

## Catalytic Conversion of Levulinic Acid and Its Esters to γ-Valerolactone over Silica-Supported Zirconia Catalysts

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Levulinic acid and its esters, important intermediate chemicals produced from biomass resources, were converted to  $\gamma$ -valerolactone via a catalytic transfer hydrogenation process over silica-supported zirconia catalysts. Silica support with a higher surface area provided highly dispersed active zirconium oxide species, which exhibited superior catalytic activity to the conventional ZrO<sub>2</sub> catalyst.

Increasing concern over the depletion of fossil fuel resources has necessitated the use of biomass as renewable, natural resources for the sustainable production of fuels and chemicals.<sup>1</sup> Among various chemicals synthesized from lignocellulosic biomass,  $\gamma$ -valerolactone (GVL) is considered one of the most appealing molecules which can be used as an ideal precursor for the production of olefins, fuels, polymers, and other valuable chemicals.<sup>2</sup> GVL can conventionally be produced by hydrogenation of cellulosic biomass-derived levulinic acid (LA) and its esters over precious metal catalysts such as Ru,<sup>3</sup> Pd,<sup>4</sup> and Ir<sup>5</sup> under the presence of high-pressure H<sub>2</sub>.<sup>6</sup>

Catalytic transfer hydrogenation (CTH) is another viable option for selective transformation of LA and its esters to GVL,<sup>7</sup> because the reaction requires alcohols as H-donors instead of high-pressure and flammable H<sub>2</sub> gas and can be catalyzed by nonprecious metal catalysts. Chia and Dumesic reported a CTH process to convert LA and its esters into GVL using bulk ZrO<sub>2</sub> and 2-propanol/2-methyl-1-propanol as H-donors at 150 °C under pressurized inert gas conditions (300 psig He, 1 Pa =  $1.45037738007 \times 10^{-4}$  psig).<sup>8</sup> However, such a system still requires high-temperature and -pressure conditions and the catalyst loses its catalytic activity during the reaction.<sup>9</sup> Previous literature regarding the CTH process using Zr-based heterogeneous catalysts have claimed that oxide supports provide

Table 1.	Conversion	of	Methyl	Levulinate	to
γ-Valer	olactone with	2-Prop	banol <sup>a)</sup>		

		ZrO <sub>2</sub> ca	at.	)~0	+	+ MeOH
Entry	Catalyst	$ZrO_2$	$S_{\rm BET}^{\rm b)}$	Т	Conv. <sup>c)</sup>	Yield <sup>c)</sup>
Linuy	Catalyst	/wt%	$/m^2 g^{-1}$	/°C	/%	/%
1	ZrO <sub>2</sub> /SiO <sub>2</sub>	9.6	250	150	93	79
2	ZrO <sub>2</sub> /MCM-41	9.7	783	150	98	88
3	ZrO <sub>2</sub> /SBA-15	9.8	863	90	6.9	5.5
4		9.8	863	120	59	49
5		9.8	863	150	98	88
6		19.4	753	150	93	84
7		49.7	597	150	54	46
8	$ZrO_2/\gamma$ - $Al_2O_3$	10.0	211	150	96	83
9	ZrO <sub>2</sub> /TiO <sub>2</sub>	10.0	91	150	61	48
10	ZrO <sub>2</sub>	100	112	150	45	42
11	SBA-15		1040	150	no rea	action

a) Reaction conditions: catalyst (40 mg as ZrO<sub>2</sub>), methyl levulinate (2 mmol), 2-PrOH (10 mL), Ar (1.0 MPa), 2 h. b) Determined by BET method from  $N_2$  adsorption isotherms. c) Determined by GC.

improved dispersibility of active Zr sites and thus afford increased catalytic activities.<sup>10,11</sup> In particular, mesoporous materials having large surface areas are expected to be suitable supports for creating highly-dispersed active Zr sites.<sup>12</sup>

In this work, we report a CTH process for the production of GVL from LA and its esters using several alcohols as H-donors over silica-supported Zr oxide catalysts, which are cheap and readily prepared. Optimization of support type, catalyst composition, and reaction conditions was performed, and the scope of substrates and alcohols was also investigated.

