

CHAPTER VI
PREFERENTIAL CO OXIDATION OVER Au/ZnO AND Au/ZnO-Fe₂O₃
CATALYSTS PREPARED BY PHOTODEPOSITION*

6.1 Abstract

Preferential CO oxidation in a H₂-rich stream was studied over Au/ZnO and Au/ZnO-Fe₂O₃ catalysts prepared by photodeposition under UV-vis light. The high catalytic activities of both Au/ZnO and Au/ZnO-Fe₂O₃ catalysts are presented over a temperature range of 30–130°C. TEM results revealed that the average particle size of Au over the Au/ZnO and Au/ZnO-Fe₂O₃ catalysts, is in the range of 3 to 5 nm. Moreover, DR/UV-vis spectra showed that the prepared catalysts contained Au^{δ+} and Au⁰ (active sites for the PROX reaction) on the catalyst support. Based on the experiment observations, it can be concluded that the catalysts prepared by photodeposition exhibited excellent catalytic activity, even when both CO₂ and H₂O were added to the simulated stream.

Keywords: Preferential CO oxidation; Photodeposition; Au catalyst; ZnO; Fe₂O₃

6.2 Introduction

Hydrogen (H₂), a very clean, highly efficient, and environmentally friendly (emission-free) fuel [1], has attracted much attention from many scientists, especially for its use in proton exchange membrane (PEM) fuel cells applications. The PEM fuel cells convert the chemical energy (H₂ and O₂) directly into electricity without combustion. This is deemed the most suitable process for powering vehicles and portable systems [2]. However, the major problem in the utilization of PEM fuel cells is the supplying of high-purity H₂ that is needed as a fuel. The method used for producing H₂ and the type of feedstock available, play a vital role in the design of the

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fuel processor unit [3–5]. In particular, a low CO content in hydrogen stream generated by reforming process deteriorates the efficiency of the Pt anode catalyst via CO poisoning [6, 7].

Many types of fuel processing systems were developed to produce pure hydrogen that is fast enough to supply the PEM fuel cell operation by passing through auxiliary units [8, 9]. These auxiliary units were integrated into the H₂ production unit (reformer) in order to effectively remove CO from the H₂ stream and also to minimize H₂ loss in the H₂-rich stream. The preferential CO oxidation (PROX) reaction has been widely studied for automobile applications [10, 11] because of their numerous advantages. These include not only keeping the cost low, but also the decreasing of the CO content to the acceptance level (<10 ppm) without excess hydrogen consumption. The ideal catalyst for this reaction needs to be active and selective at the practical temperature between the outlet temperature of the water-gas shift reactor and the inlet temperature of the PEMFC.

Although all of the platinum group metals were found to have high activity in this reaction, the ultrafine Au particles dispersed on the appropriate metal oxide supports were found to be more active for CO oxidation reaction at low temperatures [12–14]. In addition, it has been reported that the presence of a small Au particle size in its catalytic CO oxidation where the turnover frequency increases remarkably at a size smaller than 5 nm [15]. The catalytic activities of Au markedly depend on the preparation method, which brings about a significant difference in the size of Au particles and the interaction with support. Furthermore, they also observed that the deposition-precipitation (DP) technique had an advantage over co-precipitation (CP) in that all active Au remained on the support surface indicated, and none of the active Au was buried within it. However, the process in the preparation method requires the calcination step at a higher temperature in order to decompose the Au precursor and eliminate the undesired component on the support surface.

In the last few years, several studies have reported that the addition of Au to some oxidic catalyst supports leads to an increase in their catalytic activity in many reactions. These include: CO oxidation [16, 17], benzene oxidation [18], hydrocarbon catalytic combustion [19], and water-gas shift [20, 21]. In the last years our group has been involved in investigating gold catalysts for the PROX [22, 23]. It

was also revealed that the key role of catalyst support is to provide oxygen adsorption and activation sites; and probably the oxygen vacancies and/or the perimeter sites at the Au-oxide interface [24, 25]. Wang *et al.* reported that Au/ZnO exhibits good activity and stability in CO oxidation [26] and our earlier work dealt with the preparation of Au/ZnO catalysts by the DP method for the PROX [23]. In the present work, the photodeposition (PD) technique was applied to prepare the Au/ZnO catalysts in order to find a new route in which to deposit nano-size Au particles onto the catalyst support. The advantages of the PD over the DP, for example, are that a higher amount of Au is loaded and the heat treatment is not required. This is because $\text{Au}(\text{OH})_4^-$ is reduced by UV-vis irradiation [27]. Many parameters were considered for the PD technique such as the power of the light source, irradiation time, precipitation agent, and catalyst support.

Therefore, it is interesting to investigate the catalytic activity of the supported Au catalysts prepared by PD in the PROX. Additionally, it is worth remarking that, while many of the published studies have concentrated on processes involving CO with H_2 and O_2 , CO_2 and H_2O may need to be included as reactants to obtain more realistic image. The selected catalysts were tested under the realistic reformat containing both CO_2 and H_2O at a constant temperature to observe the stability with time on stream.

6.3 Experimental Methods

6.3.1 Catalyst Preparation

ZnO and ZnO- Fe_2O_3 supports were synthesized by precipitation using aqueous solutions of $\text{Zn}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (Sigma-Aldrich) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Fluka). The pH of the solutions was adjusted to 8.0 by the addition of 0.1 M Na_2CO_3 (Riedel-de Haen). After aging, washing, and drying, the precipitate was calcined at 400°C for 4 h in order to obtain a ZnO catalyst support. Nano-size Au deposition on synthesized supports with an Au loading of 1%atom was prepared by a PD technique under UV-vis light. ZnO was then added to an aqueous solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$

(ACROS). Subsequently, the pH was adjusted to 8.0 by the addition of 0.1 M Na_2CO_3 .

The suspensions were irradiated under a UV-vis lamp with the power of 11 W in the photo-reactor, and vigorously stirred at ambient temperature in series of 1, 3, and 5 h. The prepared catalysts were denoted as Au/ZnO-11W-1h, Au/ZnO-11W-3h, and Au/ZnO-11W-5h, respectively. Moreover, the power of UV-vis light effect (which ranged from 11 to 176 W) was investigated with the shortened irradiated time of 0.2 to 3 h in order to maintain the same supply of power. The prepared catalysts were denoted as Au/ZnO-11W, Au/ZnO-44W, Au/ZnO-88W, and Au/ZnO-176W, respectively.

