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Article

Effective production of γ -valerolactone from biomass-derived methyl levulinate over $\text{CuO}_x\text{-CaCO}_3$ catalyst

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ABSTRACT

The production of γ -valerolactone (GVL) from lignocellulosic biomass has become a focus of research owing to its potential applications in fuels and chemicals. In this study, $(n)\text{CuO}_x\text{-CaCO}_3$ (where n is the molar ratio of Cu to Ca) compounds were prepared for the first time and shown to function as efficient bifunctional catalysts for the conversion of biomass-derived methyl levulinate (ML) into GVL, using methanol as the in-situ hydrogen source. Among the catalysts with varied Cu/Ca molar ratios, $(3/2)\text{CuO}_x\text{-CaCO}_3$ provided the highest GVL yield of 95.6% from ML. The incorporation of CaCO_3 with CuO resulted in the formation of Cu^+ species in a $\text{CuO}_x\text{-CaCO}_3$ catalyst, which greatly facilitated the hydrogenation of ML. Notably, $\text{CuO}_x\text{-CaCO}_3$ also displayed excellent catalytic performance in the methanolysis products of cellulose, even in the presence of humins. Therefore, a facile two-step strategy for the production of GVL from cellulose could be developed over this robust and inexpensive catalyst, through the integration of cellulose methanolysis catalyzed by sulfuric acid, methanol reforming, and ML hydrogenation in methanol medium.

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1. Introduction

There has been a surge in demand for carbon resources for production of transportation fuels, commodity chemicals, and polymeric materials [1]. However, traditional fossil resources are being increasingly exhausted, with associated problems including excessive emissions of greenhouse gases and other environmental pollution. As a renewable carbon source, biomass can be regenerated in a relatively short span of time and

has great potential to partially replace fossil resources [2–7]. For example, γ -valerolactone (GVL) derived from inedible lignocellulose can serve as a flexible building block to manufacture various value-added chemicals and biofuels, including pentenoic acid, butane, 5-nonanone, 1,4-pentanediol, and aromatics [8,9]. Previous work has shown C8–C18 branched/straight-chain hydrocarbons fuels from GVL can be synthesized by sequential condensation and hydrodeoxygenation [10]. In addition, the application of GVL as a novel and

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green solvent in biomass conversion has recently received widespread attention [11–13].

A large number of studies have been devoted to GVL production by the hydrogenation of levulinic acid (LA) and its esters, which can be readily formed by the acid-catalyzed hydrolysis or alcoholysis of biomass-derived carbohydrates [14–16]. Several review articles have provided comprehensive overviews of the hydrogenation of LA and its esters to GVL in terms of the diversity of hydrogen sources, which mainly include molecular H_2 , alcohols, formic acid, and water [17]. For instance, various supported noble metals (Ru, Pt, Ir, and Au) have proved to be effective catalysts for the hydrogenation of LA and its esters to GVL, using external molecular H_2 [18–20]. However, the high costs of noble catalysts set limits on their applications [17,19,21–24]. In this light, inexpensive non-noble catalysts such as Cu, Mo_2C , Ni, Co, and Zr are desirable alternatives [25–30]; nevertheless, relatively harsh reaction conditions are required to obtain GVL yields comparable to those in the case of noble catalysts. Recently, the use of alcohols, such as ethanol and isopropanol, as the solvent and hydrogen source for GVL production is gaining momentum, because the management and use of alcohols are convenient compared with those of H_2 . For example, Meerwein-Ponndorf-Verley (MPV) reduction of levulinate esters to GVL can be achieved over various Zr-based catalysts by using ethanol or isopropanol as the in-situ hydrogen source [16,31].

Methanol (MeOH) is also an appealing hydrogen source that can be catalytically reformed to H_2 and CO_2/CO [32]. For instance, Barta et al. [33,34] reported a one-pot conversion of woody biomass to aromatics and/or liquid fuels in supercritical MeOH in the presence of a Cu-based catalyst. The advantages of employing Methanol (MeOH) as the hydrogen source for the GVL production include the fact that methyl levulinate (ML) can be easily produced by the methanolysis of carbohydrates in MeOH catalyzed by sulfuric acid [35]. Therefore, a facile two-step strategy for GVL production from biomass can be developed in MeOH by the integration of acid-catalyzed methanolysis of biomass to ML and the subsequent reduction of ML to GVL. In this respect, we previously reported that CuO could serve as a bi-functional catalyst for MeOH reforming and ML hydrogenation, giving a nearly complete ML conversion and a GVL selectivity up to 87.6% at 240 °C in 1 h. However, the CuO could be completely reduced to metallic Cu, losing its activity for MeOH reforming. Hence, it is highly desirable to prepare robust catalysts for GVL production using MeOH as the in-situ hydrogen source.

In this work, $(n)CuO_x-CaCO_3$ (where n is the molar ratio of Cu to Ca) compounds were prepared by an oxalate gel-coprecipitation method and were verified as effective and robust catalysts for H_2 production through MeOH reforming and ML hydrocyclization to GVL. Incorporation of the $CaCO_3$ with CuO resulted in the formation of Cu^+ species in the CuO_x-CaCO_3 catalyst, which greatly promoted the hydrogenation of ML to GVL, even in the methanolysis products of cellulose. Hence, a facile two-step strategy for the production of GVL from cellulose could be developed over the effective and robust CuO_x-CaCO_3 catalyst, through the integration of acid-catalyzed

methanolysis of cellulose, MeOH reforming, and ML hydrocyclization in MeOH medium.

2. Experimental

2.1. Chemicals

MeOH, ethanol, oxalic acid, and all metallic nitrates, including $Cu(NO_3)_2 \cdot 3H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, $Mg(NO_3)_2 \cdot 6H_2O$, $Ba(NO_3)_2$, $Ni(NO_3)_2 \cdot 6H_2O$, $Zn(NO_3)_2 \cdot 6H_2O$, and $Al(NO_3)_3 \cdot 9H_2O$, were purchased from Sinopharm Chemical Reagent Co. Ltd. GVL (98%) and ML (99%) were supplied by Aladdin Reagent Co. Ltd. (Shanghai, China) and TCI (Shanghai) Development Co. Ltd. (Shanghai, China), respectively. All the chemicals were analytical reagents and used without further purification.

