



Conversion of Glycerol to Lactic Acid Catalyzed by Different-Sized Cu₂O Nanoparticles in NaOH Aqueous Solution

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Different-sized Cu_2O nanoparticles with the average particle sizes ranging from 115 to 423 nm were prepared starting from $CuSO_4$ using ascorbic acid as the reductant at room temperature. When Cu_2O nanoparticles were used as the catalysts for hydrothermal conversion of glycerol at 230 °C in a NaOH aqueous solution, Cu_2O nanoparticles effectively catalyzed the hydrothermal conversion of glycerol to lactic acid as compared to the conventional hydrothermal conversion of glycerol in a "pure" NaOH aqueous solution. Small-sized Cu_2O nanoparticles showed higher catalytic activity than the large-sized ones. In a wide glycerol concentration range of 1–2.5 mol/L and a low mole ratio of Cu_2O nanoparticle to glycerol of 2.5:100, the glycerol conversion and lactic acid selectivity were more than 86.2% and 87.2%, respectively, after reacting at 230 °C for 2 h.

Keywords: Cu₂O Nanoparticles, Glycerol, Lactic Acid, Hydrothermal Conversion.

1. INTRODUCTION

With the depletion and rising price of fossil fuels and the consciousness of environmental protection, conversion of biomass to valuable chemicals has attracted much attention. The annual production of glycerol, as a biomaterial, is *ca.* 2,500 kt from biodiesel industry, which is oversupplied in the market. Glycerol can be converted to valuable chemicals, such as lactic acid, propanediols, hydroxyacetone, acrolein, acrylic acid, and glyceric acid, by hydrothermal conversion in alkaline solution,^{1,2} catalytic hydrogenolysis,^{3–5} catalytic dehydration,^{6–8} and catalytic oxidation.^{9–11} These chemicals are useful intermediates in organic synthesis and are still being obtained by either expensive processes or enzymatic ways.

Among the glycerol derivatives, lactic acid is a useful chemical, which can be used as a food additive, a starting material for the synthesis of pharmaceutical, and a monomer for the synthesis of biodegradable polylactic acid. The world-wide market demand for lactic acid reached 500 kt/a in 2010.¹² Lactic acid is usually produced by the fermentation of carbohydrates and glycerol at high production cost, accompanied with the formation of a large amount of waste salt. As an alternative to the conventional fermentation process, chemical method for lactic acid production with high production rate has attracted researcher's great attention.

Kishita et al.^{1,2} first reported that glycerol with an initial concentration of 0.33 mol/L could be converted to lactic acid with high yield of 90% by hydrothermal reaction in an alkaline solution at 300 °C. Alkaline metal hydroxides, such as KOH, NaOH, and LiOH, were more active than alkaline earth metal hydroxides, such as Ba(OH)₂, $Sr(OH)_2$, $Ca(OH)_2$, and $Mg(OH)_2$, for the hydrothermal reaction.² Ramírez-López et al.¹³ reported that lactic acid yield of 84.5% was obtained at high initial glycerol concentration of 2.5 mol/L with a mole ratio of NaOH to glycerol of 1.1:1 after reacting at 280 °C for 90 min. However, when the reaction temperature was decreased to 260 °C, the lactic acid yield was less than 20% even in 1.25 mol/L NaOH aqueous solution.¹ It is clear that high reaction temperature is necessary for effectively hydrothermal conversion of glycerol to lactic acid in alkaline aqueous solutions.

To effectively convert glycerol to lactic acid under mild reaction condition, different types of catalysts were investigated with or without O_2 . Noble metals were used for

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the oxidation of glycerol to lactic acid with O₂ under alkaline or acidic condition.^{12, 14, 15} When Au/TiO₂, Pt/TiO₂, and Au-Pt/TiO2 were used as the catalysts for the oxidation of glycerol (0.22 mol/L) at 90 °C and 0.1 MPa of O₂ in an alkaline solution, the lactic acid selectivities ranged from 73.8% to 85.6% at the glycerol conversion of ca. 30%.¹⁴ When AuPd/TiO₂ and AlCl₃ were used as the catalysts under acidic condition for the oxidation of glycerol (1 mol/L) with O₂ at 160 °C, the lactic acid yield of 66.6% was obtained at the glycerol conversion of 13.6%.¹⁵ When carbon-supported Ir and Rh catalysts were used for the hydrothermal conversion of glycerol at 200 °C, the lactic acid yield was more than 60% at the glycerol conversion of *ca*. 100% under He atmosphere.¹² Noble metal catalysts showed high catalytic activities for the conversion of glycerol to lactic acid at low reaction temperature.

