



## Research Paper

Catalytic transfer hydrogenation of ethyl levulinate to  $\gamma$ -valerolactone over a novel porous Zirconium trimetaphosphateYongdi Xie<sup>a</sup>, Fan Li<sup>b</sup>, Jianjia Wang<sup>a</sup>, Ruiying Wang<sup>a</sup>, Haijun Wang<sup>a,\*</sup>, Xiang Liu<sup>a</sup>, Yongmei Xia<sup>c</sup><sup>a</sup> The Key Laboratory of Food Colloids and Biotechnology, Ministry of Education, School of Chemical and Material Engineering, Jiangnan University, Wuxi 214122, China<sup>b</sup> School of Food Science and Technology, Jiangnan University, Wuxi 214122, China<sup>c</sup> State Key Laboratory of Food Science & Technology, Jiangnan University, Wuxi 214122, China

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## ABSTRACT

The synthesis of  $\gamma$ -valerolactone (GVL) from catalytic transfer hydrogenation (CTH) of levulinic acid (LA) and its esters is attracting more and more attention due to its wide application in additive, solvent, and precursor. Herein, a novel Zirconium trimetaphosphate (Zr-TMPA) was successfully synthesized and characterized by Fourier transform infrared, N<sub>2</sub> adsorption-desorption, powder X-ray diffraction, scanning electron microscopy, transmission electron microscopy, and NH<sub>3</sub>/CO<sub>2</sub>-TPD. The as-synthesized Zr-TMPA was used to catalyze the CTH reaction of EL to GVL using isopropanol as the hydrogen donor and solvent. Experimental results shown that Zr-TMPA could catalyze the CTH reaction and 96.2% GVL yield could be achieved at 160 °C for 8 h. Key to this success was attributed to the acid sites and basic sites of the prepared catalyst (Zr-TMPA). Finally, a possible reaction mechanism was proposed.

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## 1. Introduction

At present, the chemical and energy industries rely heavily on the use of fossil resources, which brings a lot of serious problems, so we need to seek an alternative resource for the production of valuable chemicals [1–3]. Biomass, which is a carbon-neutral resource, has been regarded as the renewable resource for the production of valuable chemicals [4,5]. Such as the most common levulinic acid (LA) [6], 5-hydroxymethylfurfural (HMF) [7], 2,5-dimethylfuran [8], furfural [9], furfuryl alcohol [10],  $\gamma$ -valerolactone (GVL) [11], and lactic acid [12], etc. Among them, GVL is one of the most valuable platform molecules, which can be applied directly as a food and fuel additive [13,14]. What's more, it has been used as a precursor for the production of 1,4-pentanediol, 2-methyltetrahydrofuran, perfume, and valeric acid [15–17].

Generally, GVL was mainly prepared from LA and its esters by direct or transfer hydrogenation. The former was usually conducted using various metal catalysis (such as Ru, Ni, Au, Ir, Pt, Pd, Rh) in the presence of external hydrogen [18]. Among them, the Ru- and Ni-based catalysts showed the highest catalytic activity. Tan et al.

developed a highly active and stable r-Ru-NH<sub>2</sub>- $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst, which obtained 99.1% yield of GVL at 25 °C for 13 h [19]. Jiang et al. found that mixed MgO–Al<sub>2</sub>O<sub>3</sub> supported Ni catalysts could achieve 99.7% yield of GVL at 160 °C, 1 h, and 3 MPa H<sub>2</sub> [20]. Although these catalysts have achieved good yield, they are still very difficult to apply in the industry because of the use of precious metals or molecular hydrogen. On the contrary, transfer hydrogenation, which using alcohols or formic acid (FA) as hydrogen donors, has aroused great concern [21]. Ruppert et al. reported the catalytic hydrogenation of LA with FA as a hydrogen source over Ru/C catalysts [22]. But the corrodibility of FA has limited the application in the CTH reaction. In recent years, the use of alcohol as a hydrogen donor has become mainstream in the CTH of LA and its esters to GVL. Most of them are secondary alcohols, for example, Cai et al. reported that 10Cu-5Ni/Al<sub>2</sub>O<sub>3</sub> had the highest activity for the CTH reaction of EL to GVL with 2-butanol as the hydrogen donor [23]. Chia and Dumesic found that reduction of LA and its esters to GVL could be achieved using secondary alcohols as the hydrogen donor over ZrO<sub>2</sub> catalysts [24]. It was not difficult to find that the non-precious metals catalysts have caused widespread concern. Recently, many catalysts, such as RANEY<sup>®</sup> Ni [25], Zr-beta zeolites [26], Zr(OH)<sub>4</sub> [27], Ni-Zr [28], Al-Zr [29], Ni-Fe/AC [30], and SnO<sub>2</sub>/SBA-15 [31], had been successfully applied to the reduction of LA and its esters to GVL. Especially, song and co-workers continuously reported that

