Zirconium-Gallic Acid Coordination Polymer: Catalytic Transfer Hydrogenation of Levulinic Acid and Its Esters into y-Valerolactone

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Abstract

The conversion of ethyl levulinate (EL) to produce γ -valerolactone (GVL) through catalytic transfer hydrogenation (CTH) reaction plays a crucial role in the field of biomass catalytic conversion. In this work, a novel Zr-base catalyst with phenate group, phenolic hydroxyl and carboxyl in its structure was prepared by the co-precipitation of natural sources gallic acid and ZrCl₄. It was found that Zr-GA has an excellent catalytic performance for this reaction and satisfactory GVL yield could be achieved. Besides, Zr-GA could be easily separated from the reaction system and reused at least six times without a significantly decrease in activity. Meanwhile, various characterizations had proved that Zr-GA is a porous material with acid-base bifunctional sites. The main reason for the high catalytic activity of the Zr-GA was that the synergetic effects of Lewis acid/ base sites and Brønsted acid sites and appropriate textural properties. In addition, a possible reaction mechanism was proposed in conjunction with the poisoning experiment and previous reports. The heterogeneous catalyst Zr-GA prepared with gallic acid as a raw material has low cost and recyclability, and has great potential in green chemistry.

Graphical Abstract



Extended author information available on the last page of the article



Keywords Ethyl levulinate \cdot $\gamma\text{-valerolactone}$ \cdot Zr-GA \cdot Catalytic transfer hydrogenation

1 Introduction

Due to the increasingly serious problems between the exploitation and use of fossil fuels and the environment, economy and politics, one of the most serious challenges of the 21st century is to replace fossil fuels with more sustainable alternatives [1, 2]. As the world's most important sustainable renewable green resource, biomass accounts for about 14% of the world total annual energy consumption. It is the fourth largest energy source after oil, coal, and natural gas, and becoming a kind of renewable substitutes that can replace petroleum-based resources are valued and favored by all countries [3, 4]. So far, various value-added chemicals have been obtained from biomass, such as 5-hydroxymethylfurfural, lactic acid, furfural, furfuryl alcohol, levulinic acid (LA), alkyl levulinate, and γ -valerolactone (GVL), etc. [5–11]. Among them, GVL has the property of non-toxic and biodegradable, which can be used as a green solvent and an intermediate for the production of high value-added chemicals and high-performance liquid fuels [12-14].

Carbonyl compounds can be reduced to alcohols through catalytic transfer hydrogenation (CTH) reactions. In this reaction, the alcohols used as a solvent and hydrogen source, and finally dehydrogenated to a ketone. CTH is a typical Meerwein-Ponndorf-Verley reaction and it is widely used in the reduction of carbonyl compounds. The use of a large number of safe secondary alcohols instead of dangerous gaseous hydrogen as H-donor makes it an ideal reduction technology for carbonyl compounds [15-17]. The methods of producing GVL mainly include direct hydrogenation and transfer hydrogenation. Between them, direct hydrogenation uses H_2 as a hydrogen source, which is not only costly, but has safety risks. At present, most of the researchers have solved the above-mentioned problems by means of transfer hydrogenation, using LA and its esters to prepare GVL through CTH. A large number of catalysts have been reported for this reaction, such as Zr-containing zeolite, ZrO₂, MOFs, GO, zirconium phosphates, supported heteropolyacid, metal hydroxides, organic-inorganic hybrid catalysts, etc. [18–26]. Among them, zirconium-based materials have received extensive attention due to their wide range of applications, in addition to being used for catalysis, they can also be used for adsorption and separation [27, 28]. So far, numerous Zr-containing organic-inorganic hybrid catalysts have been developed for the CTH reaction of LA and its esters, such as Zr-PhyA, Zr-HBA, Zr-CA, Zr-TMPA, Zr-TPPA-3, Zr-HPAA, etc. [29–34].

