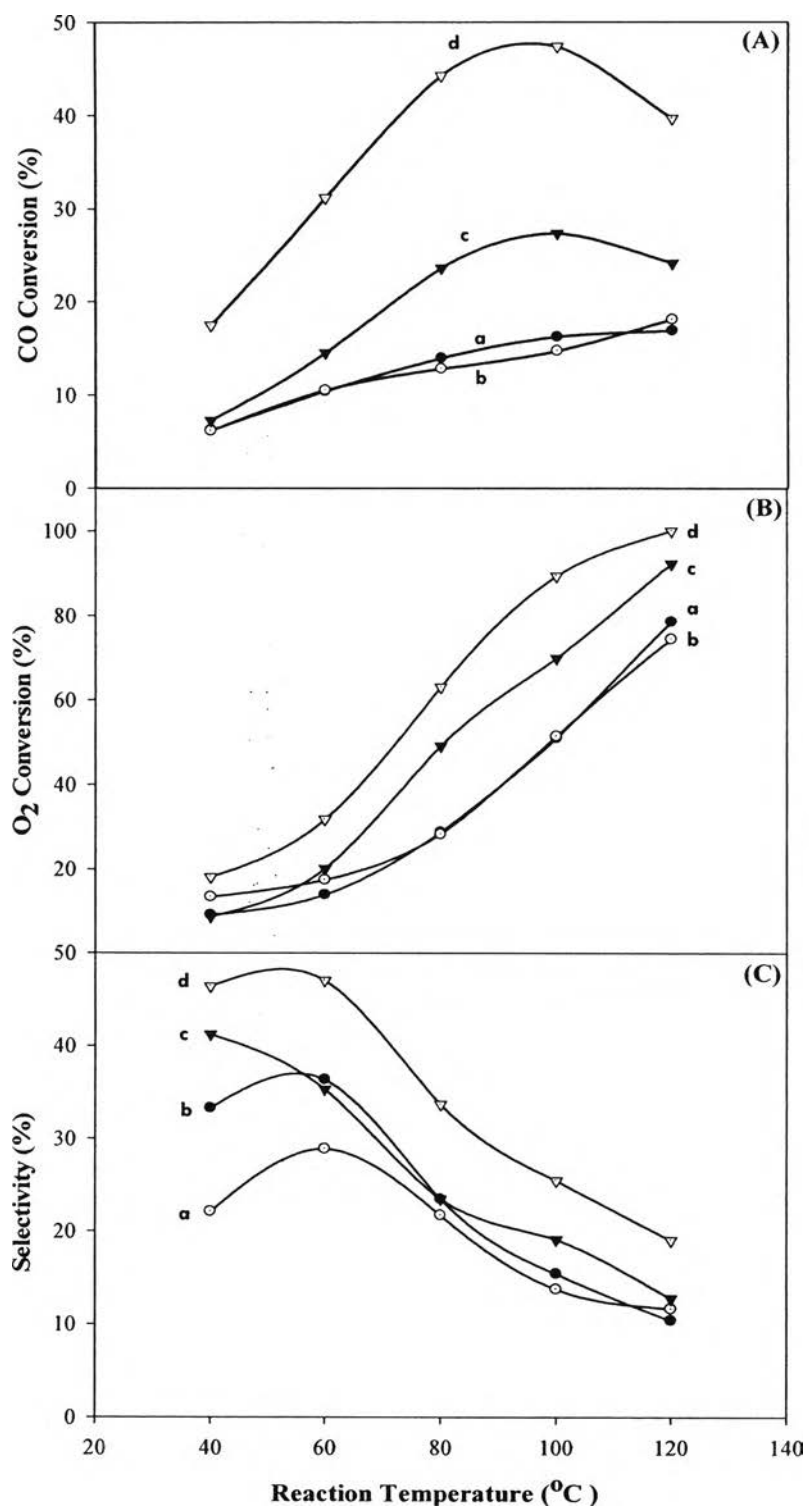
### RESULTS AND DISCUSSION

The prepared Au/ZnO catalysts were denoted in a short name, as shown in appendix A. All series of samples were tested the catalytic activity in terms of CO conversion, O<sub>2</sub> conversion, and CO selectivity in order to study the effects of irradiation time (30, 90, 120, and 240 minutes), concentration of a precipitant agent (0.05 and 0.1 M Na<sub>2</sub>CO<sub>3</sub>), calcination (without calcination and with calcination under air at 300°C for 3 hours), and storage conditions (exposed and unexposed to light for 3 months) on the catalytic performance of Au/ZnO. The catalysts were characterized by several techniques including X-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), UV-vis spectroscopy, nitrogen sorption analysis, and temperature-programmed reduction (TPR) to ascribe the characteristic of the prepared catalysts.

#### 4.1 Influence of Irradiation Time

##### 4.1.1 Measurements of Catalytic Activities for CO Oxidation

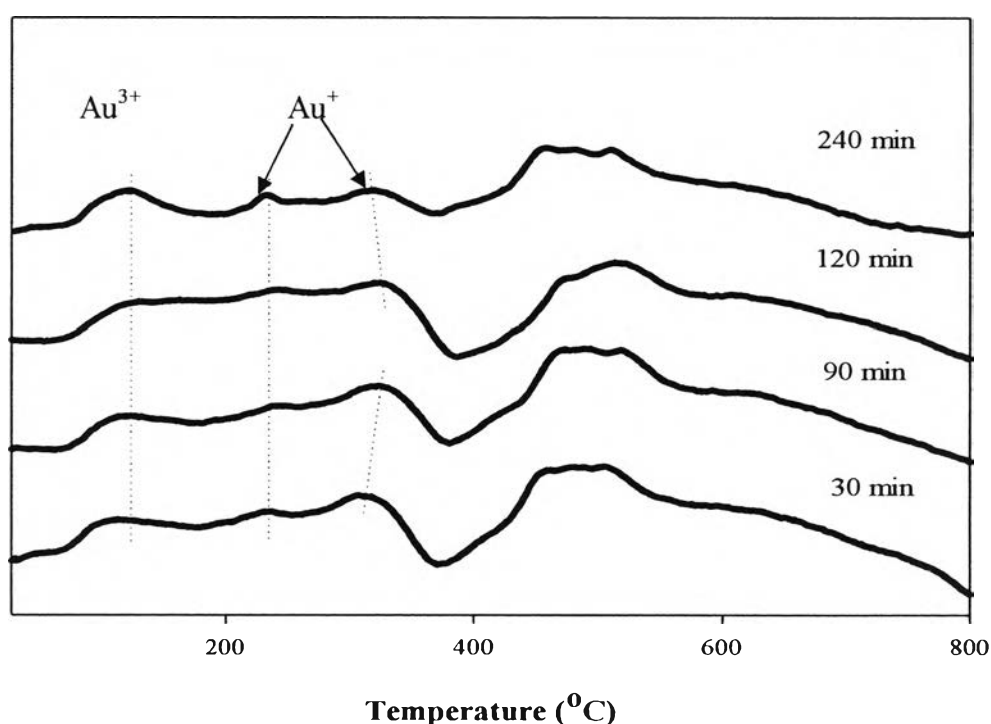
The Au/ZnO catalysts with various irradiation times were monitored the catalytic activity on the PROX. The reactant gases consisted of 1% CO, 1% O<sub>2</sub>, 40% H<sub>2</sub> balanced in He with a total flow rate of 50 ml/min. The activity measurement was preceded at the temperature range of 30 to 120°C. Figure 4.1 shows the CO conversion of the uncalcined Au(0.1)/ZnO(0.1) catalysts with different irradiation times. The CO conversion increased with increasing reaction temperature. It was found that the maximum CO conversions were obtained at ~90°C and subsequently started to decrease with further increasing temperature. The CO conversion results are in accordance with the O<sub>2</sub> conversion and CO selectivity, as shown in Figure 4.1 (B, C). It is clearly seen that the activity of Au/ZnO increased with increasing irradiation times and Au(0.1)/ZnO(0.1)-240 exhibited the highest activity.



**Figure 4.1** Catalytic activity of the Au(0.1)/ZnO(0.1)—(A) CO conversion, (B) O<sub>2</sub> conversion, and (C) CO selectivity— with different irradiation times (a) 30, (b) 90, (c) 120, and (d) 240 min.

#### 4.1.2 Catalyst Characterizations

The reducibility of Au/ZnO irradiated with different period of time. It can be seen that all of samples in this series showed a weak intensity of H<sub>2</sub> consumption. The possible reason is that prepared catalysts with 0.1 M Na<sub>2</sub>CO<sub>3</sub> made residual Cl ions from the gold precursor suppressed the reducibility of Au cations although increased the irradiation time to 240 minutes, in agreement with Oh *et al.* (2002). However, as shown in Figure 4.2, the longest irradiation time of 240 minutes was likely to display the highest reducibility of Au and the reduction peak of Au<sup>3+</sup> at low temperature distinctly separated from other temperature peaks of Au<sup>+</sup>. As a result, the presence of Au cationic form, more importantly Au<sup>3+</sup>, was a significant population, which caused uncalcined Au(0.1)/ZnO(0.1)-240 catalysts showed higher catalytic activities. Moreover, the reduction peak of ZnO of the uncalcined Au(0.1)/ZnO(0.1)-240 shifted to low temperature.



**Figure 4.2** TPR profiles of the uncalcined Au(0.1)/ZnO(0.1) irradiated at different times.

Additionally, diffuse reflectance spectra were recorded by UV-vis spectrophotometer-2550 to determine quantitatively the amount of the transition metal ions and to make an evaluation the simplistic metallic Au particle sizes. In general, UV-vis spectroscopy can be used to investigate the oxidation state of Au, which are Au<sup>3+</sup> species, Au clusters, and Au nanoparticles (plasmon), appearing at around <250 (Park *et al.*, 2006), 280 to 380 (Logunov *et al.*, 1997 and Zenella *et al.*, 2004), and 480 to 600 nm (Shen *et al.*, 2007), respectively. However, the absorption band at 200 to 350 nm can be assigned to ZnO; therefore, assigning Au species on Au/ZnO catalysts using UV-vis spectroscopy is not straightforward.

Figure B1 in appendix B demonstrates that uncalcined Au(0.1)/ZnO(0.1) catalysts with different irradiation times (30, 90, 120, and 240 minutes) insignificantly exhibited different intensity of the strong plasmon band related to the reducibility results. A strong plasmon resonance band around 480–600 nm (Shen *et al.*, 2007) of all samples is clearly seen and it referred to the amount of metallic Au and Au particle sizes, as mentioned by Logunov *et al.* (1997). However, it was reported that diffuse reflectance spectra of UV-vis were not accomplished with particle size less than 1.9 nm, which are in accordance with our UV-vis results. From UV-vis data, it can be suggested that the uncalcined Au(0.1)/ZnO(0.1) samples have the particle size of Au larger than 1.9 nm.

