Porous Ti/Zr Microspheres for Efficient Transfer Hydrogenation of Biobased Ethyl Levulinate to \( \gamma \)-Valerolactone

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ABSTRACT: \( \gamma \)-Valerolactone (GVL) is one of the versatile platform molecules and biofuel additives derived from the lignocellulosic biomass. Herein, the efficient synthesis of GVL from biobased ethyl levulinate (EL) using alcohol as both H-donor and solvent without an external hydrogen source has been achieved over porous Ti/Zr microspheres. The catalysts (Ti\(_x\)Zr\(_y\)) with different Ti/Zr molar ratios were synthesized using hexadecylamine (HDA) as a structure-directing agent via a sol–gel process combined with solvothermal treatment and characterized by scanning electron microscopy, transmission electron microscopy, X-ray diffraction, thermal gravimetric analysis, NH\(_3\)/CO\(_2\)-TPD, N\(_2\) adsorption–desorption, and pyridine-IR. A high GVL yield of 90.1% at 100% EL conversion was obtained at 180 °C for 6 h over Ti\(_3\)Zr\(_8\) in 2-propanol. The microspheric and porous structure, enhanced surface areas, and acid/base contents by the proper introduction of Ti species into Zr oxide were demonstrated to be responsible for the pronounced performance. The microspheric Ti\(_3\)Zr\(_8\) porous catalyst could be reused at least six times with no decrease in catalytic activity.

INTRODUCTION

With the gradual consumption of fossil resources and the growing demand for energy, great efforts have been made to produce biofuels and chemicals from renewable biomass resources.\(^1\)–\(^3\) In the past decades, much attention has been paid to catalytic conversion of biomass resources into a number of value-added chemicals, such as 5-hydroxymethylfurfural (HMF),\(^4\) 2,5-dimethylfuran,\(^5\) lactic acid,\(^6\) levulinic acid (LA) or its esters,\(^7,8\) \( \gamma \)-valerolactone (GVL),\(^9,10\) fural,\(^11\) and 5-ethoxymethylfurfural (EMF).\(^12\) Among these platform molecules, GVL has been considered to be one of the most promising candidates because of its widespread application.\(^13\) It has been used as a green solvent,\(^14\) fuel additive,\(^15,16\) and food additive.\(^17\) In addition, it can be further hydrogenated to 2-methyltetrahydrofuran (MTHF) and valeric biofuels.\(^18–20\)

Currently, GVL is primarily synthesized from LA or its esters by using various hydrogen sources such as molecular hydrogen, formic acid, and alcohols.\(^21–24\) However, the use of formic acid and hydrogen as H-donors has some disadvantages, including, for example, costly and unsafe characters, employment of precious metals (e.g., Pt, Pd, Au, and Ru) and unfriendly environmental solvents, and involvement of harsh reaction conditions.\(^25–27\) In this respect, increasing attention has been paid to the use of inexpensive and plentiful alcohols as H-donors, which are free from contamination and are particularly not dependent on a zero valence metal catalyst.\(^28\)

Catalytic transfer hydrogenation (CTH) of LA or its esters to GVL using alcohols as H-donors typically proceeded via Meerwein–Ponndorf–Verley (MPV) reduction. This reaction pathway was initiated though the hydrogenation of LA or its esters, followed by lactonization to produce GVL.\(^29\) For this transformation route, Zr-containing oxides [e.g., ZrO\(_2\),\(^32\) Zr-HBA\(_x\),\(^33\) ZrO\(_2\)/SBA-15,\(^34\) Zr–\( \gamma \)-\( \beta \)-\( \alpha \)-Cu-ZrO\(_2\),\(^35\) ZrFeO\(_2\),\(^36\) Zr–CA\(_x\), and Zr(OH)\(_x\)::xH\(_2\)O\(^39\)] showed superior activity to other catalysts on account of their acid/base amphoteric property.\(^40\) In addition, the pore architecture of the catalysts might affect the flowing rate of reaction systems through the porous network.\(^41\)