The synthesis of multifunctional materials using natural sources of chemical substances is becoming more and more important in the field of synthetic chemistry, especially multifunctional materials formed by chelating with metal ions [35]. Gallic acid is a kind of polyphenol compound, which is widely found in tea and it has been widely used in anti-oxidation and medicine [36]. In this work, we used gallic acid and ZrCl_4 as raw materials to synthesize a series of Zr-GA-x catalysts with different molar ratios in N,Ndimethylformamide and triethylamine. Using alcohol as a solvent and H-donor, LA and its esters were converted to GVL through CTH. It was found that the prepared Zr-GA-x can catalyze the CTH reaction to provide a satisfactory yield of GVL. As far as we know, this is the first report about the organic–inorganic hybrid catalyst Zr-GA-x has been used in the CTH reaction of LA and its esters to produce GVL, and the catalyst has the advantages of wide source of raw materials, easily assemble synthesis and high stability.

2 Experimental Section

2.1 Chemicals

Methyl levulinate (ML), ethyl levulinate (EL), butyl levulinate (BL), LA, ZrCl₄, gallic acid (GA), GVL, N,N-dimethylformamide (DMF), triethylamine, methanol, ethanol, n-propanol, isopropanol, 1-butanol, tert-butanol, 3-pentanol, benzoic acid, 2,6-lutidine, pyridine and naphthalene are of analytical grade and used without further treatment.

2.2 Catalyst Preparation

The preparation method of the as-prepared catalyst was referred to the previous literature and was modified [29]. In a general procedure, 0.476 g (2 mmol) of $ZrCl_4$ and 0.344 g (1 mmol) of GA dissolve in DMF (20 mL) with the aid of ultrasound, respectively. Then, the GA solution was added dropwise to the $ZrCl_4$ solution. After the mixture was clarified, 3 mL of triethylamine was added dropwise, stirred vigorously at room temperature for 2 h and then aged at 80 °C for 8 h. The mixed solution after aging was filtered, washed with DMF and ethanol. The obtained solid was placed in a vacuum drying oven at 80 °C for 14 h and then grounded to obtain Zr-GA. For comparison, different Zr-GA-x catalysts were synthesized by changing the raw material ratio, using x mmol of ZrCl₄ and 1 mmol of GA (x = 1, 2, 3, 4), named Zr-GA-1, Zr-GA-2/Zr-GA, Zr-GA-3, Zr-GA-4, respectively.

2.3 Catalyst Characterization

Fourier transform infrared (FT-IR) spectra were detected with a Nicolet 360 FT-IR instrument (KBr pellet) in the

range of 4000–600 cm⁻¹. X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advance diffractometer with Cu Ka radiation and 20 recorded from 5° to 90° at 30 kV and 10 mA. Scanning electron microscopy (SEM) images were obtained using a HITACHI S-4800 scanning electron microscope at 3 kV. Transmission electron microscopy (TEM) measurement was performed on a JEOL JEM-2100 microscope at 200 kV. The N₂ adsorption-desorption isotherm (BET) was measured using a Micromeritics ASAP 2020 instrument, samples were degassed at 120 °C for 12 h in a vacuum before N₂ absorption. Temperature-programmed desorption of ammonia/carbon dioxide (NH₃/CO₂-TPD) was performed on Micromeritics AutoChem II 2920 Chemisorption analyzer, the sample (50 mg) was charged into quartz reactor and preheated at 300 °C for 1 h at a rate of 10 °C min⁻¹ under a flow of He (50 cm³ min⁻¹). Then the temperature was dropped to 50 °C, NH₃/CO₂ (50 cm³ min⁻¹) was pulsed into the reactor in He flow until the acid sites was saturated. The absorbed NH₃ was removed with He and the temperature was raised from 60 to 600 °C at a rate of 10 °C min⁻¹ after waiting for baseline stabilization. The concentration of Zr in the reaction solution were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) which performed on PE Optima 8000.

