

1 Atom-economical synthesis of γ -valerolactone with self- 2 supplied hydrogen from methanol

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4 Zheng Li, Xing Tang, Yetao Jiang, Yanjun Wang, Miao Zuo, Wei Chen, Xianhai Zeng*, Yong
5 Sun and Lu Lin*

6 College of Energy, Xiamen University, Xiamen 361102, China

7 Email: xianhai.zeng@xmu.edu.cn, lulin@xmu.edu.cn

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9 Supporting information

10 Experimental Section

11 Materials

12 All chemicals were analytical reagents and purchased from Sinopharm Chemical
13 Reagent Co., Ltd., China.

14 Cu-Cr catalyst was prepared by impregnation method. CuSO_4 (99%) and $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
15 (99%) with a mole ratio of 2:1 were mixed in water and stirred at room temperature.
16 Then an equivalent amount of ammonium hydroxide (10 wt%) was slowly added to
17 the solvent. The system was then aged at 45 °C for 4 h followed by filtrating and a
18 brown solid precursor was obtained. The precursor was vacuum dried at 70 °C
19 overnight, calcined at 350 °C for 4 h and then stored in a desiccator. Chromium (VI)
20 in Cu-Cr precursor was totally reduced to Chromium (III) during calcination.

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22 Reaction

23 In a typical experiment, 17.5 g ML (99%) and 1.25 g MeOH was added to a 100 mL
24 stainless steel reactor (Parr, USA) accompanied by 0.35 g catalyst. The weight of the
25 reactor with reactant was recorded before reaction. The reactor was then sealed by N_2
26 and heated to 250 °C within 25 min. The reaction time was started recorded as soon as
27 the system reached working temperature. The stirring rate was 500 rpm.

28 After reaction, the system was quickly cooled down to room temperature and the
29 gaseous product was collected by an aluminium foil bag for GC analysis. Then the
30 reactor was weighted again to calculate the mass change during the reaction. The
31 liquid product was separated with used catalyst by filtration and stored for later
32 analysis. The catalyst was washed by ethanol and stored in a vacuum drying oven for
33 subsequent characterization.

34 For the recycle experiments, the used catalysts was separated from the liquid product,
35 washed by ethanol and then stored in a vacuum drying oven at room temperature. The
36 recycled catalyst was directly used without any calcination or hydrogenation process.

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38 Characterization

39 The component of gaseous product was analyzed with a Shimadzu GC-2010
40 instrument equipped with an Agilent CP-7429 column and a TCD.

41 The liquid product was diluted with ethanol and quantitatively analyzed by a
42 Thermofisher Trace 1300 & ISQ LT GC-MS instrument with an TR-5MS column
43 (15.0 m × 250 μm × 0.25 μm). The following programmed temperature was used in
44 the analysis: 313 K (2 min) – 10 K/min – 553 K (2 min). The carrier gas was He with
45 a flow rate of 1.2 mL min⁻¹ and the split ratio was 1:50. The mass spectra were
46 obtained by electron impact ionization (EI), at an electron energy of 70 eV and with a
47 25 μA emission current.

48 External standard method was applied to measure the mass of GVL and unreacted ML
49 in the product. C_{ML} and S_{GVL} were calculated as the following equations.

$$50 \quad C_{ML} (\%) = \left(1 - \frac{m_{ML}}{n_{ML_initial}} \right) \times 100\%$$

$$51 \quad S_{GVL} (\%) = \left(\frac{m_{GVL}}{m_{ML_initial} - m_{mL}} \right) \times 100\%$$

52 XRD spectra of catalyst was acquired on a Rigaku Ultima IV X-ray diffractometer
53 with Ni-filtered Cu K radiation operated at 40 kV and 30 mA. The data was collected
54 from $2\theta=10^\circ$ to 90° with a scan rate of $10^\circ \text{ min}^{-1}$.

55 SEM-EDX analysis was carried out by a Zeiss Sigma OXFORD X-Max scanning
56 electron microscope with an accelerating voltage of 15 kV.