The catalytic activities depended not only on the conditions of the preparation method, but also on the precipitating agent. Therefore, urea (NH_2CONH_2) was used and denoted as Au/ZnO-urea. Otherwise, ZnO- Fe_2O_3 support at the Zn:Fe atomic ratio of 5:1 was prepared by co-precipitation method. The support was dried at 110°C overnight and then calcined at 400°C for 4 h. For Au supported on ZnO- Fe_2O_3 , the catalysts were prepared by the same method as mentioned above, which was denoted as Au/ZnO- Fe_2O_3 -11W-3h. The precipitate was filtered and washed carefully with deionized warm water. Finally, the resulting solid was left to dry overnight. No catalyst pretreatment process was applied before all the reaction tests.

6.3.2 Catalyst Characterization

The X-ray powder diffraction (XRD) of the prepared catalysts was carried out on a JEOL X-Ray diffractometer system (JDX-3530) with CuK_α (1.5406 Å) X-ray source operating at 40 kV and 30 mA. The size and distribution of Au particle deposited on the supports were directly observed by a Transmission electron microscope (JEOL, JEM 2010) at an accelerating voltage of 200 kV in bright field mode. Before being transferred into the TEM chamber, the samples were dispersed in ethanol and were then dropped onto a copper grid. The average Au size diameter (d_{TEM}) was calculated from the following formula: $d_{\text{TEM}} = \Sigma(n_i d_i) / n_i$, where n_i is the number of Au particles of diameter d_i . The DR/UV-vis spectroscopy experiments

allow for checking the presence of different states of oxidation of the contained metals (which were recorded on a Shimadzu UV spectrophotometer 2550). The measurements were performed on air-exposed samples at an ambient temperature of between 200 and 800 nm. The absorption intensity was expressed using the Kubelka-Munk function. $F(R_{\infty}) = (1-R_{\infty})^2/2R_{\infty}$, where R_{∞} is the diffuse reflectance from a semi-infinite layer. Atomic Absorption Spectrometer (Varian/SpectraAA 300) was used to determine the actual Au metal content. The H₂ pulse chemisorption analysis determines the percent of Au dispersion by applying measured pulses of H₂ gas to the prepared catalysts. The amount of chemisorbed H₂ is the difference between the total amount of reactant gas injected and the amount that did not react with the active sites of the prepared catalysts. The size of each pulse of H₂ gas is determined by the loop on an operated valve.

6.3.3 PROX Reaction Testing

All catalytic activity measurements for PROX were performed in a fixed-bed U-tube micro-reactor by packing with 100 mg of the catalyst of 80–120 mesh inside. The activity was investigated at various temperatures in the range of 30 to 130°C under atmospheric pressure. The reactant gas mixture for the simulated reformat gas was composed of CO (1%), O₂ (1%), H₂ (40%), CO₂ (0–10%), and H₂O (0–10%) balanced in He with a total flow rate of 50 ml min⁻¹. The influent and effluent gases were analyzed by auto-sampling in an on-line gas chromatograph, which was equipped with a packed carbosphere column (80/100 mesh and 10 ft x 1/8 inch) and a thermal conductivity detector (TCD). The CO and O₂ conversion calculations were based on the CO and O₂ consumption, respectively. The CO selectivity was calculated by the ratio of O₂ consumption for the desired CO oxidation reaction to the total O₂ consumption.

6.4 Results and Discussion

6.4.1 Catalyst Characterization

Figure 6.1 (a–h) shows the XRD diffractograms of ZnO and the prepared catalysts. The patterns display characteristic peaks that matched perfectly with ZnO. It is clear that ZnO was not reduced under the same preparation conditions. Au (111), Au (200), and Au (311) peaks cannot be observed at 2θ of 38.10, 44.37, and 77.55°. This suggests that Au particles are highly dispersed on the surface or that the Au peaks are overlapped by zincite [28]. There is even the possibility that the Au particles were too small to be detected by the X-ray diffractometer.

Additionally, Tabakova *et al.* [29] reported that the catalytic activity of the Au supported on metal oxide catalysts relies not only on the dispersion of the Au particles, but also on the state and the structure of the supports. The TEM analysis and the Au particle size distributions shown in Figure 6.2 (a–e) demonstrated that nano-size Au particles are ultra finely dispersed (1–6 nm) on the ZnO and ZnO-Fe₂O₃ supports (The results for Au photodeposition are summarized in Table 6.1). An increase in an irradiation time from 3 to 5 h leads to a increase in the average diameter of the Au particles from 3.2 to 4.0 nm, suggesting that the difference in the contact time under irradiation has an effect on the growth of Au particles on the catalyst support.

Moreover, the Au^{δ+} on the catalyst support was reduced to Au⁰. This is confirmed by the TEM observations shown in Figure 6.2a and 6.2f, where the difference between exposed catalysts and an unexposed catalyst can clearly be seen. The mechanism of this phenomenon can be explained by the electrons in the conduction band of ZnO reduce partly Au^{δ+} to form Au⁰ under UV-vis light irradiation. Deeper studies showed that Au deposited on the ZnO surface to form the Au⁰ nano-structure, change in the Fermi level equilibration and the band structure of ZnO through shuttling photogenerated e⁻ from the ZnO to acceptors in the photodeposition process [30]. The DR/UV-vis spectra of the prepared catalysts can briefly ascertain the oxidation state of Au, which are Au⁺, Au^{δ+}, bulk Au, and Au⁰.

DR/UV-vis spectra of the prepared catalysts shows a weak band of around 520–570 nm, which is within the surface plasmon resonance band of Au⁰ (gold nanoparticles) [31]. The background noise was minimized by subtracting the ZnO spectra. Boccuzzi *et al.* [32] studied the role of Au⁰ via the investigation of the CO oxidation mechanism over the Au/ZnO by FT-IR, which concluded that CO molecules are found to be activated on the Au⁰ at both of the normal terrace sites and the borderline of the Au particles. Additionally, Au⁰ sites are able to adsorb both O₂ and CO molecules simultaneously. This action demonstrated that the direct oxidation of CO was to occur rapidly at the surface of the Au⁰ particles, while the CO oxidation between CO molecule and the surface lattice oxygen species of the catalyst support, was induced more slowly.

