

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Fresh Catalyst Characterization

4.1.1 Brunauer–Emmett–Teller Method (BET)

Textual properties of Al_2O_3 support and $\text{Cu-ZnO/Al}_2\text{O}_3$ catalyst (surface area, total pore volume, and mean pore diameter) obtained from the Brunauer–Emmett–Teller surface area analyzer are shown in Table 4.1. The surface area and pore volume of $\text{Cu-ZnO/Al}_2\text{O}_3$ catalyst were lower than those of alumina support, this loss of pore volume could be due to the high amount of metal loading. However, the pore diameter remained invariant indicating that the loaded metal particles may partially block the pores.

Table 4.1 Textural properties of the catalysts

Catalyst	BET surface area(m^2/g)	Total pore volume(cm^3/g)	Mean pore diameter(nm)
Al_2O_3	256	0.834	8.94
$\text{Cu-ZnO/Al}_2\text{O}_3$	130	0.394	8.92

4.1.2 Atomic Absorption Spectroscopy (AAS)

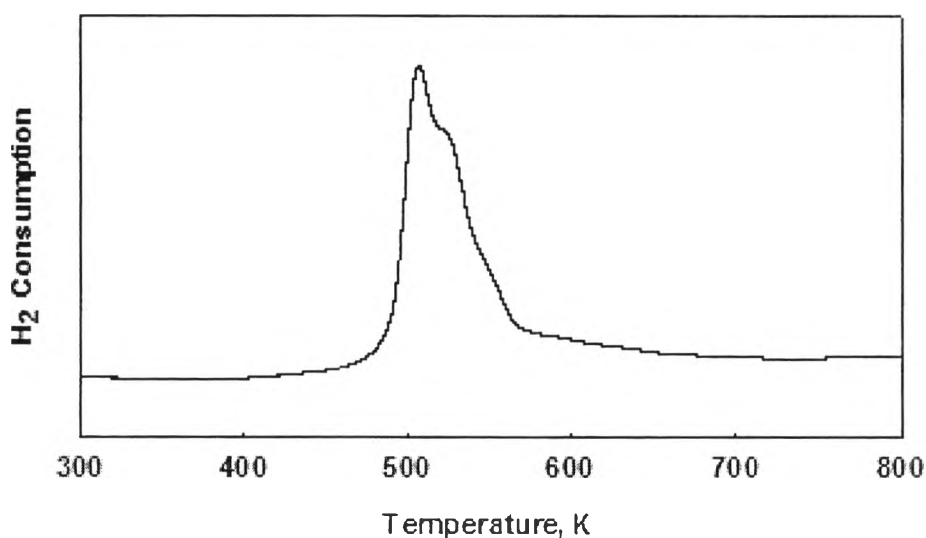
Atomic absorption spectroscopy (AAS) was employed to determine the actual metal loading of the Cu and Zn supported Al_2O_3 catalysts. The AAS results are summarized in Table 4.2. The results indicated that the amount of Cu and Zn loading on Al_2O_3 support lower to expected metal loading amount due to metal precursor impurities.

Table 4.2 The actual and expected metal loading of the catalysts

Cu-ZnO/Al ₂ O ₃	Cu (wt. %)	Zn (wt. %)
Expected loading	10.00	41.38
Actual loading	8.43	31.28

4.1.3 Temperature Programmed Reduction (TPR)

The TPR profile of the fresh catalyst is shown in Figure 4.1. The fresh catalyst showed the reduction peaks at temperature below 623 K, indicating the reduction of highly dispersed copper oxide clusters on the catalyst, while the reduction of pure CuO used as a reference appeared at 667 K. This result is in good agreement with the Cu-ZnO/Al₂O₃ prepared by co-precipitation investigated earlier in literature. The catalyst exhibited a main reduction peak at 523 K represents the small uniform of CuO grains. While the shoulder peak at 543 K represents the larger grains of CuO, which correspond to the reaction of bulk CuO. From TPR result, the suitable reduction temperature is 623 K (Panyad, S., 2011).

**Figure 4.1** TPR profile of fresh Cu-ZnO/Al₂O₃ catalyst.

4.2 Feed Characterization

Types of glycerol vary depend on the properties of feedstocks in biodiesel production and catalyst using in biodiesel production. In this work, glycerol feedstocks were characterized for their glycerol content by gas chromatograph and their impurities contents ICP-OES technique.

4.2.1 Gas Chromatograph (Flame Ionization Detector)

The amount of glycerol in each feedstock was analyzed by gas chromatograph equipped with a flame ionization detector. The amounts of glycerol content with different feedstocks are shown in Table 4.3. Refined glycerol with 95.58 % was used as reference. The result showed that refined glycerol had more glycerol content as compared to yellow grade glycerol, technical grade glycerol, and crude glycerol, respectively.

