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# Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to $\gamma$ -valerolactone over $ZrO_2$ catalyst supported on SBA-15 silica

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## ABSTRACT

A series of  $ZrO_2$  catalysts supported on mesoporous SBA-15 silica were synthesized and examined as catalysts in the production of  $\gamma$ -valerolactone (GVL) from biomass-derived levulinic acid and its esters via a catalytic transfer hydrogenation (CTH) using several alcohols as hydrogen donors. Among the catalysts examined,  $ZrO_2$  supported on high-surface-area SBA-15 silica bearing highly-dispersed zirconium species exhibited the highest catalytic activity, of which reaction rate was 1.7 times higher than that of the conventional bulk  $ZrO_2$  catalyst. Zr K-edge XAFS analysis revealed that  $Zr^{4+}$ -oxide species with a low-coordination state anchored on silica surface is the dominant active species. Such a Zr species efficiently converted levulinic acid and its esters to GVL (~95% yields) under mild reaction conditions (150 °C, 1.0 MPa Ar), and was reusable over multiple catalytic cycles without significant loss of catalytic performances. Comparative experiments, combined with detailed characterizations using  $NH_3/CO_2$ -TPD and *in-situ* FTIR, proposed a plausible reaction mechanism where basic Zr–OH site triggers the CTH reaction involving a six-member ring transition state.

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## 1. Introduction

Due to the depletion of fossil fuel resources, rapid increase of anthropogenic  $CO_2$  emissions and the associated deterioration of environmental quality, the search for renewable resources is a matter of worldwide concern. Lignocellulosic biomass is a promising feedstock for the production of fuels and chemicals, since it is an abundant, inexpensive and carbon-neutral source and is available worldwide. Recent efforts in the catalysis field have found a number of promising approaches for the catalytic transformation of lignocellulosic biomass to produce various chemicals industrially valuable (so-called “biomass refinery”) [1–7]. Among a wide range of chemicals obtained from lignocellulosic biomass,  $\gamma$ -valerolactone (GVL) has been identified as one of the most allur-

ing platform molecules [8,9], since it can be used as a fuel additive, solvent for biomass processing [10], as well as a versatile intermediate for the production of olefins [11], polymers [12,13], and other value-added chemicals [14,15]. Moreover, GVL can be used as a precursor to produce various liquid hydrocarbon fuels suitable for gasoline, diesel and aviation kerosene *etc.* [16,17].

GVL is typically obtained through the reduction of levulinic acid (LA) and its esters, which are intermediate molecules produced by acid-catalyzed solvolysis of various carbohydrate fractions of lignocelluloses, such as glucose, fructose, as well as 5-hydroxymethylfurfural (HMF), in water [18–20] and alcohols [21–25], respectively. There are two possible pathways to produce GVL from LA and its esters; (i) the hydrogenation (using molecular  $H_2$ ) and (ii) the catalytic transfer hydrogenation (CTH) (using alcohols). The former hydrogenation reaction is conventionally performed over homogeneous/heterogeneous noble metal catalysts (such as Pd [26–28], Pt [26], Ru [29–34], Ir [35]), which allow GVL production with high yields. However, the noble metal catalysts are expensive and inevitably suffer from deactivation, and the systems require flammable, high-pressure  $H_2$  (>30 bar), limiting large-scale operation requisite for biomass refinery. In contrast, the latter CTH

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process is a better alternative route for energy-saving and scalable production of GVL, since the reaction proceeds under milder conditions using low-cost metal oxides as catalysts and alcohols as cheaper and safer H-donors [36,37]. In addition, in an ideal process for the production of levulinate derivatives from lignocellulosic carbohydrates, use of alcohol media (methanol and ethanol *etc.*) is preferred rather than water because of higher yields and an easier isolation of the produced levulinate esters than LA [21–23]. Furthermore, the alcohols spent at this stage are supposed to be reused as H-donors in the following CTH process. Thus, CTH process would meet both the economic and technical requirements needed for GVL production from biomass.

Regarding the production of GVL *via* a CTH process, several catalytic systems have recently been reported. A pioneering work was done by Chia and Dumesic et al. who reported a CTH process to convert LA and its esters into GVL using bulk ZrO<sub>2</sub> and *iso*-propanol/*iso*-butanol as H-donors at 150 °C under pressurized inert gas conditions (300 psig He) [38]. Sun and Lin et al. reported that hydrated zirconia acts as an efficient heterogeneous catalyst for a CTH reaction of ethyl levulinate in a supercritical ethanol at around 250 °C [39,40]. However, these works revealed that bulk zirconia catalysts hold critical drawbacks such as high catalyst loading, relatively high reaction temperature/pressure, moderate GVL selectivity and appreciable catalyst deactivation during the reaction. Recently, Román-Leshkov et al. and Chuah et al. reported that microporous molecular sieve bearing isolated Zr sites (Zr-β) is a more effective catalyst compared with bulk zirconia [41,42], giving us an idea that dispersed Zr sites immobilized on oxide support can afford increased catalytic activities. According to these works, we recently reported that low-cost and readily-prepared silica-supported ZrO<sub>2</sub> catalyst works as a better alternative for CTH reaction of LA and its esters under relatively mild reaction conditions (150 °C, 1.0 MPa of Ar) [43]. Although the catalytic activity was found to be significantly influenced by altering type of the oxide supports, a deep insight to the activity–structure relationship has not been obtained, and the local structure of the active Zr species and the associated reaction mechanism have not fully been understood.