2.2. Catalyst preparation

CuO_x-CaCO_3 with varied Cu/Ca molar ratios and other Cu-based bimetallic catalysts were prepared by an oxalate gel-coprecipitation method. For preparation of the $(3/2)CuO_x-CaCO_3$, the desired amounts of $Cu(NO_3)_2 \cdot 3H_2O$ and $Ca(NO_3)_2 \cdot 4H_2O$ (Cu and Ca precursors) were dissolved into absolute ethanol (0.1 M of the total nitrates) under vigorous magnetic stirring (1000 rpm) at room temperature. Then, the saturated oxalic acid/ethanol solution (oxalic acid/($Cu^{2+} + Ca^{2+}$) molar ratio = 1.5) was rapidly added into the prepared metal precursor solution. The resultant gel-like precipitates were formed within several seconds. The gel-like precipitates were aged at room temperature for 30 min and separated by centrifugation to give the catalyst precursor, which was dried at 110 °C overnight. The dried gel was ground to pass through 100 mesh and calcined at 500 °C for 5 h in air atmosphere to give the target $(3/2)CuO_x-CaCO_3$ catalyst [36–38]. CuO and $CaCO_3$ were also prepared by the same oxalate gel-coprecipitation method. CaO was obtained by the calcination of $CaCO_3$ at 900 °C for 5 h.

2.3. Catalyst characterization

Chemical compositions of the fresh and spent catalysts and possible elemental leaching in the reaction filtrates were measured using inductively coupled plasma optical emission spectrometry (ICP-OES, Agilent Technologies 7700X) after digestion in concentrated HNO_3 . The X-ray diffraction (XRD) patterns of the catalysts were obtained using a Rigaku Ultima IV diffractometer with a $Cu K\alpha$ radiation source and the following parameters: 40 kV, 30 mA, 2θ from 10° to 80°, at a scanning speed of 10°/min. The specific surface areas of the catalysts were determined by N_2 adsorption-desorption analysis at –196 °C on a Micromeritics ASAP 2020 HD88. Degassing was performed before sorption measurements for all samples. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope with an accelerating voltage of 15 kV. Energy dispersive X-ray spectrometry (EDS) and energy-dispersive X-ray (EDX) element mapping images were obtained using a ZEISS SUPRA 55 SAPPHIRE field emission scan-

ning electron microscope. X-ray photoelectron spectroscopy (XPS) spectra were recorded with a Thermo Scientific ESCALAB 250Xi electron spectrometer under a base pressure $<2 \times 10^{-9}$ mbar. A monochromatic Al K_{α} ($h\nu = 1486.6$ eV) excitation energy source was used. NH_3 temperature-programmed desorption (NH_3 -TPD) and H_2 temperature-programmed reduction (H_2 -TPR) were performed on a Micromeritics AutoChem II 2920, equipped with a thermal conductivity detector (TCD). For NH_3 -TPD, after loading into the quartz tube, a sample (40 mg) was first pretreated at a rate of $20^\circ\text{C}/\text{min}$ up to 550°C in He gas flow for 1 h to remove adsorbed species on its surface. Then, the temperature was reduced to 120°C at a rate of $50^\circ\text{C}\cdot\text{min}^{-1}$ and the sample was treated with 10% NH_3 -He (vol%) mixture for 0.5 h. After NH_3 adsorption, the remaining or weakly adsorbed NH_3 was purged by high-purity He for 1 h at 120°C . TPD was performed in He flow by raising the temperature to 800°C at a rate of $20^\circ\text{C}/\text{min}$ and then holding at 800°C for 0.5 h. H_2 -TPR was performed using a similar procedure under 10% H_2/Ar . Elemental analysis for C and H was conducted with an Elementar Vario EL III (Elementar Analysensysteme GmbH, Germany), and all samples were measured twice for averaging.

2.4. Catalytic reaction

2.4.1. Conversion of ML to GVL in MeOH

All experiments were carried out in a 100-mL stainless steel high-pressure reactor (PARR, USA). After loading of ML (4 mmol), MeOH (19.5 g), and catalyst (0.25 g), the reactor was weighed, and then purged five times with N_2 before being sealed and heated to the target temperature with stirring (500 rpm). The reactor was naturally cooled to room temperature after the reaction, and the pressure was recorded before the collection of gaseous products. Gaseous products were analyzed by gas chromatography (GC) methods. The reactor was weighed again upon opening, and the weight loss compared with before the reaction was calculated. The weight loss in the present study was ascribed to the consumption of MeOH by reforming. The used catalyst was recovered by vacuum filtration, and washed with MeOH and ethanol before being dried at 60°C for 2 h. Liquid products were centrifuged at 8000 rpm for 6 min before analysis by GC-mass spectrometry (GC-MS) and GC methods, respectively.

2.4.2. Methanolysis of cellulose to ML and hydrogenation of ML to GVL

About 16 g microcrystalline cellulose (MCC) (90 μm) was added into a 400 mL Hastelloy-C high pressure reactor (Dalian-controlled plant), followed by 200 g MeOH solution with a H_2SO_4 concentration of 0.01 mol/L. The autoclave was heated to 200°C and maintained at that temperature for 4 h under vigorous stirring (500 rpm). The reactor was cooled to room temperature after the reaction, and only a small quantity of insoluble humins was observed. Excess CaCO_3 was added to neutralize H_2SO_4 , and the resulting CaSO_4 was separated by vacuum filtration. The resultant filtrate was also centrifuged and analyzed by the GC method. Based on the glucose units in

cellulose, the weight yield of ML was 32.4% (44.8% molar yield), and the resulting liquid products contained around 3.7 wt% ML.

Next, 13.9 g of the methanolysis product (containing around 4 mmol ML) and 0.25 g catalyst were placed in the Parr reactor as described above. The subsequent procedure for the GVL production was the same as that detailed in Section 2.4.1.

