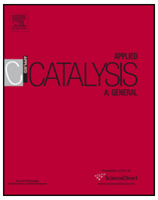
Applied Catalysis A: General 510 (2016) 11–19

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata



Cascade catalytic transfer hydrogenation–cyclization of ethyl levulinate to γ-valerolactone with Al–Zr mixed oxides

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ARTICLE INFO

Article history:
Received 7 June 2015
Received in revised form 30 October 2015
Accepted 30 October 2015
Available online 11 November 2015

Keywords:
γ-Valerolactone
Ethyl levulinate
Mixed metal oxide
Catalytic transfer hydrogenation

ABSTRACT

A series of Al–Zr mixed oxides with different molar ratios were prepared by co-precipitation method and utilized to catalyze conversion of ethyl levulinate (EL) to γ-valerolactone (GVL). Those as-prepared catalysts were characterized by XRD, SEM, N_2 adsorption–desorption, XPS, TG, NH_3-TPD, CO_2-TPD and pyridine-IR. The introduction of Al into ZrO_2 was demonstrated to enlarge surface areas, as well as increase the number of acid and base sites that were catalytically active for transfer hydrogenation. Effects of Al–Zr molar ratio, calcination temperature, reaction temperature and time, catalyst dosage, and alcohols used as hydrogen donors on the catalytic performance were investigated. A high GVL yield of 83.2% at EL conversion of 95.5% could be achieved at 220 °C in 4 h over Al_7Zr_3-300 using 2-propanol as hydrogen donor and solvent. Poisoning experiments verified that acid–base sites played a synergic role in producing GVL from EL. Moreover, the Al–Zr mixed oxide catalyst was able to be reused for several times with a slight loss in its catalytic activity.

1. Introduction

The depletion of fossil fuel reserves and environmental deterioration have stimulated researchers around the world to search for renewable resources to produce fuels and chemicals [1,2]. Considerable attention has been laid on the production of value-added chemicals and biofuels from biomass resources because of its renewable, abundant and widely distributed properties [3–6]. Various valuable compounds such as 5-hydroxymethylfurfural (HMF) [7–10], levulinic acid [11–13], 5-(ethoxymethyl) furfural (EMF) [14–16], sorbitol [17–18], and γ-valerolactone (GVL) [19] have been demonstrated to be capable of producing from biomass in recent years. Among those compounds, GVL with high boiling point (207 °C) and flash point (96 °C), as well as low melting point (−31 °C) and vapor pressure (3.5 kPa at 80 °C) is considered as a promising fuel additive [20]. More importantly, a number of value-added chemicals (e.g., methyl pentenoate [21] and ϵ-caprolactam [22]), and bio-based liquid fuels such as 2-methyltetrahydrofuran [23], valeric esters [24], and long chain liquid alkenes [25] were able to be produced from GVL.

The catalytic hydrogenation–cyclization of levulinic acid or its esters, capable of producing from carbohydrates [26–30], is a key step in production of GVL from biomass (Scheme 1) [31]. Unlike levulinic acid, alkyl levulinates possess relatively lower boiling points, as well as easy recovery and acid-free characteristics. Moreover, relatively higher yields of alkyl levulinate can be achieved from acid-catalyzed alcoholysis of carbohydrates [32–35]. In this respect, the catalytic conversion of alkyl levulinates to GVL seems to be more attractive, wherein hydrogenation of 2-ketone group to 2-CH_2OH is considered to be an important step, and various hydrogen sources including hydrogen, formic acid and alcohols are involved [36,37]. In the atmosphere of hydrogen gas, metal catalysts like Ru [38–41], Pd [42,43], Ag [44], Cu [45,46], Ni [47,48], Co [49] and Mo [50] particles have been demonstrated to be efficient for converting levulinic acid or its esters to GVL. However, some drawbacks are suffered when H_2 is used as the H-donor. For example, the procedure for catalyst preparation is somehow complicated, as it used to be reduced at the atmosphere of hydrogen at high temperatures. Moreover, the storage/usage of H_2 is expensive and unsafe. As an alternative way, more attention has been paid to use formic acid as H-donor, which is able to be produced from biomass-derived sugars [51–56]. However, acid-resistant catalysts bearing high selectivity to decompose formic acid into H_2 rather than CO and H_2O are highly demanded. In this case, only limited number of noble or non-noble

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http://dx.doi.org/10.1016/j.apcata.2015.10.049
0926-860X/

metal-based heterogeneous or homogeneous catalysts can satisfy these conditions.

Recently, the use of alcohols as hydrogen donor for the hydrogenation/hydrogenolysis of biomass derivatives such as furfural, HMF, and sugars to produce hydrogenates [57,58] has attracted a widespread attention, which is mostly ascribed to the sustainable catalytic process with alcohols obtainable from biomass [59]. Besides, the carbonyl products (e.g., acetone), which are formed from oxidation of alcohols, can be separated by simple distillation and reused elsewhere. Catalytic production of GVL from biomass derivatives through Meerwein–Ponndorf–Verley (MPV) reduction using alcohol as hydrogen donor, on the other hand, is highly chemo-selective reduction of carbonyl groups to alcoholic hydroxyl groups in organic chemistry [60]. This reaction pathway is generally called a catalytic transfer hydrogenation (CTH) process. In comparison to use H_2 or formic acid as hydrogen source, the catalytic transfer hydrogenation process offers many advantages. For example, inexpensive and abundant alcohol can be used as both hydrogen donor and solvent. What is more, MPV reduction reaction does not rely on zero valence metal catalysts, especially precious metals [60]. Various catalysts such as ZrO_2 [61,62], Raney Ni [63], Zr-Beta [64,65], $ZrO(OH)_2{\cdot}xH_2O$ [66], in situ generated $ZrO(OH)_2$ [67], $Ru(OH)_x/TiO_2$ [68] and Zr-HBA [69] have been explored for the production of GVL from levulinic acid and its esters. But, it is still necessary to improve the stability and reactivity of the catalysts. Thus, developing low-cost and more efficient catalysts for GVL production from levulinic acid and its esters by the CTH reaction is significant.

