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Zr/Ti-catalyzed efficient synthesis of fuel additive γ -valerolactone from bio-based ethyl levulinate

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ABSTRACT

This study focuses on conversion of ethyl levulinate (EL) to γ -valerolactone (GVL) in 2-propanol with catalysts comprising of Zr and Ti. In this context, a series of Zr_xTi_{10-x} mixed oxides were prepared via a simple co-precipitation method and further examined as potential acid-base bifunctional heterogeneous catalysts for cascade reaction of hydrogenation and cyclization of EL into GVL in 2-propanol. A high GVL yield of 93% at a conversion of 99% EL was achieved over Zr_5Ti_5 at 210 °C after 4 h. Several characterization techniques including XRD, N_2 -physisorption and thermogravimetric (TG), NH_3/CO_2 -temperature programmed desorption (TPD), along with different reaction parameters (e.g., Zr/Ti ratio, reaction temperature and time) were performed to investigate the activity-structure relationship between prepared catalytic materials and the conversion of EL-to-GVL. Moreover, the recycling experiments revealed that the Zr_5Ti_5 catalyst could maintain a near constant selectivity toward on the yield of GVL for at least five consecutive catalytic runs.

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1. Introduction

Presently, abundant and renewable lignocellulosic biomass has been considered to be one of promising candidates to replace fossil-based sources for the synthesis of liquid fuels and valuable chemicals [Kunkes et al., 2008]. A variety of pivotal platform molecules such as 5-hydroxymethylfurfural (HMF), levulinic acid (LA), sorbitol and GVL can be obtained from carbohydrates through reactions like hydrolysis, dehydration, rehydration, partial and complete hydrogenation [Li et al., 2016a]. In connection with this, GVL has a wide range of applications in the production of liquid fuels [Bond et al., 2010], bulk chemicals [Zhao et al., 2012], and polymers [Vobecka et al., 2015]. In addition, GVL is recognized as a sustainable solvent for organic synthesis, due to its low vapor pressure and high stability [Qi et al., 2014].

LA and its esters derived from sugars are frequently used as substrates for the synthesis of GVL, wherein a cascade hydrogenation-cyclization reaction is involved [Yan et al., 2015]. Commonly, molecular H_2 is used as hydrogen donor for producing GVL, and metal nanoparticles especially noble metals were demonstrated to exhibit high efficiency [Xiao et al., 2016]. However, potential safety hazard with respect to flammable and explosive H_2 , and high cost in transportation and storage of H_2 and in the use of noble metals are forcing to develop alternative and efficient methods for GVL production.

Instead of using gaseous H_2 as H-donor, catalytic transfer hydrogenation (CTH) of LA and its esters to yield GVL has been recently investigated. This strategy involving liquid molecules as H-donors (e.g., formic acid

and alcohols) possesses some significant advantages from the view point of cost and handling [Bui et al., 2013; Tang et al., 2014a; Valekar et al., 2016]. Particularly, the utilization of non-toxic, easily accessible, cheap alcohol for the hydrogenation of LA or its ester to GVL via Meerwein-Ponndorf-Verley (MPV) reduction is more fascinating, through which carbonyl groups can be hydrogenated to alcoholic hydroxyl ones with high chemo-selectivity [Chia and Dumesic, 2011].

In general, MPV reduction can take place over Lewis acidic or basic sites [Ruiz et al., 2007]. Recently, a single bifunctional catalyst containing acid-base couple sites, which play a concerted role in forming a six-membered cyclic transition state, was demonstrated to be more favorable for the reduction process [Song et al., 2015; Li et al., 2016b]. In this context, zirconium-containing catalysts (e.g., ZrO_2 , $ZrO(OH)_2$, Zr-Al, and Zr-B) having acid-base couple sites exhibited pronounced catalytic performance for producing GVL via MPV reduction [Tang et al., 2014b; He et al., 2016a, 2016b]. Among those catalysts, $ZrO(OH)_2$ served as a promising catalyst for the production of GVL from LA and its esters due to the advantage of facile synthesis procedure and low cost. However, relatively low stability of $ZrO(OH)_2$ in alcoholic solvent with moderate GVL yields becomes less attractive. Therefore, designing a suitable bifunctional catalyst for efficient synthesis of GVL is highly interesting.