2.5. Liquid and gaseous products analysis

The analysis for gaseous products was performed on a Shimadzu GC-2010 Plus analyzer equipped with an Agilent CP-7429 column and a TCD. GC analysis for liquid samples was conducted on an Agilent 7890 series equipped with a DB-Waxetr column (30.0 m $\times$ 0.25 mm $\times$ 0.25 μm) and a flame ionization detector operated at 270°C . The carrier gas (N_2) had a flow rate of 1.0 mL/min. Temperatures were programmed as follows: 40°C (4 min), $15^\circ\text{C}/\text{min}$, 250°C (5 min). The qualitative analysis of products after reaction was conducted using a Thermofisher Trace 1300 & ISQ LT GC-MS instrument with a TR-5MS column (15.0 m $\times$ 0.25 mm $\times$ 0.25 μm). Temperatures were programmed as follows: 40°C (2 min), $150^\circ\text{C}/\text{min}$, 280°C (2 min). The flow rate was 1.2 mL/min and the split ratio was 1:50 for the carrier gas (He). The mass spectra were obtained by electron impact ionization (EI) at an electron energy of 70 eV and with a 25 μA emission current. The operating parameters for the GC-MS analysis were consistent with those of the GC analysis. Note that the quantitative analysis of the by-products (hydrocarboxylation products and ring-opening products) was performed according to the standard curve of GVL, because these by-products were not commercially available. ML conversion (X_{ML} , %), GVL selectivity (S_{GVL} , %), and MeOH loss (L_{MeOH} , wt%) before and after the reaction were calculated by the following equations:

$$X_{\text{ML}} = \left(1 - \frac{\text{mol of ML in products}}{\text{initial mol of ML}} \right) \times 100\% \quad (1)$$

$$S_{\text{GVL}} = \left(\frac{\text{mol of GVL in products}}{\text{initial mol of ML} - \text{mol of ML in products}} \right) \times 100\% \quad (2)$$

$$L_{\text{MeOH}} = \left(1 - \frac{\text{total mass of products}}{\text{total mass of initial input}} \right) \times 100\% \quad (3)$$

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Crystallinity

In this study, CuO , CaCO_3 , and $\text{CuO}_x\text{-CaCO}_3$ catalysts were prepared by an oxalate gel-coprecipitation method, followed by calcination at 500°C (Figs. 1 and S1). When the calcination temperature increased to 900°C , CaCO_3 was further degraded to afford CaO (Figure S1). As shown in Fig. 1, all the $\text{CuO}_x\text{-CaCO}_3$ catalysts displayed characteristic peaks of CuO ($2\theta = 35.5^\circ$ and 38.7°) and CaCO_3 ($2\theta = 29.3^\circ$). The Cu/Ca molar ratio had a significant influence on the degree of ordering and crystallite size of CuO in these catalysts. As shown in Fig. 1 and Table 1,

Fig. 1. XRD patterns of (4)CuO_x-CaCO₃ (a), (3/2)CuO_x-CaCO₃ (b), (2/3)CuO_x-CaCO₃ (c), and (1/4)CuO_x-CaCO₃ (d).

Table 1

Specific surface area (S_{BET}), total pore volume (V_p), mean pore radius (r), and crystallite size (D) of various catalysts.

Catalyst	S_{BET}^a (m ² /g)	V_p^a (10 ⁻³ cm ³ /g)	r^a (nm)	D^b (nm)
CuO	10.3	120.3	44.6	11.5
CaO	8.1	102.7	39.4	37.6
(1/4)CuO _x -CaCO ₃	2.6	6.1	9.5	1.0
(2/3)CuO _x -CaCO ₃	4.6	15.9	13.8	1.4
(3/2)CuO _x -CaCO ₃	6.3	102.1	64.9	13.7
(4)CuO _x -CaCO ₃	7.0	106.3	68.3	11.7
CaCO ₃	6.5	82.4	34.9	77.6

^a Determined by BET analysis of N₂ adsorption isotherms.

^b The crystallite size was calculated using Scherrer equation, and the crystallite size of CuO phase was calculated for CuO_x-CaCO₃ catalysts.

the intensity of diffraction peaks and crystallite size of CuO decreased with the increase of CaCO₃ content. Notably, all the catalysts (except for (4)CuO_x-CaCO₃) gave an apparent diffraction peak of Cu₂O at around $2\theta = 42.1^\circ$, which became more visible with increasing CaCO₃ content (Fig. 1), indicating that the incorporation of CaCO₃ is conducive to the formation of Cu₂O even after the calcination of catalyst precursor at 500 °C. Moreover, XPS analysis of (3/2)CuO_x-CaCO₃ further consolidated the above observation, as will be discussed later (Fig. 4).

3.1.2. Surface area and porosity

The textural properties of catalysts prepared by an oxalate gel-coprecipitation method were measured by N₂ adsorption-desorption isotherms. As shown in Table 1, CuO had the highest specific surface area (10.3 m²/g) among all these catalysts, with a total pore volume of 120.3×10^{-3} cm³/g and a mean pore radius of 44.6 nm (Table 1, entry 1). Both CaO and CaCO₃ had relatively lower specific surface areas, smaller pore volume, and mean pore radius compared with CuO (entries 2 and 7, Table 1). The specific surface area, pore volume, and mean pore radius of (n)CuO_x-CaCO₃ catalysts gradually increased with increasing CuO content. For example, (1/4)CuO_x-CaCO₃ had a specific surface area of only 2.6 m²/g with a total pore volume of 6.1×10^{-3} cm³/g, whereas

(4)CuO_x-CaCO₃ had a specific surface area of only 7.0 m²/g with a total pore volume of 106.3×10^{-3} cm³/g.

3.1.3. H₂-TPR analysis

The reduction behavior of Cu-based catalysts and its counterparts was studied using H₂-TPR. All the CuO_x-CaCO₃ catalysts exhibited broad bands for H₂ consumption; CuO showed a single peak at about 220 °C, which was attributed to one-step reduction of Cu²⁺ to Cu⁰ [39]. No obvious peaks were observed in the pure CaO, whereas a notable peak at around 740 °C appeared in the H₂-TPR profile of CaCO₃ (Fig. 2(f) and (g)). It is known that Ca²⁺ species cannot be reduced in an H₂ atmosphere; thus, the peak at around 740 °C was attributed to CO₂ formed by the degradation of CaCO₃ at elevated temperatures. This was verified by TG analysis for the CaCO₃ and (3/2)CuO_x-CaCO₃ catalysts, as shown in Fig. S2. On the other hand, the reduction peak for Cu²⁺ species in CuO_x-CaCO₃ catalysts was slightly shifted to a lower-temperature region, probably owing to an interaction between Cu and Ca species [40]. Overlapping shoulders in (4)CuO_x-CaCO₃ were observed in the temperature range of 150–250 °C, indicating the existence of two types of Cu species in the oxidation state. This finding was in line with the characterization of XRD (Fig. 1).

