

# Development of Ru/CeO<sub>2</sub> catalyst for selective C–C bond scission of biomass-derived oxygenates

**Tomoo Mizugaki,<sup>a\*</sup> Kohei Uesugi,<sup>a</sup> Kodai Nitta,<sup>a</sup> Zen Maeno,<sup>a</sup> Takato Mitsudome,<sup>a</sup> Koichiro Jitsukawa,<sup>a</sup> and Kiyotomi Kaneda<sup>b</sup>**

<sup>a</sup>Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan

<sup>b</sup>Research Center for Solar Energy Chemistry, Osaka University, Toyonaka, Osaka 560-8531, Japan

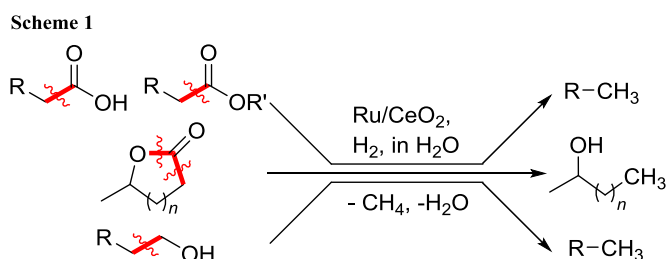
\*Corresponding author: Fax +81-6-6850-6260, E-mail: mizugaki@cheng.es.osaka-u.ac.jp

**Abstract:** Highly selective hydrogenative carbon–carbon bond scission of various biomass-derived oxygenates was achieved with a CeO<sub>2</sub>-supported Ru nanoparticle catalyst in water. The present catalyst system enabled the selective cleavage of carbon–carbon  $\sigma$  bonds adjacent to carboxyl, ester, and hydroxymethyl groups. The high selectivity for such a carbon–carbon bond scission over carbon–oxygen bonds was attributed to the multiple roles of the Ru nanoparticles assisted by the in situ formed Ce(OH)<sub>3</sub>.

**Keywords:** C–C Bond scission, Ruthenium, Cerium oxide.

## 1. Introduction

Recent requirements to reduce carbon dioxide emissions have led to the utilization of renewable resources, such as plant biomass, as carbon-neutral feedstocks for commodity chemicals. To date, much effort has been devoted to the direct C–O bond cleavage of high-oxygen containing biogenic oxygenates to produce valuable chemicals by hydrogenolysis and deoxydehydration. We have reported the highly selective transformation of biogenic chemicals into valuable ones via the catalytic C–O bond scission reaction.<sup>1–5</sup> On the other hand, selective cleavage of C–C bonds has not yet been widely investigated despite its great potential for extending the utility of biomass-derived oxygenates. The existing C–C bond cleavage methods often suffer from low selectivity toward the desired chemicals, limited substrate scope, and severe reaction conditions. Therefore, the development of selective and versatile C–C bond scission catalysts working under milder conditions is highly desired to open a new avenue for industrially important chemicals from a wide range of biomass derivatives. Herein, we found that cerium oxide-supported ruthenium nanoparticles (Ru/CeO<sub>2</sub>) efficiently promoted the selective C–C bond scission of levulinic acid (LA) to 2-butanol (**1**) in water.<sup>6</sup> This Ru/CeO<sub>2</sub> catalyst system has broad substrate scope not only for carboxylic acids, but also for esters and primary alcohols. The cleavage of C–C bonds occurs chemospecifically at positions adjacent to carboxyl, ester, and hydroxymethyl groups of oxygenated compounds (Scheme 1), leading to new eight routes for common industrial chemicals from biomass-derived oxygenates.



## 2. Experimental

The Ru/CeO<sub>2</sub> catalyst was prepared by the deposition–precipitation method using CeO<sub>2</sub> and an aqueous solution of RuCl<sub>3</sub> with NH<sub>4</sub>OH solution. The obtained powder was calcined at 573 K under static air atmosphere (Ru: 2 wt%). Other metal oxide-supported Ru catalysts were also prepared by the similar procedures. The C–C bond scission reactions were carried out in a 50 mL stainless steel autoclave equipped with a Teflon® vessel. The conversion and yields were analyzed by GC-MS using internal standard methods.

## 3. Results and discussion

Table 1 shows the results of the hydrogenative decarboxylation of LA using various supported metal catalysts. Ru/CeO<sub>2</sub> afforded **1** in water as the major product in 85% yield (entry 1). The promising catalysis

of Ru/CeO<sub>2</sub> was compared with those of the Ru-based heterogeneous catalysts. Ru/HAP (hydroxyapatite), Ru/C (activated carbon), Ru/ZrO<sub>2</sub>, Ru/TiO<sub>2</sub>, and Ru/La(OH)<sub>3</sub> gave moderate yields of **1** (entries 3–7). Ru/SiO<sub>2</sub> and Ru/Al<sub>2</sub>O<sub>3</sub> resulted in low yields of **1** and  $\gamma$ -valerolactone (**2**) was the major product (entries 8 and 9). Among the CeO<sub>2</sub>-supported noble metal catalysts, Ru/CeO<sub>2</sub> afforded the highest yield of **1**, while Rh, Pd, Ir, and Pt on CeO<sub>2</sub> gave **2** as the major product, respectively. The Ru/CeO<sub>2</sub> was reusable without appreciable loss of its activity and selectivity (entry 2). Interestingly, water was the best solvent for the production of **1**. These results clearly suggest that the combination of Ru, CeO<sub>2</sub>, and water is indispensable to achieve the selective transformation of LA into **1**. This is the first example on the highly selective production of 2-butanol from LA.