Binary metal oxides or hydroxides usually showed superior catalytic activity than their individual counterpart, due to enhanced surface area and acid/base density [Tagusagawa et al., 2010; Tagusagawa et al., 2011; Li and Wang, 2012]. In the present study, a series of Zr-Ti mixed oxides with different mole ratio were synthesized and characterized with various

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techniques, such as XRD, TGA, N_2 -sorption, and Temperature Programmed Desorption (TPD) of NH_3 and CO_2 . The characterized materials were applied for CTH of ethyl levulinate (EL) to GVL in 2-propanol and found that Zr_xTi_y catalyst exhibited a pronounced catalytic performance of yielding above 90% of GVL from EL, as compared with other Zr-Ti catalysts including $ZrO(OH)_2$ and $Ti(OH)_4$. The recyclability studies demonstrated that Zr_xTi_y catalyst was able to reuse for four consecutive runs, however, a significant loss of activity was observed after third run, revealing that the activity of the material needs to be improved.

2. Material and Methods

2.1 Materials

$ZrOCl_2 \cdot 8H_2O$ (98%), ethyl levulinate (99%), γ -valerolactone (98%) and naphthalene (99%) were purchased from Aladdin Industrial Inc (Shanghai). $Ti(SO_4)_2 \cdot 8H_2O$ (98%) was provided by Maya Reagent Co. Ltd (Zhejiang). 2-Propanol and other reagents were analytically pure grade and obtained from Chuandong Chemical Reagent Co. Ltd (Chongqing).

2.2 Catalyst preparation

Zr-Ti mixed hydroxides with different mole ratios were synthesized by a co-precipitation method [Vishwanathan et al., 2004]. In a typical procedure, $ZrOCl_2 \cdot 8H_2O$ (30 mmol) and $Ti(SO_4)_2 \cdot 8H_2O$ (30 mmol) were placed in a 250 ml flask and dissolved in deionized water (100 mL) at room temperature. Aqueous ammonia (25-28 w/w %) was then slowly added to the resultant solution under vigorous stirring. The slurry was then kept stirring for 5 h at room temperature after the final pH value of the slurry was adjusted to 9. The resulting white precipitate was filtered off, followed by washing with deionized water until the filtrate was neutral, and subsequently dried at 110 °C overnight to afford the final catalyst (Zr_xTi_y). Other mixed hydroxides, denoted as Zr_xTi_{10-x} , were also prepared by following the similar synthesis protocol by varying the molar ratios of metal precursors.

2.3 Catalyst characterization

XRD patterns ($5^\circ \leq 2\theta \leq 80^\circ$) of those as-prepared catalysts were recorded using Tongda TD-3500 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm). N_2 adsorption-desorption isotherms were obtained using a Micromeritics ASAP2020 instrument with the samples degassed at 100 °C for 2 h in a vacuum prior to N_2 adsorption. Thermal gravimetric

analysis (TGA) was conducted on NETZSCHSTA 429 instrument in the temperature range 30-600 °C with a heating rate of 10 °C/min under a dynamic nitrogen atmosphere (30 mL/min). TPD measurements were performed on an AutoChem 2920 chemisorption analyzer. The sample was preheated at 300 °C for 1 h prior to the adsorption of NH_3 or CO_2 at 50 °C for 1 h. The physisorbed NH_3 or CO_2 was then flushed out with helium for 1 h prior to the measurement, and then the sample was heated from 50 to 300 °C with a ramp rate of 10 °C/min, and kept at 300 °C for 1 h.

2.4 Catalytic reaction and product analysis

In a typical experiment, EL (1 mmol), catalyst (0.072 g) and 2-propanol (5 mL) were charged into a stainless steel autoclave with teflon lined reactor (25 mL) equipped with a magnetic stirrer. After setup, the reactor was placed in a temperature-controlled oil bath and zero time was defined as the reactor was immersed in the preheated oil bath at a desired temperature. The autoclave was cooled down to room temperature in cold water after having reacted for certain time.