3.1.4. NH₃-TPD analysis

Acidic sites on the catalysts are conducive to the intramolecular cyclization of intermediates to form GVL during hydrogenation [41]. However, no peaks and an almost straight line were observed in the NH₃-TPD profile of CuO over the full range of test temperatures, indicating that there were no active acidic sites on the surface of CuO (Fig. 3(a)). Only a small peak representative of a moderate acidic site for pure CaO was observed. Notably, a broad peak in the range of 650–750 °C was observed in the CaCO₃. This peak was ascribed to the release of CO₂ resulting from the decomposition of CaCO₃ at high temperatures, according to the TPD test, which was conducted under the same conditions but without NH₃ during the adsorption process (Fig. S2(c)). TG analysis of CaCO₃ and (3/2)CuO_x-CaCO₃ gave the same results (Fig. S2(a) and (b)). Therefore, no acidic sites were detected on the surface of CuO_x-CaCO₃. Interestingly,

Fig. 2. H₂-TPR profiles of CuO (a), (4)CuO_x-CaCO₃ (b), (3/2)CuO_x-CaCO₃ (c), (2/3)CuO_x-CaCO₃ (d), (1/4)CuO_x-CaCO₃ (e), CaCO₃ (f), and CaO (g).

Fig. 3. NH_3 -TPD profiles of CuO (a), $(4/3)\text{CuO}_x\text{-CaCO}_3$ (b), $(3/2)\text{CuO}_x\text{-CaCO}_3$ (c), $(2/3)\text{CuO}_x\text{-CaCO}_3$ (d), $(1/4)\text{CuO}_x\text{-CaCO}_3$ (e), CaCO_3 (f), and CaO (g).

the decomposition temperature of CaCO_3 was lower in the presence of Cu species (Fig. 3(b)–(f)), which could be regarded as evidence of an interaction between Cu species and CaCO_3 .

3.1.5. XPS analysis

As expected, Cu, Ca and O were detected in the survey scan of $(3/2)\text{CuO}_x\text{-CaCO}_3$ (Fig. 4(a)). Binding energy (BE) values centered at 934.2 and 954.0 eV were attributed to $\text{Cu } 2p_{3/2}$ and

$\text{Cu } 2p_{1/2}$ of $(3/2)\text{CuO}_x\text{-CaCO}_3$, respectively (Fig. 4(b)). Each Cu $2p$ emission line could be fitted by using two Gaussian components, which were representative of Cu^{2+} and Cu^0/Cu^+ species, respectively. Compared with CuO (954.2 eV for Cu $2p_{1/2}$), the Cu $2p_{1/2}$ spectrum of $(3/2)\text{CuO}_x\text{-CaCO}_3$ showed a drift toward lower binding energies, confirming the interaction between Ca and Cu [42]. Specifically, partial electrons probably transferred from Ca to Cu species in $\text{CuO}_x\text{-CaCO}_3$, owing to the stronger electronegativity of Cu (1.9) compared with that of Ca (1.0) [43,44]. A higher proportion of Cu^0/Cu^+ species was observed in the high-resolution spectrum of Cu $2p$ of $(3/2)\text{CuO}_x\text{-CaCO}_3$ (Fig. 4(b)), indicating that CaCO_3 has a crucial role in stabilizing Cu^0/Cu^+ species. There were known to be defects on the surface of metal oxides, which could result in local charge imbalance of the surface species; therefore, Cu^+ species were detected on the surface of CuO by XPS. However, trace amounts of Cu^+ species cannot be detected by XRD.

3.1.6. Surface morphology

The SEM images showed that the CuO mainly consisted of secondary particles with diameter of around 50 nm, and the particles were relatively uniform (Fig. 5(a)). In the case of $(3/2)\text{CuO}_x\text{-CaCO}_3$, the distribution of the particle size was non-uniform, and particles with a diameter greater than 100 nm were clearly present (Fig. 5(b)). Similar phenomena were observed for other $\text{CuO}_x\text{-CaCO}_3$ catalysts (Fig. S3). To gain more

Fig. 4. XPS spectra of survey scan of $(3/2)\text{CuO}_x\text{-CaCO}_3$ (a), Cu $2p$ high-resolution spectra of $(3/2)\text{CuO}_x\text{-CaCO}_3$ (b), survey scan of CuO (c), and Cu $2p$ high-resolution spectrum of CuO (d).

Fig. 5. SEM images of CuO (a) and (3/2)CuO_x-CaCO₃ (b).

Fig. 6. SEM images (a), O (b), Cu (c), and Ca (d) elemental mappings of (3/2)CuO_x-CaCO₃.

insight into the elemental distribution on the surface of CuO_x-CaCO₃ catalysts, EDX elemental mapping for these catalysts was carried out. As shown in Figs. 6 and S4, both Cu and Ca, in all the CuO_x-CaCO₃, were evenly connected and dispersed with O, respectively, in all regions.

3.2. Reaction pathway for ML hydrogenation to GVL in MeOH

MeOH acts as both a solvent and an in-situ H-donor for the conversion of ML to GVL in all experiments. The reforming of

MeOH to produce H₂ and the subsequent hydrocyclization of ML to GVL are both catalyzed by CuO_x-CaCO₃. A plausible reaction pathway can be elucidated as in Scheme 1, based on the identification of products via GC-MS. It can be seen that methyl 4-hydroxypentanoate (MHP) occurs as an intermediate, although it is undetectable by GC-MS, indicating that the hydrogenation of ML to MHP is the rate-limiting step, while the ring closing of MHP to GVL is a fast step under the conditions used in this study [45,46]. As well as the main product GVL, small amounts of by-products are formed through the hydrocarboxylation/alkoxycarbonylation of GVL followed by hydrogenation (Scheme 1) [47].