57 TEM images was acquired on a JEOL 1400 transmission electron microscopy with an
58 accelerating voltage of 100 kV.

59 CHN elemental analysis was performed on a Vario EL III instrument.

60 BET surface area and BJH adsorption curves were measured on a Micromeritics
61 ASAP 2020 physisorption apparatus. The samples (about 500 mg) were degassed at
62 363 K for 4 h in a vacuum before N₂ adsorption.

63 ICP-MS experiment was conducted on a HP/AGILENT 4500 instrument. Considering
64 that only aqueous sample could be tested, the liquid product containing GVL and
65 methanol was filtrated twice by filter membrane (220 nm) and then combusted in a
66 crucible. Then 10 mL 10 wt% HNO₃ was added to the vessel and stirred for 4 h. The
67 solvent was then filtrated twice by filter membrane (220 nm) and diluted to pH=1
68 before testing.

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70 **Supplementary tables and figures**

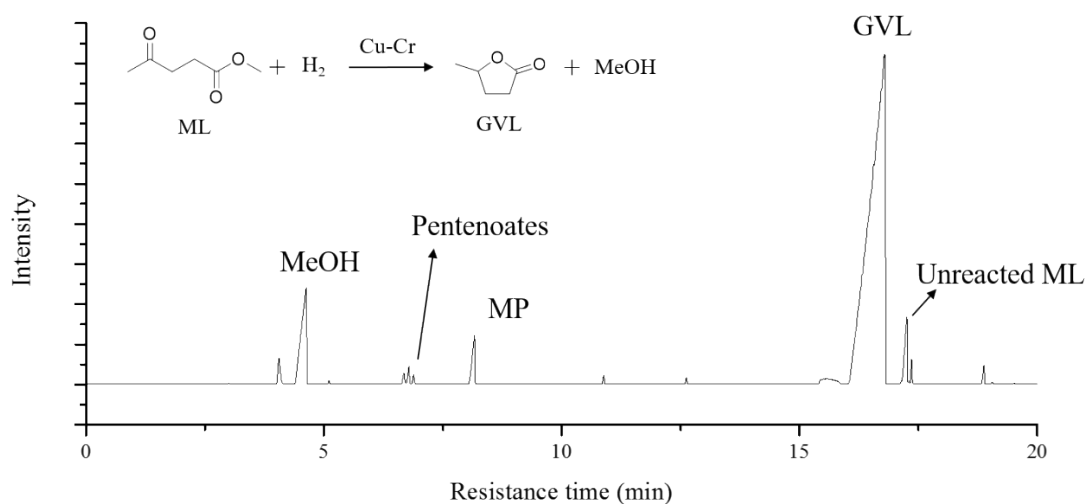
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72 **Table S1.** The equivalent ratio of H-donor and substrate for GVL production in recent reports

Substrate	H-donor	H-donor:substrate Ratio	Catalytic conditions	Ref.
26.4 mmol LA	H ₂	3.3 ^a	Homo, in 40 ml water	1
8.6 mmol LA	H ₂	2.0 ^a	Hetero, in 15 ml water	2
8.8 mmol LA	H ₂	6.1 ^a	Hetero, in 5 ml water	3
43.1 mmol LA	H ₂	6.4 ^a	Hetero, in 95 ml water	4
20.0 mmol LA	H ₂	2.8 ^a	Hetero, solvent-free, 24 h	5
13.7 mmol EL	EtOH ^b	60.3	Hetero, in 38 g EtOH	6, 7
1.0 mmol LA	2-PrOH ^b	65.4	Hetero, in 5 ml 2-PrOH	8
1.0 mmol EL	2-PrOH ^b	26.2	Hetero, in 2 ml 2-PrOH	9
0.34 mmol ML	2-BuOH ^b	24.1	Hetero, in 0.75 ml 2-BuOH	10
200.0 mmol LA	FA ^c	1.0	Homo, in 25 ml water, 12 h	11
18.0 mmol LA	FA ^c	1.0	Hetero, in 40 ml water	12
4.0 mmol ML	MeOH ^c	158.4 ^d	Hetero, in 19.5 g MeOH	13
134.6 mmol ML	MeOH ^c	0.29 ^d	Hetero, solvent-free	This work

73 a: calculated by high pressure gas state equation. b: MPV transfer hydrogenation. c: in-situ hydrogen supplied by
 74 decomposition of H-donor. d: the mole ratio of MeOH:ML.

