



Short communication

Transfer hydrogenation of methyl levulinate into gamma-valerolactone, 1,4-pentanediol, and 1-pentanol over Cu–ZrO₂ catalyst under solvothermal conditions



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ARTICLE INFO

Article history:

Received 3 November 2015

Received in revised form 17 December 2015

Accepted 18 December 2015

Available online 24 December 2015

Keywords:

Solvothermal conditions

Isopropanol

Copper–zirconium catalysts

Methyl levulinate

Transfer hydrogenation

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.

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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, the use of noble metal catalysts is not suitable for commercial

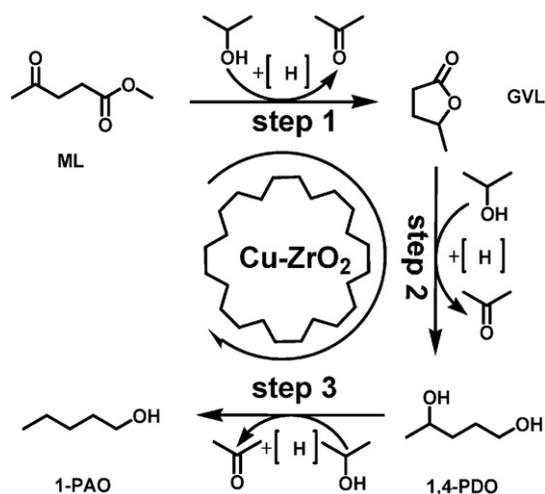
application, because of their high cost. Thus, studies on transition metal oxide catalysts attracted research attention [12–17]. Recently, non-noble metal catalyst Cu–ZrO₂ has been found to exhibit a unique feature for transfer hydrogenation of LA and its ester [15–17], because of its strong interaction force between Cu and ZrO₂, 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–ZrO₂, 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.

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Scheme 1. The hypothetical reaction sequence for the conversion of ML into GVL, 1,4-PDO and 1-PAO over Cu-ZrO₂.

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 H₂-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, entries 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, entries 6–10). From the yield of 1,4-PDO (Table 1, entries 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, entries 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 (entries 8, 15–20). It can be concluded that secondary alcohol is a more suitable substitute for H₂ 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–ZrO₂ catalysts calcined at elevated temperatures from 400 to 700 °C and the corresponding H₂-activated Cu–ZrO₂ (R-CZ-T) catalysts are depicted in Fig. 1. After exposure to H₂, the appearance of indexed diffraction lines at $2\theta = 43.5^\circ$ (111), 50.6° (200), and 74.3° (220) indicates the presence of the crystalline phase of metallic Cu in Fig. 1(B). A weak diffraction peak of Cu₂O ($2\theta = 36.5^\circ$) was found, partly due to slight oxidation of the sample, matching the results of X-ray photoelectron spectroscopy (XPS) analysis data in Fig. S2. A progressive transformation of the crystalline phase of ZrO₂ was identified, from amorphous ZrO₂ (A-ZrO₂) to tetragonal ZrO₂ (T-ZrO₂) and finally monoclinic ZrO₂ (M-ZrO₂) [18]. It is obvious that only weak and broad diffraction peaks of CuO in Fig. 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-ZrO₂ ($2\theta = 30.2^\circ$ and 60.4°) appear. When the temperature was further increased to 600 °C, the peaks become stronger and A-ZrO₂ completely transforms into T-ZrO₂, 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–ZrO₂ catalysts decreased sharply from 61 to 28 m² g^{−1}, which confirmed that calcination temperature affects specific surface area of coprecipitation-derived Cu–ZrO₂ materials [18]. The results presented in Fig. 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–ZrO₂ catalysts.

Fig. S2 presents the NH₃-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

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 ₂ O	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.

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