Zr-DBS with Sulfonic Group: A Green and Highly Efficient Catalyst for Alcoholysis of Furfuryl Alcohol to Ethyl Levulinate

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Abstract



The alcoholysis of furfuryl alcohol (FA) produce ethyl levulinate (EL) plays a crucial role in the field of biomass conversion. In this work, a novel Zr-base catalyst with sulfonic groups in its structure was prepared by the co-precipitation of sodium dodecyl benzene sulfonate and ZrOCl₂ (Zr-DBS) under non-toxic conditions. It was found that Zr-DBS has an excellent catalytic performance for this reaction and an EL yield of 95.27% could be achieved. Besides, Zr-DBS could be easily separated from the reaction system and reused at least four times without a significantly decrease in activity. Meanwhile, Zr-DBS was characterized by Fourier transform infrared spectroscopy (FT-IR), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N₂ adsorption–desorption, inductively coupled plasma optical emission spectroscopy (ICP-OES) and Temperature-programmed desorption of ammonia (NH₃-TPD). The main reason for the high catalytic activity of the Zr-DBS was that the synergetic effects of Lewis and Brønsted acid sites and appropriate textural properties.

Graphic Abstract



Keywords Furfuryl alcohol · Alcoholysis · Zr-DBS · Ethyl levulinate

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1 Introduction

The gradual decrease in fossil fuels indicates the need to find wide variety of renewable and alternative energy sources to meet the increase of energy demand. Therefore, researchers around the world have paid more attention to the technology

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of utilizing various cheap and available substances, such as convert biomass and waste CO2 into value-added chemicals [1, 2]. Among them, as one of the most abundant renewable energy sources available, biomass is not only cheap and easy to obtain, but also uses agricultural waste, and is regarded as the raw material of green chemistry in the future [3]. So far, a variety of value-added chemicals can be obtained from biomass, such as furfural, furfuryl alcohol (FA), levulinic acid (LA), alkyl levulinate (AL), y-valerolactone (GVL), etc. [4-8]. Among them, AL is a series of short-chain biomass platform chemicals, and it has many applications in industry, including biofuel additive, lubricants, spices, plasticizing and flavoring agents [9-12]. Owing to its two functional groups, ester group and carbonyl group, it can be converted into other more valuable biomass platform chemicals through substitution, addition, condensation, hydrolysis and other reactions, such as the conversion of ethyl levulinate to GVL by Meerwein–Ponndorf–Verley reaction [13].

There are three main ways to produce AL: direct alcoholysis of biomass, esterification of LA and alcoholysis of furfuryl alcohol [14, 15]. The most common raw materials for direct alcoholysis from biomass are cellulose, glucose and fructose. The problems faced by this process are low yield of target product, a lot of impurities and difficult separation. Direct esterification from LA is a typical acid-catalyzed reaction, but LA is expensive which makes it cannot be widely used. The alcoholysis of FA is an acid-catalyzed reaction of FA and alcohol. Witnessed tremendous progress in alcoholysis in recent years, it has significant advantages compared with the conventional hydrolysis, such as inhibiting the formation of humins as well as increasing the reaction rate and product yield [14]. In the last decade, various catalysts have been gradually applied to this reaction, such as zeolite, metal triflates, metal salt, metal oxides, ionic liquid, resin, graphene, arylsulfonic acid functionalized hollow mesoporous carbon spheres, supported TPA catalysts, sulfonated carbon materials, etc. [16-24].

Zr-containing organic-inorganic hybrid materials have been applied in several catalytic reaction in the field of biomass conversion, such as using phytic acid and humic acid as building blocks were reported for the production of γ -valerolactone from ethyl levulinate [13, 25]. To date, several Zr-based catalysts have been reported for the alcoholysis of FA to AL, including ZPS, SZF, PW₁₂/ZrO₂-Si(Et)Si-NTs and MZM [26-29]. However, the complex and time-consuming preparation and high energy consumption are still serious problems. Therefore, it is crucial to find an efficient and cost-effective catalyst in the present research. As a common anionic surfactant, Sodium dodecylbenzene sulfonate (SDBS) has a sulfonic group in its structure, which can coordinate with metals. Herein, we use co-precipitation method to synthesizes SDBS with ZrOCl₂ in water to synthesize a catalyst for the alcoholysis of FA in ethanol to produce

EL. The catalyst has the advantages of abundant and easily obtained raw materials, simple preparation process without excessive energy loss, non-toxic solvent and cost-effective.