Table 4.3 The amounts of glycerol content with different feedstocks

Feedstocks	Glycerol content (wt. %)
Refined glycerol	99.58
Yellow grade glycerol	79.85
Technical grade glycerol	80.44
Crude glycerol	58.14

4.2.2 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The inductively coupled plasma optical emission spectrometry (ICP-EOS) was used to detect the amount of trace metals in feedstocks. The metals investigated in this work are Mg, Na, P, Ca, and K. The amount of metals in each feedstocks are shown in Tables 4.4 and 4.5. The results showed the amount of Mg, Ca, and P in crude glycerol feedstock was slightly different as compared to rapeseed

crude glycerol from literature (Thompson, J.C., 2006). However, the amount of Na in crude glycerol is much lower than those from literature (Thompson, J.C., 2006). Moreover, the amount of K in crude glycerol is much higher than those from literature. Since, different catalyst was used in biodiesel production. The results also showed that the amount of metal impurities in crude glycerol was higher than technical grade glycerol, yellow glycerol, and refined glycerol, respectively. Especially, the amount of Na and K in crude glycerol and technical glycerol are much higher than yellow glycerol and refined glycerol. In addition, the amounts of impurities in products are lower than glycerol feedstocks due to some impurities deposited on the catalysts.

Table 4.4 Concentration of impurities in feedstocks analyzed by ICP-OES compared with literature

Feedstock	Mg (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	P (ppm)
Refined glycerol	< 1	4	< 1	16	< 1
Yellow grade glycerol	< 1	1	< 1	16	< 1
Technical grade glycerol	2	1,034	4,853	24	24
Crude glycerol	6	1,054	10,180	51	35
Crude glycerol, Rapeseed	4	10,600	< 40	24	65

(Thompson, J.C., 2006)

Table 4.5 Concentration of impurities in products analyzed by ICP-OES

Feedstock	Mg (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	P (ppm)
Refined glycerol	3	6	2	22	6
Yellow grade glycerol	2	8	< 1	16	7
Technical grade glycerol	14	410	4,005	24	7
Crude glycerol	2	1,438	5,024	51	13

4.3 Catalytic Activity Testing

4.3.1 Standard Analysis

The chemical standard such as propanol, acetol, propylene glycol, and glycerol were analyzed by gas chromatograph equipped with an FID detector (Agilent 6890) to identify peaks of compositions of feedstocks, intermediates, and products. A chromatogram of glycerol dehydroxylation to propylene glycol analyzed is shown in Figure 4.2. The retention time and response factor for the standards are shown in Table 4.5.

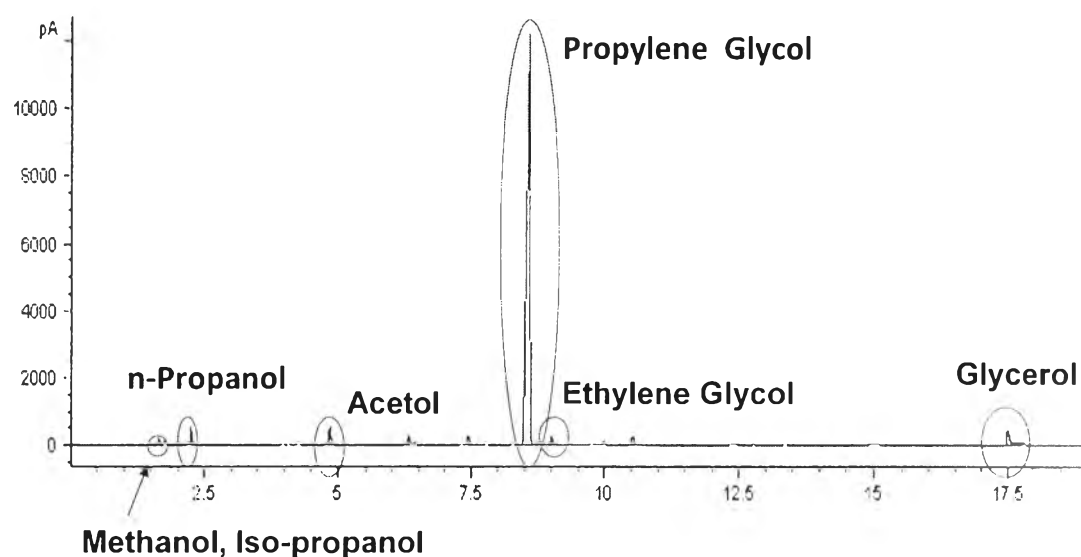


Figure 4.2 Typical GC chromatogram of liquid products obtained from the dehydroxylation to propylene glycol.