2.4 CTH of EL to GVL

The CTH reaction from EL to GVL was carried out in a 25 mL Teflon-lined stainless-steel reactor equipped with a magnetic stirrer. In a typical procedure, EL (1 mmol), isopropanol (5 mL), and the catalyst (0.2 g) were added into the reactor. The reactor was sealed and placed into a preheated oil-bath at a desired temperature for a known time. At the end of the reaction, the reactor was cooled to room temperature and the liquid samples were collected and analyzed by gas chromatography (GC 9790) using naphthalene as the internal standard, and identification of the liquid products was identified by GC–MS (ULTRA QP2010). The

conversion of EL and yield of GVL were calculated by the formula following:

$$Yield of \ GVL = \frac{Moles \ of \ GVL \ formed}{Moles \ of \ EL \ used} \times 100\% \tag{1}$$

Conversion of
$$EL = \frac{Moles \ of \ EL \ converted}{Moles \ of \ EL \ used} \times 100\%$$
 (2)

2.5 Leaching Test and Reusability Test

To investigate the heterogeneity of the catalyst, it was removed from the reaction mixture after 7 h and then the reaction was continued. In the reusability tests, the spent catalyst was recovered by centrifugation and washed three times with isopropanol. After drying under vacuum at 80 °C for 14 h, the catalyst was reused for the next run.

3 Results and Discussion

3.1 Catalyst Characterization

The FT-IR spectra of GA and Zr-GA-x are shown in Fig. 1a. The strong peak at about 3400 cm⁻¹ was the stretching vibration of the sample physically adsorbing water and hydroxyl groups [19]. The peak at 1670 cm⁻¹ was attributed to the stretching vibration of the –COOH group, indicating that –COOH was present in both of GA and Zr-GA-x, demonstrating Zr was not coordinated with –COOH. At the same time, the FT-IR spectra of Zr-GA-x and GA all showed the characteristic asymmetric and symmetric stretching vibration of the phenolic hydroxyl group, and the corresponding ranges were 1613–1580 cm⁻¹ and 1499–1467 cm⁻¹, respectively. Compared with GA, the wavenumber difference of Zr-GA-x was reduced from 155 to 85 cm⁻¹, 87 cm⁻¹, 87 cm⁻¹ and 84 cm⁻¹, respectively, which proved that Zr and





the phenolic hydroxyl group in GA were successful coordinated [37]. According to the previously reported related



Fig. 2 SEM of Zr-GA-1 (a), Zr-GA (b), Zr-GA-3 (c), Zr-GA-4 (d) and TEM of Zr-GA $\left(e \right)$

literature, it was inferred that only two adjacent phenolic hydroxyl groups in GA coordinate with Zr [38-41]. In addition, the peak appearing at 477 cm⁻¹ was attributed to the Zr–O bond.

The crystal form of Zr-GA-x was explored by X-ray diffractometer. It can be seen from the Fig. 1b that Zr-GA-x had broad diffraction peaks, indicating that Zr-GA-x was an amorphous material with low crystallinity, and the low crystallinity might be due to the weak coordinating group (phenolic hydroxyl) in the structure [42]. The surface morphology and internal composition of Zr-GA-x catalyst were observed by SEM and TEM, the images are shown in Fig. 2. It can be seen that Zr-GA-x had no uniform shape, and the gap between the aggregated particles leaded to the porosity of the catalyst, which is consistent with the XRD result [32].

Meantime, the pore structure of the Zr-GA-x catalyst was checked by N_2 adsorption–desorption, and the results are shown in Fig. 3 and Table 1. It can be seen that the isotherms of Zr-GA-x exhibited type IV mode, showing obvious hysteresis loops, indicating that there was an irregular mesoporous structure in the Zr-GA-x catalyst. Consistent with the SEM and XRD results, the pores of the catalyst originated from the gaps between the aggregated particles. It can be seen from Table 1 that Zr-GA has the largest specific surface area, which is conducive to the abundant contact of the substrate with the active sites of Zr-GA, hence improving the catalytic activity.



