



# Relay catalysis of copper-magnesium catalyst on efficient valorization of glycerol to glycolic acid

Shuguang Xu, Yuan Xiao, Wenyu Zhang, Shengqi Liao, Ruofeng Yang, Jianmei Li<sup>\*</sup>, Changwei Hu<sup>\*</sup>

Key Laboratory of Green Chemistry and Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, Sichuan 610064, PR China

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## ABSTRACT

The exploration of potential application of glycerol is of particular importance for solving the oversupply of glycerol as an unavoidable byproduct of biodiesel and affording profitable possibilities for sustainable biodiesel. Herein, we developed a simple, cheap but robust  $\text{Cu}_1\text{Mg}_4$  catalyst, which exhibited outstanding catalytic activity for the selective conversion of glycerol towards valuable glycolic acid, eliminating the addition of extra inorganic base. As high as 71.8% yield of glycolic acid was achieved, the highest value to date as far as we know. In combination of experiment and DFT calculations, it was revealed that Cu, Mg species in catalyst enabled the relay catalysis for the cascade reactions in glycerol transformation. Cu species in catalyst dominated the first dehydrogenation reaction of glycerol to glyceraldehyde, which was promoted by Mg species. Mg species followed to catalyze the next cleavage of C2-C3 bond in glyceraldehyde to generate glycolaldehyde. The final oxidation of glycolaldehyde to glycolic acid was achieved by the catalysis of Cu species. This relay catalysis of  $\text{Cu}_1\text{Mg}_4$  catalyst significantly inhibited the formation of glyceric acid and lactic acid by-products, thereby enabling the selective generation of glycolic acid.

## 1. Introduction

The drastically rising demand for biodiesel as an attractive renewable energy resource has led to the generation of glycerol as an unavoidable byproduct in great quantities, which approximately accounts for about 10 wt% of the total biodiesel production.[1,2] It is estimated that the worldwide production of glycerol reaches to about 6.14 billion liters in 2017, and continuously increases with an annual rate of 10–20% in future.[3] This offers promising opportunities to upgrade the surplus glycerol byproduct. Typical advances have been achieved in recent years, in which lactic acid [4–7] and glyceric acid[8–11] with satisfied yield could be obtained via the selective dehydration and oxidation of glyceraldehyde, respectively. Nevertheless, the applications of glycerol in current commercial market are quite limited, in which only ~4% of the total glycerol production has been utilized.[12] As a result, the oversupplied glycerol is treated as a waste stream by burning it without any further value. This makes biodiesel less economically competitive to petro-diesel, and seriously impedes the sustainability of biodiesel production.[13,14]

Several recent attempts have been paid to produce glycolic acid

(GcA) using glycerol as feedstock, due to the wide applications of GcA in cosmetics, pharmaceutical industry and fine chemicals.[15–17] Especially, GcA can be used as a monomer in the preparation of biocompatible homopolymer polyglycolic acid and copolymer, which have widespread applications in biomedical engineering, such as irrigate in endodontics, drug control-release system, repairs of bone defects, and suture of tissues (blood vessels, muscles, etc.).[18–20] Glycerol is a highly promising feedstock for the production of GcA due to its high functionalization, low cost and sustainability.[21–23] However, glycerol is quite difficult to be activated, in which inorganic base with high concentration is usually required.[24–27] To the best of our knowledge, only a handful of researches, relating to GcA production from glycerol, could be found, whereas the yield of GcA is still low. Even in the presence of noble metal catalyst ( $\text{Ag}/\text{Al}_2\text{O}_3$ ), only 57.0% selectivity of GcA with 85% glycerol conversion was obtained.[28] Unfortunately, four-fold of strong alkaline (e.g. NaOH) was necessary to activate the H in glycerol,[29] while little glycerol conversion to GcA was found in the absence of strong alkaline. This inevitably leads to the serious equipment corrosion and environmental hazards under harsh conditions. Moreover, other byproducts (e.g.  $\text{C}_3$  acids like lactic acid, glyceric acid)

<sup>\*</sup> Corresponding author.

E-mail addresses: [lijianmei@scu.edu.cn](mailto:lijianmei@scu.edu.cn) (J. Li), [changwei@scu.edu.cn](mailto:changwei@scu.edu.cn) (C. Hu).