Table 4.6 Retention times and response factors of standard chemicals analyzed by a GC/FID (Agilent GC 6890)

Standard chemical	Retention time (min)	Response factor
Hexane	0.96	1
Methanol	1.00	0.74
Acetone	1.19	1.64
Propanol	1.45	1.78
Acetol	4.72	1.11
Propylene glycol	8.66	0.80
Glycerol	17.94	0.83

4.3.2 Catalytic Activity Testing

4.3.2.1 *Effect of Feed Purity*

Prior to catalyst testing, blank test with pure Al_2O_3 was investigated under the identical catalyst testing conditions. No glycerol conversion was observed over the pure substrate. Therefore, conversion of glycerol observed over the catalysts is due to the presence of Cu–ZnO/ Al_2O_3 catalyst. The major products observed in this study were propylene glycol, acetol and propanol. The plots of glycerol conversion, propylene glycol selectivity, acetol selectivity and propanol selectivity as a function of time on stream with the different glycerol feedstocks—refined glycerol, yellow grade glycerol, technical grade glycerol and crude glycerol are illustrated in Figures 4.3-4.6, respectively. The results showed that the refined glycerol exhibited higher conversion and selectivity as compared to yellow grade glycerol, technical grade glycerol and crude glycerol, respectively. Moreover, catalytic activity of refined glycerol and yellow grade glycerol exhibited high and almost constant during the test but catalytic activity of technical grade glycerol and crude glycerol is moderate at the beginning, and then dropped considerably. As the conversion decreased, the propylene glycol selectivity

decreased with increasing acetol and propanol selectivity. The results agreed well with the mechanism proposed by Dasari *et al.* (Dasari, M.A., 2005) as shown in Figure 4.7. The result also indicated the higher the impurities (Na and K) deposited on the catalyst the lower the catalytic activity and coke formation.

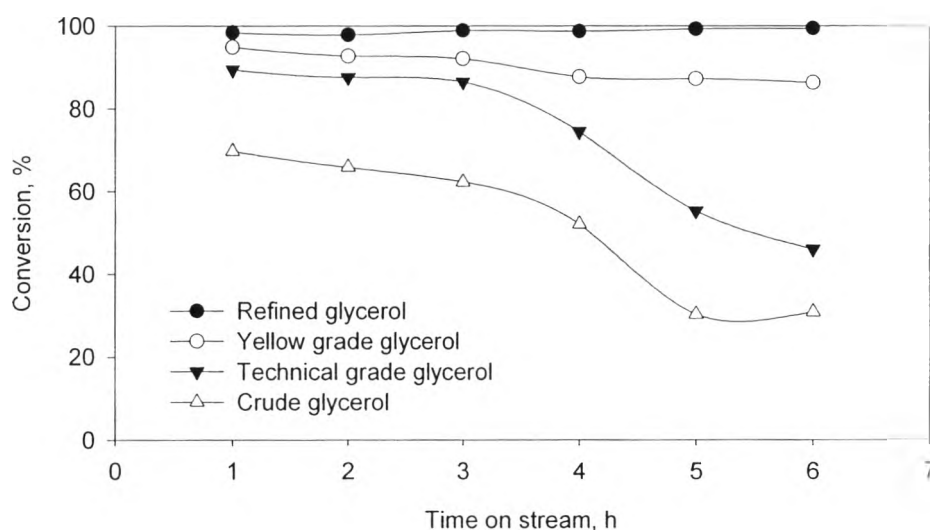


Figure 4.3 The plot of glycerol conversion as a function of time on stream with the different glycerol feedstocks (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2\text{:glycerol} = 4\text{:}1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

