



CHAPTER IV

RESULTS AND DISCUSSION

In the previous study (Chirddilok, 2009), copper-based catalysts were developed for dehydroxylation of glycerol to produce propylene glycol. The Cu-ZnO/Al₂O₃ catalyst showed the highest catalytic activity compared with Cu/Al₂O₃ and Cu/ZnO catalysts. When compared with the catalyst prepared by co-precipitation, the stability of the impregnated catalyst was lower than the co-precipitated catalyst. The better performance of the co-precipitated catalyst might be attributed the presence of CuO highly dispersed in spinel-like matrix. Therefore, in the present study, we focus on sol-gel method with intention to improve the dispersion of CuO species.

4.1 Incipient Wetness Impregnation (IWI) and Co-precipitation (COP)

Figure 4.1 shows the comparison of catalytic activity between the catalyst prepared by co-precipitation and impregnation. The co-precipitated catalyst shows higher stability than the impregnated catalyst at LHSV of 1.5 h⁻¹.

By definition, LHSV refers to the ratio between the hourly flow of liquid (ml/h) and the volume of catalyst (ml). Due to the difference in bulk density, at the same volume, the weights of catalysts prepared by co-precipitation and impregnation are different, as shown in Table 4.1.

Table 4.1 Catalyst weights and volumes obtained by different preparation methods

Preparation method	Volume (ml)	Catalyst weight (g)
IWI	2.0	1.31
COP	2.0	2.40

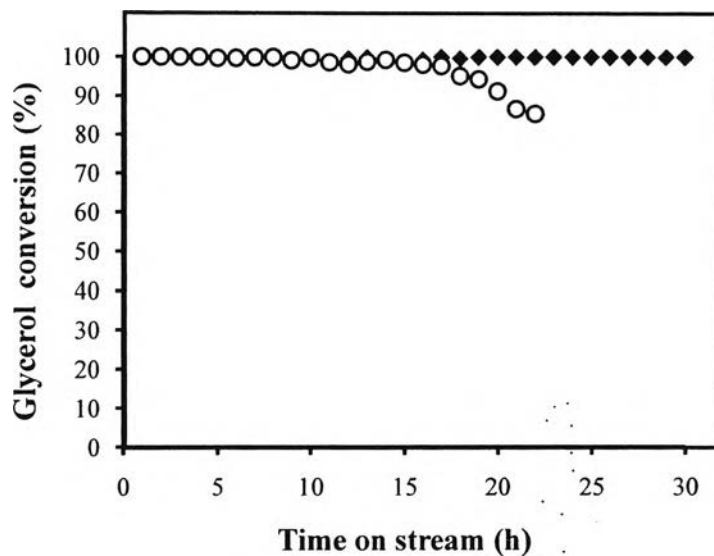


Figure 4.1 Glycerol conversion as a function of time on stream over Cu-ZnO/Al₂O₃ catalysts prepared by different preparation methods: (○) incipient wetness impregnation, and (◆) co-precipitation. Reaction conditions: 250°C, 500 psig, H₂:glycerol = 4:1, and LHSV = 1.5 h⁻¹.

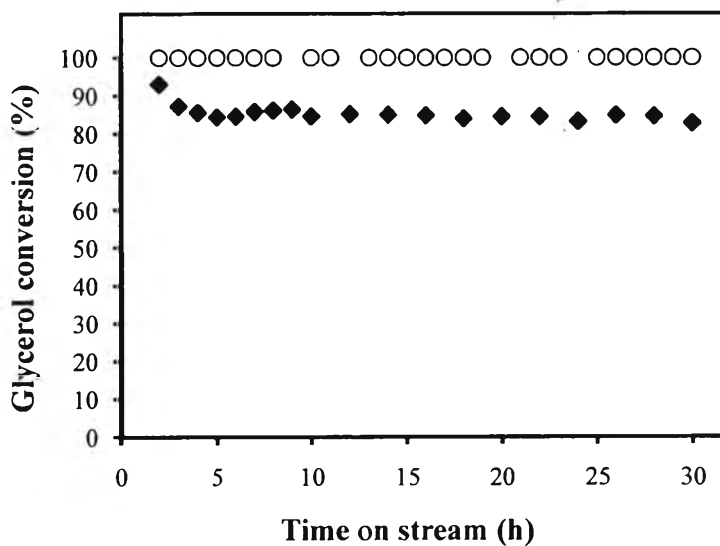


Figure 4.2 Glycerol conversion as a function of time on stream over Cu-ZnO/Al₂O₃ catalysts prepared by different preparation methods: (○) incipient wetness impregnation, and (◆) co-precipitation. Reaction conditions: 250°C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹.

The weight of co-precipitated catalyst is almost two times of impregnated catalyst at the same volume. The higher the weight of catalyst is used, the higher the active sites are available. Thus, the catalytic activity of co-precipitated catalyst may be enhanced by this effect.

From the reason above, the activities of both catalysts were tested again and WHSV which fixes the weight of catalyst were used instead of LHSV (WHSV refers to the ratio between the hourly flow of liquid (g/h) and the weight of the catalyst (g)). The result shows that the stability of co-precipitated catalyst is lower than that of impregnated catalyst at WHSV of 2.78 h^{-1} , as shown in Figure 4.2.

4.2 Sol-Gel Method

4.2.1 Effect of Aluminium Isopropoxide (AIP) to Water Molar Ratio

The activities of the sol-gel Cu-ZnO/Al₂O₃ catalysts prepared at different AIP to water molar ratios are shown in Figure 4.3. Among the catalysts tested, it is found that the catalyst prepared with an AIP-to-water molar ratio of 1:150 shows the highest activity. This result is in agreement with the work of Gonzalez *et al.* (1997). They found that the extent of polymerization was largely dependent on the number of moles of water which was added. In the case of substoichiometric quantities of water, the hydrolysis of the alcoxide was not complete, and linear oligomers were obtained. When the water to alcoxide ratio was in excess of that required for stoichiometry, the time required for the formation of the gel was also observed to increase. Therefore, the formation of the gel obtained from the catalysts prepared with 1 to 100 and 1 to 200 of AIP to water molar ratios may not be complete due to the non-stoichiometric quantities of water.