Instead of expensive noble metals, metallic copper and copper oxides were used as catalysts for the hydrothermal conversion of glycerol to lactic acid in an alkaline solution. Cu/SiO₂, CuO/Al₂O₃, and Cu₂O catalysts gave the lactic acid selectivities of 79.7%, 78.6%, and 78.1% at the glycerol conversions of 75.2%, 97.8%, and 93.6%, respectively, when the initial concentration of glycerol was 1 mol/L and the reaction temperature was 240 °C.¹⁶ The copper-based catalysts favored the hydrothermal conversion of glycerol to lactic acid at low reaction temperature as compared to those in "pure" alkaline aqueous solution. Unfortunately, silica and alumina supports are known to leach out under alkaline condition and high reaction temperature, forming sodium silicate (Na₂SiO₂) and aluminates (e.g., NaAlO₂), respectively. Interestingly, commercial Cu₂O powders with large particle sizes ranging from 100 to 125 μ m had good reusability for catalytic conversion of glycerol to lactic acid in an alkaline solution.¹⁶ However, to the best of our knowledge, the effect of particle sizes of Cu₂O nanoparticles on the catalytic conversion of glycerol to lactic acid has not been investigated until now.

In our present work, we report the hydrothermal conversion of glycerol to lactic acid catalyzed by differentsized Cu₂O nanoparticles in a NaOH aqueous solution and an aerobic atmosphere. Different-sized Cu₂O nanoparticles were facilely synthesized starting from CuSO₄ with ascorbic acid as the reductant in aqueous solution at room temperature.^{17–19} The effect of reaction parameters, such as reaction temperature, reaction time, catalyst loading, and NaOH and glycerol concentrations, on the catalytic conversion of glycerol, was investigated in detail. Possible reaction routes were also discussed.

2. EXPERIMENTAL DETAILS

2.1. Materials

Glycerol (99%), copper sulfate (CuSO₄ \cdot 5H₂O, 99%), oxalic acid (99.5%), cuprous oxide (90%), lactic acid (85%), ascorbic acid (99.7%), 1,2-propanediol (99%),

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acetic acid (99.5%), *n*-butanol (99.5%), polyvinylpyrrolidone (K-30, 95%), and NaOH (96%) were of reagent grade and were purchased from Sinopharm. Chem. Reagent Co., LTD. Formic acid (88%) was supplied by China Henli Reagent Factory. All chemicals were used as received without further purification. Deionized water was used through all of the experiments.

2.2. Preparation of Catalysts Cu₂O Nanoparticles

The preparation of Cu₂O nanoparticles was illustrated as follows.¹⁷⁻¹⁹ NaOH aqueous solution (250 mL) with the concentrations of 0.1-0.4 mol/L was added into 250 mL of CuSO₄ aqueous solution with the concentrations of 0.05-0.2 mol/L under stirring with a constant flow rate pump at 25 °C for 30 min to form Cu(OH)₂ suspension. Then 250 mL of ascorbic acid aqueous solution with the concentrations of 0.1-0.4 mol/L was added into the resultant suspension with a constant flow rate pump under stirring at 25 °C for 30 min to prepare Cu₂O nanoparticles. To change particle sizes of Cu₂O nanoparticles, given amount of polyvinyl pyrrolidone was first dissolved in CuSO₄ aqueous solution. Then NaOH and ascorbic acid solutions were added subsequently. The as-prepared Cu₂O nanoparticles were washed with water and ethanol for three times, and then kept in an ethanol solution. After drying in an vacuum oven at 60 °C for 60 min, the asprepared Cu₂O nanoparticles were used as the catalysts for the hydrothermal conversion of glycerol. The detailed preparation conditions are listed in Table I.

