



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Au/ZnO Catalysts

In this work, Au/ZnO catalysts prepared by a deposition-precipitation (DP) were characterized by several techniques. The catalysts were tested in methanol steam reforming reaction and the influences of reaction parameters, such as Au content, calcination temperature, gas pretreatment and reaction temperature on the catalytic performance of Au/ZnO catalyst were studied in detail.

The catalytic activity tests were carried out in a vertical pyrex glass micro-reactor by packing with 100 mg catalyst of 80-120 mesh inside. The activity was investigated at varied temperature in the range of 250-450°C under atmospheric pressure. The characterization results from several techniques, including XRD, TEM, and BET of the prepared catalysts will be used to explain the catalytic activity and selectivity of the prepared catalysts in this part.

4.1.1 Effect of Au Content and Calcination Temperature

For the effect of Au Content, the Au/ZnO catalysts were prepared by a deposition-precipitation technique with various Au contents of 1%, 3% and 5% atom. All of these catalysts were calcined at 400°C for 4 hours and pretreated with hydrogen at 400°C for 1 hour. Figure 4.1 shows the methanol conversion and hydrogen selectivity in steam reforming of methanol at 250-450°C over ZnO and Au/ZnO catalysts with different Au contents.

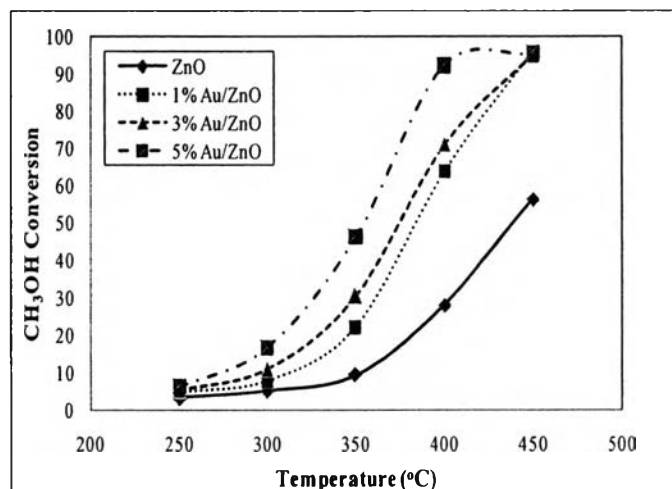
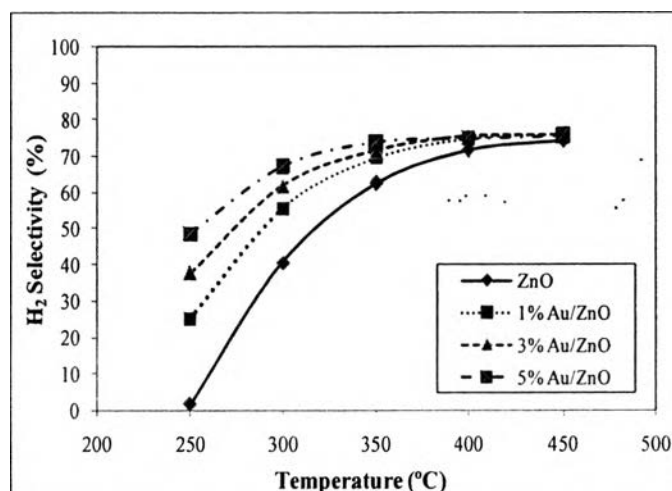
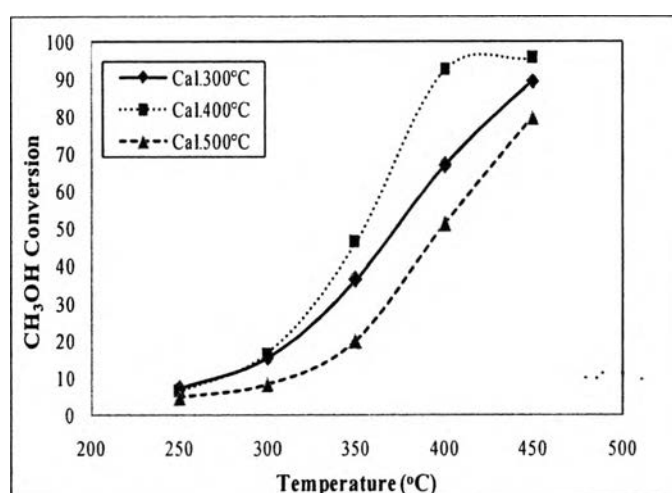
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.1 Effect of Au content on the activity and selectivity of Au/ZnO catalysts.

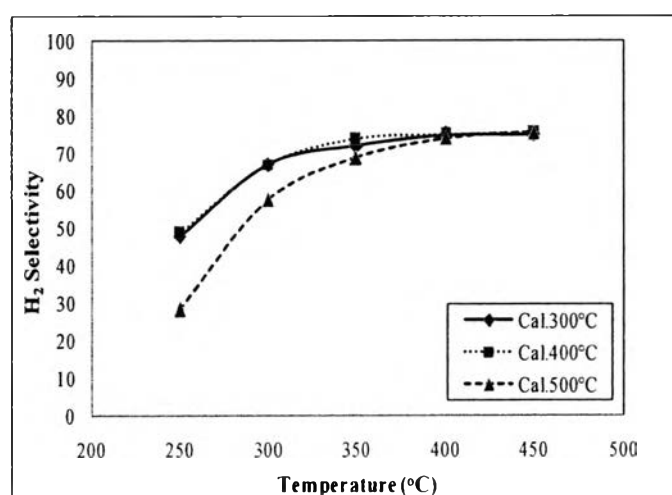
It can be seen that a remarkable improvement of catalytic activity in terms of methanol conversion and hydrogen selectivity was observed by the addition of Au. With increasing Au content, the methanol conversion and hydrogen selectivity were increased until it reached the maximum values of 95.58% and 75.53% at 450°C, respectively. Wang *et al.*, (2006) studied the selective oxidation of CO in hydrogen-rich mixtures on Au supported on ZnO catalysts. They found that the catalytic activity of Au/ZnO was improved slightly with increasing Au content until 1.5 wt.%; however, CO selectivity was constant and declined after the Au content exceeded 1.5 wt.%.

After this part, Au content of 5% atom was selected as the appropriate condition for Au/ZnO catalyst.

For the effect of calcination temperature, the 5% Au/ZnO catalyst were prepared by a deposition-precipitation technique with various calcination temperatures of 300, 400 and 500°C. All of these catalysts were pretreated with hydrogen at 400°C for 1 hour.



(a) CH₃OH Conversion



(b) H₂ Selectivity

Figure 4.2 Effect of calcination temperature on the activity and selectivity of Au/ZnO catalysts.

Figure 4.2 (a-b) shows the effect of calcination temperature on the activity and selectivity of Au/ZnO catalysts. It is clearly seen that calcination temperature significantly influenced on the catalytic performance of Au/ZnO catalyst for this reaction. Both methanol conversion and hydrogen selectivity increased as the calcination temperature increased; however, when the calcination temperature up till 400°C, its activity decreased. Wang *et al.* (2006) reported that the increasing of calcination temperature would change Au₂O₃ into Au, then the activity and selectivity of 5% Au/ZnO catalysts would be expected to increase with increasing calcination temperature.

After this part, calcination temperature of 400°C was selected as the appropriate condition for Au/ZnO catalyst.

4.1.1.1 X-ray Diffraction (XRD)

The XRD patterns of Au/ZnO catalysts prepared by a deposition-precipitation method at different Au contents (1%, 3% and 5% atom) and different calcination temperatures (300, 400 and 500°C) are shown in Figure 4.3. Almost the diffraction peaks of Au/ZnO can be assigned to pure ZnO. The presence of Au in the face-centered cubic crystal size at 2θ of 38.10° detected for only 5% Au/ZnO catalysts. For all samples, the XRD analysis did not reveal the presences of any oxidic Au species at 2θ of 25.5°, 30.2° and 32.5°. The XRD patterns of all samples were almost the same but have a little difference in term of peak intensity. The main diffraction peaks at 2θ of 31.77°, 34.42° and 36.25° were corresponding to ZnO (100), ZnO (002) and ZnO (101) planes for CuK α (1.5406 Å) radiation, respectively. The metallic Au species attributed to Au (111), Au (200) and Au (311) peaks are observed at 2θ of 38.10°, 44.37° and 77.55° for only 5% Au/ZnO catalysts, suggesting that Au particles are highly dispersed on the surface, or the Au peaks are overlapped by zincite (Yang *et al.*, 2007), or the Au particles are too small to be detected by this instrument. TEM technique was subsequently employed to confirm the Au particle size in the prepared catalysts. For 5% Au/ZnO calcined at 500°C, the metallic Au peaks are obviously presented and this result agrees well with the average particle sizes of this catalyst, as confirmed by TEM technique which the particle sizes are larger than 5 nm. The presence of Au and ZnO peaks indicated the existing species in

the prepared catalysts and the crystallite size of these species were calculated by the Scherrer Equation, as summarized in Table 4.1.

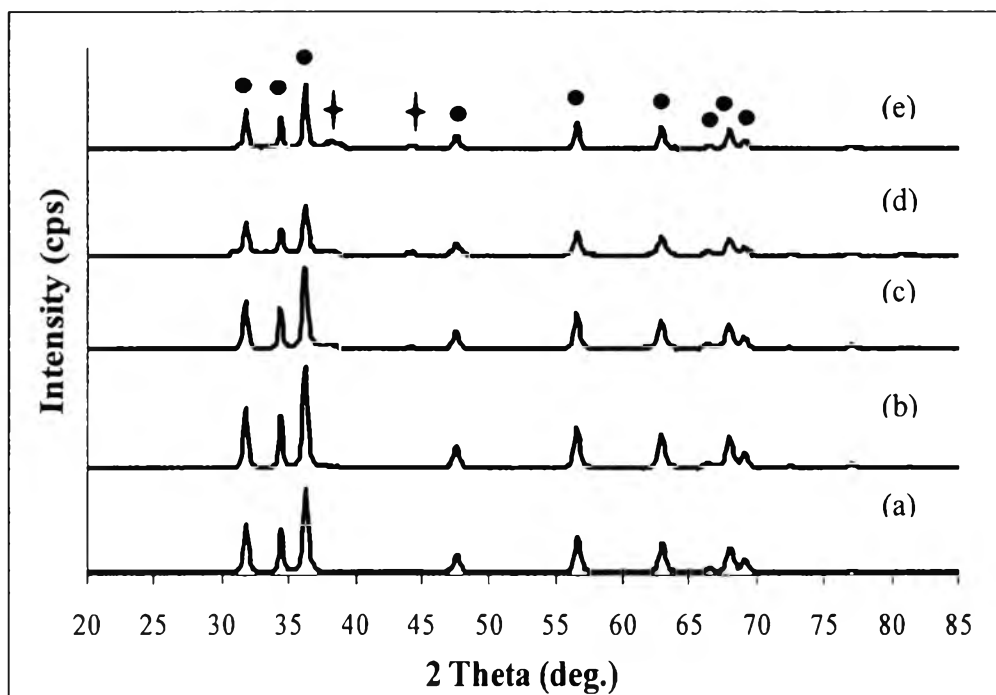


Figure 4.3 XRD patterns of the prepared Au/ZnO catalysts at various Au content and calcination temperature: (●) ZnO; (†) Au; (a) 1% Au/ZnO, calcined at 400°C; (b) 3% Au/ZnO, calcined at 400°C; (c) 5% Au/ZnO, calcined at 300°C; (d) 5% Au/ZnO, calcined at 400°C; (e) 5% Au/ZnO, calcined at 500°C.

Table 4.1 The Au and ZnO crystallite sizes of the prepared Au/ZnO catalysts

Catalysts	Crystallite sizes (nm)				
	ZnO (100)	ZnO (002)	ZnO (101)	Au (111)	Au (200)
1% Au/ZnO, Calcined at 400°C	20.24	24.45	19.15	< 5	< 5
3% Au/ZnO, Calcined at 400°C	21.17	24.82	19.34	< 5	< 5
5% Au/ZnO, Calcined at 400°C	20.34	23.22	19.36	< 5	< 5
5% Au/ZnO, Calcined at 300°C	21.39	25.34	19.16	< 5	< 5
5% Au/ZnO, Calcined at 500°C	23.19	25.19	22.64	8.10	8.14

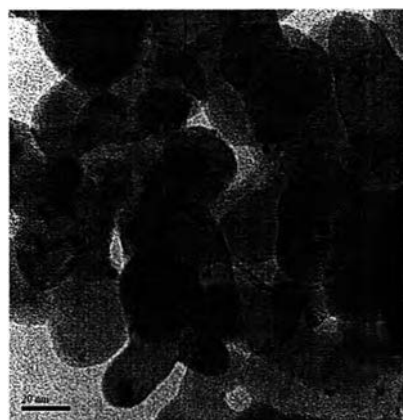
From Table 4.1, it was found that the crystallinity of the ZnO and Au phases were not much difference among the prepared catalysts calcined at 300 and 400°C. However, the catalyst calcined at 500°C had the crystallite sizes of ZnO and Au larger than the others, suggesting that at high calcination temperatures, the sintering effect could occur. Therefore, ZnO and Au crystallites were agglomerated to form the larger sizes. This sintering effect is in accordance with the TEM images in Figure 4.4 (e).