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Zr-PhyA, Zr-HBA, and Hf-ATMP were used as efficient catalyst for the CTH of ethyl levulinate (EL) to GVL with isopropanol (IPA) as the hydrogen source and solvent [32–34]. Xue et al. synthesized a porous Zr-CA catalyst that has very high activity for the CTH of LA and its esters to GVL [35]. Although good yield of GVL and conversion of LA and its esters have been achieved, it is still necessary to overcome the low catalyst stability and harsh reaction conditions. Therefore, developing more efficient and stability catalysts for the CTH reaction of LA and its esters to GVL is significant.

Sodium trimetaphosphate (STMP, Schemes 1), which have three phosphate groups in its structure, is mainly used as a starch modifier, dispersant, and stabilizer in the food industry. The strong complexation of phosphoric acid makes it easy to combine with the four-valent metals [36]. In this work, we synthesized a novel Zirconium trimetaphosphate (Zr-TMPA) catalyst by the reaction of Sodium trimetaphosphate and  $ZrOCl_2$  for the CTH reaction of LA and its esters to GVL in the presence of isopropanol. As far as we know, Zr-TMPA as a catalyst for this reduction has not been reported. In addition, the effect of reaction time, temperature, and catalyst dosage for the CTH reaction of EL to GVL were investigated, and a possible reaction mechanism was put forward.

## 2. Experimental section

### 2.1. Materials

Sodium hexametaphosphate (SHMPA, AR),  $\gamma$ -valerolactone (98%), Sodium trimetaphosphate (STMPA, 95%), levulinic acid (99%), methyl levulinate (98%), ethyl levulinate (98%), butyl levulinate (98%),  $ZrOCl_2 \cdot 8H_2O$  (AR), and  $ZrO_2$  (AR) were purchased from Aladdin Industrial Inc. (Shanghai, China).  $SnCl_4 \cdot 5H_2O$  (AR),  $TiSO_4$  (AR), pyridine (AR), benzoic acid (AR), ethanol (AR), isopropanol (AR), and naphthalene (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). Deionized water was produced with a laboratory water-purification system (RO DI Digital plus). All reagents were commercially available and without further purification.

### 2.2. Catalyst preparation

#### 2.2.1. Synthesis of the Zr-TMPA

In a typical procedure, 10 mmol STMPA and 30 mmol  $ZrOCl_2 \cdot 8H_2O$  were dissolved in deionized water (200 mL), respectively. Then, the solution of STMPA was dropwise added to the solution of  $ZrOCl_2 \cdot 8H_2O$  in a stirred state. After that, the mixture was continuously stirred for 4 h and then aged for 12 h at room temperature. The white precipitate was separated by centrifugation, thoroughly washed with water and ethanol, and dried at 80 °C under vacuum for 12 h. For comparison, we synthesized three other Zr-TMPA with different Lewis acidity and basicity by the reaction of 10 mmol STMPA and X mmol  $ZrOCl_2 \cdot 8H_2O$  (X = 10, 20, 40), which denoted as Zr-TMPA-1, Zr-TMPA-2 and Zr-TMPA-4, respectively. Meanwhile, other catalysts with different metal ions were synthesized using a similar route for Zr-TMPA.