2 Experimental Section

2.1 Chemicals

Furfuryl alcohol, methyl levulinate, ethyl levulinate (EL), butyl levulinate, levulinic acid, $ZrOCl_2 \cdot 8H_2O$, $Ti(SO_4)_2$, SDBS, Sodium dodecyl sulfonate (SDS), methanol, ethanol, iso-propanol, 1-butanol, naphthalene and deionized water are of analytical grade and used without further treatment.

The esterification of iso-propanol and LA is catalyzed by HCl to synthesize isopropyl levulinate (IPL), which is then purified by distillation. The purity was analyzed by gas chromatography-flame ionization detection (GC-FID) and proved to be greater than 99%.

2.2 Catalyst Preparation

The preparation method of the as-prepared catalyst is referred to the previous literature and is modified [30]. In a general procedure, 1 mmol SDBS and 2 mmol ZrOCl₂·8H₂O were dissolved in deionized water (25 mL) respectively. Then, the ZrOCl₂·8H₂O solution was dropwise added to the stirring solution of SDBS. After that the mixture was stirred vigorously for 5 h and then aged for 5 h at room temperature. The white precipitate obtained was isolated by centrifugation and then washed several times with water and ethanol, and finally dried at 60 °C under vacuum for 14 h, denoted as Zr-DBS. For comparison, other catalysts were prepared using the same raw material molar ratio as Zr-DBS and similar methods. One was to use $Ti(SO_4)_2$ instead of ZrOCl₂·8H₂O to coordinate with SDBS, named Ti-DBS and the other was to use SDS instead of SDBS to coordinate with ZrOCl₂·8H₂O, named Zr-DS.

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 and10 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 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 (NH₃-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 (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 700 °C at a rate of 10 °C min⁻¹ after waiting for baseline stabilization. The contents of Zr, S, C in Zr-DBS and 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 Alcoholysis of FA to EL

The alcoholysis reaction from FA to EL was carried out in a 25 mL Teflon-lined stainless-steel reactor equipped with a magnetic stirrer. In a typical procedure, FA (1 mmol), ethanol (10 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 known temperature for the desired 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 FA and yield of EL were calculated by the formula following:

$$YieldofEL = \frac{Moles \ of \ EL \ formed}{Moles \ of \ FA \ used} \times 100\%$$
(1)

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

2.5 Leaching Test and Reusability Test

To investigate the heterogeneity of the catalyst, the catalyst was removed from the reaction mixture after 1 h and then the reaction was continued. The Zr specie leached into the reaction mixture were analyzed by ICP-OES. In the reusability tests, the spent catalyst was recovered by centrifugation and washed three times with ethanol. After drying under vacuum at 60 °C for 14 h, the catalyst was reused for the next run.

3 Results and Discussion

3.1 Catalyst Characterization

The FT-IR spectrum of SDBS and Zr-DBS were shown in Fig. 1a. Strong peaks at 3418 cm^{-1} was ascribed to the

physically adsorbed water [31, 32]. A multitude of bands in the region 2840–2930 cm⁻¹ was assigned to the stretching vibrations of aliphatic C-H and band in 1600 cm⁻¹ was assigned to the vibrations of benzene [33, 34]. The band at 1460 cm⁻¹ was due to C=C stretching vibration in aromatic carbon. The sample also had a band at about 670 cm⁻¹ arose from –C–S– bonds vibration of sulfonic groups [35]. Both Zr-DBS and SDBS showed the characteristic bands of S=O symmetric stretching vibration of sulfonic groups, and the as-prepared catalyst showed the characteristic absorption peaks of sulfonate anions at 1156 cm⁻¹ and 1036 cm⁻¹ [34–36]. Compared with the FT-IR spectrum of SDBS, the difference in the wavenumber of the vibration of the sulfonate anion is narrowed, indicating that the sulfonate was coordinated with Zr⁴⁺ ions [37, 38].