4.1.1.2 Transmission Electron Micrograph (TEM)

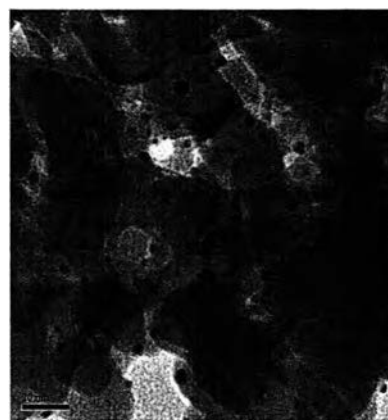
The catalytic activity of supported Au catalysts strongly depends on the Au particle size. The particle size of Au on the metal oxide supports can be controlled by the selection of a suitable Au content and suitable calcination temperature. Therefore, it is essential to study the effect of Au content and calcination temperature on the average Au particle size and particle size distribution by using TEM analysis. Figure 4.4 shows the TEM images of Au/ZnO catalysts and all Au particles are clearly observed. Deposited Au particles appeared as small black spots in the TEM micrograph and seem to be well dispersed on the surface of ZnO support.

The TEM images of the Au/ZnO catalysts with various Au contents (1%, 3% and 5% atom) are presented in Figure 4.2 (a-c). The mean particle size of Au of Au/ZnO catalysts with Au contents of 1%, 3% and 5% atom were 3.46, 3.69 and 3.96 nm, respectively. With increasing the Au content, a slight increase in Au particle size was observed. In this present work, the increasing in methanol conversion and hydrogen selectivity are related with increasing of Au particles size, as confirmed by Figure 4.1 (a-b). Therefore, it can be suggested that a large size of Au particle on the Au/ZnO catalyst was preferred for methanol steam reforming reaction.

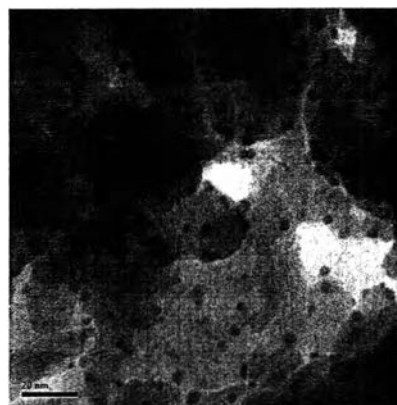
For the catalysts calcined at 300, 400 and 500°C (Figure 4.4 (c-e)), the mean particle sizes were 3.67, 3.96 and 6.59 nm, respectively. This result clearly indicated that at a higher calcination temperature, the sizes of Au particles were increased. Especially, the catalyst calcined at 500°C has the highest average Au particle size, suggesting that at this temperature the agglomeration of Au particles occurred to become larger due to the sintering effect. From this result it can be indicated that the decreasing of methanol conversion and hydrogen selectivity at the calcination temperature 500°C affected from the sintering effect of Au particles.



(a) 1% Au/ZnO, Calcined at 400°C



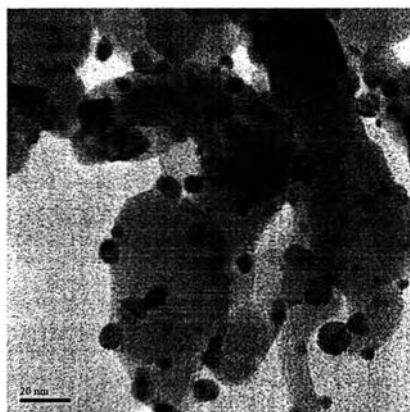
(b) 3% Au/ZnO, Calcined at 400°C



(c) 5% Au/ZnO, Calcined at 400°C



(d) 5% Au/ZnO, Calcined at 300°C



(e) 5% Au/ZnO, Calcined at 500°C

Figure 4.4 TEM images of Au/ZnO catalysts at various Au contents and calcination temperatures.

The comparison of Au particle size for Au/ZnO catalysts at different Au contents and calcination temperatures was summarized in Table 4.2.

Table 4.2 Comparison of Au particle sizes for Au/ZnO catalysts at different Au contents and calcination temperatures from XRD and TEM analysis

Catalysts	Au (111) (nm)*	Au (200) (nm)*	Au particle size (nm)**
1% Au/ZnO, Calcined 400°C	< 5	< 5	3.46 ± 0.95
3% Au/ZnO, Calcined 400°C	< 5	< 5	3.69 ± 1.00
5% Au/ZnO, Calcined 400°C	< 5	< 5	3.96 ± 0.72
5% Au/ZnO, Calcined 300°C	< 5	< 5	3.67 ± 0.89
5% Au/ZnO, Calcined 500°C	8.10	8.14	6.59 ± 2.51

* as measured by XRD, ** as measured by TEM

It was found that the particle sizes of the prepared Au/ZnO catalysts from TEM analysis were close to the crystallite sizes that determined by the XRD measurement, calculated from the half-width of the main peak (Au (111) and Au (200)) according to the Scherrer Equation.

4.1.1.3 Surface Area Measurement (BET)

The surface areas of the Au/ZnO catalysts with various Au contents of 1%, 3%, 5% atom are summarized in Table 4.3. The BET surface areas showed a slight decrease of total surface area after adding the Au on the catalysts. However, when the Au content was increased, there is no significant difference in BET surface areas.

Table 4.3 BET surface areas of ZnO and Au/ZnO catalysts

Catalysts	BET surface area (m²/g)
ZnO	37.39 ± 0.03
1% Au/ZnO, calcined 400°C	32.18 ± 0.01
3% Au/ZnO, calcined 400°C	32.23 ± 0.01
5% Au/ZnO, calcined 400°C	32.46 ± 0.05

4.1.2 Effect of Catalyst Pretreatment

The pretreatment of catalyst is very important for many chemical reactions. The different pretreatment will provide different state of Au catalysts. It is of interest to investigate the effect of pretreatments on the catalytic activity of the 5% Au/ZnO catalyst, which are H₂ reduction at 400°C and O₂ oxidation at 200°C for 1 hour. The catalyst would be fully Au metallic form for H₂ pretreatment and partial Au metallic form for O₂ pretreatment. The effect of catalysts pretreatment on the activity and selectivity of 5% Au/ZnO catalyst are shown in Figure 4.5 (a-b).

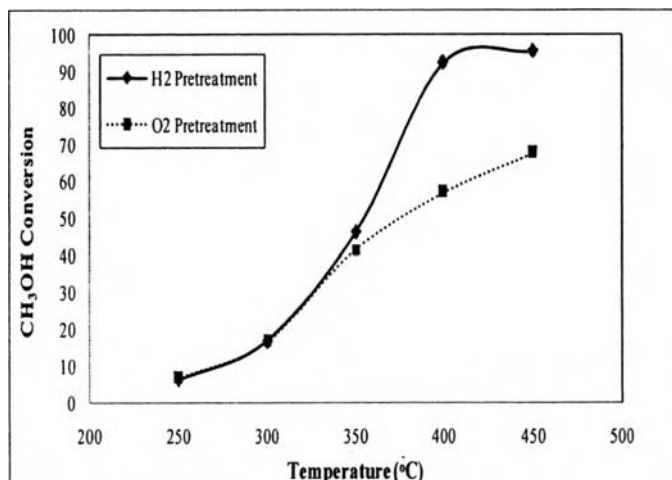
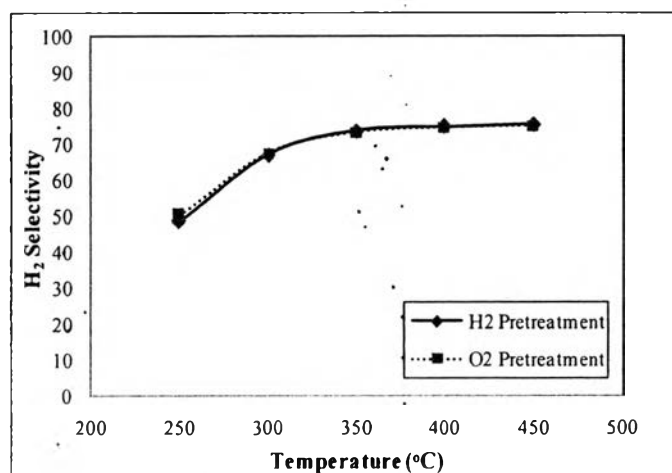
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.5 Effect of catalyst pretreatment on the activity and selectivity of Au/ZnO catalysts.

It can be observed that the methanol conversion was strongly dependent on pretreatment conditions, especially at high temperatures. It shows that H₂ pretreated achieved a higher maximum methanol conversion than O₂ pretreated catalyst. The methanol conversion increased with increasing temperature reaching a maximum, which was 95.58% for H₂ pretreated catalyst and 67.79% for O₂ pretreated catalyst at 450°C, respectively. However, the influence of pretreatment on the H₂ selectivity was, instead, negligible. The H₂ selectivity was being only related to the reaction temperature.

After this part, pure H₂ pretreatment at 400°C for 1 hour was selected as the appropriate pretreatment condition for this method.

4.1.2.1 X-ray Diffraction (XRD)

The XRD patterns of Au/ZnO catalysts prepared by a deposition-precipitation method at different gas pretreatment (O₂ pretreatment and H₂ pretreatment) are shown in Figure 4.6. For all samples, the XRD pattern presence Au in the face-centered cubic crystal size and ZnO in hexagonal crystal size. The main diffraction peaks at 2θ of 31.77°, 34.42°, 36.25° and 38.10° were corresponding to ZnO (100), ZnO(002), ZnO(101) and Au(111) planes for CuK α (1.5406 Å) radiation, respectively. The XRD patterns of all samples were almost the same but have a significant difference in term of metallic Au peak at 38.10°, H₂ pretreatment has the highest intensity of metallic Au peak while O₂ pretreatment has the lowest intensity of metallic Au peak. In this present work, the increasing of methanol conversion and hydrogen selectivity are related with increasing of intensity of metallic Au peak. Therefore, it indicated that after H₂ pretreatment the catalyst would be fully Au metallic form and enhanced the methanol steam reforming reaction. From this result, it can be concluded that, gas pretreatment affect to the crystalline structure of the prepared catalyst and affected to the activity and selectivity of this catalyst in methanol steam reforming reaction.

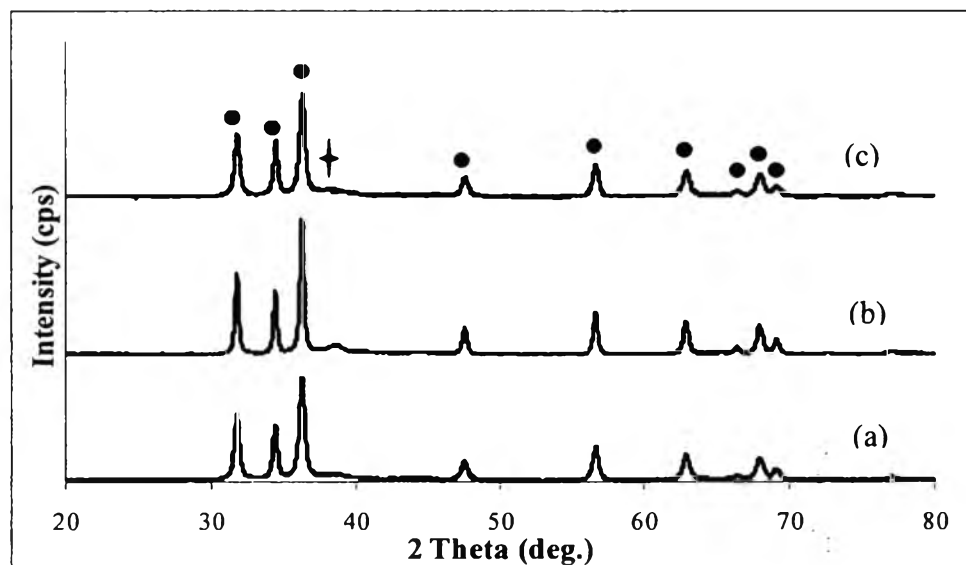


Figure 4.6 XRD patterns of the prepared Au/ZnO catalysts: (●) ZnO; (◆) Au; (a) fresh catalyst; (b) H₂ pretreatment; (c) O₂ pretreatment.

4.1.3 Effect of Reaction Temperature

The 5% Au/ZnO catalysts prepared by a deposition-precipitation technique, calcined at 400°C, and pretreated with hydrogen at 400°C for 1 hour were used to study in this part. The reaction temperature was varied in the range of 250-450°C.

Figure 4.7 (a-b) shows the activity and selectivity of 5% Au/ZnO catalyst versus temperature. When the reaction temperature was increased, there was an increase in both methanol conversion and hydrogen selectivity. Methanol conversion increased from 6.35 to 95.58% and hydrogen selectivity increased from 48.49 to 75.53% while the reaction temperature increased from 250 to 450°C. There was no CO detected at 350°C. However, at high temperatures, a trace amount of CO was detected. The CO selectivity (~0-0.93%) is very low throughout the temperature ranges (350-400°C). The CO selectivity is relatively low compared to the amount of CO produced over Cu-based catalysts (Papavasiliou *et al.*, 2007) and Pd-based catalysts (Karim *et al.*, 2006).

