Supplementary Material

The Promoting Effect of Ni on Glycerol Hydrogenolysis to 1,2-Propanediol with *in situ* Hydrogen from Methanol Steam Reforming Using a $Cu/ZnO/Al_2O_3$ Catalyst

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[#] Deceased November 2, 2018, this paper is dedicated to the memory of Professor Garry L. Rempel

A1. Calculation of methanol content in crude glycerol

Estimation of Methanol Content in Crude Glycerol before Methanol Recovery:

Triolein + 3Methanol ⇔ 3FAME + Glycerol

885.43 96.12 889.51 92.04

Assume Every 100g of Triolein and 100% Conversion:

If Methanol/Triolein Molar Ratio = 6:1

Unreacted Methanol = 100*96.12/885.43 = 10.86g

FAME Produced = 100*889.51/885.43 = 100.46g

Glycerol Produced = 100*92.04/885.43 = 10.39g

Distribution Coefficient = 0.2 [1], assume glycerol and FAME are not soluble.

Mass of methanol in glycerol is x, mass of methanol in FAME is y:

$x + y = 10.86$

$\{y/(y+100.46)\}/\{x/(x+10.39)\} = 0.2$

By Matlab ‘solve’ function: x = 4.45; y = 6.41

Methanol% in crude glycerol = 4.45/(4.45+10.86)*100% = **29.07%**

If Methanol/Triolein Molar Ratio = 12:1

Unreacted Methanol = 100*96.12/885.43*3 = 32.58g

$x + y = 32.58$

$\{y/(y+100.46)\}/\{x/(x+10.39)\} = 0.2$

By Matlab ‘solve’ function: x = 17.99, y = 14.59

Methanol% in crude glycerol = 17.99/(17.99+10.86)*100% = **62.36%**

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Laboratory Test Report

Methanol/Oil Feed Ratio: 6:1 (25wt% of methanol with respect to oil)
Methanol Content in Crude Glycerol before Methanol Recovery:
37.10%

Methanol/Oil Feed Ratio: 9:1 (35wt% of methanol with respect to oil)
Methanol Content in Crude Glycerol before Methanol Recovery:
51.35%

Methanol/Oil Feed Ratio: 12:1 (45wt% of methanol with respect to oil)
Methanol Content in Crude Glycerol before Methanol Recovery:
56.40%

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A2. Calculation of P value [2]

$P = \beta S_0/FC_0$

Where,

β = heat rate = 0.083K/s

F = flow rate = $0.5cm^3/s$

C_0 = initial H_2 concentration = $2.23\mu mol/cm^3$

For $CuO/ZnO/Al_2O_3$-OA catalyst:

S_0 = amount of CuO = 0.000244mol = 244μmol

P = 18.16molH_2/molCuO

For $NiO/CuO/ZnO/Al_2O_3$-OA catalyst:

S_0 = amount of CuO and NiO = 0.000262mol = 262μmol

P = 18.82 molH_2/molCuO

For NiO catalyst:

S_0 = amount of NiO = 0.000267mol = 267μmol

P = 19.88 molH_2/molNiO

Based on the calculation of characteristic P value, they are all below 20K. As suggested by Bravo-Suarez et al., the experiments were carried out with the absence of significant reducing gas concentration gradients along the sample bed [2].

A3. Verification for absence of mass transfer limitation

Weisz-Prater Criterion for Internal Diffusion

The Weisz-Prater criterion was used to determine if internal diffusion is limiting the reaction. This criterion was calculated by the equation below:

$$C_{WP} = \frac{-r'_{G(OBS)}\rho_c R^2}{D_e C_{As}}$$

Where,

$r'_{B(OBS)}$ = observed reaction rate = $-6.085e10^{-6}$ mol.g_{cat}^{-1}.s^{-1}

$\rho = 2.21 g_{cat}/cm^3$

R = 100μm = 0.01cm

$C_{AS} = 1.0x10^{-3} mol/cm^3_{cat}$

D_e – Effective Diffusivity (cm^2/s)

$$D_e = \frac{D_{AB}\varphi_p\sigma_c}{\tau}$$

Typical Values of the constriction factor $\sigma_c = 0.8$, tortuosity $\tau = 3.0$ and porosity $\varphi_p = 0.40$ suggested by Fogler Elements of Chemical Reaction Engineering (p. 815-p.816) [3].

The diffusion coefficient was calculated using the WILKE – CHANG equation:

$D_{AB} = 1.48e^{-4} cm^2/s$ for the diffusion coefficient of glycerol to water at 220°C (493.15K)

$D_e = 1.579e^{-5} cm^2/s$

$C_{WP} = 0.039 << 1$

According to the Weisz-Prater criterion, the calculated C_{PW} is significantly smaller than the criterion 1, therefore, it is verified that the reaction is with absence of internal mass transfer limitation.

Verification of Absence of Liquid to Solid Mass Transfer Limitations

$$P = \frac{-r_G}{k_s a_p B^*}$$

Where,

$-r_G$ = volumetric reaction rate = $1.8255e10^{-7}$ mol.$(cm^3)^{-1}.s^{-1}$

a_p = external area of particles per unit volume of reactor, cm^2/cm^3 = 5640 cm^2/cm^3

B^* = concentration of glycerol in the liquid, mol/cm^3 = 0.00217mol/cm^3

k_s = mass transfer coefficient estimated from *Frössling* Correlation (Fogler, p.774-p.777)[1]

Reynolds number: $Re = \frac{U\rho d_p}{\mu}$

U = 0.785m/s

ρ = density of the mixture at 220°C = 908.95kg/m^3

$d_p = 1e^{-4}m$

μ = dynamic viscosity of mixture at 220°C = 0.00017056$kg.s^{-1}m^{-1}$

Re = 418.34

Schmidt number: $Sc = v/D_{AB}$ = 12.679

Sherwood number = $Sh = 2 + 0.6Re^{1/2}Sc^{1/3}$ = 30.618

$$Sh = \frac{k_s d_p}{D_{AB}} => k_s = \frac{Sh \cdot D_{AB}}{d_p} = 0.453 cm/s$$

$P = 3.293e^{-8} << 0.3$

According to Hu et al. reported on 2010 [4] as well as the criteria defined by Ramachandran and Chaudhari [5], the calculated parameter is far smaller than the criteria 0.3, it is believed that the reaction system is with absence of external mass transfer limitation.