2.3. Characterization

The X-ray powder diffraction (XRD) spectra of all the catalysts were recorded on a diffractometer (D8 super speed Bruke-AEX Company, Germany) using Cu K α radiation ($\lambda = 1.54056$ Å) with Ni filter, scanning from 10 to 90° (2 θ). Scanning electron microscopy (SEM) was performed on a scanning electron microscope (JSM 7001F) operated at an acceleration voltage of 10 kV to characterize the morphologies of Cu₂O nanoparticles. The average particle sizes of Cu₂O nanoparticles were measured from the SEM images. The average particle sizes of Cu₂O nanoparticle sizes of Cu₂O nanoparticles were measured from the SEM images. The average particle sizes of Cu₂O nanoparticles were calculated by a weighted-average method according to the individual particle sizes of the all counted particles.

2.4. Catalytic Activity Test

Firstly, 100 mL of distilled water was added in a stainless steel reactor with the capacity of 500 mL, then given amounts of glycerol, NaOH, and Cu₂O catalyst were added into it. The reactor was flushed with N₂ to replace air for 10 min. The stirring speed was set at 300 rpm. The reaction mixture was heated to prescribed temperatures in *ca.* 1 h. Then the reaction time was counted. The reported reaction time did not include the corresponding heating time. After reacting for a prescribed period, the Table I. Preparation conditions and average particle sizes of Cu_2O nanoparticles and their catalytic activities in the hydrothermal conversion of glycerol in an alkaline aqueous solution.

Sample no.	Cu ₂ O nanoparticles ^a							Product selectivities ^c (mol%)					
	PVP (g/L)	CuSO ₄ (mol/L)	NaOH (mol/L)	Ascorbic acid (mol/L)	Average particle sizes of Cu_2O nanoparticles (nm)	Reaction time (h)	Glycerol conv. ^b (%)	LA	OA	FA	AA	1,2-PDO	Others (CO ₂ , coking etc.)
a	0	0.2	0.4	0.4	115	2	92.5	89.1	1.5	1.2	1.5	1.5	5.2
						4	94.2	85.8	1.7	1.4	1.5	1.4	8.2
						6	100	80.4	1.8	1.5	1.5	1.0	13.7
						8	100	77.2	2.0	1.7	1.5	0.9	16.6
b	0	0.1	0.2	0.2	161	2	89.6	88.3	1.4	1.2	1.5	1.6	6.0
						4	92.0	84.8	1.5	1.3	1.5	1.4	9.4
						6	96.5	79.6	1.6	1.5	1.5	1.2	14.6
						8	100	76.8	1.6	1.6	1.6	1.0	17.4
с	0.33	0.05	0.1	0.1	224	2	84.5	86.1	1.2	1.1	1.5	1.6	8.4
						4	90.2	82.4	1.4	1.3	1.5	1.5	11.9
						6	94.6	78.5	1.5	1.4	16	1.3	15.7
						8	99.1	75.4	1.6	1.6	1.6	1.1	18.8
d	0	0.05	0.1	0.1	423	2	80.1	83.4	1.2	1.0	1.6	1.9	11.0
						4	83.8	80.1	1.3	1.1	1.6	1.8	14.1
						6	89.6	76.8	1.4	1.2	1.6	1.5	17.5
						8	94.1	74.3	1.5	1.3	1.7	1.4	19.7
e	Commercial Cu ₂ O powder				2570	2	65.8	82.0	0.3	0.7	1.8	2.0	13.2
						4	74.2	79.3	0.4	0.7	1.8	2.0	15.7
						6	81.5	77.8	0.6	0.9	1.9	1.9	17.0
						8	90.1	76.3	0.7	1.0	2.1	1.8	18.1
f	Without Cu ₂ O catalyst					2	5.0	82.2	_	_	_	0	17.8
						4	10.8	81.5	_	_	_	0	18.5
						6	17.5	79.2	_	_	_	0	20.8
						8	25.2	76.0	_	_	_	0	24.0

Notes: ^aThe volumes of CuSO₄, NaOH, and ascorbic acid aqueous solutions were 250 mL, respectively. ^bReaction conditions: glycerol, 9.2 g; NaOH/glycerol mole ratio, 1.2:1; Cu₂O, 5 mmol; reaction temperature, 230 °C; H₂O, 100 mL, ^cLA, lactic acid; OA, oxalic acid; FA, formic acid; AA, acetic acid; 1,2-PDO, 1,2-propanediol.

reaction mixture was quickly cooled down with cooling water through a coil in the reactor.