Fig. 3 N_2 adsorption-desorption isotherm of Zr-GA-x. **a** Zr-GA-1, **b** Zr-GA, **c** Zr-GA-3 and **d** Zr-GA-4

Table 1	Textural	properties	of Zr-GA-x
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Entry	Catalyst ^a	Surface area (m ² /g) ^b	Pore diameter (nm) ^c	Pore volume (cm ³ /g) ^d
1	Zr-GA	142.1	9.39	0.35
2	Zr-GA-1	117.2	4.224	0.395
3	Zr-GA-3	133.14	6.427	0.433
4	Zr-GA-4	30.03	4.015	0.058

^aThe samples were degassed at 120 $^{\circ}\text{C}$ for 12 h

^bSurface area based on multipoint BET method

^cPore volume based on BJH method

^dPore diameter based on BJH method

3.2 Catalyst Screening

In the CTH reaction of converting EL to GVL, it is of great importance to select an excellent catalyst. Therefore, we explored the effects of different types of catalysts on the reaction in the initial investigation. As shown in Table 2, without the addition of catalyst, no reaction occurred (entry1). When using Zr-GA-x as the catalyst (entries 2–5), it can be seen that Zr-GA has the highest catalytic activity, the EL conversion and the GVL yield were reached 98.58% and 94.23%, respectively. Other Zr-GA-x also reached satisfactory EL conversion, meantime, the GVL vield was ranked as Zr-GA>Zr-GA-4>Zr-GA-1>Zr-GA-3, which can be seen that the catalytic effect had a wireless relationship with the magnitude of x. When ZrO₂ was used as a catalyst, a medium yield of GVL was obtained (entry 7), indicating that Zr was the active site of the reaction. Conversely, when GA was used as a catalyst and added to the reaction system (entry 6), there was almost no catalytic activity. These above results all indicated that the Lewis acid-base sites $(Zr^{4+}-O^{2-})$ obtained by the coordination of Zr and GA was essential for the CTH reaction for the conversion of EL to GVL. Therefore, Zr-GA was used as a catalyst to study the influence of other parameters on the reaction. Besides, the results of reaction conditions and activities of the Zr-GA catalyst and other reported catalytic systems have been summarized in Table S1.

3.3 Effect of Reaction Temperature and Time

During the reaction process, the trend of EL conversion and GVL yield with the reaction temperature and time is shown in Fig. 4. When the temperature increased from 140 to 160 °C, both the conversion of EL and the yield of GVL showed a rapid upward trend. The yield of GVL reached the maximum at 160 °C, indicating that high temperature promoted the reaction. However, when the temperature further increased to 170 °C, the yield of GVL began to decrease (Table 2, entry 8), which may be that higher temperature would cause the presence of side reactions and other by-products. Through the previous reports and the analysis of the substrate, we can infer that the by-product was isopropyl levulinate produced by the transesterification of EL and isopropanol [25, 32]. The effect of reaction time on the CTH reaction of EL was studied in the range of 5–10 h. It can be seen from Fig. 4 that when the reaction temperature is 140-150 °C, both the EL conversion and the GVL yield continue to increase with the extension of the reaction time. As the temperature continued to rise to 160 °C, the EL conversion and GVL yield increased steadily and reached the maximum at 8 h, 98.58% EL conversion and 94.23% GVL yield were obtained, respectively. When the reaction time was further extended to 10 h, both the EL conversion and GVL yield decreased, which may be due to the beginning of GVL converted into other byproducts. Therefore, the optimal reaction temperature was 160 °C, and the optimal reaction time was 8 h.

Entry	Catalyst	Temperature (°C)	Time (h)	C _{EL} (%)	Y _{GVL} (%)	S _{GVL} (%)
1	None	160	8	0	0	0
2	Zr-GA	160	8	98.58	94.23	95.59
3	Zr-GA-1	160	8	96.24	63.56	66.04
4	Zr-GA-3	160	8	97.61	60.01	61.48
5	Zr-GA-4	160	8	98.88	78.44	79.33
6	GA	160	8	10.42	1.16	11.13
7	ZrO_2	160	8	36.46	30.42	83.43
8	Zr-GA	170	8	99.46	87.56	88.04

 C_{EL} conversion of EL; Y_{GVL} yield of GVL; S_{GVL} selectivity of GVL

^aReaction condition: EL (0.144 g, 1 mmol), catalyst 0.2 g, iso-propanol 5 mL

Table 2Comparison ofdifferent catalysts for the CTHreaction of EL to produce GVL^a







Fig.5 Effect of catalyst amount. Reaction conditions: EL (0.144 g, 1 mmol), isopropanol 5 mL, reaction temperature 160 °C, reaction time 8 h

