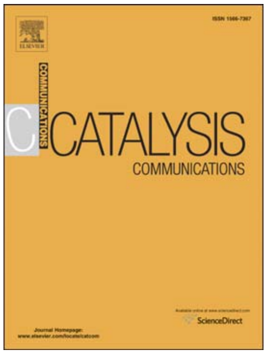

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Highlights

1. A simple solvothermal method was introduced into the sequential conversion of methyl

levulinate (ML).

2. Various yields of diverse products were obtained by tuning a series of factors.
3. Catalyst 2.5-CZ-550 showed a better performance for the conversion of ML, because of its rich acid content and Cu^0 species on the surface.

Abstract

Diverse products were obtained from transfer hydrogenation of methyl levulinate (ML) by adjusting different factors under solvothermal conditions. Excellent yields of gamma-valerolactone (GVL, 75%), 1,4-pentanediol (1,4-PDO, 39%), and 1-pentanol (1-PAO, 13.8%) could be obtained using zirconium-supported copper catalyst calcined at 550°C and under optimal conditions.

Keywords: solvothermal conditions, isopropanol, copper–zirconium catalysts, methyl levulinate, transfer hydrogenation

1. Introduction

With the decline of fossil fuels, numerous scientists have recently focused their attention toward seeking new energy resources and strategies to meet the increasing demand of energy. At the same time, bio-refinery also attracts researchers' attention. One of the degradation products of biomass[1,2] is levulinic acid (LA), which is a versatile raw material and platform molecule[3] with tremendous market efficiency, because the available clean products such as gamma-valerolactone (GVL), 1,4-pentanediol (1,4-PDO), and 1-pentanol (1-PAO) are streaming down, with applications in the fields of agriculture, cosmetics, and dyestuff.[4,5]

Synthesis of GVL from LA is the first step of hydrogenation, posing a challenge to researchers with the combined effect of the carbonyl and ester groups on selective hydrogenation. The high stability of ring structure in GVL indeed inhibits some hydrogenation catalysts[6]; therefore, the yield of 1,4-PDO depends on the activity of catalysts as well as some strict reaction conditions. Numerous studies have been conducted since the early years of the 20th century to explore the catalytic process of producing 1,4-PDO from LA and its ester, including homogeneous catalysis[7,8] and heterogeneous catalysis.[9–11] However, use of noble metal catalysts is not suitable for commercial application, because of their high cost. Thus, studies on transition metal oxide catalysts attracted research attention.[12–17] Recently, non-noble metal catalyst Cu–ZrO_2 has been found to exhibit a unique feature for transfer hydrogenation of LA and its ester,[15–17] because of its strong interaction force between Cu and ZrO_2, unique structure, and moderate acid–base property.[15,18,19] In this study, which aims at the transfer hydrogenation of methyl levulinate (ML), we conduct experiments with a special hydrogen source, isopropanol, for its accessibility and operability in a simple solvothermal treatment[20] with Cu-ZrO_2, providing a possible route to produce derived chemicals. It is interesting to note that we have obtained not only GVL and 1,4-PDO, but also 1-PAO, a critical product undergoing three steps of hydrogenation. The hypothetical reaction sequence for the conversion of ML into GVL, 1,4-PDO, and 1-PAO is shown in Scheme 1, where steps 1 and 2 involve copper coupling effect and transfer hydrogenation, respectively, and step 3 represents diol hydrogenolysis. It was generally accepted that, through the coupling of dehydrogenation and hydrogenation on Cu-based catalysts, a sequence of alcohol was efficiently used as hydrogen source.[21–24] Detailed process parameters on the reaction and the copper–zirconium catalysts were characterized.

2. Experimental

A detailed description of the materials, synthesis, characterization, catalytic test, and product analysis is presented in Supporting Information (SI) M1–M5.