In this study, an array of ZrO<sub>2</sub> catalyst supported on SBA-15 silica were prepared and examined in CTH reaction of LA and its esters to produce GVL. The structure of the catalysts, including local information concerning the overall porous properties and the state of the supported Zr atoms, were investigated in detail to draw a relationship between the structure and catalytic performances and to identify the real active Zr species. Furthermore, detailed characterizations using NH<sub>3</sub>/CO<sub>2</sub>-TPD and *in-situ* FTIR were performed to propose a plausible reaction mechanism. In addition, the scope of substrates and alcohols as well as catalyst recyclability was also investigated to demonstrate broad applicability of the catalyst.

## 2. Experimental

### 2.1. Materials

All commercially available chemical reagents for material synthesis and catalytic tests were purchased from Wako Pure Chemical Ind., Ltd. unless otherwise noted and used without further purification. A pure siliceous SBA-15 was prepared by a hydrothermal synthesis method using Pluronic P123® (PEO<sub>20</sub>-PPO<sub>70</sub>-PEO<sub>20</sub>, Aldrich, *M<sub>w</sub>* = 5800) as an organic template and tetraethoxyorthosilicate (TEOS) as a silicon source according to the previous literature [44]. A pure siliceous MCM-41 was prepared by a hydrothermal synthesis method using cetyltrimethylammonium bromide (CTAB) as an organic template and TEOS as a silicon source with the molar ratio of Si: NH<sub>3</sub>: CTAB: H<sub>2</sub>O = 1.0: 3.3: 0.1: 66 [45].

### 2.2. Catalyst preparation

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, Tokyo Chemical Industry Co., Ltd.) on oxide support in an organic solvent according to a previously reported method [43]. In a typical synthesis, SBA-15 silica was carefully treated at 150 °C under vacuum to remove physisorbed water. To a glass flask containing dried SBA-15 support (2.0 g), 60 mL of 2-propanol containing desired amount of Zr(O<sup>*n*</sup>Bu)<sub>4</sub> was added, followed by stirring at room temperature for 1 h in Ar atmosphere and further stirring at 80 °C for 5 h in air. The obtained suspension was filtered, washed with ethanol, and dried at 100 °C overnight, and was finally calcined in air at 400 °C for 6 h to afford ZrO<sub>2</sub>(X)/SBA-15, where X represents the ZrO<sub>2</sub> content in the initial synthesis gel. Other types of silica (MCM-41 and fumed SiO<sub>2</sub>) were also used as supports for ZrO<sub>2</sub>.

For comparison, pure ZrO<sub>2</sub> was synthesized by a precipitation method under basic conditions; briefly, a total of 13.5 g of ZrO(NO<sub>3</sub>)<sub>2</sub>·2H<sub>2</sub>O (99.5%) was dissolved in 500 mL of deionized water, followed by precipitation at pH 9.0 with 10% NH<sub>3</sub> solution with vigorous stirring and aging at room temperature for 48 h. The obtained precipitate was filtered, thoroughly washed with deionized water, dried at 100 °C overnight, and was finally calcined in air at 400 °C for 6 h to give pure ZrO<sub>2</sub> [25].

### 2.3. Characterization

X-ray diffraction (XRD) measurements were performed using a Bruker AXS D8 Advance X-ray diffractometer with CuKα radiation (λ = 1.54056 Å). Nitrogen adsorption-desorption isotherms were measured at –196 °C by using Micromeritics ASAP2020 system. Prior to the measurements, the samples were degassed at 300 °C under vacuum for 4 h to remove physisorbed water. The specific surface area was calculated by the BET (Brunauer–Emmett–Teller) method by using adsorption data ranging from *p/p*<sub>0</sub> = 0.05 to 0.30. The pore size distributions were obtained from the adsorption branches of the nitrogen isotherms by the BJH (Barret–Joyner–Halenda) method. Transmission electron microscope (TEM) images were taken with a FEI TITAN80–300 operated at 200 kV. Thermal gravimetric analysis and differential thermal gravimetric analysis (TG/DTG) were carried out on a MAC Science TG-DTA2000 S system under a flow of air (50 mL/min) with a heating rate of 10 °C/min.

Zr K-edge X-ray absorption fine structure (XAFS) measurement was performed in transmission mode at room temperature at the BL01B1 beam line of SPring-8, Japan. A Si(311) single crystal was used to obtain the monochromated X-ray beam. The Fourier transformation of *k*<sup>3</sup>-weighted normalized EXAFS data (FT-EXAFS) from *k* space to *r* space was performed over the range 3.0 < *k* (Å<sup>–1</sup>) < 13.0 to obtain the radial structure function (RDF). For the curve-fitting analysis, the empirical phase shift and amplitude functions for Zr–O and Zr · · · Zr were extracted from the data for monoclinic ZrO<sub>2</sub>. The analysis of the XAFS data was performed by using Rigaku REX2000 software.

The acidity and basicity of the samples were quantified by temperature programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) and CO<sub>2</sub> (CO<sub>2</sub>-TPD), respectively, using a BELCAT-B system (BEL Japan, Inc.). Approximately 100 mg of sample mounted in a quartz tube was pretreated at 600 °C in a He gas flow (50 mL/min) for 1 h, allowed to cool to 50 °C, and subsequently exposed to either 5% NH<sub>3</sub>/He gas or 100% CO<sub>2</sub> gas (50 mL/min) for 1 h. After being flushed with He for 0.5 h to eliminate weakly-adsorbed NH<sub>3</sub>/CO<sub>2</sub> molecules, TPD was carried out between 50 and 600 °C under a He flow (30 mL/min) with a ramping rate of 10 °C/min, and the desorbed NH<sub>3</sub>/CO<sub>2</sub> was detected by a thermal conductivity detector.

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