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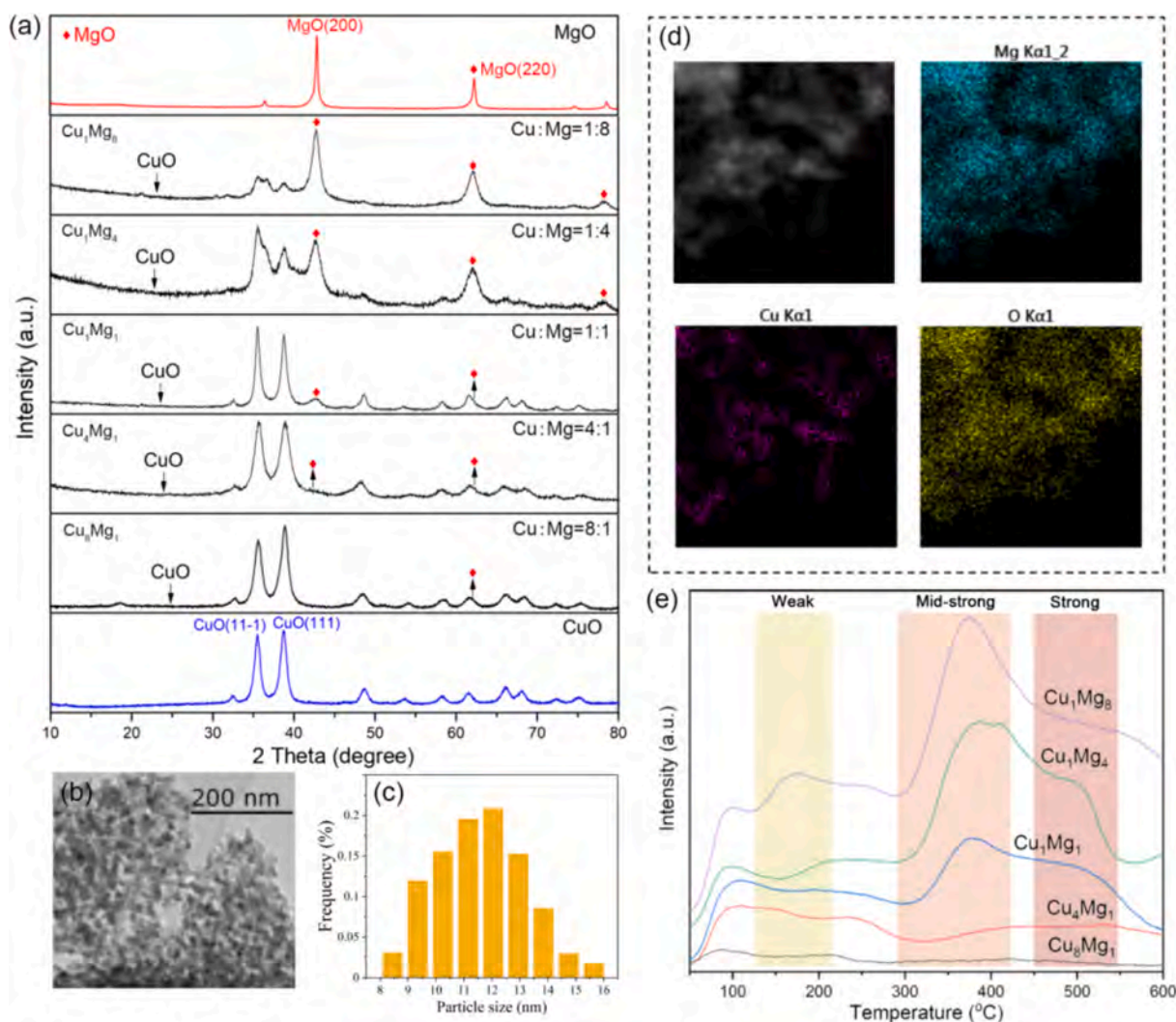
can be produced together with GcA, thereby leading to the low selectivity. For instance, only 31% selectivity of GcA with full glycerol conversion was obtained over Cu(Ni)/CNF catalyst, accompanying with the formation of a comparable amount (24%) of lactic acid.[30] The key factors to block the high selectivity towards GcA are attributed to the side reactions such as inadequate C–C cleavage of glycerol yielding lactic acid, glyceric acid, as well as the over-oxidation reaction giving oxalic acid.[31–33] The development of efficient and environmentally friendly catalytic strategy for glycerol conversion to GcA is therefore highly desirable to solve the flood of glycerol and meets the substantial demand for GcA.

Herein, we develop a cheap, multi-functional Cu-Mg catalyst, possessing appropriate oxidation ability and alkali active sites in a simple chemical technology, which exhibited outstanding activity to enable the relay catalysis for the cascade reactions in glycerol conversion towards the selective formation of GcA, eliminating the addition of inorganic base for assistance. A three-step reaction pathway is proposed, including dehydrogenation to glyceraldehyde (GLA), the breaking of C–C bond to glycolaldehyde, and the further oxygenation to GcA. Combining experimental and DFT results, we have revealed the specific role of Cu and Mg species in the three steps, and also explored the favorable pathway of the competitive reactions, explaining the origin of GcA selectivity.