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77 **Figure S1.** Product distribution of Cu-Cr catalyzed hydrogenation of ML in external H₂ (Table 1, Entry 1) detected
 78 by GC. The amount of MeOH was less than GVL because some MeOH was decomposed during the reaction and,
 79 evaporated during the vacuum filtration process.

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82 **Table S2.** Effect of catalyst on the reaction

Catalyst	C _{ML} (%)	S _{GVL} (%)	Δ _m (g)
Typical	93.5	96.1	2.1

CuO	15.2	25.6	0.5
Cr ₂ O ₃	10.5	0	0.1
Blank	0	-	0.1
Blank ^a	3.2	95.0	-

83 Typical reaction conditions: 17.5 g ML, 1.25 g MeOH, 0.35 g catalyst (2 wt% of ML), 250 °C, N₂ (1 bar), 500 rpm, 4 h. a: 20 g
 84 ML, 4 MPa H₂, no MeOH added.

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86

87 **Table S3.** Composition of gaseous product in a typical reaction

Composition	H ₂	O ₂	N ₂	CH ₄	CO	CO ₂
Content (v/v %)	9.6	-	15.4	1.6	38.9	33.5

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90 **Table S4.** Metal concentration in the product detected by ICP-MS

Entry	Concentration of Cu (µg/cm ³)	Concentration of Cr (µg/cm ³)
Product (Table 1, Entry 7)	1.1	ND

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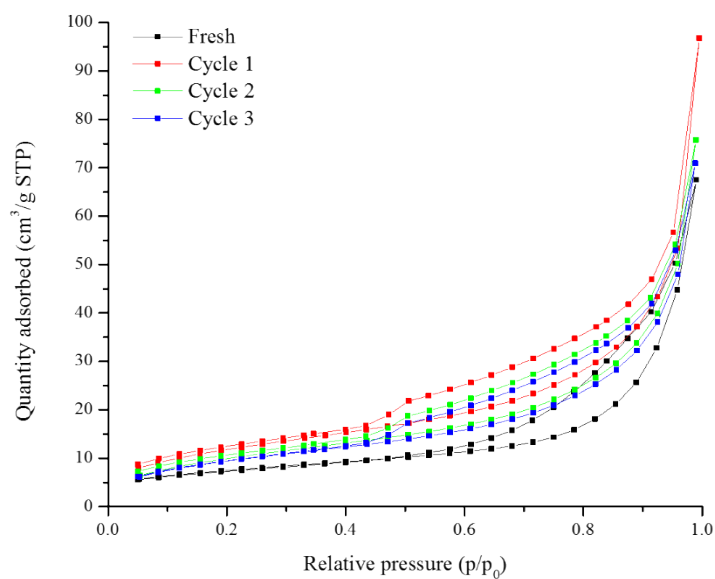
93 **Table S5.** Effect of impurities on the reaction

Conditions	C _{ML} (%)	S _{GVL} (%)	Δ _m ^c (g)
Typical	93.5	96.1	2.1
N ₂ (2 MPa)	34.2	39.4	1.3
Air (0.1 MPa)	93.5	86.1	2.1
O ₂ (0.1 MPa)	15.5	48.7	0.4
Water (0.2 g)	21.0	51.5	0.7