The high generality of this selective C–C bond scission reaction was also demonstrated using various oxygenated compounds (Table 2). For example, hydroxycarboxylic acids, keto and hydroxy esters, and lactones selectively afforded the corresponding secondary alcohols in high yields. In the case of diols, the chemospecific cleavage occurred at the C–C bond adjacent to the primary hydroxyl group. Notably, new eight routes for common industrial chemicals from biomass-derived oxygenates were successfully established with the Ru/CeO<sub>2</sub> catalyst (Table 2, entries 1–5, 7–9). Physicochemical analyses (XRD, XAFS, IR, and TEM) of Ru/CeO<sub>2</sub> catalyst revealed that the Ru nanoparticles (RuNPs) were formed on Ce(OH)<sub>3</sub> generated from CeO<sub>2</sub> support under the reaction conditions, which would be responsible for the high catalytic performance.

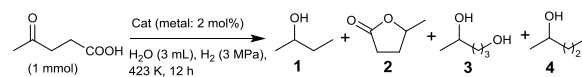
#### 4. Conclusions

Selective C–C bond scission over C–O bond of variety of carboxylic acids, esters, lactones, and polyols bearing primary hydroxy groups were achieved by Ru/CeO<sub>2</sub> catalyst, establishing eight new transformation from biomass derivatives to valuable chemicals. Both the RuNPs and in situ generated Ce(OH)<sub>3</sub> in water were crucial for the highly selective C–C bond cleavage.

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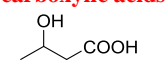

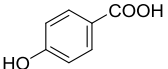

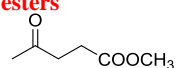

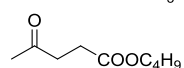

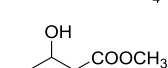

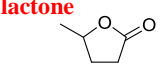

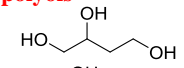

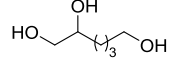

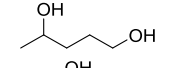

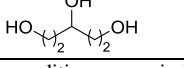

**Table 1.** Reaction of LA using various catalysts



| entry | catalyst                          | conv. [%] <sup>a</sup> | yield [%] <sup>a</sup> |    |    |   |
|-------|-----------------------------------|------------------------|------------------------|----|----|---|
|       |                                   |                        | 1                      | 2  | 3  | 4 |
| 1     | Ru/CeO <sub>2</sub>               | >99                    | 85                     | 0  | 0  | 5 |
| 2     | Reuse                             | >99                    | 83                     | 0  | 0  | 5 |
| 3     | Ru/HAP                            | >99                    | 59                     | 16 | 3  | 1 |
| 4     | Ru/C                              | >99                    | 58                     | 0  | 0  | 2 |
| 5     | Ru/ZrO <sub>2</sub>               | >99                    | 57                     | 16 | 3  | 8 |
| 6     | Ru/TiO <sub>2</sub>               | >99                    | 45                     | 29 | 5  | 1 |
| 7     | Ru/La(OH) <sub>3</sub>            | >99                    | 34                     | 27 | 16 | 2 |
| 8     | Ru/SiO <sub>2</sub>               | >99                    | 6                      | 81 | 11 | 1 |
| 9     | Ru/Al <sub>2</sub> O <sub>3</sub> | >99                    | 1                      | 92 | 5  | 0 |

<sup>a</sup>Analyzed by GC-MS using an internal standard.

**Table 2.** Selective C–C bond scission of various oxygenates catalyzed by Ru/CeO<sub>2</sub><sup>a</sup>

| entry                   | substrate  | main product  | yield [%] <sup>b</sup> |
|-------------------------|--|---|------------------------|
| <b>carboxylic acids</b> |  |   |                        |
| 1                       |  |  | 81                     |
| 2                       |  |  | 75                     |
| <b>esters</b>           |  |   |                        |
| 3                       |  |  | 82                     |
| 4                       |  |  | 82                     |
| 5                       |  |  | 82                     |
| <b>lactone</b>          |  |   |                        |
| 6                       |  |  | 83                     |
| <b>polyols</b>          |  |   |                        |
| 7                       |  |  | 72                     |
| 8                       |  |  | 72                     |
| 9                       |  |  | 97                     |
| 10                      |  |  | 82                     |

<sup>a</sup>Reaction conditions were similar to those of Table 1, entry 1.

<sup>b</sup>Yield of the main product was determined by GC-MS using internal standard technique.