#### 2.2.2. Synthesis of the Zr-HMPA

In a typical procedure, 10 mmol SHMPA and 60 mmol  $ZrOCl_2 \cdot 8H_2O$  were dissolved in deionized water (200 mL), respectively. Then, the solution of SHMPA was dropwise added to the solution of  $ZrOCl_2 \cdot 8H_2O$  in a stirred state. After that, the mixture was firstly stirred for 4 h and then aged for 12 h at room temperature. The white precipitate was separated by centrifugation, thoroughly washed with water and ethanol, and dried at 80 °C under vacuum for 12 h.

### 2.3. Catalyst characterization

Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 360 FT-IR instrument (KBr discs) in the wavenumber range of 4000–500  $cm^{-1}$ . Powder X-ray diffraction (XRD) patterns were obtained on a Bruker D8 Advance diffractometer with Cu-K $\alpha$  radiation with a scanning rate of 4°/min at 40 kV and 20 mA. Scanning electron microscopy (SEM) images were obtained using a HITACHI S-4800 field-emission scanning electron microscope operated at 15 kV. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2100 microscope operated at 120 kV. The  $N_2$  adsorption-desorption isotherm using a Micromeritics ASAP 2020 provided the porosity properties of catalysts. The X-ray photoelectron spectroscopy (XPS) measurements were implemented on Perkin Elmer PHI 5000 ESCT System. The contents of P and Zr in Zr-HMPA and Zr-TMPA were determined by ICP-AES (Optima 8300). Temperature-programmed desorption of carbon dioxide ( $CO_2$ -TPD) was performed on Micromeritics AutoChem II 2920 Chemisorption analyzer. In the experiment, the catalyst was charged into the quartz reactor, and the temperature was increased from room temperature to 300 °C at a rate of 10 °C/min under a flow of He (50  $cm^3$ /min), and then the catalyst was kept at 300 °C for 5 h. After that, the temperature was decreased to 100 °C.  $CO_2$  (50  $cm^3$ /min) was pulsed into the reactor at 100 °C under a flow of He (10  $cm^3$ /min) until the basic sites were saturated with  $CO_2$ . The adsorbed  $CO_2$  was removed by a flow of He (50  $cm^3$ /min). When the baseline was stable, the temperature was increased from 60 °C to 600 °C at a rate of 10 °C/min.

Temperature-programmed desorption of ammonia ( $NH_3$ -TPD) was performed on Micromeritics AutoChem II 2920 Chemisorption analyzer. The catalyst was charged into the quartz reactor, and the temperature was increased from room temperature to 300 °C at a rate of 10 °C/min under a flow of He (50  $cm^3$ /min), and then the catalyst was kept at 300 °C for 5 h. After that, the temperature was decreased to 100 °C.  $NH_3$ /He (10/90, 50  $cm^3$ /min) was pulsed into the reactor at 100 °C under a flow of He (10  $cm^3$ /min) until the acid sites were saturated with  $NH_3$ . The adsorbed  $NH_3$  was removed by a flow of He (50  $cm^3$ /min). When the baseline was stable, the temperature was increased from 60 °C to 700 °C at a rate of 10 °C/min.

### 2.4. Catalytic transfer hydrogenation reaction

In a typical experiment, EL (1 mmol), isopropanol (5 mL) and the catalyst (200 mg) were charged into a stainless reactor of 25 mL equipped with a magnetic stirrer. The reactor was sealed and placed into a preheated oil-bath at a known temperature for the desired time. After the reaction, the liquid samples were analyzed quantitatively by gas chromatography (GC 9790) using naphthalene as the internal standard, and identification of the products was done by GC-MS (ULTRA QP2010). The yield of GVL and the conversion of EL were calculated using the following equations:

$$\text{Yield} = \frac{\text{Moles of GVL formed}}{\text{Moles of EL used}} \times 100\%$$

$$\text{Conversion} = \frac{\text{Moles of EL converted}}{\text{Moles of EL used}} \times 100\%$$

### 2.5. Reusability of the Zr-TMPA

To investigate the reusability of the Zr-TMPA catalyst, the catalyst was recovered by centrifugation and washed with ethanol. After drying under vacuum at 80 °C for 18 h, the catalyst was reused for the next run.

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