

Electronic Supplementary Material

Reconstruction of Cu-ZnO catalyst by organic acid and deactivation mechanism in liquid-phase hydrogenation of dimethyl succinate to 1,4-butanediol

Fan Sun, Huijiang Huang, Wei Liu, Lu Wang, Yan Xu (✉), Yujun Zhao (✉)

Key Laboratory for Green Chemical Technology of Ministry of Education, Collaborative Innovation Center of Chemical Science and Engineering, School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, China

E-mails: xuyan040506@tju.edu.cn (Xu Y); yujunzhao@tju.edu.cn (Zhao Y)

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1 Catalyst Preparation

2 **Preparation of Cu-ZnO-F, Cu₁Zn₉O_x, Cu₉Zn₁O_x and ZnO:** The catalysts were prepared
3 via a co-precipitation method. In a typical procedure, 1 M (mol/L) Na₂CO₃ solution and 1
4 M (mol/L) mixed solution of copper and zinc nitrates were added dropwise simultaneously
5 into a flask with 100 ml deionized water under vigorous stirring at 70 °C and a constant pH
6 of 7 (the pH was 8 for the preparation of ZnO). The precipitates obtained were then stirred
7 gently at the same temperature for 1 h aging. The precipitates were filtered, washed with
8 deionized water several times and dried at 90 °C overnight. The dried precipitates were
9 calcined at 417 °C for 2 h. The resulted powder was granulated into 20-40 mesh pellet
10 before catalytic evaluation.

11 The catalysts with atomic Cu/Zn ratios of 1:1, 1:9 and 9:1 were denoted as Cu-ZnO-F,
12 Cu₁Zn₉, and Cu₉Zn₁, separately.

13 **Preparation of Cu-ZnO-P:** The catalyst was prepared via an organic acid reconstruction
14 method. In a typical procedure, 1 g (20-40 mesh) unreduced Cu-ZnO-F and 5 g (40-60 mesh)
15 silica dioxide were packed in a stainless-steel tubular reactor. The Cu-ZnO-F was reduced
16 in situ at 250 °C for 4 h in pure hydrogen atmosphere (80ml/min). Then, the organic acid
17 solution (10wt.% mono-methyl succinate in 1,4-dioxane) was injected into the reactor
18 through a high-pressure pump. The organic acid reconstruction was performed at 200 °C,
19 and the system pressure was kept at 8MPa in pure hydrogen atmosphere. The organic acid
20 reconstruction was performed for 4 h with the weight hourly space velocity (WHSV) of 0.5
21 $\text{g}_{\text{mono-methyl succinate}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$. After the reactor cooled down to room temperature, the catalyst
22 was taken out of the tubular reactor. The catalyst obtained was denoted as Cu-ZnO-P.

23 Catalyst Characterization

24 The specific surface area, pore volume and pore size data of the catalyst were collected on a
25 Micromeritics Tristar II 3000 Analyzer instrument. The samples were outgassed at 100 °C
26 for 6 h before the measurement.

1 X-ray diffraction (XRD) analysis of the samples were performed on a Smartlab with a Cu
2 radiate at 60 kV and 220 mA. All the samples were scanned from $2\theta=10-80^\circ$ at a rate of 8°
3 /min.

4 The specific area of Cu was estimated with the equation^[1]:

$$5 \quad S_{cu} = (6000 \cdot Cu \text{ loading}) / (8.96 \cdot d_{cu})$$

6 The actual qualitative ratio of Cu/Zn in the catalysts was measured by inductively coupled
7 plasma optical emission spectrometry (ICP-OES, Thermo Fisher iCAP PRO).

8 Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) images were
9 collected with a JEM-F200 field emission TEM.

10 The surface morphologies of samples were obtained on a Regulus 8100 field emission
11 scanning electron microscopy (SEM). All the samples were sprayed with gold for 90 s
12 before characterization.

