

In Situ Generated Catalyst System to Convert Biomass-Derived Levulinic Acid to γ-Valerolactone

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This is the first report of HCI/ZrO(OH)₂ catalysts prepared in situ by the autonomous decomposition of ZrOCl₂·8H₂O in levulinic acid (LA)/2-butanol solution, which catalyzed the esterification of LA in tandem with hydrocyclization to γ -valerolactone (GVL) by Meerwein–Ponndorf–Verley (MPV) reduction without the use of external H₂. A maximum GVL yield of 92.4% from neat LA and a GVL formation rate of

Introduction

Cellulosic biomass, the most abundant available biomass resource on earth, is receiving attention with the goal to produce chemicals and liquid fuels to alleviate the overwhelming dependence on nonrenewable fossil resources.^[1] It is known that the chemocatalytic conversion of cellulosic biomass to various platform molecules, such as 5-hydroxymethylfurfural (HMF),^[2] furfural,^[3] and γ -valerolactone (GVL),^[4] promises to be a key step to realize this fascinating prospect. One such platform compound is GVL that could be synthesized by the hydrocyclization of biomass-derived levulinic acid (LA) and its esters. GVL has received the attention of society and industry because of its potential applications: 1) GVL can be employed as a sustainable carbon source for the manufacture of hydrocarbon transportation fuels;^[5] 2) GVL can be converted to various polymeric monomers for Nylon production;^[6] 3) valueadded chemicals can be synthesized from GVL, such as 2methyltetrahydrofuran,^[7] methyl 4-methoxypentanoate,^[8]

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1092.2 μ mol g⁻¹min⁻¹ were achieved in 2-butanol at 240 °C in 2 h. The in situ generated ZrO(OH)₂ was characterized comprehensively and its unexpected catalytic efficiency was attributed mainly to its extremely high surface area. A crude LA stream from the acid hydrolysis of cellulose was extracted into 2-butanol and subjected to this catalyst system to give a GVL yield of 82.0% even in the presence of humins.

adipic acid,^[9] and aromatic hydrocarbons;^[10] 4) GVL can be used instead of water as an eco-friendly and renewable solvent for the production of furfural,^[11] LA,^[12] and sugars^[13] with unexpectedly high yields from lignocellulosic biomass. Recently, GVL was applied as a renewable solvent in organic synthesis, such as the Hiyama reaction^[14] and Sonogashira reaction.^[15]

In recent years, multiple catalytic strategies have been developed to produce LA from biomass materials with high yields in the lab or on a pilot scale.^[16] Therefore, the future role of GVL in biorefinery will depend strongly on the efficient conversion of biomass-derived LA to GVL through an affordable and concise process. To date, numerous precious- or base-metal catalysts have been employed to hydrogenate LA to GVL under an external reducing atmosphere (H₂).^[4b, 17] Among these catalysts, Ru-based catalysts are superior to other noble-metal catalysts for the selective hydrogenation of LA to GVL.^[6c, 18] However, both precious-metal catalysts and the management of external molecular H₂ are expensive. In this regard, the noble-metal-free or H₂-independent production of GVL from biomass-derived LA is highly desirable.

Recently, a catalytic transfer hydrogenation (CTH) strategy for GVL synthesis by Meerwein–Ponndorf–Verley (MPV) reduction has received increasing attention. Dumesic et al. reported that alkyl levulinates (ALs) could be subjected to MPV reduction to yield GVL using ZrO₂ and alcohols as the catalyst and in situ H donors, respectively.^[19b] This strategy provides a costeffective alternative for GVL production in which precious metals and H₂ are replaced by low-cost catalysts and alcohols, respectively. However, LA displayed a very poor performance for MPV reduction using ZrO₂ as the catalyst^[19b] because organic acids inhibit MPV reduction to produce GVL.^[20] Notably, intractable ammonium hydroxide or alkaline liquor is environmentally unfriendly and high-temperature calcination is energy-intensive but essential for the preparation of these metal oxides by conventional precipitation and calcination

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methods. With regard to these issues, we have developed an in situ generated catalyst system to convert biomass-derived LA to GVL, in which HCI/ZrO(OH)₂ catalysts were prepared in situ by the autonomous decomposition of ZrOCl₂·8H₂O in LA/2-butanol (2-BuOH) solution and then catalyzed the esterification of LA in tandem with the hydrocyclization of AL to GVL using 2-BuOH as an in situ hydrogen source by MPV reduction. The catalytic strategy described above is environmentally friendly and economical because unit operations that include the ex situ preparation of catalyst and the introduction of external H₂ are eliminated.

