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APPENDICES

Appendix A The Actual and Expected Metal Loading of the Catalysts by XPS

Table A1 The Actual and Expected Metal Loading of the Catalysts

Catalysts	Cu (wt.%)		Zn (wt.%)		Mg (wt.%)		Al (wt.%)	
	Expected loading	Actual loading	Expected loading	Actual loading	Expected loading	Actual loading	Expected loading	Actual loading
$CuZnO/Al_2O_3$	10.00	9.01	41.38	36.80	-	-	28.75	22.50
$CuZnO/MgO(5)-Al_2O_3(95)$ $CuZnO/MgO(11.84)-Al_2O_3(98.16)$*	10.00	8.54	41.38	34.90	1.64	3.33	27.11	21.30
$CuZnO/MgO(10)-Al_2O_3(90)$ $CuZnO/MgO(19.7)-Al_2O_3(80.3)$*	10.00	8.04	41.38	32.20	3.25	6.08	25.50	21.00
$CuZnO/MgO(15)-Al_2O_3(85)$ $CuZnO/MgO(27.8)-Al_2O_3(72.2)$*	10.00	8.15	41.38	32.70	4.84	8.53	23.91	18.40
$CuZnO/MgO(20)-Al_2O_3(80)$ $CuZnO/MgO(35.7)-Al_2O_3(64.3)$*	10.00	8.18	41.38	33.10	6.41	11.00	22.34	16.00
$CuZnO/MgO(30)-Al_2O_3(70)$ $CuZnO/MgO(47.4)-Al_2O_3(52.6)$*	10.00	8.00	41.38	31.90	9.48	15.40	19.27	13.00
CuZnO/MgO	10.00	7.39	41.38	28.80	28.75	32.80	-	-

* The actual compositions

Appendix B The Metal Interaction on the Surface of the Catalysts

X-ray photoelectron spectroscopy (XPS) technique was employed to study metal support interaction. The XPS spectra of CuZnO/MgO(x)-Al_2O_3(y) and CuZnO/MgO is illustrated in Figure B1. By fitting the XPS spectra, MgO(15)-Al_2O_3(85) mixed oxide support showed the only one peak at 1302.58 eV, dedicated to MgO species. After adding CuO on the mixed oxide support, the increase in MgO showed the formation of new peak at higher binding energy. The appearance of these peaks obviously confirmed the effect of interaction of copper metal with support. This XPS results clearly explained the reason why the reduction peaks of catalysts shifted to the higher temperature as observed in TPR profiles.

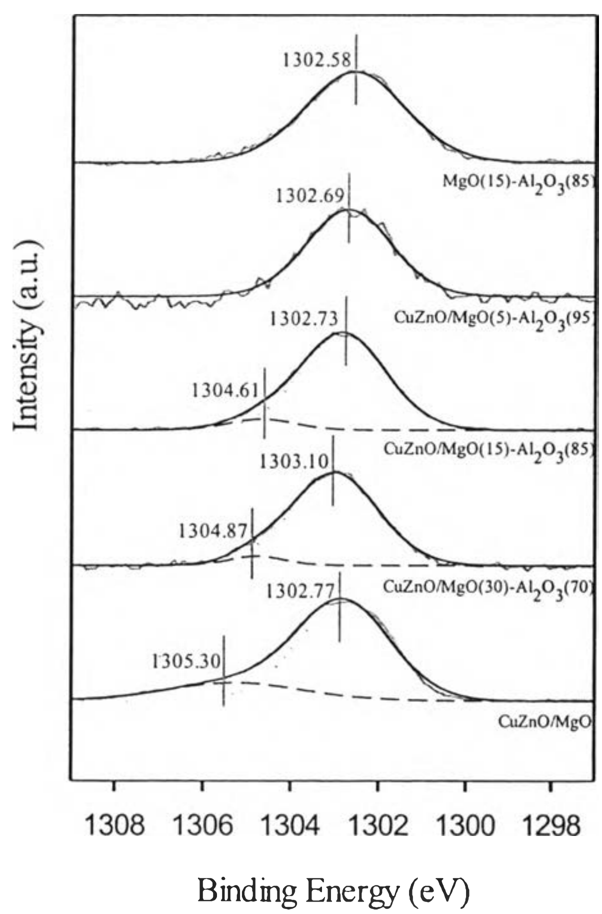

Figure B1 The XPS spectra of Mg (1s) of CuZnO/MgO(x)-Al_2O_3(y) and CuZnO/MgO.