EL conversions and GVL yields were analyzed quantitatively by gas chromatography (GC, Agilent 7890B) using naphthalene as internal standard, equipped with HP-5 column (30 m \times 0.320 mm \times 0.25 μ m) and FID detector operating at 270 °C. The injection volume of the sample was 1 μ L, the flow rate of nitrogen as carrier gas was 1.0 mL/min, and the oven temperature program was 60 °C for a minute and then increased to 230 °C with a ramp of 10°C/min, dwelling for 5 minutes.

3. Results and discussion

3.1 Characterization of as-prepared catalyst

Fig. 1a shows the XRD patterns of Zr-Ti catalysts with different Zr/Ti molar ratios, and no obvious crystal diffraction peaks can be seen, indicating the amorphous structure of prepared materials as in line with previous reports [Maity et al., 2001; Afanasiev 2008]. The N_2 adsorption-desorption isotherms of synthesized catalysts are depicted in Fig. 1b. The presence of irregular mesoporous in samples was verified by the classical type IV isotherms with the typical H1 hysteresis loops. The surface areas were determined by BET (Brunauer-Emmett-Teller) method and the mean pore sizes were evaluated by BJH (Barrett-Joyner-Halenda) method. All the obtained values are presented in Table 1. As can be seen that the surface areas of Zr-Ti mixed oxides are higher than those of $Zr_{10}Ti_0$ and Zr_0Ti_{10} , and Zr_5Ti_5 possessed the largest surface area (380.7 m²/g; entry 3). Notably, all the mean pore sizes were centered in the range of 3.2-3.6 nm.

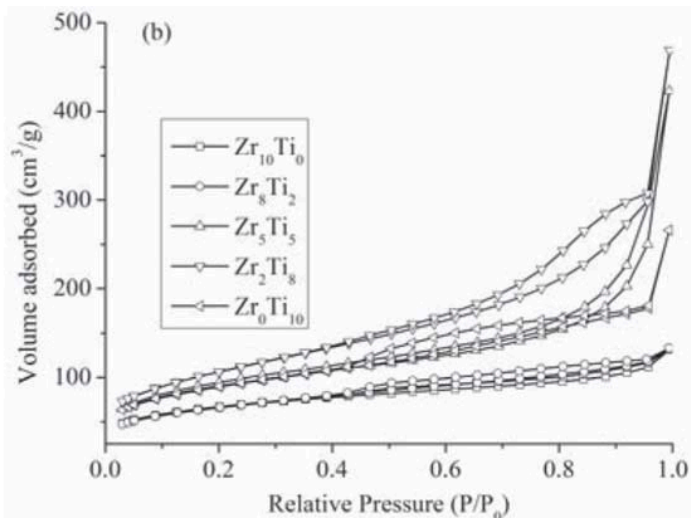
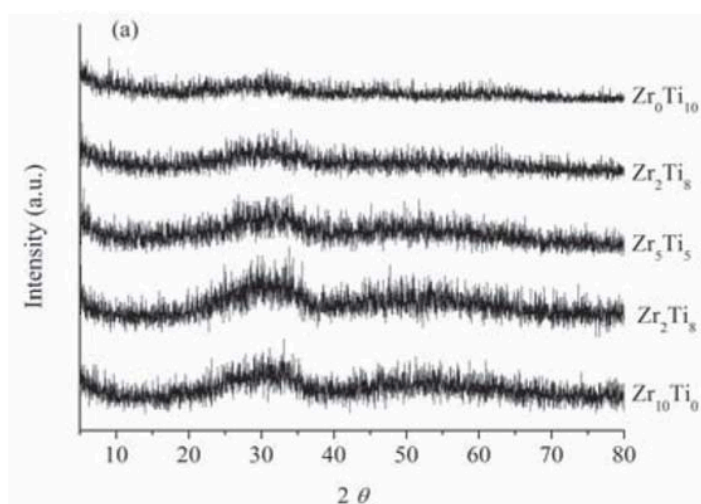


Fig. 1. XRD patterns (a) and N_2 adsorption-desorption isotherms (b) of different Zr-Ti catalysts