Results and Discussion

Study of various salts as catalyst precursors

Among various metal salts used, Zr salts, which include ZrOCl₂·8H₂O and Zr(NO₃)₄·5H₂O, showed unparalleled performance as catalyst precursors, and GVL yields as high as 84.5 and 72.3% were obtained at 240°C in 1 h, respectively (Table 1, entries 10 and 11). No GVL was detected if sorbed a certain amount of organics and had C contents of 0.2-27.1 wt% (Table 1). The atomic ratios of metal (M)/O/Cl of the recovered catalyst solids were altered dramatically compared with the parent salts. For instance, the atomic ratio of M/O/Cl was measured as 23.69:72.30:4.01, 20.81:73.88:5.31, and 23.25:73.16:3.59 if the recovered solid was derived from AlCl₃·6H₂O, SnCl₂·2H₂O, and ZrOCl₂·8H₂O, respectively (Table 1, entries 7, 8, and 10). In these cases, the CI content of the recovered solid became negligible compared to that of the parent salts. Based on these observations, we can infer that these recovered solid catalysts no longer exist in the form of the parent salts.

Mechanism for the in situ formation of HCI/ZrO(OH)₂ catalysts in alcohol

The recovered catalyst derived from ZrOCl₂·8H₂O is composed of Zr and O in a ratio (23.25:73.16) that is roughly consistent with a formula of $ZrO(OH)_2$ (1/3), and the content of CI was negligible (Table 1, entry 10). FTIR spectra of these recovered catalyst solids show absorption peaks centered at $\tilde{\nu} = 1540$ and

sis

1450 cm^{-1} (Figure 1, top), which are representative of ZrO(OH)₂.^[20] In the thermogravimetric analy-(TGA) curves

bottom), the catalyst solid recovered from 2-BuOH shows a total weight loss of 29.5% during heat treatment. This

is similar to 29.4%, which is the theoretical weight loss of ZrO(OH)₂ (12.8%), carbon deposits (14.6%), and water absorbed physically on the surface of the recovered catalyst (2%). The Xray photoelectron spectra (XPS) also corroborate that the in situ generated catalyst in 2-BuOH is composed mainly of Zr, O, and C

(Figure 2). We can thus conclude

that the recovered catalysts that originate from ZrOCl₂·8H₂O exist

(Figure 1,

value

Table 1. tal analy	Catalytic conversion sis of the recovered	of LA to GVL i catalyst solids.	n 2-BuOH usin	g various salts as the cat	alyst precu	rsors and e	elemen-
Entry	Precursor salt	Carbon content ^[a]		Atomic ratio M/O/Cl ^(b)	X _{LA} [%]	Y _{SBL} [%]	Y _{GVL} [%]
		C [wt%]	H [wt %]		[,]	[,]	
1	blank	_	_	-	59.3	44.8	1.0
2	$BaCl_2 \cdot 2H_2O$	0.7	2.9	34.88:4.44:60.67	59.1	39.7	8.9
3	MgCl ₂ •6H ₂ O	11.4	5.3	23.05:63.34:13.61	98.0	64.1	11.4
4	CuCl ₂ •2H ₂ O	0.2	0.9	46.95:16.47:36.58	67.8	46.4	11.7
5	MnCl ₂ •2 H ₂ O	0.5	1.2	30.40:34.58:35.01	99.3	65.5	16.8
6	CrCl ₃ •6H ₂ O	27.1	4.0	28.02:67.35:4.62	93.1	48.2	20.0
7	AICI ₃ •6 H ₂ O	13.5	4.3	23.69:72.30:4.01	99.9	44.3	46.1
8	SnCl ₂ •2H ₂ O	4.1	1.2	20.81:73.88:5.31	99.2	35.4	56.0
9	SnCl₄•5 H₂O	4.2	1.4	20.56:74.81:4.63	99.4	59.0	25.2
10	ZrOCl ₂ •8H ₂ O	14.6	3.5	23.25:73.16:3.59	99.9	11.7	84.5
11	$Zr(NO_3)_4 \cdot 5H_2O$	19.6	3.4	23.05:76.95	99.9	19.0	72.3
12	$Zr(SO_4)_2 \cdot 4H_2O$	3.6	2.7	13.59:77.88:8.53 ^[c]	80.3	74.3	0.0

Reaction conditions: LA (43 mmol), salt precursors (5 mol%, relative to LA) and 2-BuOH (95 g) were heated to 240 °C for 1 h. [a] Determined by using an Elementar Vario EL III (Germany). [b] Measured by EDS. [c] Atomic ratio of Zr/O/S.

Zr(SO₄)₂·4H₂O was used, and sec-butyl 4-oxopentanoate (SBL) was confirmed to be the main product rather than GVL. This is formed by the esterification reaction between LA and 2-BuOH (Table 1, entry 12). Apparently, hydrogen transfer was suppressed thoroughly in this case, probably because of catalyst poisoning in the presence of sulfur, which agrees well with a previous report. $^{\scriptscriptstyle [19a]}$ Moderate GVL yields of 46.1 and 56.0% were obtained if AlCl₃·6H₂O and SnCl₂·2H₂O were used as the catalyst precursors, respectively (Table 1, entries 7 and 8). In the blank test and with the use of other salts, SBL was confirmed as the major product with GVL yields below 20% (Table 1, entries 1-6).