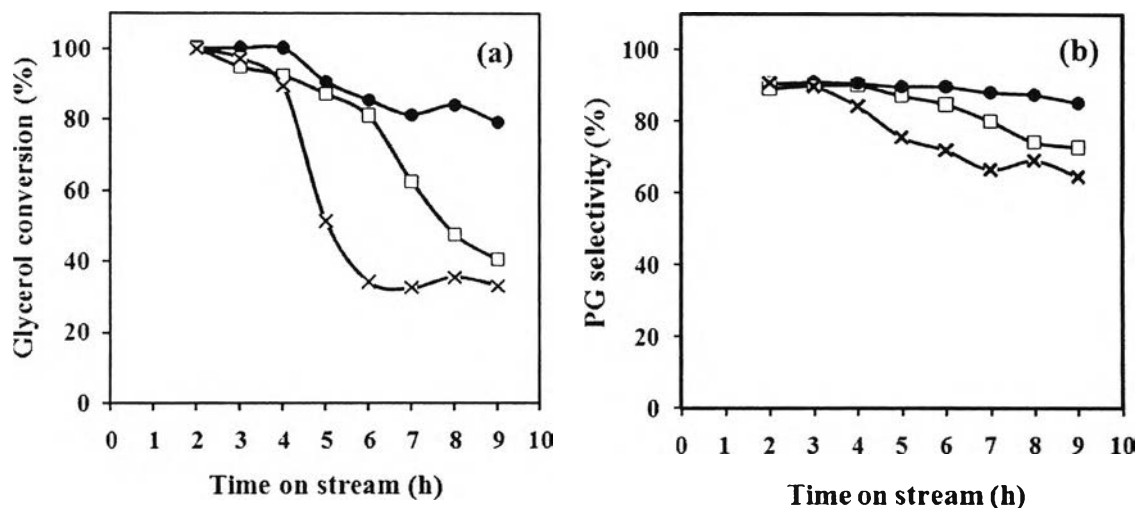


Figure 4.3 (a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream over Cu-ZnO/Al₂O₃ catalysts prepared by different AIP to water molar ratio: (□) AIP:water = 1:100, (●) AIP:water = 1:150, and (x) AIP:water = 1:200. Reaction conditions: 250°C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹.

4.2.2 Effect of Calcination Temperature

The sol-gel Cu-ZnO/Al₂O₃ catalysts with an AIP-to-water molar ratio of 1:150 was selected to study the effect of calcination temperature. The catalysts were prepared and calcined at different calcination temperatures. Figure 4.4 shows the conversion of glycerol and selectivity to propylene glycol, respectively. The catalyst calcined at 500°C shows the highest conversion and selectivity compared with the catalyst calcined at 400°C, 600°C, and 700°C.

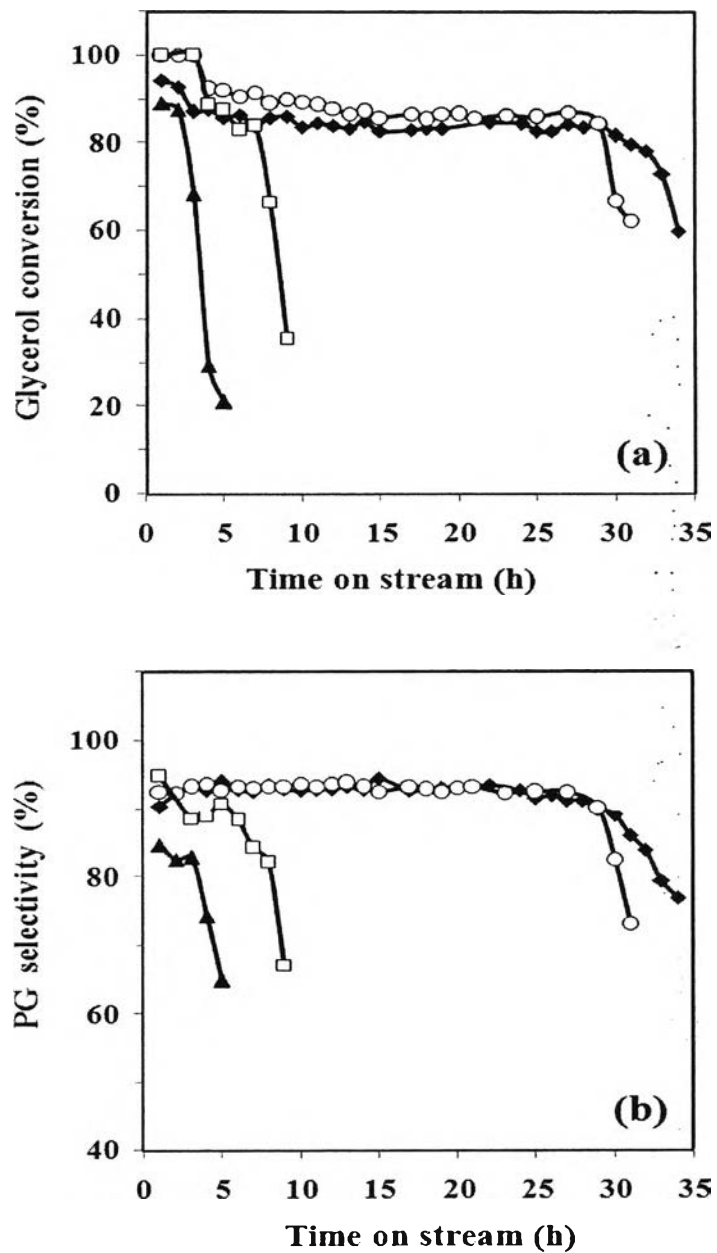


Figure 4.4 (a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream for the Cu-ZnO/Al₂O₃ catalysts prepared by sol-gel method and calcined at different temperatures: (◆) 400°C, (○) 500°C, (□) 600°C, and (▲) 700°C. Reaction conditions: 250°C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹.