Physico-chemical natures including good stability, large surface area, porous structure, and moderate acid/base density of the catalysts are most likely to be beneficial for producing GVL from LA or its esters.\(^29,35\) In this regard, the spheric catalysts having enhanced surface areas could not only improve flow properties, but also facilitate the active sites homogeneously distributed on the catalyst surface,\(^32,43\) which will definitely promote the MPV reaction. Inspired by the above findings, herein, a series of porous and microspheric Ti/Zr mixed oxides with different Ti/Zr molar ratios were synthesized by a sol–gel process combined with solvothermal treatment.
using hexadecylamine (HDA) as a structure-directing agent. After introducing Ti into Zr, the resultant \( \text{Zr}^{-}\text{O}^{-}\text{Ti}^{-}\text{O}^{-}\text{Zr}^{-} \) network not only rendered the mixed oxides adjustable porosity and a large surface area but also enhanced acidity and basicity. The direct production of GVL from ethyl levulinate (EL) in 2-propanol (2-PrOH) without using external hydrogen was further used to examine the performance of the porous Ti/Zr microspheres.

## RESULTS AND DISCUSSIONS

**Catalyst Characterization.** Figure 1 shows X-ray diffraction (XRD) patterns of sole TiO\(_2\) and ZrO\(_2\), and Ti/Zr oxides with different Ti/Zr molar ratios after calcination at 500 °C. It was clearly observed that anatase crystals were present in the samples of as-prepared TiO\(_2\) and Ti\(_8\)Zr\(_2\), while ZrO\(_2\) was composed of both tetragonal and monoclinic crystals. However, when increasing the molar amount of Zr species, the resultant Ti/Zr samples (i.e., Ti\(_2\)Zr\(_8\) and Ti\(_5\)Zr\(_5\)) showed amorphous structure after calcination at 500 °C. It was proposed that Ti mixed with Zr species could be well distributed within the microspheres, thus preventing the formation of Ti/Zr crystals during calcination. However, the probable reason for phase transition was that the formation of Zr\(^{-}\)O\(^{-}\)Ti bonds could inhibit the mobility of a single Ti/Zr atom in the inorganic framework.

Nitrogen sorption isotherms of Ti/Zr oxides are presented in Figure 2a. The isotherms belonged to type IV isothermal curves, indicating the presence of a porous structure, which was consistent with the scanning electron microscopic (SEM) image (Figure 3a,b). Besides, the shift of the hysteresis loop to lower the relative pressure in Ti/Zr oxides with the content of zirconia increased, showing the gradual decrease of pore

![Figure 1. XRD patterns of Ti/Zr oxides with different Ti/Zr molar ratios. M, T, and A stand for monoclinic zirconia, tetragonal zirconia, and anatase titania, respectively.](image)

![Figure 2. (a) N\(_2\) adsorption--desorption isotherms, (b) pyridine-IR spectra, (c) NH\(_3\)-TPD curves, and (d) CO\(_2\)-TPD curves of Ti/Zr oxides with different Ti/Zr molar ratios.](image)

![Figure 3. SEM images of Ti\(_2\)Zr\(_8\) microsphere (a,b), and TEM images of Ti\(_2\)Zr\(_8\) (c) and Ti\(_8\)Zr\(_2\) (d).](image)
Table 1. Acid/Base Content, Pore Size, and BET Surface Area of Ti/Zr Mixed Oxides with Different Ti/Zr Molar Ratios

| catalyst     | acidity (mmol/g)\(^a\) | basicity (mmol/g)\(^a\) | BET surface area (m\(^2\)/g)\(^c\) | pore size (nm)\(^d\) |
|--------------|------------------------|----------------------|---------------------------------|-------------------|
| ZrO\(_2\)    | 0.31                   | 0.21                 | 104                             | 10.8              |
| Ti\(_5\)Zr\(_3\) | 1.12                  | 0.46                 | 389                             | 6.7               |
| Ti\(_3\)Zr\(_5\) | 1.34                  | 0.47                 | 302                             | 7.6               |
| Ti\(_2\)Zr\(_8\) | 0.57                  | 0.34                 | 294                             | 12.4              |
| TiO\(_2\)    | 0.79                   | 0.20                 | 115                             | 18.9              |

\(^a\)Acid and base contents were obtained from NH\(_3\)- and CO\(_2\)-TPD, respectively. \(^b\)BET surface area and pore size were measured by N\(_2\) adsorption–desorption.