After reaction, the solid catalysts that originate from the salt precursors were recovered by filtration. These materials ab-

in the form of ZrO(OH)₂. Moreover, the liquid product was concentrated by rotary evaporation, and white floc appeared immediately if 0.01 м AqNO₃ solution was added to the concentrated 2-BuOH solution, which indicates that there was free Cl⁻ in the liquid products. Consequently, we believe that ZrOCl₂·8H₂O decomposed into ZrO(OH)₂ and HCl in LA/2-BuOH solution under the applied reaction conditions.

XRD and selected area electron diffraction (SAED) patterns showed that the insitu generated ZrO(OH)₂ existed in an amorphous state (Figures S1 and S2). Unexpectedly, in situ generated ZrO(OH)₂ in LA/2-BuOH solution had a high specific surface area of 351 m^2g^{-1} (Table 2, entry 5) compared with that of $ZrO(OH)_2$ (191.7 m²g⁻¹) and ZrO_2 (157.2 m²g⁻¹) prepared by a conventional precipitation method followed by







Figure 1. FTIR spectra (top) and TGA profiles (bottom) of in situ generated ZrO(OH)₂ catalysts recovered from different alcohols. Reaction conditions: LA (43 mmol), ZrOCl₂·8H₂O (5 mol%, relative to LA), and alcohols (95 g) were heated to 240 °C for 1 h under 1 MPa N₂.

specific surface area of in situ generated ZrO(OH)₂ catalysts.

Substrate

blank

LA

ΙA

LA

LA

EL

GVL

acetone

using an Elementar Vario EL III (Germany). [b] Measured by EDS.

Entry

2

3

4

5

6

7

8

Alcohol

2-BuOH

2-PrOH

1-BuOH

2-BuOH

2-BuOH

2-BuOH

2-BuOH

EtOH

Table 2. The effects of substrates and alcohols (H donors) on the composition and

H [wt %]

3.2

8.8

127

8.3

14.6

11.1

9.5

2.1

calcination.^[19a, 20] The higher specific surface area of the in situ

generated ZrO(OH)₂ catalyst could provide more available

active sites that are exposed to substrates to result in a better

catalytic performance for GVL production by MPV reduction. A

recycling test of the in situ generated ZrO(OH)₂ was conducted

in 2-BuOH without HCl. An LA conversion of 62.4% and a GVL yield of 37.0% were achieved at 240°C in 1 h. In contrast, only

25.6% LA was converted to GVL if ex situ prepared ZrO(OH)₂

Reaction conditions: substrate (43 mmol), ZrOCl₂·8H₂O (5 mol%, relative to substrate),

and alcohols (95 g) were heated to 240 °C for 1 h under 1 MPa N₂. [a] Determined by

Carbon content^[a]

C [wt%]

1.6

2.0

3.2

2.7

3.5

2.2

2.1

1.3

Atomic ratio

21.4:76.8:1.8

19.1:78.0:2.9

26.3:71.3:2.4

23.3:73.2:3.5

Zr/O/Cl^[b]

S_{BET}

194

363

321

303

351

204

252

 $[m^2g^{-1}]$



Figure 2. XPS spectra of the in situ generated $ZrO(OH)_2$ recovered from 2-BuOH (top) and deconvolution of the C1s emission line (bottom). Reaction conditions are the same as described in Figure 1.

was used as the catalyst under otherwise identical reaction conditions. To gain more insight into the formation of the

To gain more insight into the formation of the ZrO(OH)₂ catalyst with a high surface area, ZrOCl₂·8H₂O with different substrates and alcohols was reacted at 240 °C. The in situ generated catalysts recovered from different alcohols showed a similar IR absorption profile to that of ZrO(OH)₂ (Figure 1, top), and specific surface areas that ranged from 303 to 363 m²g⁻¹ were measured that depended on the alcohol used (Table 2). However, no solid catalyst was obtained if the reaction was conducted in methanol (MeOH). The dielectric constant of a solvent is associated strongly with the solubility of salts in the solvent and decreases in the order of water (80.37) > MeOH (33.30) > EtOH (25.09) > 2-PrOH (19.52) > 1-BuOH (17.90) > 2-BuOH (16.68).^[21] Kim et al. found that the dielectric constant of an aqueous salt solu-

tion decreased greatly with the addition of alcohols, which resulted in the supersaturation of the salt solution and ZrO(OH)₂ precipitation.^[22] Precipitation also takes place upon heating the alcohol/aqueous salt solution because the dielectric constant of the mixed solution is decreased considerably with increasing temperature.^[23] However, MeOH has a high dielectric constant and cannot be decreased enough to make precipitation occur even at a high temperature.



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Figure 3. SEM images of in situ generated $ZrO(OH)_2$ catalysts recovered from various alcohols: A) EtOH, B) 2-PrOH, C) 1-BuOH, and D) 2-BuOH. Reaction conditions are as described in Table 2.



Figure 4. SEM images for the recovered catalyst solids in the presence of different substrates: A) blank test, B) GVL, C) EL, and D) acetone. Reaction conditions are as described in Table 2.

