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## ARTICLE

# New porous Zr-containing catalyst with phenate group: efficient catalyst for catalytic transfer hydrogenation of ethyl levulinate to $\gamma$ -valerolactone

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Catalytic transfer hydrogenation (CTH) of ethyl levulinate (EL) to  $\gamma$ -valerolactone (GVL) is a very attractive reaction in the field of biomass transformation. In this work, a new porous Zr-containing catalyst with phenate group in its structure was prepared by the coprecipitation of 4-hydroxybenzoic acid dipotassium salt and  $\text{ZrOCl}_2$  (Zr-HBA) in water and characterized by powder X-Ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM),  $\text{N}_2$  adsorption-desorption, and Fourier transform infrared spectroscopy. The Zr-HBA was used as the catalyst for CTH of EL to GVL in the presence of isopropanol, and the effects of temperature, time, and amount of the catalyst on the reaction were studied. It was found that Zr-HBA was very active for the reaction and a GVL yield of 94.4% could be achieved. Meanwhile, the Zr-HBA could be reused at least five times without notable decrease in activity and selectivity. The main reason for the high catalytic activity of the Zr-HBA was that the existence of phenate in the structure of Zr-HBA increased the basicity of the catalyst, which is favourable to the CTH of EL.

## Introduction

With the gradual depletion of fossil resources and the growing concerns on global climate change, development of efficient technologies for transformation of biomass into liquid fuels and valuable chemicals has received much attention.<sup>1</sup> Up to now, various value-added chemicals could be obtained from biomass, including different alcohols,<sup>2</sup> gluconic acid,<sup>3</sup> 5-hydroxymethylfurfural,<sup>4</sup> lactic acid,<sup>5</sup> 2,5-dimethylfuran,<sup>6</sup> levulinic acid,<sup>7</sup>  $\gamma$ -valerolactone (GVL),<sup>8</sup> etc. Among these chemicals, GVL has been considered as a versatile platform chemical, which can be used as a fuel additive, solvent for biomass processing, and a precursor for the production of alkanes and valuable chemicals.<sup>9</sup>

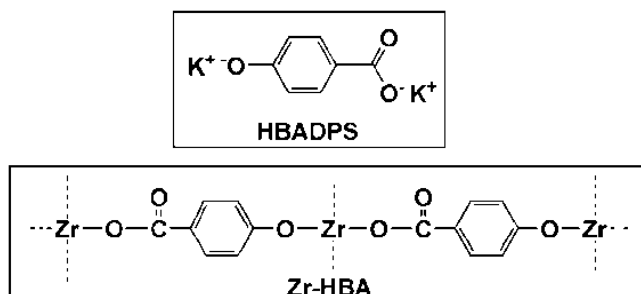
Many methods have been reported for the production of GVL. Generally, GVL is currently produced by hydrogenation of levulinic acid (LA) and its esters in the presence of various metal catalysts, such as Pd, Ru, Rh, Pt, Re, Ni, Co, Mo, and Cu.<sup>10</sup> However, these hydrogenation strategies suffer from high  $\text{H}_2$  pressure, the use of precious metals, and low catalyst stability or reactivity, which limit their large-scale application to a certain degree. Furthermore, formic acid has been used as

an alternative to  $\text{H}_2$  for the GVL production from LA over supported Au catalysts<sup>11</sup> or immobilized Ru catalysts.<sup>12</sup> Although good yields of GVL were achieved, the need of noble metals and/or harsh conditions and the corrodibility of formic acid still limited the application of this method. Therefore, development of new efficient methods for the production of GVL is highly desired.

It is well-known that catalytic transfer hydrogenation (CTH) reactions offer an attractive alternative to  $\text{H}_2$  for the reduction of carbonyl compounds.<sup>13</sup> The reduction of carbonyl group is an important step in the production of GVL from LA and its esters. Some catalysts have been developed for the CTH of LA and its esters to produce GVL. For example, Chia and Dumesic reported that CTH of LA and its esters could be carried out *via* Meerwein-Ponndorf-Verley (MPV) reduction catalyzed by  $\text{ZrO}_2$  in the presence of secondary alcohols.<sup>14</sup> Lin and co-workers found that CTH of ethyl levulinate (EL) could proceed over  $\text{ZrO}_2$  in supercritical ethanol<sup>15</sup> or metal hydroxides in alcohols.<sup>16</sup> In addition, Zr-Beta zeolite could be used as efficient catalysts for CTH of LA and its esters *via* MPV reduction for the production of GVL.<sup>17</sup> Recently, an efficient CTH route to convert EL to GVL has been reported by

using Raney Ni as the catalyst.<sup>18</sup> Although these catalysts were efficient for the CTH of LA and its esters, there existed some limitations, including long reaction time,<sup>14</sup> high reaction temperature,<sup>15,16</sup> low catalyst stability or reactivity,<sup>18</sup> etc. Therefore, it is very attractive to develop more efficient and stable catalysts for CTH reaction of LA and its esters to produce GVL.