3.4 Effect of the Dosage of Catalyst

After exploring the effect of reaction temperature and time on the CTH reaction of EL, the dosage of catalyst added to the reaction system was studied under the reaction conditions of 160 °C and 8 h. As shown in Fig. 5, when the dosage of Zr-GA was 75-200 mg, as the dosage increased, both the EL conversion and the GVL yield increased rapidly, which may be due to the presence of more available active sites in the reaction system, which promoted the progress of the reaction. Subsequently, the dosage of catalyst continued to increase to 300 mg, the EL conversion and GVL yield began to decrease, which may be due to the excessive amount of catalyst would lead to poor dispersibility of the Zr-GA particles and have a negative impact on the mass transfer of the reaction [43]. Therefore, the addition of 0.2 g of Zr-GA would be the best choice for this reaction.

Table 3 The effect of the different H-donor on the CTH reaction of EL to $\ensuremath{\mathsf{GVL}}$

Entry	Solvents	C _{EL} (%) ^b	Y _{GVL} (%) ^b
1	Methanol	77.42	9.4
2	Ethanol	74.21	19.24
3	n-propanol	74.19	24.32
4	2-butanol	85.35	73.65
5	tert-butanol	13.21	0
6	3-pentanol	68.45	83.56
7	Isopropanol	98.58	94.23

 C_{EL} conversion of EL; Y_{GVL} yield of GVL

^aReaction conditions:0.20 g Zr-GA; 5 mL H-donor; 1 mmol EL; reaction temperature:160 $^\circ$ C; reaction time:8 h

^bProduct analysis were determined by GC

3.5 Catalytic Effect of H-Donor

The H-donor is a crucial parameter in the CTH reaction which acts as both a H-donor and a solvent. Therefore, primary alcohols (methanol, ethanol, n-propanol), secondary alcohols (isopropanol, 2-butanol, 3-pentanol) and tertbutanol were used as H-donor to study their effects on the CTH reaction of EL, and the results are shown in Table 3. When using primary alcohols as H-donor, high EL conversion could be obtained, however, the yield of GVL were relatively low (entries 1-3). When tert-butanol was used as a H-donor, the EL conversion was extremely low, indicating the presence of α -H in the alcohol was essential for the CTH reaction (entries 5) [44]. Therefore, primary and tertiary alcohols were not suitable as H-donor for CTH reactions. On the contrary, when using the secondary alcohols as H-donor, satisfactory EL conversion and GVL yield could be obtained (entries 4 and 6–7). With the extension of the carbon chain in the secondary alcohol, the conversion of EL decreased slightly. The possible reason for this phenomenon was that the extension of the secondary alcohol carbon chain would cause greater negative steric hindrance, preventing the diffusion of substrate molecules into the pores of Zr-GA [37]. Therefore, in the CTH reaction of converting EL to GVL, isopropanol would be the best choice of the H-donor and solvent.

3.6 Catalytic Effect of Zr-GA on Different Substrates

It can be seen from previous studies that Zr-GA has high catalytic activity for the CTH reaction of converting EL to GVL. Therefore, the catalytic performance of Zr-GA in the reaction of preparing GVL from other substrates was examined under optimal conditions. As shown in Table 4, when ML was used as a substrate, Zr-GA had high catalytic activity for the reaction, 98.32% ML conversion and 96.63% GVL yield were obtained (entry 2). On the contrary, BL showed lower reactivity than ML and EL, which may be due to the larger steric hindrance of butyl, only 81.56% of GVL yield was obtained (entry 4). In addition, LA could be easily converted to GVL. When the reaction time was 4 h, 100% LA conversion and 96.63% GVL yield could be achieved (entry 1). This phenomenon may be caused by the acidity of LA itself, which made the key intermediate 4-hydroxyvaleric acid lactonization faster, therefore generating GVL in a shorter time [25].

