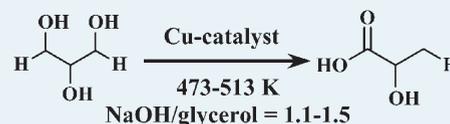


Cu-Based Catalysts Show Low Temperature Activity for Glycerol Conversion to Lactic Acid

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ABSTRACT: Cu based catalysts with a base promoter are reported for the first time for the synthesis of lactic acid from glycerol without using either a reductant or an oxidant. The catalytic route presented here gives high yields at lower temperatures (473 K) and lower molar NaOH/glycerol ratios (1.5) compared to the known hydrothermal (553–573 K) route. Further, the Cu₂O catalyst shows excellent recyclability.

KEYWORDS: glycerol, lactic acid, copper catalyst



Global biodiesel production by transesterification of fatty acid esters has increased severalfold in the past decade to partly substitute the use of fossil-derived diesel fuel.¹ The byproduct, glycerol, in this process has emerged as an important building block for chemicals.² For example, glycerol can be converted to several high value chemicals such as 1,2-propanediol,³ 1,3-propanediol,⁴ acrolein,⁵ and glyceric acid.⁶ Recently, lactic acid has emerged as another promising product from glycerol. Lactic acid (2-hydroxypropionic acid) is a platform chemical for several important commodity products such as biodegradable fibers, polylactic acid esters, and acrylic acid.² Lactic acid is mainly produced (~95% of world production) from sugars and sugar alcohols by the fermentation route which is slow and involves complex separation steps.⁷ Hydrothermal conversion of glycerol to lactic acid, wherein aqueous glycerol is treated at high temperature (573 K) under alkaline conditions, has been investigated as an alternative to the fermentation route.⁸ The hydrothermal conversion process is advantageous as it can directly use glycerol from the biodiesel production process containing water and alkali as feedstock with no need for a separation step. However, this process operates at near-critical temperature for water ($T_c = 647$ K), and the alkaline medium therefore causes severe corrosion of the reactors.⁹

The reaction pathway for glycerol to lactic acid was described earlier by Kishida et al.⁸ (Scheme 1) suggesting that dehydrogenation of glycerol to glyceraldehyde is a key step in this reaction. Ramirez-Lopez et al.¹⁰ showed that high temperatures (>550 K) are required in the hydrothermal process to convert glycerol to glyceraldehyde via glyceroxide ion as an intermediate. However, the decomposition of pyruvaldehyde and lactic acid are significant at that temperature, adversely affecting the selectivity to lactic acid. To overcome this problem, we investigated the use of a suitable dehydrogenation catalyst (in presence of a base) to facilitate conversion of glycerol to glyceraldehyde at lower temperature and then converting the glyceraldehyde to lactic acid using a base catalyst also present in the reaction mixture. We report here that copper catalysts along with NaOH provide a promising one-pot, low temperature route for glycerol conversion to lactic acid. Our finding is significant as the previous reports on metal catalyzed conversion of

glycerol to lactic acid employ Pt, Ru, PtRu, AuRu catalysts and require either oxygen¹¹ or hydrogen,^{12–14} with higher alkali concentration (molar alkali/glycerol molar ratios between 4 and 7).

Effect of Reactor Construction Material. It is well documented in the literature that NaOH leads to leaching of reactor construction materials.^{9,10} Further, the leached metals may catalyze chemical transformations. To investigate such a possibility, three reactions with an aqueous solution containing NaOH and glycerol (without Cu-catalysts) were conducted in different reactors; one made of Hastelloy-C, one of titanium, and the third with a Teflon liner inside the reactor to avoid contact of the reaction mixture with the reactor wall. The experiment in Hastelloy-C reactor showed 36.4% glycerol conversion with 90.1% selectivity to lactic acid after 6 h at 473 K. Inductively coupled plasma (ICP) analysis of the reaction mixture showed the presence of Fe (<7 ppm), Cr (<5 ppm), and Ni (<3 ppm). The titanium reactor showed very low conversion (5%), but suffered severe corrosion. In sharp contrast, the Teflon-lined reactor showed negligible conversion (0.26%) under identical conditions. These experiments clearly indicate that leached metals catalyze glycerol conversion in the Hastelloy-C reactor. Therefore, further experiments were conducted in a Teflon lined reactor.