The XRD pattern of the Zr-DBS are shown in Fig. 1b. Obviously, the Zr-DBS had a broad diffraction peak, indicating that Zr-DBS was amorphous. Generally speaking, the presence of weak coordination groups in the catalyst structure will lead to low crystallinity, indicating that the low crystallinity of Zr-DBS comes from the only weak coordination groups (sulfonic groups) in the structure [39]. The textural properties of Zr-DBS were characterized by N₂ adsorption-desorption isotherm. It could be seen that Zr-DBS belonged to typical type IV isotherms (Fig. 1c), indicating Zr-DBS is a mesoporous material with irregular pore structure, which was in consistent with the pore size distribution (Fig. 1d). The porosity of the Zr-DBS was caused by the gaps between the aggregated particles (shown in Fig. 2a). Besides, Brunauer-Emmett-Teller (BET) surface area and pore volume and the average pore size calculated from N₂ adsorption–desorption were 6.24 m² g⁻¹, 0.033 cm³ g⁻¹ and 21.65 nm, respectively. When the relative pressure (P/P_0) of N₂ adsorption is as low as 0.01, the N₂ adsorption capacity of Zr-DBS is very low in the N2 adsorption-desorption isotherm, indicating that the number of micropores in Zr-DBS is very limited [40]. This can also be seen from the SEM image (Fig. 2a). Although the specific area and pore volume is limited, its large pore size helped to enhance the diffusion of FA to the active center of the as-prepared catalyst and then promoted the reaction.

Meantime, the surface morphology and internal composition of the prepared catalyst were observed by SEM and TEM, the images are shown in Fig. 2a and b. It can be seen that Zr-DBS has no uniform shape, and the gap between the aggregated particles leads to the porosity of the catalyst, which is consistent with the XRD result [30].

3.2 Catalyst Screening

The importance of an excellent catalyst for the alcoholysis of FA to EL is conspicuous. As shown in Table 1, in the absence of catalyst, no reaction occurred (Table 1, entry 1).



Fig. 1 Characterization of Zr-DBS. a FT-IR spectra, b Powder XRD pattern, c N2 adsorption-desorption isotherm, d pore size distribution



Fig. 2 SEM image (a) and TEM image (b) of Zr-DBS

When Zr-DBS catalyst was used for this reaction, it was not difficult to find that Zr-DBS possessed the highest activity with 95.27% EL yield at 150 °C for 2 h (Table 1, entry 2). In contrary, Ti-DBS was little activity for this reaction (Table 1, entry 3). For comparison, Zr-DS, having a similar structure to Zr-DBS, was obtained a moderate yield of EL (Table 1, entry 4). Afterwards, SDBS and SDS were used to catalyze the reaction, little EL yield could be observed (Table 1, entries 5 and 6). These results demonstrated that Zr was the activity center for the alcoholysis of FA to EL and

 Table 1
 Comparison of different catalysts for the reaction of alcoholysis of FA to EL

Entry	Catalyst	Tem- perature (°C)	Time (h)	Conversion _{FA} (%)	Yield _{EL} (%)
1	None ^a	0	0	0.96	0
2	Zr-DBS ^a	150	2	98.83	95.27
3	Ti-DBS ^a	150	2	32.74	10.34
4	Zr-DS ^a	150	2	90.28	56.32
5	SDBS ^a	150	2	3.64	0.97
6	SDS ^a	150	2	30.65	1.63

 $^{\mathrm{a}}\text{Reaction}$ condition: FA (0.098 g, 1 mmol), catalyst 0.2 g, ethanol 10 mL

the addition of a sulfonic group could help to achieve high EL yield. Therefore, Zr-DBS was considered as the most suitable catalyst in the next study. The reason for the high activity of the catalyst will be discussed below. Meantime, the results of reaction conditions and activities of the present catalyst and other reported catalytic systems have been summarized in Table S2. Compared with other alcoholysis catalysts, the Zr-DBS catalyst prepared in this study can provide relatively high conversion and yield (both higher than 95%). In terms of reaction conditions and the cost of catalyst preparation materials, Zr-DBS catalyst has obvious advantages compared with other catalysts, especially the inherent sulfonic groups in SDBS could serve as Brønsted acidic sites avoiding the use of hazardous sulfonating agents.