Zr mixed oxides were larger than those of TiO\(_2\) and ZrO\(_2\), and much larger than the surface areas of commercial TiO\(_2\) and ZrO\(_2\) (Tables 1 and S1). Notably, Ti\(_2\)Zr\(_8\) had the highest BET surface area (389 m\(^2\)/g), which implied that the combination of Ti with Zr species could adjust the structural network to generate porous surfaces.\(^{50}\) Meanwhile, the pore size of Ti\(_2\)Zr\(_8\) was well distributed and centered at around 6.3 nm, while the others are presented in a relatively scattered form (Figure S1).

As shown in Figure 2c,d and Table 1, the acid and base properties of Ti/Zr oxides were evaluated from NH\(_3\)- and CO\(_2\)-TPD, respectively. Both acid and base contents of Ti/Zr oxides were initially increased and then decreased with the introduction of Ti species into ZrO\(_2\), and the highest acid and base contents (i.e., 1.34 and 0.47 mmol/g) were observed for Ti\(_2\)Zr\(_8\). The acid type and strength of Ti/Zr oxides were measured by FT-IR spectra of pyridine adsorption (Figures 2b and S2). The spectra showed three bands at around 1450, 1490, and 1610 cm\(^{-1}\) that were assigned to Brønsted acid, and a small band at 1545 cm\(^{-1}\) was allocated to Lewis acid.\(^{51,52}\) It should also be noted that Brønsted and Lewis acidity increased with the introduction of Ti species. Meanwhile, the ZrO\(_2\) calcined at 500 °C was free of Brønsted acid and had the lowest Lewis acidity, while Ti/Zr oxides remained similar in terms of Brønsted acidity and TiO\(_2\) possessed the highest Lewis acidity.

Furthermore, morphological properties of Ti/Zr catalysts were studied by SEM and transmission electron microscopy (TEM) (Figures 3 and S2). It was found that Ti/Zr oxides were spherical and commercial TiO\(_2\) and ZrO\(_2\) were ruleless in shape (Figures 3a,b, and S2). The visibly porous structure of Ti/Zr oxides was confirmed by SEM images, which well matched with that of N\(_2\) physisorption isotherms (Figure 2a). Meanwhile, because of different amounts of Ti species, Ti\(_2\)Zr\(_8\) existed in crystal shape while Ti\(_5\)Zr\(_3\) was amorphous, as illustrated by TEM images (Figure 3c,d), which were in agreement with the results of XRD patterns (Figure 1).

Conversion of EL to GVL over Different Ti/Zr Catalysts. As compared with commercial ZrO\(_2\) and TiO\(_2\), microspheric ZrO\(_2\) and TiO\(_2\) exhibited two times higher GVL selectivity for the CTH of EL in 2-propanol at 180 °C for 6 h (Table 2), which could be attributed to the larger surface area, acidity, and basicity of microspheric Ti/Zr oxides (Tables 1 and S1). In sharp contrast, Ti/Zr microspheres, by introducing Ti species into ZrO\(_2\), exhibited predominant performance in the CTH of EL to GVL (Table 2). Meanwhile, the synergistic effect of the surface area and Lewis acidity and basicity have been demonstrated to have a promotion role in CTH reaction.\(^{53}\) All of the microspheric Ti/Zr mixed oxides possessed higher GVL yields (>72.9%) than microspheric ZrO\(_2\) (71.2%) and TiO\(_2\) (9.4%), which could be ascribed to their improved surface area and moderate Lewis acidity and basicity (Tables 1, 2, and S2).