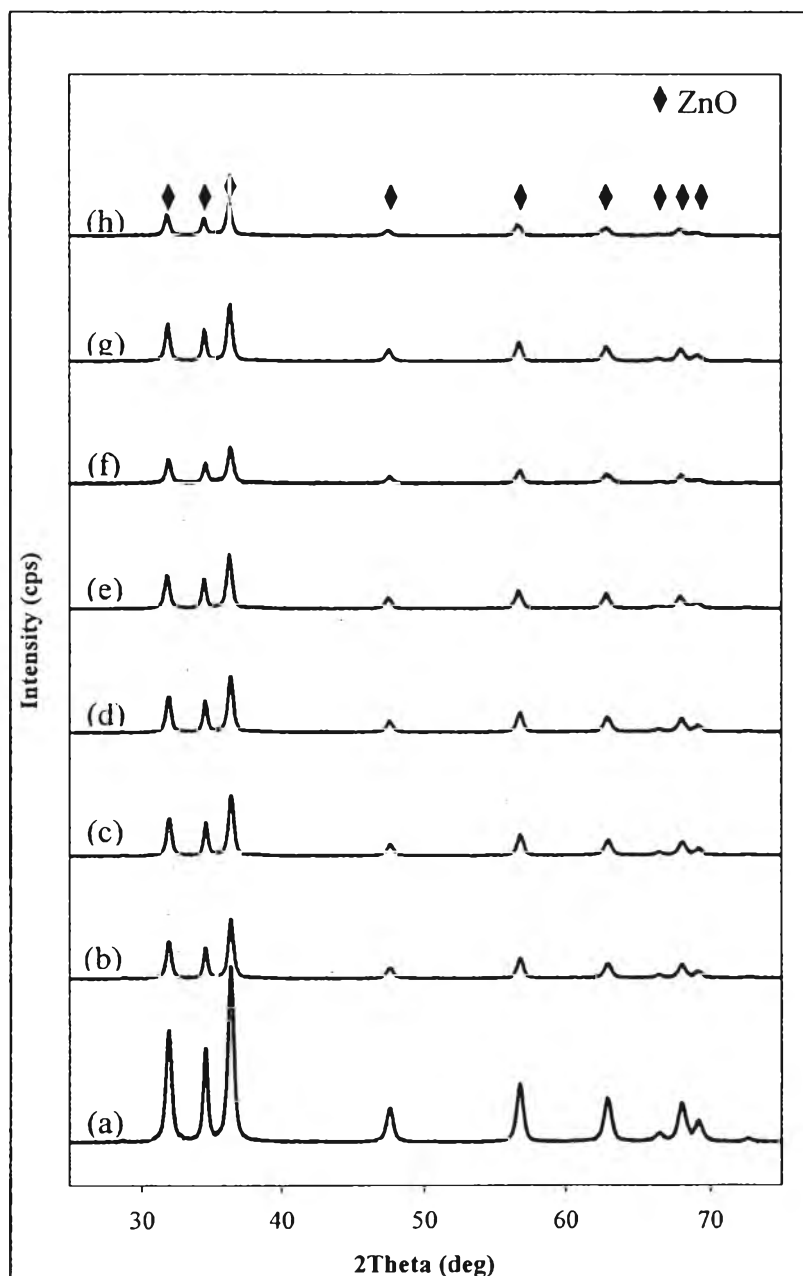


Figure 6.1 XRD diffractograms of ZnO, prepared, and spent catalysts: (a) ZnO, (b) Au/ZnO-11W-1h, (c) Au/ZnO-11W-3h, (d) Au/ZnO-11W-5h, (e) Au/ZnO-176W, (f) Au/ZnO-11W-3h_spent, (g) Au/ZnO-Fe₂O₃-11W-3h, and (h) Au/ZnO-Fe₂O₃-11W-3h_spent.