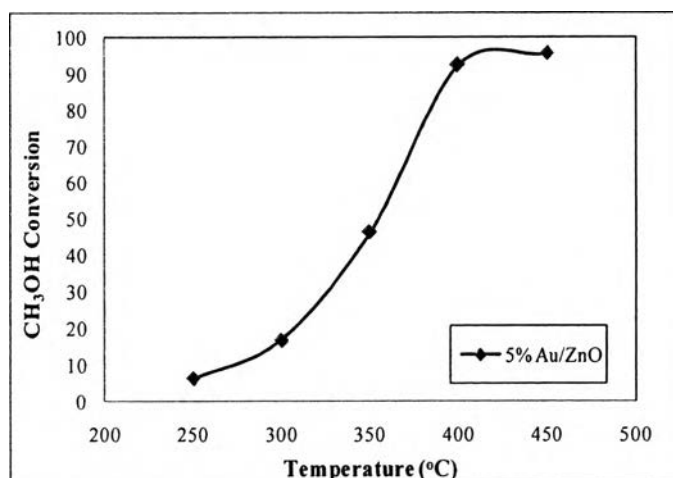
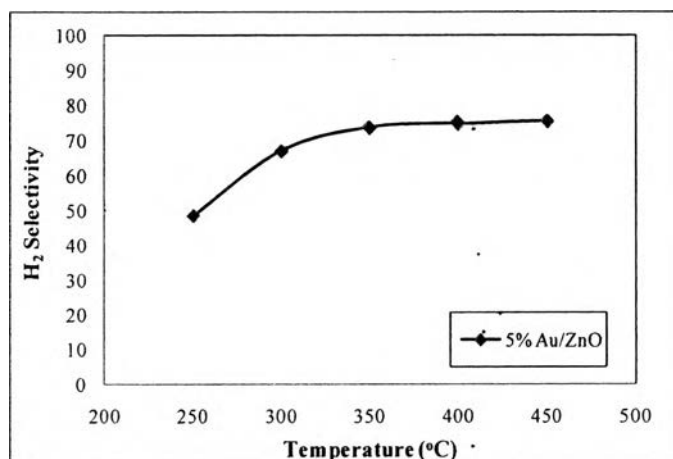
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.7 Effect of reaction temperature on the activity and selectivity of Au/ZnO catalyst.

4.1.4 Deactivation Test of the Au/ZnO Catalyst

The catalytic stability of 5% Au/ZnO catalyst calcined at 400°C for 4 hours and pretreated with hydrogen, which showed the maximum CH₃OH conversion and H₂ selectivity, was tested at the constant temperature of 450°C. As can be seen from Figure 4.8, this catalyst exhibited a stable catalytic performance during 24 hours of testing time.

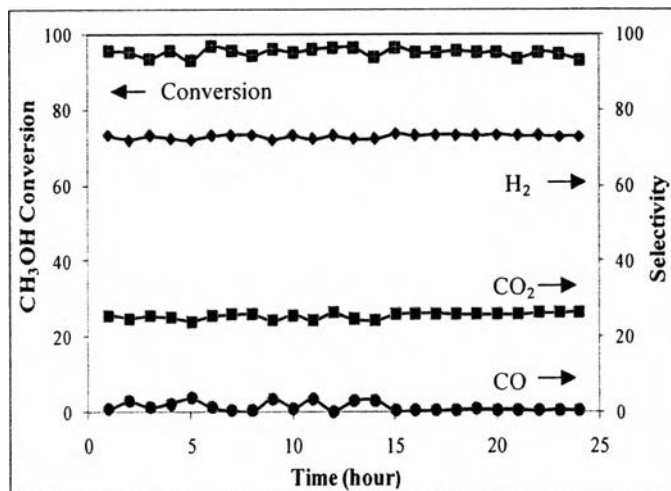


Figure 4.8 Deactivation test of the Au/ZnO catalyst at the constant temperature of 450°C.

4.2 Au/ZnO-Fe₂O₃ Catalyst

In this part, the Au/ZnO-Fe₂O₃ catalysts prepared by a deposition-precipitation (DP) were characterized by several techniques. The catalysts were tested in methanol steam reforming reaction. Moreover, the influences of ZnO-Fe₂O₃ ratio, Au content, calcination temperature, gas pretreatment, and reaction temperature on the catalytic performance of Au/ZnO-Fe₂O₃ catalyst were studied in detail.

The catalytic activity tests were carried out in a vertical pyrex glass micro-reactor by packing with 100 mg catalyst of 80-120 mesh inside. The activity was investigated at varied temperature in the range of 250-450°C under atmospheric pressure. The characterization results from several techniques, including XRD and TEM of the prepared catalysts will be used to explain the catalytic activity and selectivity of the prepared catalysts in this part.

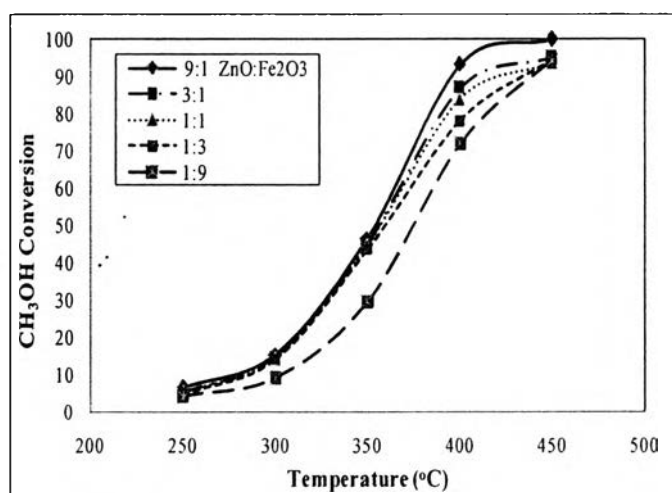
4.2.1 Effect of ZnO-Fe₂O₃ Molar Ratios

The 5% Au/ZnO-Fe₂O₃ catalysts were prepared by a deposition-precipitation technique with various ZnO-Fe₂O₃ molar ratios of 1:9, 1:3, 1:1, 3:1, and 9:1. All catalysts were calcined at 400°C and pretreated with O₂ at 200°C for 1 hour.

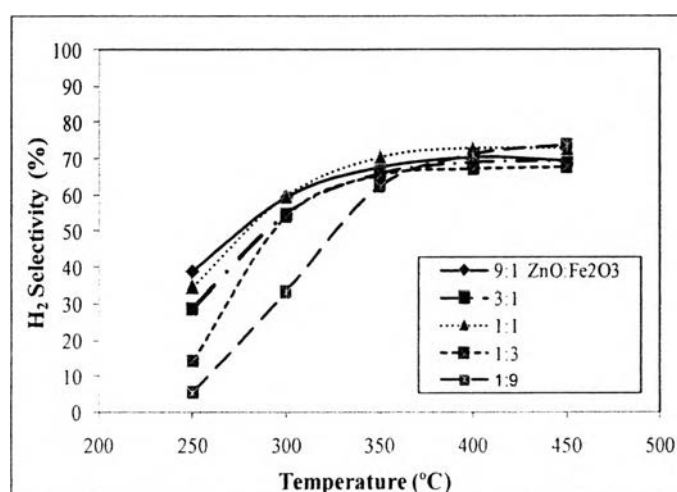
From Figure 4.9 (a-b), it can be observed that at a ratio of ZnO-Fe₂O₃ of 9:1, it achieved a higher methanol conversion than other molar ratios of ZnO to Fe₂O₃ (3:1, 1:1, 1:3, and 1:9). Moreover, the H₂ selectivity at high temperature is not relevant influenced by the molar ratios of ZnO to Fe₂O₃. On the other hand, H₂ selectivity at lower temperature was difference. The catalyst at a 9:1 ratio of ZnO-Fe₂O₃ achieved the highest selectivity of H₂ at a low temperature range. From this result, it can be concluded that the molar ratio of ZnO to Fe₂O₃ affected on the catalytic performance of Au/ZnO-Fe₂O₃ catalyst, when an amount of Fe₂O₃ decreased the activity and selectivity of Au/ZnO-Fe₂O₃ catalyst are increased. This result is supported by Chang *et al.*, (2006). they conducted the experimental of partial oxidation of methanol over Au catalyst supported on TiO₂ and they found that when a small amount of additional support such as Fe₂O₃ was added in Au/TiO₂ (Ti:Fe = 9:1), hydrogen selectivity was increased from 37.0 to 69.6%. It can be concluded that a small amount

of additional Fe_2O_3 is preferred for supported Au catalysts in methanol stream reforming reaction. Bond and Thomson suggested that both Au atoms and ions are necessary for an active supported Au catalyst. In the present work, the activity of Au/ZnO is improved by Fe_2O_3 . It is probably due to the inhibition of complete reduction of ionic Au to Au atom (Chang *et al.*, 2006) and the small crystallite size of ZnFe_2O_4 , as evidenced by XRD.

After this part, the molar ratio of ZnO to Fe_2O_3 of 9:1 was selected as the appropriate condition for Au/ZnO- Fe_2O_3 catalyst.



(a) CH₃OH Conversion



(b) H₂ Selectivity

Figure 4.9 Effect of ZnO- Fe_2O_3 ratio on the activity and selectivity of Au/ZnO- Fe_2O_3 catalyst.

4.2.1.1 X-ray Diffraction (XRD)

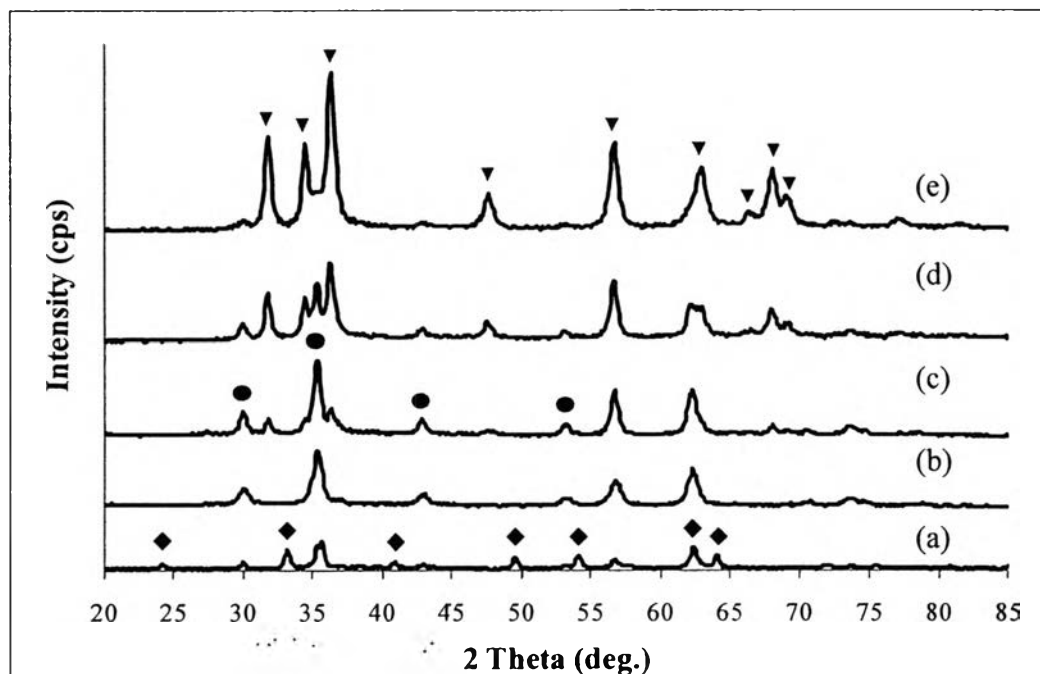


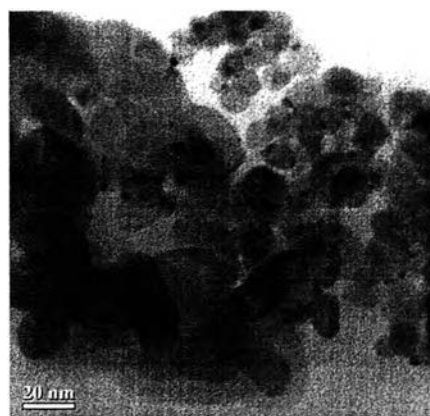
Figure 4.10 XRD patterns of 5% Au/ZnO-Fe₂O₃ catalysts at various molar ratios of ZnO to Fe₂O₃: (▼) ZnO; (●) ZnFe₂O₄; (◆) Fe₂O₃; (a) ZnO:Fe₂O₃ = 1:9; (b) ZnO:Fe₂O₃ = 1:3; (c) ZnO:Fe₂O₃ = 1:1; (d) ZnO:Fe₂O₃ = 3:1; (e) ZnO:Fe₂O₃ = 9:1.

All XRD patterns of 5% Au/ZnO-Fe₂O₃ catalysts, calcined at 400°C, prepared by a deposition-precipitation and various molar ratios of ZnO to Fe₂O₃ of 1:9, 1:3, 1:1, 1:3, and 9:1 are illustrated in Figure 4.10. The presence of ZnFe₂O₄ in the cubic crystal size and ZnO in the hexagonal crystal size was found in all molar ratios of ZnO to Fe₂O₃ samples except at a molar ratio of ZnO to Fe₂O₃ of 1:9. It showed the presence of ZnFe₂O₄ in the cubic crystal size and Fe₂O₃ in the hexagonal crystal size. From this result, it indicated that, the ZnO-Fe₂O₃ ratio affect to the crystalline structure of the prepared catalyst. Additionally, the metallic Au species of Au(111), Au(200) and Au(311) planes are not observed at 2θ of 38.10°, 44.37° and 77.55°, respectively, suggesting that Au particle are highly dispersed on the surface or the Au particles are too small to be detected by the instrument. TEM

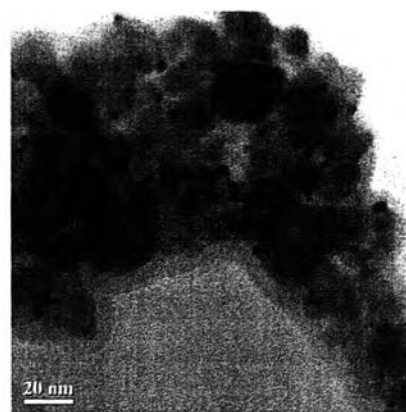
technique was subsequently employed to confirm the Au particle size in the prepared catalysts (Figure 4.11).