The acid-base properties of the materials were determined by NH_3/CO_2 -TPD (Figs. 2 and 3), and the results are summarized in Table 1. It was evidently observed that the materials contained weak acid-base sites as can be seen from Figs. 2 and 3. Interestingly, the acid density of those catalysts increased with the increase of the Ti content (entries 1-5), while the base density reached a maximum value in the case of Zr_5Ti_5 (entry 3) as Zr content ascended, further increasing the Zr content led to decrease

the basicity of the material (entry 4 and 5). The increase of acid-base sites was possibly ascribed to the enlargement of surface areas that were more accessible to NH_3 and CO_2 , and the decrease in base density after excess addition of Ti (i.e., Zr_2Ti_8 and Zr_0Ti_{10}) might be elucidated as the increase of acid density inhibiting the basicity of the catalysts [Fung and Wang, 1996].

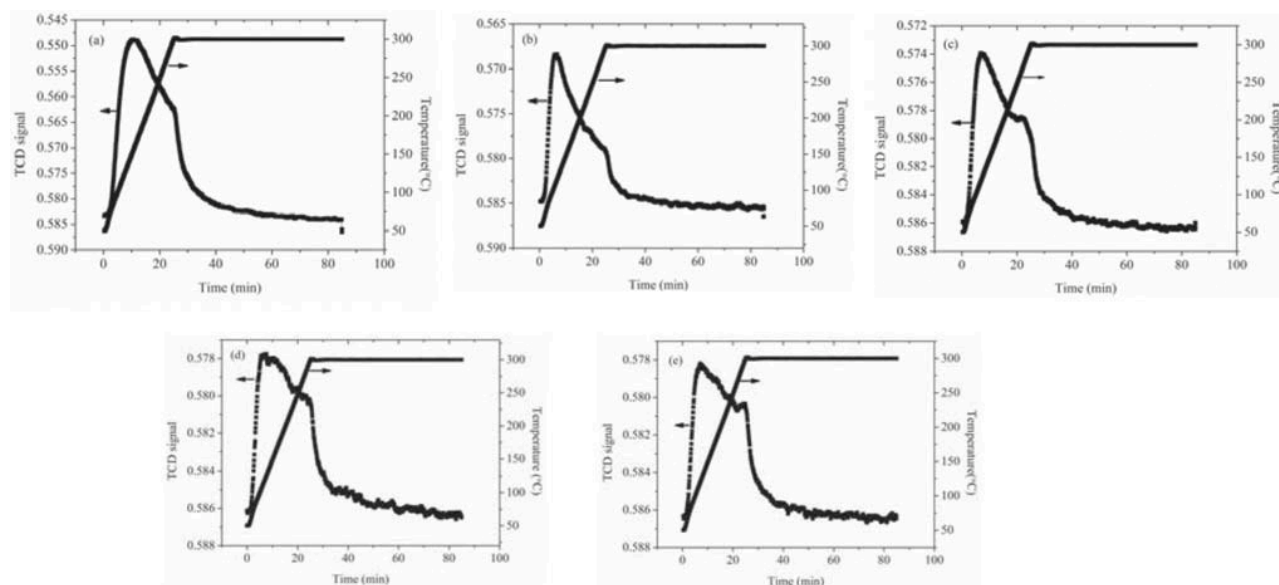


Fig. 2 NH₃-TPD profiles of Zr₀Ti₁₀ (a), Zr₂Ti₈ (b), Zr₅Ti₅ (c), Zr₈Ti₂ (d), and Zr₁₀Ti₀(e)