First, Lewis sites can promote 2-propanol deprotonation and hydride transfer through generating surface 2-propoxide, and they play a coordinated role with base sites, in combination with subsequent lactonization, to boost the production of GVL from EL. Although ZrO\(_2\) has the highest yield per m\(^2\), it has about 1/4 number of acid sites and 1/2 basic sites of Ti\(_2\)Zr\(_8\); thus, Lewis acid and base sites play a collaborative role to boost the production of GVL from EL, so the catalyst Ti\(_2\)Zr\(_8\) gets more GVL yield. The GVL yields obtained with Ti\(_5\)Zr\(_3\) (90.1%) and Ti\(_3\)Zr\(_5\) (83.3%) were >10% higher than that with Ti\(_2\)Zr\(_8\) (72.9%), implying that the higher acid/base density and enhanced surface area of the catalysts (i.e., Ti\(_5\)Zr\(_3\) and Ti\(_3\)Zr\(_5\)) were beneficial for GVL formation (Table 1, Figures 1 and 3c,d). The EL conversion (100%) and average rate (37.6 μmol g\(^{-1}\)min\(^{-1}\)) with Ti\(_2\)Zr\(_8\) were higher than that with Ti\(_5\)Zr\(_3\) (94% conversion and 31.1 μmol g\(^{-1}\)min\(^{-1}\) average rate), which was probably attributed to the relatively improved surface area of Ti\(_5\)Zr\(_3\) than that of Ti\(_2\)Zr\(_8\) (Table 2). In addition, the relatively higher Lewis acidity in Ti\(_2\)Zr\(_8\) seemed to be more beneficial for producing GVL, as compared with Ti\(_5\)Zr\(_3\) (Figure 2b, Table S2). As a result, Ti\(_2\)Zr\(_8\) (with appropriate acidity/basicity and enhanced surface area) possessed the highest activity (100% EL conversion, 90.1% GVL yield) among the different molar Ti/Zr catalysts. Meanwhile, Ti\(_5\)Zr\(_3\) (90.1% GVL yield, 180 °C) showed better performance than Zr/B (88.5% GVL yield, 200 °C), Al–Zr (83.2% GVL yield, 220 °C), and ZrO\(_2\) (81.5% GVL yield, 250 °C) under the same reaction system.\(^{31,32,54}\) Therefore, the Ti\(_2\)Zr\(_8\) catalyst was chosen for subsequent investigations.

Effect of Reaction Time and Temperature. The CTH reactions of EL to GVL were further carried out over Ti\(_2\)Zr\(_8\) at different reaction temperatures in the range of 160–200 °C with the reaction time of 1–10 h (Figure 4). Gas chromatography (GC)–mass spectrometry (MS) showed that isopropyl levulinate (IPL) was the primary byproduct (20% yield) after reacting at 160 °C for 4 h (Figure S3), which could be promoted by acid and base sites of Ti\(_5\)Zr\(_3\) through transesterification. A moderate GVL yield of 84% was obtained

Table 2. Results of EL-to-GVL Conversion with Different Ti/Zr Catalysts

| catalyst     | EL conv (%) | GVL yield (%) | GVL select (%) | average rate (μmol g\(^{-1}\)min\(^{-1}\))\(^d\) |
|--------------|-------------|---------------|----------------|---------------------------------|
| commercial ZrO\(_2\) | 7.3        | 2.9           | 39.7           | 1.1                             |
| microspheric ZrO\(_2\) | 86.0       | 71.2          | 82.8           | 27.9                            |
| Ti\(_5\)Zr\(_3\) | 100        | 90.1          | 90.1           | 37.6                            |
| Ti\(_3\)Zr\(_5\) | 94.0        | 83.3          | 88.6           | 31.1                            |
| Ti\(_2\)Zr\(_8\) | 87.4        | 72.9          | 83.4           | 28.3                            |
| microspheric TiO\(_2\) | 16.2        | 9.4           | 58.0           | 3.5                             |
| commercial TiO\(_2\) | 4.5        | 1.1           | 24.4           | 0.4                             |

\(^d\)Reaction conditions: 1 mmol EL, 0.072 g catalyst, 5 mL 2-PrOH, 180 °C, and 6 h. Average rate is defined as GVL mol/(catalyst weight × time).
for a long duration (10 h) at 160 °C (Figure 4a), and IPL (∼14% yield) without other byproducts was obtained. It seemed that the generation of IPL (9%) could be suppressed at a relatively higher temperature of 180 °C, giving higher yields of GVL (∼90% after 6 h; Figure 4b). However, the IPL yield slightly decreased with no visible increase in EL conversion and GVL yield after further increasing the temperature to 200 °C for 6 h (Figures S4 and 4c). Hence, 180 °C and 6 h were chosen for the following measurements.