The liquid reaction mixture was filtered and the filtrate was acidified with hydrochloric acid (37%) to the pH value of 2–3. Carboxylic acids were analyzed by HPLC with an Agilent HPLC system equipped with a tunable absorbance UV detector and a C18 column. The mobile phase was methyl cyanide aqueous solution (20:80, V/V) with a flow rate of 1.0 mL/min. The pH value of mobile phase was 2.0, which was adjusted with phosphate buffer. The detection wavelength was 210 nm. GC analysis was performed with SP-6800A equipped with a FID detector and a PEG-20M capillary column to analyze the contents of glycerol and 1,2-propanediol.

3. RESULTS AND DISCUSSION

3.1. XRD Analysis

The as-prepared copper oxides and commercial Cu₂O powder were analyzed by powder X-ray diffraction technique (Fig. 1). The XRD patterns of the samples were consistent with those of standard Cu₂O (JCPDS 05-0667), indicating that the as-prepared copper oxides had the chemical structure of cuprite. The crystallite sizes (111) of the as-prepared Cu₂O samples (a–d) under different conditions were 17.9, 30.3, 29.2, and 24.8 nm, respectively.

The crystallites size (111) of the commercial Cu_2O sample was 55.9 nm. Under our present experimental conditions, the as-prepared Cu_2O had smaller crystallite sizes than the commercial Cu_2O sample.



Figure 1. XRD patterns of the copper oxide catalysts prepared under different conditions. Sample preparation conditions: (a) $CuSO_4 0.2 \text{ mol/L}$, NaOH 0.4 mol/L, ascorbic acid 0.4 mol/L; (b) $CuSO_4 0.1 \text{ mol/L}$, NaOH 0.2 mol/L, ascorbic acid 0.2 mol/L; (c) $CuSO_4 0.05 \text{ mol/L}$, NaOH 0.1 mol/L, ascorbic acid 0.1 mol/L, PVP 0.33 g/L; (d) $CuSO_4 0.05 \text{ mol/L}$, NaOH 0.1 mol/L, ascorbic acid 0.1 mol/L; (e) commercial Cu_2O powder.

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3.2. SEM Analysis

The SEM images of the as-prepared Cu₂O samples and commercial Cu₂O powder are shown in Figure 2. The SEM images show that when Cu₂O samples (a and b) were prepared with high CuSO₄ concentrations of 0.2 and 0.1 mol/L, respectively, small-sized Cu₂O nanoparticles with the average particle sizes of 115 and 161 nm were prepared. When the CuSO₄ concentration was decreased to 0.05 mol/L, large-sized Cu₂O nanoparticles (sample (d)) with the average particle size of 423 nm were prepared. High CuSO₄ concentration favored the formation of smallsized Cu₂O nanoparticles. When sample (c) was prepared in the presence of PVP as an organic modifier under the same conditions as those for sample (d), the average particle size of sample (c) was 224 nm. The presence of PVP favored the formation of small-sized Cu₂O nanoparticles.

The SEM image of commercial Cu_2O powders (sample (e)) shows that their average particle size was 2570 nm, much larger than those prepared under our present experimental conditions. Small-sized Cu_2O nanoparticles with



Figure 2. SEM images of Cu₂O samples prepared under different conditions. The preparation conditions of samples (a–d) were the same as those mentioned in Figure 1. Sample (e) was the commercial Cu₂O powder. Sample (f) was the used sample (a) (reaction conditions: glycerol, 9.2 g; NaOH/glycerol mole ratio, 1.2:1; reaction temperature, 230 °C; H_2O , 100 mL).

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the average particle sizes of 115 nm (sample (a)) after taking reaction was also characterized by SEM analysis, and the SEM image showed average diameter slightly increased to 121 nm, indicating the used catalyst was almost no agglomeration.