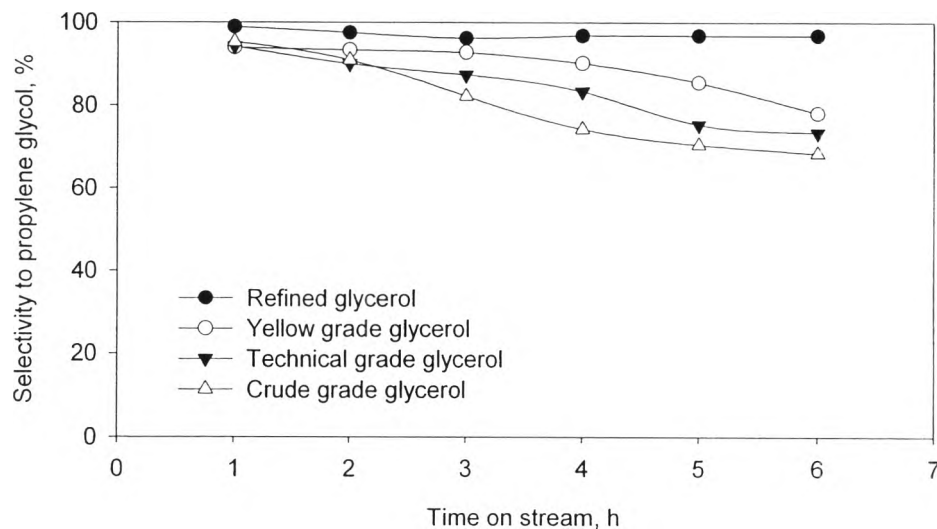


Figure 4.4 The plot of propylene glycol selectivity as a function of time on stream with the different glycerol feedstocks (reaction conditions: $T = 523$ K, $P = 3.2$ MPa, H_2 :glycerol = 4:1, and $WHSV = 3$ h⁻¹).

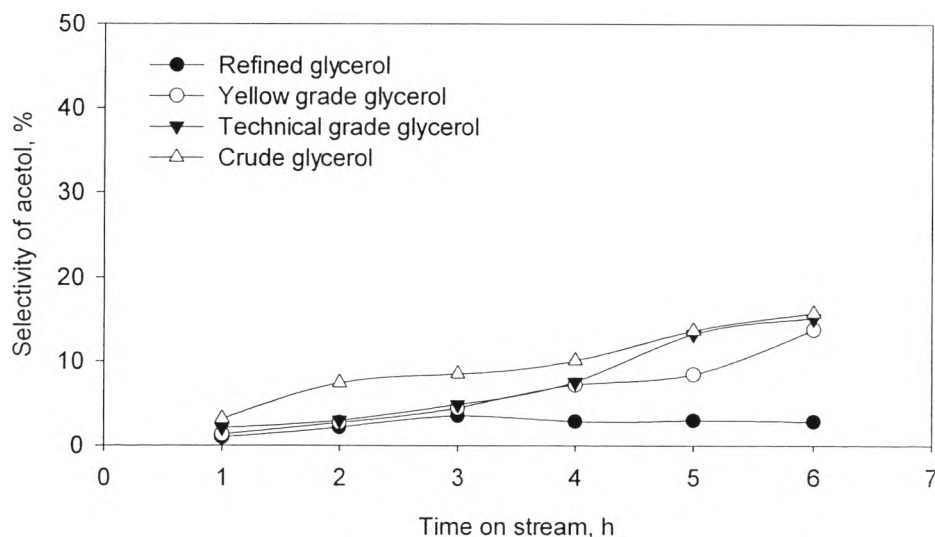


Figure 4.5 The plot of acetol selectivity as a function of time on stream with the different glycerol feedstocks (reaction conditions: $T = 523$ K, $P = 3.2$ MPa, H_2 :glycerol = 4:1, and $WHSV = 3$ h⁻¹).

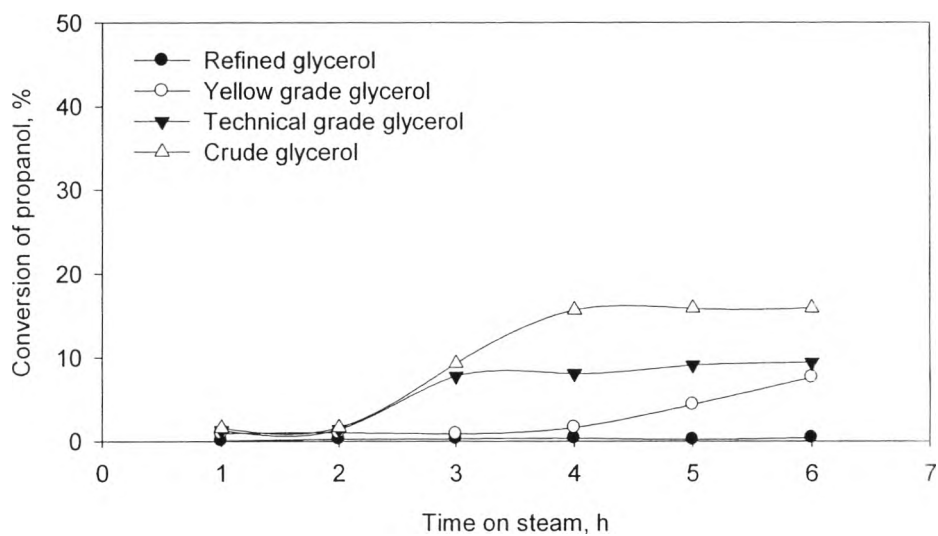


Figure 4.6 The plot of propanol selectivity as a function of time on stream with the different glycerol feedstocks (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2:\text{glycerol} = 4:1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