The TPR profiles of the calcined and uncalcined catalysts are shown in Figure 4.5. The catalysts calcined at 500 °C, 600 °C, and 700 °C show the combination of two reduction peaks. The first peak is attributed to the reduction of highly dispersed CuO species, and the second at higher temperature is attributed to the reduction of CuO which strongly interacts with ZnO and/or Al₂O₃ support (Yang *et al.*, 2008). By increasing calcination temperature, the reduction peaks are shifted to lower temperature which might be attributed to the formation of the Cu²⁺ ion in a distorted octahedral geometry of CuAl₂O₄ spinel which has been observed at much lower temperatures (Marchi *et al.*, 2003). Moreover, for the catalyst calcined at 400 °C, a large broad peak at around 320 °C may be the reduction peak of incomplete calcination of precursor at this temperature. This result corresponds to the TPR profile of uncalcined catalyst, which shows the peak of H₂ consumption of precursor at around 330 °C.

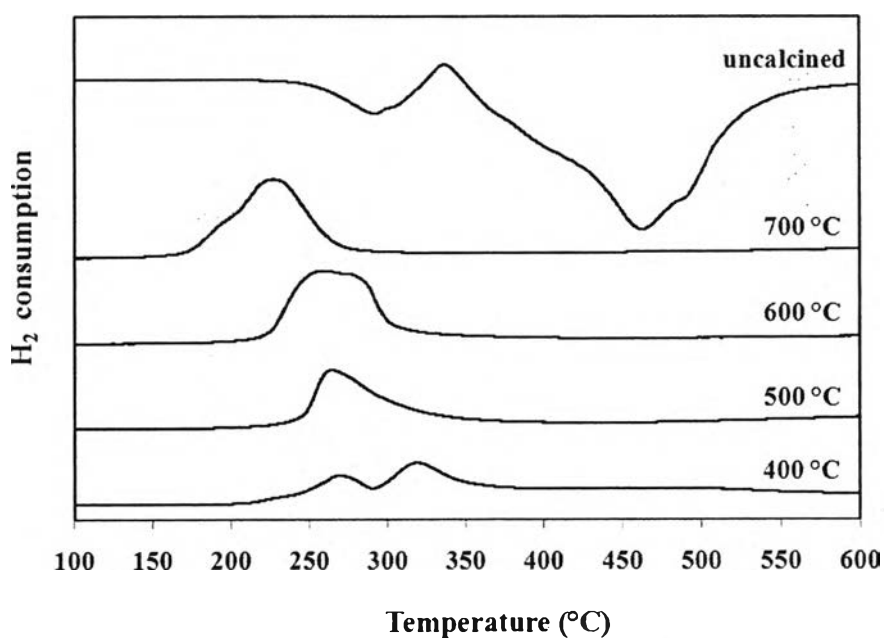


Figure 4.5 TPR profiles of the Cu-ZnO/Al₂O₃ catalysts prepared by sol-gel method and calcined at different temperatures.