3.3 Effect of Reaction Temperature and Time

As we all known, the reaction temperature and time are critical to the reaction. Consequently, the alcoholysis of FA to EL was performed at different temperature and time over Zr-DBS (Fig. 3). As shown in Fig. 3, the yield EL and the conversion of FA continuously increased when the temperature increased from 120 to 150 °C, which suggested that the alcoholysis of FA to EL was easier to proceed at high temperature. However, the FA conversion only slightly increased and the EL yield began to decrease when the temperature rose to 160 °C, which may be because the high temperature promoted the side reaction. Therefore, 150 °C was the optimal reaction temperature. Obviously, the yield of EL and conversion of FA increased rapidly as the reaction time increased from 1 to 2 h. Although the conversion rate of FA remains constant, when the reaction time is extended to 4 h, the EL yield began to decreased, indicating that 2 h is the most suitable reaction time to obtain the target product. As a result, 150 °C and 2 h were the best reaction conditions.

3.4 Effect of the Amount of Catalyst

The effect of the Zr-DBS dosage was investigated in the range of 0.1 to 0.4 g and the results have presented in Fig. 4. It was obvious that the conversion of FA and the yield of EL increased from 89.18 and 82.26% to 98.83 and 95.27%, respectively. When the amount of catalyst increased from 0.1 to 0.2 g, the conversion of FA and the yield of EL increased rapidly, which could be attributed to more available active sites. However, further increasing the amount of catalyst led to a slight decrease in EL yield. It may be due to the excessive amount of catalyst, resulting in poor dispersion of heterogeneous catalyst particles, which has a negative impact on the mass transfer of the reaction. Hence, 0.2 g of the Zr-DBS would be the best choice in the next experiments.



Fig. 3 Effect of reaction time and temperature on the FA conversion (a) and EL yield (b). Reaction conditions: FA (0.098 g, 1 mmol), catalyst 0.2 g, ethanol 10 mL



Fig.4 Effect of catalyst amount. Reaction conditions: FA (0.098 g, 1 mmol), 10 mL ethanol, reaction temperature 150 $^{\circ}C$, reaction time 2 h

3.5 Catalytic Effect of Zr-DBS on Different Substrates

Due to the high activity of Zr-DBS for the alcoholysis of FA to EL, other alcohols were also used as substrate to produce other AL. As displayed in Fig. 5, methanol and 1-butanol were easily converted to corresponding levulinate in 2 h with yields of 89.76% and 80.89% respectively. Hence, methanol and 1-butanol could achieve good results like ethanol. On the contrary, only 73.39% furfuryl alcohol conversion and 63.84% IPL yield could be observed at the same reaction conditions because of the steric hindrance of isopropyl [41]. These discussions have fully demonstrated that the Zr-DBS has an excellent catalytic activity for the production of AL from the alcoholysis of furfuryl alcohol and different alcohols.

3.6 The Leaching Test and Reusability of the Catalyst

To investigate the stability and reusability of the Zr-DBS, a leaching test and recycle experiment were conducted under the optimal reaction conditions, respectively. As shown in Fig. 6a, after the removal of Zr-DBS, no further reaction proceeded, and the EL yield remained at about 60.02%, indicating that there are no or few active sites in the reaction system. On the contrary, as the catalyst remains in the reaction system, the yield of EL increases steadily. The ICP-OES results showed that the Zr/S molar ratio in fresh and spent Zr-DBS was about 2:1, and there was no significant compositional change in the filtered sample, implying that a little active species was leached into the reaction mixture and the heterogeneous character of Zr-DBS (Table 2).



Fig. 5 Effect of catalyst with different substrates. Reaction conditions: 1 FA (0.098 g, 1 mmol), catalyst 0.2 g, ethanol 10 mL, reaction temperature 150 $^{\circ}$ C, reaction time 2 h

The stability of the Zr-DBS catalyst used for the alcoholysis of FA was also checked under the optimal reaction conditions. Although the EL yield in the reaction system decreased systematically after the catalyst was reused 4 times (Fig. 6b), the catalyst remained active in each cycle, indicating that the Zr-DBS in the reaction was stable. The decrease in EL yield in the recycling run probably due to the deposition of carbonaceous products produced by the reaction process deactivating the catalyst surface [41]. The Zr-DBS used after four cycles was characterized by FT-IR, XRD and SEM. It can be seen from Fig. 7 that the amorphous morphology and microstructure of the recovered Zr-DBS remain basically unchanged compared with the fresh catalyst. Meantime, ICP-OES result showed that less than 2.8 ppm of Zr specie leached into the filtrate after the fourth round of reaction, indicating that a small amount of Zr active sites were lost, resulting in a slight decrease in catalytic performance. These findings demonstrate that the Zr-DBS can be recovered and reused very well in the alcoholysis of furfuryl alcohol and the active site of the Zr-DBS was insoluble in the reaction system.