For the actual Au loading (0.56% atom) result has a proclivity to be frivolously different, as presented in Table B1 (appendix B). All in all, it is feasible to deem that the ample of Au loading over ZnO was not complied with increasing irradiation time, which is contrast to Chang *et al.* (2008) work. Whereas, it was reported by Comotti *et al.* (2006) that the deposition time is clearly not dependent on the point of zero charge (p.z.c) of ZnO support. Accordingly, from the AAS results of the catalysts with different irradiation time, which can be referred to the deposition time, relate to Comotti *et al.* (2006) report .

#### **4.2 Influence of Precipitating Agent Concentration**

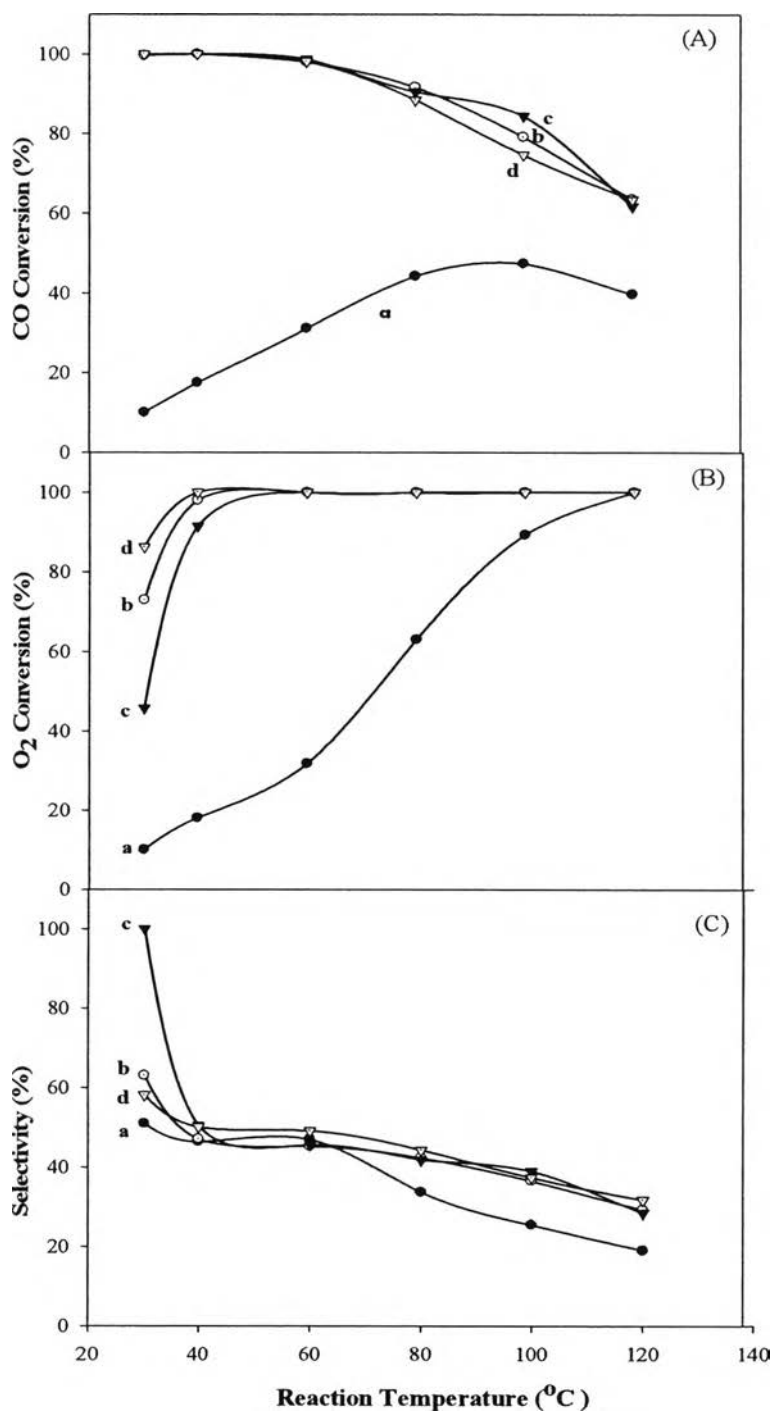
It has been reported that the size distribution of metal particles is influenced by the concentration of precursor, pH value, and irradiation time. In this work, it is

likely that the  $\text{Na}_2\text{CO}_3$  concentration has an influence on both support morphology and Au particles. A series of catalysts in this study was prepared by using 0.05 and 0.1 M  $\text{Na}_2\text{CO}_3$  as a precipitant agent. The pH of suspension was adjusted until reached 8, and the irradiation time were fixed at 240 minutes.

#### 4.2.1 Measurements of Catalytic Activities for CO Oxidation

The CO conversion,  $\text{O}_2$  conversion, and CO selectivity of the catalysts are presented in Figure 4.3. From Figure 4.3 (A), when high concentration of 0.1 M  $\text{Na}_2\text{CO}_3$  was used in both support preparation and Au loading procedure, it gave the lowest catalytic activity. On the other hand, when low concentration of 0.05 M  $\text{Na}_2\text{CO}_3$  was used in the catalyst preparation, high CO conversion was obtained even though 0.1 M  $\text{Na}_2\text{CO}_3$  was used in one of these two steps.

Figure 4.3 (B) depicts the  $\text{O}_2$  consumption of the Au/ZnO catalysts, at low temperature the uncalcined Au(0.05)/ZnO(0.1)-240, uncalcined Au(0.1)/ZnO(0.05)-240, and uncalcined Au(0.05)/ZnO(0.05)-240 showed different  $\text{O}_2$  conversions, although their CO conversions are almost the same value at low temperature. As Daté and Haruta (2001) reported that water adsorbed on the catalyst influences the activity and they suggested that water-derived species on the catalyst surface are involved in the reaction mechanism. Moreover, Neri *et al.* (2004) have studied the influence of water on CO response and their results are consistence with the indication that CO oxidation may proceed through two reaction pathways: (i) reaction of the adsorbed CO on the noble metal with adsorbed oxygen; (ii) reaction of adsorbed CO with the neighboring hydroxyl groups on the oxide support by a likeformate or carboxylate intermediate. The results here may involve with the presence of reactive hydroxyl groups and hence at low temperature adsorbed water promotes CO oxidation and further increasing reaction temperature CO oxidation will act as the first pathway. And due to the  $\text{O}_2$  consumption of CO and  $\text{H}_2$  at high reaction temperature, the uncalcined Au(0.05)/ZnO(0.1)-240, uncalcined Au(0.1)/ZnO(0.05)-240, and uncalcined Au(0.05)/ZnO(0.05)-240 show a hundred-percent  $\text{O}_2$  conversion. Similarly,  $\text{O}_2$  is consumed rapidly by the uncalcined Au(0.1)/ZnO(0.1)-240 catalyst because of the  $\text{H}_2$  oxidation occurrence with increasing of reaction temperature.



**Figure 4.3** Catalytic activity of the (a) uncalcined Au(0.1)/ZnO(0.1)-240, (b) uncalcined Au(0.1)/ZnO(0.05)-240, (c) uncalcined Au(0.05)/ZnO(0.05)-240, and (d) uncalcined Au(0.05)/ZnO(0.1)-240—(A) CO conversion, (B) O<sub>2</sub> conversion, and (C) CO selectivity.

#### 4.2.2 Catalyst Characterizations

Support preparation and Au loading procedure with different precipitant concentrations were totally different in many aspects: specific surface areas, Au particle sizes, Au size distributions, and reducibility.

One obvious difference is specific surface areas (Table C1 in appendix C), the specific surface areas of bare ZnO, prepared with different precipitant concentrations (0.05 and 0.1 M Na<sub>2</sub>CO<sub>3</sub>) showed different specific surface areas. Likewise, when Au was deposited on ZnO by using different precipitant concentrations (0.05 and 0.1 M Na<sub>2</sub>CO<sub>3</sub>) cause the BET surface area of the prepared catalysts to vary between 39.19–64.21 m<sup>2</sup>/g and determine the extent of morphology of the catalyst. Using 0.1 M Na<sub>2</sub>CO<sub>3</sub> in both of two preparation steps (uncalcined Au(0.1)/ZnO(0.1)-240) is the cause of pressingly low specific surface areas as low as 39.19 m<sup>2</sup>/g. Dissimilar to the uncalcined Au(0.1)/ZnO(0.1)-240, the uncalcined Au(0.05)/ZnO(0.1)-240 (53.82 m<sup>2</sup>/g) showed higher specific surface areas as well as the uncalcined Au(0.05)/ZnO(0.05)-240 (64.21 m<sup>2</sup>/g) and uncalcined Au(0.1)/ZnO(0.05)-240 (54.74 m<sup>2</sup>/g) as a consequence of low precipitant concentration of 0.05 M Na<sub>2</sub>CO<sub>3</sub>. Here we believed that low concentration of precipitating agent could produce the small particle size of ZnO, which is beneficial for Au catalysis preparation, and the small particle size of Au.