4.2.1.2 Transmission Electron Micrograph (TEM)

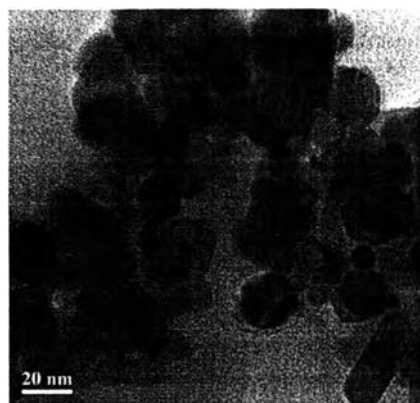
The Au crystallite sizes of 5% Au/ZnO-Fe₂O₃ catalysts with various molar ratios of ZnO to Fe₂O₃ could be clearly observed in TEM micrographs as shown in Figure 4.11 (a-e). The Au particles are seen as dark contrasts on the surface of ZnO-Fe₂O₃ support. The presence of Au on the ZnO-Fe₂O₃ support was confirmed by energy dispersive spectroscopy (EDS). From Figure 4.11 (a-e), the mean particle sizes of Au for Au/ZnO-Fe₂O₃ catalysts with ZnO:Fe₂O₃ molar ratios of 9:1, 3:1, 1:1, 1:3, and 1:9 are 3.45, 4.05, 4.15, 4.17, and 4.24 nm, respectively. With increasing content of Fe₂O₃, a slightly increase in Au particle size was observed. The increase in Au particle size when increasing the Fe₂O₃ content was also reported for Au/TiO₂-Fe₂O₃ catalyst in partial oxidation of methanol reaction (POM) (Chang *et al.*, 2006).



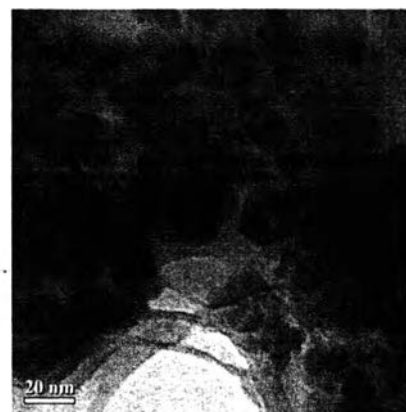
(a) $\text{ZnO}:\text{Fe}_2\text{O}_3 = 9:1$



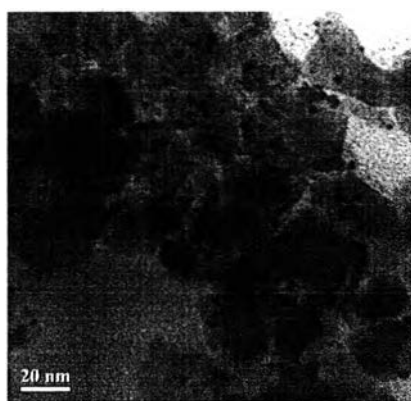
(b) $\text{ZnO}:\text{Fe}_2\text{O}_3 = 3:1$



(c) $\text{ZnO}:\text{Fe}_2\text{O}_3 = 1:1$



(d) $\text{ZnO}:\text{Fe}_2\text{O}_3 = 1:3$



(e) $\text{ZnO}:\text{Fe}_2\text{O}_3 = 1:9$

Figure 4.11 TEM images of the 5% Au/ZnO-Fe₂O₃ catalysts at various molar ratios of ZnO to Fe₂O₃.

A comparison of Au particle sizes for 5% Au/ZnO-Fe₂O₃ catalysts at various molar ratios of ZnO to Fe₂O₃ is summarized in Table 4.4 and the EDS pattern of Au/ZnO-Fe₂O₃ catalyst is shown in Appendix C.

Table 4.4 Comparison of Au particle sizes for Au/ZnO-Fe₂O₃ catalysts at various molar ratios of ZnO to Fe₂O₃ from XRD and TEM analysis

Au/ZnO-Fe₂O₃ Catalysts (molar ratio)	Au (111) (nm)*	Au (200) (nm)*	Au particle size (nm)**
ZnO:Fe₂O₃ = 9:1	< 5	< 5	3.45 ± 1.20
ZnO:Fe₂O₃ = 3:1	< 5	< 5	4.05 ± 1.07
ZnO:Fe₂O₃ = 1:1	< 5	< 5	4.15 ± 1.07
ZnO:Fe₂O₃ = 1:3	< 5	< 5	4.17 ± 0.57
ZnO:Fe₂O₃ = 1:9	< 5	< 5	4.24 ± 1.10

* as measured by XRD, ** as measured by TEM

It was found that the particle sizes of the prepared Au/ZnO-Fe₂O₃ catalysts with various molar ratios of ZnO to Fe₂O₃ from TEM analysis agrees well with the crystallite sizes obtained from the XRD measurement.

4.2.2 Effect of Au Content and Calcination Temperature

For the effect of Au Content, the Au/ZnO-Fe₂O₃ catalysts with a 9:1 molar ratio of ZnO to Fe₂O₃ were prepared by a deposition-precipitation technique with various Au contents of 1%, 3% and 5% atom. All of this catalyst were calcined at 400°C for 4 hours and pretreated with oxygen at 200°C for 1 hour. Figure 4.12 shows methanol conversion and hydrogen selectivity during steam reforming of methanol at 250-450°C over ZnO-Fe₂O₃ and Au/ZnO-Fe₂O₃ catalysts with different Au contents.

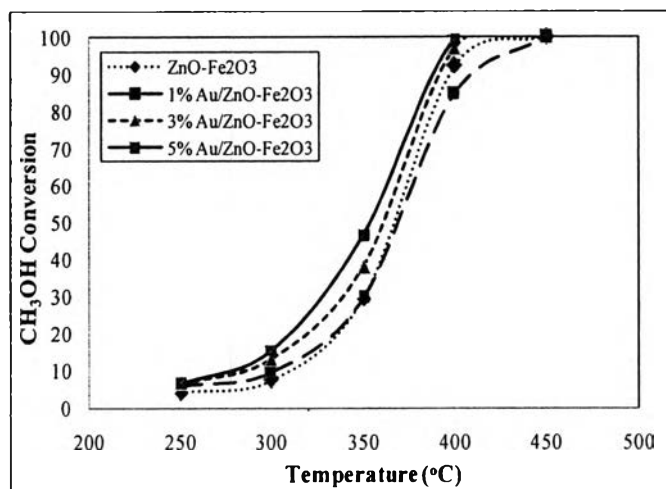
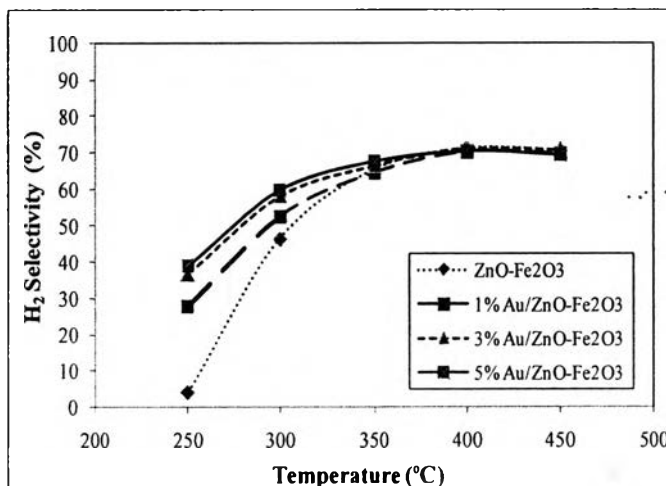
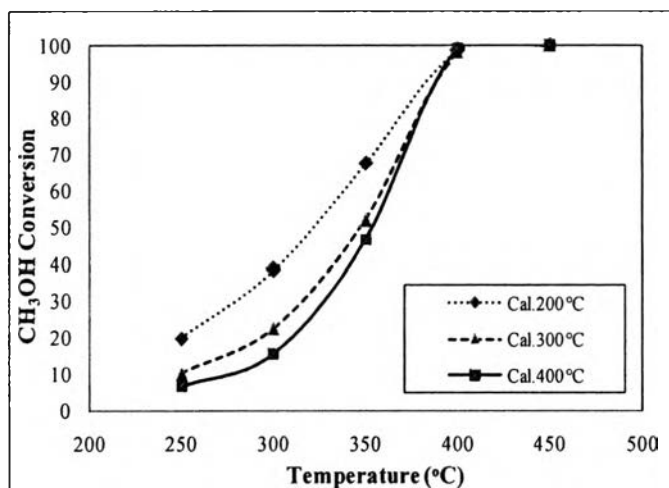
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.12 Effect of Au content on activity and selectivity of Au/ZnO-Fe₂O₃ catalysts.

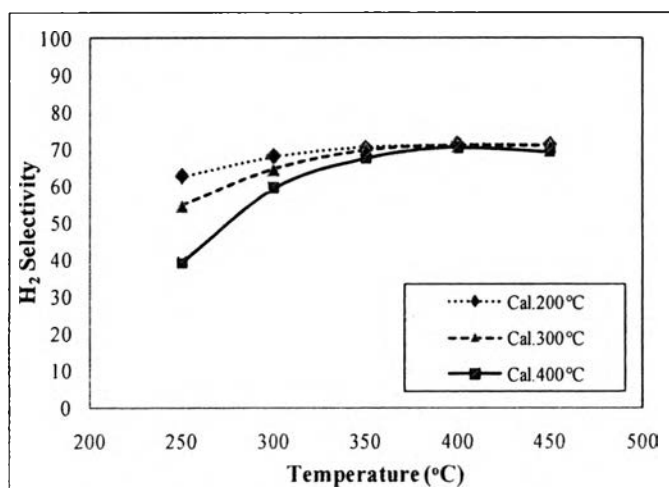
The effect of Au content on the performance of Au/ZnO-Fe₂O₃ catalysts showed a significant improvement on both methanol conversion and hydrogen selectivity, as shown in Figure 4.12 (a-b). This figure clearly indicates that the catalytic activity of ZnO-Fe₂O₃ was improved slightly in the presence of Au. With increasing Au content, methanol conversion and hydrogen selectivity are increased until it reaches the maximum values of 100% and 70%, respectively.

After this part, the Au content of 5% atom was selected as the appropriate condition for Au/ZnO-Fe₂O₃ catalyst.

For the effect of calcination temperature, the 5% Au/ZnO-Fe₂O₃ catalysts with a 9:1 molar ratio of ZnO to Fe₂O₃ were prepared by a deposition-precipitation technique and calcined at various calcination temperatures of 200, 300 and 400°C. All of these catalysts were pretreated with oxygen at 200°C for 1 hour.



(a) CH₃OH Conversion



(b) H₂ Selectivity

Figure 4.13 Effect of calcination temperature on the activity and selectivity of 5% Au/ZnO-Fe₂O₃ catalysts.

Figure 4.13 (a-b) shows the effect of calcination temperature on the activity and selectivity of Au/ZnO-Fe₂O₃ catalysts. It is clearly seen that calcination temperature significantly influences the catalytic performance of Au/ZnO-Fe₂O₃ cat-

alyst. Methanol conversion and hydrogen selectivity increased as the calcination temperature decreased. Methanol conversion was increased from 46.47 to 67.43% and hydrogen selectivity increased from 67.49 to 70.51% while the calcination temperature decreased from 400 to 200°C at the reaction temperature of 350°C.

After this part, the calcination temperature of 200°C was selected as the appropriate condition for Au/ZnO-Fe₂O₃ catalyst.

4.2.2.1 X-ray Diffraction (XRD)

Figure 4.14 shows the XRD patterns of Au/ZnO-Fe₂O₃ catalysts prepared by a deposition-precipitation method at different Au contents (1%, 3% and 5% atom) and different calcination temperatures (200, 300 and 400°C). The XRD patterns of Au/ZnO-Fe₂O₃ catalysts were almost the same but have a little difference in term of peak intensity. All XRD patterns of Au/ZnO-Fe₂O₃ catalysts show the presence of ZnFe₂O₄ in the cubic crystal size and ZnO in the hexagonal crystal size. Those additional peaks observed at 2θ of 29.85°, 31.82°, 36.49°, 43.04°, and 51.17° were corresponding to ZnFe₂O₄ (220), ZnO (100), ZnO (101), ZnFe₂O₄ (400) and ZnO (110) for CuK α (1.5406 Å) radiation, respectively. Additionally, no evidence of metallic Au peaks was observed, suggesting that the Au particle was smaller than 5 nm.

