catalysts

Supplementary Material

Glycerol Hydrogenolysis with In Situ Hydrogen Produced via Methanol Steam Reforming: The Promoting Effect of Pd on a $Cu/ZnO/Al_2O_3$ Catalyst

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Table S1. Specific reaction rates of different products yields and glycerol conversion using the CZA catalysts with different Pd loading for glycerol hydrogenolysis with in situ hydrogen from methanol steam reforming [1].

Catalysts	Specific Rate of Glycerol Conversion $mmol.h^{-1}.gcat^{-1}$		Specific Rate of 1,2-PD Formation $mmol.h^{-1}.gcat^{-1}$		Specific Rate of EG Formation $mmol.h^{-1}.gcat^{-1}$	
	1 h	6 h	1 h	6 h	1 h	6 h
CZA [2]	7.29	8.47	1.62	5.34	0.22	0.27
0.5Pd-CZA [3]	12.87	9.71	7.00	6.76	0.34	0.38
1Pd-CZA [3]	18.09	10.86	12.02	8.64	0.58	0.45
2Pd-CZA [3]	38.40	11.99	27.39	9.87	1.72	0.54
3Pd-CZA [3]	39.96	12.07	28.41	9.98	1.93	0.82
2Pd-ZnO	16.79	10.01	5.38	4.97	0.00	0.29
CZA [2, 4]	1.39	1.32	0.00	0.51	0.00	0.00
2Pd-CZA [3, 4]	31.56	11.94	18.64	9.24	1.13	0.42

[1] Reaction conditions: 220 °C, 218 psi N_2, 20 wt% glycerol, water/methanol molar ratio = 1.2, 3 wt% catalyst with respect to total feed mixture, 6 hours reaction time, 500 RPM. [2] Cu/Zn/Al (molar) = 35/35/30. [3] Support: CZA [2]. [4] Unreduced catalyst.

Table S2. Specific reaction rates of acetol conversion using the CZA and 2Pd-CZA catalysts for acetol hydrogenation [1].

Catalysts	Acetol Concentration wt%	Hydrogen Pressure MPa	Specific Rate of Acetol Conversion mmol.h^{-1}.gcat^{-1}	
			1 h	6 h
CZA [2]	10%	400	106.64	41.79
2Pd-CZA [3]	10%	400	263.72	45.00
CZA [2]	20%	400	80.46	41.40
2Pd-CZA [3]	20%	400	225.88	44.67
CZA [2]	20%	600	138.31	45.00
2Pd-CZA [3]	20%	600	254.66	45.00

[1] Reaction conditions: 200 °C, 500 RPM, 6 hours reaction time, 5 wt% of catalyst with respect to acetol weight, aqueous acetol solution. [2] Cu/Zn/Al (molar) = 35/35/30. [3] Support: CZA [2].

Table S3. Specific reaction rates of different products yields and glycerol conversion using recycled 2Pd-CZA catalysts for glycerol hydrogenolysis with in situ hydrogen from methanol steam reforming [1].

Hydrogen pressure	Specific Rate of Glycerol Conversion mmol.h^{-1}.gcat^{-1}		Specific Rate of 1,2-PD Formation mmol.h^{-1}.gcat^{-1}		Specific Rate of EG Formation mmol.h^{-1}.gcat^{-1}	
	1 h	**6 h**	**1 h**	**6 h**	**1 h**	**6 h**
Fresh	38.4	12.0	27.4	9.9	1.7	0.5
First recycle	32.3	11.3	20.4	9.2	1.4	0.5
Second recycle	34.2	11.3	23.6	9.2	1.0	0.5
Third recycle	29.8	11.2	18.3	8.8	1.1	0.4

[1] Reaction conditions: 220 °C, 1.5 MPa total pressure balanced with N_2 if necessary, 20 wt% glycerol, water/methanol molar ratio = 1.2, 3 wt% catalyst with respect to total feed mixture, 6 hours reaction time, 500 RPM. Catalyst: 2Pd-CZA, Cu/Zn/Al (molar) = 35/35/30.

A1. Effect of Pd loading onto the CZA catalyst.