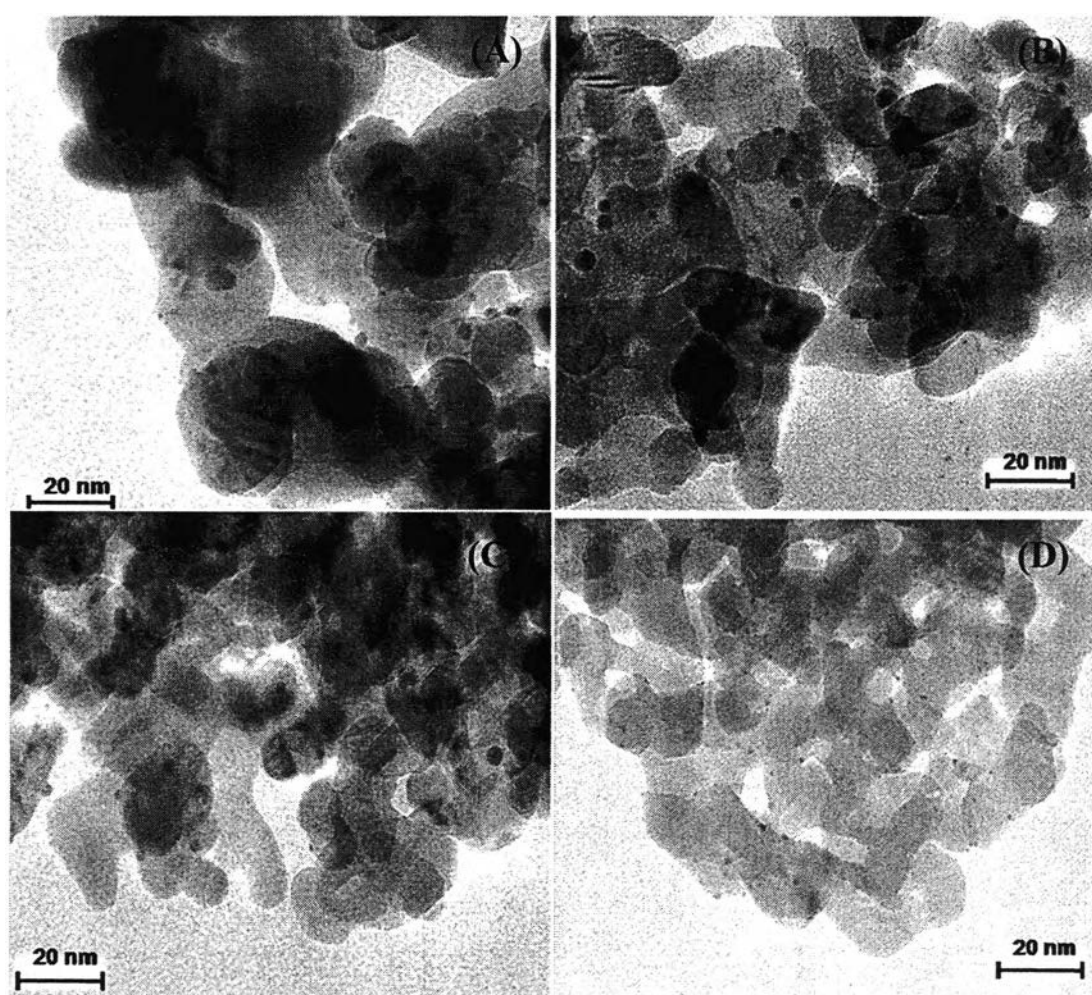
In addition, both ZnO morphology and structure were investigated by SEM (Figure C1 in appendix C). It was found that the prepared ZnO with different precipitant concentrations produced the flake-like structure (Sepulveda-Guzman *et al.*, 2009). Both supports consisted of different thickness of folds with different Na<sub>2</sub>CO<sub>3</sub> concentrations. In this work, a thinner and smaller fold of ZnO was obtained by 0.05 M Na<sub>2</sub>CO<sub>3</sub>, leading to the increasing of specific surface areas. Another technique of particle comparison is UV-vis spectroscopy, as presented in Figure C2 (appendix C), it can be seen that there is a pronounced shift in the absorption edge of 3.06 (0.1 ZnO) to 3.12 eV (0.05 ZnO). According to Viswaratha *et al.* (2003), the absorption edge systematically shifts to the lower wavelength or higher energy with decreasing size of the nanocrystal, which is consistence with the SEM images and BET results of 0.05 ZnO (49.24 m<sup>2</sup>/g). It showed a thinner fold and higher specific surface area than the 0.1 ZnO (45.49 m<sup>2</sup>/g).

Accordingly, the morphology and specific surface areas are controlled by the precipitant agent concentration. From this result, it is reasonable to mention that a low concentration of  $\text{Na}_2\text{CO}_3$  can make a nano-sized Au, which is related to TEM results. The TEM images of the samples are shown in Figure 4.4, which the nano-Au could be prepared by photodeposition. There are no strong obvious differences in the sizes for using different precipitant concentrations. However, the particle size distribution of the uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.1)$ -240 and the uncalcined  $\text{Au}(0.1)/\text{ZnO}(0.05)$ -240 are deeply observed, which showed the particle sizes of about 2.59 and 1.32 nm, respectively, while the catalytic activities insignificantly different. This means that the Au particle size may be not of importance because previous catalytic activity results. Differences between the activities of the four samples may thus be attributed to different morphology and structure of prepared ZnO supports. It is clearly seen that prepared ZnO and Au/ZnO by using 0.1 M  $\text{Na}_2\text{CO}_3$  seem to be possible change the morphology to form a nano-rod ZnO (observed by TEM, Figure C3 in appendix C), leading to the low catalytic activities compared to the other conditions. According to Glaspell *et al.* (2005), they claimed that the formation of long nano-rod ZnO did not allow for a uniform dispersion of Au and aggregation of metal nanoparticles causing the catalytic activities to be lower than prepared by 0.05 M  $\text{Na}_2\text{CO}_3$ .

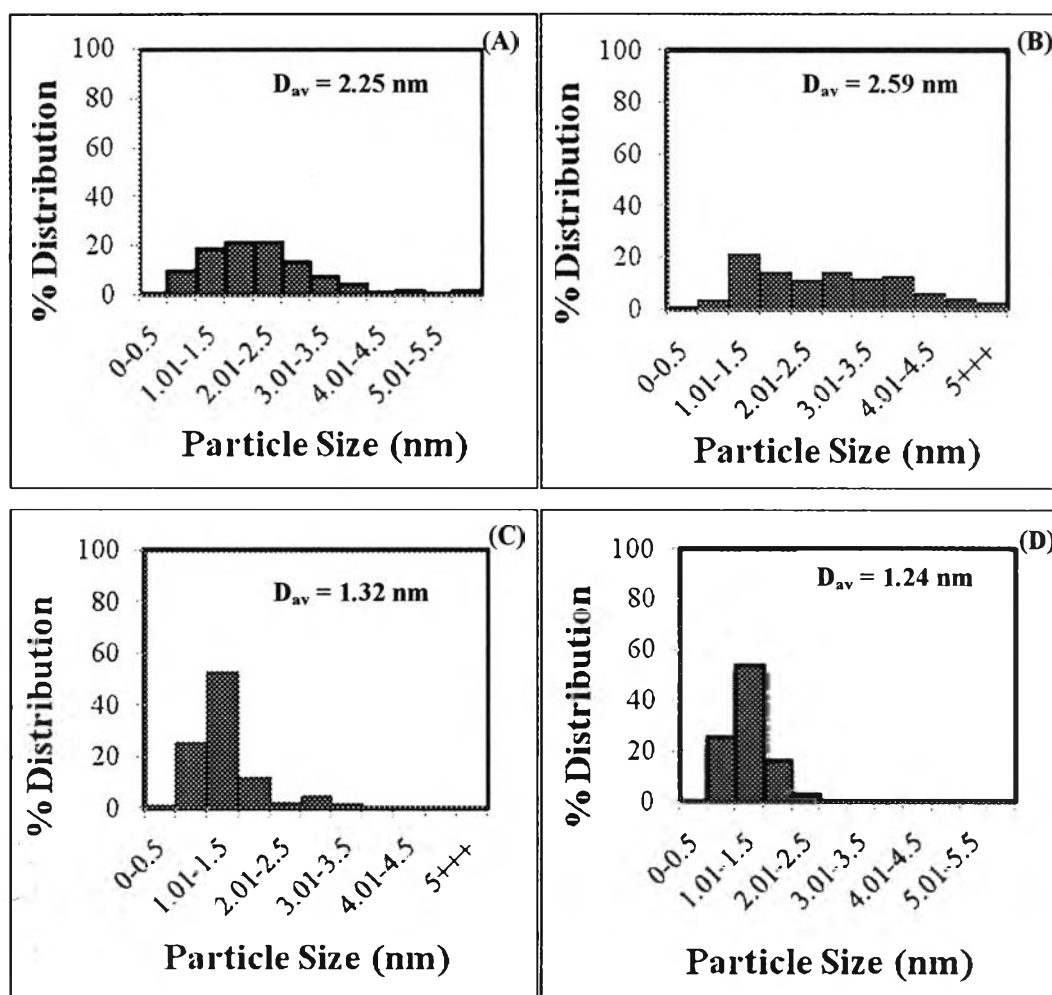
The calculated average Au particle size (formula in appendix C) of the uncalcined  $\text{Au}(0.1)/\text{ZnO}(0.1)$ -240, uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.1)$ -240, uncalcined  $\text{Au}(0.1)/\text{ZnO}(0.05)$ -240, and uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$ -240 are 2.25, 2.59, 1.32, and 1.24 nm, respectively, as presented in Figure 4.5. Uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$ -240 catalyst performs the smallest particle size and well dispersion of Au, which is in accordance with the absence of corresponding XRD peaks at  $2\theta = 38.2^\circ$ ,  $44.5^\circ$ , and  $64.6^\circ$  (Figure C4 in appendix C). On the contrary, the uncalcined  $\text{Au}(0.1)/\text{ZnO}(0.1)$ -240 catalyst displayed a feeble diffraction, it suggested that with this preparation condition produced a small Au with bad dispersion. Moreover, UV-vis absorption was used to investigate the Au particle sizes. Figure 4.6 shows that when 0.05 M  $\text{Na}_2\text{CO}_3$  was used, the maximum absorption of  $\text{Au}^0$  was weaker compared to the sample with 0.1 M  $\text{Na}_2\text{CO}_3$ . The results showed that the uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$ -240 had a smaller particle size of Au with a weak



absorbance, which is related to TEM and XRD data. In Figure 4.6, it seems likely to be explained that the simplistic particle sizes investigated by UV-vis spectra of the uncalcined Au(0.05)/ZnO(0.1)-240 and uncalcined Au(0.1)/ZnO(0.1)-240 might not be related to the average size distributions. However, the uncalcined Au(0.05)/ZnO(0.1)-240 has the particle size in the range of 1.01 to 1.50 nm higher than other ranges, whereas the uncalcined Au(0.1)/ZnO(0.1)-240 exhibited the highest particle sizes in the range of 1.51 to 2.50 nm.



**Figure 4.4** TEM images of the (A) uncalcined Au(0.1)/ZnO(0.1)-240, (B) uncalcined Au(0.05)/ZnO(0.1)-240, (C) uncalcined Au(0.1)/ZnO(0.05)-240, and (D) uncalcined Au(0.05)/ZnO(0.05)-240.

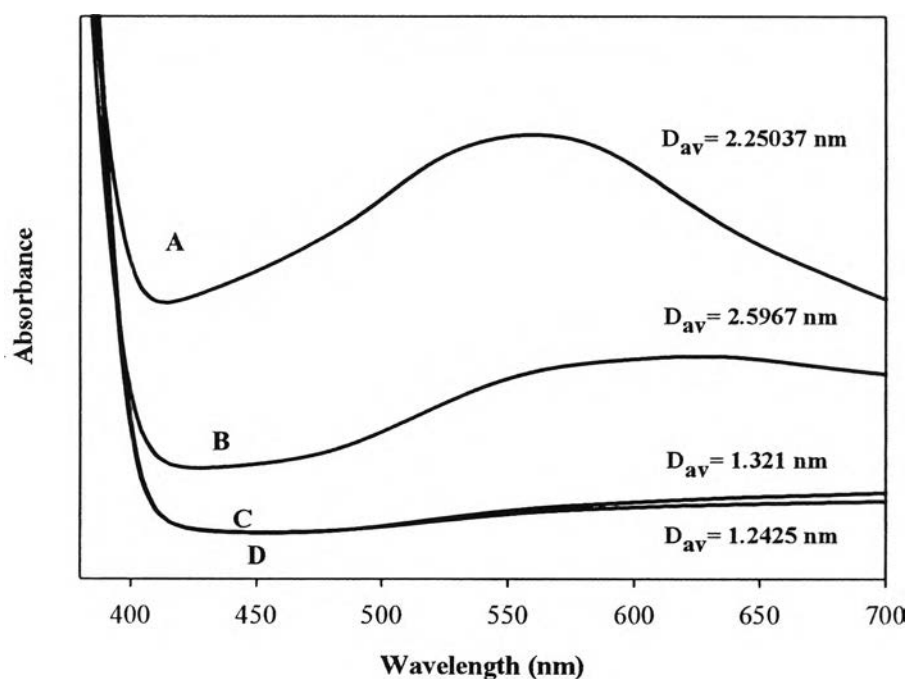


**Figure 4.5** Au particle size distribution of the (A) uncalcined Au(0.1)/ZnO(0.1)-240, (B) uncalcined Au(0.05)/ZnO(0.1)-240, (C) uncalcined Au(0.1)/ZnO(0.05)-240, and (D) uncalcined Au(0.05)/ZnO(0.05)-240.