Table 4 The conversion of LA and its eaters into GVL through CTH reaction catalyzed by $Zr\text{-}GA^a$

Entry	Substrate	Time (h)	$C_{EL} \left(\%\right)^b$	Y _{GVL} (%) ^b
1	LA	4	100	96.63
2	ML	8	98.32	93.38
3	EL	8	98.58	94.23
4	BL	8	91.48	81.56

 C_{EL} conversion of EL; Y_{GVL} yield of GVL

^aReaction conditions: substrate (1 mmol), isopropanol (5 mL), Zr-GA (0.20 g), temperature (160 $^{\circ}$ C)

^bProduct analysis were determined by GC

Fig. 6 Leaching test of Zr-GA for the CTH of EL to produce GVL (**a**) and recycle experiment of the Zr-GA (**b**). Reaction conditions: EL (0.144 g, 1 mmol), catalyst 0.2 g, isopropanol 5 mL, reaction temperature 160 °C, reaction time 8 h

3.7 The Leaching Test and Reusability of the Catalyst

The heterogeneous catalyst has the advantages of easy recycling, cost reduction, and extremely good potential application value in the reaction of converting biomass into high value-added chemicals. Firstly, the heterogeneity of Zr-GA was checked by leaching test. It can be seen from Fig. 6a that the yield of GVL was around 85.23% after removing the Zr-GA, indicating that no active sites were leached into the reaction solution and Zr-GA had excellent heterogeneity. On the contrary, as the Zr-GA remained in the reaction system, the GVL yield increased continuously and eventually decreased. Secondly, the reusability of the catalyst was explored, and the results have shown in Fig. 6b. It was found that Zr-GA still had great catalytic activity after six cycles, and the yield of GVL was only slightly lower than that of the first cycle. The reaction solution after the sixth cycle was checked by ICP-OES, and it was found that the concentration of Zr was lower than 1.7 ppm. The decrease in catalyst activity may be due to the leaching of a small amount of Zr active sites. In addition, the Zr-GA after six cycles was characterized by FT-IR, XRD, SEM, and TEM. It can be seen from Fig. 7 that the amorphous morphology and microstructure of Zr-GA did not change much. In addition, the new peak around 2900 cm⁻¹ appeared in recovered Zr-GA in Fig. 7a might be due to the deposition of humins on the surface of Zr-GA. In summary, Zr-GA had outstanding heterogeneity and could be reused several times.

3.8 Explanation of the High Activity of Zr-GA

According to previous reports, the influence of the acidity and basicity of the catalyst on the CTH reaction of EL cannot be ignored. First, we checked the acidity of Zr-GA by NH₃-TPD. It can be seen from Fig. 8a that Zr-GA has two desorption peaks at 160 °C and 377 °C, corresponding to the weak acid site and the medium strong acid site, and the acidity was 1.55 and 2.70 mmol g⁻¹, respectively. The







Fig. 8 NH_3 -TPD (a) and CO_2 -TPD (b) of Zr-GA

first peak at 160 °C corresponded to a weak acid site, which was derived from Zr^{4+} and the phenolic hydroxyl group that were not coordinated with Zr in the GA structure. Generally speaking, the metal in the metal–ligand coordination polymer is Lewis acidic [45]. The second desorption peak was related to the -COOH group which was not coordinated with Zr in the GA structure. The existence of a large number of acidic sites can activate the activation of C=O in the substrate, therefore improving the reactivity [29].

Secondly, the basicity of Zr-GA was checked by CO_2 -TPD. It can be seen from Fig. 8b that there are a large number of basic sites in the Zr-GA catalyst, and the total amount is 4.98 mmol g⁻¹, which was originated from the

large number of phenate groups present in Zr-GA. According to reports, the phenate group can increase the basicity of the catalyst [30]. Higher basicity was conducive to the dissociation of the hydroxyl group in the isopropanol molecule, consequently increasing the CTH reactivity of EL [29, 46].

Except for the acidity and basicity of the catalysts, the textural properties of the catalyst might also affect the catalytic activity. As shown in Table 1, compared with other Zr-GA-x, Zr-GA has the largest specific surface area, which promotes the diffusion of the substrate to the active center of Zr-GA, hence achieving a better catalytic effect [31].