It has been reported that the carboxylate and phenate on benzene ring could be coordinated with metal ions.<sup>19</sup> It was also proved that the existence of phenate could increase the basicity of the synthesized catalyst.<sup>19c</sup> Meanwhile, increasing the basicity of the catalyst could enhance the activity of CTH reaction.<sup>14</sup> Herein, we synthesized a new porous Zr-containing catalyst (Zr-HBA hereafter) using 4-hydroxybenzoic acid dipotassium salt (HBADPS, Scheme 1) and  $\text{ZrOCl}_2$  in water for the CTH reaction of EL to produce GVL using isopropanol as the hydrogen source and solvent. The reason for using EL as reactant instead of LA was that the catalyst prepared was sensitive to acid. At the same time, the production of ester levulinate from lignocellulose has higher yield and the product separation is easier.<sup>20</sup> The as-prepared catalyst contained both carboxylates and phenates, leading to high active, selective and stable of the Zr-HBA for the reaction. To the best of our knowledge, this is the first report for the synthesis of the novel porous Zr-containing catalyst (Zr-HBA) and its application to catalyze the CTH reaction of EL to produce GVL.

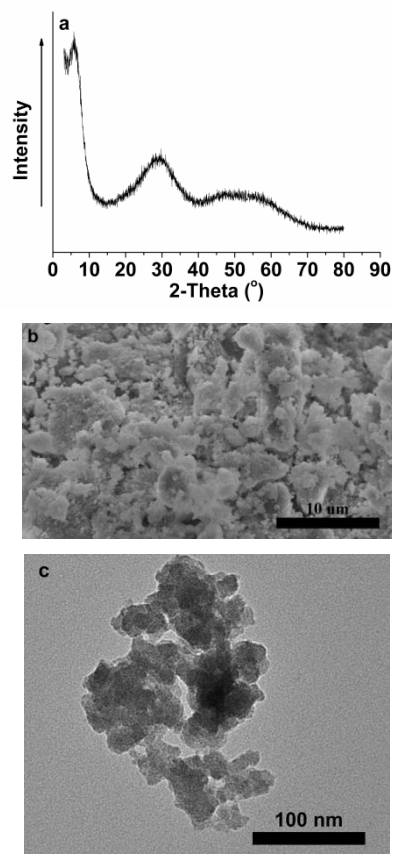


**Scheme 1.** The structure of HBADPS and Zr-HBA.

## Results and discussion

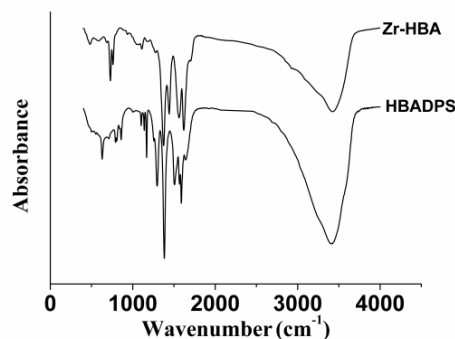
### Catalyst characterization

The synthetic procedure for Zr-HBA was presented in detail in the Experimental section. The powder XRD pattern of the synthesized catalyst is shown in Fig. 1a. It could be seen that the catalyst had no X-ray crystal structure. In the structure of HBADPS, there are only one strong coordination group (carboxylate) and one weak coordination group (phenate). Less strong coordination groups resulted in the lower degree of crystallinity for the as-prepared catalyst. Meanwhile, the XRD pattern showed one broad diffraction peak, indicating that the obtained catalyst was amorphous. The scanning electron microscopy (SEM) and transmission electron microscopy (TEM) demonstrated that the catalyst had no uniform shape (Fig. 1b, 1c and Fig. S4).



**Fig. 1.** Powder XRD pattern (a), SEM image (b) and TEM image (c) of the as-prepared Zr-HBA.

Fourier transform-infrared (FT-IR) technique was also used to characterize the as-prepared catalyst (Fig. 2). The FT-IR spectrum of the as-prepared catalyst displayed the characteristic asymmetric ( $1624\text{cm}^{-1}$ ,  $1556\text{cm}^{-1}$ ) and symmetric vibration ( $1445\text{cm}^{-1}$ ,  $1379\text{cm}^{-1}$ ) of carboxylate anions. In comparison with the FT-IR spectrum of HBADPS, the wavenumber difference of asymmetric and symmetric vibration of carboxylate anions is narrowed.<sup>21</sup> This indicated that carboxylate groups were coordinated to  $\text{Zr}^{4+}$  ions. The observed strong peaks at about  $3450\text{cm}^{-1}$  should be assigned to the adsorbed water.