From TEM, SEM, BET surface areas, and UV-vis results might confirm that the concentration of  $\text{Na}_2\text{CO}_3$  influences on morphology and finer size of ZnO, because of the absent diffraction. And also the morphology of ZnO can affect the particle sizes and dispersion of Au. Moreover, precipitant concentration can be proposed as the rate of the deposition of Au over ZnO, which ZnO can adsorb Au in a short period of time as Comotti *et al.* (2006) referred that the deposition was independent on the point of zero charge (p.z.c) of ZnO although it has high p.z.c of

about 11. Consequently, the higher precipitant concentration is, the less fine, the more nanorod shaped ZnO, and the larger Au particle are formed, and thus the lower the catalytic performance of the catalysts.

As Imai *et al.* (2008) reported that the CO conversion might be governed by the number of specific sites available for CO oxidation at the interface between the Au nanoparticles and the support surface; the length of this interface depends on the Au particle size. Additionally, Qian *et al.* (2008) claimed about the Au-ZnO interaction that the stronger the Au-ZnO interaction, the finer the supported Au nanoparticles, and the better the catalytic performance of the catalysts in low-temperature CO oxidation.



**Figure 4.6** UV-vis spectra of the (A) uncalcined Au(0.1)/ZnO(0.1)-240, (B) uncalcined Au(0.05)/ZnO(0.1)-240, (C) uncalcined Au(0.1)/ZnO(0.05)-240, and (D) uncalcined Au(0.05)/ZnO(0.05)-240.

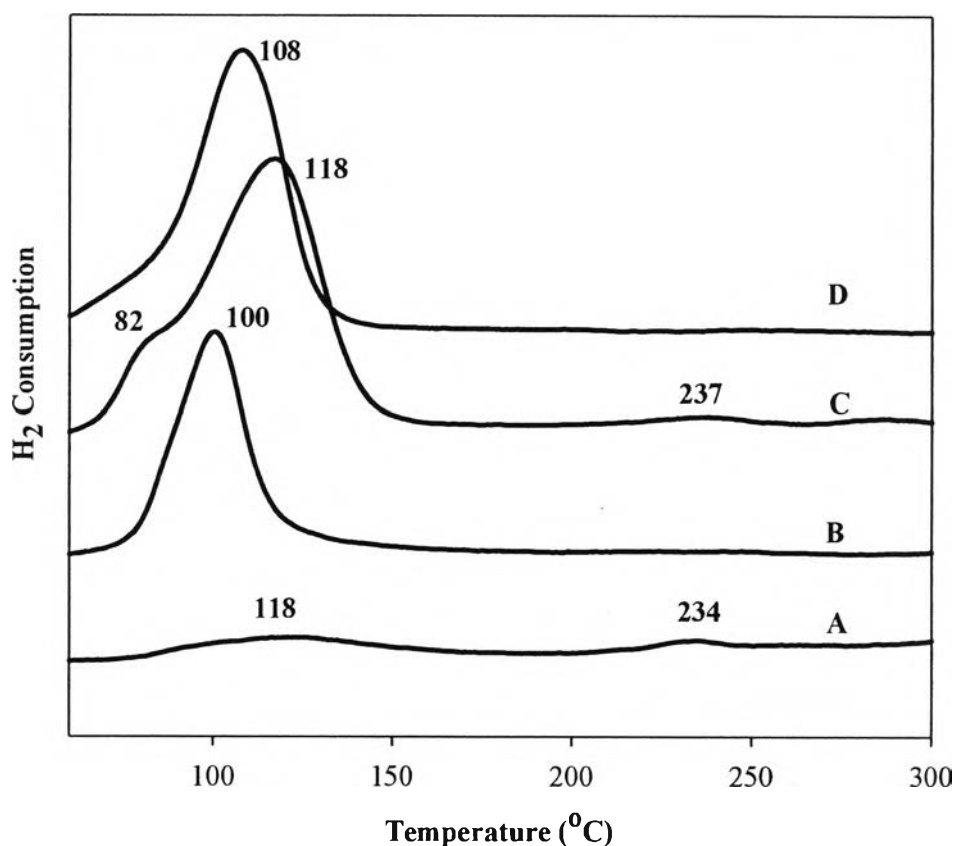
Above all, it can be reported that the morphology of the prepared ZnO could affect the particle size of Au. Using 0.05 M Na<sub>2</sub>CO<sub>3</sub> as a precipitant in

preparing Au over ZnO, the differences in both of catalytic activities and Au particle sizes between the uncalcined Au(0.05)/ZnO(0.1)-240 (2.59 nm) and the uncalcined Au(0.1)/ZnO(0.05)-240 (1.32 nm) was clearly observed. Furthermore, the results of the average size distribution and catalytic activities are consistent with the specific surface areas, suggesting that the appropriate condition in preparing ZnO supports and Au/ZnO catalysts was taken an action by 0.05 M Na<sub>2</sub>CO<sub>3</sub> and irradiated for 240 minutes in Au loading procedure.

Another major difference with the different preparation procedures is the reducibility of Au since the high catalytic activities can not be achieved from small Au particles alone. The reduction properties of the catalysts are studied by TPR. Figure 4.7 displays the TPR profiles of different samples, which provided the reducibility of charged Au species at different temperatures. The reduction temperatures of the uncalcined Au(0.1)/ZnO(0.1)-240, uncalcined Au(0.05)/ZnO(0.1)-240, uncalcined Au(0.1)/ZnO(0.05)-240, and uncalcined Au(0.05)/ZnO(0.05)-240,  $T_{\max}$  are 118, 100, 118, and 108°C, respectively. These peaks are attributed to the reduction of Au<sup>3+</sup> into Au<sup>+</sup> species (Mohamed *et al.*, 2001). Because of an unstable of Au oxide, the Au oxide had a low reduction temperature (Baatz *et al.*, 2008). Uncalcined Au(0.1)/ZnO(0.05)-240 has a peak at about 82°C, which was reported by Tabakova *et al.* (2006) that hydrogen is dissociated already at room temperature on Au sites, which can react with the adsorbed oxygen atoms or spillover on the supports and reduce the surface sites. And they described that the reduction at 82°C is the reduction of oxygen species, which the Au particles smaller than 3 nm are able to adsorb oxygen during calcination in air. From this discussion, it is obviously to propose that the peak at 82°C occurs from the spillover of hydrogen on the supports. A second peak exhibited at 234–237°C is observed in the uncalcined Au(0.1)/ZnO(0.1)-240 and uncalcined Au(0.1)/ZnO(0.05)-240, which relate to the reduction of Au<sup>+</sup> to Au<sup>0</sup>. This is in accordance with Sandoval *et al.* (2007).

From the different activity of the uncalcined Au(0.1)/ZnO(0.1)-240 and Au(0.05)/ZnO(0.1)-240, it was found that using different concentrations of Na<sub>2</sub>CO<sub>3</sub> in Au loading procedure is the cause of its difference. And also, it was clearly seen that using 0.1 M Na<sub>2</sub>CO<sub>3</sub> in Au loading step suppress the reducibility of

Au and the reduction temperature was shifted to higher temperature with a broad peak. In the same way, a similar peak of uncalcined Au(0.1)/ZnO(0.05)-240 and uncalcined Au(0.05)/ZnO(0.05)-240 was observed and the reduction temperature was shifted from  $T_{\max} = 108^{\circ}\text{C}$  to  $118^{\circ}\text{C}$  with using 0.1 M  $\text{Na}_2\text{CO}_3$ . It can be suggested that the prepared catalysts with low concentration of a precipitant agent in the Au loading step can enhance the reducibility of Au by shifting the reduction peaks to lower temperature, especially the uncalcined Au(0.05)/ZnO(0.05)-240.



**Figure 4.7** TPR patterns of the (A) uncalcined Au(0.1)/ZnO(0.1)-240, (B) uncalcined Au(0.05)/ZnO(0.1)-240, (C) uncalcined Au(0.1)/ZnO(0.05)-240, and (D) uncalcined Au(0.05)/ZnO(0.05)-240.

These features suggested that using a low concentration of  $\text{Na}_2\text{CO}_3$  in both of support preparation and Au loading step makes an active catalyst, which can be observed in the TPR profile of the uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$ -240. It showed a symmetric shape, high intensity, and low reduction temperature, which means that the catalyst with a good dispersion and narrow size distribution of Au can be observed. This result is consistent with TEM results.