3. Results and discussion

3.1 Hydrogenation of ML catalyzed by various Copper–Zirconium (CZ) catalysts

Initially, we assume Cu/Zr molar ratio as a variable and conduct a study on the catalytic performance of the corresponding R-CZ-T catalysts. (The preparation of catalyst is shown in SI; we defined our H_2-activated catalyst as R-CZ-T, where R denotes the Cu/Zr molar ratio and T denotes the calcination temperature.) With a reaction temperature of 200°C (a better parameter for 1,4-PDO formation discussed hereinafter) and reaction time of 12 h, we found that the optimum Cu/Zr molar ratio is 2.5:1 (Table 1, entry 1–5, 8). In this context, 2.5-CZ-550 had a better performance than other R-CZ-T catalysts, producing 39% yield of 1,4-PDO. Similarly, on the basis of this Cu/Zr molar ratio, a series of activated catalysts upon different calcination temperatures ranging from 400 to 700°C (preparation of catalyst shown in SI) were tested (Table 1, entry 6–10). From the yield of 1,4-PDO (Table 1, entry 1–10), we conducted a further study on the catalytic performance of 2.5-CZ-550 (Section 3.2).

3.2 Effects of the reaction conditions

In order to investigate the maximum yield of single product, tunable factors (e.g., reaction temperature, reaction time, and H-donor) were taken into account. The optimum reaction time for GVL, 1,4-PDO, and 1-PAO was 12 h, and their corresponding optimum reaction temperatures were 120, 200, and 240°C, found by solvothermal methods (Fig. S1 (a–c) SI M6, Table 1, entry 8, 11–14). When the temperature was increased to 240°C, the number of by-products formed, such as 1,7-octanediol and gamma-octanoic lactone, increased, thereby resulting in a sharp decrease in the yield of the main product. Under optimum reaction conditions, GVL, 1,4-PDO, and 1-PAO could be achieved with yields of 75%, 39%, and 13.8%, respectively. During hydrogenation, trials on different H-donors were conducted, and the result is shown in Table 1 (entry 8, 15–20). It can be concluded that secondary alcohol is a more suitable substitute for H_2 than primary alcohol. To the best of our knowledge, isopropanol performs better than other H-donors, because of its better utilization of H atoms and good H-balance during the catalytic process.[25,26]

3.3 Catalyst characterization

Results of characterizations are displayed in SI M6.

X-ray diffraction (XRD) patterns of Cu–ZrO_2 catalysts calcined at elevated temperatures from 400 to 700°C and the corresponding H_2-activated Cu–ZrO_2 (R-CZ-T) catalysts are depicted in Figure 1. After exposure to H_2, the appearance of indexed diffraction lines at 2θ = 43.5° (111), 50.6° (200), and 74.3° (220) indicates the presence of the crystalline phase of metallic Cu in Figure 1(B). A weak diffraction peak of Cu_2O (2θ = 36.5°) was found, partly due to slight oxidization of the sample, matching the results of X-ray photoelectron spectroscopy (XPS) analysis data in Figure S2. A progressive transformation of the crystalline phase of ZrO_2 was identified, from amorphous ZrO_2

(A-ZrO_2) to tetragonal ZrO_2 (T-ZrO_2) and finally monoclinic ZrO_2 (M-ZrO_2).[18] It is obvious that only weak and broad diffraction peaks of CuO in Figure 1(A) can be observed for the catalyst calcined at 400 and 500°C; however, when the temperature was increased to 550°C, the peaks become strong and narrow, and simultaneously, diffraction peaks of T-ZrO_2 (2θ = 30.2° and 60.4°) appear. When the temperature was further increased to 600°C, the peaks become more stronger and A-ZrO_2 completely transforms into T-ZrO_2, and, to some degree, the sample confronts sintering after further calcination at 700°C. As shown in Table 2, with increasing calcination temperature from 400 to 700°C, the BET surface areas of the Cu–ZrO_2 catalysts decreased sharply from 61 to 28 m^2 g^{-1}, which confirmed that calcination temperature affects specific surface area of coprecipitation-derived Cu-ZrO_2 materials.[18] The results presented in Figure 1 and Table 2 confirm that, as the temperature increases, crystallinity increases with the decrease of BET surface areas of the samples. Thus, comprehensive factors will be considered because the properties of surface areas and crystallinity significantly affect the activity of Cu–ZrO_2 catalysts.