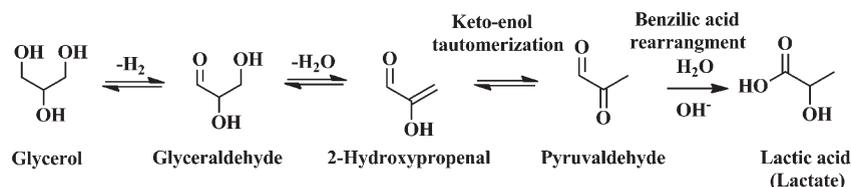
Cu-Based Catalysts. To investigate our hypothesis that a good dehydrogenation catalyst and alkali can convert glycerol to lactic acid at lower temperatures compared to the hydrothermal process, three different copper catalysts (viz. Cu/SiO₂, Cu₂O, and CuO/Al₂O₃) were tested, and the results are shown in Table 1. It is important to mention here that Cu catalysts without a base did not lead to any detectable liquid phase product, which indicates that both Cu and the base are required for the transformation of glycerol to lactic acid. CuO and Cu₂O catalysts showed higher conversion (~95%) of glycerol than Cu/SiO₂ catalyst (75%) with identical lactic acid selectivity (75–80%) at a significantly lower temperature compared to hydrothermal synthesis,¹⁰ and also without the need

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Scheme 1. Reaction Pathway for Conversion of Glycerol to Lactic Acid

Table 1. Comparison of Different Cu-Based Catalysts^a

	Cu/SiO ₂	CuO/Al ₂ O ₃	Cu ₂ O
glycerol conversion, %	75.2	97.8	93.6
Liquid Phase Product Selectivity, %			
glyceraldehyde	0.43	0.01	0.03
pyruvaldehyde	4.44	3.52	0.00
ethylene glycol	0.39	0.00	0.32
1,2-propanediol	2.15	1.54	6.03
lactic acid	79.7	78.6	78.1
acetic acid	2.61	1.33	1.90
formic acid	0.13	0.02	0.15
methanol	5.15	0.72	0.69
ethanol	0.52	0.00	0.53
propanol	0.00	0.00	0.00
Gas Phase Product Selectivity, %			
methane	0.90	1.04	3.86
ethane	0.01	0.02	0.04
propane	0.00	0.02	0.03
butane	0.01	0.05	0.11

^a Reaction conditions: glycerol: 3g; NaOH/glycerol molar ratio: 1.1; Cu: 3.5 mmol; P_{N₂}: 14 bar; 513 K; solvent: H₂O; initial liquid volume: 30 mL; batch reaction time: 6 h.

for a reductant^{12,13} or an oxidant.¹¹ The silica and alumina supports are known to leach out under alkaline conditions and high temperature forming sodium silicate (Na₂SiO₃) and aluminates (e.g., NaAlO₂), respectively.¹⁵ ICP analyses of the liquid phases, following runs with Cu/SiO₂ and CuO/SiO₂ catalysts under our reaction conditions, reveal complete dissolution of silica and alumina in the reaction mixture. However, only a negligible amount of Cu (less than 0.1 wt % of Cu in the catalyst) leached into the liquid phase. The problem of support dissolution clearly does not exist with the unsupported Cu₂O catalyst, which was hence used for further studies.