### 4.3 Influence of Calcination

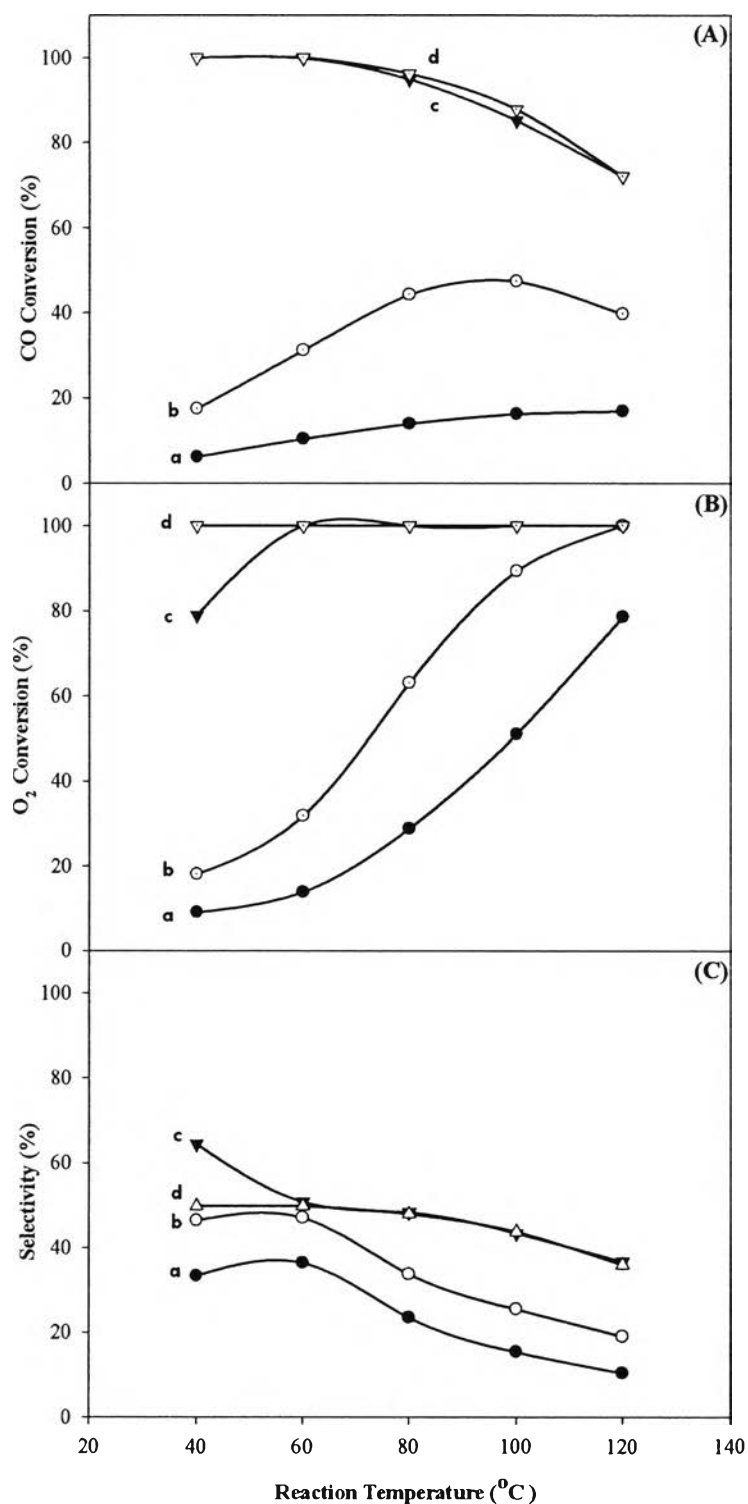
#### 4.3.1 Measurements of Catalytic Activities for CO Oxidation

From previous results, it was found that the  $\text{Au}(0.1)/\text{ZnO}(0.1)$  catalysts performed high activity, as the irradiation time increased. It was reported by Chang *et al.* (2008) that the heat treatment is unnecessary since gold is reduced by UV irradiation, which was almost same with the series of the  $\text{Au}(0.1)/\text{ZnO}(0.1)$ , confirmed by a strong plasmon band of UV-vis results. Nevertheless, with this condition showed the lowest reducibility, it may be because prepared catalysts by using 0.1 M  $\text{Na}_2\text{CO}_3$ , a lot of residual Cl ions were presented (Oh *et al.*, 2002). Calcination might remove them; therefore, it is interesting to study the effect of calcination on the activities of  $\text{Au}(0.1)/\text{ZnO}(0.1)$ . Prior to a catalytic test, each catalyst was activated by calcination in an oven under air at  $300^\circ\text{C}$  for 3 hours. However, according to literature reviews, the disputed observations are that the calcination is either desirable or essential. In this study, the highest activity with uncalcined catalysts are found when the catalyst was prepared by lower concentration of  $\text{Na}_2\text{CO}_3$  and the catalytically active gold species zero-valent atoms ( $\text{Au}^0$ ) or oxidized species ( $\text{Au}^{\text{I}}$  or  $\text{Au}^{\text{III}}$ ) are the active species due to the presence of  $\text{Au}^0$  and oxidized species in the calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)$  and the uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.1)$ -240,  $\text{Au}(0.1)/\text{ZnO}(0.05)$ -240, and  $\text{Au}(0.05)/\text{ZnO}(0.05)$ -240.

Figure 4.8 shows the catalytic activities of the calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)$ -30 and  $\text{Au}(0.1)/\text{ZnO}(0.1)$ -240, indicating that the catalytic activities of CO oxidation were more sensitive only after they were calcined at  $300^\circ\text{C}$  as compared to the uncalcined catalysts.

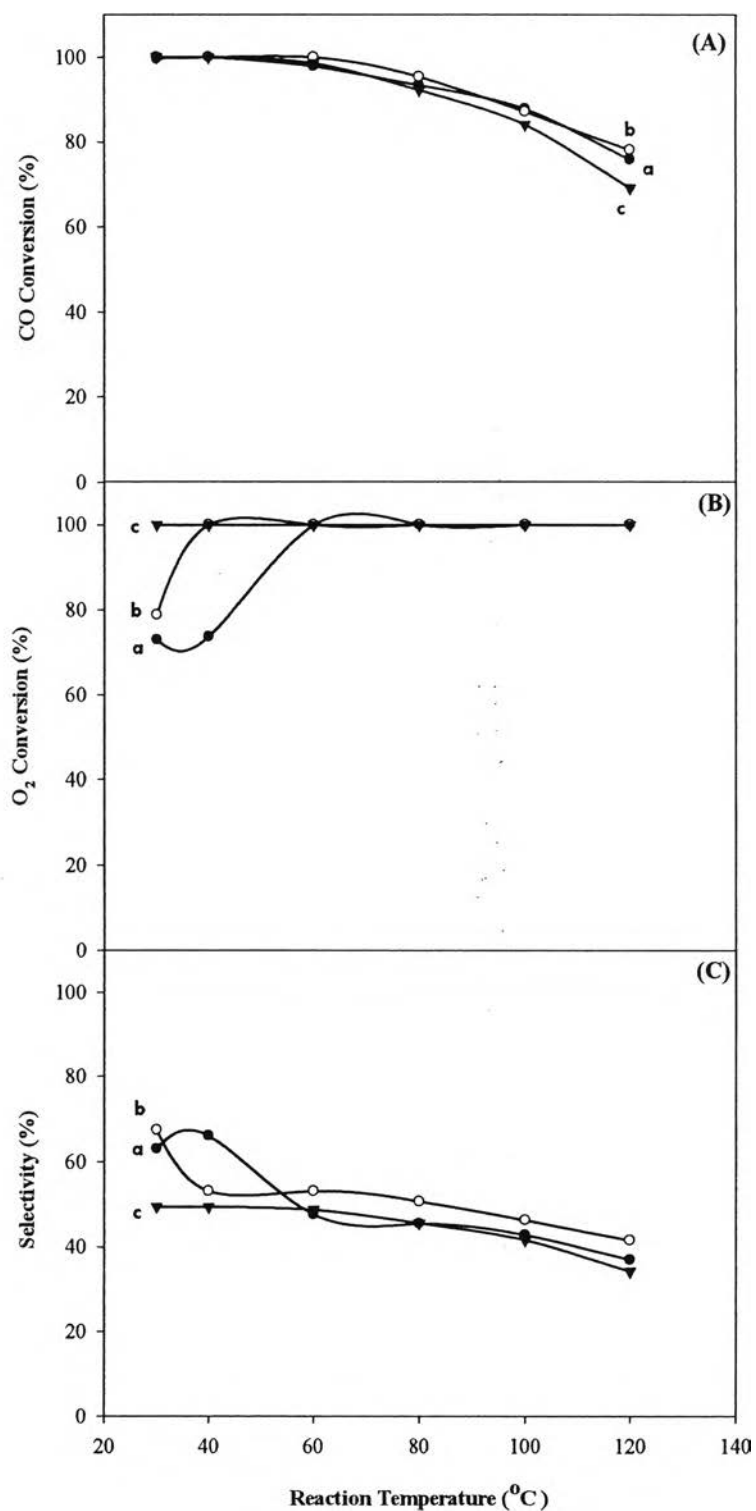
Moreover, the catalysts prepared with different concentrations of  $\text{Na}_2\text{CO}_3$ , were also tested. It can be seen that the calcined catalysts precipitated with lower concentration of  $\text{Na}_2\text{CO}_3$  were slightly different. The activity of the calcined  $\text{Au}(0.1)/\text{ZnO}(0.05)$  and  $\text{Au}(0.05)/\text{ZnO}(0.1)$  seem likely to be higher than that of the calcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$ , as shown in Figure 4.9.

All in all, in this study, the calcination is very essential for active catalysts, in particular  $\text{Au}(0.1)/\text{ZnO}(0.1)$  catalysts.



**Figure 4.8** Catalytic activity of the uncalcined (a) Au(0.1)/ZnO(0.1)-30 and (b) Au(0.1)/ZnO(0.1)-240 and the calcined (c) Au(0.1)/ZnO(0.1)-30 and (d) Au(0.1)/ZnO(0.1)-240—(A) CO conversion, (B) O<sub>2</sub> conversion, and (C) selectivity.

