Supporting Information

Cleaner One-Pot Transformation of Glycerol to Acrylic Acid and 1,2-Propanediol over Cu_2O/Montmorillonite Bifunctional Catalysts without External Oxygen and Hydrogen

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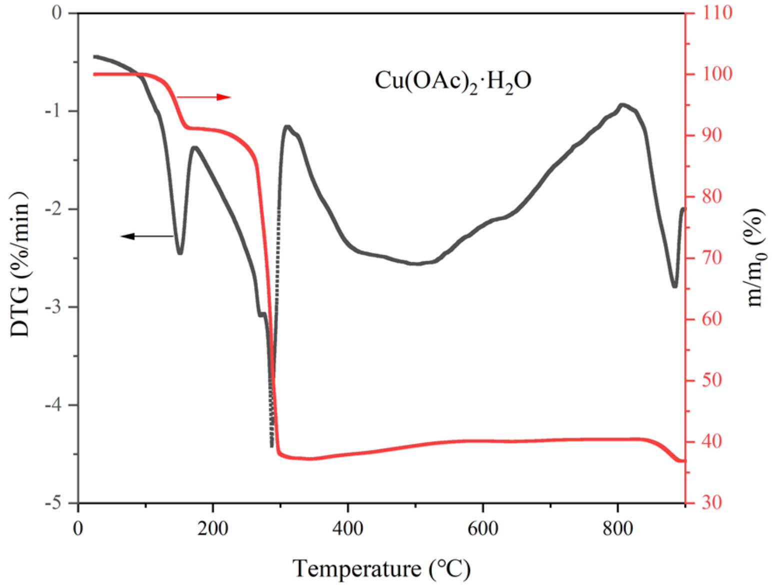

Fig. S1 Thermogravimetric analysis of Cu(OAc)$_2$·H$_2$O.

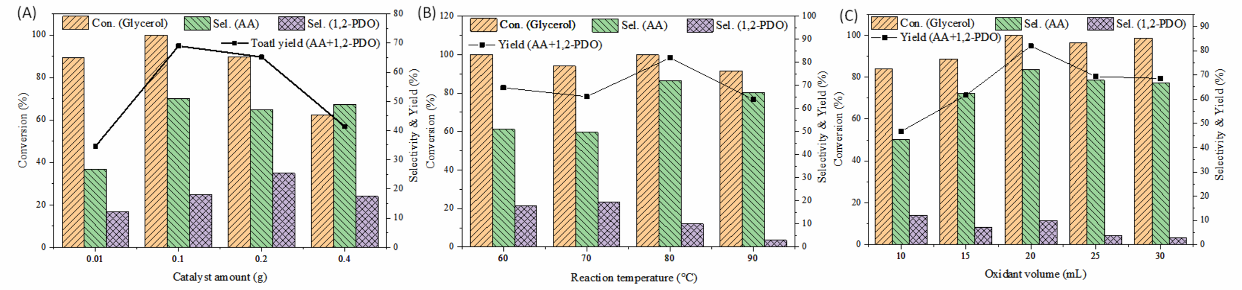

Fig. S2 Catalytic performance of Cu_2O/MMT-H-150 catalyst. (A) Oxydehydration and hydrogenolysis of glycerol over different amounts of catalyst. Reaction conditions: glycerol: 0.67 g, DMF: 10 mL, H_2O_2: 20 mL, reaction time: 3 h, reaction temperature: 60 °C. (B) Temperature dependence of glycerol conversion. Reaction conditions: glycerol: 0.67 g, DMF: 10 mL, H_2O_2: 20 mL, reaction time: 3 h, catalyst amount: 0.1 g. (C) The influence of oxidant volume on glycerol conversion. Reaction conditions: catalyst amount 0.1 g; reaction temperature: 80 °C; glycerol amount: 0.67 g; reaction time: 3 h; DMF: 10 mL. (Agent abbreviation: MMT: montmorillonite, AA: acrylic acid, 1,2-PDO: 1,2-propanediol)

In the experiment, the decomposition of H_2O_2 over the Cu_2O/MMT-H catalysts was observed, which would affect the conversion of glycerol. Therefore, the amount of Cu_2O/MMT-H-150 catalyst was worthy to be studied for investigating the effects of this parameter on oxydehydration and hydrogenolysis of glycerol, and the results were shown in Fig. S2 (A). The conversion of glycerol increased upon a decrease in the amount of Cu_2O/MMT-H-150 catalyst from 0.4 g to 0.1 g, because excess catalysts would catalyze the decomposed of H_2O_2 [1], which can lead to an insufficient amount of oxidant. In the case of continuing to decrease the amount of catalyst to 0.01 g, the selectivity of AA and 1,2-PDO decreased to 27 % and 12 %, especially for the total yield for AA and 1,2-PDO, it decreased to 35 % from 69 % on the case of 0.1 g Cu_2O/MMT-H-150 catalyst, which indicated the importance of catalyst amount. 100 % conversion of glycerol and 69 % yield for AA and 1,2-PDO were obtained using 0.1 g Cu_2O/MMT-H-150 catalyst. Hence, the optimal glycerol conversion of 100 % with AA selectivity of 51 % and 1,2-PDO selectivity of 18 % was obtained when the amount of the catalyst was 0.1 g.