3.3. Catalytic activity evaluation

3.3.1. Catalyst screening

In this study, both the gaseous and liquid products were collected for analysis. Gaseous products contained H₂, CO, and/or CO₂; no methyl ether was detected (Fig. S5). As shown in Table 2, the CuO could provide a ML conversion (X_{ML}) of 91.5% with a GVL selectivity (S_{GVL}) of 82.2% at 240 °C in 1 h (Table 2, entry 6). Some by-products (S_{ROP} of 7.3%, S_{HCP} of 6.3%) derived from the hydrocarboxylation and ring-opening of GVL were also detected. However, a low L_{MeOH} with negligible X_{ML} and Y_{GVL} was obtained over CaO or CaCO₃ (Table 2, entries 7 and 8), indicating the poor catalytic performance of CaO or CaCO₃ in H₂ production and ML hydrogenation. Interestingly, an X_{ML} of 96.8% with a S_{GVL} up to 88.9% was achieved over (3/2)CuO_x-CaCO₃ under the same reaction conditions (Table 2, entry 3); S_{HCP} decreased to only 3.2% and Y_{GVL} increased to 86.1% in this case. The above observation clearly indicates that (3/2)CuO_x-CaCO₃ is highly active for ML hydrogenation to GVL.

To determine the role of CaCO₃ in the catalytic performance of (3/2)CuO_x-CaCO₃, several blank experiments were carried out. When a physical mixture of CuO and CaCO₃ was used as the catalyst, X_{ML} was reduced to 71.7% while the hydrocarboxylation by-product increased dramatically to 16.2%, but selectivity towards ring-opening by-product declined compared with CuO

Scheme 1. The reaction pathway of the conversion of ML to GVL, as well as by-products, using MeOH as in-situ hydrogen source over CuO_x-CaCO₃.

Table 2 Catalytic performance of CuO, CaO, CaCO₃, CuO-CaO and CuO_x-CaCO₃ catalysts.

Entry	Catalyst	X_{ML} (%)	S_{GVL} (%)	S_{ROP} (%)	S_{HCP} (%)	Y_{GVL} (%)	L_{MeOH} (%)
1	(1/4)CuO _x -CaCO ₃	44.4	57.4	27.5	10.1	25.5	3.6
2	(2/3)CuO _x -CaCO ₃	73.0	73.4	16.7	9.0	53.6	4.6
3	(3/2)CuO _x -CaCO ₃	96.8	88.9	7.6	3.2	86.1	6.0
4	(4)CuO _x -CaCO ₃	93.2	86.1	7.6	4.4	80.2	6.3
5	(3/2)CuO-CaO ^a	67.3	79.8	3.7	16.2	53.7	5.4
6	CuO	91.5	82.2	7.3	6.3	75.2	6.5
7	CaO	2.9	59.8	2.1	35.2	1.7	2.5
8	CaCO ₃	5.3	89.4	4.3	–	4.7	3.1
9	(3/2)CuO-CaCO ₃ ^b	71.7	83.6	2.8	4.1	59.9	5.2
10	(3/2)CuO _x -CaCO ₃ ^c	49.6	43.3	29.8	19.2	21.5	3.9
11	(3/2)CuO-CaO ^d	70.2	79.6	3.4	12.9	55.9	5.1

Reaction conditions: 4 mmol ML, 19.5 g MeOH, 0.25 g catalyst, 1 h, 500 rpm, 240 °C.

^a Physical mixture of CuO and CaO with a Cu/Ca molar ratio of 3:2.^b Physical mixture of CuO and CaCO₃ with a Cu/Ca molar ratio of 3:2.^c Pre-reduced (3/2)CuO_x-CaCO₃ at 300 °C for 2 h.^d (3/2)CuO-CaO was prepared by the same method with the calculation temperature at 900 °C for 5 h.

(Table 2, entries 6 and 9). This indicates that a simple physical mixture of CaCO₃ with CuO not only harms the catalytic activity of CuO for ML conversion, but also favors the side reaction of GVL hydrocarboxylation. Therefore, there are probably strong interactions between Cu species and CaCO₃ in the (3/2)CuO_x-CaCO₃, which may be responsible for the outstanding catalytic performance. (3/2)CuO-CaO was obtained by the calcination of (3/2)CuO_x-CaCO₃ at 900 °C for 5 h; its catalytic performance was inferior to that of (3/2)CuO_x-CaCO₃, which confirmed the importance of CaCO₃ during the hydrogenation of ML to GVL with MeOH as the in-situ H-source.

In addition, X_{ML} and S_{GVL} gradually increased as the molar ratio of Cu to Ca increased (from 1/4 to 3/2 CuO_x-CaCO₃), and then decreased with a further increase of the molar ratio of Cu to Ca to 4 (Table 2, entries 1–4). Notably, the (3/2)CuO-CaCO₃ catalyst also outperformed other Cu-based bimetallic catalysts for ML hydrogenation in MeOH (Table S1).

3.3.2. Effect of reaction temperature, time and the ML dosage

Given the outstanding performance of (3/2)CuO-CaCO₃, the effects of reaction temperature and time on the hydrogenation of ML to GVL were investigated. When the reaction was conducted at 200 °C for 1 h, an X_{ML} of only 76.1% with an S_{GVL} of 92.3% was obtained (Table 3, entry 1). The low X_{ML} was mainly ascribed to the poor catalytic activity of the catalyst for ML hydrogenation at a relatively low temperature [48]. Moreover, only a small number of by-products were detected in this case. Notably, an increase in the reaction temperature to 240 °C brought about a significant improvement of X_{ML} to 96.8%, with a small decline in S_{GVL} compared with the case at 200 °C (Table 3, entries 1–3). Further increasing the temperature to 260 °C resulted in the gradual decrease of S_{GVL} to 84.7%, although the X_{ML} reached 99.1% (Table 3, entry 4). It appears that elevated temperatures greatly favor side reactions, indicating that these side reactions have higher activation energies than that of ML

Table 3

Conversion of ML into GVL in MeOH.

Entry	T (°C)	Time (h)	ML (mmol)	X_{ML} (%)	S_{GVL} (%)	S_{HCP} (%)	S_{ROP} (%)	Y_{GVL} (%)	L_{MeOH} (%)
1	200	1	4	76.1	92.3	3.5	1.8	70.3	4.1
2	220	1	4	91.3	90.8	8.2	0.0	82.8	4.8
3	240	1	4	96.8	88.9	7.6	3.2	86.1	6.0
4	260	1	4	99.1	84.7	9.9	1.5	83.9	6.1
5	280	1	4	99.4	70.3	17.8	8.1	69.9	7.9
6	240	2	4	97.8	90.6	7.8	1.7	88.5	6.5
7	240	3	4	99.5	96.1	3.0	0.0	95.6	6.6
8	240	4	4	100.0	89.4	3.2	2.9	89.4	6.9

Reaction conditions: 19.5 g MeOH, 0.25 g catalyst, 500 rpm.

hydrogenation. An excess of gaseous products containing H₂, CO, and CO₂ formed by MeOH reforming could further promote the hydrocarboxylation of GVL (Scheme 1). Elevation of the temperature to 280 °C resulted in complete reduction of CuO and Cu₂O to Cu in (3/2)CuO-CaCO₃ (Fig. S6), and the side reaction was greatly promoted because of the inadequate Cu⁺ species, revealing that Cu⁺ species are conducive to suppressing the side reaction. When pre-reduced (3/2)CuO-CaCO₃ was used as the catalyst, an ML conversion of only 49.6% was obtained, along with a poor GVL selectivity (43.3%), at 220 °C in 1 h (Table 2, entry 10); this is specific evidence for the suppression of side reactions by Cu⁺.