Figure S2 presents the NH_3-TPD profiles of various activated catalysts. The figure indicates that 2.5-CZ-400 and 2.5-CZ-500 exhibit an abundant weak acidic site at around 223°C and an incisive strong acidic site at around 609°C, whereas 2.5-CZ-600 and 2.5-CZ-700 exhibit a lower amount of weak acidic site and a medium strong acidic site at around 337°C. Because of the higher calcination temperature, acidic sites would transit and sintering finally results in loss of acid content as well as surface area.[27] It is surprising that 2.5-CZ-550 possesses the most abundant acidic sites (Table S1) and more acid content

(Table 2) than other R-CZ-T samples. The rich acidic sites and acid content in the copper-containing catalysts have a high promotion on the hydrogenolysis mechanism of lactone and some categories of esters.[17,28]

XPS analysis data of 2.5-CZ-T are shown in Figure S3(a–e). From the Cu 2p spectra, probably because of its high activity on surface, in addition to Cu^0 (around 932.3 eV[29]), Cu_2O (933.5 eV[29]) and CuO (935.5 eV[30]) passivation layers were detected. Data on the fraction of Cu species (Table 2) were in good agreement with the catalytic performance of 2.5-CZ-T (Table 1, entry 6–10).

Inductively coupled plasma (ICP) spectroscopy analysis of 2.5-CZ-T samples (Table S2) reflects the experimental Cu/Zr molar ratio. H_2-TPR (temperature-programmed reduction) and thermogravimetric/differential thermal analysis (TG-DTA) results of 2.5-CZ-550 catalyst are shown in Figure S4 and S5, respectively. It is evident from the figure that the H_2-TPR profile of the catalyst exhibited a broad band of H_2 consumption at 207°C, because of the sequential reduction of CuO to Cu via Cu_2O. No distinct decomposition was found before 900°C (Fig. S5 (A)), and an exothermic peak was observed at around 180°C for the process of conversion of Cu and Cu_2O to CuO in DTA. Finally, catalytic performance, XRD patterns, and XPS analysis of the recycled 2.5-CZ-550 catalysts were tested and the results are shown in Figures S6–S8, respectively. Although encountering inevitable leaching of copper particles, CZ catalyst still exhibited a good performance, producing 17% yield of 1,4-PDO in the third run at 200°C.

4. Conclusions

Cu–ZrO_2 catalyst calcined at 550°C with 2.5:1 Cu/Zr molar ratio exhibits a higher activity for transfer hydrogenation of ML, because it possesses more abundant acid content (1.603 mmol/g) and Cu^0 species (28%) than other CZ catalysts. By tuning a series of factors (e.g., reaction temperature, reaction time, and H-donor), various yields of the diverse products were obtained. As a H-donor, isopropanol becomes the best substitute for H_2, making the reaction more operable with 2.5-CZ-550 catalyst. Further experiments to understand the mechanism and improve the yields of main product under relatively mild solvothermal conditions are ongoing.