In the initial studies, several ZrO<sub>2</sub> catalysts supported on various oxide supports were prepared and tested in the CTH reaction of methyl levulinate with 2-PrOH (Table 1). Supported ZrO<sub>2</sub> catalysts were prepared by in situ hydrolysis of zirconium n-butoxide (Zr(O<sup>n</sup>Bu)<sub>4</sub>, 70% in n-butanol) on oxide support in an organic solvent, followed by filtration, washing, drying, and calcination. The reaction was carried out using a stainless autoclave reactor under 1.0 MPa of Ar. As shown in Table 1, GVL was synthesized from methyl levulinate over various ZrO<sub>2</sub> catalysts. Transesterification compounds (i.e., isopropyl levulinate ester and 4-hydroxypentanoic acid isopropyl ester) were produced as main by-products, and acetone and methanol were also detected, suggesting that the reaction proceeds via a CTH reaction and the following dealcoholation steps. Supported ZrO<sub>2</sub> catalysts showed higher catalytic activities than bulk ZrO<sub>2</sub>, although the selectivity to GVL slightly decreased (Entries 1 and 8–10). ZrO<sub>2</sub> supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (S<sub>BET</sub> = 211  $m^2 g^{-1}$ ) showed as high an activity as that on SiO<sub>2</sub> (S<sub>BET</sub> =  $250 \text{ m}^2 \text{g}^{-1}$ ), whereas ZrO<sub>2</sub> supported on TiO<sub>2</sub> (S<sub>BET</sub> = 91 m<sup>2</sup>g<sup>-1</sup>) gave a modest catalytic activity. A further improvement of catalytic activity was achieved by enlarging surface area of silica support; ZrO<sub>2</sub> supported on typical hexagonal mesoporous silica, such as MCM-41 and SBA-15, both afforded 88% yield of GVL with 98% conversion at 150 °C for 2h (Entries 2 and 5), while silica support itself is inactive



**Figure 1.** (A) Zr K-edge XANES spectra and (B) Zr K-edge radial distribution functions of monoclinic ZrO<sub>2</sub>, ZrO<sub>2</sub>/SiO<sub>2</sub>, and ZrO<sub>2</sub>/SBA-15 with varied ZrO<sub>2</sub> content.

for this reaction (Entry 11). The pore size of mesoporous silica had little effect on the catalytic activity (For reaction kinetics data, see Figure S1). These results clearly indicate that surface area of oxide support alters the local structure of Zr species and consequently affects the catalytic activity.

Optimization of catalyst composition and reaction conditions was performed on  $ZrO_2/SBA-15$  catalyst (Table 1). Reaction rate in the CTH process increased as the reaction temperature increased (Entries 3–5). On the other hand, increasing  $ZrO_2$  content from 9.8 to 49.7 wt % led to an appreciable reduction of catalytic activity (Entries 5–7), despite retaining most of its surface area. This result also suggests a strong link between the dispersion state of Zr species and the catalytic activity.

To obtain insights to the local structure of Zr species supported on silica, X-ray diffraction (XRD) and X-ray absorption fine structure (XAFS) measurements were performed. In the XRD patterns of the catalysts, no crystalline zirconia phase was identified below 20 wt % of ZrO<sub>2</sub> loading levels, but a tetragonal ZrO2 phase was observed at 49.7 wt % of ZrO2 loading (Figure S2). The Zr K-edge X-ray absorption near edge structure (XANES) spectra of the supported ZrO<sub>2</sub> samples resembled to that of ZrO<sub>2</sub>, suggesting that Zr species exist on silica surface as zirconium(IV) oxides (Figure 1A). In the radial distribution functions, the peaks corresponding to Zr-O and Zr-Zr bonds were observed at around r = 1.6 and 3.0 Å (the phase shift was uncorrected), respectively (Figure 1B). Curve-fitting analysis of the signals showed that the average coordination number (C.N.) of the first Zr-O shell was 4.5-5.5 at low ZrO<sub>2</sub> content, but was 7.1 at 49.7 wt % ZrO2 content, which is similar to that of bulk ZrO2 (Table 2), suggesting a different coordination state of Zr.13 The FT magnitude of the Zr-Zr shell signal for the supported ZrO<sub>2</sub> samples was considerably damped compared to that for bulk ZrO2. As for 9.8 wt % ZrO2 loaded SBA-15, the interatomic distance between two zirconium atoms was calculated to be 3.40 Å and the C.N. was 0.9, suggesting the presence of highly dispersed Zr oxide species. As the ZrO<sub>2</sub> content increased from 9.8 to 49.7 wt %, the C.N. for the Zr–Zr shell became higher  $(0.9 \rightarrow 3.2)$ , clearly evidencing the formation of agglomerated ZrO<sub>2</sub> species at higher ZrO<sub>2</sub> level. It should be also noted that ZrO2/SBA-15 (49.7 wt%) sample exhibited the Zr–Zr shell signal at r = 3.3 Å (R = 3.69 Å)

Table 2. EXAFS Curve-Fitting Parameters of  $ZrO_2$ ,  $ZrO_2/SiO_2$ , and  $ZrO_2/SBA-15^{a}$ 

Sample	Phase <sup>b)</sup>	Shell	C.N. <sup>c)</sup>	$R/Å^{d)}$
ZrO <sub>2</sub>	monoclinic	Zr–O	7	2.160
		Zr–Zr	7	3.460
$ZrO_2/SiO_2$	amorphous	Zr–O	5.5	2.122
(9.6 wt %)		Zr–Zr	1.6	3.431
ZrO <sub>2</sub> /SBA-15	amorphous	Zr–O	4.5	2.121
(9.8 wt %)		Zr–Zr	0.9	3.401
ZrO <sub>2</sub> /SBA-15	amorphous	Zr–O	5.1	2.121
(19.4 wt%)		Zr–Zr	1.0	3.404
ZrO <sub>2</sub> /SBA-15	amorphous	Zr–O	7.1	2.128
(49.7 wt %)	+ tetragonal	Zr–Zr	3.2	3.693

a)  $k^3$ -weighted EXAFS,  $3.0 \le k(\text{\AA}^{-1}) \le 13.0$ . b) Determined by XRD. c) Average coordination number. d) Average interatomic distance.