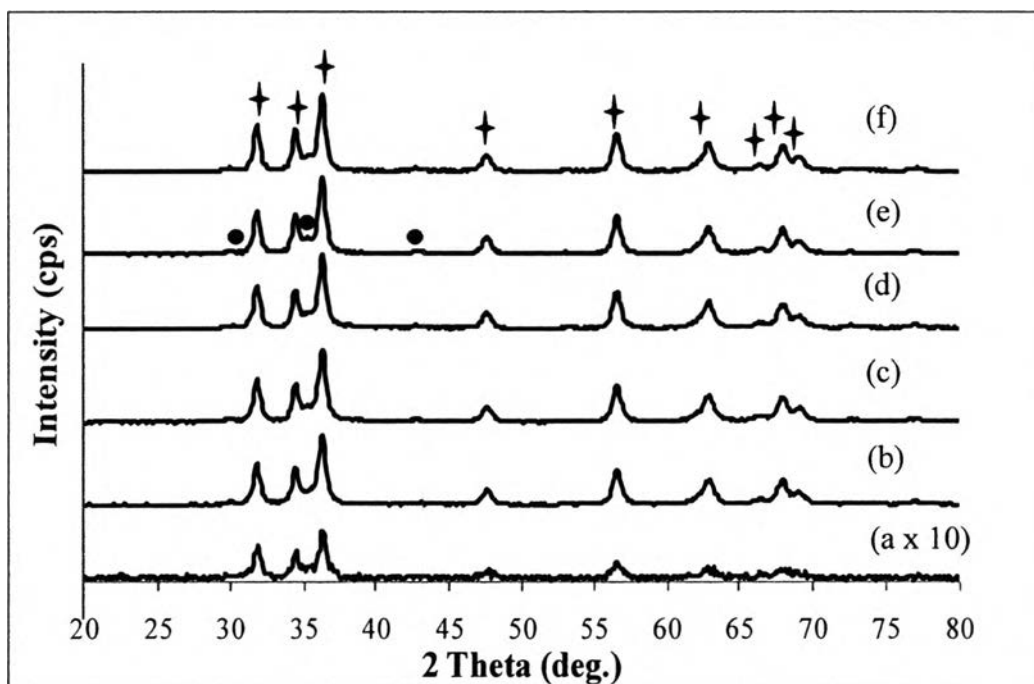


Figure 4.14 XRD patterns of the prepared Au/ZnO-Fe₂O₃ catalysts at various calcination temperatures and Au contents: (†) ZnO; (●) ZnFe₂O₄; (a) ZnO-Fe₂O₃; (b) 5% Au/ZnO-Fe₂O₃, calcined at 200°C; (c) 5% Au/ZnO-Fe₂O₃, calcined at 300°C; (d) 3% Au/ZnO-Fe₂O₃, calcined at 400°C; (e) 1% Au/ZnO-Fe₂O₃, calcined at 500°C.

For ZnO-Fe₂O₃ support, it shows only ZnO in the hexagonal crystal size, whereas ZnFe₂O₄ in the cubic crystal size were not observed in ZnO-Fe₂O₃ support. Moreover, the low peak intensity of ZnO was significantly different from other samples, compared to the XRD patterns of Au/ZnO-Fe₂O₃ catalysts. The crystallite sizes of ZnO and ZnFe₂O₄ calculated from X-ray line-broadening by using the Scherrer Equation are summarized in Table 4.5.

Table 4.5 The metal crystallite sizes of the prepared Au/ZnO-Fe₂O₃ catalysts

Catalysts	Metal crystallite sizes (nm)	
	ZnO (101)	ZnFe ₂ O ₄ (400)
ZnO-Fe ₂ O ₃	17.21	-
1% Au/ZnO-Fe ₂ O ₃ , Calcined at 400°C	13.88	13.55
3% Au/ZnO-Fe ₂ O ₃ , Calcined at 400°C	15.27	14.19
5% Au/ZnO-Fe ₂ O ₃ , Calcined at 400°C	16.48	16.87
5% Au/ZnO-Fe ₂ O ₃ , Calcined at 300°C	16.10	13.40
5% Au/ZnO-Fe ₂ O ₃ , Calcined at 200°C	15.39	11.10

It was found when Au was deposited onto ZnO-Fe₂O₃ support, the crystallite size of the ZnO(101) tended to decrease due to the interaction between Au and ZnO atom. Moreover, it was observed that the crystallite sizes of the ZnO(101) and ZnFe₂O₄(400) phases slightly increased when increasing Au content and calcination temperature. Therefore, it indicated that Au content and calcination temperature affected to the crystalline structure of the prepared catalyst.

4.2.1.2 Transmission Electron Micrograph (TEM)

TEM micrographs of the Au/ZnO-Fe₂O₃ catalysts with various Au contents and calcination temperatures are shown in Figure 4.15. From Figure 4.15 (a-c), TEM images of the Au/ZnO-Fe₂O₃ catalysts with various Au contents (1%, 3% and 5% atom) revealed that the mean particle sizes of Au are 2.45, 2.94, and 3.45 nm, respectively. With increasing the Au content, a slight increase in Au particle size was observed. In this present work, the increasing in methanol conversion and hydrogen selectivity are related with increasing of Au particles size, as confirmed by Figure 4.12 (a-b). Therefore, it can be suggested that a large size of Au particle on the Au/ZnO catalyst was preferred for methanol steam reforming reaction.

For the catalysts calcined at 200, 300 and 400°C (Figure 4.15 (c-e)), the mean particle sizes are 3.00, 3.20 and 3.45 nm, respectively. This result clearly indicates that at a higher calcination temperature, the sizes of Au particles are increased. In addition, Change *et al.*, (2006) studied the effect of calcination temperature on the particle size of Au for Au/TiO₂-Fe₂O₃ catalyst; They found that the particle size of Au increased from 2.5 to 2.8 nm, when the calcination temperature increased from 200 to 400°C.

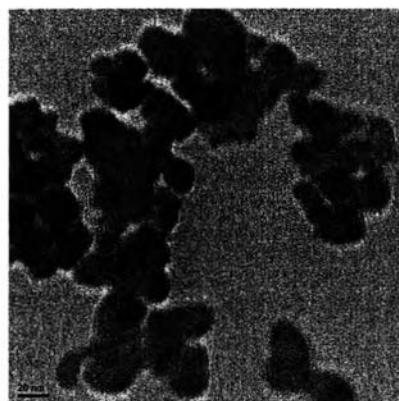
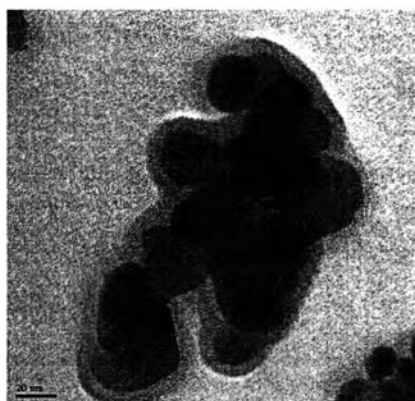
A comparison of Au particle size for Au/ZnO-Fe₂O₃ catalysts with different Au contents and calcination temperatures is summarized in Table 4.6.

Table 4.6 Comparison of Au particle sizes for Au/ZnO-Fe₂O₃ catalysts at different Au contents and calcination temperatures from XRD and TEM analysis

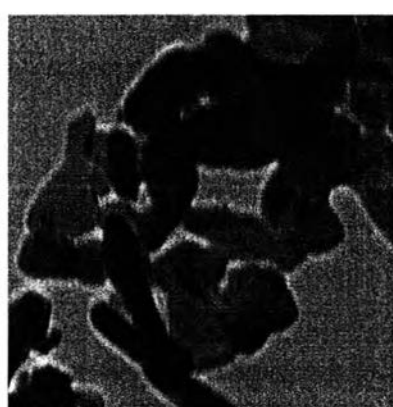
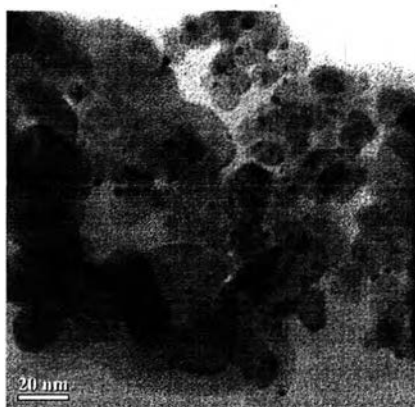
Catalysts	Au (111) (nm)*	Au (200) (nm)*	Au particle size (nm)**
1% Au/ZnO-Fe ₂ O ₃ , Calcined 400°C	< 5	< 5	2.45 ± 0.60
3% Au/ZnO-Fe ₂ O ₃ , Calcined 400°C	< 5	< 5	2.94 ± 0.76
5% Au/ZnO-Fe ₂ O ₃ , Calcined 400°C	< 5	< 5	3.45 ± 1.20
5% Au/ZnO-Fe ₂ O ₃ , Calcined 300°C	< 5	< 5	3.20 ± 0.71
5% Au/ZnO-Fe ₂ O ₃ , Calcined 200°C	< 5	< 5	3.00 ± 0.88

* as measured by XRD, ** as measured by TEM

The particle sizes of the prepared Au/ZnO-Fe₂O₃ catalysts at various Au contents and calcination temperatures from TEM analysis were close to the crystallite sizes determined by the XRD measurement.



(a) 1% Au/ZnO-Fe₂O₃, calcined at 400°C (b) 3% Au/ZnO-Fe₂O₃, calcined at 400°C



(c) 5% Au/ZnO-Fe₂O₃, calcined at 400°C (d) 5% Au/ZnO-Fe₂O₃, calcined at 300°C



(e) 5% Au/ZnO-Fe₂O₃, calcined at 200°C

Figure 4.15 TEM images of the Au/ZnO-Fe₂O₃ catalysts at various Au contents and calcination temperatures.

4.2.3 Effect of Catalyst Pretreatment

The different pretreatment will provide different state of Au catalysts. It is of interest to investigate the effect of pretreatments, which are H₂ pretreatment at 400°C and O₂ pretreatment at 200°C for 1 hour on the activity and selectivity of 5% Au/ZnO-Fe₂O₃ catalysts with a 9:1 molar ratio of ZnO to Fe₂O₃, calcined at 400°C for 1 hour. After pretreatment, the catalyst would be fully gold metallic and partial gold metallic form for H₂ pretreatment and O₂ pretreatment, respectively. The effect of catalyst pretreatment on the activity and selectivity of 5% Au/ZnO-Fe₂O₃ catalyst is shown in Figure 4.16 (a-b).

It can be observed that O₂ pretreated achieved a higher methanol conversion and H₂ selectivity than H₂ pretreated catalyst, especially at low temperatures range. From this result, it can be indicated that Fe₂O₃ preferred the O₂ pretreatment than H₂ pretreatment.

After this part, pure O₂ pretreatment at 200°C for 1 hour was selected as the appropriate pretreatment condition for this method.

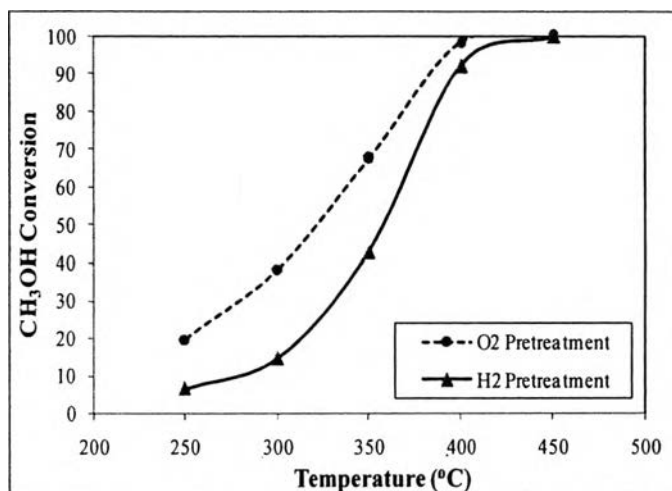
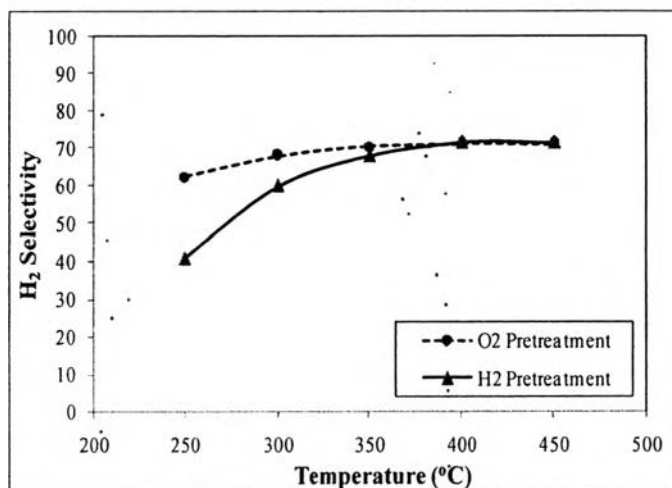
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.16 Effect of catalyst pretreatment on the activity and selectivity of 5% Au/ZnO-Fe₂O₃ catalysts.

4.2.3.1 X-ray Diffraction (XRD)

The XRD patterns of Au/ZnO-Fe₂O₃ catalysts prepared by a deposition-precipitation method at different gas pretreatment (O₂ pretreatment and H₂ pretreatment) are shown in Figure 4.17. The XRD pattern of fresh catalyst shows the presence of ZnFe₂O₄ in the cubic crystal size and ZnO in the hexagonal crystal size. Those additional peaks observed at 2θ of 29.85°, 31.82°, 36.49°, 43.04°, and 51.17° were corresponding to ZnFe₂O₄ (220), ZnO (100), ZnO (101), ZnFe₂O₄ (400) and ZnO (110) for CuKα (1.5406 Å) radiation, respectively. After pretreatment the

XRD patterns were almost the same but have a significant difference in term of peak intensity of ZnFe_2O_4 , higher intensity of ZnFe_2O_4 peak was observed after O_2 pretreatment, while no evidence of ZnFe_2O_4 was observed after H_2 pretreatment. From this result, suggesting that O_2 pretreatment enhanced the ZnFe_2O_4 phase and enhanced the activity and selectivity of this catalyst in methanol steam reforming reaction, especially at low temperature. Additionally, the metallic Au specie attributed to Au (200) peaks was observed at 2θ of 44.58° after H_2 pretreatment.