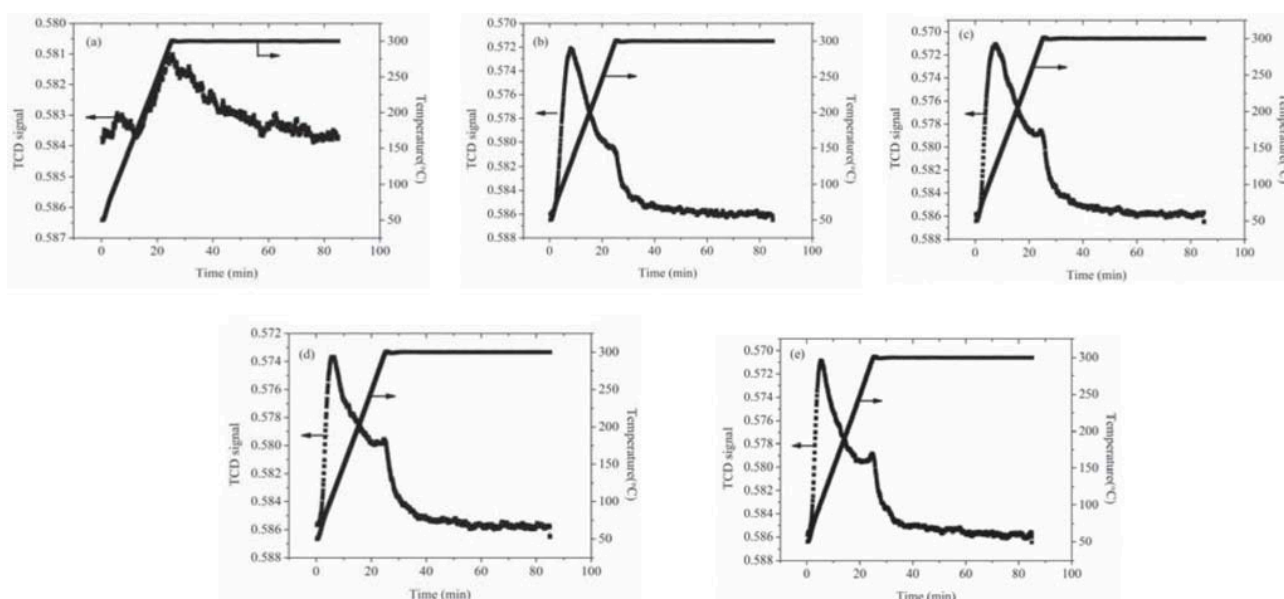


Fig. 3 CO₂-TPD profiles of Zr₀Ti₁₀ (a), Zr₂Ti₈ (b), Zr₅Ti₅ (c), Zr₈Ti₂ (d), and Zr₁₀Ti₀(e)

Table 1. Texture and acid-base properties of as-prepared Zr-Ti catalysts

Entry	Sample	BET surface area (m ² /g) ^a	Mean pore size (nm) ^b	Acidity (mmol/g) ^c	Basicity (mmol/g) ^d
1	Zr ₀ Ti ₁₀	320.2	3.578	1.46	0.01
2	Zr ₂ Ti ₈	326.4	3.584	0.73	0.24
3	Zr ₅ Ti ₅	380.7	3.289	0.55	0.27
4	Zr ₈ Ti ₂	237.1	3.581	0.38	0.16
5	Zr ₁₀ Ti ₀	240.5	3.581	0.36	0.15

^a The BET surface areas were obtained by N₂ adsorption-desorption

^b Calculated by the Barrett-Joyner-Halenda method

^c Acid contents were determined by NH₃-TPD

^d Base contents were determined by CO₂-TPD

3.2 Effect of Zr/Ti ratio

Initially, the catalytic hydrogenation of EL to GVL over Zr-Ti catalysts were conducted at 180 °C for 6 h, and the results are presented in Fig. 4. It can be apparently seen that the GVL yield first increased with the increase of Ti content, which can be ascribed to the presence of high surface area and acid-base couple site contents. A pronounced catalytic performance was observed with Zr_5Ti_5 (91.2% yield of GVL at 99.2% EL conversion) among the catalysts employed, indicating that higher surface area and acid-base site content favored towards GVL. In case of Zr_0Ti_{10} catalyst, a low GVL yield was observed despite of possessing largest number of acid sites, implying that the enhanced activity of MPV reduction also took place substantially on the basic sites of the material.