In addition, quantitative analysis of the metal on the catalyst surface is presented in Table B1. The $CuZnO/Al_2O_3$ provided a greater amount of Cu atom, indicating the highly dispersion of loaded CuO grains on the surface of catalyst. This is probably due to its high surface area. It is interesting to note that Cu concentration on the surface of catalysts increased with increasing magnesium oxide in mixed oxide supports. This also confirmed that the strong metal support interaction improved the dispersion of Cu particles, good agreement with TPR results. In case of $CuZnO/MgO(30)-Al_2O_3(70)$ catalysts, the lower in surface area of support caused the agglomeration of Cu particles, resulted in lower metal dispersion. However, the highest amounts of copper oxide in CuZnO/MgO could be due to the minimal surface area of CuZnO/MgO, leading to almost completely covered by CuO. This result was accorded with the lowest hydrogen consumption of CuZnO/MgO in TPR profiles.

Table B1 Quantitative analysis of the metal on the catalyst surface

Catalysts	**Cu (wt. %)**	**Zn (wt. %)**	**Mg (wt. %)**	**Al (wt. %)**	**O (wt. %)**
$CuZnO/Al_2O_3$	5.94	35.07	-	20.87	38.13
$CuZnO/MgO(5)-Al_2O_3(95)$	4.99	27.70	1.58	23.05	42.69
$CuZnO/MgO(15)-Al_2O_3(85)$	5.60	28.90	6.59	17.74	47.17
$CuZnO/MgO(30)-Al_2O_3(70)$	3.48	26.96	7.64	13.75	48.17
CuZnO/MgO	10.69	14.27	18.52	-	56.52

Appendix C Specification of Various Glycerol Feedstocks

The specifications of different purities glycerol feedstocks (refined glycerol and yellow grade glycerol) using in this research were obtained from PTT Global Chemical Public Company Limited.

Table C1 The specifications of glycerol feedstocks

Feedstocks	Glycerol (wt. %)	Methanol (wt. %)	MONG* (wt. %)	Water (wt. %)	Ash (wt. %)
Refined glycerol	99.5	< 0.5	< 1	< 0.5	< 0.5
Yellow grade glycerol	80	< 1	< 20	< 1	< 0.1

*MONG = Matter Organic Non Glycerol

Appendix D Product Analysis

The chemical products of $CuZnO/Al_2O_3$, $CuZnO/MgO(15)-Al_2O_3(85)$, CuZnO/MgO catalysts on 3 h TOS. in refined glycerol feedstock were analyzed using a gas chromatograph equipped with an FID detector (Agilent 6890) to identify peaks of compositions of feedstocks, intermediates, and products. Chromatograms of glycerol dehydroxylation to propylene glycol analyzed are shown in Figures D1-D3.