The space time conversion (STC) of glycerol and space time yield (STY) of 1,2-PD are calculated using the following equations:

$$STC_{Glycerol} = \frac{n_{Glycerol_{in}} * Conversion_{Glycerol}}{Reaction\ Time * Catalyst\ Weight}$$

$$STY_{1,2-PD} = \frac{n_{Glycerol_{in}} * Yield_{1,2-PD}}{Reaction\ Time * Catalyst\ Weight}$$

Where,

$$Yield_{1,2-PD} = Conversion_{Glycerol} * Selectivity_{1,2-PD}$$

Table S1 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Cu/ZnO/Al_2O_3$-Na catalyst[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
2	16.0	16.7	0.00097	0.00581
4	42.2	31.7	0.00243	0.00764
8	60.3	29.1	0.00159	0.00546

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Cu/Zn/Al (molar) = 35/35/30.

Table S2 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
1	30.3	53.9	0.0118	0.0219
2	47.6	57.2	0.0099	0.0173
4	70.2	65.7	0.0084	0.0127
6	80.1	67.0	0.0065	0.0097
8	87.1	70.7	0.0056	0.0079

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, 500RPM, Cu/Zn/Al (molar) = 35/35/30.

Table S3 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
2	43.9	62.3	0.00991	0.01591
4	63.9	66.2	0.00766	0.01157
6	77.7	68.4	0.00642	0.00939
8	82.7	69.9	0.00524	0.00749

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Cu/Zn/Al (molar) = 25/25/50.

Table S4 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
2	35.2	54.9	0.00700	0.01275
4	56.4	62.1	0.00635	0.01022
6	70.6	63.7	0.00544	0.00853
8	80.2	65.7	0.00477	0.00726

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Cu/Zn/Al (molar) = 45/45/10.

Table S5 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Ni/Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
1	20.6	73.7	0.0110	0.0149
2	38.3	77.9	0.0108	0.0139
4	57.2	81.3	0.0084	0.0104
6	67.4	83.3	0.0068	0.0081
8	70.0	85.5	0.0054	0.0063

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Ni/Cu/Zn/Al (molar) = 5/32.5/32.5/30.

Table S6 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Ni/Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
1	22.7	66.2	0.0109	0.0165
2	41.0	72.7	0.0108	0.0149
4	61.3	78.5	0.0087	0.0111
6	72.3	81.6	0.0071	0.0087
8	77.4	82.8	0.0058	0.0070

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Ni/Cu/Zn/Al (molar) = 3/33.5/33.5/30.

Table S7 Space Time Yields for glycerol hydrogenolysis with *in situ* H_2 from methanol steam reforming over $Ni/Cu/ZnO/Al_2O_3$-OA catalysts[1]

Time	Glycerol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Glycerol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
1	24.4	57.3	0.0101	0.0177
2	46.4	63.5	0.0107	0.0168
4	66.3	66.6	0.0080	0.0120
6	76.9	69.6	0.0065	0.0093
8	85.5	76.7	0.0059	0.0077

[1]Reaction Conditions: 220°C, 1.5MPa N_2, 100g feedstock mixture, 20wt% glycerol, 32.2wt% of water and 47.8wt% methanol (water/methanol molar ratio = 1.2), 3g catalyst, 500RPM, Ni/Cu/Zn/Al (molar) = 1/34.5/34.5/30.

Table S8 Space Time Yields for acetol hydrogenation over $Cu/ZnO/Al_2O_3$-OA catalyst[1]

Time	Acetol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Acetol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0.0	N/A	0.0	0.0
0.5	12.8	57.3	0.0107	0.0692
1	29.8	63.5	0.0318	0.0806
2	65.3	66.6	0.0430	0.0882
4	81.0	69.6	0.0290	0.0548
6	92.0	76.7	0.0230	0.0414
8	97.7	63.1	0.0208	0.0330

[1]Reaction Conditions: : 200°C, 500RPM, 100g feedstock mixture, 20wt% aqueous acetol, 1g catalyst, H_2 pressure 2.8PMa, Cu/Zn/Al (molar) = 35/35/30.

Table S9 Space Time Yields for acetol hydrogenation over $Ni/Cu/ZnO/Al_2O_3$-OA catalyst[1]

Time	Acetol Conversion	1,2-PD Selectivity	1,2-PD Space Time Yield	Acetol Space Time Conversion
hour	%	%	$mol.gcat^{-1}.hr^{-1}$	$mol.gcat^{-1}.hr^{-1}$
0	0	0	0.0	0.0
0.5	60.0	66.0	0.2141	0.3243
1	79.7	69.6	0.1498	0.2153
2	87.4	69.5	0.0822	0.1182
3	93.3	68.4	0.0575	0.0840
4	97.8	71.1	0.0470	0.0661
6	100.0	72.6	0.0327	0.0450
8	100.0	75.1	0.0254	0.0338

[1]Reaction Conditions: : 200°C, 500RPM, 100g feedstock mixture, 20wt% aqueous acetol, 1g catalyst, H_2 pressure 2.8PMa, Ni/Cu/Zn/Al (molar) =5/32.5/32.5/30.

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