**Fig. 2.** FT-IR spectra of Zr-HBA and HBADPS.

The textural parameters of the synthesized Zr-HBA were investigated by N<sub>2</sub> adsorption-desorption method after the sample was degassed at 100 °C for 24 hours. It can be seen that the N<sub>2</sub> adsorption-desorption isotherm of the catalyst exhibited a type IV mode, showing pore condensation with pronounced adsorption-desorption hysteresis (Fig. 3). The result in Fig. 3 indicates that the Zr-HBA prepared was porous. The porosity of the catalyst could result from the gaps between the aggregated particles (shown in Fig. 1c). The average pore diameter, Brunauer-Emmett-Teller (BET) surface area, and pore volume calculated from the N<sub>2</sub> adsorption-desorption were 8.0 nm, 87.3 m<sup>2</sup>g<sup>-1</sup>, and 0.21 cm<sup>3</sup>g<sup>-1</sup>, respectively. The low BET of the as-prepared catalyst was due to use of water as the solvent.<sup>22</sup> The amount of micropores in the Zr-HBA was very limited, which can be known from the fact that the Zr-HBA had a very low N<sub>2</sub> adsorption capacity when the relative pressure (P/P<sub>0</sub>) was as low as 0.01 in the N<sub>2</sub> adsorption-desorption isotherm (Fig. 3).<sup>23</sup>

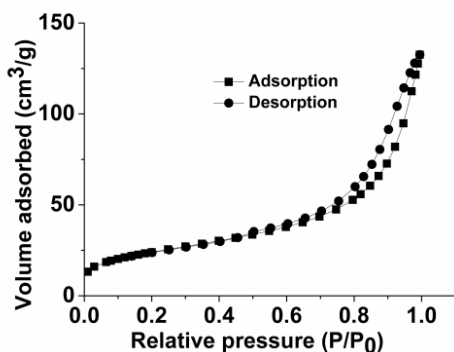


Fig.3. N<sub>2</sub> adsorption-desorption isotherm for Zr-HBA.

### Catalytic performance of different catalysts

The activity and selectivity of various catalysts were tested for the CTH reaction of EL to produce GVL using isopropanol as the hydrogen source and solvent, and the results are given in Table 1. The reaction did not occur in the absence of the catalyst (entry 1, Table 1). When HBADPS was used as the catalyst, the main product was isopropyl levulinate generated from transesterification of EL with isopropanol (entry 2, Table 1). Although GVL could be produced with moderate yields when Zr-containing compounds, such as ZrOCl<sub>2</sub>, ZrO<sub>2</sub> and Zr-BDC, were used as the catalysts, the selectivity for GVL was not satisfactory because large amounts of isopropyl levulinate were produced as by-products in the reaction process (entries 3-5, Table 1). Surprisingly, the reaction proceeded with much higher conversion and selectivity when the as-prepared Zr-HBA was used as the catalyst (entry 6, Table 1). Less transesterification product was formed over Zr-HBA, which may result mainly from the high activity of Zr-HBA for CTH reaction of EL and isopropyl levulinate. The main reason for the excellent performance was probably that the existence of carboxylate and phenate in the structure of Zr-HBA increased the basicity of the catalyst,<sup>19c</sup> which has been proved by that increasing the basicity could increase the yield and selectivity of the CTH reaction.<sup>14</sup> In order to prove the effect of phenate, we synthesized a Zr-containing metal-organic framework (Zr-BDC), which was formed by the coordination between Zr<sup>4+</sup> and benzene-1,4-dicarboxylic acid (BDC) in the absence of phenate. The result showed that the Zr-BDC had lower activity than the Zr-HBA (entry 5, Table 1) although Zr-BDC had similar pore volume and higher surface area than the Zr-HBA (Fig. S1 and

Table S1). Thus, we can deduce that the phenate could increase the reaction activity. Furthermore, it has also been reported that Sn-containing compounds could catalyze the CTH reaction. In this work, we also synthesized Sn-HBA for comparison and found that Zr-HBA had better catalytic activity than Sn-HBA (entry 7, Table 1), which was consistent with the results obtained from the catalytic systems of zeolites.<sup>17</sup> Furthermore, it was also demonstrated that the Zr-HBA prepared in our work had better performance than other Zr-based catalysts reported in the literature when the reaction was conducted under comparable reaction conditions (entries 8-13, Table 1).

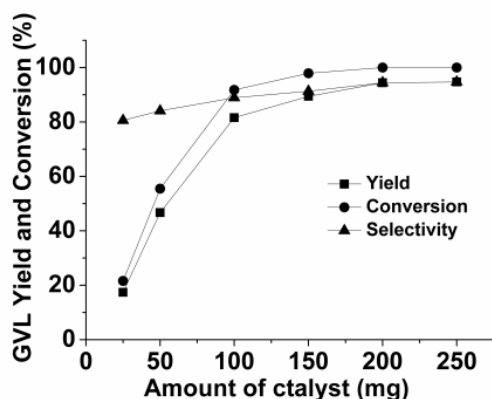
Table 1. CTH reaction of EL in isopropanol catalyzed by different catalysts.<sup>a</sup>