To investigate the effect of Pd loading method on the Pd promoted catalyst activity, Pd was in situ reduced and directly added to the catalyst support. A pre-calculated amount of palladium (II) acetate (≥98%) in acetone solution was added drop wise into the slurry containing the calcined support and ethanol solution. The palladium acetate was reduced to metallic palladium as the ethanol acted as a reducing agent. The dried particles were powdered and screened via a 250 mm opening sieve and then calcined in stationary air at 360 for 4 hours. The experimental results were listed in Table A1 below.

Table A1-1. Effect of Pd loading method on the promoted CZA catalyst activity[1].

Catalysts	Glycerol Conversion %	Selectivity 1,2-PD %	Acetol %	EG %	Others %
CZA	70.2	63.0	8.0	3.2	25.7
1Pd-CZA[2,3]	90.0	79.6	1.8	4.1	14.5
1Pd-CZA[2,4]	80.4	63.0	9.7	3.4	24.0

[1] Reaction conditions: 220 °C, 1.5 MPa N_2, 20 wt% glycerol, water/methanol molar ratio = 1.2, 3 wt% catalyst with respect to total feed mixture, 6 hours reaction time, 500 RPM. [2] Cu/Zn/Al (molar) = 35/35/30. [3] Impregnation method. [4] In situ reduction method.

A2. Repeatability of the reaction process using the 2Pd-CZA catalyst.

The glycerol hydrogenolysis of glycerol into 1,2-PD with in situ hydrogen produced via methanol steam reforming using the 2Pd-CZA catalyst has been repeated for 4 times to check the repeatability of this reaction system. The repeated results are listed in Table A2-1 below. The data has been statistically analyzed by calculating the standard error (SE) and the margin of error (ME) for 95% confident interval (C.I.). The t-test was used for the sample SE with 3 degree of freedom. The ME for 95% C.I. was calculated by the equation below:

$$ME = t_{3,0.025} \times \frac{SE}{\sqrt{n}}$$

Where, n is the number of replicate.

Table A2-1. Repeatability of the glycerol hydrogenolysis with in situ hydrogen from methanol steam reforming using the 2Pd-CZA catalyst[1].

Run No.	Glycerol Conversion %	Selectivity 1,2-PD %	Acetol %	EG %	Others %
1	98.9	81.1	0.9	5.0	13.0
2	100.0	83.1	0.0	3.7	13.2
3	100.0	84.1	0.0	5.0	10.9
4	98.5	81.2	0.8	4.3	13.7
Average[2]	99.4 ± 1.2	82.4 ± 2.3	0.4 ± 0.8	4.5 ± 1.0	12.7 ± 2.0
SE[3]	0.4	0.7	0.3	0.3	0.6
ME[2]	1.2	2.3	0.8	1.0	2.0

[1] Reaction conditions: 220 °C, 1.5 MPa N_2, 20 wt% glycerol, water/methanol molar ratio = 1.2, 3 wt% catalyst with respect to total feed mixture, 6 hours reaction time, 500 RPM. [2] 95% confident interval. [3] t-test.

A3. Methematical Equations:

Glycerol Conversion:

$$Conversion_{Glycerol} = 100\% - \frac{n_{Glycerol,f}}{n_{Glycerol,f} + n_{1,2-PD} + n_{Acetol} + n_{EG} + n_{Propanol} + n_{Others}} \times 100\%$$

Where,

$$n_{Others} = n_{Glycerol,in} - \left(n_{Glycerol,f} + n_{1,2-PD} + n_{Acetol} + n_{EG} + n_{Propanol}\right)$$

Product Yield:

$$Yield_i = \frac{n_i}{n_{Glycerol} + n_{1,2-PD} + n_{Acetol} + n_{EG} + n_{Propanol} + n_{Others}} \times 100\%$$

Where, i = each product/by-product formed from glycerol

Product Selectivity:

$$Selectivity_i = \frac{Yield_i}{Conversion_{Glycerol}} \times 100\%$$

Specific rate of glycerol conversion:

$$R_{Glycerol} = \frac{n_{Glycerol_{in}} \times Conversion_{Glycerol}}{Reaction\, Time \times Catalyst\, Weight}$$

Specific rate of acetol conversion:

$$R_{Glycerol} = \frac{n_{Acetol_{in}} \times Conversion_{Acetol}}{Reaction\, Time \times Catalyst\, Weight}$$

Specific rate of product yield:

$$R_i = \frac{n_{Glycerol_{in}} \times Yield_i}{Reaction\, Time \times Catalyst\, Weight}$$

Where, i = each product/by-product formed from glycerol.