The influence of reaction time was investigated at 240 °C. When the reaction time was prolonged from 1 to 4 h, X_{ML} gradually increased from 96.8% to 100%, whereas S_{GVL} continuously increased to 96.1% in 3 h and then decreased 89.4% in 4 h (Table 3, entry 3 and entries 6–8). Further prolonging the reaction time to 4 h would result in more ring-opening of GVL at the cost of S_{GVL} .

3.3.3. Catalytic performance of (3/2)CuO_x-CaCO₃ in the methanolysis product of cellulose

In view of the excellent catalytic performance of (3/2)CuO_x-CaCO₃ in neat ML/methanol solution, it was highly desirable to test the catalytic activity of (3/2)CuO_x-CaCO₃ in the methanolysis product of carbohydrates. A detailed procedure is given in Section 2.4.2. The biggest challenge for the hydrogenation of ML to GVL in methanolysis products is the presence of humins, which are inevitable and complicated by-products that are formed during acid-catalyzed degradation of carbohydrates [49]. Humins can be easily adsorbed onto solid catalysts, leading to their deactivation. As shown in Table 4, an X_{ML} of 72.9% was obtained over (3/2)CuO_x-CaCO₃ at 240 °C in 1 h in the methanolysis product (Table 4, entry 1), while S_{HCP} sharply increased to 17.6% at the cost of S_{GVL} , compared with the case of neat ML/MeOH feedstock (Table 3, entry 3). The above observations clearly reveal that the presence of humins facilitates side reactions over (3/2)CuO_x-CaCO₃. With extension of the reaction time to 4 h, both X_{ML} and S_{GVL} gradually increased to 86.5% and 82.4%, respectively (Table 4, entries 2–4). In the methanolysis of MCC, the formation of humins is inevitable. We assumed that the adsorption of humins on the catalysts led to the indirect adsorption of ML, as the humins coated the cata-

Table 4

Production of GVL from ML in methanolysis product of MCC.

Time (h)	X_{ML} (%)	S_{GVL} (%)	S_{HCP} (%)	S_{ROP} (%)	Y_{GVL} (%)	L_{MeOH} (%)
1	72.9	61.0	17.6	13.8	44.5	4.9
2	77.5	69.7	11.6	10.2	54.0	5.1
3	83.7	75.8	10.0	4.1	63.4	5.4
4	86.5	82.4	8.9	5.1	71.3	5.6
6	89.2	87.8	7.2	4.4	78.3	6.1
8	92.5	85.6	7.9	4.8	79.2	6.4

Reaction conditions: 13.9 g methanolysis product of MCC (containing about 4 mmol ML), 0.25 g catalyst, 500 rpm, 240 °C.

lysts with a loose structure and improved their overall specific surface area. This would have resulted in a reduced amount of ML in the solution. The adsorbed ML would not have been converted into GVL; thus, the X_{ML} values (Table 4) for the first several hours were inevitably higher than the real ones, while the opposite was true for S_{GVL} . A desorption experiment was conducted to verify the above assumption. After the reaction had proceeded for 1 h in methanolysis product, the catalyst was separated by centrifugation and washed by methanol with ultrasonic cleaning. About 7.1 wt% ML was washed out (based on the initial ML dosage). The overall selectivity ($S_{GVL}+S_{HCP}+S_{ROP}$) did not reach 100%, and the hydrocarboxylation and alkoxycarbonylation of GVL were reversible. Some by-products/intermediates were eventually converted into GVL when the reaction time was prolonged.

Notably, the initial black methanolysis product changed to a canary yellow and transparent liquid product after the reaction in the presence of (3/2) CuO_x-CaCO_3 (Fig. S7), suggesting that most humins in the methanolysis product were adsorbed onto the catalyst during the reaction, along with the ML. The carbon content of the used (3/2) CuO_x-CaCO_3 in methanolysis product was measured as 6.5 wt% by elemental analysis after the reaction. According to NH_3 -TPD analysis, the adsorption of humins conferred a number of acid sites on the spent (3/2) CuO_x-CaCO_3 catalyst (Fig. S8), which were thought to be responsible for the improvement in the selectivity of by-products compared with that in the neat ML/MeOH group [47].

3.4. Leaching and reusability tests

Leaching tests were performed to investigate the stability of the CuO_x-CaCO_3 catalyst. Hydrogenation of ML in both ML/MeOH solution and the methanolysis solution were conducted at 240 °C in 1 h, after which the reaction was stopped and the solid catalyst was separated from the reaction mixture by centrifugation. The resulting filtrate was reloaded into the reactor and then reacted at 240 °C for another 3 h. As shown in Figs. 7 and S9, only negligible fluctuation was observed, indicating that no soluble catalytic active species leached into the resulting filtrates. Element leaching (Cu and/or Ca species) was also verified by ICP-OES. The Cu and Ca contents in the reaction mixture were measured as 3.92 and 6.01 ppm for neat ML/MeOH solution, while there was almost no leaching of Cu and Ca species in the methanolysis solution (0.48 and 0.85 ppm, respectively) (Table S2). Therefore, the leaching of the

Fig. 7. Leaching test of (3/2) CuO_x-CaCO_3 for hydrogenation of ML to GVL using MeOH as the in-situ H-source. Reaction conditions: 19.5 g MeOH, 4 mmol ML, 0.25 g catalyst, 240 °C, 500 rpm.

catalyst was negligible during the reaction. The possible leaching of active metals during the reusability tests was also investigated; the results are provided in Table S2. The Cu and Ca contents of the filtrate did not increase during the recycling test, which clearly indicates that CuO_x-CaCO_3 is a robust catalyst.

