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Conversion of biomass to γ-valerolactone by catalytic transfer hydrogenation of ethyl levulinate over metal hydroxides

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ABSTRACT

A series of low-cost readily-assembled eco-friendly metal hydroxides were examined as catalysts in the synthesis of a novel platform molecule, γ-valerolactone (GVL), from biomass-derived ethyl levulinate (EL) via hydrogen transfer reaction. Among these catalysts, $ZrO(OH)_2 \cdot xH_2O$ was found to be most active. EL conversion of 93.6% and GVL selectivity of 94.5% were achieved when 2-propanol was used as a hydrogen donor at 473 K with a reaction time of only 1 h. The complete reaction pathway and the probable main by-products for the conversion of EL to GVL were clearly deduced for the first time. The $ZrO(OH)_2 \cdot xH_2O$ catalyst could be reused at least ten times without any significant loss of catalytic activity. Furthermore, characterizations were carried out on the fresh and spent $ZrO(OH)_2 \cdot xH_2O$ catalysts with XRD, FT-IR, BET, TGA-DTA. Combined with the results of poisoning experiments, a plausible mechanism for catalytic transfer hydrogenation (CTH) of EL to GVL was proposed to be consisted of a catalytic cycle involving a six member ring transition state.

1. Introduction

Depletion of fossil-based resources and deterioration of environmental have raised the concerns on the sustainability of our society, economy and environment. In recent decades, various renewable resources were studied and developed in order to meet the growing energy demands. Among them, abundant and inexpensive biomass is the only renewable resources on the earth that can be converted to liquid fuels and chemicals which are conventionally derived from fossil resources [1,2]. The transformation of biomass to platform molecules, the precursor for the synthesis of a substantial number of value-added chemicals and transportation fuels, has attracted increasing attention of researchers worldwide [2–6]. In recent years, a variety of catalytic strategies have been developed for the generation of platform chemicals, including 5-hydroxymethylfurfural (HMF) [7–10], levulinic acid (LA) [11,12] and γ-valerolactone (GVL) [13,14], which can be readily derived from carbohydrates or even directly from biomass. GVL is identified as a versatile building block that can be applied to produce various value-added chemicals which are well-suited as organic solvents and bio-oxygenates [15,16]. Moreover, GVL can also be used to synthesize various liquid hydrocarbons with a suitable molecular weight to meet the qualities for gasoline, diesel and aviation kerosene [17–19], respectively. GVL itself has also been described as an excellent green solvent in biomass conversion, which resulted in a higher yield and effective separation of desired products from biomass due to its outstanding physicochemical properties [20–23].

GVL is usually produced through selective reduction of biomass-derived LA under high-pressure H_2 in homogeneous and/or heterogeneous systems [24,25]. Until now, a variety of catalytic systems have been developed for the production of GVL from LA, and Ru-based catalysts were confirmed as most active [26–28]. However, the drawbacks of being high cost, prone to deactivation and difficult to regenerate limited the applications of noble metal catalysts in a commercial scale GVL production. Moreover, there are safety concerns on the use of corrosive LA and hazardous H_2. For instance, the cost of transportation and storage of hydrogen are probably more expensive than the biomass feedstock itself [29]. A cost-efficient separation and purification process of LA from biomass seems impossible due to its high acidity and low volatility. Thus, EL, which can also be derived from biomass via ethanolysis [30,31], is a better alternative than LA for the production of GVL as EL is acid-free and easy-separable [32,33]. However, a poor performance was observed for the selective hydrogenation of levulinate esters under high-pressure H_2 [34,35]. Therefore, it is important to develop a new catalytic process for the production of GVL from EL.

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Recently, Yao Fu's group was reported an effective catalytic transfer hydrogenation (CTH) route to convert biomass-derived EL to GVL over Raney Ni under room temperature [36]. Differing from the CTH route employed by Yao Fu, the CTH of carbonyl compounds via Meerwein–Ponndorf–Verley (MPV) reduction was extensively studied in the organic synthesis [37]. Carbonyl compounds can be converted to their corresponding alcohols by MPV reduction with a high selectivity over low-cost metal oxides [38]. Using abundant and safe alcohols as hydrogen donor is another unique advantage for the MPV reduction of carbonyl compounds. Although high yields of the desired alcohols were obtained when this CTH approach was applied to an open system through a solvent refluxing method, an extended reaction time (longer than dozens of hours) was essential [39]. Nevertheless, MPV reaction in a sealed reactor under high temperature and saturated pressure was rarely studied, especially for the reduction of biomass-derived EL to GVL [40]. Recently, our group has reported the CTH of EL to GVL over metal oxides [41]. In this work, we discovered that metal hydroxides were more effective than metal oxides for the CTH of EL. Herein, an effective and green process was developed for the conversion of biomass-based EL to GVL via MPV reduction in various subcritical alcohols over the low-cost eco-friendly metal hydroxides. The effects of varied experiment parameters on the selectivity of products were systematically investigated and a detailed characterization of the fresh and used catalysts was conducted. Finally, based on the results of the poisoning experiments, a plausible mechanism for the CTH of levulinate esters to GVL via MPV reduction over metal hydroxides was proposed.