Figure 2. Catalyst reusability of  $ZrO_2/SBA-15$  and bulk  $ZrO_2$ . Reaction conditions are the same as those shown in Table 1.

which corresponds to that of tetragonal  $ZrO_2$  (C.N. = 12, R = 3.63 Å),<sup>14</sup> being consistent with the XRD result. The estimated C.N., rather than the surface area, provided a more distinct relationship toward the catalytic activity (Figure S3). These combined analyses suggest that high-surface-area silica support provides a surface environment suitable for generating highly-dispersed zirconium oxide species with a low-coordination state which is highly active for the CTH reaction.

To evaluate catalyst reusability,  $ZrO_2/SBA-15$  (9.8 wt%) and bulk  $ZrO_2$  catalysts were used 5 times repeatedly for the CTH reaction (Figure 2).<sup>15</sup> The supported  $ZrO_2$  catalyst retained more than 70% of its initial activity even after 4 repeated cycles, while unsupported  $ZrO_2$  lost most of its activity during the same number of cycles. The observed loss of catalytic activity is due to strong adsorption of organic residues on catalyst surface, which inhibits the access of organic substrate to the Zr active sites (Figure S4).

Table 3 shows the scope of substrates and alcohols for the production of GVL over ZrO<sub>2</sub>/SBA-15 (9.8 wt%) catalyst. Among various alcohols, secondary alcohols such as 2-butanol and cyclohexanol worked as efficient H-donors (Entries 4–6). Primary alcohols such as methanol, ethanol, and 1-propanol gave quite low GVL yields (Entries 1–3), mainly affording transesterification products. When 2-propanol was used as a

Table 3. Scope of Substrates and Alcohols for the Production of  $\gamma$ -Valerolactone over ZrO<sub>2</sub>/SBA-15 (9.8 wt %) Catalyst<sup>a)</sup>

ZrO <sub>2</sub> cat. Alcohol	+	ROH

R = H, Me, Et, <sup>n</sup>Bu

Entry	Substrate <sup>c)</sup>	Alcohol	Conv. <sup>d)</sup> /%	Yield <sup>d)</sup> /%
1 <sup>b)</sup>	ML	MeOH	4.7	1.2
2	ML	EtOH	87	19
3	ML	1-PrOH	88	31
4	ML	2-PrOH	98	88
5	ML	2-BuOH	95	79
6	ML	СуОН	97	88
7	EL	EtOH	10.4	9.7
8	EL	2-PrOH	86	81
9	BL	2-PrOH	68	58
10	LA	2-PrOH	99	83

a) Reaction conditions: catalyst (40 mg as  $ZrO_2$ ), substrate (2 mmol), alcohol (10 mL), Ar (1.0 MPa), 150 °C, 2 h. b) At 90 °C. c) ML: methyl levulinate, EL: ethyl levulinate, BL: *n*-butyl levulinate, LA: levulinic acid. d) Determined by GC.

H-donor, GVL could be synthesized from ethyl levulinate (EL), butyl levulinate (BL), and levulinic acid (LA) (Entries 8–10). Moreover, GVL could be produced from EL by using EtOH as a H-donor, although the reaction rate is considerably low (Entry 7). In an ideal biomass conversion process, levulinate esters are produced by alcoholysis of sugars, which results in a mixture of alcohols and the corresponding levulinate esters.<sup>16</sup> Expanding the scope of substrates and alcohols would open up a simple and low-cost way to produce GVL, because, if the alcohol media could directly be used as H-donors in CTH process, several energy-consuming steps associated with isolation and purification can be skipped.

In summary, GVL, an important feedstock chemical, was produced from biomass-derived levulinic acid and its esters using alcohols as H-donors via a CTH process over supported ZrO<sub>2</sub> catalysts, which are cheap and readily prepared. In particular, ZrO<sub>2</sub> supported on high-surface-area silica was demonstrated to be a more active and reusable catalyst compared to the conventional bulk ZrO<sub>2</sub>.

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## **Supporting Information**

Reaction kinetics data, XRD patterns, activity-structure relationships, and thermogravimetric measurement data. These materials are available electronically on J-STAGE.

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