Acknowledgments

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Scheme:

Scheme 1 Hypothetical reaction sequence for the conversion of ML into GVL, 1,4-PDO, and 1-PAO over Cu–ZrO_2 catalyst

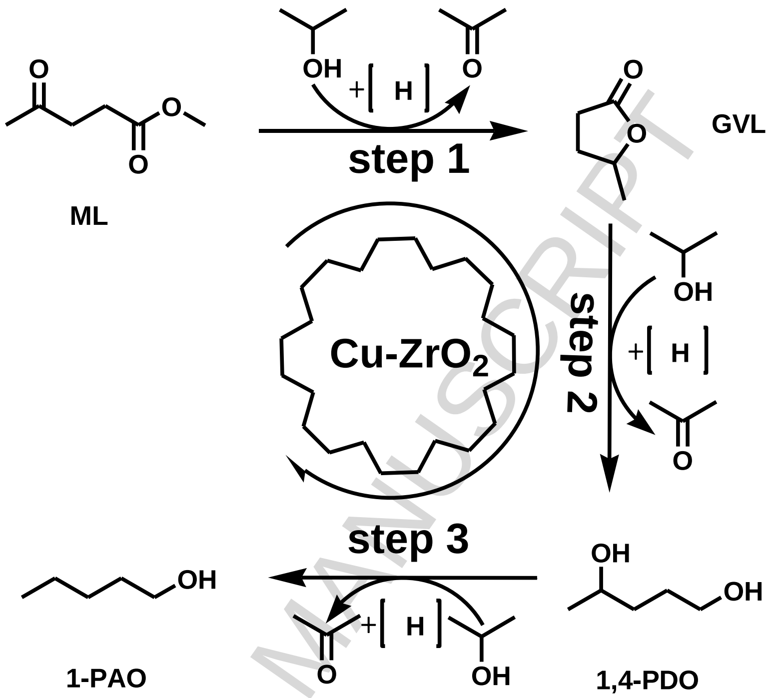
Figure:

Fig.1 XRD patterns of (A) 2.5-CZ catalysts after calcination and (B) further exposure to H_2

List of tables:

Table 1 Hydrogenation of ML over various R-CZ-T catalysts

Table 2 Physicochemical properties of 2.5-CZ-T catalysts calcined at different temperatures



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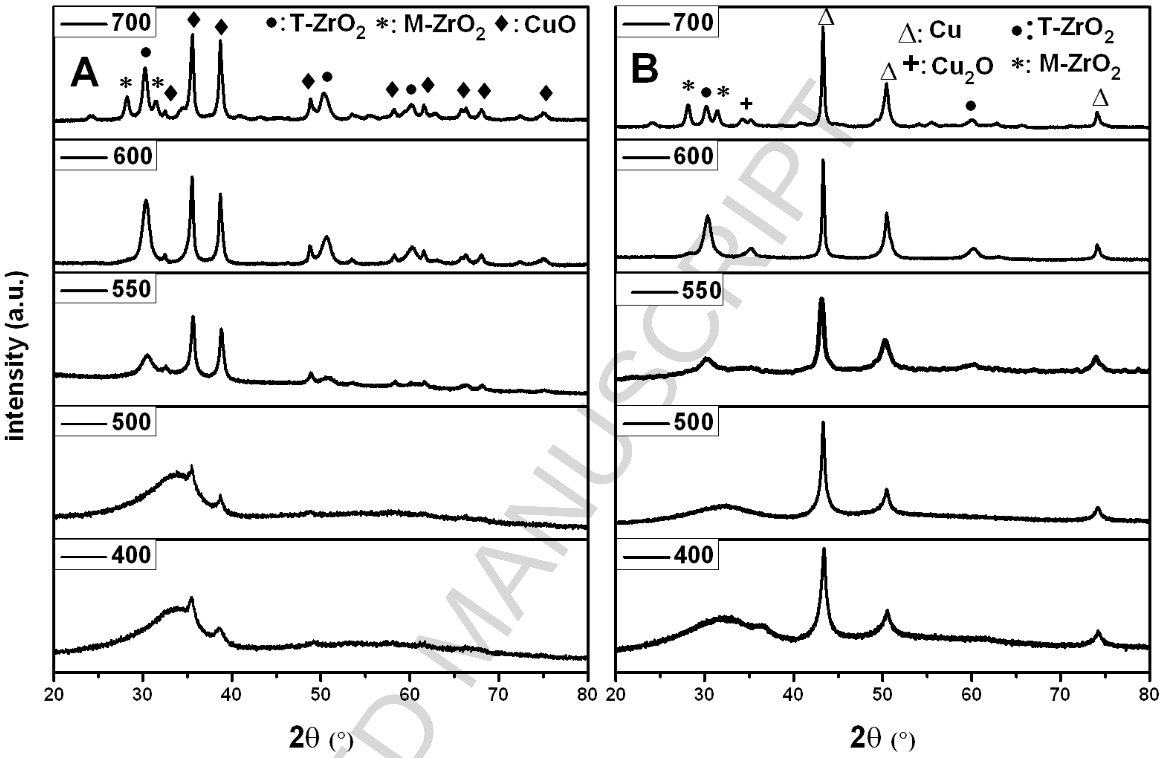