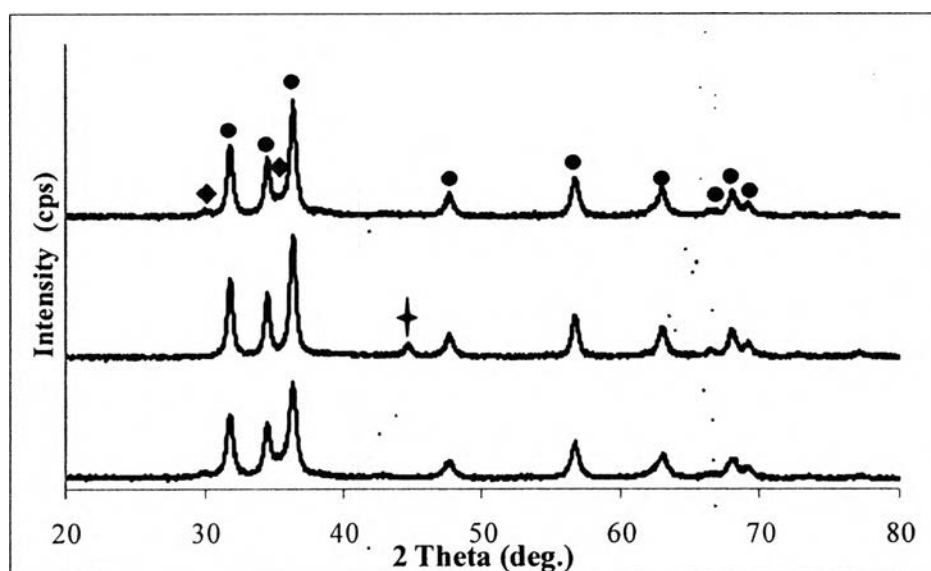


Figure 4.17 XRD patterns of the prepared Au/ZnO- Fe_2O_3 catalysts: (●) ZnO; (†) Au; (◆) ZnFe_2O_4 ; (a) Fresh catalyst; (b) H_2 pretreatment; (c) O_2 pretreatment.

4.2.4 Effect of Reaction Temperature

The 5% Au/ZnO- Fe_2O_3 catalysts with a 9:1 molar ratio of ZnO to Fe_2O_3 prepared by a deposition-precipitation technique, calcined at 400°C and pretreated with oxygen at 200°C for 1 hour were used to study in this part.

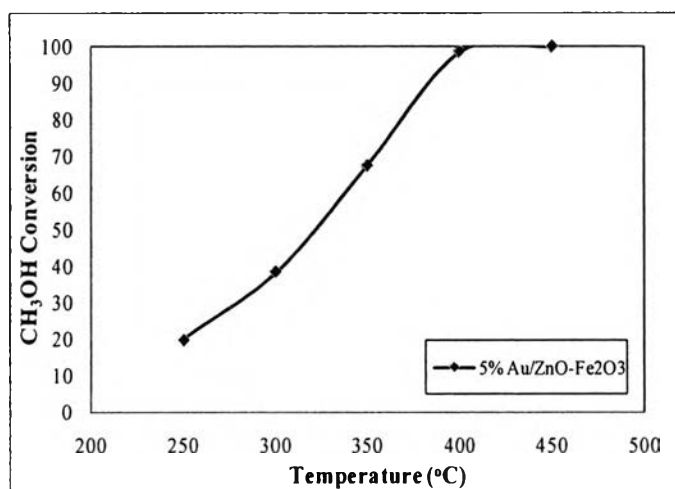
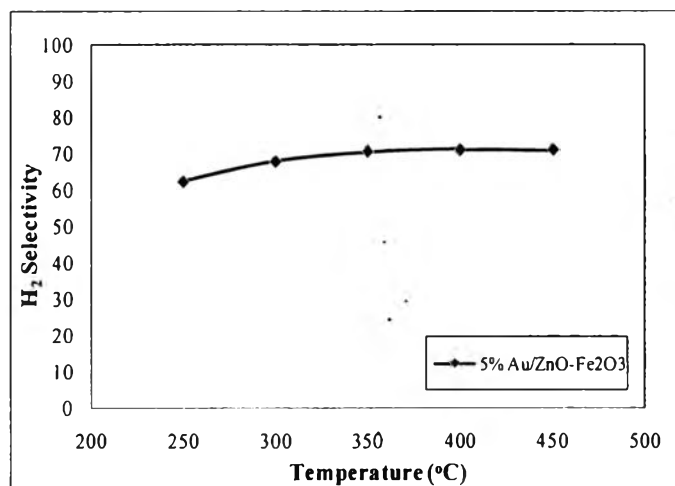
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.18 Effect of reaction temperature on the activity and selectivity of Au/ZnO-Fe₂O₃ catalyst.

Figure 4.18 (a-b) shows the activity and selectivity of 5% Au/ZnO-Fe₂O₃ catalyst versus temperature. When the reaction temperature increased, there is an increase in both methanol conversion and hydrogen selectivity. Methanol conversion increased from 19.72 to 100% and hydrogen selectivity increased from 62.25 to 71.12% while the reaction temperature increased from 250 to 450°C. The maximum methanol conversion reached 100% at 450°C and H₂ selectivity reached 71.12% at 450°C. There was no CO detected at 350°C. However, at high temperatures, a trace amount of CO was detected. The CO selectivity increased from 0 to 3.45%, when the

temperature increased from 350 to 450°C. The CO selectivity is relatively less compared to the amount of CO produced over Cu-based (Papavasiliou *et al.*, 2007) and Pd-based catalysts (Karim *et al.*, 2006).

After this part, reaction temperature at 450°C was selected as the appropriate reaction temperature for studying the deactivation test.

4.2.5 Deactivation Test of Au/ZnO-Fe₂O₃ Catalyst

The catalytic stability of 5% Au/ZnO-Fe₂O₃ catalyst with a 9:1 molar ratio of ZnO to Fe₂O₃ calcined at 200°C for 4 hours and pretreated with oxygen, which showed the maximum CH₃OH conversion and H₂ selectivity, was tested at the constant temperature of 450°C. As can be seen from Figure 4.19, this catalyst exhibited a stable catalytic performance during 24 hours of testing time.

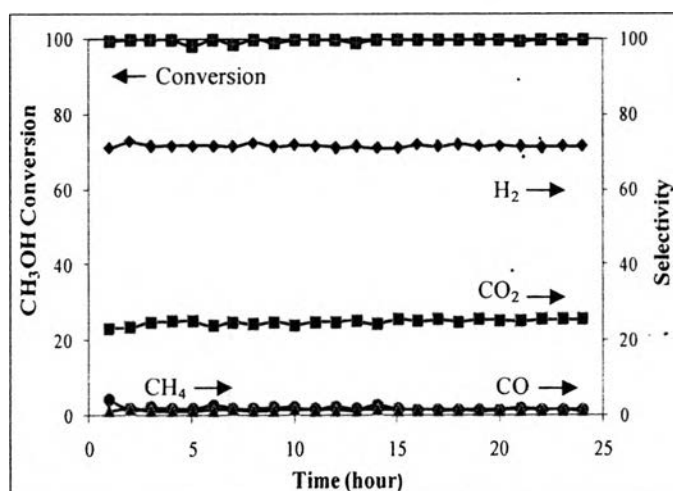


Figure 4.19 Deactivation test of Au/ZnO-Fe₂O₃ catalyst at the constant temperature of 450°C.

4.3 Comparison of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts

In this part, the performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts at the optimum conditions were compared in methanol steam reforming reaction (SRM), decomposition of methanol (DM), and water gas shift (WGS) reactions. The optimum conditions for Au/ZnO catalysts were 5% Au loading, calcined at 400°C for 4 hours, and H₂ pretreatment at 400°C for 1 hour. For Au/ZnO-Fe₂O₃ catalyst, the optimum conditions were 5% Au loading with a 9:1 molar ratio of ZnO to Fe₂O₃, calcined at 200°C for 4 hours, and O₂ pretreatment at 200°C for 1 hour.

The catalytic activity tests were carried out in a vertical pyrex glass micro-reactor by packing with 100 mg catalyst of 80-120 mesh inside. The activity was investigated at varied temperature in the range of 250-450°C under atmospheric pressure. The characterization results from several techniques, including XRD, TEM, TPR and TPO of the prepared catalysts will be used to explain the catalytic activity and selectivity of the prepared catalysts in this part.

4.3.1 Methanol Steam Reforming Reaction (SRM)

The catalytic performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts at the optimum conditions were compared in Figure 4.20. The results showed that the catalytic performance of the Au/ZnO-Fe₂O₃ is higher than that of the Au/ZnO catalyst. A maximum methanol conversion of 95.58% was achieved with Au/ZnO catalyst, while Au/ZnO-Fe₂O₃ gave 100% methanol conversion at the reaction temperature of 450°C. Moreover, the H₂ selectivity of Au/ZnO-Fe₂O₃ catalyst was higher than that of Au/ZnO at low temperature range H₂ produced was maintained from 300-450°C. From this result, it can be concluded that the addition of Fe₂O₃ to the ZnO would greatly enhance the catalytic activity of methanol steam reforming.

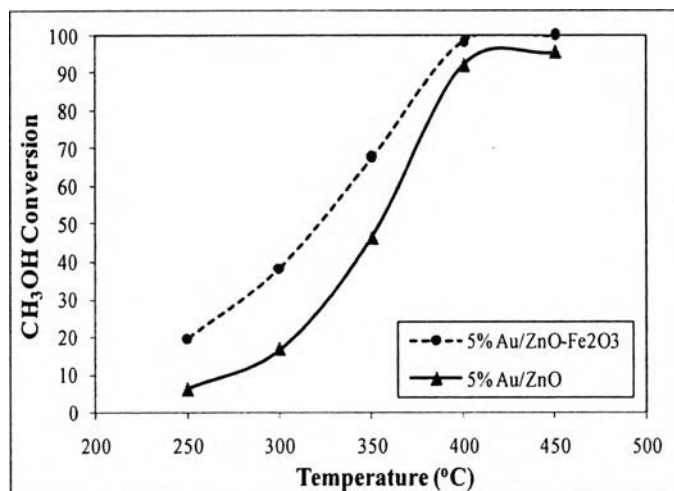
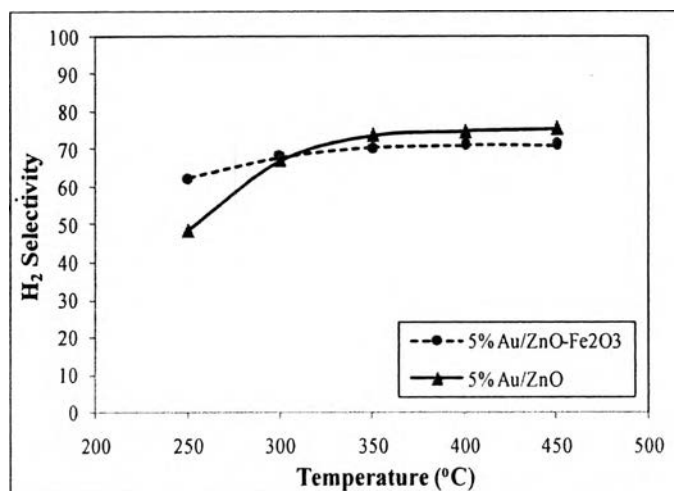
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.20 Catalytic performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in methanol steam reforming reaction.

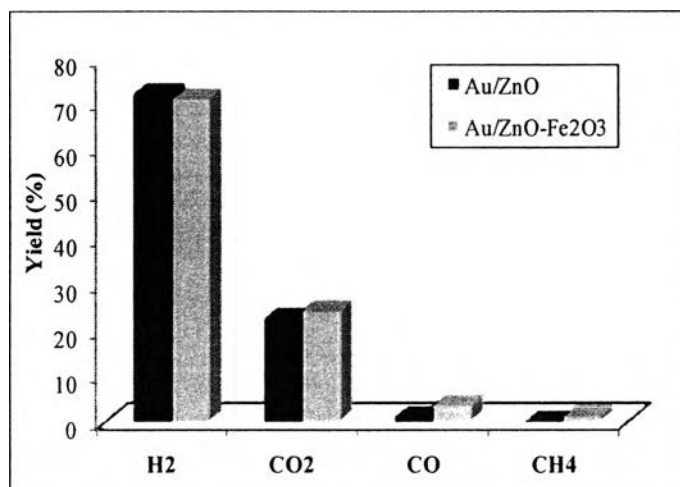


Figure 4.21 Product distribution of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in methanol steam reforming reaction at 450°C.

Figure 4.21 shows the product distribution of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in methanol steam reforming reaction at 450°C. At this temperature, Au/ZnO catalyst gave a higher H₂ production and lower CO production than Au/ZnO catalyst. The results showed that CH₄ formation was observed in the product stream of Au/ZnO-Fe₂O₃ catalysts. By considering the formation of CH₄, it formed through reaction (4.1) because the available of reactants (CO and H₂) and heat source at high temperatures.



4.3.1.1 X-ray Diffraction (XRD)

The XRD patterns of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts at the optimum conditions were compared in Figure 4.22. The XRD pattern of Au/ZnO catalyst shows the presence of Au in the face-centered cubic crystal size and ZnO in hexagonal crystal size. But for the XRD pattern of Au/ZnO-Fe₂O₃ catalysts, it shows the presence of ZnFe₂O₄ in the cubic crystal size and ZnO in the hexagonal crystal size. These XRD patterns are different in term of ZnFe₂O₄ phase, suggesting that this phase could affect the differences in the catalytic performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts. In Addition, for Au/ZnO-Fe₂O₃ catalysts the metallic Au

were not presented, suggesting that the particles size of Au of Au/ZnO-Fe₂O₃ are smaller than that of Au/ZnO catalyst, as confirmed by TEM images.