## 2. Results and discussion

We first characterized the as-prepared Cu-Mg catalysts with different Mg/Cu ratios (the preparation procedures were illustrated in Fig. S1). The XRD patterns (Fig. 1a) showed the peaks at  $2\theta = 35.5^\circ, 38.8^\circ$ , assigning to  $(\bar{1}11)$  and  $(111)$  lattice plane of CuO, the calculated particle size of which gradually increased with the increment of Cu content. The peaks at  $2\theta = 42.8^\circ, 62.3^\circ$  corresponding to the  $(200)$  lattice plane of MgO gradually strengthened with increasing MgO content.[34,35] This demonstrated the presence of cubic phase CuO (PDF 48–1548) and MgO (PDF 45–0946) in Cu-Mg catalyst. The result of  $H_2$ -TPR showed that the reduction temperature

of  $Cu^{II}$  in  $Cu_1Mg_4$  catalyst was higher than that of bulk CuO (Fig. S2), reflecting the strong interaction between Cu and Mg with increasing Mg percentage in the catalysts.[35] TEM analysis and the elemental mappings for  $Cu_1Mg_4$  catalyst demonstrated the well dispersion of CuO (Fig. 1b, 1c and 1d). XPS analysis showed the binding energy centered at 933.5 and 941.6 eV, corresponding to the core level of Cu 2p<sub>3/2</sub> (Fig. S3) and the shakeup satellite peak, respectively; further confirming the existence of  $Cu^{II}$  in the catalyst.[34,36] These results indicated the existence of CuO/MgO as main species in catalyst. ICP-AES analysis demonstrated that the actual ratio of Mg/Cu in catalyst was quite close to the designed amount (Table S1).  $N_2$  adsorption–desorption isotherms of the catalyst showed that the prepared Cu-Mg catalysts were in



**Fig. 1.** The characterizations of the prepared catalysts. (a) The XRD patterns of the catalysts. (b) The TEM image of  $Cu_1Mg_4$  catalyst. (c) The distribution of particle size of  $Cu_1Mg_4$  catalyst. (d) Elemental mappings of  $Cu_1Mg_4$  catalyst. (e)  $CO_2$ -TPD profiles of the prepared catalysts.

mesoporous state (Fig. S4), [37] and the BET surface area slightly decreased with increasing Mg percentage (Table S1). CO<sub>2</sub>-TPD analysis (Fig. 1e, Table S2) indicated that the amount of alkaline sites in catalyst (especially the mid-strong alkalinity) increased obviously with the increment of Mg percentage in the catalysts.

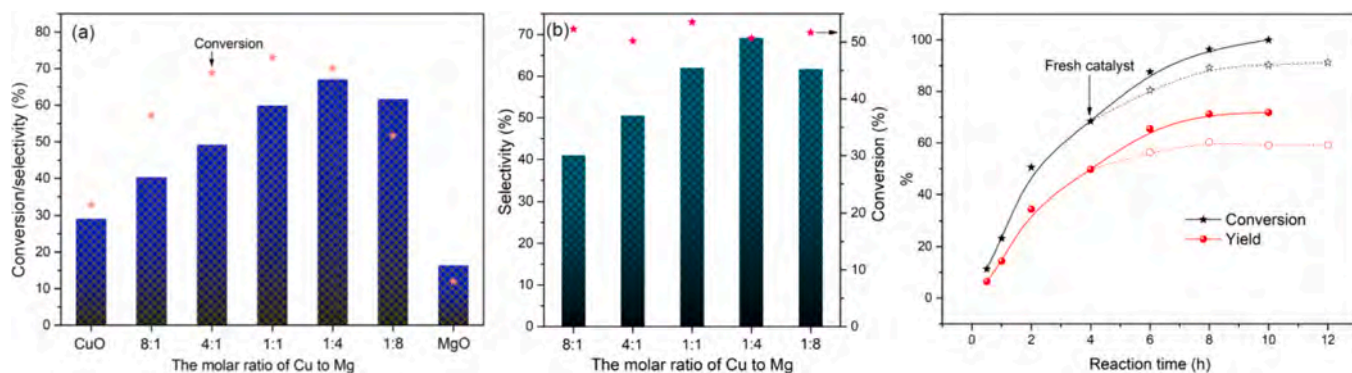
We next studied the catalytic activity of Cu-Mg catalysts with different Cu/Mg ratios for the conversion of glycerol to GcA, and found that single CuO gave only 9.6% of GcA yield. Interestingly, increasing Mg percentage (the Cu content gradually decreased) led to the great increment of GcA yield, which reached up to the maximum (51.7%) at Cu:Mg = 1:4 (Fig. 2a). However, continuously increasing Mg content obviously decreased GcA yield, and only 2.0% yield of GcA was obtained in the presence of pure MgO. We also compared the catalysts with different Cu/Mg ratios at about 50% conversion, the results showed that the highest selectivity of GcA (67.1%) was also achieved at Cu:Mg = 1:4 (Fig. 2b). In contrast, scarce GcA (1.2% yield) with 28% glycerol conversion was obtained in blank reaction, in which much glycerol might be