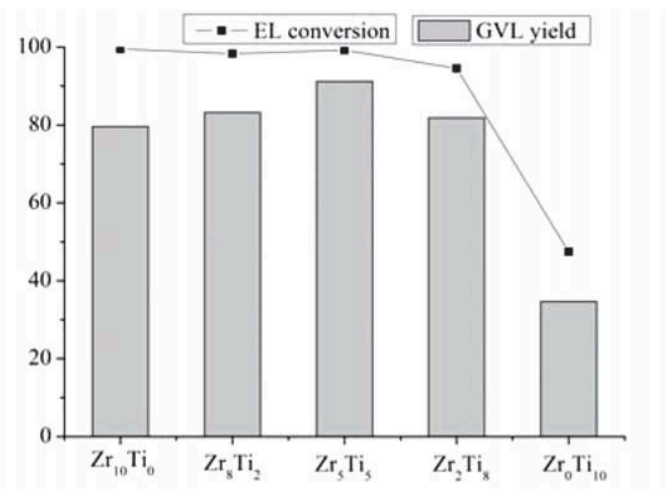


Fig. 4 Effect of Zr/Ti molar ratio on producing GVL from EL. Reaction conditions: EL (1 mmol), 2-propanol (5 mL), catalyst (0.072 g), 180 °C, and 6 h.

3.3 Effect of reaction temperature

Fig. 5 shows the effect of reaction temperature on the yield of GVL from EL over Zr_5Ti_5 after having reacted for 6 h. In general, high temperature facilitates the formation of GVL from EL, as expected, a sharp increase in GVL yield (from 59.6 to 91.2%) was observed as the reaction temperature increased from 150 to 180 °C, and further increasing the temperature to 210 °C slightly improved the GVL yield (94.7%). Nevertheless, a significant decline in GVL yield (from 94.7% to 86.5%) at full EL conversion was found when the reaction temperature increased to 240 °C. The undesired side reactions (e.g., aldol) seemed to be promoted at relatively high reaction temperatures as found in previous article [He et al., 2016b]. The optimized reaction temperature of 210 °C was chosen for further investigation.

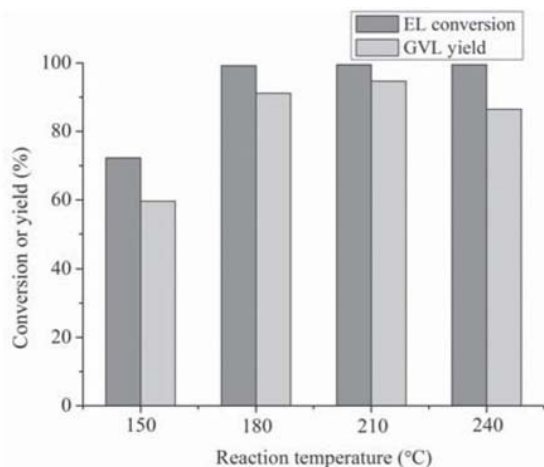


Fig. 5 Effect of reaction temperature on the yield of GVL from EL. Reaction conditions: EL (1 mmol), Zr_5Ti_5 (0.072 g), 2-propanol (5 mL), and 6 h.

3.4 Effect of reaction time

The influence of reaction time on the yield of GVL from EL at 210 °C was studied between 1 and 8 h and the obtained results are shown in Fig. 6. Only 64.7% yield of GVL was attained in 1 h, and the yield heightened with prolonging the reaction time and reached a plateau (93.3%-94.7%) between 4 and 6 h. Nevertheless, a slight decrease in GVL yield was observed when the reaction time was further extended to 8 h, which might be attributed to the occurrence of undesirable side reactions.

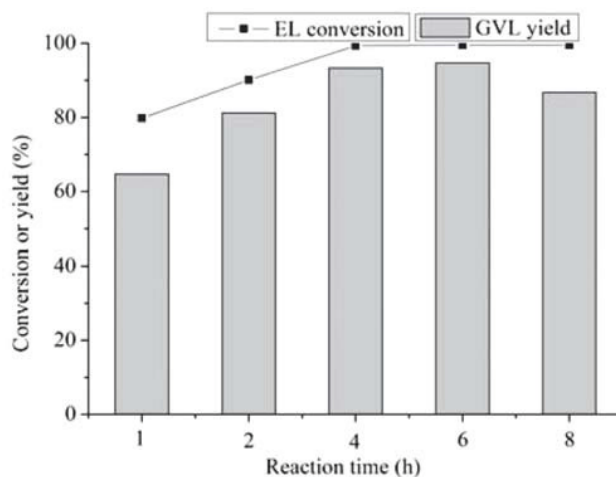


Fig. 6 Effect of reaction time on producing GVL from EL. Reaction conditions: EL (1 mmol), Zr_5Ti_5 (0.072 g), 2-propanol (5 mL), and 210 °C.