On the basis of positive identification of glyceraldehyde in the reaction mixture, it is reasonable to speculate that glyceraldehyde is an intermediate under our reaction conditions, as shown in Scheme 1. Acetol, a glycerol dehydration product, may also be an intermediate during glycerol conversion to lactic acid via a C₆-adduct.¹⁶ However, it has been demonstrated that the C₆ adduct from acetol does not react in alkaline conditions to produce lactic acid.¹⁰ On Cu-based catalysts, glycerol has been reported to form acetol under reactive distillation conditions, thereby overcoming equilibrium limitations due to the presence of water in the liquid phase.¹⁷ In the present study, water is employed as a solvent, and hence acetol formation will be severely hindered by equilibrium limitations. Thus, it is clear

Table 2. Effect of NaOH/Glycerol Molar Ratio on Lactic Acid Formation^a

	NaOH/glycerol molar ratio		
	0.5	1.1	1.5
glycerol conversion, %	46.2	75.2	93.5
Liquid Phase Product Selectivity, %			
glyceraldehyde	0.81	0.43	0.79
pyruvaldehyde	4.84	4.44	2.99
ethylene glycol	0.00	0.39	0.42
1,2-propanediol	1.95	2.15	2.99
lactic acid	67.6	79.7	73.0
acetic acid	3.25	2.61	2.31
formic acid	0.68	0.13	1.18
methanol	2.06	5.15	2.26
ethanol	0.00	0.52	0.73
propanol	0.00	0.00	0.00
Gas Phase Product Selectivity, %			
methane	0.50	0.90	0.02
ethane	0.01	0.01	0.01
propane	0.00	0.00	0.00
butane	0.02	0.01	0.00
CO ₂	6.41	0.00	0.00

^a Reaction conditions: glycerol: 3g; Cu/SiO₂: 0.4 g; P_{N₂}: 14 bar; 513 K; solvent: H₂O; initial liquid volume: 30 mL; batch reaction time: 6 h.

from reported studies that acetol is not a viable intermediate at high water concentrations in the liquid phase. A detailed investigation of intermediates is required to further elucidate the reaction mechanism.

Effect of NaOH/Glycerol Molar Ratio. As shown in Scheme 1, the base accelerates lactic acid formation by (i) favoring the transformation of pyruvaldehyde to lactic acid, and (ii) shifting the equilibrium toward lactic acid formation (by reducing the lactic acid concentration as a result of Na-lactate formation). As lactate formation reduces the effective base concentration in the reaction mixture, the effect of NaOH/glycerol molar ratio was studied.

Table 2 shows a gradual increase in conversion of glycerol with increase in NaOH/glycerol ratio; however, the lactic acid selectivity remained constant above NaOH/glycerol ratio of 1. At NaOH/glycerol ratio <1, the final reaction mixture was neutral (pH: 7) indicating that there was no base left to catalyze the pyruvaldehyde to lactic acid reaction or scavenge lactic acid to shift the equilibrium. Consequently, conversion of glycerol decreased. At higher NaOH/glycerol ratios, the base catalyzed reactions should be able to proceed farther thereby reducing the

Table 3. Effect of Temperature on Glycerol Conversion to Lactic Acid in Presence of Cu/SiO₂ Catalyst and NaOH^a

temperature	glycerol conversion, %	lactic acid selectivity, %
473 K	35.5	81.6
493 K	44.5	81.5
513 K	75.2	79.7

^a Reaction conditions: glycerol: 3 g; NaOH/glycerol molar ratio: 1.1; Cu/SiO₂: 0.4 g; P_{N₂}: 14 bar; solvent: H₂O; initial liquid volume: 30 mL; batch reaction time: 6 h.

Table 4. Cu₂O Catalyst for Conversion of Glycerol to Lactic Acid under Different Temperature and NaOH/Glycerol Molar Ratio^a

temperature	NaOH/glycerol molar ratio	glycerol conversion, %	lactic acid selectivity, %
473 K	1.1	70.2	79.2
	1.5	95.1	80.3
493 K	1.1	88.2	76.2
	1.5	94.8	77.6
513 K	1.1	93.6	78.1

^a Reaction conditions: glycerol: 3 g; Cu₂O: 0.2 g; P_{N₂}: 14 bar; solvent: H₂O; initial liquid volume: 30 mL; batch reaction time: 6 h.

effective concentration of glyceraldehyde, which indirectly favors the dehydrogenation equilibrium for glycerol conversion to glyceraldehyde. This might be a reason for the improved conversion of glycerol at the NaOH/glycerol molar ratio of 1.5. These results are significant compared to the hydrothermal synthesis¹⁰ in which not only higher NaOH/glycerol ratio and high temperature (>543 K) are required, but the lactic acid selectivity is also lower because of decomposition of pyruvaldehyde and lactic acid.