The oxydehydration and hydrogenolysis of glycerol were made up of dehydration-oxidation steps and dehydration-hydrogenation steps, respectively [2, 3]. The dehydration of glycerol is an endothermic process, the oxidation and hydrogenation of dehydration products are exothermic processes [4, 5]. Hence, the high temperature contributed to the dehydration of glycerol, nevertheless, the oxidation and hydrogenation processes proceed effectively at a lower temperature. Besides, the optimal temperatures for these steps are different [6, 7]. Thereby, it is meaningful to trace the distributions of products over the Cu_2O/MMT-H-150 catalyst at different reaction temperatures. The catalytic results were shown in Fig. S2 (B). In all tests, the conversion of glycerol was higher than 90 %. Specifically, the conversions of glycerol at 60 °C, 70 °C, 80 °C, 90 °C were 100 %, 94 %, 100 % and 92 %, respectively. On this basis, it is worth comparing the selectivity of target products because the reaction was consecutive. Increasing reaction temperature from 60 °C to 80 °C, the selectivity to AA increased from 51 % to 72 %. A further increase in temperature to 90 °C led to a decrease in the selectivity of AA to 67 %, because H_2O_2 could be decomposed at high temperatures [8]. Hence, the highest selectivity to AA was 72 % when the reaction temperature was 80 °C, and the total yield of AA and 1,2-PDO was 82 %.

The effect of oxidant dosage was studied and the corresponding results were shown in Fig. S2 (C). When increasing the volume of oxidant from 10 to 20 mL, the conversion of glycerol gradually increased, reaching 100 % with 72 % selectivity to AA from 84 % with 44 % selectivity to AA. And the selectivity of 1,2-PDO was not significantly different, the range of change was within 2 %. With a further increase in the volume of oxidant to 30 mL, the selectivity of AA and 1,2-PDO decreased to 67 % and 3 %, respectively. This may be due to excessive oxidation of the product. Hence, the selectivity of target products was closely related to the amount of oxidant. Insufficient oxidant could result in an uncompleted reaction, while excessive H_2O_2 may further oxidize the AA and 1,2-PDO to total oxidation products, such as CO and CO_2, etc., reducing the selectivity of target products. The optimal conversion of glycerol and total yield was 100% and 82 % using 20 mL H_2O_2, respectively.

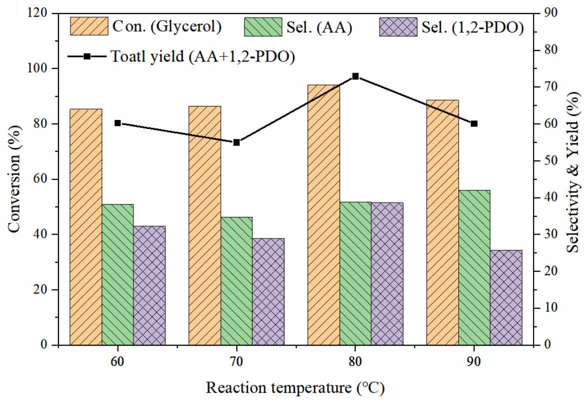

Fig. S3 The effect of temperature on glycerol conversion for 30 min. Reaction conditions: glycerol: 0.67 g, DMF: 10 mL, H_2O_2: 20 mL, catalyst amount: 0.1 g. (Agent abbreviation: MMT: montmorillonite, AA: acrylic acid, 1,2-PDO: 1,2-propanediol)

As shown the Fig. S2 (B), full conversion of glycerol at all tested temperatures was obtained. Hence, we repeated the experiments at reaction time of 30 min in order to reveal the dependence of this reaction on the reaction temperature, and the results were shown in Fig. S3. The conversion of glycerol, the selectivity of AA, and the total yield of AA and 1,2-PDO decreased compared to that of reaction time of 3 h, which was consistent with the effect of reaction time (Fig. 6). The increased selectivity to 1,2-PDO and decreased selectivity to AA indicated that 1,2-PDO could be an intermediate for the conversion of glycerol to AA. Although the significant difference was not obtained at different temperatures, similar trends between the reaction time of 30 min and 3 h were observed, which indicated the reproducibility of the experiment.