**Effect of Different H-Donors.** The influence of various alcohols including methanol (MeOH), ethanol (EtOH), n-propanol (n-PrOH), 2-PrOH, n-butanol (n-BuOH), and 2-butanol (2-BuOH) on the CTH of EL to GVL was investigated. Compared with primary alcohols, the secondary alcohols showed an outstanding performance for the CTH reaction because of their lowest reduction potential (Figure 5). It was not difficult to find that 2-BuOH (86.1%) and 2-PrOH (90.1%) afforded high selectivity toward GVL at near-complete EL conversions. Although a high EL conversion could be obtained by using methanol as the H-donor, extremely poor GVL selectivity with the majority of methyl levulinate formed via transesterification was observed. Owing to stronger steric effects of n-propyl levulinate (PL) and n-butyl levulinate (BL), the CTH of PL in n-PrOH and BL in n-BuOH to GVL was more difficult than EL-to-GVL conversion in EtOH, thus resulting in inferior selectivity toward GVL in n-PrOH and n-BuOH. Meanwhile, it was clear that some other side reactions took place in EtOH besides transesterification and MPV reaction. In addition, 2-PrOH possessed the lowest reduction potential, resulting in the best reduction capacity that ensures the highest GVL yields. Therefore, 2-PrOH was the best H-donor in this reaction system.

**Effect of Catalyst Dosage and Substrate.** Catalyst dosage is one of the important parameters to measure the activity of the reaction system among various factors. As shown in Figure 6, the effect of the mass ratio of EL to the catalyst in the range of 1:1 to 8:1 on GVL production was examined. When the EL/catalyst mass ratio increased from 1:1 to 2:1, GVL selectivity and EL conversion remained almost constant. However, both EL conversion and GVL yield showed a remarkable reduction as the mass ratio of EL/catalyst reached 4:1, and IPL with a yield of about 10% was also formed. When the mass ratio of EL/catalyst further increased to 6:1 and 8:1, both EL conversion and GVL yield revealed continuous decrease, while the IPL yield remain unchanged (∼10%).

![Figure 4](https://example.com/figure4.png)

**Figure 4.** Catalytic production of GVL from EL by varying reaction time at temperatures of 160 (a), 180 (b), and 200 °C (c). Reaction conditions: 1 mmol EL, 0.072 g Ti$_2$Zr$_6$, and 5 mL 2-PrOH.

![Figure 5](https://example.com/figure5.png)

**Figure 5.** The effect of different alcohols as H-donors on the production of GVL from EL. Reaction conditions: 1 mmol EL, 0.072 g Ti$_2$Zr$_6$, 5 mL alcohol, 180 °C, and 6 h.
Hence, the subsequent experiments were set the mass ratio of EL and catalyst at 2:1. Notably, LA was also used as a substrate under the above-mentioned identical reaction conditions (Figure S3), and complete LA conversion with comparable yields of GVL (81.2%) and IPL (11.6%) were achieved.

Recyclability of the Catalyst. The multiple reusability and long-term stability of the catalyst are extraordinarily significant considerations for the production of GVL from EL in order to save the economic costs. In this recycling test, the reused catalyst was separated from the reaction mixture by centrifugation, washed by methanol and N,N-dimethylformamide (DMF), dried for 2 h at 80 °C, and subsequently calcined for 2 h at 500 °C. The catalytic performance of regenerate catalyst for the next cycle reaction was conducted under the same conditions. The catalyst recycling study under a relatively low EL conversion was also conducted with the decrease of the catalyst dosage to 0.018 g; the results are presented in Figure 7.