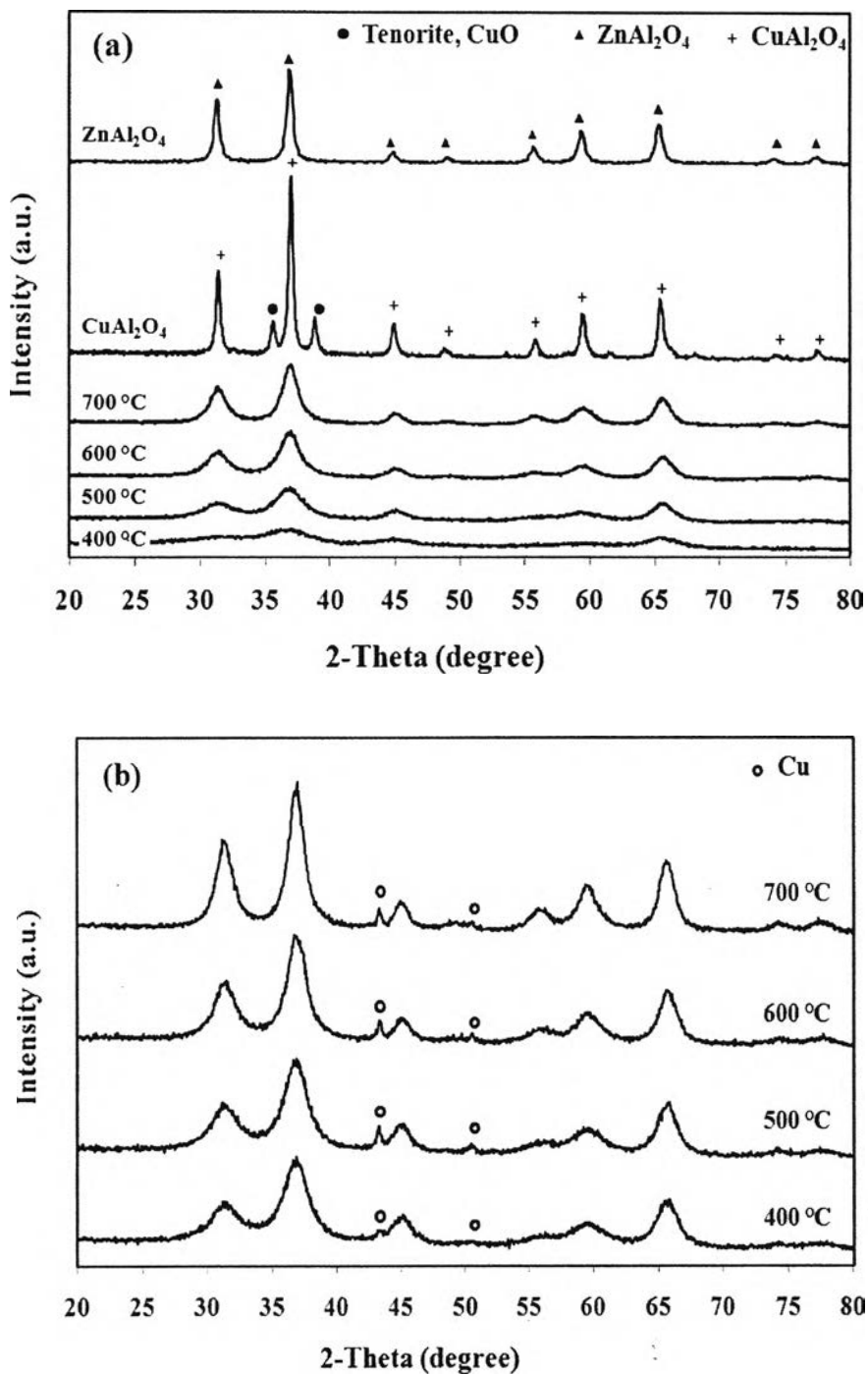


Figure 4.6 XRD patterns of the (a) fresh and (b) reduced Cu-ZnO/Al₂O₃ catalysts prepared by sol-gel method and calcined at different temperatures.

The XRD patterns of the Cu-ZnO/Al₂O₃ catalysts calcined at 400–700 °C are illustrated in Figure 4.6. All samples exhibit diffraction patterns consistent with the presence of aluminate-like spinel species as shown in Figure 4.6 (a). Since, ZnAl₂O₄ and CuAl₂O₄ display nearly coincident diffraction patterns. Therefore, the spinel phase is difficult to specify from X-ray results. It has been reported that bulk CuAl₂O₄ spinel is thermodynamically unstable below 600 °C and an intermediate CuO phase precede to the copper aluminate formation up to 900 °C (Barroso *et al.*, 2006). However, the possible interaction between ZnO and Al₂O₃ to form ZnAl₂O₄ might decrease the possibility of the CuAl₂O₄ formation because the amount of ZnO is larger than Cu by 4 times (El-Shobaky *et al.*, 1999). For XRD patterns of the reduced catalysts in Figure 4.6 (b), the increase in calcination temperature leads to the sharper of XRD diffraction peak which can indicate that the crystalline size of each species increases excepting the catalyst calcined at 400 °C, the intensity of Cu diffraction peak is lower than the other three catalysts. This could be due to unburned precursor present in the catalyst.

Moreover, the result from XRD corresponds with that from BET. Table 4.2 shows the decrease in specific surface area with increasing calcination temperature. The decrease in surface area could be due to the loss of active sites or increasing crystalline size as shown in Figure 4.6

Table 4.2 BET surface areas of the Cu-ZnO/Al₂O₃ catalysts calcined at different temperatures

Calcination Temperature (°C)	BET surface area (m ² /g)
400	224
500	185
600	130
700	104

4.2.3 Effect of Solution pH

In this study, catalysts were prepared with different solution pH and calcined at 500°C. The activities of them are shown in Figure 4.7. From the results, the prepared catalyst with solution pH of 10 shows the highest stability as the conversion starts to decay at 35 hours of time on stream.

This result is in agreement with Kim *et al.* (2000). They found that the performance of Pd-Al₂O₃ prepared in a basic condition showed an activity higher than the one prepared in an acidic condition. The results indicated that the highly dispersed and uniform clusters were formed on the Pd-Al₂O₃ catalyst prepared at pH of 10.

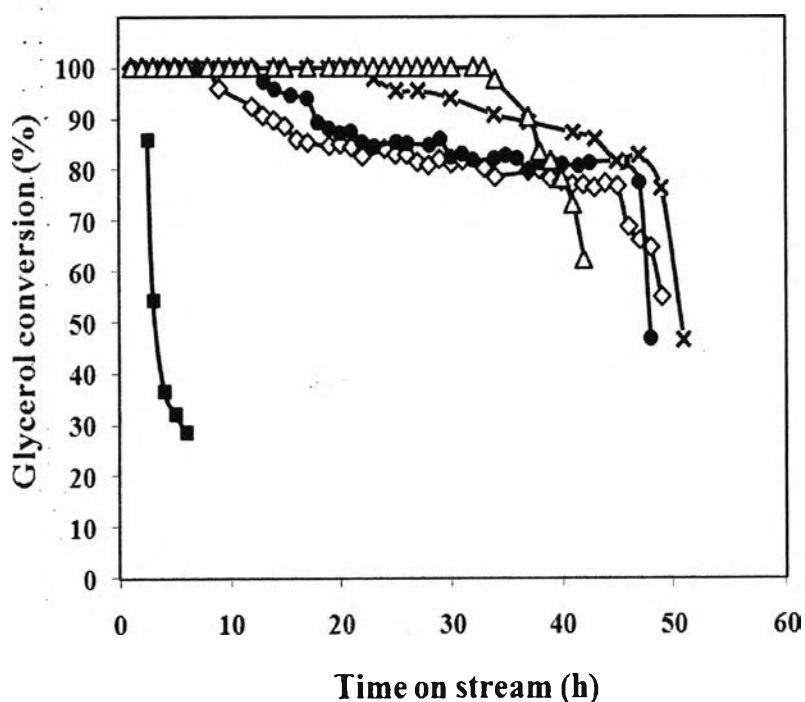


Figure 4.7 Glycerol conversion as a function of time on stream over Cu-ZnO/Al₂O₃ catalysts prepared by different solution pH: (◇) pH = 1, (●) pH = 2, (■) pH = 3, (x) pH = 6, and (△) pH = 10. Reaction conditions: 250°C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹.

It has been known that under acidic condition hydrolysis occurs at a faster rate than condensation and the resulting gel is weakly branched. Under basic condition, the condensation rate is higher than hydrolysis rate and the resulting gel is highly branched and contains colloidal aggregates (Ertl *et al.*, 1999).

As pH value increased, the network structures were developed in the gels. The three-dimension networks were completely formed. The gel precursors become the network structures with a lot of pores. The formation of the porous network structures may be originated from the release of gasses, such as NH_3 and H_2O during drying process. In fact, during calcination, the NH_4NO_3 can decompose to release NH_3 , NO_x and water vapor. For the case of high pH value much NH_4NO_3 remains in dried gels. Thus, a lot of gasses will be released from the precursors during calcinations, resulting in high porous materials (Yue *et al.*, 2004).