13 Temperature-programmed reduction (TPR) was performed on a Micromeritics Autochem II
14 2920 instrument. 50 mg sample was loaded into the instrument for analysis. The catalyst
15 loaded was dried in an argon stream at 200 °C for 1 h and then heated to 700 °C in 10 %
16 H₂-Ar at a ramp rate of 10 °C/min. The H₂ consumed was monitored with a thermal
17 conductivity detector.

18 The basicity of the samples was measured by CO₂ temperature programmed desorption
19 (CO₂-TPD) performed on a Micromeritics Autochem II 2920 instrument. About 50 mg
20 sample was loaded into the instrument for analysis. The catalyst loaded was reduced at
21 250 °C for 4 h, and then pretreated at 250 °C with argon followed by exposure to 10 %
22 CO₂-He for 15 min at 50 °C. The system was then purged with He to remove the CO₂
23 physically adsorbed on the catalyst. The TPD was performed in a He stream at a ramp rate
24 of 10 °C/min up to 700 °C. The desorption of CO₂ was monitored with a thermal
25 conductivity detector.

26 X-ray photoelectron spectroscopy (XPS) profile and Auger electron spectroscopy (XAES)
27 were obtained on a Thermo Fisher Scientific ESCALAB Xi⁺ instrument with an Al K α
28 X-ray radiate. The binding energies were corrected by the C 1s peak at 284.8 eV. The ratio

1 of surface Cu^+/Cu^0 was obtained by deconvoluting the XAES spectra. The catalysts were
2 protected by Ar in glovebox after reduction in pure H_2 or organic acid processing, and then
3 the catalysts were transferred into sample tubes in the glovebox and then transferred into
4 the XPS analysis chamber.

5 **Catalytic Performance**

6 **Liquid phase hydrogenation of dimethyl succinate:** 1 g unreduced Cu-ZnO-F (20-40
7 mesh) was loaded into a stainless-steel tubular reactor and reduced in situ at 250°C for 4 h
8 in pure hydrogen atmosphere (80ml/min). The reactant (10wt.% dimethyl succinate in
9 1,4-dioxane) was injected into the reactor through a high-pressure pump. The reaction was
10 performed at 200°C , the system pressure was kept at 8MPa in pure hydrogen atmosphere
11 and the atomic ratio of H_2 /dimethyl succinate was fixed at 50, and the weight hourly space
12 velocity (WHSV) was $0.5 \text{ g}_{\text{dimethyl succinate}} \text{ g}_{\text{cat}}^{-1} \text{ h}^{-1}$. The liquid product was collected in a
13 condenser for further analysis. For the Cu-ZnO-P, the in-situ reduction was performed at
14 200°C for 2 h, then, its catalytic performances were evaluated at the same conditions as
15 above Cu-ZnO-F catalyst.

16 **Transesterification of dimethyl succinate and 1,4-butanediol:** The transesterification
17 was investigated in a stainless-steel tubular reactor and a 100 ml batch reactor. For the
18 transesterification investigated in the tubular reactor, the reactant injected was a 1,4-dioxane
19 solution containing 5wt.% dimethyl succinate and 5wt.% 1,4-butanediol, and the other
20 reaction conditions are the same with the liquid phase hydrogenation of dimethyl succinate.
21 For the transesterification investigated in the batch reactor, 0.5 g reduced catalyst and 30 ml
22 reactant (5wt.% dimethyl succinate and 5wt.% 1,4-butanediol in 1,4-dioxane) were loaded
23 into the batch reactor, then the reactor was purged with nitrogen to remove the air. The
24 initial system pressure was 0.1 MPa at room temperature. The reactor was then heated to
25 120°C with an 800 rpm stirring. After reaction, the liquid product was collected for further
26 analysis.