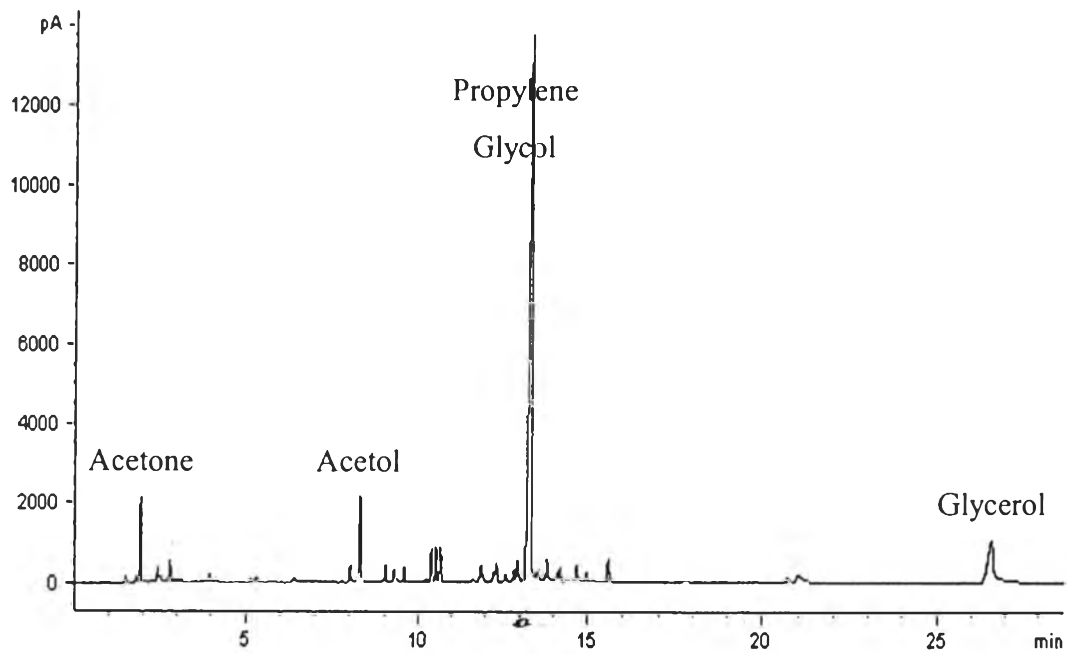

Figure D1 Chromatogram of $CuZnO/Al_2O_3$ on 3 h TOS. in refined glycerol feedstock analyzed by a GC/FID (Agilent GC 6890).

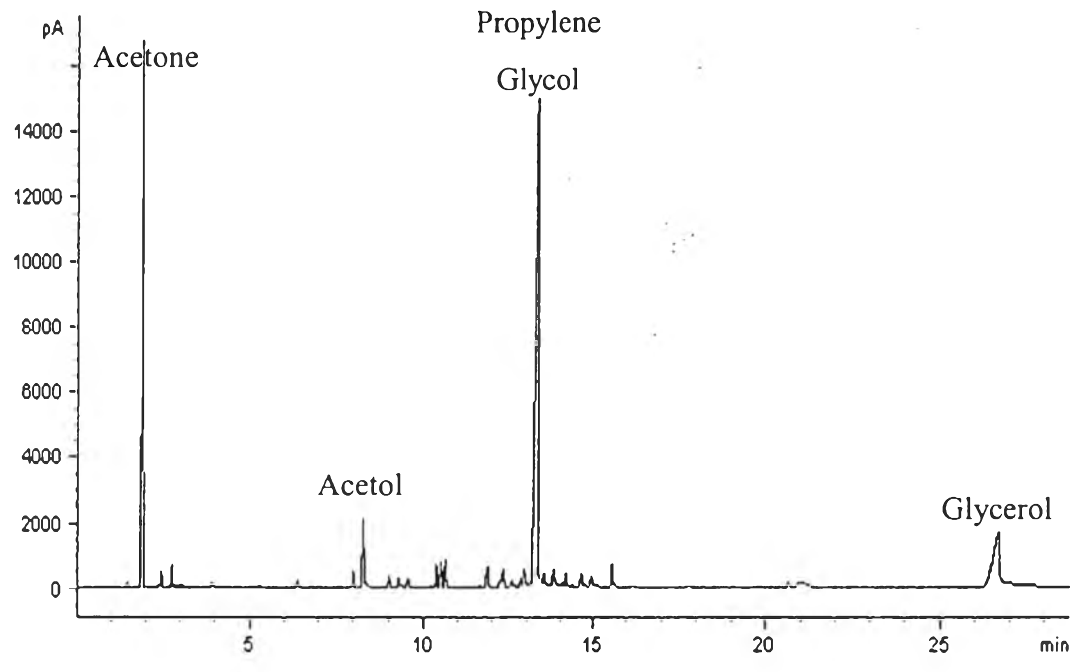

Figure D2 Chromatogram of CuZnO/MgO(15)-Al_2O_3(85) on 3 h TOS. in refined glycerol feedstock analyzed by a GC/FID (Agilent GC 6890).