3.5 Catalyst recyclability

The reusability of a catalyst is of significant importance in practical production. A recycling test of Zr_5Ti_5 for producing GVL from EL through MPV reduction was thus investigated under the optimized reaction conditions. In a typical recycling test, the catalyst was collected by centrifugation after each run, followed by washing with anhydrous ethanol and acetone for three times (3×10 mL) under ultrasonic conditions. After drying at 80 °C for 2 h, the recovered catalyst was directly used for the subsequent runs. As illustrated in Fig. 7, an almost constant GVL selectivity was observed in five consecutive cycles despite GVL yield and EL conversion significantly dropped down.

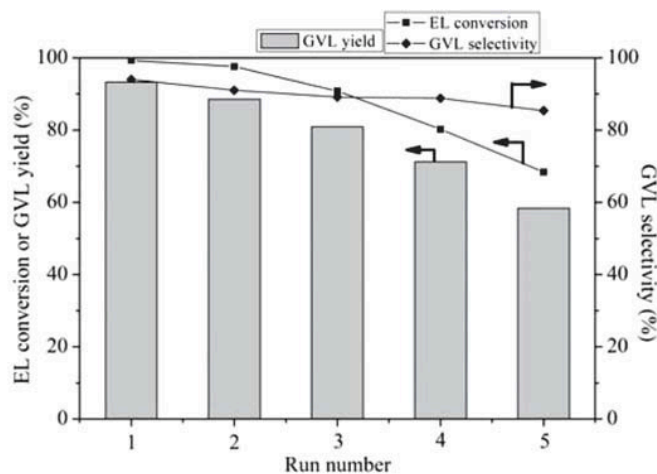


Fig. 7 Recyclability of Zr_5Ti_5 in the synthesis of GVL from EL. Reaction conditions: EL (1 mmol), Zr_5Ti_5 (0.072 g), 2-propanol (5 mL), 210 °C, and 4 h

XRD patterns indicated that the used Zr_5Ti_5 catalyst still possessed amorphous nature of the material and no new phase was generated (Fig. 8a). Moreover, the mesoporous structure of Zr_5Ti_5 catalysts was retained after five runs (Fig. 8b). The decline in EL conversion and GVL yield from the first to fifth run was speculated that deposition of organic species onto the surface of Zr_5Ti_5 during the reaction could have hampered the active sites. As illustrated by TG analysis (Fig. 8c & d), more mass loss (about 15.2%) was observed in fresh Zr_5Ti_5 catalyst compared to the used Zr_5Ti_5 catalyst (~14.2%), which indicated less water absorbed on the used Zr_5Ti_5 catalyst than the fresh one [Tang et al., 2014a]. For fresh catalyst,

the exothermic peak appearing in the range of 50-300 °C could be attributed to stripping of physical adsorbed water molecules on the surface of the catalyst along with the release of hydroxyl groups. With regard to the used Zr_5Ti_5 catalyst, another exothermic peak could be observed at around 330 °C, which was possibly assigned to the decomposition of deposited carbon residues. Therefore, the deposited carbon residues might result in the decline of EL conversion and GVL yield, which was consistent with the obtained BET surface area (191.2 m²/g) of the used Zr_5Ti_5 catalyst, which is significantly lower than that of the fresh one (380.7 m²/g).