Entry	Catalyst	Tem. (°C) <sup>b</sup>	Time (h)	Con. (%) <sup>c</sup>	GVL yield (%) <sup>c</sup>	Sel. <sup>d</sup>
1	None	150	4	0	0	---
2	HBADPS	150	4	62.1	1.8	2.9
3	ZrOCl <sub>2</sub>	150	4	84.7	43.7	51.6
4	ZrO <sub>2</sub>	150	4	24.7	21.3	86.2
5	Zr-BDC <sup>e</sup>	150	4	62.9	15.9	25.3
6	Zr-HBA	150	4	100	94.4	94.4
7	Sn-HBA	150	4	43.1	30.7	71.2
8 <sup>f</sup>	Zr-HBA	150	4	100	95.9	95.9
9 <sup>f,g</sup>	Zr-Beta	150	6	100	92	92
10	Zr-HBA	200	1	100	96.8	96.8
11 <sup>h</sup>	Zr(OH) <sub>4</sub>	200	1	93.6	88.5	94.5
12	Zr-HBA	120	4	82.1	50.1	61.0
13 <sup>i</sup>	ZrO <sub>2</sub>	120	4	36.6	12.2	33.3

<sup>a</sup>Reaction conditions: a stainless reactor of 22 mL; catalyst 0.2 g; EL 1 mmol; isopropanol 100 mmol. <sup>b</sup>Tem.=Temperature. <sup>c</sup>Conversion (Con.) and GVL yield were determined by GC. <sup>d</sup>Sel.=Selectivity and the other products were mainly isopropyl levulinate produced by transesterification of EL with isopropanol. <sup>e</sup>Zr-BDC was obtained from ZrCl<sub>4</sub> and BDC in N,N-dimethylformamide. <sup>f</sup>The hydrogen donor was 2-butanol. <sup>g</sup>The data was obtained from reference 17b. <sup>h</sup>The data was obtained from reference 16. <sup>i</sup>The data was obtained from reference 14.

### Effect of catalyst amount

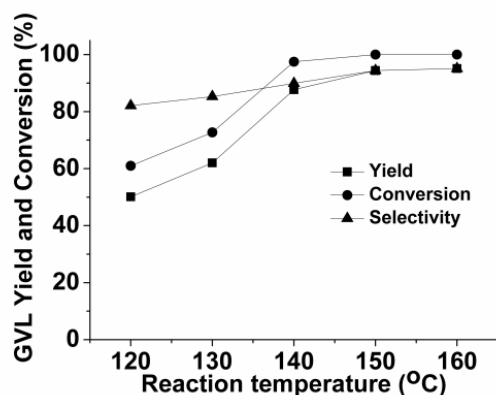
Effect of the amount of Zr-HBA on the CTH reaction of EL was studied in isopropanol at 150 °C with a reaction time of 4 h, and the results are shown in Fig. 4. It can be known from the figure that the conversion of EL and the yield and selectivity of GVL increased with the amount of the catalyst at the beginning. 100% conversion of EL and 94.4% yield and selectivity of GVL were obtained as the catalyst amount was 200 mg. Our experiments indicated that the by-products were mainly isopropyl levulinate produced from transesterification of EL with isopropanol in the reaction process, which could also be converted into GVL with a lower reaction rate under a similar process with EL. Therefore, 200 mg of the catalyst would be an appropriate amount at the reaction conditions.



**Fig. 4.** Effect of Zr-HBA amount. Reaction conditions: EL 1 mmol; isopropanol 100 mmol; reaction temperature 150 °C; reaction time 4 h.

### Influence of reaction temperature

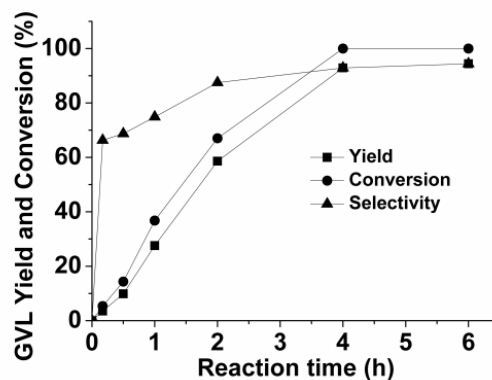
Fig. 5 demonstrates the influence of reaction temperature on the CTH reaction of EL in the range of 120-160 °C with a reaction time of 4 h. It can be seen that the reaction temperature affected the reaction significantly. The conversion of EL and the yield and selectivity of GVL increased with increasing temperature, and was nearly independent of temperature after 150 °C.



**Fig. 5.** Influence of reaction temperature. Reaction conditions: EL 1 mmol; isopropanol 100 mmol; Zr-HBA 200 mg; reaction time 4 h.

### Influence of reaction time

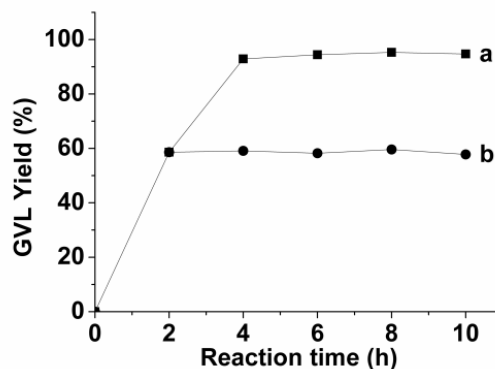
The influence of reaction time was investigated at the reaction temperature of 150 °C in the presence of 200 mg Zr-HBA (Fig. 6). In a relatively short reaction time, the conversion of EL was incomplete and the selectivity was low with isopropyl levulinate produced. It is shown in Fig. 6 that the conversion of EL and the yield and selectivity of GVL increased with increasing reaction time from 0 to 4 h. Full conversion of EL and 94.4% yield of GVL could be achieved with a reaction time of 4 h. No obvious increase in the yield and selectivity of GVL was observed with prolonged reaction time because nearly all of the EL could be converted in 4 h.