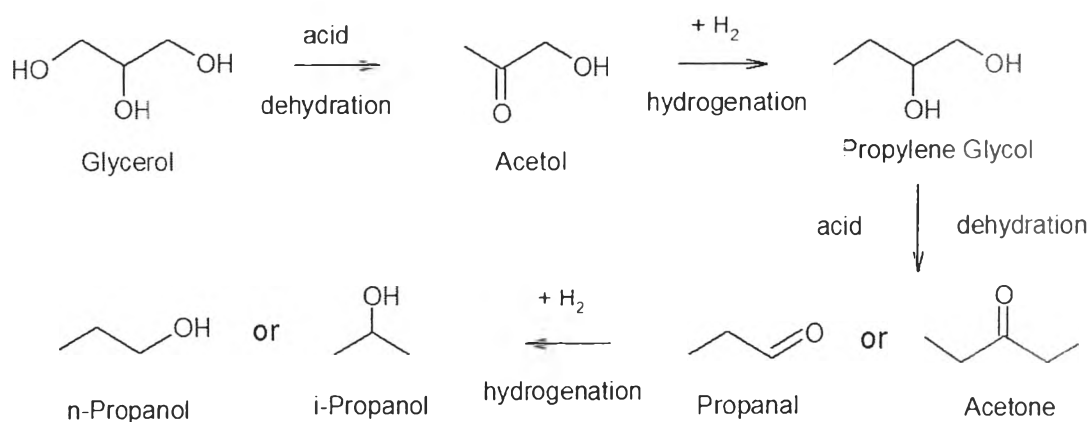


Figure 4.7 The glycerol conversion mechanism by $\text{Cu-ZnO/Al}_2\text{O}_3$ catalyst (Dasari, M.A., 2005).

4.3.2.2 Effect of Na and K

From ICP-OES and catalytic activity with different feedstocks results, the higher impurities (Na and K) contained in glycerol, the lower catalytic activity. Therefore, the effect of Na and K were investigated. The plots of glycerol conversion as a function of time on stream with the different purity glycerols—refined glycerol, refined glycerol mixed with 0.1% Na and refined glycerol mixed with 0.1% K are illustrated in Figure 4.8. The results showed that refined glycerol exhibited higher conversion compared to the one mixed with 0.1% Na and with 0.1% K, respectively. The results revealed that Na and K deposited on catalyst lowered conversion the glycerol conversion. The results indicated that Na and K may poison the active site of catalysts so that the conversion of glycerol decreased. However, K had more influence on conversion of glycerol than Na. Since the atom radius of K (220 pm) is higher than Na (190 pm). So K atom might be blocking the pores of the catalyst easier than Na (Slater J.C., 1964).

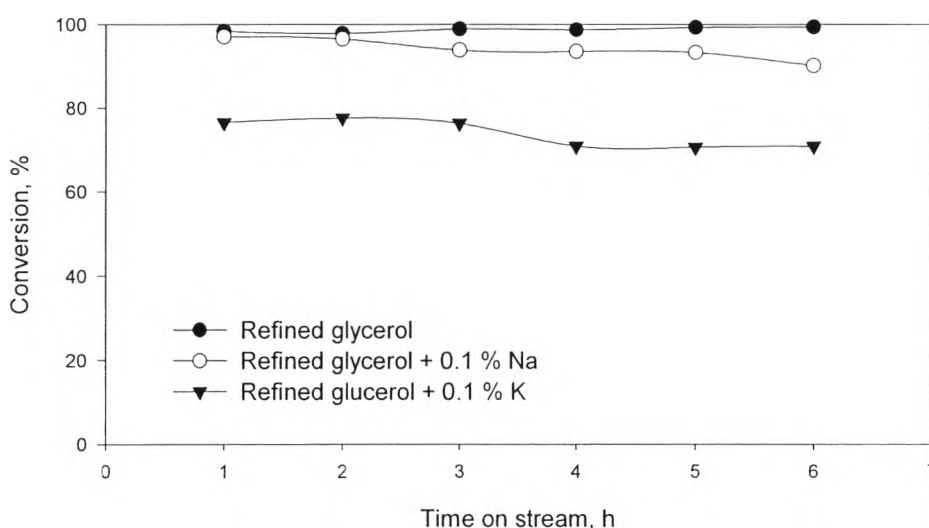


Figure 4.8 The plot of glycerol conversion as a function of time on stream with the different glycerol impurities (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2\text{:glycerol} = 4\text{:}1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

The plots of propylene glycol selectivity, acetol selectivity, and propanol selectivity as a function of time on stream with the different grades glycerol—refined glycerol, refined glycerol mixed with 0.1% Na and refined glycerol mixed with 0.1% K are illustrated in Figures 4.9-4.11. The results show refined glycerol exhibited higher conversion and selectivity as compared to refined glycerol mixed with 0.1% Na, and refined glycerol mixed with 0.1% K, respectively. As the conversion decreased, the propylene glycol selectivity decreased with increasing acetol and propanol selectivity. The results agreed well with the mechanism proposed by *et al.* (Dasari, M.A., 2005) as shown in Figure 4.7.