A recyclability test was also conducted to evaluate the catalytic stability of (3/2) CuO_x-CaCO_3 in both the neat ML/MeOH solution and the methanolysis solution. In a typical reusability test, the used catalyst was separated by vacuum filtration and then directly reused in the next run. Unexpectedly, only negligible decreases in X_{ML} and S_{GVL} were observed with the recycling tests in both neat ML methanol solution and methanolysis product of cellulose (Tables 5 and S3); this was ascribed to the limited carbon deposition on the surface of the catalysts. This insignificant reduction in the catalytic ability of (3/2) CuO_x-CaCO_3 could be easily recovered by calcination of the used catalyst at 500 °C (Table 5, entries 8; Table S3, entry 7).

In view of the catalytic performance of (3/2) CuO_x-CaCO_3 , the spent catalysts were further characterized for neat ML/MeOH solution and methanolysis solution. As shown in Fig. 8, the characteristic diffraction peaks for Cu^+ species of the

Table 5 Recycling test of (3/2) CuO_x-CaCO_3 in neat ML/MeOH solution.

Cycle	X_{ML} (%)	S_{GVL} (%)	S_{HCP} (%)	S_{ROP} (%)	Y_{GVL} (%)	L_{MeOH} (%)
Fresh	99.5	96.1	3.0	0.0	95.6	6.6
1 st	96.5	94.0	4.5	1.5	90.7	6.4
2 nd	95.2	92.1	6.6	1.3	87.6	6.4
3 rd	94.3	90.3	7.1	2.0	85.1	6.3
4 th a	97.4	96.6	1.9	1.0	94.1	6.5
5 th	97.1	95.3	2.9	1.2	92.5	6.6
6 th	95.8	94.5	4.2	0.0	90.5	6.4
7 th	94.2	92.8	5.1	1.7	87.4	6.4
8 th a	98.9	95.7	2.1	1.3	94.6	6.7

Reaction conditions: 19.5 g MeOH, 0.25 g catalyst, 3 h, 500 rpm, 240 °C, 4 mmol ML.

^a Spent catalyst was regenerated by calcination at 500 °C before reaction.

Fig. 8. XRD patterns of the fresh (a) and the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ after first (b) and 8th cycle (c), the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ after first cycle in methanolysis solution (d), the spent (1/4) $\text{CuO}_x\text{-CaCO}_3$ after first cycle (e), the spent (2/3) $\text{CuO}_x\text{-CaCO}_3$ after first cycle (f), the spent (4) $\text{CuO}_x\text{-CaCO}_3$ after first cycle (g), and the spent CuO after first cycle (h). Reaction conditions: 19.5 g MeOH, 4 mmol ML, 0.25 g catalyst, 240 °C, 3 h, 500 rpm; all the spent catalysts were recycled from neat ML/MeOH solution, except for sample (d).

spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ in both neat ML/MeOH solution and methanolysis solution were markedly intensified after the reaction compared with those of the fresh catalyst (Figure 1). Note that the majority of Cu species in the used (3/2) $\text{CuO}_x\text{-CaCO}_3$ existed in the form of Cu^+/Cu^0 instead of Cu^{2+} (Fig. 8(b)–(d)). However, the intensity of diffraction peaks for Cu^+ or Cu^0 species remained almost unchanged even after the eighth recycling test (Fig. 8(c)). On the contrary, CuO was completely reduced to metallic Cu after the first run under the same conditions (Fig. 8(h)). Interestingly, the Ca proportions in the catalysts greatly influenced the state of copper species after the reaction. Based on XRD patterns, there was no Cu phase for (1/4) $\text{CuO}_x\text{-CaCO}_3$ and (2/3) $\text{CuO}_x\text{-CaCO}_3$ (Fig. 8(e)–(f)); however, apparent peaks for Cu^+ around $2\theta = 36.2^\circ$ were observed for all the catalysts, with relatively moderate Ca percentages (Fig. 8(b)–(d), g), especially in the case of (3/2) $\text{CuO}_x\text{-CaCO}_3$, whose Cu^+ proportion was the highest among the three catalysts. The above observations reveal that the incorporation of moderate Ca by an oxalate gel-coprecipitation method effectively prevents the reduction of CuO to Cu in a reducing atmosphere, and greatly favors the stabilization of Cu^+ species. Note that Cu^{2+} species were observed in the XPS spectra for the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ catalysts, probably owing to the difference in limit of detection between XPS and XRD analysis. This result also indicates that there was a small quantity of Cu^{2+} species dispersed on the catalyst surface, and that the particle size of the CuO in the spent catalysts was too small to be detected by XRD.

As shown in Fig. 9(b), the deconvolution of Cu 2p emission

lines clearly indicates that both metallic and oxidized Cu crystallite species were present in the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$, similar to the fresh one (Fig. 4(b)). The proportion of Cu^0/Cu^+ species in Cu 2p_{3/2} drastically increased in the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ (Fig. 9(b)), indicating that more Cu^{2+} species were reduced to Cu^0/Cu^+ species after the reaction. Notably, no satellite peak for Cu^{2+} species of spent CuO was observed alongside the Cu 2p_{3/2} and 2p_{1/2} peaks (Fig. 9(d)). These observations agree well with the XRD analysis of the spent catalysts (Fig. 8), according to which the oxidation state species of Cu in the spent CuO catalyst were almost entirely reduced into metallic copper. This confirms the promotion of Ca species in stabilizing Cu^+ species in (3/2) $\text{CuO}_x\text{-CaCO}_3$. On the other hand, BE signals of Ca 2p in the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ obviously shifted to higher values compared with the fresh (3/2) $\text{CuO}_x\text{-CaCO}_3$ or CaO (Fig. S10), suggesting an elusory interaction between Ca species and Cu species.

