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Appendix A Analysis Report Obtained from X-ray Fluorescence Spectrometer

Sample : Catalyst

Objective : To quantitate concentration of Al, Cu, and Zn

Analysis Method : Wavelength dispersive X-ray fluorescence spectrometry

Instrument : X-ray fluorescence spectrometer, Philips model PW 2400

Table A1 The concentration of element in the fresh and spent Cu-ZnO/Al_2O_3 catalysts prepared by different methods

Sample	Concentration (wt%)*		
	Al_2O_3	CuO	ZnO
Fresh IWI	49.86	11.26	38.33
Fresh COP	50.22	12.29	37.25
Fresh SG	54.05	10.46	35.29
Spent IWI	50.38	11.16	37.15
Spent COP	51.86	11.34	35.95
Spent SG	57.40	6.58	35.44

* 1. Quantitation method used theoretical formulas, "fundamental parameter calculations"

2. The concentration of elements is expressed as oxide equivalent

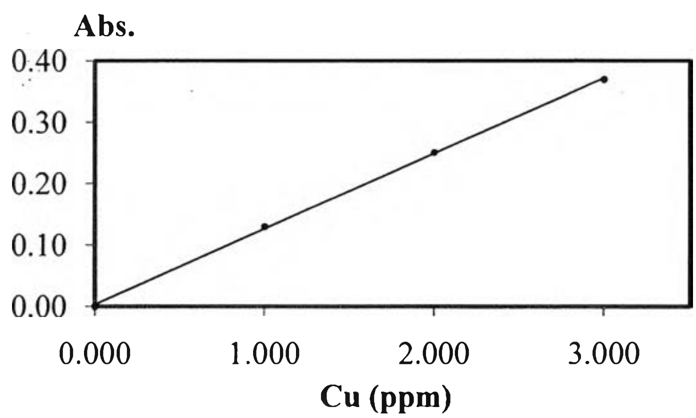
Appendix B Copper Leaching Calculation from AAS Analysis

Raw Data Obtained from Atomic Absorption Spectrophotometer

Method: Cu (Flame)		STANDARD 1:	1.000 ppm
		STANDARD 2:	2.000 ppm
Element-Matrix:	Cu-	STANDARD 3:	3.000 ppm
Instrument Type:	Flame	Re slope Rate:	50
Conc. Units:	ppm	Re slope Standard No.:	2
Instrument Mode:	Absorbance	Re slope Lower Limit:	75.0 %
Sampling Mode:	Manual	Re slope Upper Limit:	125.0 %
Calibration Mode:	Concentration	Re calibration Rate:	100
Measurement Mode:	Integrate	Calibration Algorithm:	Linear Origin
Replicates Standard:	3	Cal. Lower Limit:	20.0 %
Replicates Sample:	3	Cal. Upper Limit:	150.0 %
		SIPS:	Off
Expansion Factor:	1.0		
Minimum Reading:	Disabled	Measurement Time:	5.0 s
Smoothing:	7 point	Pre-Read Delay:	5 s
Conc. Dec. Places:	3	Flame Type:	Air/Acetylene
		Air Flow:	13.50 L/min
Wavelength:	324.8 nm	Acetylene Flow:	2.00 L/min
Slit Width:	0.5 nm	Burner Height:	13.5 mm
Gain:	31 %		
Lamp Current:	5.0 mA	RSD Limit:	5.0 %
Lamp Position:	6	RSD Test Min. Abs:	0.1000 Abs
Background		Cor. Coeff. Limit:	0.9950
Correction:	BC On		

Sample ID	Conc. (ppm)	%RSD	Mean Abs.
CAL ZERO	0.000	>100	0.0000
	Readings		
	0.0000	-0.0001	0.0000
STANDARD 1	1.000	0.4	0.1297
	Readings		
	0.1302	0.1292	0.1296
STANDARD 2	2.000	0.6	0.2508
	Readings		
	0.2511	0.2491	0.2521
STANDARD 3	3.000	0.3	0.3698
	Readings		
	0.3701	0.3687	0.3705

