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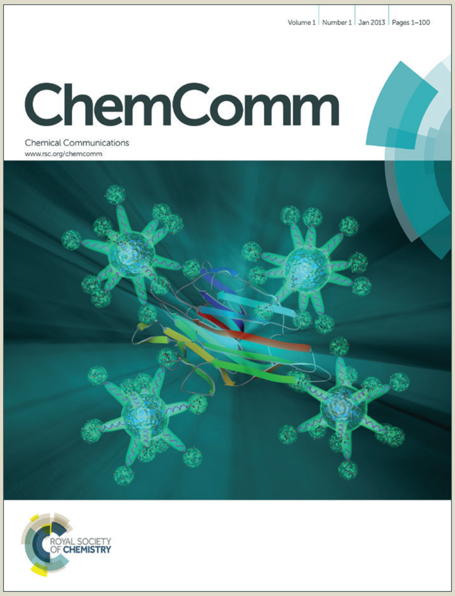

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Atom-economical synthesis of γ-valerolactone with self-supplied hydrogen from methanol

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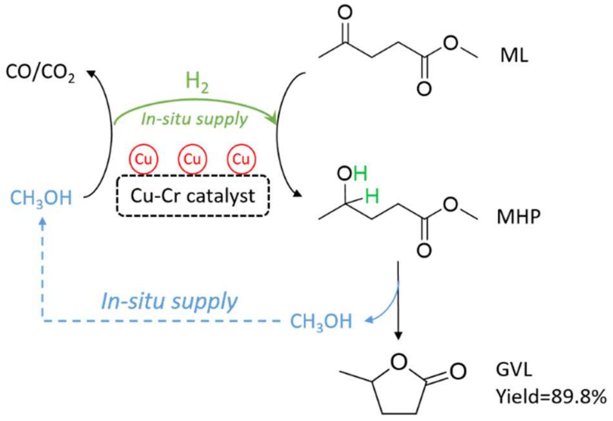
γ-Valerolactone (GVL), a versatile biomass derived platform molecule, was synthesized with a highest yield of 89.8% from methyl levulinate (ML) using self-supplied H_2 coming from the decomposition of MeOH derived partially from ML. Cu-Cr acted as a bi-functional catalyst for both H_2 production from MeOH and carbonyl hydrogenation. An extremely low amount of MeOH (29 mol% relative to ML) was initially necessary to start up the hydrocyclization of ML to GVL and MeOH, which is in turn employed as an in-situ H_2 source for ML hydrogenation, providing an atom-economical pathway for GVL production.

Biomass derived γ-valerolactone (GVL), which can be synthesized from levulinic acid (LA) and levulinate esters (LE), is acknowledged as a potential building block for the production of biofuels, biochemicals and polymeric materials. [1-4] Recently, the conversion of LA and LE to GVL has been carried out with various hydrogen sources. Ru and Ir-based catalysts, especially in mild homogeneous systems, showed high hydrogenation efficiencies in the presence of molecular H_2. [5, 6] Heterogeneous catalysts containing transition metals such as Ru, Pd, Cu, Ni also provided promising GVL production efficiencies in aqueous phase and alcohols under H_2 pressure ranged from 2 to 100 bar or, in vapour phase under ambient pressure. [7-10] Otherwise, multiple efforts were devoted to eliminate the reliance on external H_2. The δ-carbonyl of LA and LE can be reduced to hydroxyl through Meerwein–Ponndorf–Verley (MPV) reaction, which was conducted in H-donor solvents such as ethanol, 2-propanol or 2-butanol. Zr based catalysts showed high catalytic capability for the MPV reaction. [11, 12] Formic acid (FA) has also been adopted as hydrogen source owing to its co-production with LA during the acid promoted decomposition of carbohydrates. Several impressive reports have shown that FA was in-situ decomposed into H_2 and CO_2 over metal catalysts and LA could be hydrogenated to GVL. [13-15] However, to the best of our knowledge, methanol (MeOH) has been rarely reported as an in-situ hydrogen supplier, [16, 17] especially for GVL production. Our previous research demonstrated that Cu nanoparticles prepared from CuO acted as a bi-functional catalyst for both MeOH reforming and ML hydrogenation in MeOH, which is much less corrosive against reactor and catalyst comparing to LA-FA system. [18]