**Fig. 6.** Influence of reaction time. Reaction conditions: EL 1 mmol; isopropanol 100 mmol; Zr-HBA 200 mg; reaction temperature 150 °C.

### The leaching and heterogeneity of the catalyst

To study the leaching of the catalytic species and heterogeneity of the catalysis, the effect of reaction time on the CTH reaction of EL in the presence of isopropanol catalyzed by Zr-HBA at 150 °C was compared with that of another reaction where the reaction was stopped after 2 h, and then continued after filtering out the solid catalyst. The results are shown in Fig. 7. It is obvious that there was no further increase in the product yield after the solid catalyst was removed, confirming that the active site in Zr-HBA was not soluble in the reaction mixture and the reaction was proceeded with heterogeneous catalysis. The thermogravimetric analysis in this work indicated that the decomposition temperature of the as-prepared catalyst was 350 °C, which was much higher than the reaction temperature.

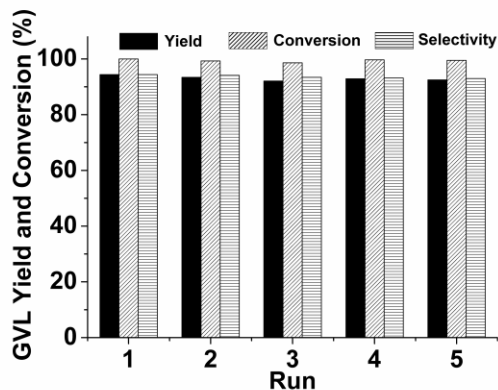


**Fig. 7.** (a) Time-yield plots for the CTH reaction of EL catalysed by Zr-HBA. Reaction conditions: EL 1 mmol; isopropanol 100 mmol; Zr-HBA 200 mg; reaction time 4 h; reaction temperature, 150 °C. (b) The line shows the GVL yields upon removing the solid catalyst after 2 h and continued up to 10 h.

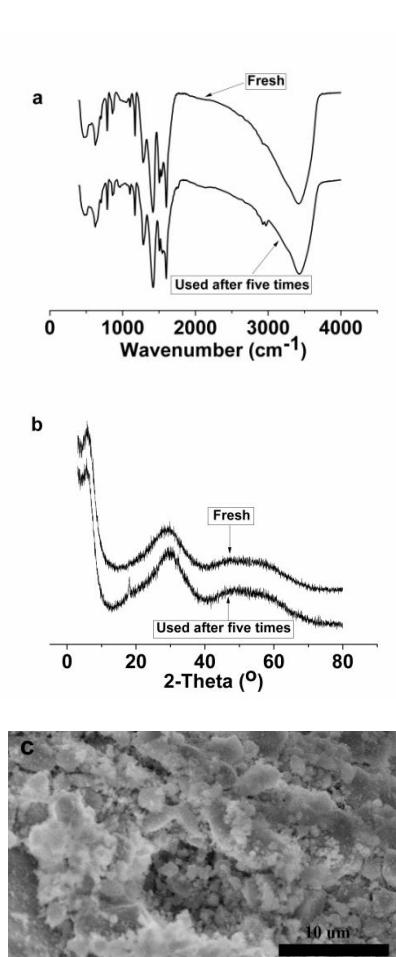
### Reusability of the catalyst

Experiments were also carried out to examine the reusability of the Zr-HBA. In each cycle, Zr-HBA was recovered by centrifugation. Then, the catalyst was reused directly after washed by ethyl ether and dried for the next run. The conversion of EL and the yield and selectivity of GVL for the

five repeated runs are shown in Fig. 8. There was no notable decrease in the conversion, yield and selectivity after five cycles, indicating that the catalyst was very stable. The Zr-HBA recovered after reused five times was characterized by FT-IR (Fig. 9a), XRD (Fig. 9b) and SEM (Fig. 9c). It can be known that the properties of the Zr-HBA were not changed after being used. These results provided further evidences that the catalyst was stable in our reaction system.



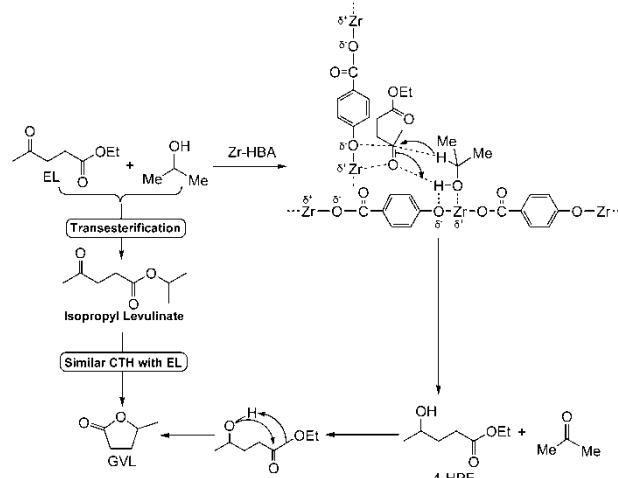
**Fig. 8.** Reusability of the catalyst. Reaction conditions: EL 1 mmol; isopropanol 100 mmol; Zr-HBA 200 mg; reaction temperature 150 °C; reaction time 4 h.