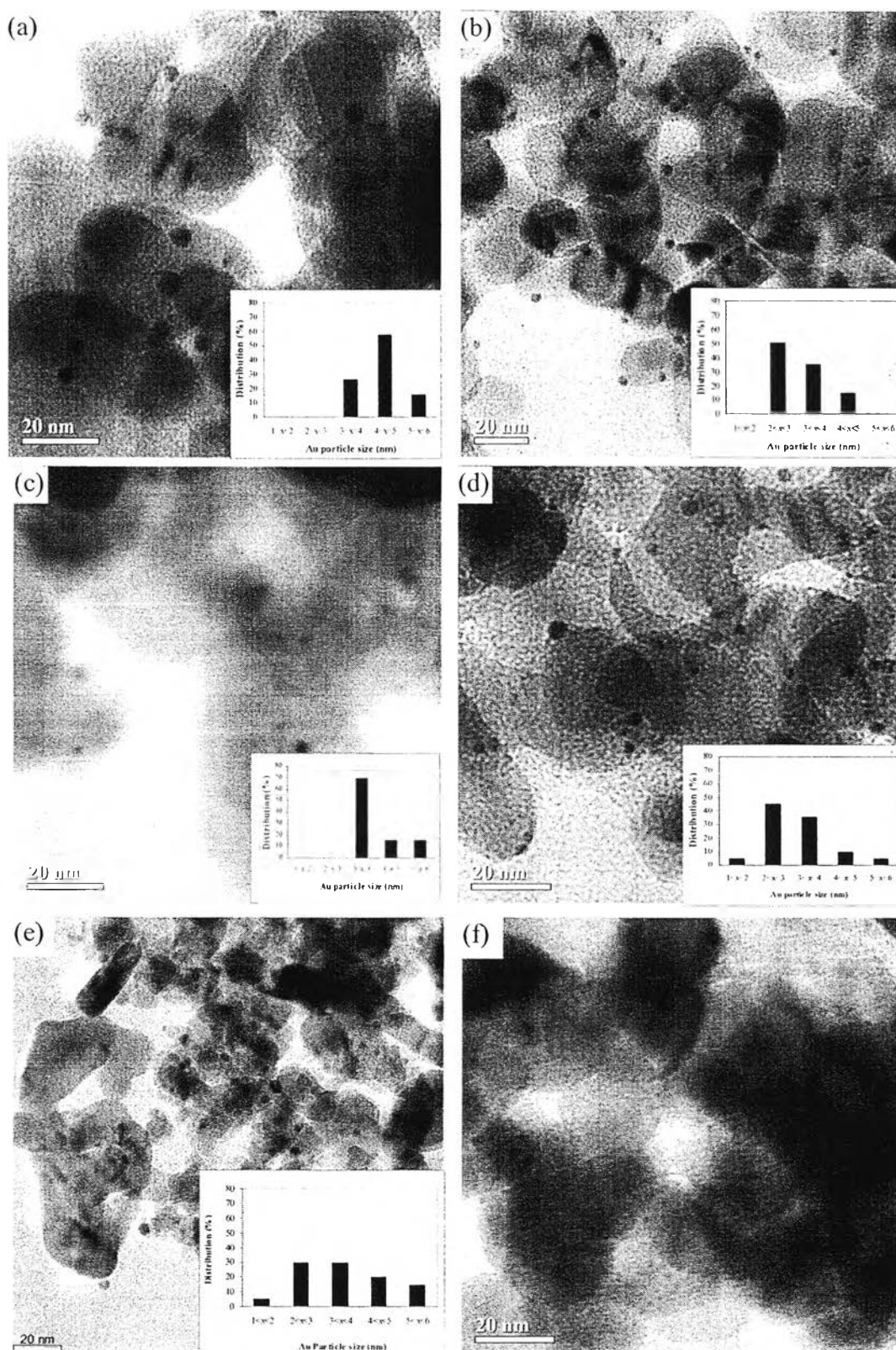


Figure 6.2 Transmission electron micrographs of the prepared catalysts: (a) Au/ZnO-11W-1h, (b) Au/ZnO-11W-3h, (c) Au/ZnO-11W-5h, (d) Au/ZnO-176W-0.2h, (e) Au/ZnO-Fe₂O₃-11W-3h, and (f) Au/ZnO-not exposed to UV-vis light.

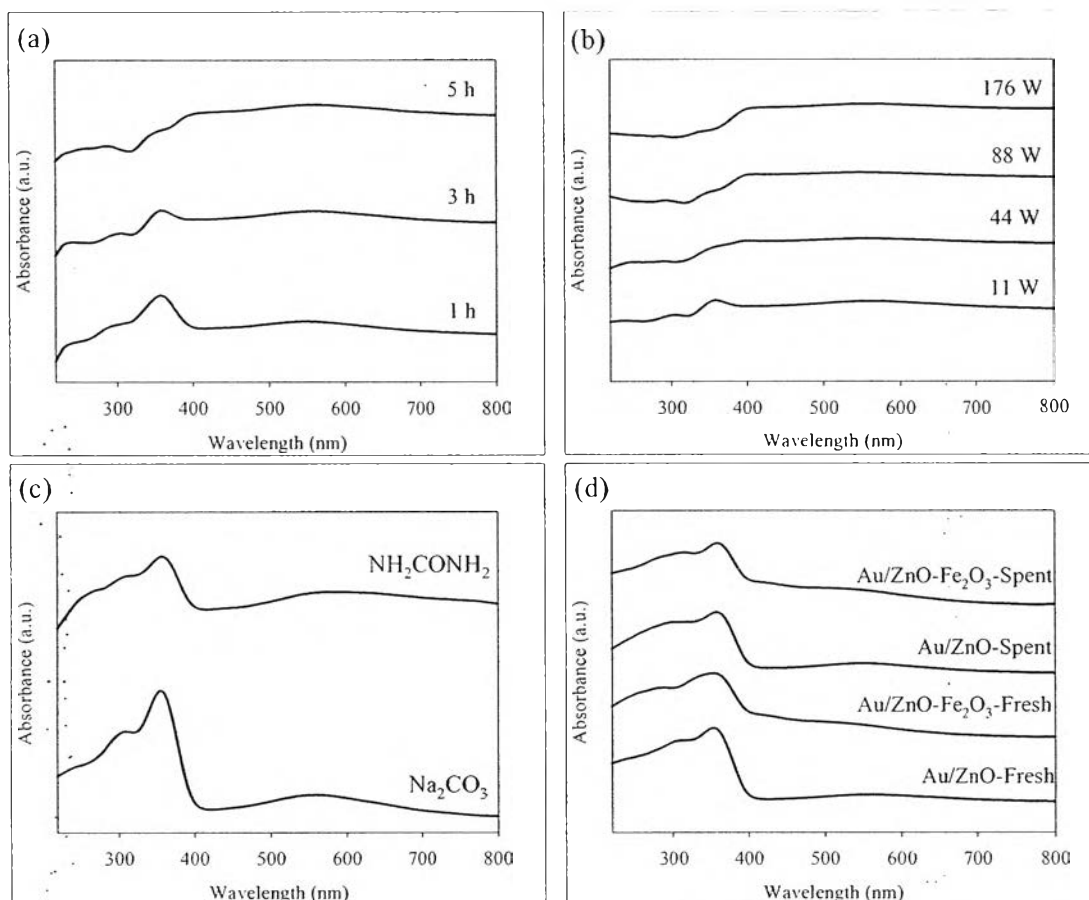


Figure 6.3 UV-vis spectras of the prepared catalysts: (a) Effect of irradiation time, (b) Effect of UV light power, (c) Effect of precipitating agent, and (d) Effect of catalyst support.

The actual amount of deposited Au on the catalyst was evaluated by AAS (Table 6.1) and the results showed that the amount of Au was noticeably lower than the calculated value. This result was due to Au loss in the preparation and/or the washing steps.

Also, it was evident that Au and metal oxide interface play an important role in the presence of PROX activity. The deposition of Au on the supports by using Na_2CO_3 is an effective method for creating smaller Au particles that result in an increase of the number of Au-oxide interfaces. These, in turn, enhanced the catalytic activity for this reaction.