As far as we know, recent approaches for converting LA or LE to GVL are facing an H-donor excessive issue, that is, the mole ratio of H-donor to LA (LE) is generally much higher than equivalent ratio (1:1), leading to an atom-economical issue, as Table S1 summarized. In this article, a Cu-Cr oxide was applied in ML-MeOH system, in which initial amount of MeOH is only relative to 29 mol% of ML, for GVL production with self-supplied H_2 from MeOH decomposition. The initial MeOH could theoretically only provide 58% H_2 required for a complete ML conversion; [19] however, a highest GVL yield of 89.8% was achieved in this study, which leaves no doubt that MeOH generated by the hydrocyclization of ML also acted as an in-situ H_2 source (Scheme 1). As compared to previous reports, one can thus conclude that this is an atom-economical synthesis of GVL from ML, which is feasible for large-scale application.



Scheme 1. In-situ hydrogen supplied conversion of ML to GVL

In the present study, reactions were conducted in a batch reactor. The fresh Cu-Cr oxide catalyst was in-situ reduced at the beginning of the reaction. We found that Cu-Cr showed very high hydrogenation activity in the conversion of ML to GVL in the presence of external H_2 with a catalyst dosage of 1 wt% (Table 1, Entry 1). Given the highly effective activity of Cu based catalyst in MeOH reforming and carbonyl hydrogenation, MeOH was added to the system to eliminate the reliance of external H_2. Unexpectedly, Cu-Cr, as a bi-functional catalyst, showed a significantly higher catalytic activity compared to CuO (Table S2), which provided high GVL yield with a much lower MeOH dosage. During the reaction, MeOH was decomposed on the catalyst and the in-situ generated H_2 was immediately consumed by the reduction of ML to methyl 4-hydroxypentanoate (MHP), which was then cyclized to form GVL, as scheme 1 implied.

Equivalent mass of MeOH and ML as substrates led to a complete ML conversion (C_{ML}), but the GVL selectivity (S_{GVL}) was only 63.6% (Table 1, Entry 2). Considerable amount of GVL-derived molecules such as pentanoates and hydrocarboxylation products were observed, which was in accordance with our previous report. [18] S_{GVL} was significantly increased as MeOH:ML mole ratio reduced (Table 1, Entries 3-7), suggesting that the decreasing MeOH input would inhibit the downstream conversion of GVL to by-products. Interestingly, a C_{ML} of 93.5% and S_{GVL} up to 96.1% were still achieved even through the initial dosage of MeOH was only 1.25 g (29 mol% of ML, Table 1, Entry 7). Meanwhile, a mass loss of reactant (Δm) of 2.1 g was observed after reaction, which was ascribed to the decomposition of MeOH during the reaction. However, further reducing the amount of MeOH to 1.0 g (23 mol% of ML) required a prolonged reaction time for ML conversion (Table 1, Entries 8 and 9). When the dosage of MeOH was decreased to 0.5 g, only 24.5 % C_{ML} was achieved within 4 h (Table 1, Entry 10).

Table 1. In-situ H_2 supplied GVL production from ML

Entry	Mass ratio of MeOH:ML (g/g)	mole ratio of MeOH:ML	$C_M{}^a$ (%)	$S_{GVL}{}^b$ (%)	Δm^c (g)
1	H_2 (4 MPa)/20	-	95.0	97.6	-
2	10/10	4.06	99.6	63.6	2.1
3	5/15	1.35	99.5	74.9	3.0
4	2.5/17.5	0.58	99.2	85.4	3.0
5	2/17.5	0.46	96.2	85.6	2.8
6	1.5/17.5	0.35	92.6	96.4	2.4
7	1.25/17.5	0.29	93.5	96.1	2.1
8	1.0/17.5	0.23	70.9	97.0	1.4
9[d]	1.0/17.5	0.23	91.3	87.0	2.0
10	0.5/17.5	0.12	24.5	77.3	0.7

Reaction conditions: 2 wt% catalyst (relative to ML), 250 °C, N_2 (0.1 MPa), 500 rpm, 4 h. a: percentage conversion of ML. b: selectivity to GVL. c: mass loss of the reactant after reaction. d: 6 h.