Effect of Temperature. Glycerol conversion increased significantly with increase in temperature (493–513 K) while, the selectivity to lactic acid remained more or less constant (Table 3).

Several experiments were also carried out using Cu₂O catalyst with different NaOH/glycerol ratios at different temperatures. As shown in Table 4, the Cu₂O catalyst provides high yield of lactic acid even at 473 K, a temperature at which the Cu/SiO₂ catalyst displays much lower yield (see Table 3). When compared to the hydrothermal route, the Cu₂O catalyst provides similar yield of lactic acid (~80%) but at temperatures that are 80–100 K lower than those required for the hydrothermal route.

Reuse of Cu₂O Catalyst. The reusability of the Cu₂O catalyst was tested by several recycle experiments at 473 K with a molar NaOH/glycerol ratio of 1.1. As shown in Figure 1, the glycerol conversion and lactic acid selectivity remained virtually identical during the recycle runs, indicating very good catalyst stability under reaction conditions.

In conclusion, Cu based catalysts have been demonstrated for low temperature (473 K) conversion of glycerol to lactic acid with high yields (~80%). Compared to the hydrothermal process, this new catalytic route requires lower temperatures and lower glycerol/alkali ratios without the need for adding either oxygen or hydrogen. The Cu₂O catalyst showed very good stability for prolonged use.

EXPERIMENTAL SECTION

Materials. Glycerol (≥99.5%), Cu₂O in powder form, and 13 wt % CuO/Al₂O₃ were purchased from Sigma-Aldrich. 60 wt % Cu/SiO₂ was supplied by Evonik Degussa and powdered

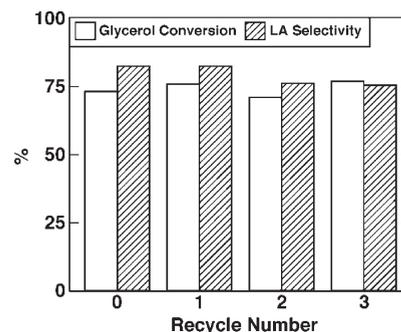


Figure 1. Recycle study with Cu₂O catalyst. Reaction conditions: glycerol: 3 g; Cu₂O: 0.2 g; NaOH/glycerol molar ratio: 1.1; P_{N₂}: 14 bar; 473 K; solvent: H₂O; initial liquid volume: 30 mL; batch reaction time: 6 h.

(to 100–125 μm) before use. Hydrogen (>99.5%) and nitrogen (>99%) were procured from Air Gas Inc. and Linweld, respectively.

Reaction Experiments. The reactions were conducted in a high temperature, high pressure multiple batch slurry reactor setup.³

For the reactions with Cu/SiO₂ catalyst, the catalyst was activated inside the reactor at 513 K and 70 bar H₂ partial pressure for 12 h. Following the activation step, the reactor was cooled down, H₂ was released, and the reactor was purged three times with N₂. A known amount of glycerol and NaOH, dissolved in a predetermined volume of water, were injected into the reactor. The reactor was purged three times with N₂. The reactor was first heated to a desired temperature. N₂ was then introduced into the reactor up to 14 bar and reaction started by increasing the agitation speed to 9 Hz. N₂ pressurization allows convenient sampling of the gas phase for GC analysis at the end of the run. To investigate the effect of N₂ pressure on the reaction, a run at 473 K with Cu₂O catalyst and 1.1 molar ratio of NaOH/glycerol under 14 bar N₂ pressure was compared with a run without N₂ addition. Both runs showed nearly identical conversion of glycerol (70.2% and 67.8% respectively) and selectivity to lactic acid (79.2% and 77.9% respectively). At the end of the run, the reactor was cooled, and the reactor pressure was noted. The gas phase sample was analyzed offline by GC.¹⁸ The reactor was opened, and the pH of the reaction mixture was measured. Liquid phase sample for analysis was prepared by diluting the reaction mixture with 20 mL aqueous H₂SO₄ solution to lower the pH of the HPLC sample to ≤7 as the HPLC column used in the analysis is unsuitable for basic samples. The final volume and pH of the mixture were noted. Part of the liquid sample was passed through syringe filters and analyzed by HPLC.¹⁸ Calibrations for glycerol and the expected gas and liquid phase products were performed for quantitative analysis. The analytical procedure is able to account for ~90% of the starting glycerol. It is important to note that carbonate can form during the reaction¹⁰ and is indirectly confirmed by the bubbles (CO₂) formed when the reaction mixture was diluted with aqueous H₂SO₄ solution.