4.3 Effect of Catalyst Preparation Technique on Catalytic Performance

In this part, the activities of catalysts prepared by different methods were compared. The sol-gel Cu-ZnO/ Al_2O_3 catalyst with an AIP-to-water molar ratio of 1:150, solution pH of 10, and calcination temperature of 500 °C was selected to compare with the catalyst prepared by co-precipitation and impregnation. Due to the difference in bulk density as shown in Table 4.3, the catalytic activity of the catalysts prepared by different methods cannot directly be compared because of the difference in contact time between reactant and catalyst.

Table 4.3 Bulk density of the catalysts prepared by different methods

Preparation method	Bulk density (ml/g)
IWI	1.45
SG	1.80
COP	0.80

To solve this problem, SiC, an inert material, is used as a diluent to increase catalyst volume, while the weight of catalyst is still the same. To obtain the same volume of all catalysts, the difference of dilution ratio is required and the details are shown in Appendix C.

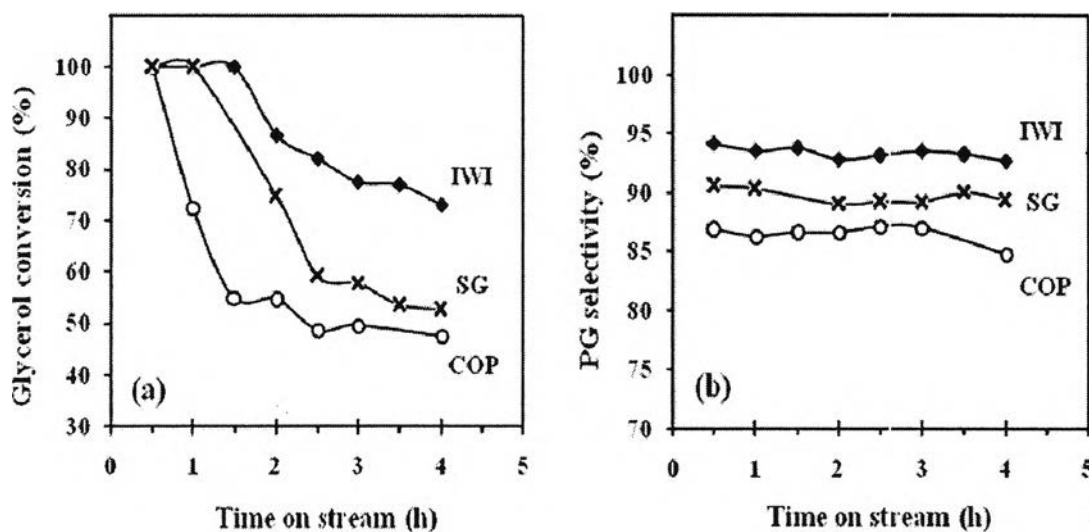


Figure 4.8 Plot of (a) glycerol conversion and (b) propylene glycol selectivity as a function of time on stream over Cu-ZnO/Al₂O₃ catalysts prepared by different preparation methods. Reaction conditions: 250 °C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹.

Figure 4.8 shows the catalytic activity and product selectivity of the Cu-ZnO/Al₂O₃ catalysts prepared by incipient wetness impregnation, co-precipitation, and sol-gel methods. The experimental results demonstrate that the impregnated Cu-ZnO/Al₂O₃ catalysts showed the highest conversion and selectivity compared to the catalyst prepared by co-precipitation and sol-gel methods. This can be possibly attributed to more Cu species exposed on the catalyst surface—in case of the impregnated Cu-ZnO/Al₂O₃ catalyst—instead of entering the bulk as in sol-gel and co-precipitated catalysts leading to more active site for reaction.

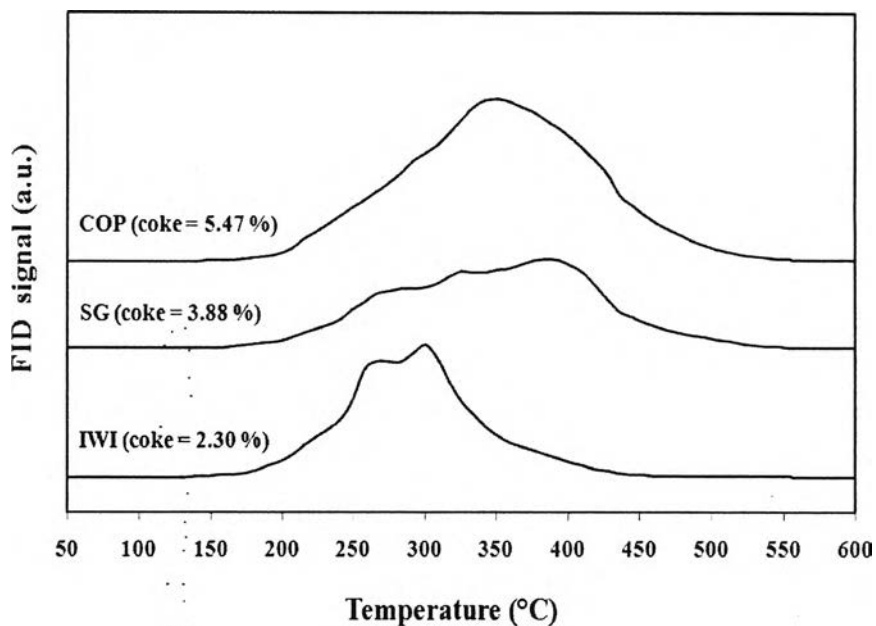


Figure 4.9 Temperature-programmed oxidation (TPO) profiles of the spent Cu-ZnO/Al₂O₃ catalysts prepared by different preparation methods. (Reaction conditions: 250 °C, 500 psig, H₂:glycerol = 4:1, and WHSV = 2.78 h⁻¹).