The results indicated that Na and K contained in glycerol may decrease active site of dehydration of glycerol and basicity property of Na and K can alter dehydration of propylene glycol to propanol or acetone. Therefore, conversion and selectivity to propylene glycol decreased and the selectivity of acetol and propanol increased. Na seemed to have more influence to selectivity than K. Since molar of Na is higher that it of K even amount of Na and K are equal as 0.1 wt. %. Moreover, Na has stronger basicity than K.

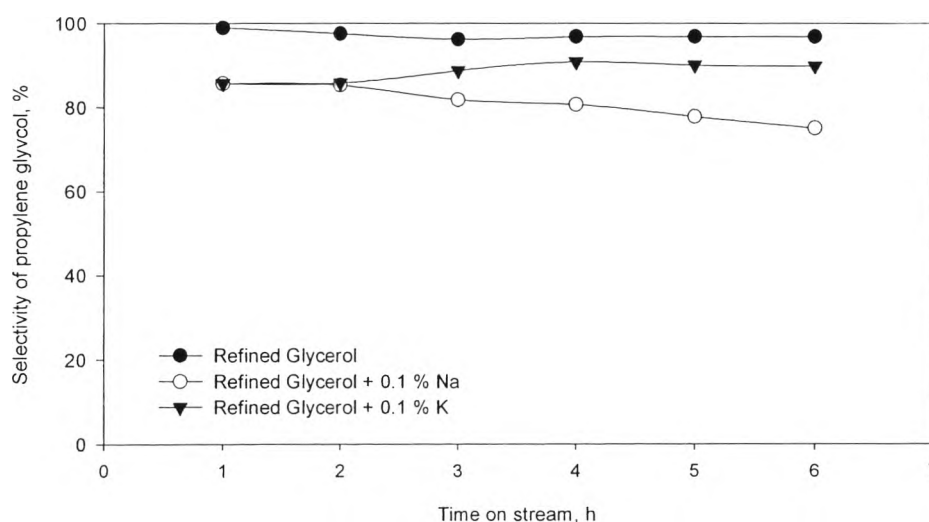


Figure 4.9 The plot of propylene glycol selectivity as a function of time on stream with the different glycerol impurities (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2\text{:glycerol} = 4\text{:}1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

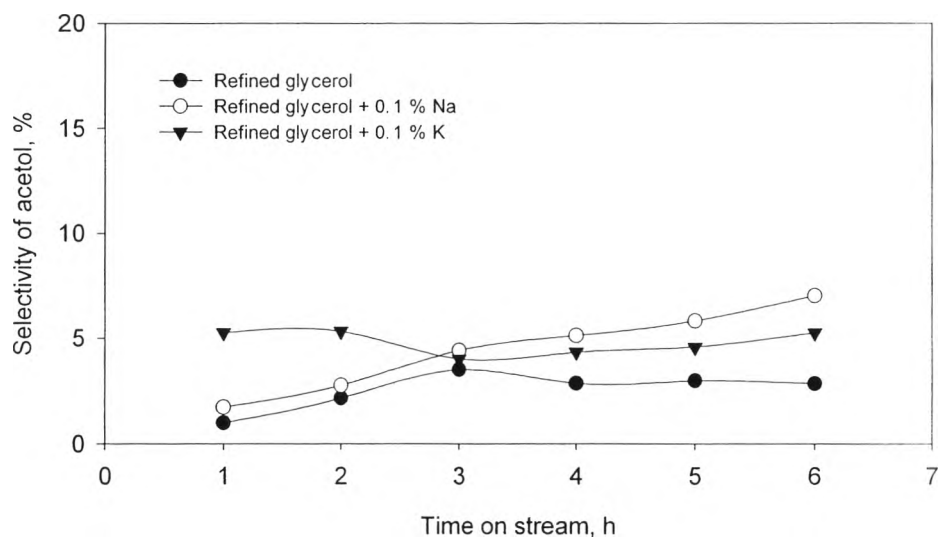


Figure 4.10 The plot of acetol selectivity as a function of time on stream with the different glycerol impurities (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2\text{:glycerol} = 4\text{:}1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