27

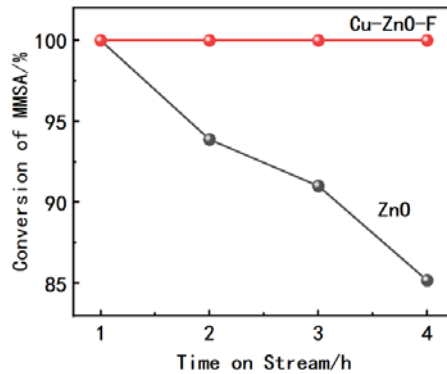
1 **Liquid sample analysis:** A gas chromatography (Beifen-Ruili) equipped with an Agilent
 2 DB-624 column (30m×0.53mm×3μm) was used to analyze the low-boil substances
 3 (boiling point < 240 °C) in the liquid sample. The polyester in the liquid sample was
 4 analyzed by Matrix Assisted Laser Desorption Ionization Time of Flight Mass
 5 Spectrometry (MALDI-TOFMS, Autoflex tof/tofIII). The conversion of mono-methyl
 6 succinate (MMSA) and DMSA and selectivity of product were defined as the following
 7 equations:

$$8 \text{ Conversion (MMSA)} = \frac{(\text{moles of MMSA})_{in} - (\text{moles of MMSA})_{out}}{(\text{moles of MMSA})_{in}} \times 100\% \quad (1)$$

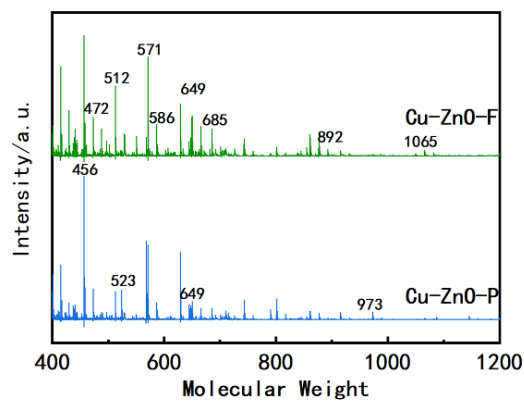
$$9 \text{ Conversion (DMSA)} = \frac{(\text{moles of DMSA})_{in} - (\text{moles of DMSA})_{out}}{(\text{moles of DMSA})_{in}} \times 100\% \quad (2)$$

$$10 \text{ Selectivity (i)} = \frac{\text{moles of product } i}{(\text{moles of DMSA})_{in} - (\text{moles of DMSA})_{out}} \times 100\% \quad (3)$$

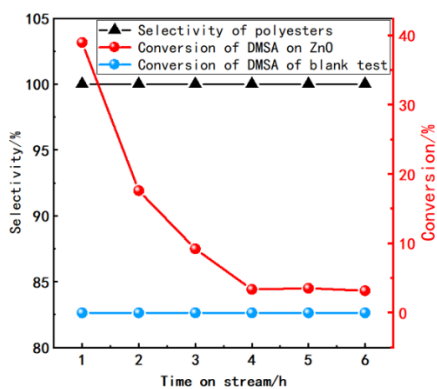
$$11 \text{ Selectivity (others)} = [1 - \sum \text{Selectivity}(i)] \times 100\% \quad (4)$$



13
 14 **Figure S1.** Esterification of MMSA on ZnO and Cu-ZnO-F. Reaction conditions: T = 200 °C, P = 8
 15 MPa, H₂/MMSA=200, WHSV = 0.5 h⁻¹. Reactant: 10 wt.% MMSA in 1,4-dioxane.



1
 2 **Figure S2.** MALDI-TOFMS analysis ^a of the product (after 2 h on stream) of the liquid-phase
 3 hydrogenation.
 4 a: The number near the peak presents the molecular weight of the compound detected, and the intensity of the peaks represents the
 5 relative content.



6
 7 **Figure S3.** Transesterification between DMSA and BDO in a trickle -bed reactor. Reaction
 8 conditions: T = 200 °C, P = 8 MPa, H₂/DMSA = 50, WHSV = 0.5 h⁻¹. Reactant: 5wt.% DMSA-5wt.%
 9 BDO in 1,4-dioxane.