The TPO profiles and percentages of carbon deposit on the spent Cu-ZnO/Al₂O₃ catalysts as analyzed by temperature-programmed oxidation (TPO) are shown in Figure 4.9. It was found that the highest amount of coke was observed on the spent co-precipitated catalyst. Moreover, the coke obtained over the impregnated Cu-ZnO/Al₂O₃ catalyst can be removed at relatively lower temperature. This result is in agreement with the loss in catalytic activities of the Cu-ZnO/Al₂O₃ catalysts as mentioned earlier. This coke may be formed by unwanted polymerization of unsaturated intermediates (Ertl *et al.*, 2008). The TPO results indicate that the poor stability of the sol-gel and co-precipitated catalysts could be due to high amount of coke which can plug the catalyst pores. Therefore, they cannot easily remove at low temperature.

As shown in Table 4.4, the impregnated Cu-ZnO/Al₂O₃ catalyst has a lower surface area and pore volume compared with γ -Al₂O₃ support, while pore diameter is

still the same. This is possibly due to loss of pore size caused by Cu and ZnO impregnation (Zhang *et al.*, 2009). In spite of the lowest BET surface area, the Cu-ZnO/Al₂O₃ prepared by incipient wetness impregnation shows the highest activity. Therefore, the surface area is not an important parameter for this reaction. It can be observed that, catalytic activities of the Cu-ZnO/Al₂O₃ catalysts decreased with a decrease in pore diameter. This may lead to pore plugging of carbon deposition when large amount of coke was formed and result in losing the active sites for reaction (Ertl *et al.*, 2008).

4.4 Catalyst Regeneration

In this study, the spent Cu-ZnO/Al₂O₃ catalysts were regenerated in-situ in order to eliminate the deposited carbon on the surface. After that the regenerated Cu-ZnO/Al₂O₃ catalysts were re-tested at the same condition as the fresh catalysts.

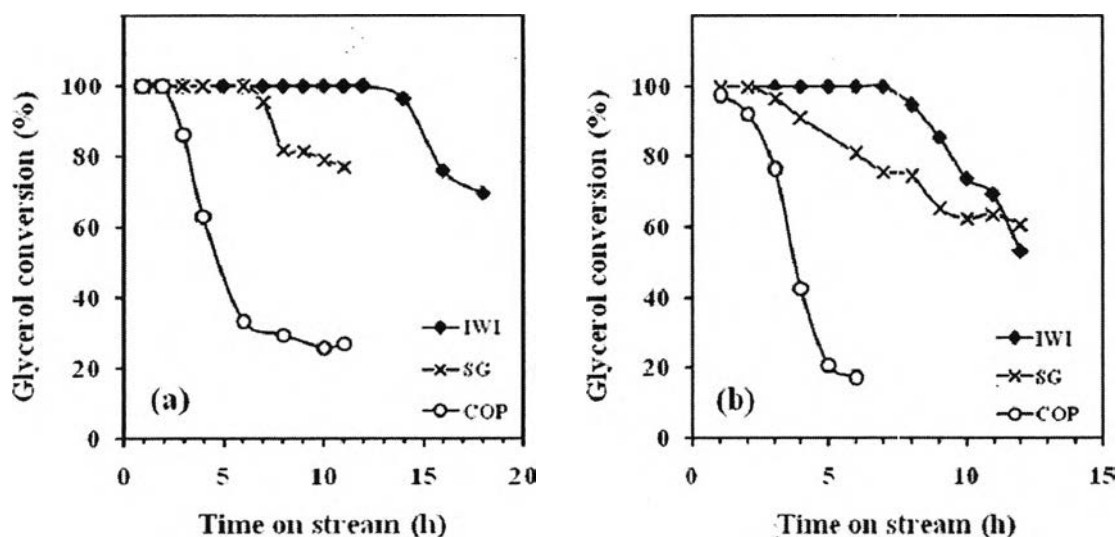


Figure 4.10 Time course of conversion of glycerol over the (a) fresh, and (b) regenerated Cu-ZnO/Al₂O₃ catalysts: Reaction conditions: 250 °C, 500 psig, H₂:glycerol = 4:1

Figure 4.10 shows the glycerol conversion as a function of time on stream for the fresh and regenerated Cu-ZnO/Al₂O₃ catalysts. The result reveals that the regenerated catalysts give the conversion as good as the fresh catalyst at the beginning of reaction time. However, the stability of the regenerated catalysts is lower than the fresh catalysts. Therefore, it may imply that the deactivation of the first cycle is not only due to the coke formation.

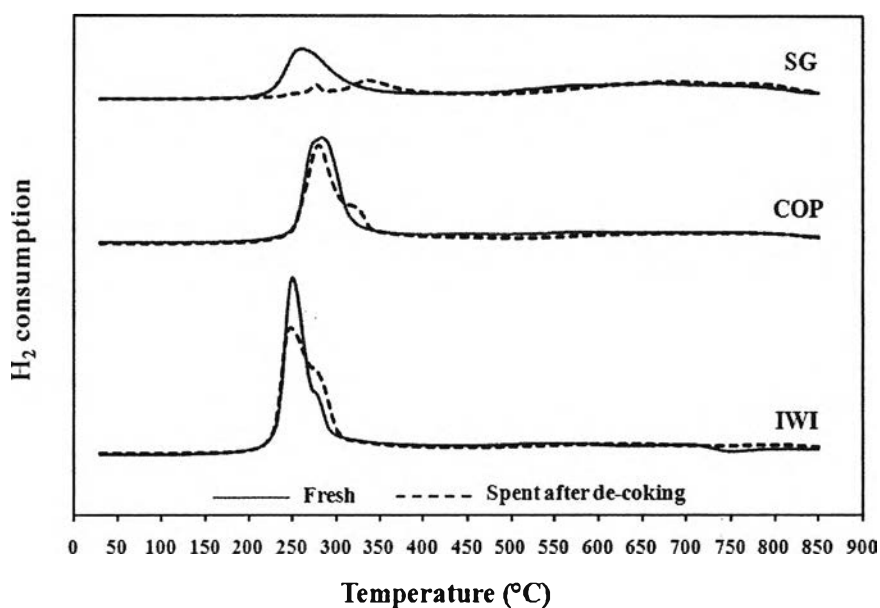


Figure 4.11 TPR profiles of the fresh and spent Cu-ZnO/Al₂O₃ catalysts prepared by different methods.