converted to oligomers and humins (Table S3). These results demonstrated the outstanding activity of Cu<sub>1</sub>Mg<sub>4</sub> catalyst, and suggested that both CuO and MgO were essential and contributed to the formation of GcA from glycerol. In addition, the smaller particle size of CuO at relatively lower content might also benefit to GcA formation. When the mixture of CuO and MgO (1:4 in mole) was employed as catalyst, the yield of GcA (37.0%, Table S3) was also much higher than that catalyzed by either single CuO or MgO, which further evidenced the predominant roles of both CuO and MgO species. Whereas, this GcA yield was slightly lower than that catalyzed by Cu<sub>1</sub>Mg<sub>4</sub> catalyst. Similarly, Cu<sub>4</sub>Mg<sub>1</sub> and Cu<sub>1</sub>Mg<sub>1</sub> catalysts gave slightly higher GcA yield than the corresponding CuO/MgO mixtures (4:1 and 1:1 in mole) from mechanical mixing. We therefore speculated that CuO and MgO exhibited a significant synergetic effect, in which, the strong interaction between the two components might promote the activity of catalyst to some extent. This could be proved by the more increment of GcA yield over Cu-Mg catalyst with increasing Mg/Cu ratio when comparing to that using the corresponding mixture as catalyst, due to the stronger interaction between MgO and CuO. Besides GcA, formic acid was co-produced as main byproduct via the catalysis of Cu<sub>1</sub>Mg<sub>4</sub> catalyst (Table S3), which could be used as potential hydrogen source in biomass hydrogenation. Glyceric acid (GA), lactic acid (LaA), tartaric acid (TA), and oxalic acid (OA) with limited yield were also obtained (Table S2), and CO<sub>2</sub> was detected as the main gas product (Table S4). In light of these results, Cu<sub>1</sub>Mg<sub>4</sub> was selected as the catalyst in the next studies relative to the optimization of reaction conditions, including reaction temperature, time, the mass ratio of reactant to catalyst and the O<sub>2</sub>

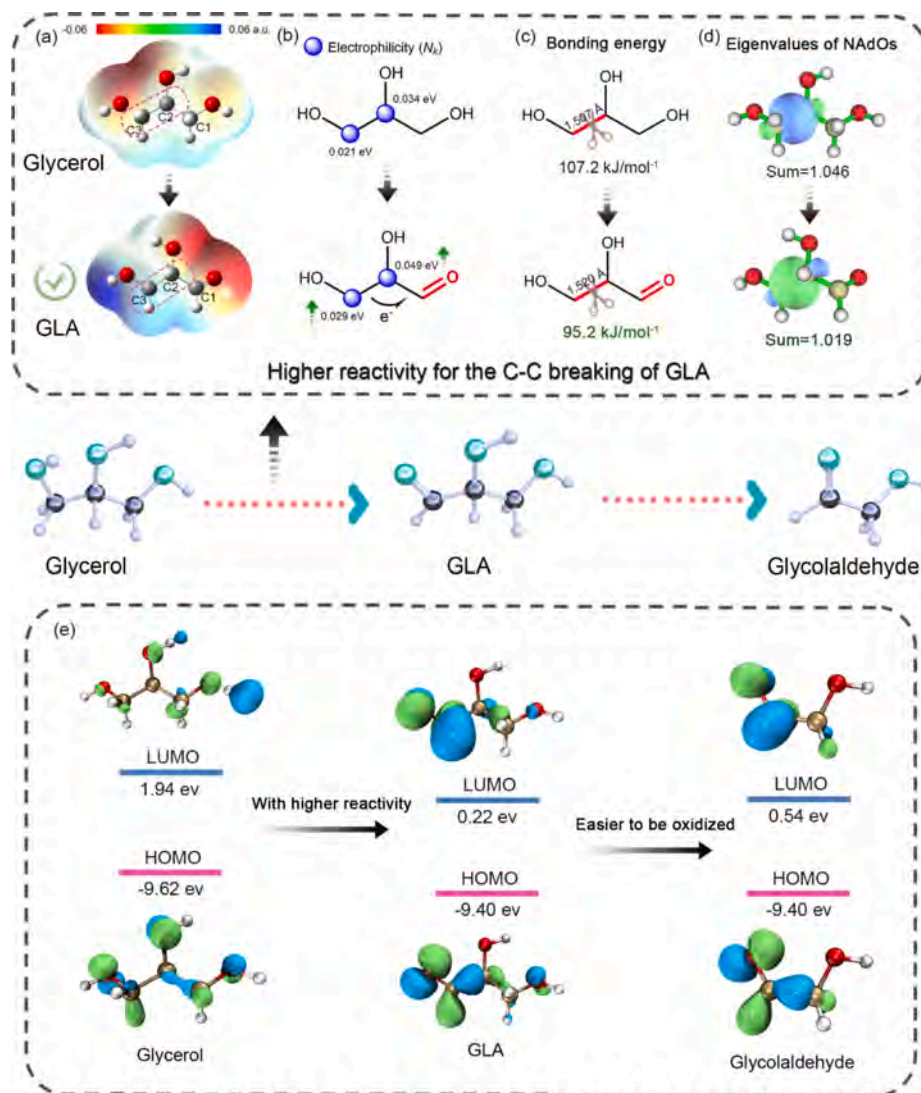
pressure (Table S15 to S9, Fig. S5). Under the optimized conditions (473 K, the mass ratio of reactant: catalyst = 1:2, 8 h, 1 MPa O<sub>2</sub>), the highest GcA yield (60.3%) was achieved with 89.2% conversion of glycerol and 85.9% of carbon balance, which was much higher than those reports previously (Table S10).