Mixed metal oxides are often preferable for heterogeneous catalysis due to their low cost and easy regeneration features [70,71]. On the other hand, the physical–chemical properties of mixed metal oxides such as surface area, thermal and chemical stability, and acid density are superior to their individual components [72–76]. Zr-based catalysts were reported to be efficient for MPV reduction [77–79], and Lewis acid or base sites were demonstrated to be responsible for the high activity of the reduction reaction [80,81]. Moreover, increasing acidity or basicity of heterogeneous catalysts is beneficial for the lactonization reaction to produce GVL [68,82]. Inspired by above findings, present work aims to incorporate aluminum into zirconia by co-precipitation method, so as to increase the Lewis acid or base contents, thus enhancing the producibility of GVL from ethyl levulinate. Gratifyingly, the combination of alumina with zirconia increases contents of both acid sites and base sites and even enlarges specific surface areas of the obtained catalysts. Importantly, all Al–Zr mixed oxides exhibit better catalytic activity than sole ZrO_2 and Al_2O_3, in which the mixed catalyst with a Zr/Al molar ratio of 3/7 shows the highest performance.

2. Experimental

2.1. Materials

Ethyl levulinate (99%), sec-butyl alcohol (AR, 98%), GVL (98%) and $ZrOCl_2{\cdot}8H_2O$ (98%) were purchased from Shanghai Aladdin Industrial Inc. $Al(NO_3)_3{\cdot}9H_2O$ (AR, ≥99%), 2-propanol (AR, ≥99.7%) and other reagents used in the work were obtained from Chongqing Chuandong Chemical Reagent Company. All chemicals were used as received without further purification.

2.2. Catalyst preparation

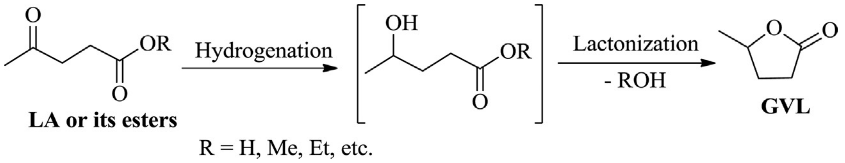
Al–Zr mixed metal catalysts were prepared by a co-precipitation method with slight modifications [83]. In a general procedure, $ZrOCl_2{\cdot}8H_2O$ (18 mmol) and $Al(NO_3)_3{\cdot}9H_2O$ (42 mmol) were dissolved in deionized water (120 mL) at room temperature. To the resulting transparent solution, aqueous ammonia (25–28%) was dropwise added under vigorous stirring, and the final pH value of the slurry was adjusted to 9. The white gel solution was aged at room temperature for 12 h, then filtered and washed with deionized water until no chloride ion was detected with $AgNO_3$ solution. The resulting precipitate was dried at 100 °C for 10 h, and then calcined at a specified temperature with a temperature gradient of 1 °C/min in air for 4 h to afford the final catalyst (7:3). By using the identical method, Al–Zr mixed oxides with different metal ratios were prepared, and denoted as Al_xZr_{10-x}-T (T on behalf of different calcination temperature). For comparison, sole Al_2O_3 and ZrO_2 catalysts were also synthesized in the same procedure.

2.3. Catalysts characterization

Powder X-ray diffraction (XRD) patterns were recorded using Bruker D8 Advance X-ray diffractometer with Cu Kα radiation ($\lambda = 1.54056$ nm) and the 2θ angle between 5 and 80°. Scanning electron microscopy (SEM) images were obtained using field-emission scanning electron microscopy (FESEM; JEOL, EOL, JSM-6700F, 5 kV). NH_3-TPD and CO_2-TPD were performed on an AutoChem 2920 chemisorption analyzer. The specific surface areas (Brunauer–Emmett–Teller) of the catalysts were obtained from nitrogen adsorption–desorption measurements, which were conducted on a Micromeritics ASAP2020 instrument, and the mean pore sizes and pore volumes were calculated from the Barrett–Joyner–Halenda method. Thermogravimetry (TG) analysis was determined by NETZSCHSTA 429 instrument in the range of room temperature to 800 °C with a heating rate of 10 °C/min under N_2 atmosphere (flow rate: 30 mL/min). The property of acid was measured by FT-IR of adsorbed pyridine, which was performed by PE Company. XPS was performed on Shandong TRW technology Co., LTD. with Thermo ESCALAB 250Xi instrument. The concentration of Al and Zr in the filtrate after removal of Al_7Zr_3-300 was measured by ICP-AES. Elemental analyses (Vario EL III, Elementar) were used to measure the carbon content of used Al_7Zr_3-300 catalysts.

2.4. Typical procedure for catalytic conversion of ethyl levulinate (EL) to GVL

Catalytic conversion of EL to GVL was performed in a 25 mL stainless steel autoclave with Teflon lined reactor under magnetic stirring, and placed in a temperature-controlled oil bath. As a typical run, 1 mmol EL, 5 mL alcohol as hydrogen donor and solvent, and 0.0721 g metal oxide catalyst were charged into the reactor, the vessel was sealed and zero time was taken as soon as the stainless steel autoclave placed into the preheated oil bath at a fixed temperature with stirring. When the reaction finished, the reactor



Scheme 1. The pathway for producing GVL from levulinic acid (LA) or its esters.