The H₂-TPR profiles of the Cu-ZnO/Al₂O₃ catalysts before and after the first cycle of reaction are shown in Figure 4.11. All of the spent catalysts from the first cycle have two reduction peaks. The low-temperature peak describes a process in which small grains of CuO were reduced into Cu. The high-temperature peak describes a process in which larger grains of CuO were reduced into Cu. The temperature of reducible CuO peaks of the spent catalysts were separated and shifted higher, compared with that of the fresh catalysts. This fact implies that some grains of Cu become larger during the course

of reaction (Dong-sheng *et al.*, 2008), which is another important cause of the catalyst deactivation. Moreover, in the case of the sol-gel Cu-ZnO/Al₂O₃ catalysts the H₂ consumption of spent catalyst is much less than that of the fresh catalyst, indicating the decrease in Cu contents.

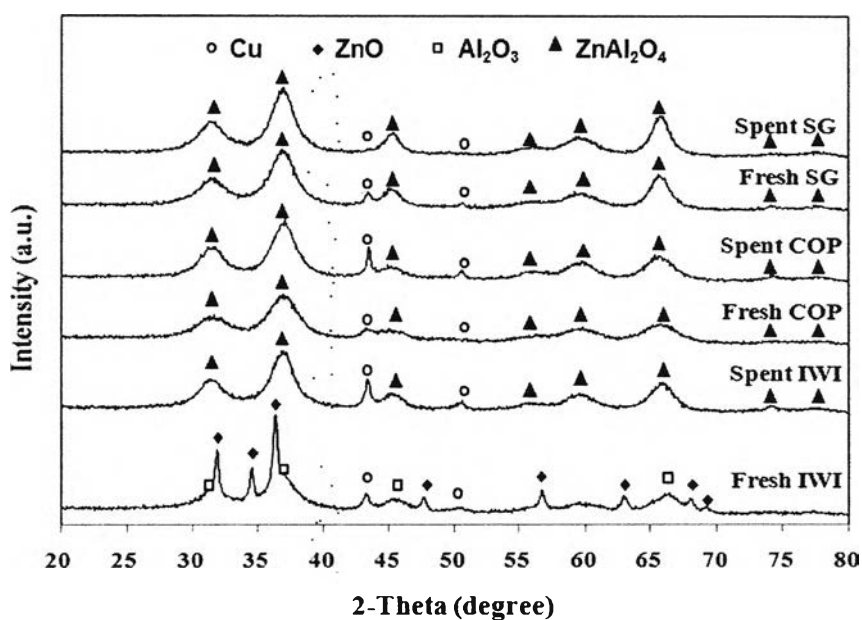


Figure 4.12 XRD patterns of the reduced Cu-ZnO/Al₂O₃ catalysts prepared by different methods: (○) Cu, (◆) ZnO, (□) Al₂O₃ and (▲) ZnAl₂O₄.

Figure 4.12 shows the XRD patterns of the reduced Cu-ZnO/Al₂O₃ catalysts, the change in diffraction lines of all catalysts before and after reaction is observed. For the impregnated and co-precipitated catalysts, the spent Cu-ZnO/Al₂O₃ catalysts after de-coking provide a higher intensity of Cu diffraction peak than the fresh catalysts. This exhibits the larger crystallize size of Cu species. While the Cu diffraction peak of the sol-gel catalyst shows the decrease in intensity after the reaction indicating the loss of Cu species which corresponds with the TPR result.

Moreover, the phase change in the spent impregnated Cu-ZnO/Al₂O₃ catalyst is observed. The diffraction peak of ZnO is absent after the course of reaction. This indicates that ZnO migrates from the upper layer of γ -Al₂O₃ support into the bulk and forms ZnAl₂O₄ phase. In addition, the catalytic activities of γ -Al₂O₃ support decrease progressively as a function of time on stream due to the formation of metal aluminate which exhibits a lower catalytic activity as compared with the metal oxide itself (El-Shobaky *et al.*, 1999).

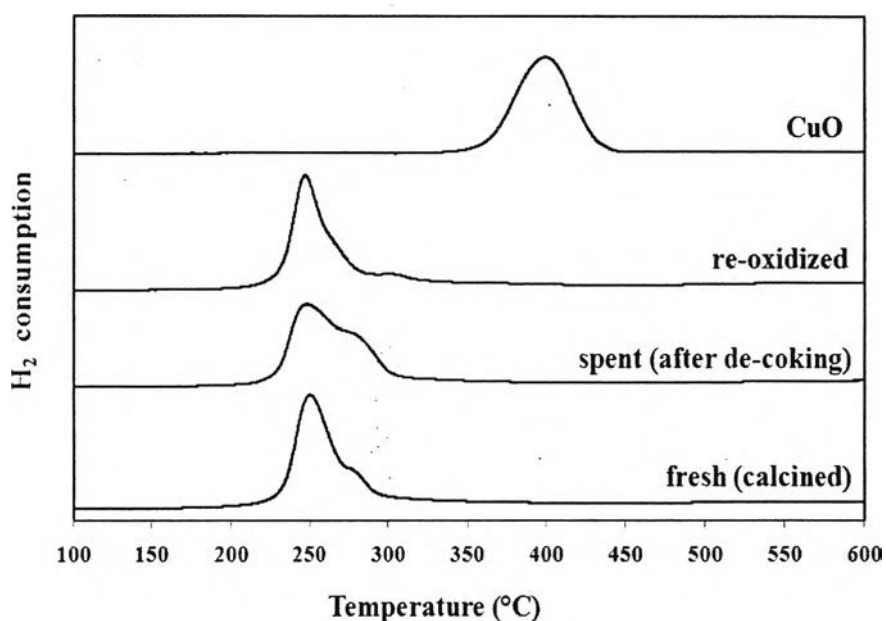


Figure 4.13 TPR profiles of the impregnated Cu-ZnO/Al₂O₃ catalysts at different conditions and the CuO reference standard.