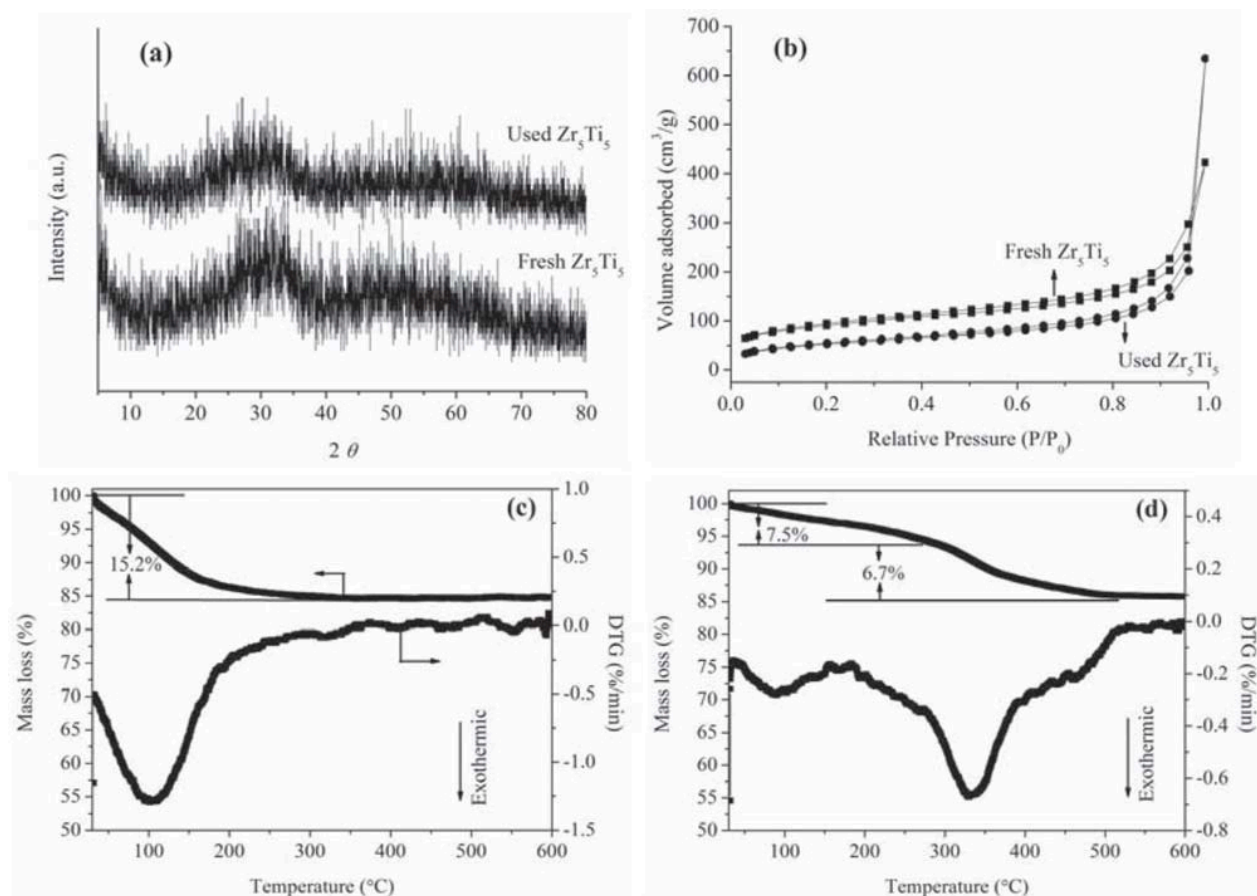


Fig. 8 XRD patterns (a) and N_2 adsorption-desorption isotherms (b) of fresh and used Zr_5Ti_5 catalysts, as well as TGA-DTG curves of fresh (c) and used (d) Zr_5Ti_5 catalysts

4 Conclusions

In summary, a series of acid-base bifunctional Zr-Ti catalysts with different Zr/Ti molar ratios were prepared by co-precipitation, and employed as heterogeneous catalysts for efficient CTH of EL to GVL by using 2-propanol as H-donor. Systematic characterizations revealed that the acid density of those as-prepared catalysts increased with the increment of Ti content, while the surface area and the base density initially increased with the increase of Ti content and then decreased. A high GVL yield of 93.3% at a conversion of 99.3% EL was obtained over Zr_5Ti_5 at 210 °C after 4 h, and the enhanced surface area and acid-base densities were demonstrated to be responsible for the pronounced catalytic performance. In addition, the Zr_5Ti_5 catalyst could be reused for at least four runs without significant changes in the selectivity of GVL. However, the yield of GVL drastically declined after third run.

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