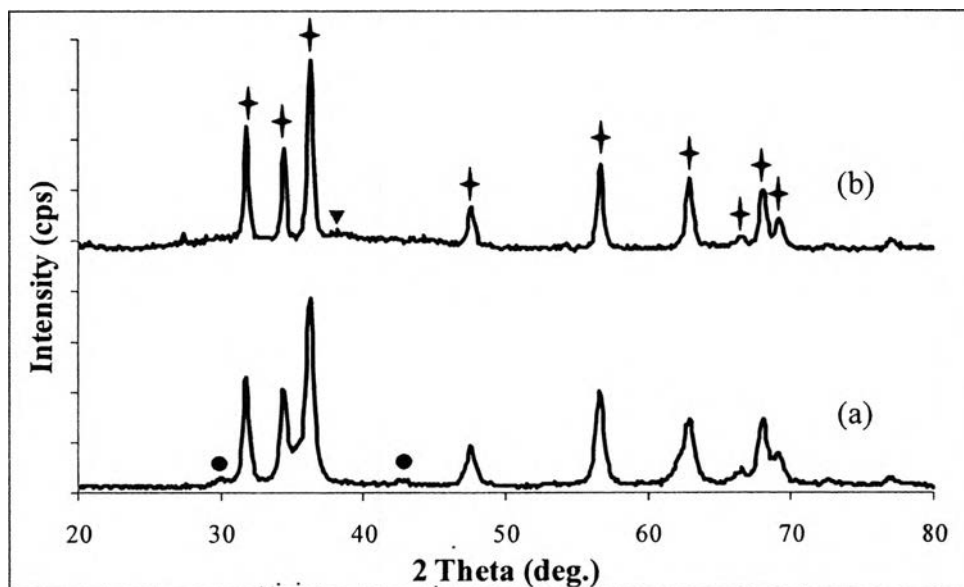


Figure 4.22 Comparison of XRD patterns of Au/ZnO-Fe₂O₃ and Au/ZnO catalysts: (▼) Au; (⊕) ZnO; (●) ZnFe₂O₄; (a) Au/ ZnO-Fe₂O₃ catalyst; (b) Au/ZnO catalyst.

4.3.1.2 Temperature Programmed Reduction (TPR)

Temperature programmed reduction experiments were performed on the prepared catalyst in order to investigate the reactivity of the metal oxide catalyst support upon Au addition. The TPR profiles of the prepared catalysts and pure metal oxide support are shown in Figure 4.23. In the TPR profile of ZnO, it presents lower H₂ consumption, which was probably the result of complete dehydroxylation and high thermal stability (Valenzuela *et al.*, 2002). It can be seen that in Au supported catalysts (Au/ZnO and Au/ZnO-Fe₂O₃), a reduction peak for Au was observed at 180°C. For Au/ZnO profile, it presents a peak in low temperature region at 180°C, assigned to the reduction of Au metal and three peaks in correspondence of three peaks of the pure ZnO support but the reduction temperature was shifted around 20°C to lower temperature, when compared to the pure ZnO support. This indicates that Au can enhance the reduction behavior of the ZnO. Moreover, TPR profile of ZnO-Fe₂O₃ support, two main peaks are observed; It corresponds to the

peak of Fe_2O_3 support but shifted significantly to the higher temperature, implying the strong interaction between ZnO and Fe_2O_3 . In the TPR profile of $\text{Au}/\text{ZnO}-\text{Fe}_2\text{O}_3$ catalyst, it can be seen that one peak appear at 180°C , which corresponds to the reduction of Au metal and one broad reduction peak starting at 380°C and ending at 800°C , which corresponds to ZnFe_2O_4 (Valenzuela *et al.*, 2002). In the TPR profile of Fe_2O_3 , the first reduction peak appear at 360°C , corresponding to the transition of Fe_2O_3 to Fe_3O_4 and a large broad peak with a maximum at 620°C obviously comprises several peaks that represent the multiple reduction steps of Fe_3O_4 to FeO and Fe (Silberova *et al.*, 2006). The H_2 consumption of $\text{Au}/\text{ZnO}-\text{Fe}_2\text{O}_3$ was lower than that of Fe_2O_3 which reveal that ZnFe_2O_4 was more stable to severe reaction treatment. XRD technique was subsequently employed to confirm the present of ZnFe_2O_4 in $\text{Au}/\text{ZnO}-\text{Fe}_2\text{O}_3$ catalysts (Figure 4.22).

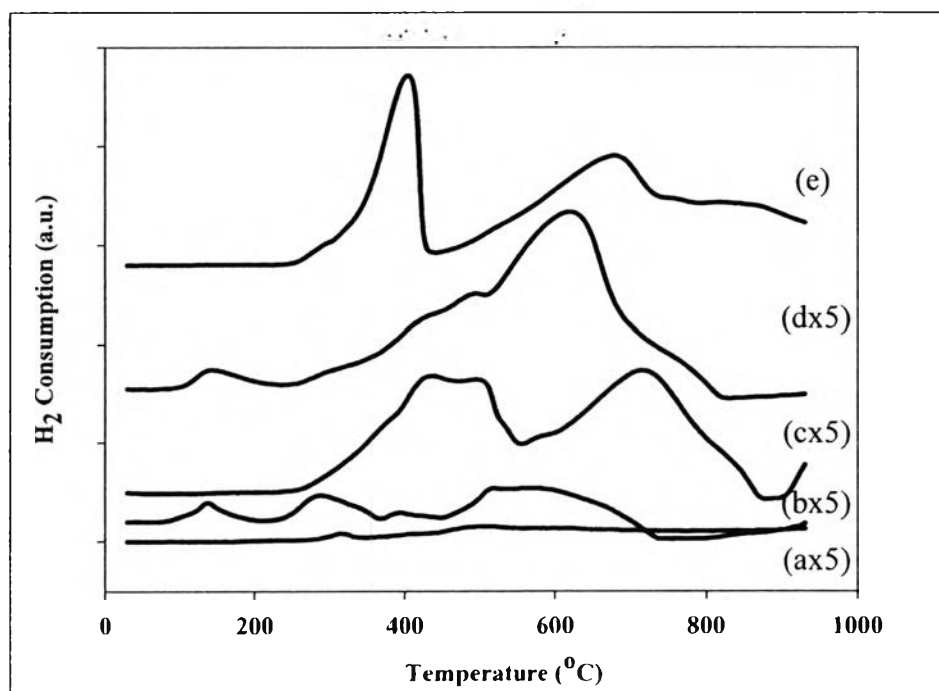


Figure 4.23 Temperature programmed reduction profiles of the prepared catalysts: (a) ZnO ; (b) Au/ZnO ; (c) $\text{ZnO}-\text{Fe}_2\text{O}_3$; (d) $\text{Au}/\text{ZnO}-\text{Fe}_2\text{O}_3$; (e) Fe_2O_3 .

According to the synergism between ZnO and Fe₂O₃ to form ZnFe₂O₄ is proposed, as evidenced by XRD and TPR results, it can be suggested that this effect would enhance the catalytic performance of Au/ZnO-Fe₂O₃ catalyst in methanol steam reforming reaction. Therefore, Au/ZnO-Fe₂O₃ catalyst has the higher methanol conversion and H₂ selectivity than Au/ZnO catalyst in this reaction. However, this effect is expected on Au/ZnO-Fe₂O₃, which comprises of a 9:1 molar ratio of ZnO to Fe₂O₃.

4.3.1.3 Temperature Programmed Oxidation (TPO)

Temperature programmed oxidation (TPO) experiments were performed on the prepared catalyst in order to investigate the amount of carbon formed (coke) on the Au/ZnO and Au/ZnO-Fe₂O₃ catalysts after the reaction was carried out at 450°C for 24 hours (deactivation test). The results showed that the amount of carbon formation on Au/ZnO and Au/ZnO-Fe₂O₃ catalysts were 0.12 and 0.88% weight, respectively. However, it can be suggested that these carbon formations had no effect on the performance of catalyst because the deactivation was not observed during 24 hours of testing. Moreover, Figure 4.24 shows the oxidation temperature of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts. One main peak at 320°C presented in the TPO profile of Au/ZnO catalyst, whereas one main peak at 450°C and a shoulder at 470°C are observed in the TPO profile of Au/ZnO-Fe₂O₃ catalyst. The peak located at 300-450 °C corresponds to the coke oxidized at the metal phase.

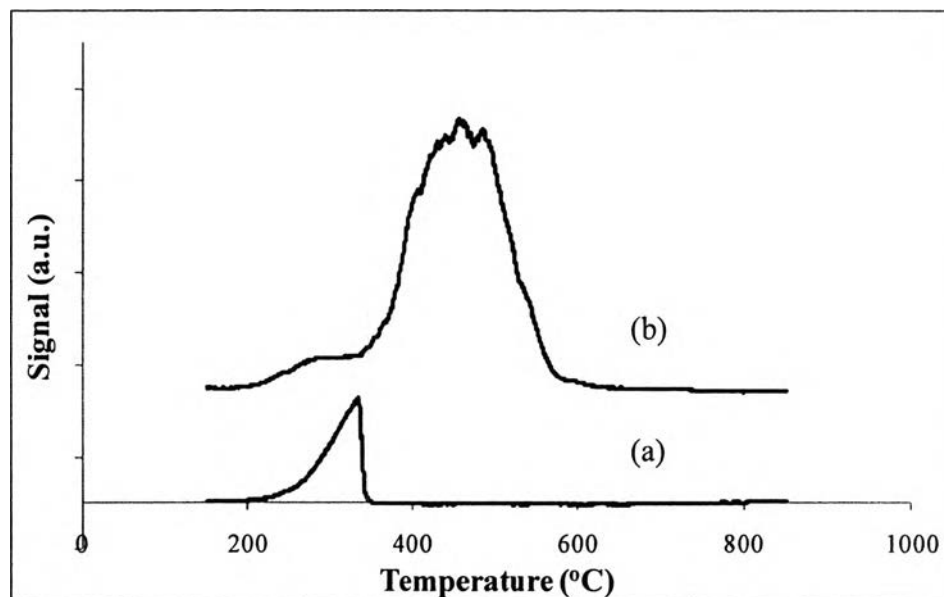


Figure 4.24 Temperature programmed oxidation profiles of the Au/ZnO and Au/ZnO-Fe₂O₃ catalysts: (a) Au/ ZnO; (b) Au/ZnO-Fe₂O₃:

4.3.2 Methanol Decomposition Reaction (DM)

Methanol decomposition reaction (Equation 4.2) is one of side reactions that affect to methanol steam reforming reaction. Therefore, it is essential to study the performance of both Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in this reaction.



The catalyst used in this part is Au/ZnO and Au/ZnO-Fe₂O₃ catalysts at the optimum conditions. The reaction condition were 1.5 ml/hour of liquid flow rate, 34 ml/min of carrier gas (He) and reaction temperature range of 250-450°C.

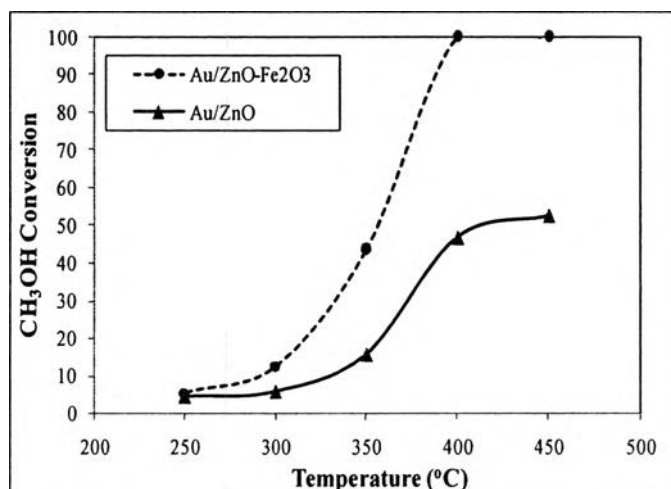
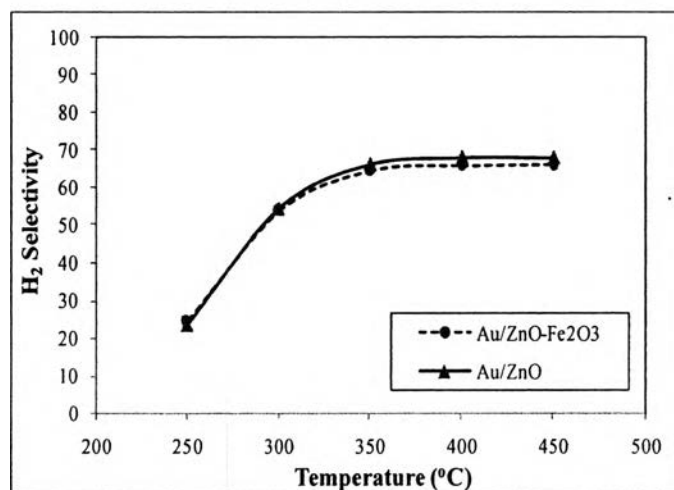
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.25 Catalytic performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in methanol decomposition reaction.

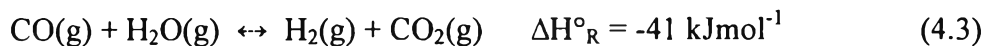
From Figure 4.25, it can be observed that the catalytic performance of the Au/ZnO-Fe₂O₃ is higher than that of the Au/ZnO catalyst in DM reaction. It can be concluded that the addition of Fe₂O₃ to the ZnO would greatly enhance the catalytic activity of methanol decomposition. It is important to mention that the same methanol conversion (100% conversion) was obtained by using Au/ZnO-Fe₂O₃ catalyst, while Au/ZnO gave 52.44% methanol conversion at the reaction temperature of 450°C. However, the selectivity of H₂ of both catalysts is not much different. It in-

creased with increasing the reaction temperature reaching constant values of 66.04% and 68% at 350°C for Au/ZnO-Fe₂O₃ and Au/ZnO catalysts, respectively.