**Fig. 9.** The characterization of the catalyst Zr-HBA after reused five times. FT-IR spectrum (a), XRD pattern (b), and SEM image (c).

## Mechanism

Acidic and basic sites in the catalyst are crucial for CTH reaction.<sup>13</sup> Through the characterizations of NH<sub>3</sub>-TPD (Fig. S2) and CO<sub>2</sub>-TPD (Fig. S3) techniques, we can conclude that there were both acid sites and basic sites on the Zr-HBA. The acid sites were mainly originated from the Zr<sup>4+</sup> and the basic sites resulted mainly from O<sup>2-</sup> in the carboxylate and phenate groups.<sup>15,19c</sup> Based on the results above and some related knowledge in the literatures,<sup>13a,15</sup> we proposed a possible mechanism of CTH reaction of EL to GVL catalyzed by Zr-HBA (Scheme 2). Firstly, the interaction of isopropanol with the acid-base sites (Zr<sup>4+</sup>-O<sup>2-</sup>) on Zr-HBA leads to its dissociation to the corresponding alkoxide. At the same time, the carbonyl group in EL can be adsorbed and activated by Zr<sup>4+</sup>-O<sup>2-</sup> on Zr-HBA. Then, hydrogen transfer takes place between the dissociated alcohol and the activated EL *via* a concerted process involving a six-link intermediate to form ethyl 4-hydroxypentanoate (4-HPE). Finally, the 4-HPE is converted into GVL through an intramolecular transesterification. Meanwhile, isopropanol is converted into acetone after losing two hydrogen atoms. In the reaction process, the by-product isopropyl levulinate can be formed by transesterification of EL with isopropanol. Similarly, the isopropyl levulinate can be transformed into GVL by CTH reaction with the similar way like EL.



**Scheme 2.** Possible mechanism for the transformation of EL to produce GVL catalyzed by Zr-HBA *via* CTH reaction.

## Conclusions

In summary, a new porous Zr-containing catalyst (Zr-HBA) with the existence of phenate group has been synthesized and used as the heterogeneous catalyst for the CTH reaction of EL to produce GVL in the presence of isopropanol. Full conversion of EL and GVL yield of 94.4% can be obtained under the optimal conditions. Catalytic activity of the Zr-HBA is very high for the reaction, mainly because the existence of phenate in the Zr-HBA structure increases the basicity of the catalyst, which was beneficial for the CTH reaction of EL. The catalyst can be reused at least five times without reducing the activity and selectivity. We believe that the catalyst has potential applications in the synthesis of GVL from CTH reaction of EL.

## Experimental section

## Material

Ethyl levulinate (98%),  $\gamma$ -valerolactone (98%), terephthalic acid (99%) and isopropanol (99.5%) were provided by J&K Scientific Ltd.  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (AR),  $\text{ZrO}_2$  (AR) and  $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$  (AR) were purchased from Beijing Chemical Reagent Company. 4-Hydroxybenzoic acid dipotassium salt (99.9%) was obtained from Beijing Institute of Chemical Reagent.

## Preparation and characterization of Zr-HBA

In a typical procedure,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  (0.1 mol) and 4-hydroxybenzoic acid dipotassium salt (0.2 mol) were dissolved in water (250 mL), respectively. Then, the solution of 4-hydroxybenzoic acid dipotassium salt was dropwise added into the solution of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  with a time of 2 h. After that, the mixture was continued stirred for 6 h. The white precipitate was separated by filtration, thoroughly washed with  $\text{H}_2\text{O}$  and ethanol, and dried at 80 °C under vacuum for 12 h.

The scanning electron microscopy (SEM) measurements were performed on a Hitachi S-4800 Scanning Electron Microscope operated at 15 kV. The samples were spray-coated with a thin layer of platinum before observation. The transmission electron microscopy (TEM) images were obtained using a TEM JeoL-1011 with an accelerating voltage of 120 kV. The sample was dispersed in ethanol with the aid of sonication and dropped on an amorphous carbon film, supported on a copper grid, for the TEM analysis. Powder XRD patterns were recorded on Rigaku D/max-2500 X-ray diffractometer using  $\text{Cu-K}\alpha$  radiation ( $\lambda=0.15406$  nm) at a scanning rate of 5 degree  $\text{min}^{-1}$ . The tube voltage was 40 kV and the current was 200 mA. FT-IR spectra were obtained using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The porosity properties were determined by nitrogen adsorption-desorption method using a Micromeritics ASAP 2020m system. The thermogravimetric analysis of the Zr-HBA catalyst was performed on a thermogravimetric analysis system (Netzsch STA 409 PC/PG, Germany) in  $\text{N}_2$  atmosphere at a heating rate of 20 °C  $\text{min}^{-1}$ .