Table 6.1 Characteristic of the prepared catalysts

Catalyst	Precipitating agent	Actual Au content (%atom) ^a	Degree of metal dispersion (%) ^b	Mean Au particle size (d _{TEM} , nm) ^c
Au/ZnO-11W-1h	Na ₂ CO ₃	0.37	12.23	4.4±0.68
Au/ZnO-11W-3h	Na ₂ CO ₃	0.36	14.87	3.2±0.58
Au/ZnO-11W-5h	Na ₂ CO ₃	0.41	9.49	4.0±0.80
Au/ZnO-44W	Na ₂ CO ₃	0.42	8.73	n.i.
Au/ZnO-88W	Na ₂ CO ₃	0.41	6.86	n.i.
Au/ZnO-176W	Na ₂ CO ₃	0.38	3.59	3.1±0.75
Au/ZnO-Urea	urea	0.57	8.62	n.i.
Au/ZnO-Fe ₂ O ₃ -11W-3h	Na ₂ CO ₃	0.48	5.31	3.6±1.1

^a Actual Au loading achieved by AAS.

^b Degree of metal dispersion evaluated by H₂ chemisorption.

^c Mean Au particle size achieved by TEM.

n.i. not indicated

Bocuzzi *et al.* [32] studied the role of Au⁰ via the investigation of the CO oxidation mechanism over the Au/ZnO by FT-IR, which concluded that CO molecules are found to be activated on the Au⁰ at both of the normal terrace sites and the borderline of the Au particles. Additionally, Au⁰ sites are able to adsorb both O₂ and CO molecules simultaneously. This action demonstrated that the direct oxidation of CO was to occur rapidly at the surface of the Au⁰ particles, while the CO oxidation between CO molecule and the surface lattice oxygen species of the catalyst support, was induced more slowly. The actual amount of deposited Au on the catalyst was evaluated by AAS (Table 6.1) and the results showed that the amount of Au was noticeably lower than the calculated value. This result was due to Au loss in the preparation and/or the washing steps.

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6.4.2 Effect of Irradiation Time

Because irradiation time is the most common parameter in the photodeposition method, in this section we will examine the role of irradiation time on the catalytic activity of Au/ZnO catalysts under atmospheric pressure in the temperature range of 30 to 130°C. Figure 6.4 displays the catalytic activities dependence of the 1% atom Au catalysts at different irradiation times ranging from 1 to 5 h. It is clearly seen that all catalysts exhibited an excellent CO conversion (100%) with a higher CO selectivity (~66–73%). With increasing irradiation times, there is no significant influence on the Au loading measured by AAS.

To obtain a more quantitative comparison of the amount of Au⁺, Au^{δ+}, and Au⁰ on the catalyst surface, the prepared catalysts were analyzed by DR/UV-vis. The results shown in Figure 6.3a reveals that Au⁺ and Au^{δ+} (at around 385 nm) drastically decreased with increasing irradiation time; however, the plasmon resonance of Au

nanoparticles at 550 nm increases with this particular effect, except when the catalyst was irradiated with UV-vis light for 5 h. All prepared catalysts did not show the band at 410 nm which was indicated in the bulk of Au. These results are in agreement with the TEM results (Figure 6.2 (a-e)) in that the bulk of Au did not appear on the catalyst surface.

Some researchers have suggested a role for Au^+ and $\text{Au}^{\delta+}$ but it is not clear that ionic species (Au^+ and $\text{Au}^{\delta+}$) and/or gold nanoparticles (Au^0) act as an active site for the reaction [33, 34]. Also, Hodge *et al.* [35] proposed that a mixed oxidation state for the Au was found and explained by the Bond-Thompson mechanism. By this method, CO molecules adsorb to Au^0 and are attacked by the OH^- group situated at $\text{Au}^{\delta+}$, resulting in the forming of a carboxylate group at the Au-support interface. The carboxylate is attacked by a superoxide from the support to produce CO_2 , and the resulting OH_2^- oxidizes another carboxylate, forming another CO_2 molecule.

Our observation indicates that metallic particles are the major cause for the increase in catalytic activity. In this study, Au/ZnO-11W-3h exhibited the highest catalytic activities for the PROX reaction in terms of CO selectivity, which is much higher than that of the other prepared catalysts. It provided almost 100% CO conversion, and 73% CO selectivity at 30°C. These results are probably due to the mixed oxidation states of Au in the suitable ratio presence on the support. TEM images show that nano-size Au particles homogeneously disperse on the catalyst support surface with the narrow particle size distribution. The size of Au particle at around 2–4 nm of Au/ZnO-11W-3h catalyst is preferred for the PROX at a low temperature of 30°C. In addition, the metal dispersion of Au/ZnO-11W-3h is higher than that of those prepared catalysts, as presented in Table 6.1. It is apparent that by increasing irradiation time, after this section, the irradiation time at 3 h was selected as the most suitable preparation condition for these catalysts.

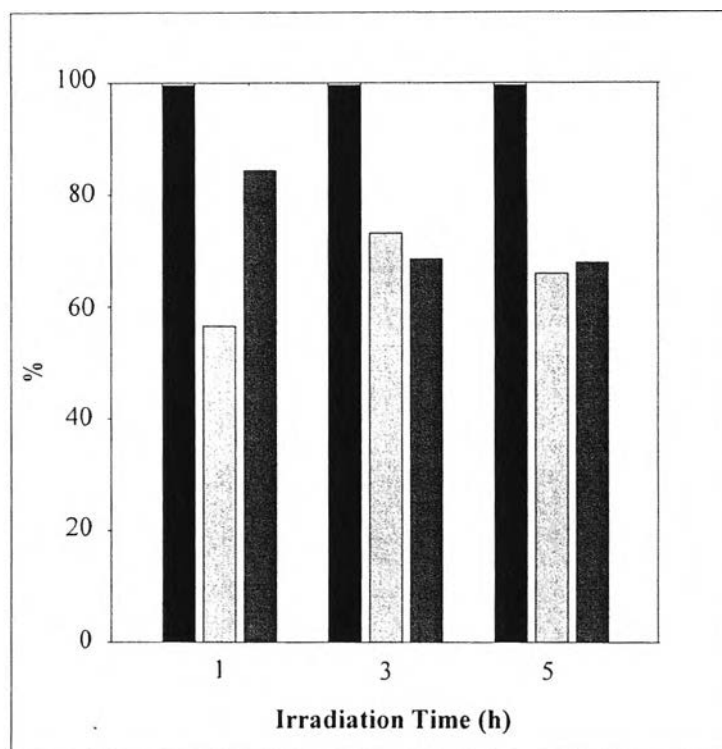


Figure 6.4 Effect of irradiation time on the Au/ZnO catalytic activities: CO conversion (■), CO selectivity (▨), and O₂ conversion (▩). The preferential CO oxidation reactions were conducted at 30°C.