3.3. Catalytic Test

3.3.1. Effect of Particle Sizes of Cu₂O Nanoparticles

To clarify the effect of the particle sizes of cuprous oxide nanoparticles on the hydrothermal conversion of glycerol into lactic acid, a series of experiments were carried out with glycerol concentration of 1 mol/L, NaOH/glycerol mole ratio of 1.2:1, and Cu₂O/glycerol mole ratio of 5:100 at 230 °C for 2–8 h. The experimental results are listed in Table I.

When the hydrothermal conversion of glycerol was carried out in "pure" NaOH aqueous solution without Cu₂O catalyst, the glycerol conversions increased from 5.0% to 25.2% with prolonging the reaction time from 2 to 8 h. The lactic acid selectivities slightly decreased from 82.2% to 76.0%. Trace amounts of oxalic, formic, and acetic acids were detected. When commercial Cu₂O powders were used as the catalysts, the glycerol conversions increased from 65.8% to 90.1% with prolonging the reaction time from 2 to 8 h. The lactic acid selectivities slightly decreased from 82.0% to 76.3%. Oxalic, formic, and acetic acids were formed with the selectivity less than 2.07%. 1,2-Propanediol was detected as a new product with the selectivity of less than 2.05%. When Cu₂O nanoparticles with the average particle sizes of 423, 224, 161, and 115 nm were used as the catalysts, the glycerol conversions increased from 80.1% to 94.1%, 84.5% to 99.1%, 89.6% to 100%, 92.5% to 100%, respectively, with prolonging the reaction time from 2 to 8 h. The lactic acid selectivities decreased from 83.4% to 74.3%, 86.1% to 75.4%, 88.3% to 76.8%, and 89.1% to 77.2%. Oxalic, formic, and acetic acids were formed with the selectivities of less than 2.04%. The selectivities of 1,2-propanediol were less than 1.91% and decreased with prolonging reaction time. The other products were carbonate and polymerlike chemicals. The results showed that nanosized Cu₂O particles had high catalytic activity for the hydrothermal conversion of glycerol to lactic acid. The catalytic activities of Cu₂O nanoparticles increased with the decrease in particle sizes. Lactic acid selectivity and glycerol conversion efficiency were heavily affected by different-sized Cu₂O particles, especially in the reaction time of 2 h (Table I). With the same loading of Cu₂O particles, the smaller nanoparticles tend to obtain higher surface area, which may induce the different efficiency. Besides, the theoretical activation energy for the glycerol conversion to lactic acid in the presence of NaOH as catalyst is in the range of $114.0-174.0\pm1.6$ KJ/mol.²⁰ Small-sized Cu₂O particles effectively catalyzed the glycerol select oxidation to lactic acid reaction by lowering the theoretical activation energy.

To investigate the effect of experimental parameters, such as reaction temperature, catalyst loading, NaOH/ glycerol mole ratio, and glycerol concentration, on the hydrothermal conversion of glycerol, Cu_2O nanoparticles (sample (a)) with the smallest average particle size of 115 nm were used as the model catalysts in the following sections. Interestingly, full glycerol conversions were obtained in reaction time of 6 h and 8 h catalyzed by Cu_2O nanoparticles (sample (a)) of 115 nm, while the selectivity decreased as the time elongated. At the same time, the byproducts of CO_2 and formic acid increased slightly, which indicated lactic acid undergoes decomposition when the reaction time increased to 8 h.

3.3.2. Effect of Reaction Temperature

Figure 3 shows the glycerol conversions and product selectivities in the hydrothermal conversion of glycerol catalyzed by Cu₂O nanoparticles with the average particle size of 115 nm at different reaction temperatures. With increasing the reaction temperatures from 190 to 230 °C, the glycerol conversions increased from 71.5% to 92.5% and the lactic acid selectivities increased from 81.5% to 89.1%, respectively. The selectivities of oxalic, formic, and acetic acids slightly increased from *ca*. 0.5% to 1.5% while the selectivities of 1,2-propanediol decreased from *ca*. 2% to 1.5%. Under the employed reaction conditions, high reaction temperature favored the hydrothermal conversion of glycerol to lactic acid. It is worth mentioning that under higher temperature, more glycerol molecules could overcome the energy barrier to be converted to target product lactic acid. However, as the reaction temperature was above 280 °C, lactic acid yield decreased quickly, because conversion routes of lactic acid and pyruvaldehyde to formate and carbonate were activated.¹⁶