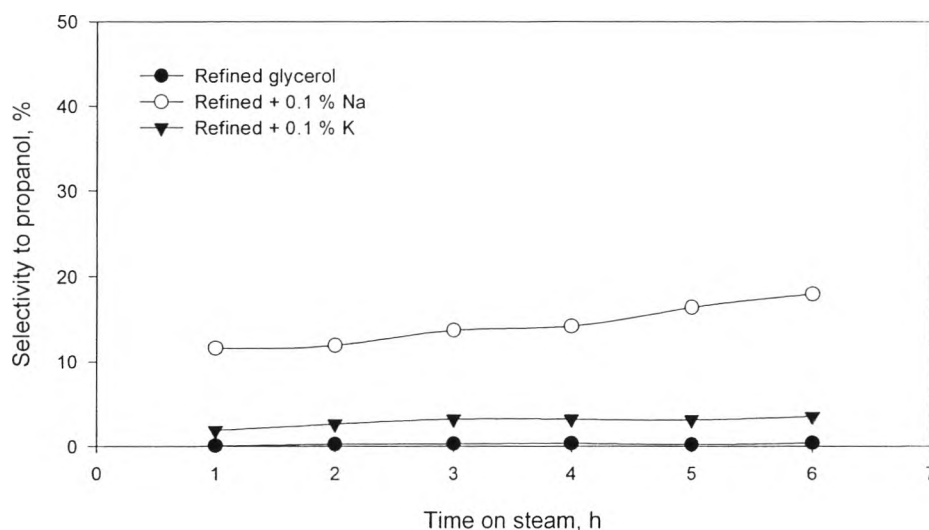


Figure 4.11 The plot of propanol selectivity as a function of time on stream with the different glycerol impurities (reaction conditions: $T = 523 \text{ K}$, $P = 3.2 \text{ MPa}$, $\text{H}_2\text{:glycerol} = 4\text{:}1$, and $\text{WHSV} = 3 \text{ h}^{-1}$).

4.4 Spent Catalyst Characterization

4.4.1 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

The inductively coupled plasma optical emission spectrometry (ICP-OES) was used to determine the amount of metal impurities in spent catalysts. The impurities investigated in this work were Mg, Na, P, Ca and K. The concentration of metal impurities on spent catalysts is shown in Table 4.6. The results showed that spent catalysts using refined glycerol and yellow grade glycerol as feedstocks contained lower amounts of impurities. Spent catalysts using technical grade glycerol and crude glycerol as feedstocks contained higher amounts of impurities, especially Na and K. These impurities may come from the feedstocks which contained some amount of Na and K. The results indicated that Na and K deposited on the spent catalysts had negative effect on glycerol conversion, especially K. The results also indicated that Na and K deposited on the spent catalysts negatively affected the propylene glycol selectivity while acetol selectivity and propanol selectivity were increased. However, Na seemed to have more influence to selectivity than K.

Table 4.7 Concentration of metal impurities on spent catalysts analyzed by ICP-OES

Feedstock	Mg (ppm)	Na (ppm)	K (ppm)	Ca (ppm)	P (ppm)
Refined glycerol	1	7	4	14	< 1
Yellow grade glycerol	1	11	6	15	< 1
Technical grade glycerol	1	191	1,105	17	20
Crude glycerol	1	198	1,028	16	31

4.4.2 Temperature Programmed Oxidation (TPO)

The TPO profiles and calculated amounts of carbon deposition on the spent Cu-ZnO/Al₂O₃ catalysts (after 7 h time on stream) with different feedstocks—refined glycerol, technical grade glycerol, yellow glycerol, and crude glycerol are shown in Figure 4.12. It was found that the spent catalyst of refined glycerol as feedstock contained the highest amount of coke compared to the spent catalyst of yellow grade glycerol, technical grade glycerol, and crude glycerol. The results showed that metal contaminated in feedstocks may poison the active site of the catalysts, thus lowering catalytic activity and coke formation.