6.4.3 Effect of Power of UV-vis Light

The dependence of the preferential CO oxidation on reaction temperature was studied over Au/ZnO catalysts with the difference in the power of UV-vis light in the dry simulated reformat. Figure 6.5 shows CO conversion and CO selectivity as a function of the reaction temperature. The CO conversion of all prepared catalysts reached 100% in the temperature range of 30–50°C except the Au/ZnO-176 W catalyst. At 70–120°C, the CO conversion decreases with the increasing of the reaction temperature. This suggests that the increasing of the temperature also facilitates H₂ oxidation, which is competitive with CO oxidation and the decreasing of CO selectivity.

The TEM results in Table 6.1 show that the Au particle size was not affected by the appliance of the high power of UV-vis light for preparation of the catalysts. Although, the Au particle size of Au/ZnO-176W was close to its Au/ZnO-

11W, the metal dispersion of Au/ZnO-11W is higher than that of Au/ZnO-176W, which suggested that the higher power of UV-vis lamp leads to a coalescing of an Au particle on the catalyst support. Furthermore, the size distribution in the prepared catalyst, which irradiated under the UV-vis light at the power of 11 W, has a narrower size distribution than that of the catalyst that was exposed in 176 W. The DR/UV-vis spectra of the prepared catalysts (Figure 6.3b) revealed that Au^+ and $\text{Au}^{\delta+}$ (at around 385 nm) decreased with increasing the power of UV-vis light. As a consequence, with the effect of irradiation time, the presence of a mixed oxidation state of Au in the Au/ZnO-11W catalyst exhibits a more impressive performance in catalytic activities than other catalysts.

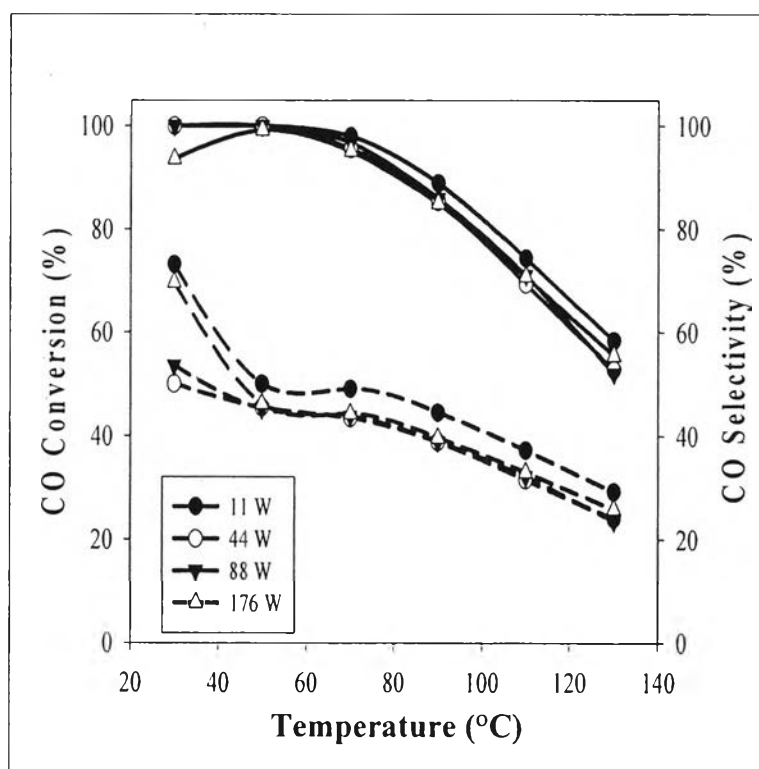


Figure 6.5 Catalytic activities of the prepared catalysts on the effect of power of UV-vis light; 11 W (●), 44 W (○), 88 W (▼), and 176 W (△): CO conversion (—) and CO selectivity (---).

6.4.4 Effect of Precipitating Agent

Since the type of the precipitating agent significantly affects the particle size of Au, it is expected that the type of precipitating agent will also have an influence on the catalytic activity. To further investigate the differences in catalytic activity between Au photodeposition on ZnO support using different precipitating agents, experiments of Au/ZnO-11W-3h prepared by Na_2CO_3 and NH_2CONH_2 (urea) were performed. At 30°C , the CO conversion of Au/ZnO- Na_2CO_3 was 100%, while the Au/ZnO-urea catalyst achieved only 78% CO conversion, as illustrated in Figure 6.6. In addition, CO selectivity profiles of the prepared catalysts also followed a similar trend in that the CO selectivity decreased with the raising of the reaction temperature. The observed effect of precipitating agent type is rather complex. We expect this to be due to the different concentrations of $\text{Au}^{\delta+}$ and Au^0 particles on the surface of catalysts, estimated by the DR/UV-vis results in Figure 6.3c. Furthermore, the Au/ZnO- Na_2CO_3 (11W, 3h) shows a higher degree of metal dispersion than Au/ZnO-urea, suggesting that the metal dispersion and the amount of $\text{Au}^{\delta+}$ and Au^0 depended on the nature of the precipitating agent, presented in Table 6.1. Using Na_2CO_3 as a precipitating agent significantly improved the performance of the catalyst in terms of CO conversion at a low temperature range of $30\text{--}50^\circ\text{C}$. Based on those results, Na_2CO_3 was selected as a suitable precipitating agent for preparing the Au/ZnO catalyst via the photodeposition under the UV-vis light irradiation.