Besides the extremely low hydrogen source demand (MeOH), we noticed that Δm was larger than the initial MeOH input (Table1, Entries 4-9). It was verified that MeOH generated during the hydrocyclization process of ML (Figure S1) was subsequently decomposed into H_2 and CO/CO_2 in the presence of Cu-Cr catalyst. As a result, MeOH greater than the initial dosage were consumed. The mass balance of MeOH was analyzed and the result showed that the initial MeOH occupied about 60% of Δm, that is, the in-situ generated MeOH contributed up to over 40% of MeOH consumption (Table 2), suggesting that H-donor utilization is rather high. The gaseous product was also analyzed and N_2, CO and CO_2 were the main components (Table S3), while H_2 only accounted for 9.6% of the gas, implying that the in-situ generated H_2 was effectively consumed. Based on Scheme 1, it could be calculated that about 0.12 mol H_2 was consumed for GVL formation which was supplied by the decomposition of ~0.07 mol MeOH. This result agrees well with Yong's report that 2 mol H_2 would be theoretically generated from the decomposition of 1 mol MeOH in oxygen and water free system. [19]

Table 2. Mass balance of MeOH based on a typical reaction

Supplied MeOH	Initial MeOH (g)	In-situ generated MeOH^a (g)	Total (g)
	1.25	3.87	5.12
Consumed and remained MeOH	Δm^b (g)	Evaporated MeOH from product^c (g)	Total (g)
	2.10	2.56	4.66

a: calculated based on GVL yield. b: the mass change of reactant during reaction was ascribed to decomposed MeOH. c: the product was vacuum evaporated at room temperature and the mass loss was ascribed to the unreacted MeOH.

To study the recycle performance of the catalyst, the catalyst was reused without any regeneration treatment process such as calcination and hydrogenation, and a slight descending of GVL yield was observed in the successive 2 cycles (Table 3). A C_{ML} of 79.4% and a S_{GVL} of 83.6% were still achieved after 6 h in the 3rd run, implying that the in-situ reduced Cu-Cr acted quite stably as a bi-functional catalyst. About 6.3% carbon deposit of the catalyst was detected after 3 cycles (Table 3). ICP-MS result showed that the concentration of Cu in liquid product was 1.1 μg/g (Table S4), probably owing to the infiltration of Cu nano-particles. Oppositely, Cr was not detected in the liquid product, implying that there was no obvious ion leaching occurred. However, the introduction of impurities, such as O_2 and water, was adverse to the system (Table S5). Besides, the reaction was severely inhibited by high N_2 pressure probably due to the suppressed H_2 production.

Table 3. Performance and properties of recycled Cu-Cr catalysts

Cycle	C_{ML} (%)	S_{GVL} (%)	Δ_m (g)	BET surface area (m^2/g)	Carbon deposit (%)
1	93.5	96.1	2.1	44.3 (27.6^a)	5.3
2	84.1	80.1	1.9	38.1	6.1
3[b]	79.4	83.6	1.6	35.8	6.3

Reaction conditions: 17.5 g ML, 1.25 g MeOH, 0.35 g catalyst, 250 °C, N_2 (1 bar), 500 rpm, 4 h. The used catalysts were washed by ethanol and dried in a vacuum oven at room temperature before reutilization. a: fresh catalyst. b: 6 h.

The fresh Cu-Cr catalyst with a surface area of 27.6 m^2/g was in-situ reduced in the first cycle. After reaction, mesoporous structure with a diameter less than 10 nm was observed (Figure S2 and S3), leading to a higher surface area of 44.3 m^2/g. The surface area declined to 38.1 and 35.8 m^2/g in the two following cycles, in keeping with the less distribution of pore structure ranges from 4 to 10 nm (Table 3 and Figure S3). SEM and TEM images revealed that there were Cu nano-particles dispersed on the surface of catalyst after in-situ activation (Figures 1 and S4), which is probably responsible for the increase of surface area of the catalyst after reaction. After 3 successive cycles, sintering of Cu into larger particles was observed, thus resulting in the loss of surface area and catalytic activity. [20]