In summary, the efficient synthesis of GVL from EL via MPV reduction catalyzed by microspheric Ti/Zr porous oxides has been developed by using 2-PrOH simultaneously as H-donor and solvent. Among various Ti/Zr microspheres with different Ti/Zr molar ratios, Ti2Zr8 possessing the largest surface area (385 m²/g), and appropriate acidity (1.12 mmol/g) and basicity (0.46 mmol/g), was more beneficial for the MPV reaction. A GVL yield of 90.1% at an EL conversion of 100% was achieved at 180 °C for 6 h over Ti2Zr8, which can be ascribed to moderate physico-chemical properties. Moreover, the Ti2Zr8 catalyst showed excellent stability and reusability in six consecutive cycles, with a GVL yield of no less than 84.4% at complete EL conversion.

EXPERIMENTAL SECTION

Materials. EL (99%), LA (99%), GVL (98%), titanium-(IV)isopropoxide (TiIPP, 97%), zirconium(IV)propoxide (ZrPP, 70 wt % in 1-propanol), hexadecylamine (HDA, 90%), sec-butyl alcohol (98%), zirconium oxide (≥99.9%), and titanium oxide (≥99.9%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). Absolute ethanol (≥99.5%), 2-PrOH (≥99.5%), and potassium chloride (KCl, ≥99.5%) were obtained from Chongqing Chuandong Chemical Reagent Company. Other chemicals were of analytical grade and used without further purification.

Preparation of Microspheric Ti/Zr Porous Oxides. The Ti2Zr8 microspheres [with Ti/Zr molar ratios of 2:8 (Ti2Zr8), 5:5 (Ti5Zr5), and 8:2 (Ti8Zr2)] were prepared through the sol-gel process combined with solvothermal treatment using HAD as a structure-directing agent. In a typical procedure for the synthesis of Ti2Zr8, 1.21 g of HDA was dissolved in 100 mL ethanol, followed by the addition of 0.43 mL KCl aqueous solution and 0.98 mL 2-PrOH. The mixture was heated to 180 °C for 6 h over Ti2Zr8, which can be ascribed to moderate physico-chemical properties. Moreover, the Ti2Zr8 catalyst showed excellent stability and reusability in six consecutive cycles, with a GVL yield of no less than 84.4% at complete EL conversion.

Figure 6. The effect of different catalyst dosage on the production of GVL from EL. Reaction conditions: 1 mmol EL, catal: Ti2Zr8, 5 mL 2-PrOH, 180 °C, 6 h.

Figure 7. Recyclability of regenerate Ti2Zr8 in the production of GVL from EL. Reaction conditions: 1 mmol EL, 0.018 g Ti2Zr8, 5 mL 2-PrOH, 180 °C, and 6 h.

EL conversion and GVL yield declined by only ~6%. In addition, the reusability of the unregenerate Ti2Zr8 is shown in Figure S5b, wherein EL conversion decreased only by 10% and GVL selectivity remained balanced in six consecutive cycles, showing a little loss of the active sites in the Ti2Zr8 catalyst. Figure S5a shows that there is no obvious difference of EL conversion (~100%) and GVL yield (decreasing only by 5%) after six consecutive cycles, showing no loss of the active sites in the Ti2Zr8 catalyst. XRD patterns of the fresh and used Ti2Zr8 indicated no obvious structural change (Figure S6), and the morphology and porous structure of used Ti2Zr8 were not alerted at all, as confirmed by SEM (Figure S7). No obvious change in the acid (0.98 mmol/g) and base (0.45 mmol/g) density of the used Ti2Zr8 was observed, compared with those (1.08 and 0.46 mmol/g) of fresh Ti2Zr8 (Figure S8). The thermal stability of the fresh and used Ti2Zr8 was verified by TG analysis, which showed only 2.3% weight loss difference between them (Figure S9). All of the above observations demonstrate that the Ti2Zr8 catalyst is very stable during the reaction and can be used for multiple recycles.

Reaction Mechanism. On the basis of above discussions and previous reports,58,54 two possible reaction pathways (i.e., hydrogenation−cyclization and cyclization−reduction) can be involved for producing GVL from EL.56 In the present catalytic systems, no angelica lactone was detected by GC−MS, and no GVL was obtained when angelica lactone was directly used as a substrate. Therefore, it can be speculated that the CTH of EL to GVL over Ti2Zr8 micropores proceeds through sequential transfer hydrogenation and intramolecular transesterification (i.e., cyclization), as shown in Scheme 1. The formation of 2-propoxyl and the activation of carbonyl group of EL are promoted by both acid and base sites (Zr4+−O2−) of the Ti/Zr catalyst, resulting in the production of 4-hydroxypentanoate (4-HPE) through a six-membered transition state, which can be further transformed into GVL via an intramolecular transesterification process.