3.3.3. Effect of Catalyst Loading

Figure 4 shows the effect of catalyst loading on the hydrothermal conversion of glycerol. With increasing the mole ratios of Cu₂O to glycerol from 1:100 to 7.5:100, the glycerol conversions increased from 74.3% to 97.2%. The lactic acid selectivities first increased from 86.5% to 89.1% and then decreased to 87.3%. The selectivities of



Figure 3. Effect of reaction temperature on hydrothermal conversion of glycerol over Cu_2O nanoparticles with the average particle size of 115 nm. Reaction conditions: glycerol (1 mol/L) aqueous solution, 100 mL; NaOH/glycerol mole ratio, 1.2:1; reaction time, 2 h; Cu_2O , 5 mmol. GLY, glycerol; LA, lactic acid; OA, oxalic acid; FA, formic acid; AA, acetic acid; 1,2-PDO, 1,2-propanediol.

Figure 4. Effect of catalyst loading on hydrothermal conversion of glycerol over Cu_2O nanoparticles with the average particle size of 115 nm. Reaction conditions: glycerol (1 mol/L) aqueous solution, 100 mL; NaOH/glycerol mole ratio, 1.2:1; reaction temperature, 230 °C; reaction time, 2 h. GLY, glycerol; LA, lactic acid; OA, oxalic acid; FA, formic acid; AA, acetic acid; 1,2-PDO, 1,2-propanediol.

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oxalic, formic, and acetic acids slightly increased from ca. 0.8% to 2% and the selectivities of 1,2-propanediol were less than 1.51%. Increasing the Cu₂O loadings enhanced the hydrothermal conversion of glycerol to lactic acid, as Cu₂O could afford more active catalytic sites. However, more active sites would probably promote the byproduct reaction involving lactic decomposition especially in high reaction temperature, inducing the decrease of lactic selectivity.

3.3.4. Effect of NaOH Concentration

When the hydrothermal conversion of glycerol was carried out over Cu₂O nanoparticles with different mole ratios of NaOH to glycerol in 100 mL of glycerol aqueous solution (1 mol/L) at 230 °C for 2 h, the glycerol conversions increased from 69.2% to 100% with increasing the mole ratios of NaOH to glycerol from 0.5:1 to 2:1 (Fig. 5). The lactic acid selectivities first increased from 76.8% to 87.2%, then slightly decreased to 84.5%. The selectivities of oxalic, formic, and acetic acids slightly

increased from ca. 0.6% to 1.6% and the selectivities of 1,2-propanediol decreased from 1.68% to 0.

Glycerol conversions increased with NaOH to glycerol of molar ratios below 2, suggesting that the reaction rate increased with this variable. This is consistent with the reports by Roy¹⁶ and Ramirez-Lopez.¹³ The behavior implied that increasing molar ratio of NaOH to glycerol other than lactic acid or the degradation of the previously generated lactic acid played the key role in products formation reactions.

3.3.5. Effect of Glycerol Concentration

When the hydrothermal conversion of glycerol was carried out under different glycerol concentrations ranging from 1 to 2.5 mol/L, the glycerol conversions slightly increased from 86.2% to 92.2% with increasing the glycerol concentrations (Fig. 6). Lactic acid selectivities slightly increased from 87.2% to 91.7%. The selectivities of oxalic acid, formic acid, acetic acid, and 1,2-propanediol were less than 2.03%. The experimental results showed that



Figure 5. Effect of NaOH concentration on hydrothermal conversion of glycerol over Cu_2O nanoparticles with the average particle size of 115 nm. Reaction conditions: glycerol (1 mol/L) aqueous solution, 100 mL; reaction temperature, 230 °C; reaction time, 2 h; Cu_2O , 2.5 mmol. GLY, glycerol; LA, lactic acid; OA, oxalic acid; FA, formic acid; AA, acetic acid; 1,2-PDO, 1,2-propanediol.