To confirm that the deactivation of the catalysts does not result from de-coking process, the fresh impregnated Cu-ZnO/Al₂O₃ catalyst was reduced, calcined and then characterized with TPR and XRD without passing the reaction.

The TPR profiles of the fresh (calcined), spent (after de-coking), and re-oxidized impregnated Cu-ZnO/Al₂O₃ catalysts are shown in Figure 4.13. The first peak of three catalysts appearing at the same temperature around 250 °C represents the reduction of small uniform CuO grains. While the second peak at higher temperature represents the larger grains of CuO, which correspond to the reduction of bulk CuO. For the spent catalyst (after de-coking), the amount of H₂ consumption at the first peak decreases while the peak at higher temperature increases compared with the fresh (calcined) and re-oxidized catalyst. This indicates that some Cu grains are sintered during the course of reaction corresponding with the work of Dong-sheng *et al.* (2008). However, the reduction and calcination of catalyst have a minor effect on the sintering of Cu which is clearly observed in the case of re-oxidized catalyst.

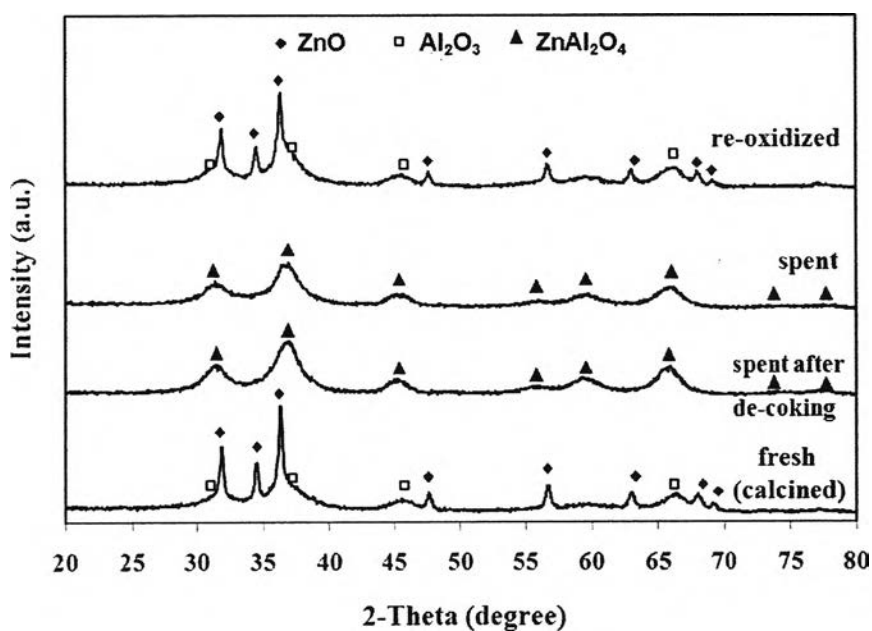


Figure 4.14 XRD patterns of the impregnated Cu-ZnO/Al₂O₃ catalysts at different conditions.

The XRD patterns of the impregnated Cu-ZnO/Al₂O₃ catalysts are shown in Figure 4.14. From the result, the diffraction lines of the fresh (calcined) and re-oxidized

catalysts are similar. This implies that de-coking process does not affect the structure of the catalyst while the phase change of ZnO and γ -Al₂O₃ to the spinel-like phase is significantly observed in the spent catalyst.

The physical properties of the catalysts obtained from BET surface area analyzer are summarized in Table 4.4. The sintering of active metals during the reaction may lead to the decrease in BET surface area. Moreover, after reaction, pore diameter of catalysts is increased while pore volume is decreased. This implies that the pore of catalyst is blocked by some deposited carbon which cannot completely remove by de-coking process. From these data, we can conclude that the decrease in surface area of the spent catalysts is caused by both the sintering of active metals on the catalyst surface and the plugging of residual carbon in the catalyst pore.

Table 4.4 Percentages of carbon deposition and physical properties of the fresh (calcined) and spent Cu-ZnO/Al₂O₃ catalysts after de-coking

Catalyst		Coke (wt%)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Pore diameter (nm)
γ -Al ₂ O ₃		-	256	0.834	8.94
IWI	Fresh	-	145	0.477	8.91
	Spent	2.30	129	0.357	8.94
SG	Fresh	-	175	0.395	6.18
	Spent	3.88	146	0.369	8.90
COP	Fresh	-	182	0.185	3.64
	Spent	5.47	128	0.144	4.64

Table 4.5 The compositions of the fresh (calcined) and spent Cu-ZnO/Al₂O₃ catalysts prepared by different methods

Catalyst		Composition (wt%) *		
		Cu	Zn	Al
IWI	Fresh	9.00	30.80	26.39
	Spent	8.92	29.85	26.66
COP	Fresh	9.82	29.93	26.58
	Spent	9.06	28.88	27.45
SG	Fresh	8.36	28.35	28.61
	Spent	5.26	28.47	30.38

* Determined by XRF

The compositions of the fresh (calcined) and spent catalysts determined by XRF are summarized in Table 4.5. The Cu, Zn, and Al contents of fresh (calcined) and spent catalyst seem to be similar for both impregnated and co-precipitated catalysts, while the content of Cu in sol-gel catalyst is decreased significantly after reaction.

Table 4.6 Percentage of copper leaching after 4 hours of reaction determined by XRF and AAS

Copper Leaching (wt%)	
XRF	AAS
3.10	2.58

To confirm that the Cu species are leached during the reaction, product from reaction of the sol-gel Cu-ZnO/Al₂O₃ catalyst was burnt in the air to eliminate organic compounds at 600 °C. Then, the residual substance was dissolved in aqueous solution of nitric acid and characterized by AAS. The amount of leaching copper obtained from

XRF and AAS are shown in Table 4.6. This result confirms that the Cu species are leached during the reaction. Although the leaching of Cu is observed in the sol-gel catalyst, its catalytic activity is greater than that of the co-precipitated catalyst. It implies that the deactivation of sol-gel catalyst is independent of the leaching of Cu species.