In this study, the addition of water to methanol markedly affected to the reaction, as confirmed by Figure 4.20 and 4.25. The total conversion underwent more significant changes for both catalysts, especially in the low temperature range (250-350°C).

4.3.3 Water Gas Shift Reaction (WGS)

In subsequent experiment, water gas shift reaction was carried out at the reaction temperature range of 250-450°C. Water Gas Shift reaction (Equation 4.3) is one of side reactions that affects to methanol steam reforming reaction because it can reduce the CO content in the product stream that occurred from DM reaction. Therefore, it is essential to study the performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in this reaction.



The catalyst used in this study was tested at the optimum conditions. The reaction condition were 1.5 ml/hour of liquid flow rate, at a 2:1 molar ratio of H₂O to CO, a flow rate of carrier gas (He) of 34 ml/min and reaction temperature range of 250-450°C.

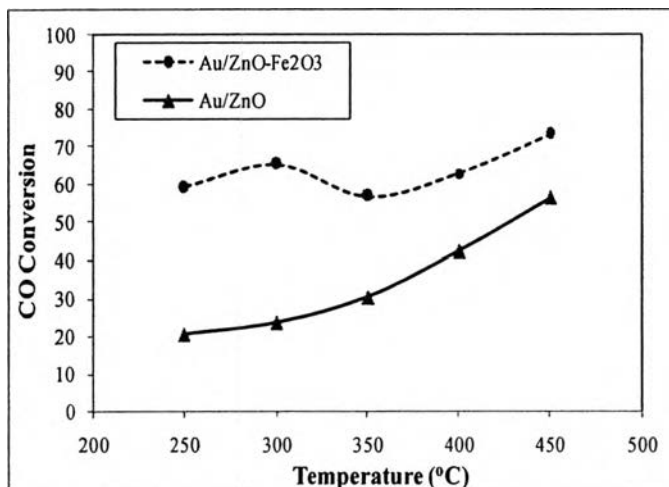
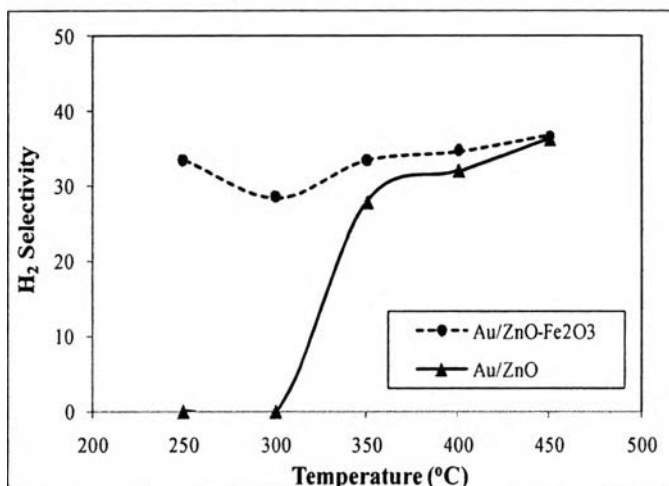
(a) CH₃OH Conversion(b) H₂ Selectivity

Figure 4.26 Catalytic performance of Au/ZnO and Au/ZnO-Fe₂O₃ catalysts in water gas shift reaction.

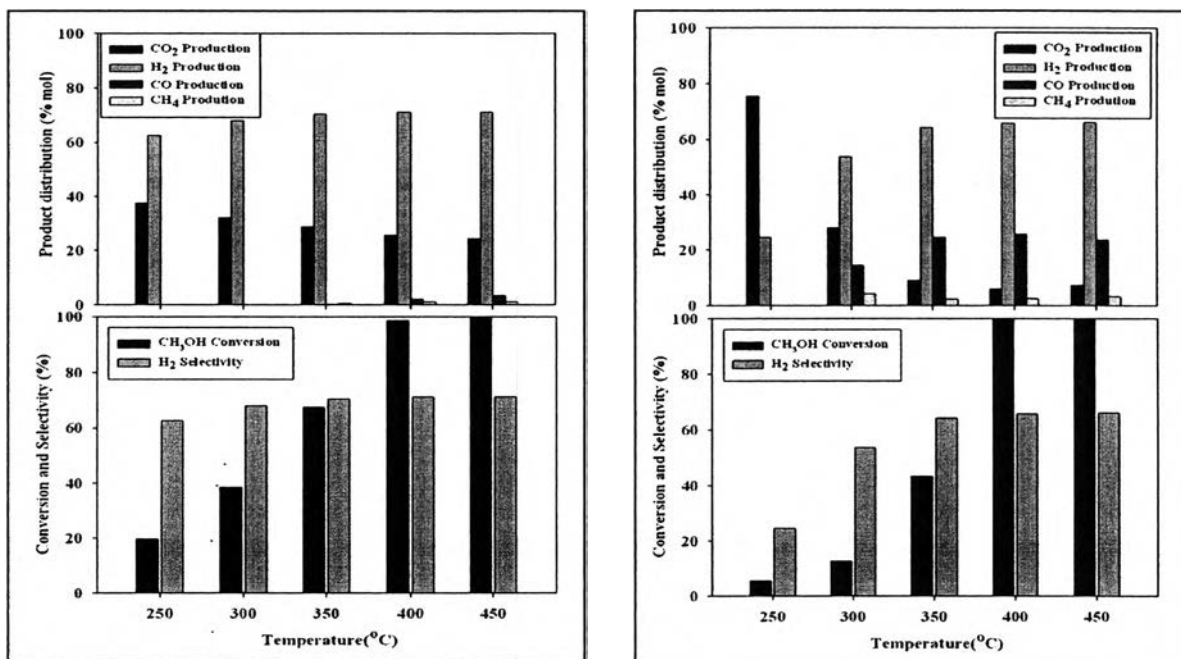
From Figure 4.26, it can be observed that the catalytic performance of the Au/ZnO-Fe₂O₃ is much higher than that of the Au/ZnO catalyst in WGS reaction. A maximum CO conversion of 73.25% was achieved with Au/ZnO-Fe₂O₃ catalyst, while Au/ZnO gave 56.48% CO conversion at the reaction temperature of 450°C. Moreover, the H₂ selectivity of Au/ZnO-Fe₂O₃ catalyst is higher than that of Au/ZnO at low temperature range. Additionally, Andreeva *et al.*, (1995) conducted the experiment of water gas shift reaction over Au/ α -Fe₂O₃, Au/Al₂O₃, and α -Fe₂O₃. It was found that Au/ α -Fe₂O₃ gave the highest catalytic activity because of a specific inte-

reaction between Au and ferric oxide support. Moreover, in 1996 Andreeva *et al.* reported the mechanism of WGS reaction proceeding on Au/ α -Fe₂O₃ catalyst that Au was formed intermetallic bond with Fe₂O₃ and the reaction occurred through the redox transfer of Fe³⁺ ↔ Fe²⁺ in Fe₃O₄.

The high performance of Au/ZnO-Fe₂O₃ catalyst in WGS reaction can enhance the performance of this catalyst in SRM reaction. Therefore, it can be suggested that a higher H₂ selectivity of Au/ ZnO-Fe₂O₃ catalyst in SRM reaction at low temperature range is influenced by WGS reaction. This enhanced CO₂ production was accompanied by an increase in H₂ only at low temperature range (250-300°C).

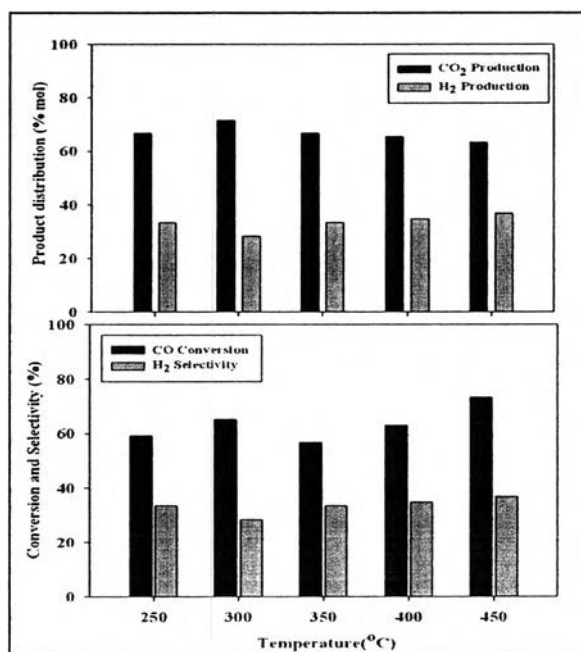
4.3.4 Comparison of Catalytic Performance in SRM, DM and WGS Reactions

The comparison of catalytic performance of Au/ZnO-Fe₂O₃ and Au/ZnO catalysts in the SRM, DM and WGS reactions at 450°C is shown in Figures 4.27 and 4.28, respectively. It can be seen that at low temperature range (250-300°C) a higher H₂ selectivity of Au/ZnO-Fe₂O₃ catalyst in SRM reaction is produced with a higher selectivity in the WGS and DM reaction, whereas the production of H₂ were not observed for Au/ZnO catalyst in the WGS reaction. Therefore, it can be concluded that addition of Fe₂O₃ to Au/ZnO catalyst was enhanced the H₂ selectivity in the WGS reaction at low temperature range. However, at high temperature range (350-450°C) the formation of CH₄ and CO was observed in the product stream of Au/ZnO-Fe₂O₃ catalyst in SRM reaction. It can be suggested that this formation is influenced by a higher CH₄ and CO selectivity in DM reaction.



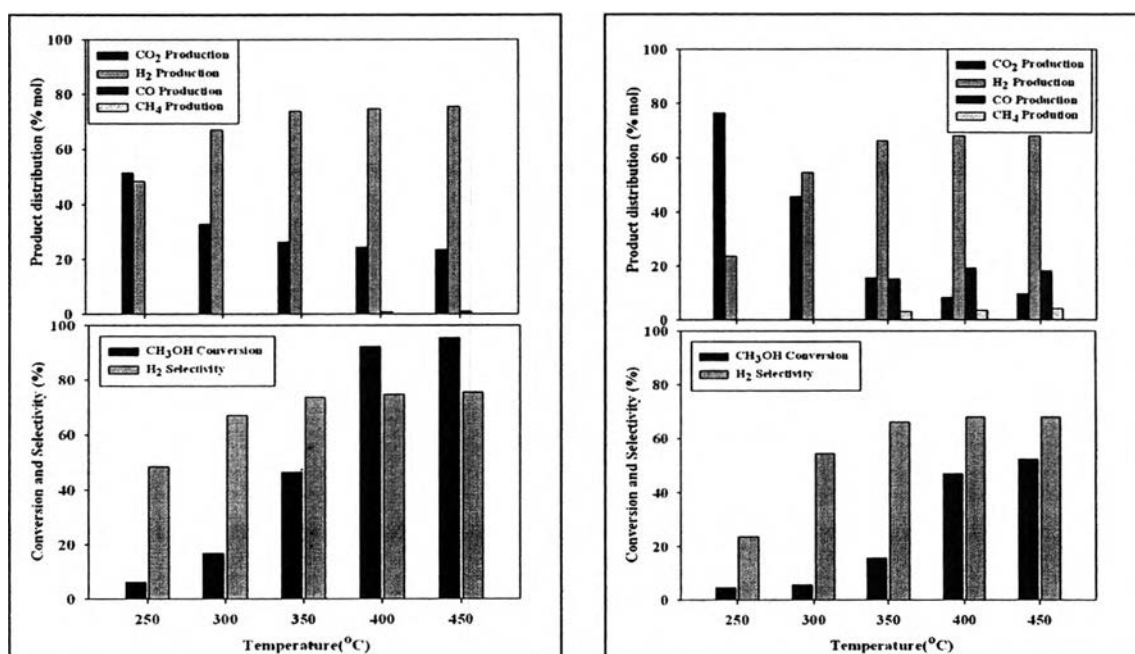
(a) SRM reaction

(b) DM reaction



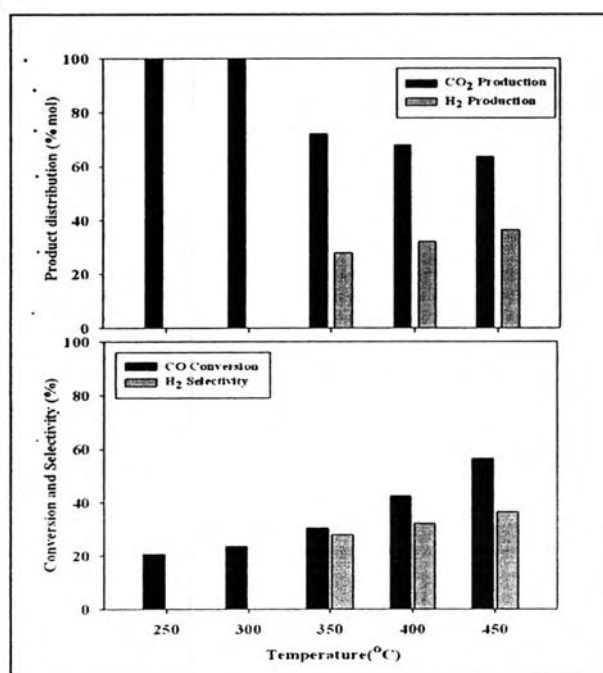
(c) WGS reaction

Figure 4.27 Comparison of catalytic performance of Au/ZnO-Fe₂O₃ catalysts in SRM, DM, and WGS reactions.



(a) SRM reaction

(b) DM reaction



(c) WGS reaction

Figure 4.28 Comparison of catalytic performance of Au/ZnO catalysts in SRM, DM, and WGS reactions.