SEM images reveal that the catalyst recovered from EtOH is composed of ultrafine primary particles (Figure 3). However, spherical secondary particles with a diameter of 200–500 nm are observed if $ZrO(OH)_2$ was generated in 2-PrOH or 2-BuOH. $ZrO(OH)_2$ recovered from 1-BuOH shows large, clumpy aggregations and the lowest surface area (303 m²g⁻¹) compared with that generated in other alcohols (Table 2).

However, the specific surface area and morphology of the in situ generated catalysts showed a strong dependence on the substrates. In a control test, the specific surface area of the recovered catalyst was measured to be $194 \text{ m}^2\text{g}^{-1}$ in the absence of substrate (Table 2, entry 1). The surface area was increased significantly to 351 m²g⁻¹ in the presence of LA in 2-BuOH (Table 2, entry 5) and to 204 and 252 m^2g^{-1} in the presence of EL and GVL, respectively (Table 2, entries 6 and 7). SEM images show that catalyst solids aggregate to much larger and rodlike particles if the catalyst was generated in the absence of LA in 2-BuOH (Figure 4), in contrast, smaller spherical particles are observed in the presence of LA (Figure 3). According to Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the morphology of colloids is dominated mainly by electrostatic repulsion forces among particles.^[22] The mechanism of MPV reduction was elucidated by considering that the adsorption of substrate and H donors onto the surface of solid catalyst took place before hydrogen transfer.^[20] At this point, the absorbed LA and H donors probably enhanced the electrostatic repulsion forces between the in situ formed ZrO(OH)₂ particles and then prevented further agglomeration in 2-BuOH.

In addition, a relatively higher C content in the recovered $ZrO(OH)_2$ catalysts was recorded if LA was used as the substrate. The C content of the recovered $ZrO(OH)_2$ catalyst was measured as 14.6 wt% if LA was added (Table 2, entry 5), whereas the C content decreased sharply to 3.2 or 2.1 wt% in the blank test or if acetone was used, respectively (Table 2, entries 1 and 8). This trend is in good agreement with the substrate dependence of the specific surface area of the in situ

generated ZrO(OH)₂ catalysts, that is, the insitu formed ZrO(OH)₂ catalyst with a high specific surface area has a high C content if LA was applied as the substrate. These carbon deposits on the surface of the recovered ZrO(OH)₂ catalysts could be attributed mainly to the adsorption of the intermediate (SBL) and/or GVL because the characteristic IR absorption peak of a carbonyl group ($\tilde{v} = 1710 \text{ cm}^{-1}$; Figure 1) and the binding energy of a C=O bond (Figure 2) were observed.

In short, the dispersity and morphology of in situ generated $ZrO(OH)_2$ particles relied strongly on the solvent and substrate used. The solvents and substrates also had a substantial influence on the GVL yield, which will be discussed at the next section.

Reaction pathway of the conversion of LA to GVL

In the recycling test, we found that the recovered ZrO(OH)₂ catalyst showed a low catalytic activity compared to its parent salt; only a GVL yield of 37.0% and an LA conversion of 62.4% were achieved with the recovered material. However, the GVL yield was increased sharply to 71.6% with the quantitative conversion of LA if a small amount of HCl (1.5 mmol) was added under the same reaction conditions. LA could not be converted immediately to 4-hydroxyvaleric acid (HVA) by MPV reduction under the reaction conditions discussed here, probably because MPV reduction is restrained by organic acids. $\ensuremath{^{[24]}}$ Apparently, in situ generated HCl along with ZrO(OH)₂ that comes from the decomposition of ZrOCl₂·8H₂O could eliminate the negative impact of the organic acid by the esterification of LA with 2-BuOH. SBL was one of the main compounds in the liquid product. This observation indicates that LA first undergoes esterification to SBL, which is followed by the CTH of SBL to sec-butyl 4-hydroxypentanoate (SHPB) and the lactonization of SHPB to yield GVL in 2-BuOH (Scheme 1). No intermediate SHPB was observed in the products because the lactonization of SHPB to GVL is fast at a temperature above 150°C in the



Scheme 1. Proposed reaction pathway for the conversion of LA to GVL by MPV reduction.

presence of acid catalysts.^[25] Therefore, the CTH of SBL to SHPB was the rate-limiting step for the conversion of LA to GVL. Moreover, a trace amount of *sec*-butyl 4-*sec*-butoxypenta-noate (SBOP), which was formed by the etherification reaction between SHPB and 2-BuOH, was detected. If GVL (43 mmol) and ZrOCl₂·8 H₂O (5 mol%, relative to GVL) were reacted at 240 °C for 3 h, a recovery rate of GVL of 93.1% was obtained and SBOP was detected by GC–MS, which indicates that the cyclization of SHPB to GVL was reversible and the reaction equilibrium was preferred significantly to the formation of GVL under the given reaction conditions.