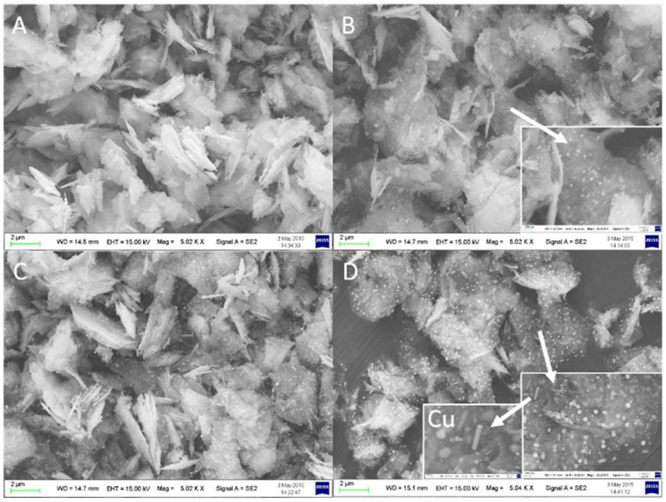


Figure 1. SEM images of: A) fresh Cu-Cr catalyst; B) in-situ reduced Cu-Cr catalyst after 1 cycle; C) used Cu-Cr catalyst after2 cycles; D) used Cu-Cr catalyst after 3 cycles

XRD spectra showed that Cu (II) in the catalyst was reduced to Cu_2O (2θ=36.6 °) and Cu (2θ=43.5, 50.6 and 74.3 °) during the reaction (Figure 2). Besides, no Cu^{2+} was detected for used Cu-Cr catalyst in XPS spectra and the peak at ~932 eV suggested the presence of Cu^0 and Cu^+ species (Figure 3). Cu LMM spectrum showed that 90% of the surface Cu was ascribed to Cu^0 (Figure S5).[20, 21]

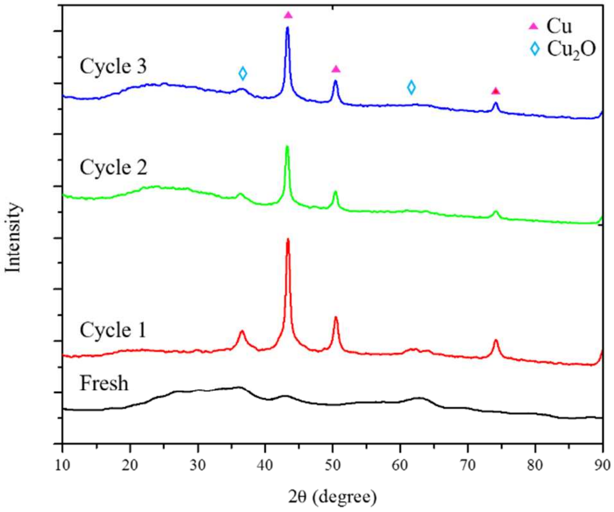


Figure 2. XRD spectra of fresh and used catalysts

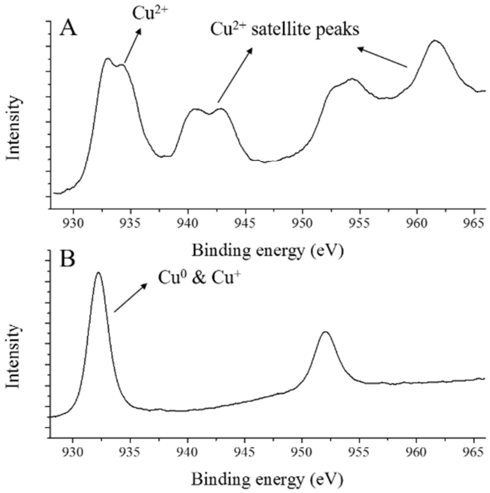


Figure 3. Cu XPS spectra of: (A) fresh catalyst and (B) in-situ reduced catalyst after 1 cycle

To summarize, we reported an atom-economical synthesis of GVL from ML with an extremely low amount of initial MeOH input (29 mol% of ML) as in-situ hydrogen source over a Cu-Cr catalyst. Mass balance analysis of MeOH proved that over 40% of consumed MeOH (for H_2 production) was contributed by the hydrocyclization of ML, which ensured a complete ML conversion and the highest GVL yield of 89.8%. Moreover, the in-situ activated Cu-Cr showed excellent catalytic activity and recyclability as a H_2 production-carbonyl hydrogenation bi-functional catalyst.

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Notes and references

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