CONCLUSION

In the efficient synthesis of GVL from EL via MPV reduction catalyzed by microspheric Ti/Zr porous oxides has been developed by using 2-PrOH simultaneously as H-donor and solvent. Among various Ti/Zr microspheres with different Ti/Zr molar ratios, Ti2Zr8 possessing the largest surface area (385 m²/g), and appropriate acidity (1.12 mmol/g) and basicity (0.46 mmol/g), was more beneficial for the MPV reaction. A GVL yield of 90.1% at an EL conversion of 100% was achieved at 180 °C for 6 h over Ti2Zr8, which can be ascribed to moderate physico-chemical properties. Moreover, the Ti2Zr8 catalyst showed excellent stability and reusability in six consecutive cycles, with a GVL yield of no less than 84.4% at complete EL conversion.
solution (0.1 M) and 0.54 mL H₂O. To the resultant solution, a mixture containing 10 mL of ethanol, 0.57 g TiPP (2 mmol), and 2.62 g ZrPP (8 mmol) was added under vigorous stirring at room temperature. The milky white suspension was acquired and kept static for 18 h, followed by centrifugation and washing by ethanol and dried in air at room temperature. The resultant white solids (1.2 g) were further dispersed into a mixed solution of 7.5 mL H₂O and 15 mL ethanol and then subjected to a solvothermal process in Teflon-lined autoclave for 16 h at 160 °C. After suction filtration, the solvothermally treated solids were immersed in ethanol, followed by desiccation at room temperature. Finally, the obtained white powder was calcined at 500 °C at a heating ramp of 2 °C/min for 2 h in air, affording the porous Ti/Zr oxide microspheres by elimination of organic components. The sole TiO₂ and ZrO₂ microspheres were synthesized with 10 mmol TiPP and 10 mmol ZrPP, respectively, and the synthetic procedures were similar to those of Ti₂Zr₈ microspheres.

Catalysts Characterization. XRD patterns of the catalysts were recorded on a Rigaku diffractometer with Cu Kα radiation source (λ = 1.5406 Å), with 2θ from 5 to 80 °. Thermal gravimetric analysis was performed on a 1000 thermal analyzer under a dynamic N₂ atmosphere. SEM was performed on EHT E200. BET surface areas of the catalysts were determined by the nitrogen adsorption–desorption method using a Micromertics ASAP2020 instrument. FT-IR spectra of fresh and used microspheric Ti₂Zr₈ were recorded on a Rigaku di-gractometer with Cu Kα radiation (λ = 1.5406 Å), with 2θ from 5 to 80 °. Thermal gravimetric analysis was performed on a 1000 thermal analyzer under a dynamic N₂ atmosphere. SEM was performed on EHT E200.

Sample Analysis. The concentrations of EL, GVL, and byproducts were analyzed by GC (Agilent 7890) equipped with FID detector and HP-5 capillary column (30 m × 0.32 mm × 0.25 μm). The carrier gas was nitrogen with a flow rate of 1.0 mL/min, the injection volume of 1 μL, injector temperature of 250 °C, detector temperature of 270 °C, and oven temperature programming from 60 °C at a rate of 10 °C/min to 230 °C and maintained for 5 min. The identification of the liquid products was conducted by GC (Agilent 6890)–MS (5973).

ASSOCIATED CONTENT
Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00469. Pore size distributions of Ti/Zr oxides with different Ti/Zr molar ratios. GC and MS spectra of reaction mixtures. SEM images of microspheric ZrO₂ and TiO₂, commercial ZrO₂ and TiO₂, and used microspheric Ti₂Zr₈. XRD patterns and NH₃-TPD patterns of the fresh and used microspheric Ti₂Zr₈ (PDF)

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Notes
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