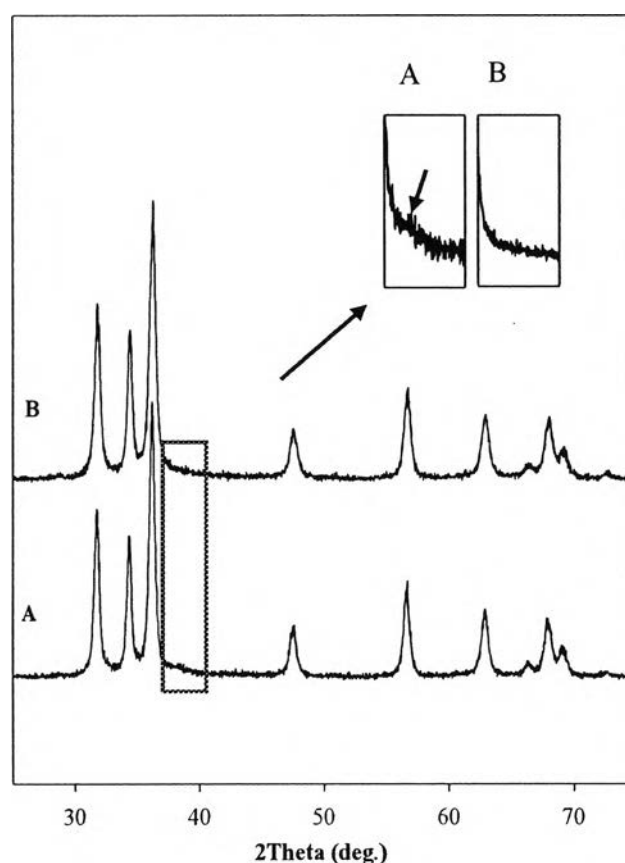




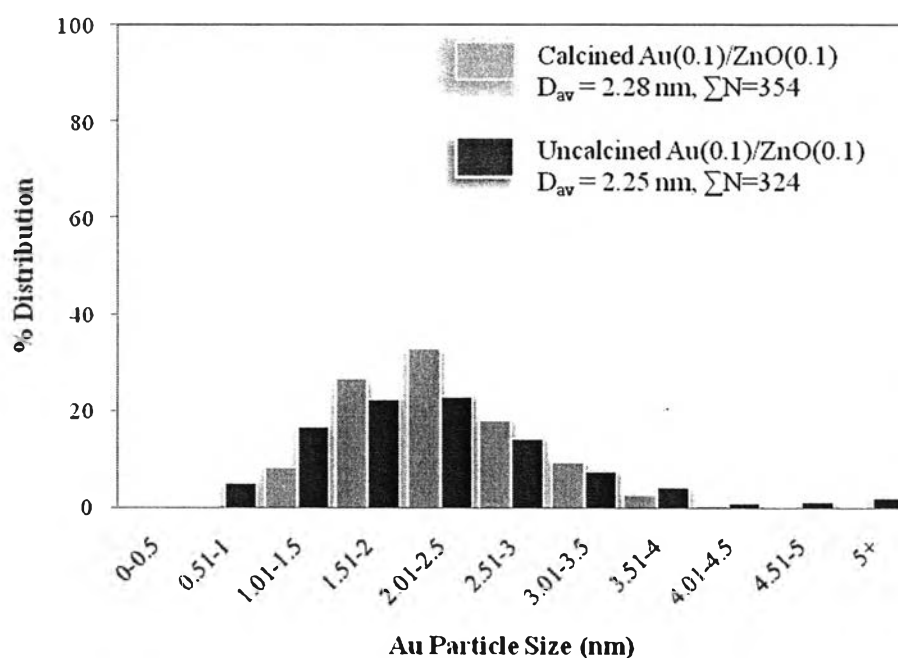
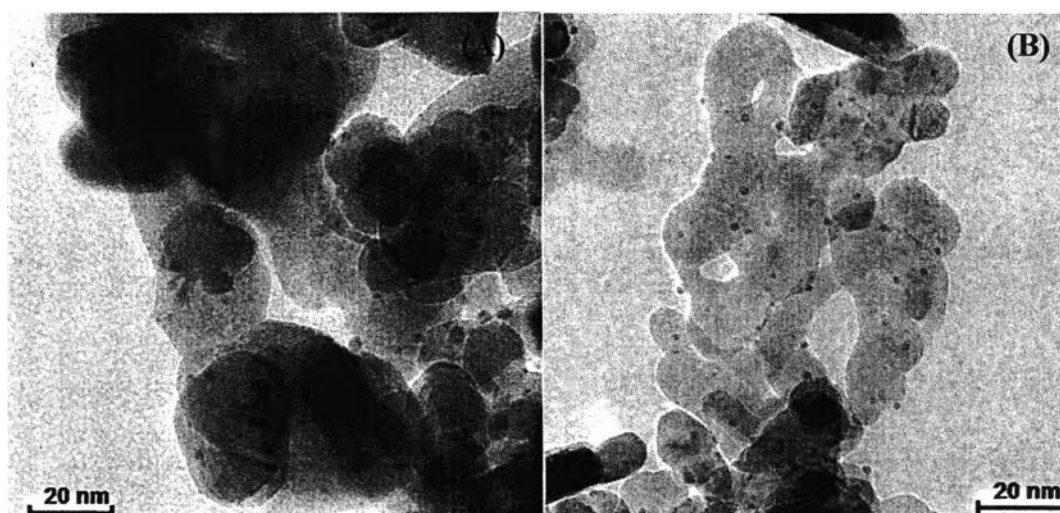
**Figure 4.9** Catalytic activity of the calcined (a) Au(0.1)/ZnO(0.05)-240, (b) Au(0.05)/ZnO(0.1)-240, and (c) Au(0.05)/ZnO(0.05)-240—(A) CO conversion, (B) O<sub>2</sub> conversion, and (C) selectivity.

#### 4.3.2 Catalyst Characterizations

As shown in Figure 4.10, the XRD patterns of the uncalcined Au(0.1)/ZnO(0.1)-240 displayed only the weak intensity of Au around  $2\theta = 38.2633^\circ$ . However, no diffraction peaks corresponding to Au metal particles in the patterns of the calcined Au(0.1)/ZnO(0.1)-240 samples can be surveilled. This is probably attributed to the low Au content, well-dispersed Au, or Au particles are too small to be detected by XRD technique. Figure 4.11 reveals the TEM images, average Au sizes, and Au size distribution of the uncalcined and calcined Au(0.1)/ZnO(0.1), indicating that the calcined Au(0.1)/ZnO(0.1) had a smaller Au particle, narrow size distribution, and well-dispersed Au on ZnO, leading to high specific surface area ( $51.68 \text{ m}^2/\text{g}$ ).



**Figure 4.10** XRD patterns of the (A) uncalcined and (B) calcined Au(0.1)/ZnO(0.1)-240.

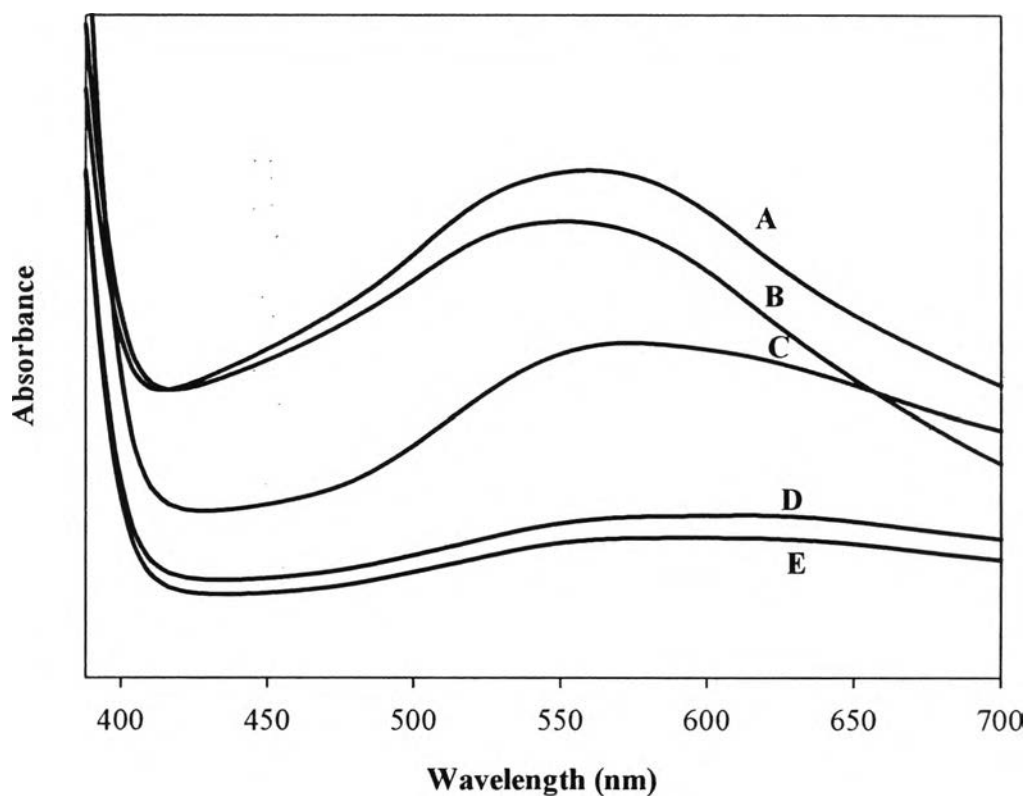


**Figure 4.11** TEM images of the (A) uncalcined and (B) calcined Au(0.1)/ZnO(0.1)-240 catalysts. At below graph showed an average Au particle sizes and Au particle size distribution.

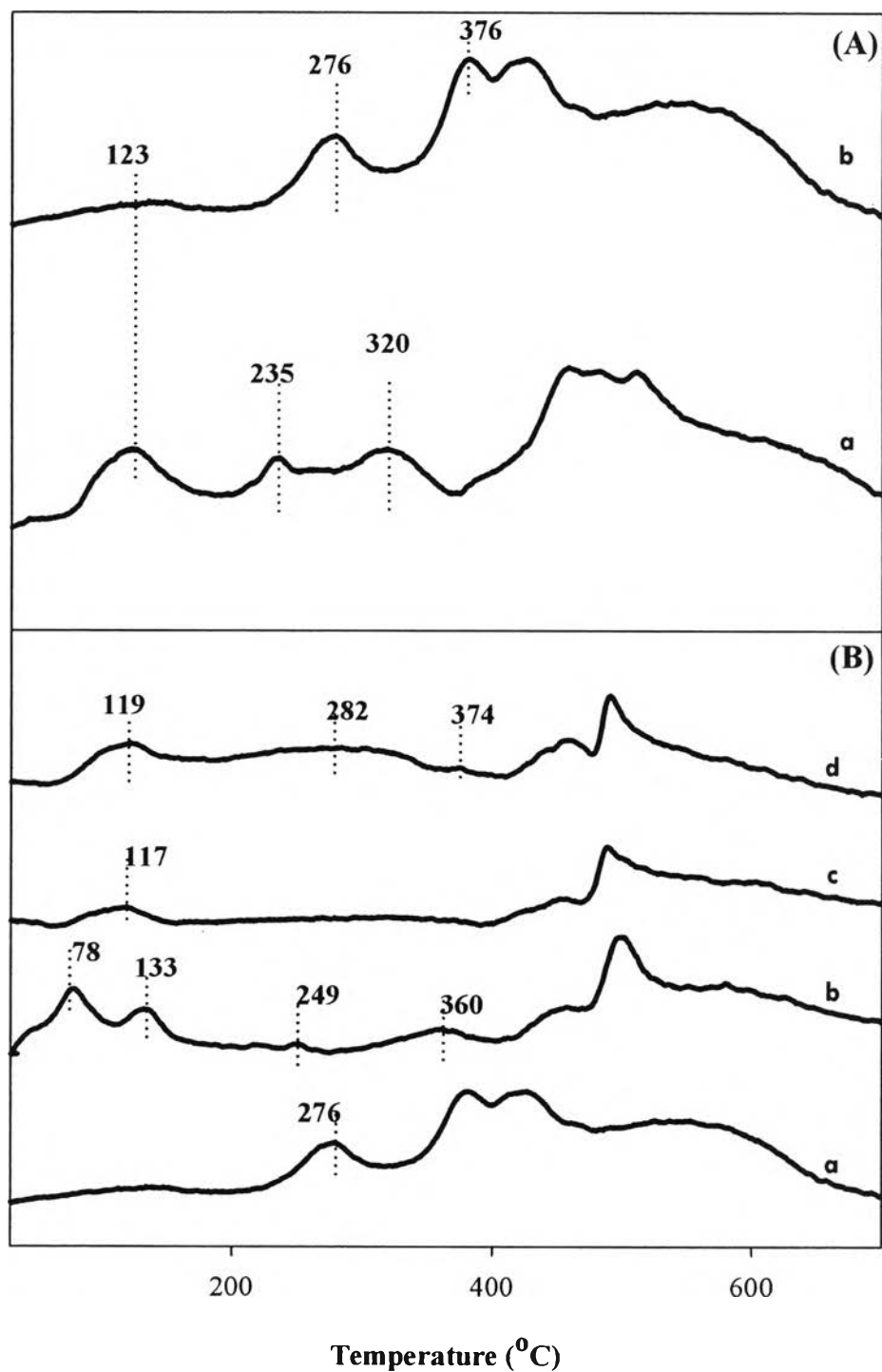
Moreover, Figure 4.12 presents the UV-vis reflectance spectra of the uncalcined and calcined Au(0.1)/ZnO(0.1). It was clearly seen that after the samples were calcined, the Au particle size of the Au(0.1)/ZnO(0.1)-240 decreased with decreasing intensity of plasmon band, which is in agreement with TEM and an

average Au particle size results. The blue shift in the surface plasmon of  $D_{av} = 2.25$  and 2.28 nm corresponds to the uncalcined Au(0.1)/ZnO(0.1) and calcined Au(0.1)/ZnO(0.1), suggesting that the calcination under air at 300°C has no significant effect on the particle size of Au.