3.9 Poisoning Experiment

From the previous discussion, it is clear that the acid-base site is critical in the reaction of EL through CTH to prepare GVL. At the same time, the results of NH₃-TPD and CO₂-TPD also indicate that Zr-GA contains a large number of acid-base sites. Meantime, the acidic sites were mainly derived from Zr^{4+} , the –COOH and phenolic hydroxyl groups originated from GA, and the basic sites were mainly derived from O^{2-} in the phenate groups. In order to explore the effect of acid-base sites on the reaction, benzoic acid. 2,6-lutidine and pyridine were used to poison Lewis basic sites, Brønsted acid sites and Lewis acid sites, respectively. As shown in Table 5, when benzoic acid was added to the reaction system, it was observed that the GVL yield and EL conversion decreased significantly. This may be due to the strong interaction between the benzoic acid and the basic sites of Zr-GA, indicating that the CTH reaction catalyzed by Zr-GA was closely related to basic sites. The addition of pyridine also reduced the GVL yield and EL conversion. When 2,6-lutidine was used to poison Brønsted acidic sites, the EL conversion and GVL yield only slightly decreased, indicating that Brønsted acid sites can promote the CTH reaction. According to previous literature reports, compared with benzoic acid, 2,6-lutidine and pyridine have weaker poisoning effects [47]. Consequently, due to the partial poisoning of acid sites, the addition of 2,6-lutidine and

 Table 5
 Study on the activity of Zr-GA by benzoic acid, 2,6-lutidine and pyridine^a

Entry	additives	C _{EL} (%)	Y _{GVL} (%)	S _{GVL} (%)
1	No	98.58	94.23	95.59
2	Benzoic acid	61.53	43.95	71.43
3	2,6-lutidine	90.25	86.34	95.67
4	Pyridine	87.32	79.65	91.22

 C_{EL} conversion of EL; Y_{GVL} yield of GVL; S_{GVL} selectivity of GVL ^aReaction environments: 0.20 g Zr-GA; 5 mL isopropanol; 1 mmol EL; reaction temperature:160 °C; reaction time: 8 h

pyridine only slightly reduced the EL conversion and GVL yield. The above poisoning experiment further proved that

the acid-base sites in the Zr-GA catalyst were significant for the high catalytic performance.

3.10 Plausible Mechanism

It can be seen from the previous discussion that acidic and basic sites are indispensable for the CTH reaction. Based on previous reports and the above analysis, we proposed a possible reaction mechanism for Zr-GA to catalyze the conversion of LA and its esters to GVL (Scheme 1) [38, 39, 41]. First, isopropanol interacts with the acid-base coupled sites (-Ar-O₂-Zr-) on Zr-GA and dissociates into alkoxide and hydrogen protons. At the same time, the electron-withdrawing Brønsted acid site (Ar-OH) activates the C=O in the structure of LA and its ester, and then the activated C=O and the dissociated isopropanol form a six-membered ring transition state and undergo hydrogen transfer to produce 4-hydroxyvaleric acid and its esters. Finally, under the action of the acidic sites of Zr-GA, 4-hydroxyvaleric acid and its esters undergo intramolecular esterification or transesterification to produce the final product GVL.

4 Conclusions

In summary, we synthesized a new Zr-based heterogeneous catalyst (Zr-GA) with natural resource gallic acid as ligand through a simple co-precipitation method, and applied it to the reaction of LA and its esters to prepare GVL through CTH reaction. Characterization and experimental results showed that Zr-GA has excellent catalytic activity. Under the optimized reaction conditions, the LA and its esters conversion and GVL yield could reach more than 90%. The high activity of the catalyst is attributed to the synergistic effect of Lewis acid sites from Zr⁴⁺, Brønsted acid sites from phenolic hydroxyl groups, and Lewis base sites from phenolate groups. In addition, the Zr-GA catalyst can be reused six times without significantly catalytic activity loss. Finally, a possible reaction mechanism for the conversion of LA and its esters to produce GVL was proposed. Due to Zr-GA has the characteristics of low cost and recyclability, it has potential applications in the catalytic conversion of biomass and its derivatives.



Scheme 1 Plausible mechanism of CTH reaction of EL into GVL over Zr-GA

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Declarations

Conflict of interest The authors declare no conflict of interests.

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