Linear Origin-Cal. Set 1



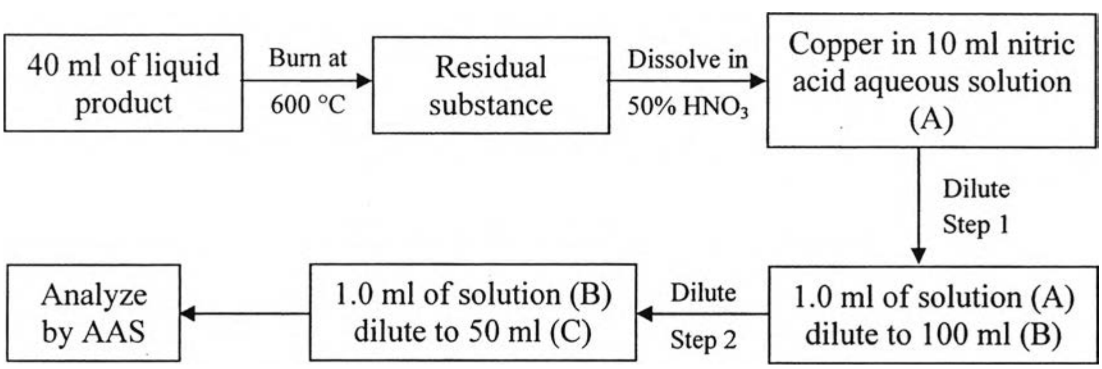
QC Test: Correlation coefficient 0.9997 within 0.9950 limit

Curve Fit	= Linear Origin			
Characteristic Conc.	= 0.035 ppm			
r	= 0.9997			
Calculated Conc.	= 0.000	1.043	2.017	2.974
Residuals	= 0.000	-0.043	-0.017	0.026

Abs. = 0.12433 x C

Sample ID	Conc. (ppm)	%RSD	Mean Abs.
Check Std.	2.031	0.3	0.2525
	Readings		
	0.2531	0.2518	0.2528
Sample	2.240	0.4	0.2785
	Readings		
	0.2795	0.2776	0.2785
Blank	0.005	11.1	0.0006
	Readings		
	0.0005	0.0006	0.0006

Flow Chart to Prepare the Sample for AAS Analysis



Back Calculation

Concentration of Copper analyzed by AAS = Cu in sample – Cu in blank

= 2.240 – 0.005 ppm

= 2.235 ppm

Thus, concentration of copper in solution (C) is 2.235 ppm.

From $C_cV_c = C_bV_b$

C_c, C_b concentration of copper in solution (C) and (B)

V_c,V_b volume of solution (C) and (B)

C_b = (2.235 ppm)(50 ml)/(1.0 ml)

= 111.75 ppm

Thus, concentration of copper in solution (B) is 111.75 ppm.

From $C_bV_b = C_aV_a$

C_b, C_a concentration of copper in solution (B) and (A)

V_b,V_a volume of solution (B) and (A)

C_a = (111.75 ppm)(100 ml)/(1.0 ml)

= 11,175 ppm

Thus, concentration of copper in solution (A) is 11,175 ppm.

It's mean, 1.0 ml of solution (A) contain copper 11,175 μg (0.011175 g)

10 ml of solution (A) contain copper 0.11175 g

Thus, 40 ml of liquid product contain copper 0.11175 g

At WHSV is 2.78 h^{-1} and 10.00 g Catalyst:

Glycerol feed rate is 23.077 ml/h

After 4 hours of reaction, total volume of product is about 92.308 ml

Thus, 92.308 ml of liquid product contain copper 0.258 g

Percentage of copper leaching = (0.258 g)(100%)/(10.00 g)

= 2.58 wt%

Appendix C Flow Criteria Calculation

To obtain the same volume of all catalysts, the difference of dilution ratio is required and the co-precipitated catalyst was selected to test in this effect. The result shows that the catalytic activities for the co-precipitated Cu-ZnO/Al_2O_3 catalyst with dilution ratio of 2.0 and 2.5 are not different, as shown in Figure C1. It can imply that dilution ratio does not affect the activity of the catalyst. Therefore, the co-precipitated, impregnated and sol-gel catalysts could be diluted by different SiC ratios to obtain the same volume of all catalysts.