Investigation of the CTH of LA to GVL under various reaction conditions

MPV reduction is associated strongly with the reducing capacity of alcohols (H donors), which decrease in the order of MeOH < EtOH < 1-BuOH < 2-BuOH \approx 2-PrOH (Table S1).^[26] In MeOH, methyl levulinate (ML) was verified as the dominant product with a negligible GVL yield (Table 3, entry 1). 2-PrOH and 2-BuOH were confirmed to be active H donors, which bring about similar GVL yields of 83.1 and 84.5 % at 240 °C in

Table 3.	The effect of a	lcohols (th	e H donors	s) on the CT	H of LA to	GVL.
Entry	Alcohol	<i>Т</i> [°С]	X _{LA} [%]	Y _{LE} ^[b] [%]	Y _{GVL} [%]	$R_{\text{GVL}}^{[c]}$ [µmol g ⁻¹ min ⁻¹]
1 ^[a]	MeOH	200	99.9	97.6	1.3	-
2 ^[a]	EtOH	200	99.9	66.2	28.9	1140.6
3	EtOH	200	99.9	40.5	34.8	822.7
4	EtOH	220	99.9	31.6	55.0	1300.9
5	EtOH	240	99.9	14.6	76.4	1806.8
6 ^[a]	2-PrOH	200	99.9	32.9	62.0	2444.5
7	2-PrOH	200	99.9	27.5	62.7	1482.3
8	2-PrOH	220	99.9	19.8	68.2	1613.2
9	2-PrOH	240	99.9	9.5	83.1	1964.9
10 ^[a]	1-BuOH	200	99.5	60.7	27.9	1099.0
11	1-BuOH	220	96.5	29.7	51.7	1222.2
12	1-BuOH	240	97.0	12.6	64.2	1517.7
13 ^[a]	2-BuOH	200	67.9	29.0	27.5	1084.5
14	2-BuOH	200	99.9	32.1	56.1	1326.2
15	2-BuOH	220	99.9	24.5	67.8	1603.5
16	2-BuOH	240	99.9	11.7	84.5	1996.8

Reaction conditions: 43 mmol LA, 95 g alcohols, catalyst loading (ZrOCl₂·8H₂O, relative to LA) 5 mol%, 1 h, 1 MPa N₂, 600 rpm. [a] Catalyst loading 3 mol%. [b] Y_{LE} is yield of levulinates, for example, Y_{LE} is the yield of methyl levulinate in entry 1. [c] Based on the mass of ZrO(OH)₂.

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1 h with a catalyst loading of 5 mol% (Table 3, entries 9 and 16). Under the same reaction conditions, GVL yields were decreased to 76.4 and 64.2% if EtOH and 1-BuOH were applied as the solvent and H donor, respectively (Table 3, entries 5 and 12). However, the GVL yield in 2-BuOH was much lower than that in 2-PrOH at a relatively low reaction temperature. For example, a GVL yield of 62.0% was achieved in 2-PrOH at 200 °C in 1 h with 3 mol% ZrOCl₂·8H₂O, in contrast, only 27.5% of LA was converted to GVL in 2-BuOH under identical reaction conditions (Table 3, entries 6 and 13). This result can be ascribed mainly to the stronger steric effect of 2-BuOH than that of 2-PrOH, and a high temperature was beneficial to overcome the steric effect of 2-BuOH. If the reaction temperature was increased to 240 $^\circ\text{C},$ a GVL yield of 84.5 % was obtained in 2-BuOH, which is similar to that obtained in 2-PrOH under the same reaction conditions (Table 3, entries 9 and 16). In addition, an elevated temperature improved the GVL formation rate markedly from 822.7 to 1806.8 μ mol g⁻¹min⁻¹ if EtOH was used as the solvent and H donor (Table 3, entries 3-5). A similar trend was observed if other alcohols were used as the H donor.

The CTH of LA to GVL in 2-BuOH was investigated in depth using in situ generated $HCI/ZrO(OH)_2$ catalysts (Table 4). The blank experiment gave only an insignificant GVL yield with an SBL yield of 28.2% at 200 °C in the absence of catalyst (Table 4, entry 1). The yields of GVL and SBL increased to 16.0 and 60.1% if 1 mol% of ZrOCl₂·8 H₂O was added (Table 4, entry 2). A further increase of the temperature to 260 °C and the catalyst loading to 5 mol%, improved the GVL yield gradually from 16.0 to 89.4% to the detriment of the SBL yield, which decreased from 60.1 to 3.1% (Table 4, entries 2–5 and 10). However, if the catalyst loading was further increased to 10 or 15 mol%, the GVL yield decreased to 73.7 or 72.2% with a slight increase of the SBL yield (Table 4, entries 11 and 12). A

relatively higher concentration of HCl, which originates from the decomposition of ZrOCl₂·8H₂O, could partially suppress the CTH of SBL to GVL (discussed in the next section). An analogous tendency was also discovered if AlCl₃·6H₂O or SnCl₂·2H₂O was employed as the catalyst precursor (Table 4, entries 13–18). In this scenario, the GVL formation rate increased and peaked at 3528.4 μ mol g⁻¹min⁻¹ (Table 4, entry 5) and then decreased to 569.0 μ mol g⁻¹min⁻¹ (Table 4, entry 12).