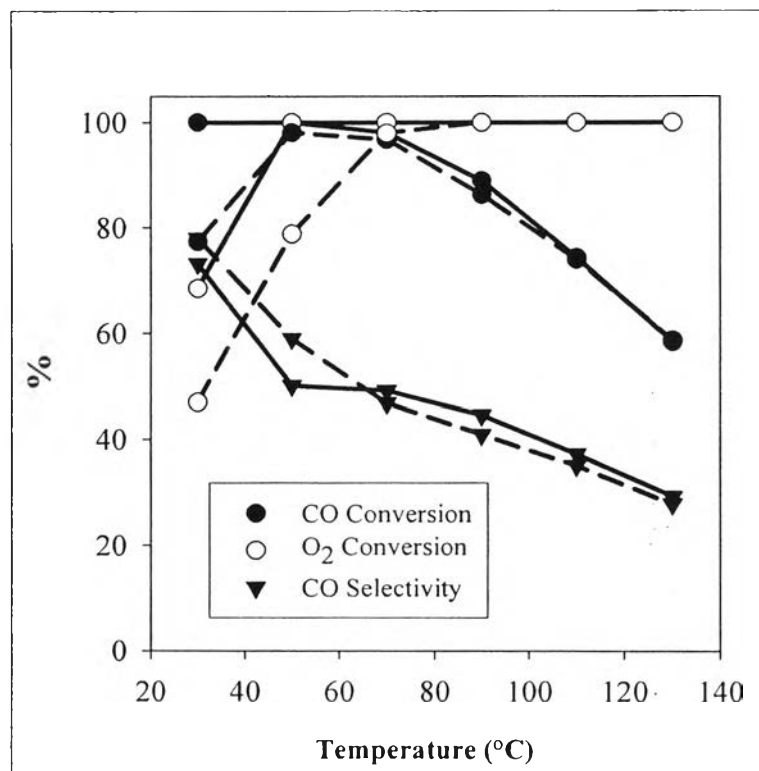


Figure 6.6 Catalytic activities of the prepared catalysts on the effect of precipitating agent; CO conversion (●), O₂ conversion (○), and CO selectivity (▼): Na₂CO₃ (—) and urea (---).

6.4.5 Effect of Mixed-Oxide Catalyst Support

The nature of the support is one of the important parameter to obtain the active catalyst. It might therefore be expected that a Au supported on Fe₂O₃, reducible oxide support that facilitates the active O₂, was more active than any other reducible oxide support for CO oxidation [33, 36]. Qiao and Deng showed that ferric hydroxide supported Au catalysts prepared without any pretreatment exhibited an excellent environment for CO oxidation in air, and also for PROX in the presence of H₂ [37]. Thus, the 1%Au/ZnO-Fe₂O₃ at a ratio of ZnO to Fe₂O₃ is 5 to 1 was prepared and investigated to determine their performance. It was found that the CO conversion of Au/ZnO and Au/ZnO-Fe₂O₃ reached 100% at 30–50°C. The CO selectivity of a Au/ZnO catalyst was higher than that of the Au/ZnO-Fe₂O₃ catalyst in all of the tested temperature ranges, as shown in Figure 6.7. We therefore suggest that Fe₂O₃ provides sufficient dissociated O₂ to enhance both the CO and H₂

oxidation. However, the catalytic performance of the Au/Fe₂O₃ in this reaction is strongly related to the support phase, being sensitive to the microcrystalline structure and the oxidation state of the Fe₂O₃, as explained by Scirè *et al.* [38].

Additionally, XRD results revealed that the phase of ZnFeO₄ present in the crystalline structure of ZnO-Fe₂O₃. It suggested that some of the Fe₂O₃ had been incorporated in ZnO lattice, resulting in an improvement of its oxygen mobility and thermal stability. The addition of Fe₂O₃ also had an influence on the electronic state of supported Au catalysts. The DR/UV-vis results (Figure 6.3d) revealed that the plasmon resonance band of Au/ZnO was more visible than that of Au/ZnO-Fe₂O₃.

In 2006, Hutchings *et al.* [39] studied the role of Au cation over Au/ α -Fe₂O₃ on the CO oxidation reaction. They proposed that Au⁺ and Au ^{δ +} play a crucial role in catalyzing that reaction at 25°C and also noted that the most active catalysts contain more cationic Au. They further concluded that the least active catalyst contained more Au⁰.

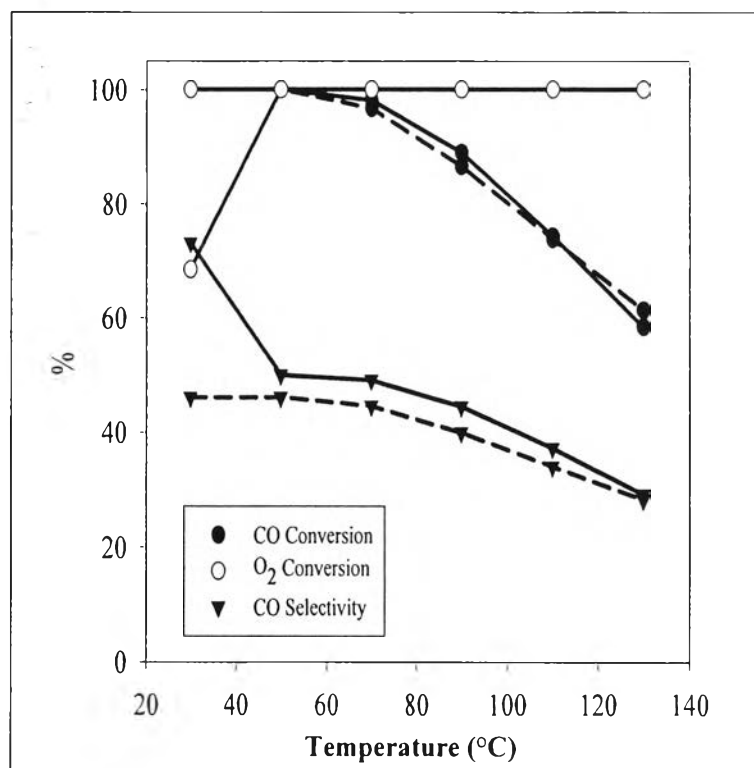


Figure 6.7 Catalytic activities of the prepared catalysts on the effect of catalyst support; CO conversion (●), O₂ conversion (○), and CO selectivity (▼): Au/ZnO (—) and Au/ZnO-Fe₂O₃ (---).

6.4.6 Influence of CO₂ and H₂O on Catalytic Activities

Within the range of reaction temperatures investigated, the catalysts exhibited the highest activity at 30°C. Therefore, the effect of CO₂ and H₂O presence in the feedstream on the catalytic performance of Au/ZnO-11W-3h and Au/ZnO-Fe₂O₃-11W-3h catalysts was investigated at a constant temperature (30°C) with time on stream. The results shown in Figure 6.8 illustrate that the catalytic activities of both catalysts for the PROX reaction, in the absence of CO₂ and H₂O in the simulated stream, are stable without significant loss of CO conversion and CO selectivity.