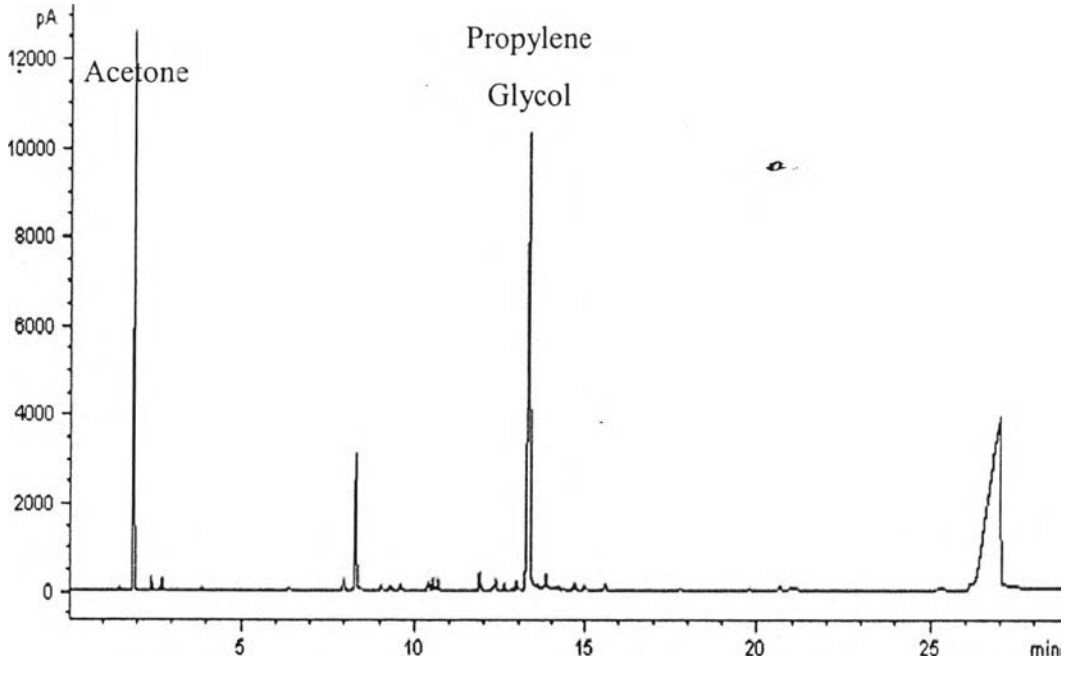

Figure D3 Chromatogram of CuZnO/MgO on 3 h TOS. in refined glycerol feedstock analyzed by a GC/FID (Agilent GC 6890).

The chemical standards were analysed by GC/FID detector (Agilent 6890) to identify peaks of compositions of feedstocks, intermediates, and products. The retention time and response factor for the standards are shown in Table D1.

Table D1 Retention times and response factors of standard chemicals analyzed by a GC/FID (Agilent GC 6890)

Standard chemical	Retention time (min)	Response factor
Hexane	1.43	1.00
Acetone	2.50	0.35
Methanol	3.78	0.13
2-propanol	4.57	0.37
Ethanol	4.74	0.26
1-propanol	7.65	0.42
Acetol	13.30	0.54
Propylene glycol	18.07	0.27
Ethylene glycol	18.60	0.16
Glycerol	27.73	0.25

Appendix E Glycerine Prices

The statistics of refined glycerine and crude glycerine prices were obtained from PTT Global Chemical Public Company Limited as shown in Table E1.

Table E1 Refined glycerine and crude glycerine prices

Year	Refined Glycerine			Crude Glycerine 80%		
	Drummed; FOB SEA (USD/ton)			Flexi bags; CIP China main (USD/ton)		
	Low	High	Average	Low	High	Average
1996	1,337	1,412	1,375	-	-	-
1997	976	1,033	1,004	-	-	-
1998	750	842	796	-	-	-
1999	873	968	921	-	-	-
2000	1,235	1,374	1,304	-	-	-
2001	858	911	885	-	-	-
2002	845	892	868	-	-	-
2003	899	966	933	-	-	-
2004	831	862	846	-	-	-
2005	683	702	692	-	-	-
2006	580	611	596	-	-	-
2007	924	970	947	-	-	-
2008	1,140	1,229	1,184	-	-	-
2009	545	600	573	183	205	194
2010	598	641	619	232	254	243
2011	740	782	761	329	362	346
2012	774	826	798	331	347	339
2013	881	927	904	402	417	409
2014	743	802	773	300	315	307

cited Mar 24, 2015

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Presentations:

1. Patharakul, C.; Tamiyakul, S.; Jongpatiwut, S. and Rirksomboon, T. (2015, April 21) Selective Conversion of Glycerol to Propylene Glycol over Copper Zinc Oxide/Magnesium Oxide-Aluminium Oxide Catalysts. Paper presented at The 5th Research Symposium on Petrochemicals and Materials Technology and the 20th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand. (Poster presentation)
2. Patharakul, C.; Tamiyakul, S.; Jongpatiwut, S. and Rirksomboon, T. (2015, June 21) Effect of strong metal support interaction in $CuZnO/MgO-Al_2O_3$ catalyst to coke resistance for dehydroxylation of glycerol to propylene glycol. Paper presented at The 5th International Colloids Conference, Amsterdam, Netherlands. (Poster presentation)