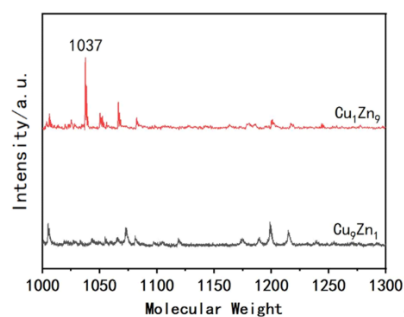
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2 **Table S1.** Transesterification between DMSA and BDO in a batch reactor^[a].

Catalyst	$X_{\text{DMSA}}/\%$	Composition of the product ^[b] /%				Selectivity of polyesters ^[c] /%
		THF	GBL	BDO	DMSA	
Cu_7Zn_9	9.34	0.35	0	57.61	42.04	100
Cu_9Zn_1	5.23	0.28	2.33	64.13	33.26	0

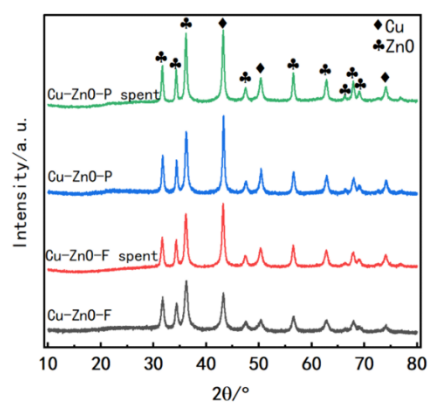
3 [a] Reaction condition: $T = 120\text{ }^\circ\text{C}$, $P = 0.1\text{ MPa}$, in a N_2 atmosphere. Reactant: 30 g of 5 wt.% DMSA-5 wt.% BDO in
 4 1,4-dioxane, 0.5g catalysts. Reaction time: 6 h. [b] Obtained by gas chromatography, and the polyesters were not
 5 counted. [c] Existence of polyesters was proved by MALDI-TOFMS (Figure S4).
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8 **Figure S4.** MALDI-TOFMS analysis of the product of the transesterification in a batch reactor.

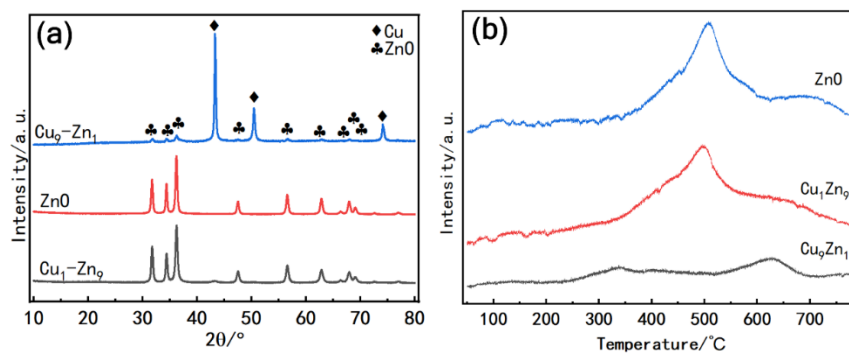
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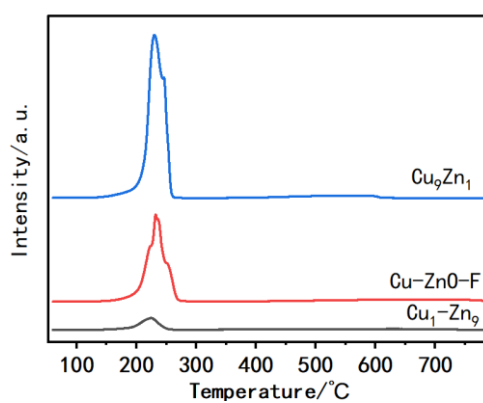
11 **Figure S5.** XRD patterns of the catalysts.

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1

2 **Figure S6.** XRD patterns (a) and CO_2 -TPD (b) of the catalysts



3

4 **Figure S7.** H_2 -TPR of the catalysts

5 **References**

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