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Figure 6. Effect of glycerol concentration on hydrothermal conversion of glycerol over Cu_2O nanoparticles with the average particle size of 115 nm. Reaction conditions: Glycerol aqueous solution, 100 mL; NaOH/glycerol mole ratio, 1.2:1; reaction temperature, 230 °C; reaction time, 2 h; Cu_2O /glycerol mole ratio, 2.5:100. GLY, glycerol; LA, lactic acid; OA, oxalic acid; FA, formic acid; AA, acetic acid; 1,2-PDO, 1,2-propanediol.

Route 1 Hydrothermal conversion of glycerol to lactic acid catalyzed by Cu₂O nanoparticles



Route 2 Oxidative cleavage of lactate to acetate, formate, and carbonate



Route 3 Oxidative cleavage of glyceraldehyde to oxalate, formate, and carbonate



Route 4 Hydrogenation of glycerol to 1,2-propanediol catalyzed by Cu₂O nanoparticles Delivered by Ingenta to: State University of New York at Binghamton OH IP: 79.110.28.91 On: Mon, 06 Mar 2017 07:34:54 Copyright: American Scientific Publishers OH H₂ OH OH H₂ OH OH I,2-propanediol

Scheme 1. Reaction routes for the hydrothermal conversion of glycerol catalyzed by Cu₂O nanoparticles in NaOH aqueous solution.

small-sized Cu₂O nanoparticles had high catalytic activity for the conversion of glycerol to lactic acid at high glycerol concentration.

3.4. Reaction Routes

According to the experimental results, the possible reaction routes for the hydrothermal conversion of glycerol over Cu₂O nanocatalyst in alkaline solution were suggested as Scheme 1. Cu₂O nanoparticles first catalyzed the dehydrogenation of terminal hydroxyl group of glycerol to form glyceraldehyde. Glyceraldehyde could be converted to form 2-hydroxypropenal via intramolecular dehydration catalyzed by OH⁻,¹⁶ which could be converted to pyruvaldehyde via keto-enol tautomerism.^{1,13,16} The resultant pyruvaldehyde could be converted to lactate via internal Cannizaro reaction.^{1,13,16} The intermediates, such as glyceraldehyde, 2-hydroxypropenal, and pyruvaldehyde, were not detected in our present experiments, indicating that the intermediates could be rapidly converted to subsequent chemicals and finally to lactate. As compared to the hydrothermal conversion of glycerol in a "pure" alkaline solution, Cu_2O nanoparticles effectively catalyzed the hydrothermal conversion of glycerol. The results revealed that glycerol dehydrogenation is a control step. Meanwhile, lactate anions could be decomposed to form acetate and formate anions in alkaline solution, accompanied with the formation of carbonate anions (Route 2).¹³ Oxalate anions were probably formed by the oxidative cleavage of glyceraldehyde in alkaline solution (Route 3).¹³ 1,2-Propanediol was produced by the catalytic hydrogenation of glycerol with resultant H₂ over Cu₂O nanoparticles because it was not detected when the hydrothermal reaction was carried out in a "pure" alkaline solution (Route 4).

4. CONCLUSIONS

Cu₂O nanoparticles effectively catalyzed the hydrothermal conversion of glycerol to lactic acid in a NaOH

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aqueous solution at low reaction temperature of 230 °C as compared to the conventional hydrothermal conversion of glycerol in a "pure" alkaline aqueous solution. In a wide glycerol concentration range of 1-2.5 mol/L, the conversions of glycerol were more than 86.2% and the selectivities of lactic acid were more than 87.2% when Cu₂O nanoparticles with the average particle size of 115 nm were used as the catalysts with the mole ratio of Cu₂O to glycerol of 2.5:100 after reacting at 230 °C for 2 h. Cu₂O nanoparticles rapidly catalyzed glycerol dehydrogenation, giving high rate of glycerol conversion. As compared to micro-sized Cu₂O particles, Cu₂O nanoparticles showed high catalytic activity for the hydrothermal conversion of glycerol to lactic acid.

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