Fig.1 XRD patterns of the (A) 2.5-CZ catalysts after calcination and (B) further exposure to H_2(2.5-CZ-T catalysts)

Table 1 Hydrogenation of ML over various R-CZ-T catalysts[a]

Entry	Sample	Solvent	T [°C]	Yield（%）		
				GVL	1,4-PDO	1-PAO
1	Cu-550	2-PrOH	200	54	19	0
2	6-CZ-550	2-PrOH	200	55	32	0
3	2-CZ-550	2-PrOH	200	46	34	0
4	1-CZ-550	2-PrOH	200	53	28	0
5	ZrO_2-550	2-PrOH	200	0	0	0
6	2.5-CZ-400	2-PrOH	200	41	32	0.5
7	2.5-CZ-500	2-PrOH	200	41	31	0.6
8	2.5-CZ-550	2-PrOH	200	47	39	1.1
9	2.5-CZ-600	2-PrOH	200	50	37	0.3
10	2.5-CZ-700	2-PrOH	200	61	17	0
11[b]	2.5-CZ-550	2-PrOH	80	0	0	0
12	2.5-CZ-550	2-PrOH	120	75	0	0
13	2.5-CZ-550	2-PrOH	160	55	34	0
14	2.5-CZ-550	2-PrOH	240	10	9	13.8
15	2.5-CZ-550	MeOH	200	14	0	0
16	2.5-CZ-550	EtOH	200	64	7	0
17	2.5-CZ-550	1-PrOH	200	49	7	0
18	2.5-CZ-550	1-BuOH	200	40	0	0
19	2.5-CZ-550	2-BuOH	200	55	27	0
20	2.5-CZ-550	H_2O	200	0	0	0

[a] 100% ML conversion, reaction conditions: solvent 20 mL, ML 0.1 mL, catalyst 0.2 g, reaction time 12 h

[b] 0% ML conversion

Table 2 Physicochemical properties of 2.5-CZ-T catalysts calcined at different temperatures

Entry	Sample	S_{BET} (m^2/g)	V_{porc} (cm^3/g)	Acid content (mmol/g)[a]	Binding Energy (eV) & fraction of Cu species (%)[b]
1	2.5-CZ-400	61	0.088	1.453	933.5 (55) 935.5 (45)
2	2.5-CZ-500	59	0.096	1.561	933.5 (55) 935.5 (45)
3	2.5-CZ-550	55	0.137	1.603	932.4 (28) 933.5 (40) 935.5 (32)
4	2.5-CZ-600	41	0.147	0.742	932.3 (20) 933.5 (48) 935.3 (32)
5	2.5-CZ-700	28	0.156	0.716	933.5 (100)

[a] Total acid content was estimated by NH_3-TPD test.

[b] Binding energy and fraction of Cu species were tested by XPS analysis.

Graphical abstract

Relatively mild and operational solvothermal conditions were used for hydrogenation of ML to GVL, 1,4-PDO, and 1-PAO over zirconium-supported copper catalysts.