94 Typical reaction conditions: 17.5 g ML, 1.25 g MeOH, 0.35 g catalyst (2 wt% of ML), 250 °C, N₂ (1 bar), 500 rpm, 4 h.

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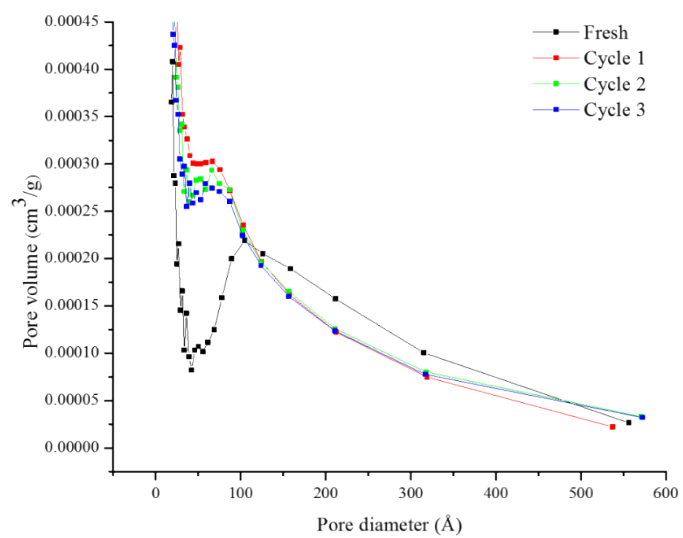


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98 **Figure S2.** Isotherms of fresh and used catalysts

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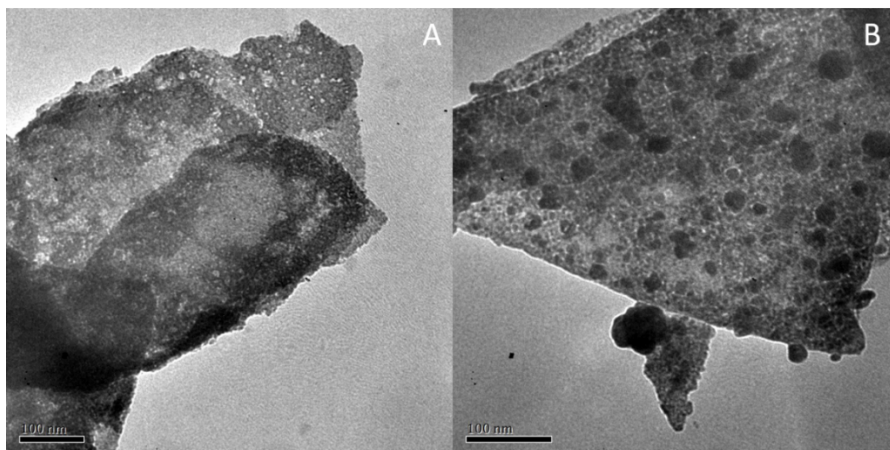


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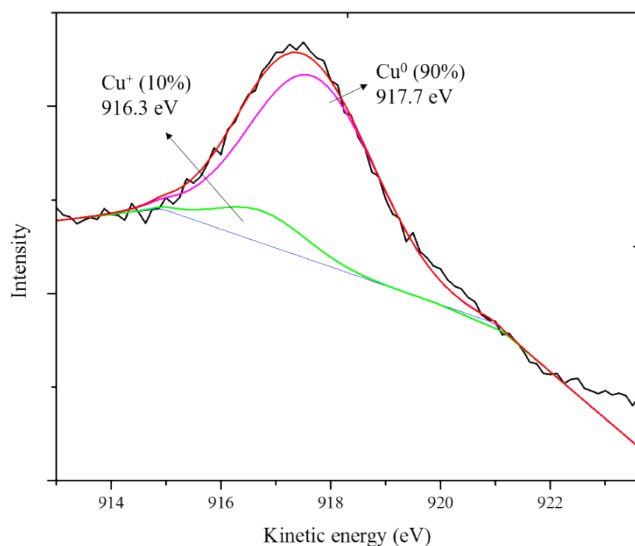
102 **Figure S3.** BJH adsorption profiles of fresh and used catalysts

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 106 **Figure S4.** TEM images of: A) fresh Cu-Cr catalyst; B) in-situ reduced catalyst after 1 cycle.
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 110 **Figure S5.** Cu LMM spectrum of in-situ reduced Cu-Cr catalyst
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