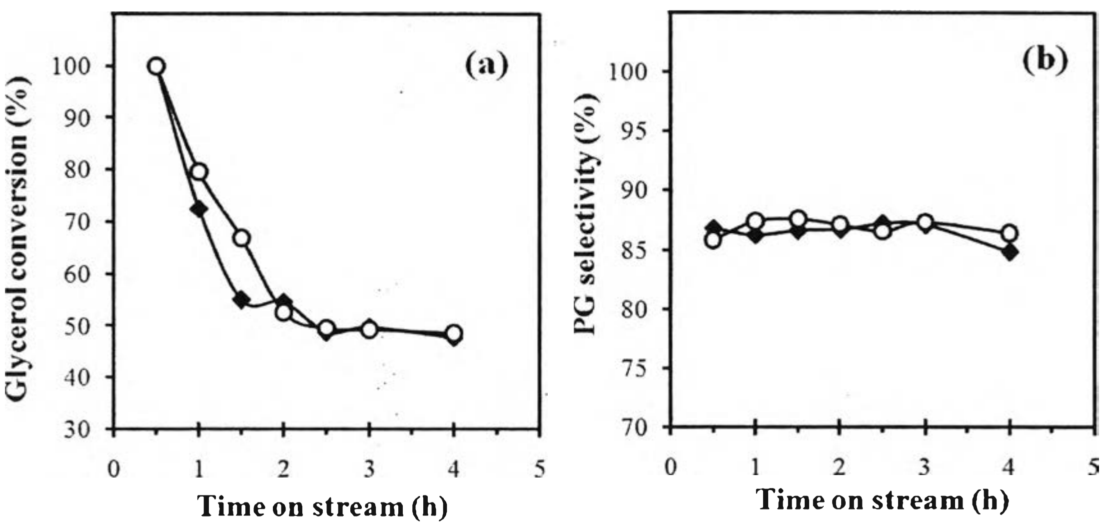


Figure C1 (a) Glycerol conversion and (b) selectivity to propylene glycol as a function of time on stream for the co-precipitated Cu-ZnO/Al_2O_3 at different dilution ratio: (♦) COP:SiC = 1:2.0 and (○) COP:SiC = 1:2.5. Reaction conditions: 250°C, 500 psig, H_2:glycerol = 4:1, and WHSV = 2.78 h^{-1}.

Moreover, flow criteria were tested to ensure the ideal behaviors in the reactor before comparing the catalytic performance of catalysts. The flow criteria determined in this study are summarized in Table C1.

Table C1 Summary of flow criteria used in this study

Flow criteria	IWI	SG	COP	Criteria *
Peclet number	74	74	74	> 50
L/D	1843	1843	1843	> 1243
	1843	1843	1843	> 695
Wall Effect	96.08	96.08	96.08	> 10.0
Wetting	8.47E-02	8.47E-02	8.47E-02	> 5.00E-06
Dilution effect	0.655	0.333	2	< 4

* Handbook of Heterogeneous Catalysis: Laboratory Testing of Solid Catalysts

From the flow criteria, we can presume that axial and radial dispersion, wetting, wall effect, and dilution effect have no any influence on the catalytic activities of the catalysts.