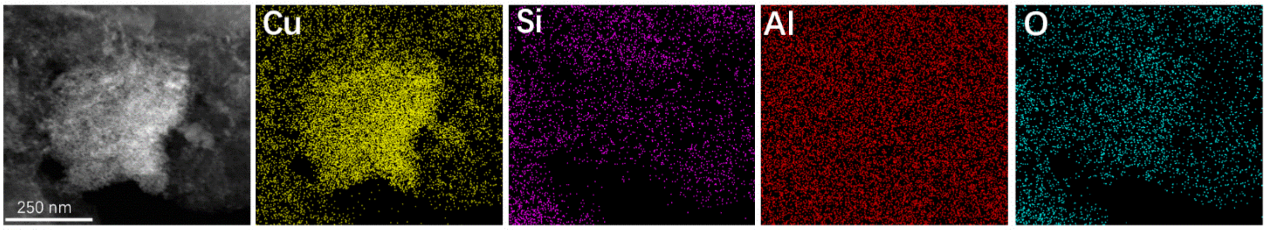

Fig. S4 The EDS-mapping of Cu_2O/MMT-H-150 catalysts. (Agent abbreviation: MMT: montmorillonite)

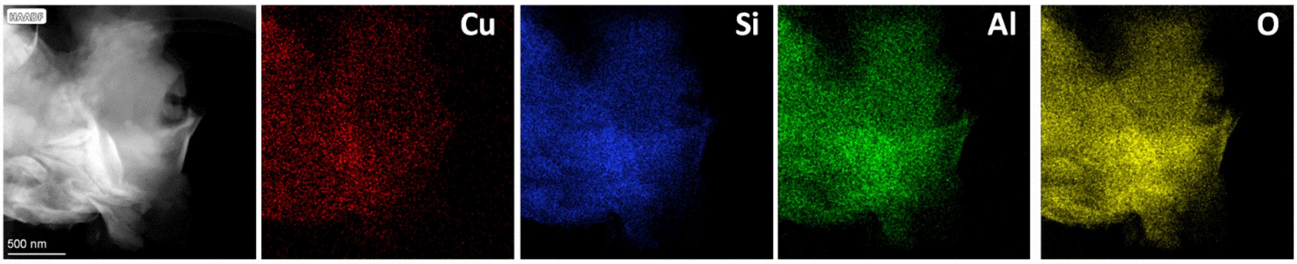

Fig. S5 The EDS-mapping of Cu_2O/MMT-H-100 catalysts. (Agent abbreviation: MMT: montmorillonite)

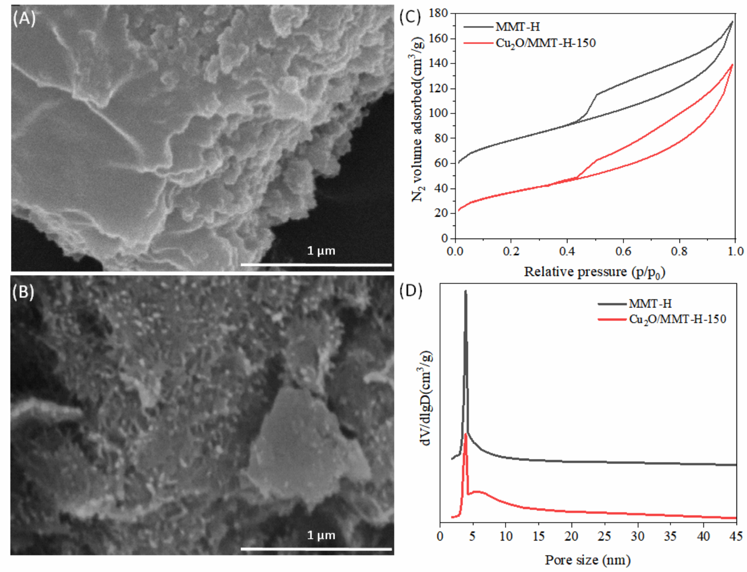

Fig. S6 The structure characterizations of MMT-H and Cu_2O/MMT-H-150. SEM micrographs for MMT-H (A) and Cu_2O/MMT-H-150 (B). N_2 adsorption-desorption isotherms (C) and corresponding BJH pore size distributions (D) of MMT-H and Cu_2O/MMT-H-150. (Agent abbreviation: MMT: montmorillonite)