Subsequently, we attempted to reveal the reaction mechanism of glycerol conversion. We conducted the reaction at lower temperature (433 K), and detected a few dihydroxyacetone (DHA) and glyceraldehyde (GLA), the amount of which showed an increasing-first and exhaustion-next tendency (Fig. S6). [38,39] We then conducted the control experiments using DHA and GLA as substrates under the optimal conditions, respectively. The results showed that GLA as reactant gave a similar conversion to DHA but much higher selectivity (73.8%) towards GcA than DHA (34.9%) (Table S11). Whereas, DHA preferred to produce lactic acid with 37.2 C-mol% yield. [40] Therefore, we speculated that GLA was the possible intermediate, in which the conversion of glycerol might firstly pass through the formation of GLA via a dehydrogenation of terminal -CHOH to -C=O. [41] This could significantly promote the reactivity of the substrate, and the result of DFT calculation further confirmed this speculation, in which the LUMO-HOMO gap (11.56 eV) of glycerol indeed became much lower after the oxidation of -CHOH to -C=O (GLA, 9.62 eV), due to the electron-pushing stabilization of terminal -OH in glycerol (Fig. 3e).

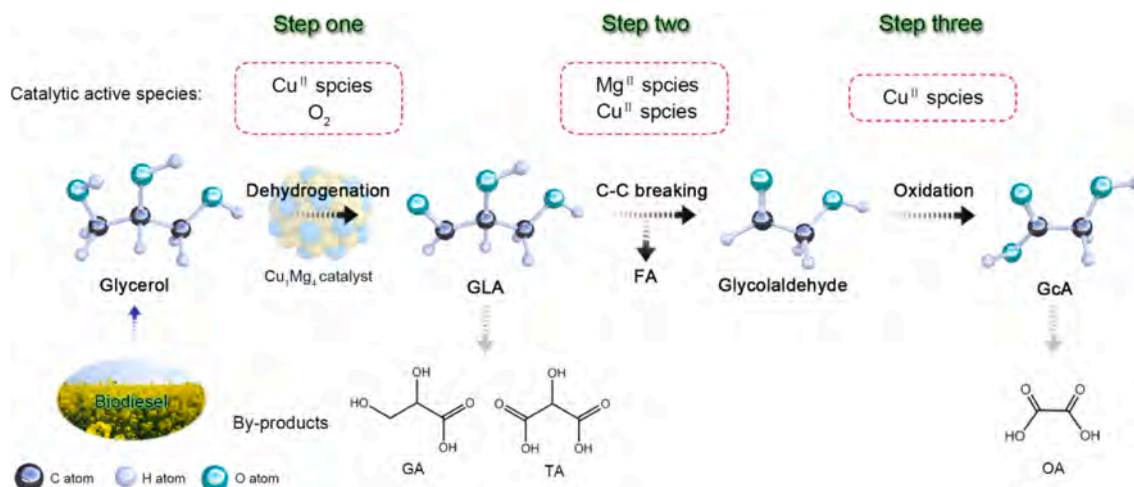
When glycerol was transformed to GLA, the ESP analysis (Fig. 3a) showed that more positive charge was concentrated at C2 and C3 in GLA, the electrophilicity of which increased from 0.034 to 0.049 eV at C2 and 0.021 to 0.029 eV at C3, respectively (Fig. 3b). This proved the electron flow from C2-C3 to around C=O after the dehydrogenation of glycerol to GLA. As a result, the bond energy of C2-C3 sharply decreased from 107.2 to 95.2 kJ mol<sup>-1</sup> (Fig. 3c). The bond length increased from 1.507 to 1.520 Å, and the bond order also decreased from 1.046 to 1.019 (Fig. 3d). These results gave strong evidences on the fact that C2-C3 bond was significantly weakened after the oxidation of terminal -C-OH in glycerol to -C=O. [42] In contrast, C1-C2 bond was strengthened after the flowing of electron around -C=O, the bond energy of which increased from 107.2 to 120.3 kJ mol<sup>-1</sup>, with bond length decreasing from 1.507 to 1.499 Å (Fig. S7). This allowed the selective cleavage of C2-C3 bond. In the case of such a breaking model, glycolaldehyde was generated. We then employed glycolaldehyde as reactant, and obtained 83.1% yield of GcA. The higher LUMO value of glycolaldehyde (0.54 eV) than that of GLA (0.22 eV) also proved that -C=O in glycolaldehyde was much easier to be oxidized than that in GLA. These results indicated the possible precursor role of glycolaldehyde, and also validated the C2-C3 breaking model in GLA. Besides glycolaldehyde intermediate, GcA could