## Catalytic reaction

In a typical experiment, EL (1 mmol), isopropanol (100 mmol) and catalyst (200 mg) were charged into a stainless reactor of 22 mL equipped with a magnetic stirrer, which was similar to that used previously.<sup>24</sup> After sealed, the reaction mixture was stirred at a known temperature for the desired time. After the reaction, the products were analyzed quantitatively by a gas chromatography (GC, Agilent 6820) using ethylbenzene as the internal standard, and identification of the products was done by GC-MS (Shimadzu QP2010). The yield of GVL was calculated by the following equation:

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

## Reusability of the Zr-HBA

In the experiments to test the reusability of the Zr-HBA, the catalyst was recovered by centrifugation, washed using ethyl ether. After drying under vacuum at 80 °C for 12 h, the catalyst was reused for the next run.

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## Notes and references

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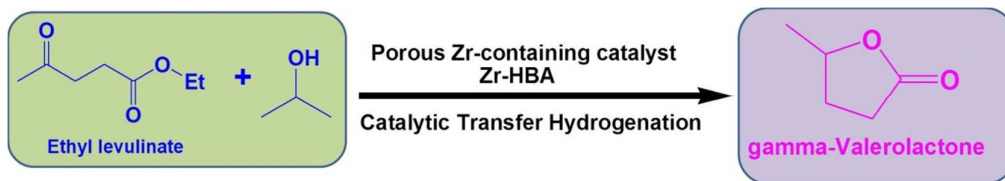
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## Graphical abstract

New porous Zr-containing catalyst (Zr-HBA) could be used as heterogeneous catalyst for efficient catalytic transfer hydrogenation of ethyl levulinate to  $\gamma$ -valerolactone.



## Supplementary Information for

### **New porous Zr-containing catalyst with phenate group: efficient catalyst for catalytic transfer hydrogenation of ethyl levulinate to $\gamma$ -valerolactone**

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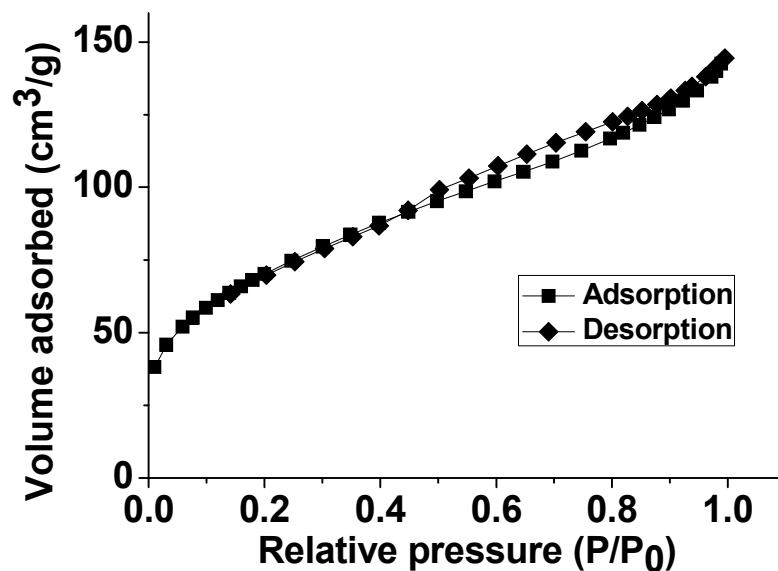
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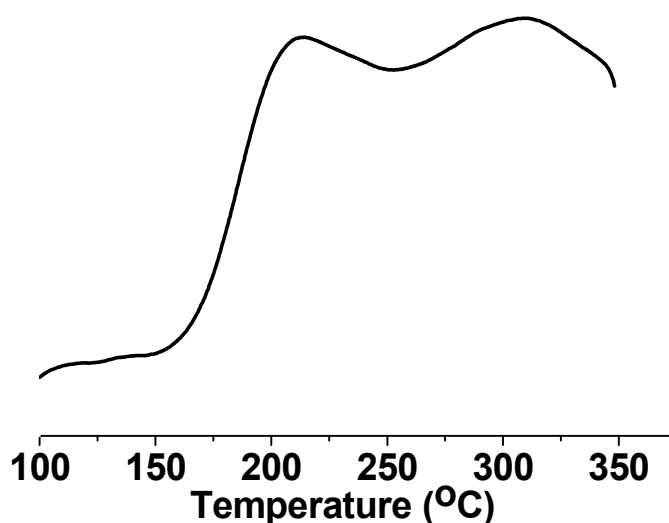
**1. Table S1.** Physical properties of Zr-BDC and Zr-HBA.

Sample <sup>a</sup>	BET surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>b</sup>	Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>c</sup>	Pore diameter (nm) <sup>d</sup>
Zr-BDC	257.9	0.20	4.5
Zr-HBA	87.3	0.21	8.0

<sup>a</sup>The sample was degassed at 100 °C for 24 h. <sup>b</sup>Surface Area based on multipoint BET method. <sup>c</sup>Pore volume and pore diameter based on BJH method.