Moreover, the GVL yield increased significantly and then peaked at 92.4% with a prolonged reaction time from 0.5 to 2 h at 240 °C (Table 4, entries 6 and 7). In this case, the GVL formation rate was 1092.2 μ mol g⁻¹min⁻¹, which is increased by nearly 100 times compared with a previous report in which Dumesic et al. demonstrated that a GVL formation rate of only 12.6 μ mol g⁻¹min⁻¹ and a GVL yield of 71% were obtained if LA and 2-BuOH reacted at 220 °C over ZrO₂ for 16 h.^[19b] If the reaction time was further prolonged to 4 h, the GVL yield decreased slightly to 86.5% (Table 4, entry 9). Meanwhile, a slight increase of the yield of the byproduct SBOP

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Entry	Catalyst ^[a] [mol %]	<i>Т</i> [°С]	<i>t</i> [h]	X _{LA} [%]	Y _{sbl} [%]	Y _{GVL} [%]	R _{GVL} ^[d] [µmol g ^{−1} min [−]
1	blank	200	1	37.4	28.2	0.6	-
2	1	200	1	84.5	60.1	16.0	1891.3
3	2	200	1	85.0	47.5	26.5	1566.2
4	2	220	1	99.9	43.2	48.7	2878.3
5	2	240	1	99.9	32.8	59.7	3528.4
6	5	240	0.5	99.9	27.9	67.2	3175.5
7	5	240	2	99.9	4.9	92.4	1092.2
8	5	240	3	99.9	4.3	92.3	727.7
9	5	240	4	99.9	3.4	86.5	511.4
10	5	260	1	99.9	3.1	89.4	2114.5
11	10	240	1	99.9	15.3	73.7	871.2
12	15	240	1	99.9	15.4	72.2	569.0
13 ^[b]	3	240	1	99.7	55.3	31.5	-
14 ^[b]	5	240	1	99.9	44.3	46.1	-
15 ^[b]	10	240	1	99.3	53.7	31.1	-
16 ^[c]	3	240	1	99.2	39.0	52.0	-
17 ^[c]	5	240	1	99.2	35.4	56.0	-
18 ^[c]	10	240	1	99.9	38.8	52.2	-

the catalyst precursor. [d] Based on the mass of ZrO(OH)₂.

was observed, which indicates that the decrease of the GVL yield can be ascribed mainly to the ring-opening of GVL to SHPB (Scheme 1). 2-sec-Butoxybutane and 2,2-di-sec-butoxybutane were also detected, which were formed by the etherification of 2-BuOH and the condensation between butanone with 2-BuOH, respectively. However, only a small amount of solvent (2-BuOH) was consumed by these side reactions even after reaction at 240 °C for 4 h (Figure S4).

CTH of crude LA derived from cellulose to GVL in 2-BuOH

With regard to the outstanding catalytic efficiency of in situ generated HCl/ZrO(OH)₂ catalysts, it is promising to utilize this catalytic strategy for the CTH of crude LA, instead of off-theshelf pure LA, which was produced by the acid-cata-

lyzed hydrolysis of biomass carbohydrates.

In general, liquid products that result from the acid-catalyzed hydrolysis of biomass carbohydrates are composed mainly of LA (desired product), formic acid (FA, byproduct), mineral acids (catalysts), H₂O (solvent), humins, and other undetectable intermediates. In light of the complexity of this hydrolysate, the conversion of LA to GVL was simulated preliminarily in 2-BuOH in the presence of typical impurities that are usually present in the hydrolysate of carbohydrates (Table 5).

A relatively high concentration of water (10 wt%) or HCl (15 mmol) was found to facilitate the aggregation of ZrO(OH)₂ to give rise to a considerable decrease of the surface area of the recovered catalysts to 146 or 98 m²g⁻¹, respectively. Consequently, the GVL yields were also reduced sharply to 68.3 and 31.6%, respectively (Table 5, entries 4 and 8). In contrast, a relatively low concentration of water (5 wt%) or HCI (1.5 mmol) impacted the LA conversion slightly and led to an acceptable decrease of GVL yield to 80.6 and 78.5%, respectively (Table 5, entries 2 and 7). A GVL yield of only 60.6% was obtained in the presence of FA (43 mmol) at 240 °C in 1 h, whereas the GVL yield was improved to 92.9% with a prolonged reaction time of 4 h (Table 5, entries 6 and 7). The negative impact of FA (organic acid) on MPV reduction was eliminated by the esterification of FA with a prolonged reaction time, similar to that of LA. However, the GVL yield was decreased dramatically to 8.3% if H₂SO₄ was introduced into the reactor, and the consumption of 2-BuOH by dehydration to butene was observed (Table 5, entry 9). H₂SO₄ could promote the dehydration of 2-BuOH and hinder hydrogen transfer from 2-BuOH to SBL.