To further probe the deactivation of $\text{CuO}_x\text{-CaCO}_3$ catalysts, the carbon content of the spent catalysts was measured by elemental analysis. The C content of the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ was only 0.514 wt% after the first cycle, and only slightly increased to 1.119 wt% after the 7th cycle in neat ML/MeOH solution. SEM images showed that the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ after the first cycle in ML/MeOH solution was composed of irregular particles with a similar diameter to those in the fresh catalyst (Figs. 5(b) and S11(a)). Cu and Ca in the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ after the fourth and eighth cycles were evenly connected and dispersed with O in all regions, as before (Fig. S12(a)–(h)). Agglomeration of the spent catalyst was negligible

Fig. 9. (a) XPS survey scan of the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$; high-resolution spectra of Cu 2p (b), O 1s (c) and Ca 2p (d) of the spent (3/2) $\text{CuO}_x\text{-CaCO}_3$ after the first cycle; survey scan (e) and Cu 2p high-resolution spectra (f) of the spent CuO after the first cycle.

with the recycling of the catalyst, which was probably a major contributor to the excellent catalytic performance of (3/2) $\text{CuO}_x\text{-CaCO}_3$ in ML/MeOH solution. However, severe carbon deposition of the catalyst occurred in the methanolysis product of cellulose. In these cases, the C content of the catalyst was 6.455 wt% after the first cycle, dramatically increasing to 38.14 wt% after the fifth cycle (Table S4). The deactivation of solid catalysts is strongly associated with the carbon deposition of the catalyst in organic solvents. Fortunately, the carbon deposits could be readily removed by calcination at 500 °C.

Leaching and reusability tests of the CuO prepared by the same method were also conducted, as described in the supporting information (experimental section). The leaching of Cu species was much more severe for CuO than for the (3/2) $\text{CuO}_x\text{-CaCO}_3$ catalyst. According to the XRD pattern and XPS spectra for the spent CuO (Figs. 8(h) and 9(f)), the CuO was completely reduced to metallic Cu after the first run (Fig. 8(h)), with significant drops for both the X_{ML} and Y_{GVL} compared with the first cycle (Table S5). This was in marked contrast to the (3/2) $\text{CuO}_x\text{-CaCO}_3$, whose Cu^+ species were retained for at least eight continuous recycling runs (Table 5, Figs. 8 and 9). These results reaffirm the superior stability and reusability of the (3/2) $\text{CuO}_x\text{-CaCO}_3$ catalyst, due to the incorporation of CaCO_3 .

4. Conclusions

The incorporation of CaCO_3 by an oxalate gel-coprecipitation method resulted in a robust dual-functional (3/2) $\text{CuO}_x\text{-CaCO}_3$ catalyst. This dual-functional catalyst could

effectively catalyze both the in-situ production of H_2 by MeOH reforming and the simultaneous hydrogenation of ML to GVL. (3/2) $\text{CuO}_x\text{-CaCO}_3$ achieved GVL yield up to 95.6% at 240 °C in 3 h. Incorporation of CaCO_3 with CuO resulted in the formation of Cu^+ species in the $\text{CuO}_x\text{-CaCO}_3$ catalyst, which greatly facilitated the hydrogenation of ML. In addition, (3/2) $\text{CuO}_x\text{-CaCO}_3$ could be reused for at least eight consecutive reaction cycles without significant loss of its catalytic activity. Notably, the presence of humins in methanolysis products has an inconspicuous influence on its catalytic performance. Therefore, it is possible to develop a facile two-step strategy for GVL production from cellulose through the integration of ML production, by methanolysis of cellulose, H_2 formation by MeOH reforming, and ML hydrogenation in an MeOH system.

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Graphical Abstract

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Effective production of γ -valerolactone from biomass-derived methyl levulinate over $\text{CuO}_x\text{-CaCO}_3$ catalyst

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Incorporation of CaCO_3 greatly stabilized Cu^+ species. The robust and stable $\text{CuO}_x\text{-CaCO}_3$ catalyst could contribute to the development of a facile two-step strategy for the production of GVL from cellulose with methanol as the in-situ hydrogen source.

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CuO_x-CaCO₃催化剂高效催化生物质乙酰丙酸甲酯制备γ-戊内酯

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摘要: γ-戊内酯(GVL)在燃料和化学品上有着巨大的潜在利用价值, 如何从生物质木质纤维素出发经济地制备GVL广受关注. 目前已有大量的研究致力于利用不同氢源从乙酰丙酸及其酯类催化加氢制备GVL的催化体系. 过去的数年里, 外加氢气条件下的乙酰丙酸及其酯类加氢制备GVL已经得到了广泛的研究. 考虑到液体醇使用和管理相比于氢气更为安全便捷, 而且醇类如甲醇、乙醇都是可以从生物质制备的绿色环保的溶剂, 利用醇类通过Meerwein-Ponndorf-Verley (MPV)还原作为生物质催化加氢过程中的溶剂和氢供体已经引起了人们的浓厚兴趣. 在脂肪醇中, 甲醇的还原势能最高, 在MPV还原里的效果不如其他醇, 但可以通过甲醇重整制氢的方式来供氢. 此外, 乙酰丙酸甲酯(ML)可以通过甲醇中酸催化醇解碳水化合物制得, 因此可以尝试将碳水化合物醇解制备ML; 甲醇重整制氢以及ML加氢结合起来, 从而省去繁琐且能耗较大的ML分离步骤. 腐殖质的存在和固体催化剂在甲醇中的稳定性是上述两步法策略的最大挑战.

本文通过草酸凝胶共沉淀法首次制备了(n)CuO_x-CaCO₃ (n为Cu/Ca摩尔比)双功能催化剂, 用于以甲醇为原位氢源, 从生物质ML一锅制备GVL反应中. 经筛选, (3/2)CuO_x-CaCO₃催化制备GVL的得率高达95.6%. 利用各种表征手段分析了催化剂使用前后的组成和结构变化. 结果显示, 新制的CuO_x-CaCO₃催化剂中即可检测到Cu⁺的存在, 且在使用过程中CaCO₃可以有效阻止二价铜在氢气氛围下被完全还原成单质铜. 对于该体系中的ML加氢, 亚铜有着比单质铜更佳的催化性能. 循环实验表明, (3/2)CuO_x-CaCO₃至少可以连续稳定使用8次, 其催化活性没有明显损失. 此外, 在纤维素醇解产物中存在腐殖质的情况下, (3/2)CuO_x-CaCO₃催化剂仍能够有效催化纤维素醇解得到的ML加氢制备GVL. 因此可以利用这个高效廉价的催化剂开发一种便捷的一锅两步法从木质纤维素生物质制备GVL, 即将酸催化的纤维素醇解、甲醇重整、ML在甲醇溶剂中加氢三者整合起来.

关键词: γ-戊内酯; 乙酰丙酸甲酯; 加氢; 甲醇重整; 纤维素甲醇解

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