And also, the average Au particle size of the calcined Au(0.05)/ZnO(0.1), calcined Au(0.1)/ZnO(0.05), and calcined Au(0.05)/ZnO(0.05) was slightly increased by calcination in comparison to the uncalcined samples describing in previous section, which consistent with the catalytic activity results.



**Figure 4.12** UV-vis spectra of the (A) uncalcined and (B) calcined Au(0.1)/ZnO(0.1)-240, (C) calcined Au(0.05)/ZnO(0.1)-240, (D) calcined Au(0.1)/ZnO(0.05)-240, and (E) calcined Au(0.05)/ZnO(0.05)-240.



**Figure 4.13** TPR patterns of (A) the Au(0.1)/ZnO(0.1)-240: (a) uncalcined and (b) calcined and (B) the calcined catalysts at different precipitant concentrations: (a) Au(0.1)/ZnO(0.1)-240, (b) Au(0.05)/ZnO(0.1)-240, (c) Au(0.1)/ZnO(0.05)-240, and (d) Au(0.05)/ZnO(0.05)-240.

The reduction properties of catalysts which depend on the nature of support were acquired by TPR. The attribution of the signals at  $T_{max} = 40\text{--}123^\circ\text{C}$  may be related with  $\text{Au}^{3+}$  reduction ( $\text{Au}^{3+} \rightarrow \text{Au}^+$ ) and  $T_{max} = 249\text{--}376^\circ\text{C}$  may be assigned to the reduction of  $\text{Au}^+$  ( $\text{Au}^+ \rightarrow \text{Au}^0$ ); however, it is not so clear. As shown in Figure 4.13 (A), Because of the instability of  $\text{Au}_2\text{O}_3$ , the catalysts calcined at  $300^\circ\text{C}$  emerged low intensities of low-temperature peaks. High-temperature peaks at higher than  $400^\circ\text{C}$  may be favorable to the reduction of surface oxygen species, bulk oxygen, and ZnO. The calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)\text{-}240$  still displayed the reduction of  $\text{Au}_x\text{O}_y$  at the temperature of  $276^\circ\text{C}$ , indicating that  $\text{Au}_x\text{O}_y$  was incompletely transformed into metallic Au. However, the high-temperature reduction of the calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)\text{-}240$  was shifted to lower temperature, resulting in the high catalytic activities of the calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)\text{-}240$ .

The influence of calcination on the reduction profiles of the  $\text{Au}(0.1)/\text{ZnO}(0.1)\text{-}240$ ,  $\text{Au}(0.05)/\text{ZnO}(0.1)\text{-}240$ ,  $\text{Au}(0.1)/\text{ZnO}(0.05)\text{-}240$ , and  $\text{Au}(0.05)/\text{ZnO}(0.05)\text{-}240$  were observed in Figure 4.13 (B). Broad peaks were observed in the calcined  $\text{Au}(0.05)/\text{ZnO}(0.05)$  because of a good dispersion of nano-Au and strong interaction. It was clearly seen that the Au oxidation states of 3 and 1 were observed on the calcined  $\text{Au}(0.05)/\text{ZnO}(0.1)\text{-}240$ ,  $\text{Au}(0.1)/\text{ZnO}(0.05)\text{-}240$ , and  $\text{Au}(0.05)/\text{ZnO}(0.05)\text{-}240$  at low-temperature peaks. Whereas, the calcined  $\text{Au}(0.1)/\text{ZnO}(0.1)\text{-}240$  showed only low-temperature peaks at around  $276$  to  $376^\circ\text{C}$ , suggesting that it is probably due to the weak interaction between  $\text{Au}_2\text{O}_3$  and ZnO.

## 4.4 Influence of Storage Conditions

### 4.4.1 Measurements of Catalytic Activities for CO Oxidation

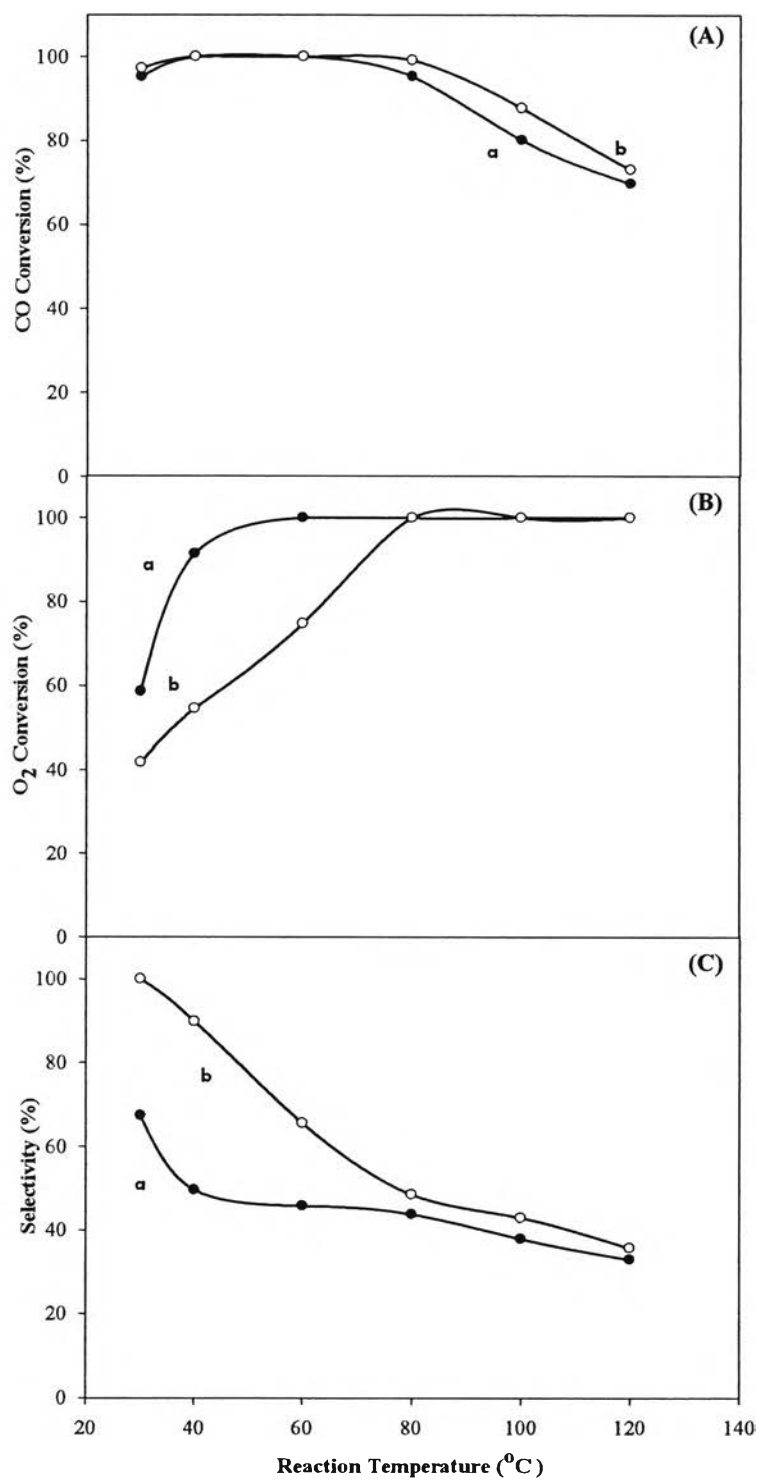
Owing to the smallest Au particle size, which is easy to be agglomerated and the instability of  $\text{Au}_2\text{O}_3$ , the storage conditions of the prepared catalysts are interesting to be investigated. In this work, the uncalcined  $\text{Au}(0.05)/\text{ZnO}(0.05)\text{-}240$  catalysts were kept in two different storage conditions. The first condition is that the catalysts was stored in the apparent glass bottle and closed with the lid for 3 months (exposed catalysts). The second condition was similar to the

previous one but the catalyst was enclosed by the black-taped to prevent the light from the ambient environment (unexposed catalysts).

The possible occurrences from the storage conditions may have two possibilities, which are (i) the further formation of metallic Au causing from the reduction of  $\text{Au}_2\text{O}_3$  by light and (ii) the sintering or agglomeration of Au by light and other parameters of environmental storage.

Figure 4.14 compares the catalytic activities of the unexposed and exposed catalysts. It can be seen that the unexposed catalysts performed higher catalytic activity. However, the 100% CO conversion of the exposed catalysts was still obtained, suggesting that the storage condition studied in this work insignificantly affected to CO conversion. On the other hand, the decreasing of CO selectivity was observed in Figure 4.19 (C).

The slightly decrease in CO conversion and extremely decrease in CO selectivity at low temperature can draw the scientist attention to study how to property store the prepared catalysts.