With the addition of H₂O, the CO selectivity of both catalysts was improved dramatically. Boccuzzi *et al.* [32] proposed this promotional effect. They found that the Au/ZnO catalyst could produce atomic hydrogen via CO-H₂O co-adsorption experiments. From this result, we suggest that the H₂O molecule could promote the water gas shift reaction over the Au/ZnO and Au/ZnO-Fe₂O₃ catalysts. The addition of CO₂ would then lead to a severe reduction in the catalytic activities. This effect can be explained by the accumulation of carbonate-like species on the catalyst surface. This in turn then blocks the active sites for the PROX reaction [40,41].

Au/ZnO-Fe₂O₃-11W-3h showed improved resistance towards deactivation more than that on Au/ZnO caused by the presence of CO₂ in the simulated stream. Furthermore, the catalytic activities of Au/ZnO improved even further with the addition of H₂O to the simulated stream. Daté *et al.* [42] suggested that the H₂O could attack and decompose the carbonate intermediate; moreover, the presence of OH⁻ group extends the lifetime of the catalyst and prevents the deactivation by carbonate-like species accumulation.

On the other hand, the Au/ZnO catalyst exhibited high activity, good selectivity, and high stability at low temperatures in the simulated stream with and without CO₂ and H₂O. Based on those results, it is seen that the CO₂ has stronger influence on the catalytic performance of both the Au/ZnO and Au/ZnO-Fe₂O₃ catalysts than the H₂O. To compare the structures of the spent catalysts after testing in the simulated stream, the catalysts were analyzed by XRD and UV-vis techniques. There was a slight deviation in the structure of the spent catalysts, as seen in Figure 6.2 (2f and 2h) and Figure 6.3d.

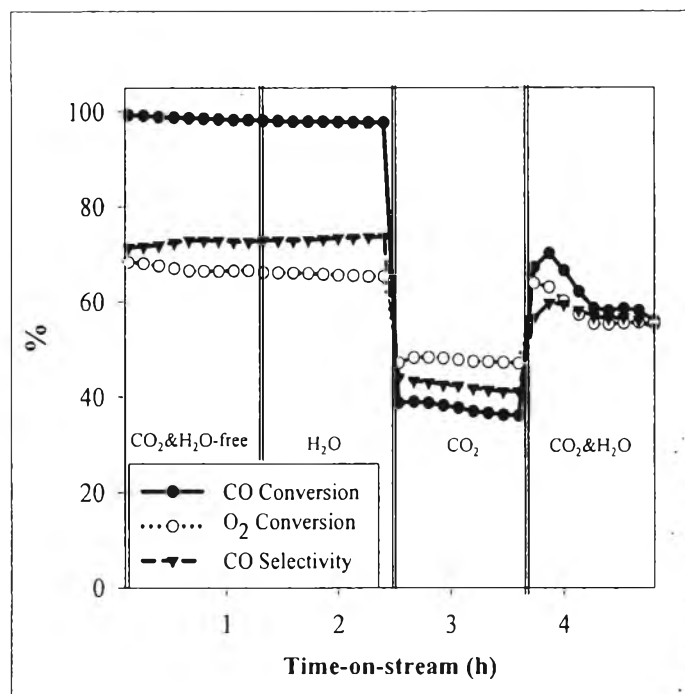


Figure 6.8 The effect of CO₂ and H₂O on the catalytic activities of Au/ZnO catalyst. The reaction was tested at constant temperature of 30°C and monitored with time on stream.

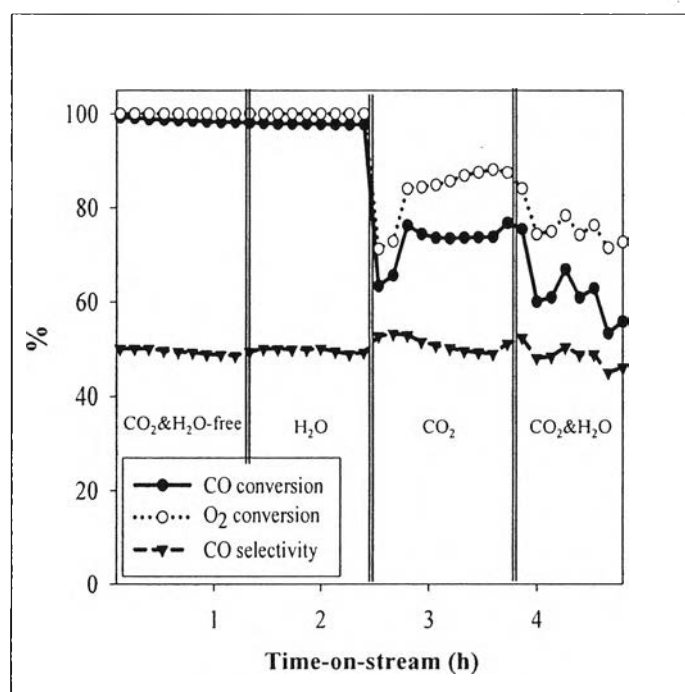


Figure 6.9 The effect of CO₂ and H₂O on the catalytic activities of Au/ZnO-Fe₂O₃ catalyst. The reaction was tested at constant temperature of 30°C and monitored with time on stream.

6.5 Conclusions

Our results showed that Au/ZnO and Au/ZnO-Fe₂O₃ catalysts can be successfully prepared via the photodeposition under UV-vis light irradiation in order to obtain Au particles that are in nanometer size (1–6 nm). Moreover, it revealed that the prepared catalysts (without heat treatment step) exhibited higher catalytic activity, where it achieves a complete conversion of the CO at 30°C and 50–73 % CO selectivity. The presence of a mixed oxidation state of Au is the active site for the PROX reaction. Na₂CO₃ can be used as an appropriate precipitating agent for the Au photodeposition under UV-vis light irradiation. In addition, the mixed metal oxide support (ZnO-Fe₂O₃) can reduce the influence of CO₂, which is present in the simulated stream.

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6.7 References

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