There was a significant decrease in the C content of the recycled catalyst formed in the presence of impurities compared with that formed in the presence of LA only (14.6 wt%; Table 2, entry 5). For example, the C content of the recovered catalyst decreased to 5.3 or 5.7 wt% if 10 wt% water or 15 mmol HCl was added to the reactor (Table 5, entries 4 and 8). This

trend is in good agreement with the decrease of the specific surface area of these recovered catalysts, which implies that $\mathrm{H_2O}$ and HCl probably disturb the interaction between LA and the in situ generated catalysts.

To minimize the negative effect of these impurities, the pretreatment of the hydrolysate that comes from the acid-catalyzed hydrolysis of biomass carbohydrates is a prerequisite to guarantee a high GVL yield. In this study, partial neutralization and extraction by 2-BuOH were employed to remove the mineral acid catalyst and water. The separation of neat LA from the synthetic hydrolysate was tested by liquid-liquid extraction systems that comprised an aqueous LA solution and the same volume of 2-BuOH. The detailed procedure for the extraction experiments is described in the Supporting Information. The

and GV	'L yield.							
Entry	Impurity	<i>t</i> [h]	Carbon content ^[a]		S_{BET} [m ² q ⁻¹]	Х _{LA} [%]	Y _{sbl} [%]	Ү _{GVL} [%]
			C [wt%]	H [wt%]	- 5 -			
1	5 wt % H ₂ O ^[b]	1	-	_	-	99.9	30.8	68.6
2	5 wt % H ₂ O ^[b]	2	10.5	3.2	-	99.9	18.2	80.6
3	10 wt % H ₂ O ^[b]	1	11.5	3.0	299	92.0	39.8	51.7
4	10 wt % H ₂ O ^[b]	3	5.3	1.1	146	99.4	30.0	68.3
5	43 mmol FA	1	12.4	3.1	319	99.9	25.3	60.6
6	43 mmol FA	4	-	-	-	99.9	5.2	92.9
7	1.5 mmol HCl	1	12.1	3.6	-	99.9	18.6	78.5
8	15 mmol HCl	1	5.7	2.7	98	99.9	58.9	31.6
9	$1.5 \text{ mmol } H_2SO_4$	1	1.2	2.4	-	89.5	57.3	8.3
Reaction conditions: LA (43 mmol), $ZrOCl_2 \cdot 8H_2O$ (5 mol%, relative to LA), and 2-But (95 g) were heated to 240 °C for the prescribed duration under 1 MPa N ₂ . [a] Det					BuOH Deter-			

Table 5. The effects of impurities in 2-BuOH on the formation of the ZrO(OH)₂ catalyst

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addition of NaCl into the aqueous phase promoted the extraction behavior of 2-BuOH greatly and decreased the solubility of H₂O in the 2-BuOH extract (Table S2), which generates a favorable environment for the CTH of LA to GVL.

Herein, microcrystalline cellulose was selected as the feedstock to produce LA, and an LA yield of 47.8% was achieved. The detailed procedure for LA production from cellulose and subsequent extraction by 2-BuOH is described in the Supporting Information. Finally, 90.2% of LA and 15.1% of FA were extracted by 2-BuOH from the hydrolysate of cellulose. A yellowbrown solution was obtained because humins also dissolved in 2-BuOH in the extraction process, and the mass concentration of LA in the 2-BuOH extract was approximately 5 wt% (Figure S6). The resulting 2-BuOH extract and ZrOCl₂·8H₂O (5 mol%, relative to LA) were reacted at 240 °C, and a GVL yield of 82.0% (based on LA) was still achieved even in the presence of humins (Scheme 2). This is the first report of the production of GVL in a high yield from crude LA by MPV reduction using alcohol as the H donor.



Scheme 2. Schematic representation of GVL production from cellulose through the integration of acid-catalyzed hydrolysis, extraction, and subsequent CTH process catalyzed by in situ generated ZrO(OH)₂ and HCl.

Conclusions

We present an in situ generated catalyst system for the conversion of biomass-derived levulinic acid (LA) to γ -valerolactone (GVL). The mechanism of the formation of the HCl/ZrO(OH)₂ catalysts from ZrOCl₂·8H₂O in alcohols was elaborated, and the catalytic transfer hydrogenation of LA to GVL catalyzed by this in situ generated HCl/ZrO(OH)₂ catalysts was investigated comprehensively using 2-butanol as the solvent and H donor. The delicate strategy reported here might minimize the costs for the production of GVL from carbohydrates by avoiding an energy-intensive LA purification process and the use of noblemetal catalysts and molecular H₂. Especially, tedious and environmentally hazardous processes for the preparation of catalysts were eliminated through the spontaneous decomposition of the inexpensive salt precursors in alcohols. The in situ generated HCI/ZrO(OH)₂ catalysts showed a high catalytic activity for the catalytic transfer hydrogenation of LA to GVL and satisfactory robustness against intractable humins that come from the acid-catalyzed hydrolysis of carbohydrates. In addition, the in situ generated catalyst system described here is also applicable to the hydrogenation of other biomass-derived molecules, which include 5-hydroxymethylfurfural and furfural.