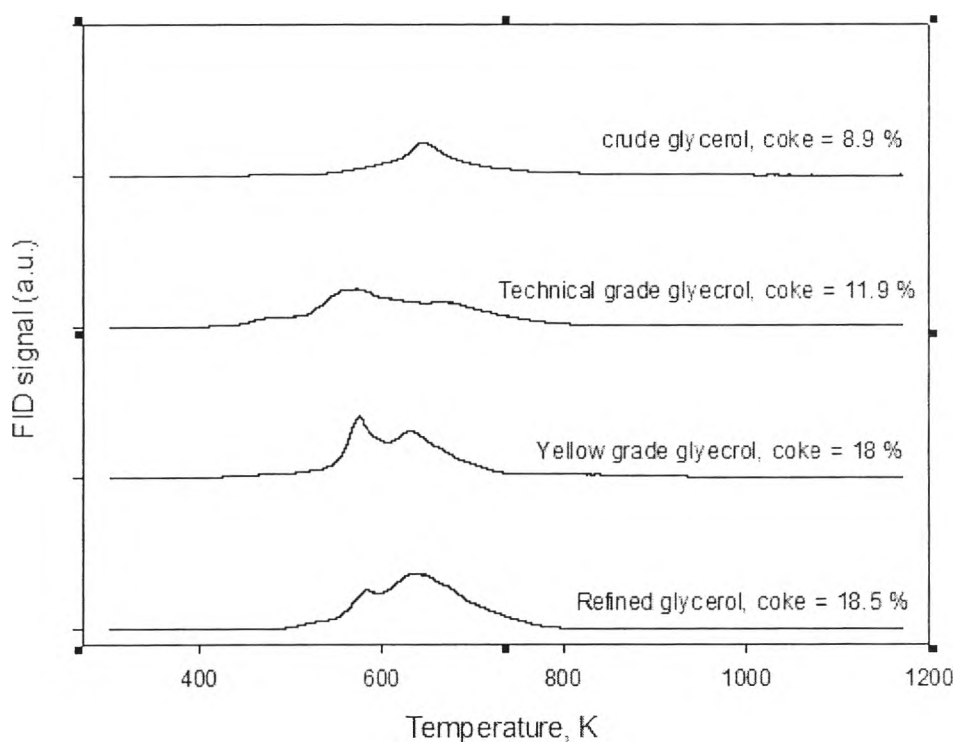


Figure 4.12 TPO profiles of the spent Cu-ZnO/Al₂O₃ catalysts with different feedstocks (refined glycerol, technical grade glycerol, yellow glycerol, and crude glycerol).

The TPO profiles and calculated amounts of carbon deposition on the spent Cu-ZnO/Al₂O₃ catalysts (after 7 TOS) with different feedstocks—refined glycerol, refined glycerol mixed with 0.1% Na, and refined glycerol mixed with 0.1% K are shown in Figure 4.13. It was found that the spent catalyst of refined glycerol as feedstock contained the highest amount of coke compared to the spent catalyst of refined glycerol mixed with 0.1% Na, and refined glycerol mixed with 0.1% K. The results showed that Na and K metal contaminated in feedstocks poisoned the active site of the catalysts, thus lowering catalytic activity and coke formation.

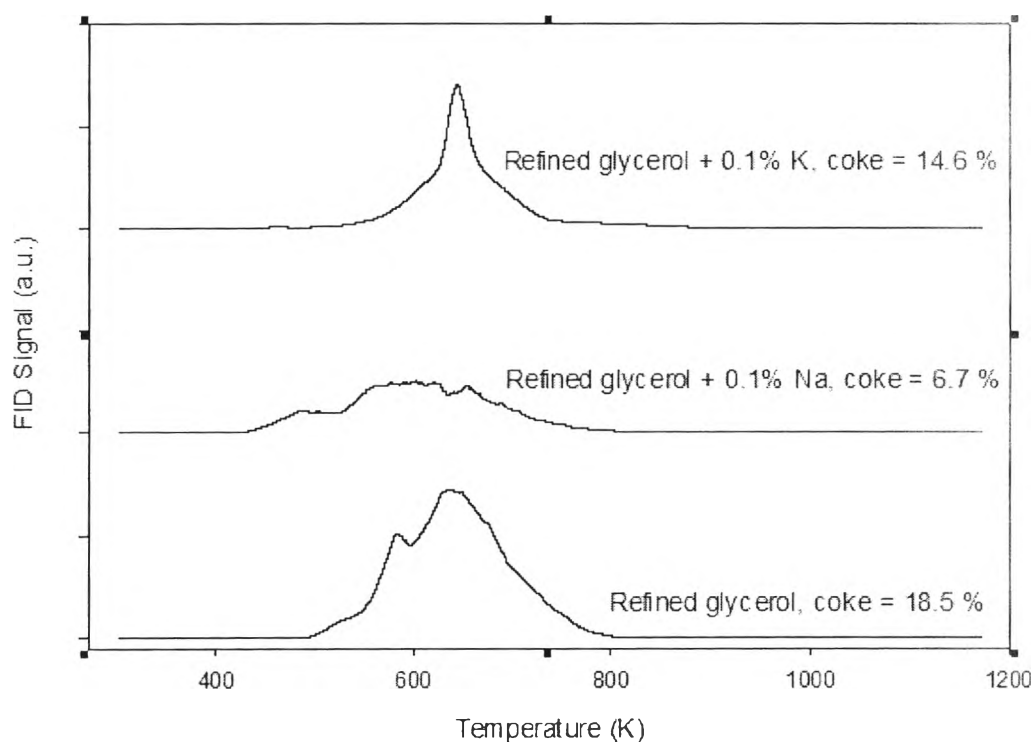


Figure 4.13 TPO profiles of the spent Cu-ZnO/Al₂O₃ catalysts with different feedstocks (refined glycerol, refined glycerol mixed with 0.1% Na, and refined glycerol mixed with 0.1% K).