For the reactions with Cu₂O or CuO/Al₂O₃, the catalyst was used as received. For these reactions, the catalyst, dissolved glycerol, and NaOH in water were charged into the reactor, and the reactor was sealed.

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REFERENCES

- (1) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Pina, C. D. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434–4440.
- (2) Bozell, J. J.; Petersen, G. R. *Green Chem.* **2010**, *12*, 539–554.
- (3) Roy, D.; Subramaniam, B.; Chaudhari, R. V. *Catal. Today* **2010**, *156* (1–2), 31–37.
- (4) Qin, L.-Z.; Song, M.-J.; Chen, C.-L. *Green Chem.* **2010**, *12*, 1466–1472.
- (5) Corma, A.; Huber, G. W.; Sauvinaud, L.; O'Connor, P. *J. Catal.* **2008**, *257* (1), 163–171.
- (6) Zhou, C.-H. C.; Beltramini, J. N.; Fan, Y.-X.; Lu, G. Q. *M. Chem. Soc. Rev.* **2008**, *37*, 527–549.
- (7) Datta, R. In *Kirk-Othmer concise encyclopedia of chemical technology*, 5th ed.; Wiley-Interscience: Hoboken, NJ, 2004; Vol. 1 pp 1324–1327.
- (8) Kishida, H.; Jin, F.; Zhou, Z.; Moriya, T.; Enomoto, H. *Chem. Lett.* **2005**, *34* (11), 1560–1561.
- (9) Shen, Z.; Jin, F.; Zhang, Y.; Wu, B.; Kishita, A.; Tohji, K.; Kishida, H. *Ind. Eng. Chem. Res.* **2009**, *48*, 8920–8925.
- (10) Ramírez-López, C. A.; Ochoa-Gómez, J. R.; Fernández-Santos, M.; Gómez-Jiménez-Aberasturi, O.; Alonso-Vicario, A.; Torrecilla-Soria, J. *Ind. Eng. Chem. Res.* **2010**, *49* (14), 6270–6278.
- (11) Shen, Y.; Zhang, S.; Li, H.; Ren, Y.; Liu, H. *Chem.—Eur. J.* **2010**, *16*, 7368–7371.
- (12) Maris, E. P.; Davis, R. J. *J. Catal.* **2007**, *249*, 328–337.
- (13) Maris, E. P.; Ketchie, W. C.; Murayama, M.; Davis, R. J. *J. Catal.* **2007**, *251*, 281–294.
- (14) Marincean, S.; Peereboom, L.; Xi, Y.; Miller, D. J.; Jackson, J. E. *Chem. Ind.* **2007**, *115*, 427–436.
- (15) Sarkar, S. *Hydrometallurgy* **2011**, *105*, 364–369.
- (16) Lux, S.; Stehring, P.; Hilber, T.; Siebenhofer, M. *Proceedings of the 2008 AIChE Annual Meeting, Fall Conference*; on CD-ROM, abstract 678c, Philadelphia, PA, November 16–21, 2008; <http://www.aiche.org/apps/pubcat/index.asp>, ISBN 978-0-816910-1050-2.
- (17) Chiu, C.-W.; Dasari, M. A.; Suppes, G. J.; Sutterlin, W. R. *AIChE J.* **2006**, *52*, 3543–3548.
- (18) Torres, A.; Roy, D.; Subramaniam, B.; Chaudhari, R. V. *Ind. Eng. Chem. Res.* **2010**, *49*, 10826–10835.