**Fig. 2.** The conversion of glycerol to GcA. (a) The influence of Cu/Mg ratio in catalysts on the conversion of glycerol as well as the selectivity to GcA. Reaction conditions: 0.2 g glycerol; 0.2 g catalyst; reaction temperature, 453 K; reaction time, 8 h; 1 MPa O<sub>2</sub>; 400 rpm; 50 mL H<sub>2</sub>O. (b) The selectivity to GcA at about 50% conversion catalyzed by Cu<sub>x</sub>Mg<sub>y</sub> catalysts. (c) The successive reaction of glycerol conversion over two batches of catalysts. Reaction conditions in segment 1: 0.2 g glycerol; Cu<sub>1</sub>Mg<sub>4</sub> catalyst (mass ratio of reactant : catalyst = 1:2); reaction temperature, 473 K; reaction time, 4 h; 1 MPa O<sub>2</sub>; 400 rpm; 50 mL H<sub>2</sub>O. After reaction, the spent catalyst was filtrated and the other batch of fresh catalyst was then added into the resultant mixture for the next conversion. Reaction conditions in segment 2: 0.2 g glycerol; Cu<sub>1</sub>Mg<sub>4</sub> catalyst (mass ratio of reactant : catalyst = 1:2); reaction temperature, 473 K; reaction time, 4 h; 1 MPa O<sub>2</sub>; 400 rpm; 50 mL H<sub>2</sub>O. The dotted line represented one-pot reaction of glycerol with only one batch of catalyst for 8 h.



**Fig. 3.** Multiple property analyses of the typical chemicals in the conversion of glycerol to GcA. (a) The electrostatic potential (ESP) analysis; (b) The reactivity index analysis; (c) Bond energy (kJ mol<sup>-1</sup>) and bond length (Å); (d) Natural adaptive orbital (NAdO) analysis; (e) Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) analysis.



**Fig. 4.** The proposed reaction pathway for the conversion of glycerol to GcA catalyzed by Cu<sub>1</sub>Mg<sub>4</sub> catalyst.

also be generated from glyceric acid via the subsequent C–C cleavage, in which glyceric acid was formed by the further oxidation of GLA.[43] However, using glyceric acid as substrate gave only 15.5% yield of GcA under the reaction conditions in present work (Table S11). These results further evidenced the proposal that GcA was formed passing through glycolaldehyde precursor rather than glyceric acid. Based on these results, it was reasonable to propose that glycerol conversion to GcA mainly involved three steps in the following: (1) Glycerol dehydrogenation to GLA; (2) C2-C3 cleavage in GLA to glycolaldehyde; (3) Glycolaldehyde further transformation to GcA (Fig. 4). In light of the proposed mechanism, the remaining C<sub>1</sub> compound was almost transformed to formic acid (30.2 C-mol% yield, Table S11). The higher ratio of formic acid/GcA (1.23:1) than the theoretical value (1:1) in our work was possibly caused by the further decomposition of GcA and the formation of some by-products like oxalic acid, tartronic acid and so on. [44,45]

To comprehensively understand the relay catalysis of Cu, Mg species in catalyst for the cascade reactions in glycerol conversion to GcA, we next carried out kinetic studies, in which glycerol, GLA, and glycolaldehyde were used as the substrates in the successive three steps of glycerol conversion to GcA, respectively. CuO and MgO mixture from mechanical mixing were used as model catalysts by varying the amount of one species while keeping the others constant, wherein, the influence of the interaction between Cu and Mg species in Cu-Mg catalyst with different Cu/Mg ratios was eliminated. When glycolaldehyde was employed as substrate, single CuO obviously enhanced the yield of GcA and slightly promoted the formation of oxalic acid byproduct, while single MgO gave little activity. This indicated that CuO species was responsible for glycolaldehyde conversion to GcA, whereas more CuO might also promote the deep oxidation of glycolaldehyde to oxalic acid. The rate for GcA formation significantly increased when gradually increasing CuO amount but keeping the amount of MgO constant. When keeping the amount of CuO constant but varying the amount of MgO, the

yield of GcA indeed showed no obvious change (Fig. S8, Table S12). These results confirmed the substantial role of CuO in glycolaldehyde transformation to GcA (Table S13).[46] Compared to that using glycolaldehyde as reactant, a key reaction step relative to C–C cleavage was required in GLA conversion to GcA. When GLA was used as substrate, it was found that single MgO gave lactic acid as the main product with just a small amount of GcA, while single CuO led to the formation of glyceric acid. In the presence of CuO with constant amount, the rate constant for GLA conversion significantly increased with the gradual increase of MgO amount (Fig. S9, Table S12), and the yield of GcA showed a similar tendency. When keeping the amount of MgO constant, the rate constant of GLA conversion showed just a slight increase with increasing amount of CuO. Notably, the yield of glycolic acid sharply increased, while the yield of LaA obviously decreased with the increment of CuO content. We therefore assumed that MgO greatly facilitated the cleavage of C2-C3 bond in GLA with the assistance of CuO, giving GcA as the main product. The great enhancement of GcA yield with increasing amount of CuO in the presence of MgO could be explained by the fact that the acceleration of glycolaldehyde oxidation to GcA by CuO substantially facilitated the promoting effect of MgO on C2-C3 cleavage in GLA. These results indicated that MgO and CuO enabled the relay catalysis of GLA to GcA, in which MgO first facilitated the cleavage of C2-C3 bond in GLA to glycolaldehyde, while CuO mainly promoted the next glycolaldehyde oxidation to GcA which in turn promoted C2-C3 cleavage.