2. Experimental procedure

2.1. Chemicals and materials

EL (98%), GVL (98%) and zirconium oxychloride (99%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Butyl levulinate (BL) and methyl levulinate (ML) were obtained from Alfa Aesar Co. Ltd. (Tianjin, China). All other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

2.2. Catalysts preparation

All metal hydroxides were prepared by precipitation using their chloride salts as the precursors. In a typical procedure, $ZrOCl_2·8H_2O$ was dissolved in deionized water to prepare a 100 g/L $ZrOCl_2·8H_2O$ solution. Concentrated NH_4OH was added to adjust the solution pH value around 9.5 with vigorous stirring, and then the resulting emulsion was aged at room temperature for 24 h before separating the white precipitate. The precipitate was thoroughly washed with deionized water until the chloride ions could not be identified in the filtrate. The washed precipitate was dried at 383 K for 12 h, and then was ground to pass a 100-mesh sieve.

2.3. Catalyst characterization

X-ray diffraction (XRD) patterns were obtained on a Panalytical X'pert Pro diffractometer using a Cu $K\alpha$ radiation source with the following parameters: 40 kV, 30 mA, 2θ from 20° to 90° at a scanning speed of 7°/min. FT-IR spectrums were recorded on a Nicolet 380 spectrometer. SEM images were performed on a Hitachi S-4800 by using 30 kV. Thermal gravimetric analysis and differential thermal gravimetric analysis (TGA/DTG) were carried out on a SDT Q600 thermal analyzer under a dynamic N_2 atmosphere (100 mL/min) at the temperature range of 293–1173 K with a heating rate of 20 K/min. BET surface areas were measured on a TriStar 3000 surface area and porosimetry analyzer (Micromeritics), the samples were degassed at 373 K for 3 h in a vacuum before N_2 adsorption. Elemental analyses were performed by an Elementar Vario EL III (Elementar Analysensysteme GmbH, Germany).

2.4. Typical procedure for the production of GVL

The experiments were carried out in a 100 mL cylindrical stainless steel high-pressure reactor (PARR instrument company, USA). In a typical reaction, the batch autoclave reactor was loaded with substrate (2 g), solvent (38 g) and catalyst (1 g), and then purged five times with N_2 at atmospheric conditions before the reaction mixture was heated to the prescribed temperature for a desired reaction time with stirring at 500 rpm. After reaction, the reactor was cooled to room temperature. The liquid products were centrifuged at 10,000 rpm for 5 min and analyzed by GC–MS and GC methods, respectively.

2.5. Sample analysis

The qualitative analysis of sample after reaction was conducted with a Shimadzu QP2010SE instrument with Rtx-5MS column (30.0 m × 0.25 μm × 0.25 mm) and electron impact ionization (EI).

The amount of levulinate esters and its products were determined on an Agilent 7890 series equipped with a HP-5 capillary column (30.0 m × 320 μm × 0.25 μm) and a flame ionization detector (FID) operating at 543 K. The carrier gas was N_2 with a flow rate of 1.0 mL/min. The following programmed temperature was used in the analysis: 313 K (4 min) – 15 K/min – 623 K (5 min). Typically, EL conversion, GVL yield, GVL selectivity and GVL formation rate were calculated using the following equations:

$$\text{EL conversion}\,(\%) = \left(1 - \frac{\text{Mole of EL}}{\text{Initial mole of EL}}\right) \times 100\% \qquad (1)$$

$$\text{GLV yield}\,(\%) = \frac{\text{Mole of GLV}}{\text{Initial mole of EL}} \times 100\% \qquad (2)$$

$$\text{GLV selectivity}\,(\%) = \frac{\text{Mole of GLV}}{\text{Innitial mole of EL} - \text{Mole of EL}} \times 100\% \qquad (3)$$

$$\text{GLV formation rate}\,(\mu\text{mol/g/min}) = \frac{\text{Mole of GLV}}{\text{Amount of catalyst} \times \text{Reaction time}} \qquad (4)$$

3. Results and discussion

3.1. Evaluation and screening of catalyst

To the best of our knowledge, the CTH of biomass-derived EL to GVL over inexpensive metal hydroxides has not been reported prior to this paper. As shown in Table 1, the catalytic activities of various metal hydroxides for the CTH of EL to GVL were largely different when ethanol was used as a hydrogen donor. The reaction mixture consisted of 2 g EL and metal hydroxide in 38 g ethanol. The reactor was heated to 473 K for 60 min. $Zr(OH)_4$ produced the most GVL yield with an EL conversion of 50.9% and a GVL yield of 43.1% (Table 1, entry 8). However, when $La(OH)_3$, $Mg(OH)_2$ and $Al(OH)_3$ were used as catalysts, EL conversions were no greater than 25% (Table 1, entries 5–7). Moreover, GVL yields were negligible in the presence of $Cr(OH)_3$, $Sn(OH)_4$ and $Ni(OH)_2$ probably due to their weak basicity (Table 1, entries 1–3). It is noticeable that EL was mostly converted in the presence of strong Bronsted bases. EL conversion of 100% was reached when NaOH was employed as the catalyst, but considerable coke, rather than GVL, was observed under the above-mentioned reaction conditions. This observation might be attributed to that condensation reactions of EL increased