3.7 Explanation of the High Activity of Zr–DBS

From the previous analysis, it can be seen that Zr-DBS has a high activity to the alcoholysis reaction of FA to produce EL. Firstly, the total acidity of Zr-DBS was checked by NH₃-TPD (Fig. 8). It can be seen, there are two desorption peaks located at 133 °C and 473 °C, indicating the coexistence of weak and strong acid sites and the acidity amounts are 0.146 and 1.04 mmol g⁻¹, respectively. The first peak corresponds to the weak acidic site. Since there were almost no hydroxyls in Zr-DBS, we consider that the weak acidic sites mainly derived from the Zr⁴⁺. In general, the metal ions



Fig. 6 Leaching test of Zr-DBS for the alcoholysis of FA to EL (a) and recycle experiment of the Zr-DBS (b). Reaction conditions: FA (0.098 g, 1 mmol), catalyst 0.2 g, ethanol 10 mL, reaction temperature 150 °C, reaction time 2 h

Table 2Composition of Zr,S, C in Zr-DBS determined by	Catalysts	Content (wt.%)		
ICP-OES		Zr	S	С
	Fresh	24.08	4.32	32.57
	Spent	23.44	4.16	34.05

in the metal-ligand coordination polymers exhibit Lewis acidity [42]. The second peak relate to the strong acid site originated from the sulfonic group showing Brønsted acidity. The high catalytic activity of Zr-DBS can be attributed to the synergistic effect of these two acid sites.

In addition, the structure of the catalyst will also affect the activity of the catalyst. The N_2 adsorption–desorption isotherm and pore size distribution of Zr-DBS has shown in Fig. 1c and d. The large pore diameter and pore volume were helpful for increasing the diffusion of the reactants to the activity center, and thus promoted the reaction with a high activity. Therefore, a large number of acid sites and appropriate texture properties result in high catalytic activity of Zr-DBS.

3.8 Plausible Mechanism

According to literatures, multiple routes for producing AL from FA have been proposed, including the key intermediate EMF. Combining the experiment results and some previous reports [43, 44], we proposed a possible reaction mechanism of Zr-DBS catalyzing FA to produce EL through alcoholysis (Scheme 1). Firstly, the hydroxyl groups of FA are protonated by acidic groups and then attacked by ethanol to form EMF. Subsequently, EMF and ethanol generate 2-ethoxy-5-methylene-2,5-dihydrofuran through 1,4-addition. In the process of 1,4-addition, an ethanol molecule is released, and then under the action of water molecules, the ring is opened and subsequent tautomerized leading to the generation of EL.



Fig. 7 The characterization of the Zr-DBS after reused for four times. a FT-IR spectrum, b XRD pattern and c SEM image



Fig. 8 NH₃-TPD of Zr-DBS



Scheme 1 Plausible mechanism of acid-catalyzed conversion of FA into EL over Zr-DBS

4 Conclusions

In summary, a novel Zr-base catalyst (Zr-DBS) has been synthesized and used as a heterogeneous catalyst for the alcoholysis of FA to produce EL. The characterization and experimental results show that Zr-DBS has excellent catalytic activity for the preparation of EL from FA. Under optimized reaction conditions, the FA conversion is 98.83% and the EL yield is 95.27%. The high activity of the catalyst was attributed to the synergistic effect of the Lewis acid sites derived from Zr⁴⁺ and the Brønsted acid sites originated from sulfonic group. Besides, the Zr-DBS catalyst could be reused four times without significantly reduce of catalytic activity. Finally, the possible reaction mechanism of FA alcoholysis to EL is proposed. As a consequence of the low-cost and pollution-free characterization of the catalyst, Zr-DBS has potential applications in the catalytic conversion of biomass.

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Compliance with Ethical Standards

Conflict of interest The authors declare no conflict of interests.

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