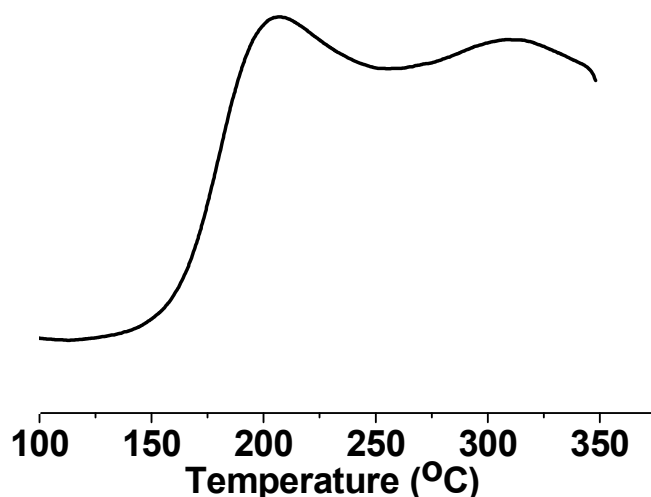
**2. Fig. S1****Fig. S1.** N<sub>2</sub> adsorption-desorption isotherm for Zr-BDC.

## 3. Fig. S2



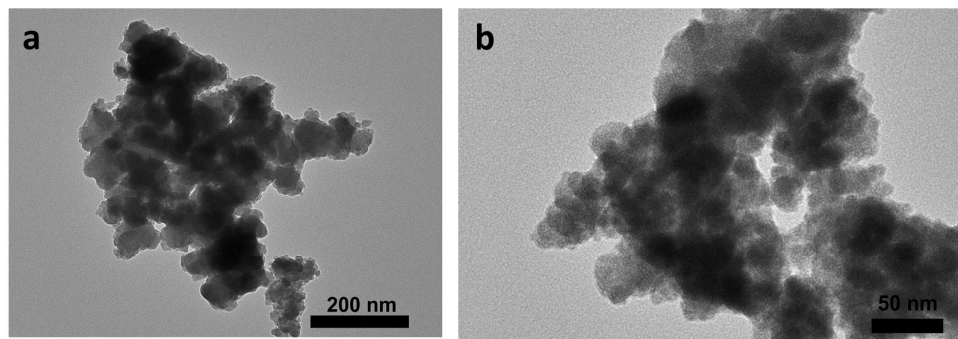
**Fig. S2.** NH<sub>3</sub>-TPD spectra of Zr-HBA. Temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. The catalysts were charged into the quartz reactor, and the temperature was increased from room temperature to 150 °C over 1 h at a rate of 10 °C min<sup>-1</sup> under a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>), and then the temperature was decreased to 50 °C. NH<sub>3</sub>/He (10/90, 50 cm<sup>3</sup>min<sup>-1</sup>) was pulsed into the reactor at 50 °C under a flow of He (10 cm<sup>3</sup>min<sup>-1</sup>) until the acid sites were saturated with NH<sub>3</sub>. The adsorbed NH<sub>3</sub> was removed by a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>). When the baseline was stable, the temperature was increased from 50 °C to 350 °C at a rate of 10 °C min<sup>-1</sup>. The NH<sub>3</sub>-TPD curve of the Zr-HBA was shown in Fig. S2. Due to the decomposition temperature of the as-prepared catalyst was about 350 °C, the test could conduct under the temperature lower than 350 °C. It could be found that there existed large amounts of acid sites, which were mainly resulted from Zr<sup>4+</sup> (*RSC Adv.*, 2013, 3, 10277).

## 4. Fig. S3



**Fig. S3.** CO<sub>2</sub>-TPD spectra of Zr-HBA. Temperature-programmed desorption of carbon dioxide (CO<sub>2</sub>-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. The catalysts were charged into the quartz reactor, and the temperature was increased from room temperature to 150 °C over 1 h at a rate of 10 °C min<sup>-1</sup> under a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>), and then the temperature was decreased to 50 °C. CO<sub>2</sub> (50 cm<sup>3</sup>min<sup>-1</sup>) was pulsed into the reactor at 50 °C under a flow of He (10 cm<sup>3</sup>min<sup>-1</sup>) until the acid sites were saturated with CO<sub>2</sub>. The adsorbed CO<sub>2</sub> was removed by a flow of He (50 cm<sup>3</sup>min<sup>-1</sup>). When the baseline was stable, the temperature was increased from 50 °C to 350 °C at a rate of 10 °C min<sup>-1</sup>. The CO<sub>2</sub>-TPD curve of the Zr-HBA was shown in Fig. S3. Due to the decomposition temperature of the as-prepared catalyst was about 350 °C, the test could conduct under the temperature lower than 350 °C. It could be found that there existed large amounts of basic sites, which were mainly resulted from O<sup>2-</sup> in the carboxylate and phenate groups (*RSC Adv.*, 2013, 3, 10277).

## 5. Fig. S4



**Fig. S4.** TEM image of the as-prepared Zr-HBA.