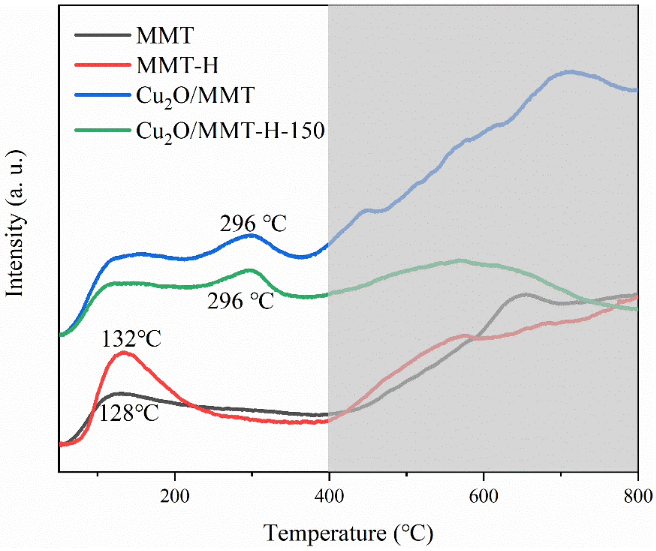

Fig. S7 NH_3-TPD profiles of MMT, MMT-H, Cu_2O/MMT, and Cu_2O/MMT-H-150 catalysts. (Agent abbreviation: MMT: montmorillonite)

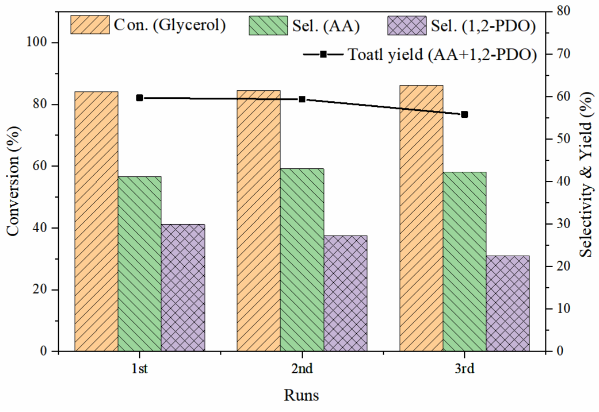

Fig. S8 Recycling test of the Cu_2O/MMT-H-150 catalyst for the conversion of glycerol to AA and 1,2-PDO. The solid catalyst was recovered by filtration, wash and dried after each run. Reaction conditions: reaction temperature: 80 °C; glycerol amount: 0.67 g; reaction time: 30 min; H_2O_2: 20 mL, DMF: 10 mL. (Agent abbreviation: MMT: montmorillonite, AA: acrylic acid, 1,2-PDO: 1,2-propanediol)

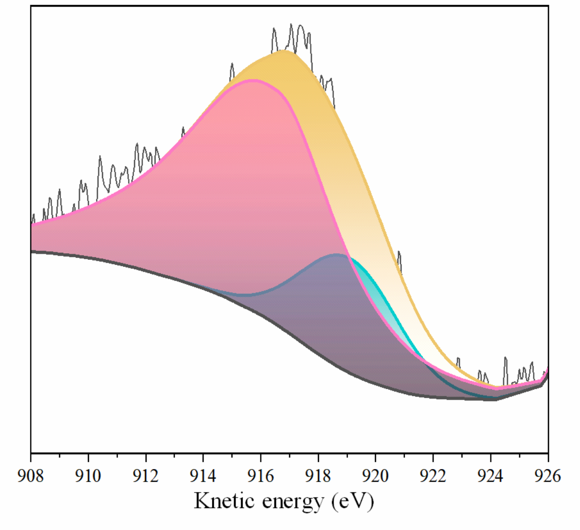

Fig. S9 The LMM spectrum of three reused Cu_2O/MMT-H-150 catalysts. (Agent abbreviation: MMT: montmorillonite)

Table S1 The chemical composition of MMT-H and Cu_2O/MMT-H prepared at 100 °C, 120 °C, 150 °C, 180 °C.

Samples	Composition (wt. %)				
	Cu_2O	SiO_2	Al_2O_3	MgO	Fe_2O_3
Cu_2O/MMT-H-100	9.99	72.60	11.87	2.03	1.89
Cu_2O/MMT-H-120	11.29	71.97	11.45	1.97	1.90
Cu_2O/MMT-H-150	11.28	71.29	12.03	2.12	1.94
Cu_2O/MMT-H-180	9.57	71.94	12.83	2.29	1.94
MMT-H	0.00	80.49	13.27	2.37	1.94

Table S2 Catalyst specific surface area and pore structure.

Sample	S_{BET}(m^2/g)	Pore volume (cm^3/g)	BJH pore size (nm)
MMT-H	171	0.20	3.9
Cu_2O/MMT-H-150	130	0.20	3.9

Note and References

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