Experimental Section

Chemicals and materials

Levulinic acid (LA, 98%), ethyl levulinate (EL, 98%), y-valerolactone (GVL, 98%), microcrystalline cellulose (90 µm), and zirconium oxychloride (ZrOCl₂·8H₂O, 99%) were purchased from Aladdin Reagent Co. Ltd. (Shanghai, China). All other chemicals were supplied by Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China) and used without further purification.

Catalytic reactions and sample analysis

All experiments were performed in a 400 mL Hastelloy-C high-pressure reactor (Dalian-controlled Plant, Dalian, China). The reactor was heated in an adjustable electric stove. The temperature of the reactor contents was monitored by using a thermocouple connected to the reactor. Typically, substrate (LA, 5 g), solvent (2-BuOH, 95 g), and catalyst salt precursor (ZrOCl₂·8H₂O, 5 mol%, relative to substrate) were charged into the reactor, which was sealed, filled with N_2 (1 MPa), and heated to the prescribed temperature for the desired reaction time with stirring at 600 rpm. After the reaction, the reactor was cooled to RT. The solid catalysts (white powder) were recovered by filtration under vacuum and dried in a vacuum oven at 60°C for 4 h, and the liquid products were centrifuged at 8000 rpm for 5 min. The liquid products were analyzed by GC-MS and GC, respectively. The conversion and product selectivity were determined using calibration curves obtained by analyzing standard solutions. Typically, the GC analysis of each sample was conducted by using an Agilent 7890 series system equipped with a DB-WAXetr column (30.0 m×0.25 mm×0.25 µm) and a flame ionization detector (FID) that was operated at 270 °C. The carrier gas was N_2 with a flow rate of 1.0 mLmin⁻¹. The following temperature program was used: 40 °C (4 min) and 15 °C min⁻¹ to 250 °C (5 min). The qualitative analysis of the products after reaction was conducted by using a Shimadzu QP2010SE instrument with an Rtx-5 MS column (30.0 m \times 0.25 mm \times 0.25 μ m) and EI-MS. The operating parameters of the GC-MS analysis were in line with that of GC analysis. LA conversion (X_{LA} [%]), GVL yield (Y_{GVL} [%]), and GVL formation rate (R_{GVL} [µmol g⁻¹ min⁻¹]) were calculated according to Equations (1)-(3):

$$X_{\rm LA} = (1 - \frac{\text{Mole of LA in the products}}{\text{Initial mole of LA}}) \times 100 \tag{1}$$

$$Y_{\rm GVL} = \frac{\text{Mole of GVL in the products}}{\text{Initial mole of LA}} \times 100 \tag{2}$$

$$R_{GVL} = \frac{\text{Mole of GVL in the products}}{\text{Mass of ZrO(OH)}_2 \times \text{Reaction time}}$$
(3)

The detailed procedure for LA production from cellulose and subsequent extraction by 2-BuOH is described in the Supporting Information.

Catalyst characterization

XRD patterns were obtained by using a Panalytical X'pert Pro diffractometer using a CuK_{α} radiation source with the following parameters: 40 kV, 30 mA, $2\theta = 20-90^{\circ}$ at a scanning speed of 7° min⁻¹. FTIR spectra were recorded by using a Nicolet 380 spectrometer. The morphology of the recovered catalyst powder was observed by SEM (Hitachi S-4800), equipped with an energy dispersive X-ray spectrometer (EDS) that was used to analyze the ele-



mental content (Zr/O/Cl) of the recovered catalyst solid. The content of each element was calculated by the average value of at least five scans on the different area of the catalyst. TEM images and the corresponding SAED patterns were obtained by using a JEOL JEM-2100 instrument operated at an accelerating voltage of 200 kV. XPS spectra were measured by using a PHI Quantum-2000 electron spectrometer (Ulvac-Phi, Japan) with 150 W monochromatized AlK_{α} radiation (1486.6 eV). TGA was performed by using a SDT Q600 thermal analyzer under a dynamic N₂ atmosphere (100 mLmin⁻¹) in the temperature range of 20–900 °C with a heating rate of 20°C min⁻¹. The surface area, pore volume, and pore size of the recovered catalysts were calculated by N₂ adsorptiondesorption isotherms measured by using a TriStar 3000 with the BET and Barrett-Joyner-Halenda (BJH) methods. The samples were degassed at 373 K for 3 h under vacuum before N₂ adsorption. Elemental analyses (C and H) were performed by using an Elementar Vario EL III (Elementar Analysensysteme GmbH, Germany), and each sample was measured twice to determine the content of C and H.

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In situ generated catalyst system: HCI/ZrO(OH)₂ catalysts are prepared in situ by the autonomous decomposition of ZrOCl₂•8H₂O in levulinic acid (LA)/2-butanol solution. The esterification of LA was catalyzed in tandem with hydrocyclization to γ-valerolactone (GVL) by Meerwein–Ponndorf–Verley reduction.