As for glycerol as substrate, single CuO gave much higher glycerol conversion than single MgO, indicating the predominant performance of CuO possibly on the dehydrogenation of glycerol, since dehydrogenation is the most crucial step in glycerol activation.[47,48] When keeping the amount of MgO constant, both the rate constant of glycerol conversion and GcA yield were enhanced sharply with increasing CuO amount. The yield of glyceric acid was also sharply raised by increasing CuO amount, indicating that higher CuO content could promote the oxidation of glycerol to glyceric acid. When keeping CuO unchanged, the

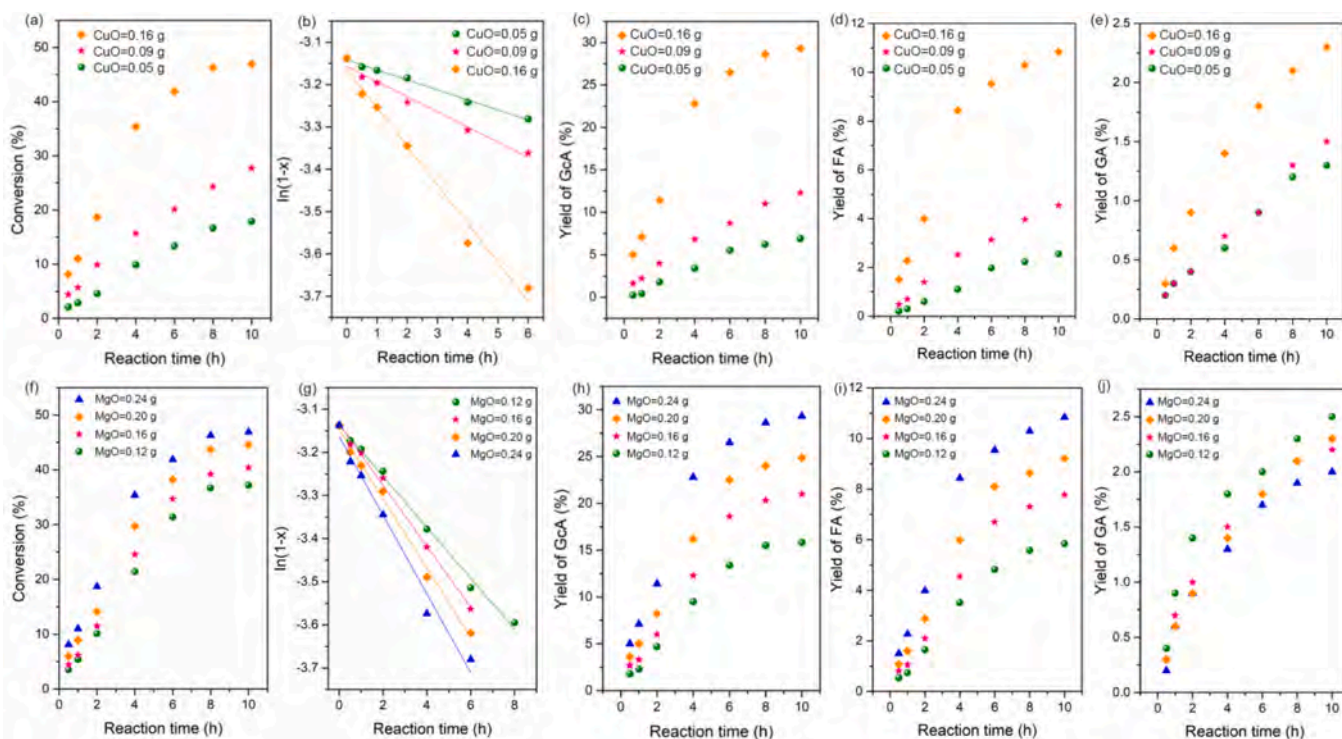


Fig. 5. Kinetic curves for the conversion of glycerol in different catalytic systems. (a) and (f): the rate of glycerol conversion with reaction time; (b) and (g): natural logarithm of the remained percentage of glycerol with reaction time, and  $x$  represented the conversion of reactant; (c) and (h): the time-course of GcA; (d) and (i): the time-course of FA; (e) and (j): the time-course of GA. (a)–(e) were conducted in the presence of MgO with a constant amount (0.24 g, equal to the amount in Cu<sub>1</sub>Mg<sub>4</sub> catalyst) while varying CuO amount; (f)–(j) were conducted in the presence of CuO with a constant amount (0.16 g, equal to the amount in Cu<sub>1</sub>Mg<sub>4</sub> catalyst) while varying MgO amount. Reaction conditions: 2.22 mmol glycerol; temperature 453 K; 1 MPa O<sub>2</sub>; 50 mL H<sub>2</sub>O.