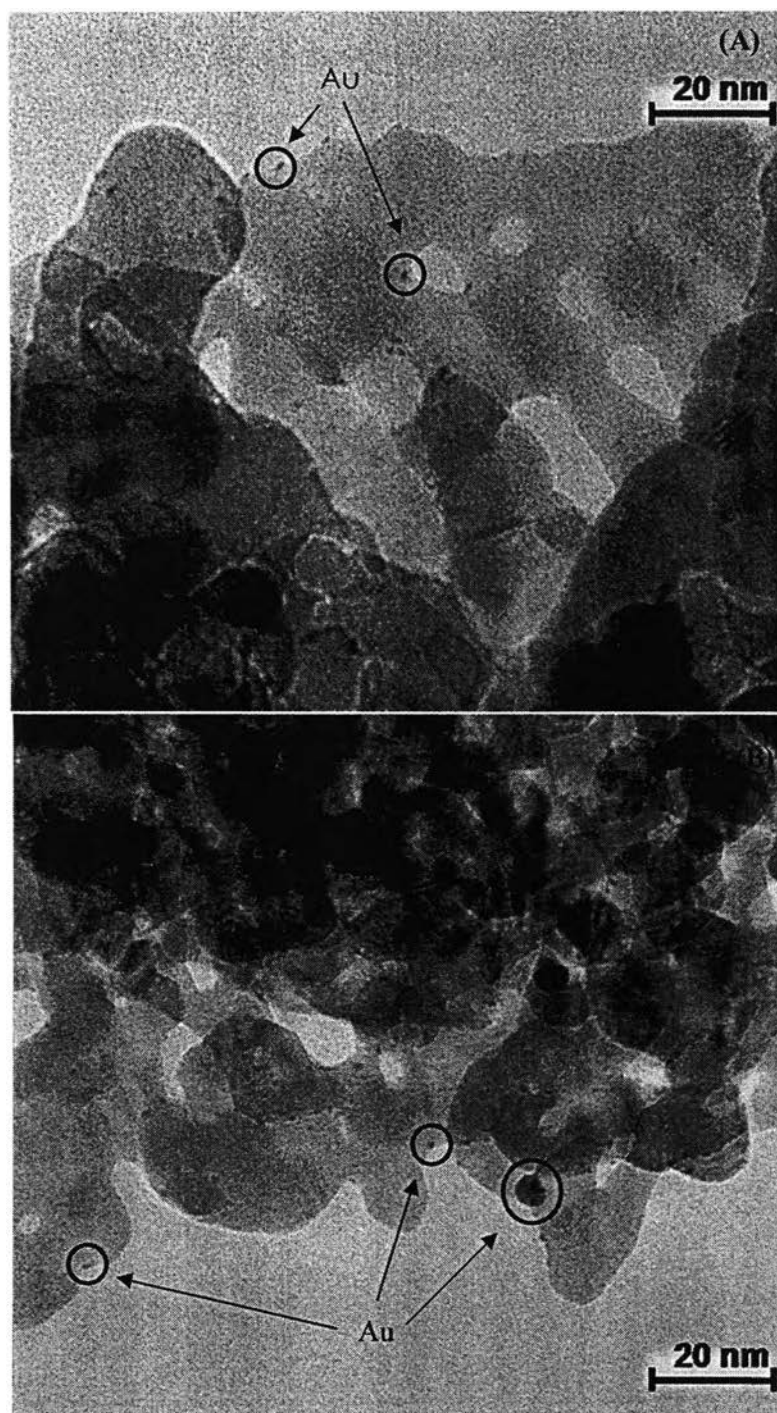
**Figure 4.14** Catalytic activity of the uncalcined Au(0.05)/ZnO(0.05)-240 (a) exposed and (b) unexposed to light for 3 months—(A) CO conversion, (B) O<sub>2</sub> conversion, and (C) CO selectivity.



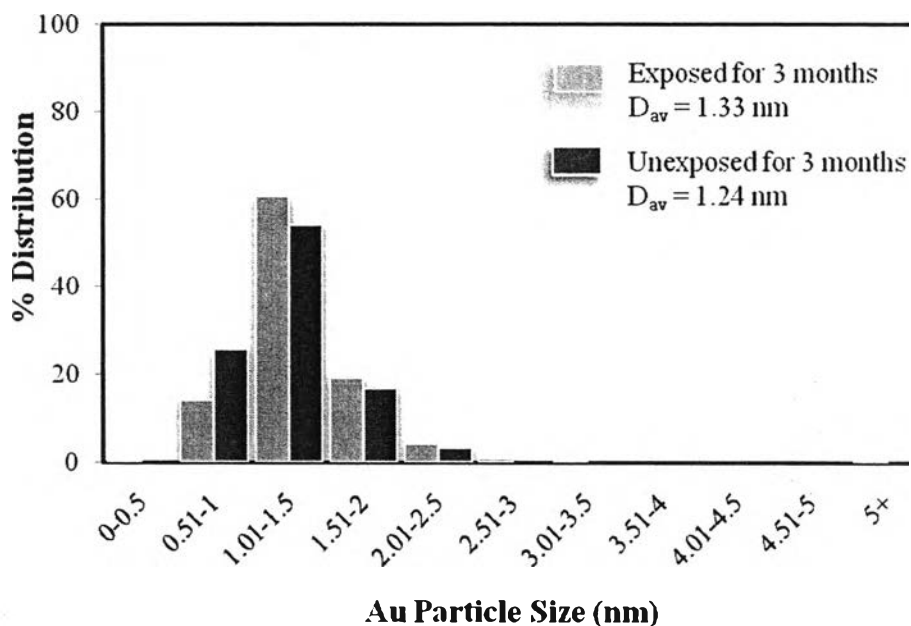
#### 4.4.2 Catalyst Characterizations

As shown in Figures 4.15, the observed particle sizes of Au from the TEM images and particle size distribution showed that the Au particles slightly formed the larger particle sizes when the catalysts was exposed to light. The average Au particle sizes of the exposed and unexposed catalysts are about 1.33 and 1.24 nm, respectively. For the increasing of Au particle size in the range of 0.51–1.00 nm and the decreasing of Au particle size in the range of 1.01–1.50 and 1.51–3.00 nm were observed in the exposed catalysts, which are in corresponding to TEM images and UV result. However, it was claimed by Lee *et al.* (2007) that the UV-vis reflectance spectrum of the sample after exposure light had a stronger plasmon band and they suggested that the nano-Au clusters were reduced to the Au metal, which is irrelevant with our UV-vis results. Therefore, it was the first time to propose that the plasmon band type of UV-vis spectra of the Au particle sizes smaller than 1.9 nm would not be observed although it had high amount of Au metallic. On the other hand, the sample with Au particle larger than 1.9 nm would show the strong plasmon band even though it had presented low amount of Au metallic. Consequently, TPR technique is necessary for observing the Au cations, which can be used to rough estimate the amount of Au metallic.

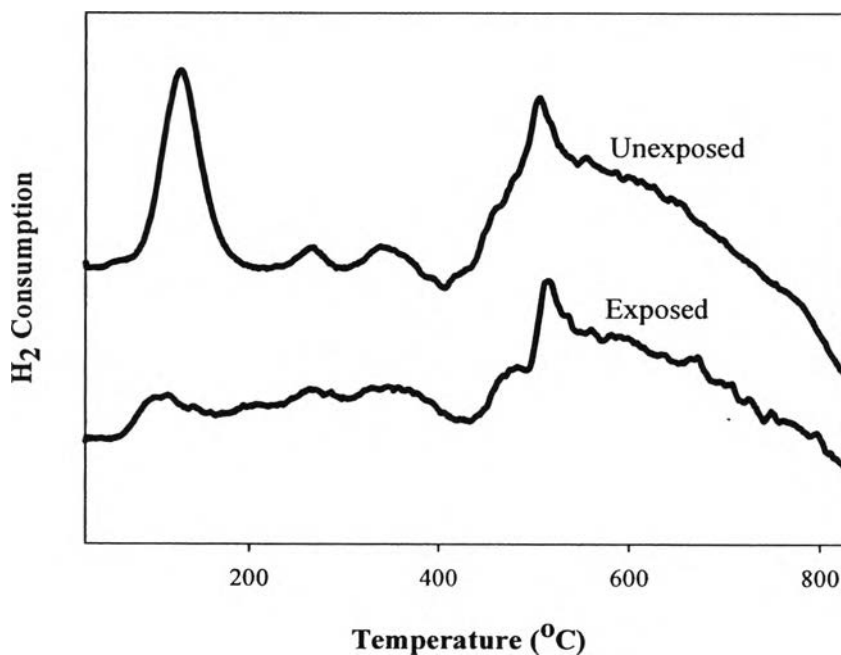
As shown in Figure 4.17, it was evidently seen that after the catalysts were exposed to light for 3 months, the reducibility of the catalyst at the temperature around 130°C was markedly decreased, suggesting that the Au<sub>2</sub>O<sub>3</sub> was reduced to the metallic Au.



**Figure 4.15** TEM images of the Au(0.05)/ZnO(0.05) (A) unexposed to light for 3 months and (B) exposed to light for 3 months.



**Figure 4.16** Au particle size distributions and Au averaged sizes of the Au(0.05)/ZnO(0.05) unexposed and exposed to light for 3 months.



**Figure 4.17** TPR profiles of the Au(0.05)/ZnO(0.05) unexposed and exposed to light for 3 months.

#### 4.5 Stability Testing

The activity of the uncalcined Au(0.05)/ZnO(0.05) catalysts were tested at room temperature range (27–30°C) for 100 hours. It was found that the Au/ZnO prepared by photodeposition gave high levels of CO removal and exhibited good stability during 100 hours time-on-stream (appendix E). This result showed that the photodeposition can generate the active Au/ZnO catalysts for the PROX reaction.

Fresh and spent catalysts were also characterized by UV-Vis and TPR techniques. As shown in Figure E2 (appendix E), spent catalyst showed a stronger plasmon band than the fresh one, which was caused by the increasing of the Au particle size and the amount of metallic Au, confirmed by TPR results in Figure E3, after reaction for 100 hours. The significant drop in the H<sub>2</sub> consumption and a shift in reduction temperature of the spent catalyst were clearly observed. There were a broad and strong reduction band centered at 108°C in the spent catalyst due to the reaction of Au<sup>3+</sup> to Au<sup>0</sup>.

Above all, from the TPR and UV-visible results of the uncalcined Au(0.05)/ZnO(0.05)-240 in the stability testing shows that the onset of reduction peak shifts to high temperature and consumes a very low level of H<sub>2</sub>, which suggests that the content of oxidized Au decreased (Figure E3, appendix E). As this reason, the intensity of absorption band can identify the amount of metallic Au also which is in accordance with Lee *et al.* (2007). They reported that the strong absorption band was observed when the Au over supports was reduced to the Au metal by no apparent difference between the sizes of Au on before and after reduced.

#### 4.6 Influence of H<sub>2</sub>O

Because of unsuitable of moisture containing in feed (10%, ~100,000 ppm), the catalytic activity of the uncalcined Au(0.05)/ZnO(0.05)-240 dramatically decreased to zero percent in particular at low temperature and thereafter CO conversion and selectivity increased with the increasing of temperature, the highest activity shows at 80°C, as shown in appendix F. As presented by Daté and Haruta (2001), the moisture

in the reactant gas has a significant effect on the activity of the Au/TiO<sub>2</sub> and the optimum moisture concentration was about 200 ppm and thereafter the catalytic activity decreased with increasing the level of moisture because of the blocking of active sites. The influence of moisture on the activities of Au/ZnO was also studied in this work; despite only one level of moisture investigation, which is higher than the Au/TiO<sub>2</sub> in Daté and Haruta report.

This results suggested that Au/ZnO can tolerate to the high level of water, which predicted from the occurrence of CO conversion of Au/ZnO even flew water through catalysts in high level.

#### **4.7 Color Observations**

It is well known that the electronic and optical properties of metal nanoparticles extremely depend on gold particle size and shape of the Au (Xu *et al.* 2007). Particularly, the specific color is a function of the size, shape, and material properties of the particles (Ahmadi *et al.*, 1996). Moreover, they suggested that the different shapes of metallic nanoparticles give the different types of catalytic reactions. In this work, the color of catalysts has been also observed the color of an active catalyst. As shown in Table G1 (appendix G), all of active catalysts in the PROX exhibited pale blue and pale purple. The color of the fresh and spent catalysts was also observed.