Data

Reactor

Outside diameter	1.905 cm
Inside diameter	1.605 cm
Wall thickness	0.150 cm
Thermowell O.D.	0.3175 cm
Space from wall to wall	0.64375 cm

Liquid Feed

Density	1.2 g/ml
Viscosity	0.697742 cP
Velocity	23.077 ml/h
Velocity	0.00641 ml/s

Assumption and Parameters

Reaction order	1	Conversion	0.998
Bodenstein number	0.04	g	980 cm/s^2
WHSV	2.78 h^{-1}	Catalyst used	10.00 g

Criteria

Peclet Number:

From equation (2) (chapter II),

$$Pe > 8n \ln\left(\frac{1}{1-x}\right)$$

Pe peclet number, n reaction order, x conversion

$$Pe > 8(1) \ln\left(\frac{1}{1-0.998}\right)$$

$$Pe > 50$$

L/D:

From equation (3) (chapter II),

$$\frac{L_b}{d_p} > \frac{8n}{Pe_p} \ln\left(\frac{1}{1-x}\right)$$

L_b bed length, d_p particle size (diluents), x conversion

Pe_p particle peclet number (also referred to as the Bodenstein number)

$$\frac{L_b}{d_p} > \frac{8(1)}{(0.04)} \ln\left(\frac{1}{1-0.998}\right)$$

$$\frac{L_b}{d_p} > 1243$$

From Chen's equation (Mederos *et al.*, 2009),

$$\frac{L_b}{d_p} > \frac{\sqrt{20}n}{Pe_p} \ln\left(\frac{1}{1-x}\right)$$

$$\frac{L_b}{d_p} > \frac{\sqrt{20}(1)}{0.04} \ln\left(\frac{1}{1-0.998}\right)$$

$$\frac{L_b}{d_p} > 695$$

Our Case

Incipient Wetness Impregnation (IWI)

Catalyst amount	14.5 ml	Diluent volume	9.5 ml
Diluent size	0.0067 cm	Dilution ratio	0.655
Total bed volume	24.0 ml	Cross section area	1.944 cm^2
Bed length	12.345 cm		

Sol-gel (SG)

Catalyst amount	18.0ml	Diluent volume	6.0 ml
Diluent size	0.0067 cm	Dilution ratio	0.333
Total bed volume	24.0 ml	Cross section area	1.944 cm^2
Bed length	12.345 cm		

Co-precipitation (COP)

Catalyst amount	8.0 ml	Diluent volume	16.0 ml
Diluent size	0.0067 cm	Dilution ratio	2.0
Total bed volume	24.0 ml	Cross section area	1.944 cm^2
Bed length	12.345 cm		

Peclet Number:

From equation (1) (chapter II),

$$Pe = \frac{L_b}{d_p} Pe_p$$

$$Pe = \frac{(12.345\ cm)(0.04)}{0.0067\ cm}$$

$$Pe = 74$$

L/D:

$$\frac{L_b}{d_p} = \frac{12.345\ cm}{0.0067\ cm}$$

$$\frac{L_b}{d_p} = 1843$$

Wall Effect:

From equation (4) (chapter II),

$$\frac{d_t}{d_p} > 10$$

d_t space from wall to wall

$$\frac{d_t}{d_p} = \frac{0.64375\ cm}{0.0067\ cm}$$

$$\frac{d_t}{d_p} = 96.08$$

Wetting:

From equation (5) (chapter II),

$$W_{tr} = \frac{v_l u_l}{d_p^2 g} > 5 \times 10^{-6}$$

u_l liquid velocity, v_l kinematic viscosity

$$W_{tr} = \frac{(0.697742\ cP)(0.00641 \frac{ml}{s})}{(1.2 \frac{g}{ml})(0.0067\ cm)^2 (980 \frac{cm}{s^2})}$$

$$W_{tr} = 8.47 \times 10^{-2}$$

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1. Panyad, S., Jongpatiwut, S., Rirksomboon, T., Sreethawong, T., and Osuwan, S. (2010, April 22) Dehydroxylation of Glycerol to Propylene Glycol over Copper/Zinc Oxide-based Catalysts: Effects of Catalyst Preparation and Regeneration. Poster presented at The 1st National Research Symposium on Petroleum, Petrochemicals, and Advanced Materials and The 16th PPC Symposium on Petroleum, Petrochemicals, and Polymers, Bangkok, Thailand.