the rate constant showed a milder increment with increasing MgO amount, as well as the yield of GcA (Fig. 5, Table S12). These results further confirmed the main performance of CuO. It was known that the dehydrogenation reaction of glycerol to GLA was a typical oxidation process, in which CuO with oxidation activity might contribute to it. We speculated that the alkalinity of MgO probably facilitated the dehydrogenation of glycerol. The higher conversion of glycerol in the presence of both CuO and NaOH than that with single CuO further confirmed this speculation. To further confirm the activity of CuO species, we replaced the O<sub>2</sub> by N<sub>2</sub> with the same pressure, and obtained 27.4% yield of GcA when Cu<sub>1</sub>Mg<sub>4</sub> was employed as catalyst. The XRD of used catalyst showed obvious peaks corresponding to Cu<sub>2</sub>O (Fig. S10). These results gave strong evidences on the mild oxidation performance of CuO species. However, this yield was much lower than that with O<sub>2</sub> (60.3%), thus proposing that CuO dominantly acted as the catalyst to active O<sub>2</sub> molecule. In addition, formic acid yield was promoted by both increasing of CuO and MgO amount, which proved that C–C cleavage and oxidation collectively contributed to promote the formation of formic acid.

The relay catalysis of Cu, Mg species in catalyst for glycerol conversion enabled the selective formation of GcA with high yield. CuO first catalyzed the dehydrogenation reaction of glycerol to GLA, and MgO followed to promote the cleavage of C2-C3 bond in GLA to yield glycolaldehyde, which greatly inhibited the further oxidation of GLA to glyceric acid. The resultant glycolaldehyde was further oxidized to GcA via the catalysis of CuO species. This significantly drove the reaction towards C2-C3 cleavage in turn. Consequently, the generation of lactic acid byproduct was also obviously inhibited, although single MgO gave lactic acid as the main product from GLA.

We also investigated the recyclability of the catalyst. Before the next run, the recovered catalyst by filtration was calcined at 400 °C for 4 h to remove the impurities deposited on the surface of the catalyst. As shown in Fig. S11, just a slight decrease of GcA yield was observed after each recycle, which was possibly due to the reduction of CuO to some extent as observed by XPS analysis (Fig. S12), giving a 56.5% yield in the fourth run. XRD patterns (Fig. S13) of the spent catalyst showed similar peaks to the fresh one. The ICP-AES analysis showed a small leaching of Mg, possibly due to the reaction with the GcA generated, but negligible Cu loss was detected in the spent catalyst (Table S14). The successive reaction via replacing the spent catalyst after 4 h by the fresh one to convert the residue glycerol could lead to further increment of GcA yield (up to 71.8%, in Fig. 2b). We finally investigated the separation and purification of GcA. The liquid mixture obtained was extracted in water-ether bi-phase system, in which formic acid as the main byproduct could be extracted into ether phase due to its good-solubility, while most of GcA was remained in aqueous phase because of the limited solubility of GcA in ether. The remained GcA could be salted out from THF (tetrahydrofuran) phase after the extraction using THF/NaCl two-phase system. [49] The detailed procedures were shown in Note S1 and scheme S1. The recovery efficiency of GcA was 86.4%. H<sup>1</sup>NMR (Fig. S14) and C<sup>13</sup>NMR (Fig. S15) analyses confirmed the high purity of separated GcA.

### 3. Conclusion

In summary, the developed Cu<sub>1</sub>Mg<sub>4</sub> catalyst exhibited outstanding activity for the selective conversion of the oversupplied glycerol towards GcA with high yield, eliminating the addition of extra inorganic base with high concentration in the conventional method. Cu, Mg species in catalyst exhibited not only a pronounced synergetic effect, but also the relay catalytic effect, which cooperatively contributed to the selective production of GcA from glycerol. Wherein, Cu species was mainly responsible for GLA formation from glycerol via dehydrogenation, and the oxidation of glycolaldehyde to GcA. Mg species dominantly contributed to the cleavage of C2-C3 bond in GLA to generate glycolaldehyde. This work might give some clues to open new potential application towards the targeted product production from glycerol,

affording profitable possibilities for sustainable biodiesel.

### Author contributions

S. X., Y. X., W. Z., S. L. performed all the experiments; S. X. and J. L. analyzed the experimental data. S. X. conducted the theoretical computations and analyzed the data. J. L. reviewed and co-wrote the manuscript. C. H. designed the study, analyzed all the experimental results, and reviewed and co-wrote the paper.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2021.132555>.

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