Dehydration of biomass-derived butanediols over rare earth zirconate catalysts

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Supplementary Materials

Additional results and discussion

In the reaction at 325 °C, the mass recovered in the effluent liquid at −78 °C was achieved more than 98% of the mass feed, while that at 0 °C was lower than 96%. Total mass balance including recovered liquid and gaseous 1,3-butadiene achieved higher than 99% using a cold trap at −78 °C. However, it was at most 97% using ice-water trap because volatile 3-buten-1-ol was not recovered completely at 0 °C. Thus, a comparison of the difference in the temperature of the cold trap was shown in Table S1. 1,3-Butadiene was underestimated in the experiment using a cold trap at −78 °C, while 3-buten-1-ol was underestimated at 0 °C. In this work, we used a cold trap at −78 °C to correctly estimate the selectivity to 3-buten-1-ol.

In the TPD measurements of YZrO calcined at 600 and 900 °C, a blank TPD profile was obtained in the TPD measurement without adsorption (Figure S1). Even though the samples had been preheated in the blank test at 500 °C, desorption signal appeared from 100 °C. Thus, the desorption signal could be a gas desorbed YZrO sample. The desorbed gases were CO₂ and H₂O, which were detected by using mass spectrometer. In the TPD measurements, molar sensitivity of CO₂ was 1.64 times as large as that of NH₃ because of the difference of thermal conductivity of NH₃ and CO₂ gases. The detection of CO₂ and H₂O was individually conducted with mass spectrometer (not shown in Figure). Thus, we obtained TPD profiles in Figure 9 in the main text.

We discussed the intrinsic activity of REZrO catalyst, which is defined as the formation rate of UOLs per unit surface area. For the calculation of the formation rate, the conversion data less than 80% was used not to underestimate the rate. For example, some of the data over 80% conversion in Table 3 provided about a half of the datum. In the case of YZrO, the value is 0.82 and 1.58 mmol h⁻¹ m⁻² at a conversion of 93.8 and 73.0% (Table 3 and S2), respectively.
Figure S1. N$_2$ adsorption-desorption isotherm of YZrO calcined at 900 °C.

Figure S2. XRD pattern of YZrO calcined at 900 °C together with PDF data.
Figure S3 Changes in catalytic activity of YZrO calcined at 900 °C with TOS. NH$_3$ pre-adsorption prior to the reaction (A) and without NH$_3$ pre-adsorption (B). Reaction temperature, 300 °C; W/F, 0.31 h; N$_2$ carrier gas flow rate, 30 cm$^3$ min$^{-1}$.

Figure S4 TCD signal profiles in the TPD measurement of NH$_3$ and CO$_2$ desorbed from YZrO calcined at 600 (a) and 900 °C (b).
Table S1 Dehydration of 1,4-BDO over YZrO calcined at different temperatures.

| Calcination (°C) | Conv. (%) | Selectivity (mol%) | Formation rate of UOLs (mmol m⁻² h⁻¹) |
|------------------|-----------|--------------------|--------------------------------------|
|                  | 3B1ol | 2B1ol | UOLs | THF | Others |
| 600              | 59.0  | 75.3  | 3.5  | 78.8| 18.1  | 3.1  | 0.18 |
| 800              | 68.4  | 85.0  | 3.8  | 88.8| 10.2  | 1.0  | 0.42 |
| 900              | 77.6  | 87.7  | 2.8  | 90.5| 7.5   | 2.0  | 0.69 |
| 1000             | 68.5  | 90.2  | 3.1  | 93.3| 4.7   | 2.0  | 1.2  |
| 1050             | 54.0  | 90.7  | 1.4  | 92.1| 5.8   | 2.1  | 1.1  |

Conversion and selectivity are averaged between 1-5 h.

Reaction conditions: temperature, 325 °C; W/F, 0.31 h; N₂ carrier gas flow rate, 30 cm³ min⁻¹.

3B1ol, 3-buten-1-ol; 2B1ol, 2-buten-1-ol; UOLs = 3B1ol + 2B1ol; THF, tetrahydrofuran. Others include 1,3-butadiene, γ-butyrolactone, ethanol, and some unidentified products.

Table S2 Dehydration of 1,4-BDO over YZrO calcined at 900 °C with different space-time.

| Space time, W/F (h) | Conv. (%) | Selectivity (mol%) | Formation rate of UOLs (mmol m⁻² h⁻¹) |
|---------------------|-----------|--------------------|--------------------------------------|
|                     | 3B1ol | 2B1ol | UOLs | BD | THF | GBL | Others |
| 0.19                | 51.5  | 85.9  | 2.9  | 88.8| 0.7 | 8.9 | 0.6 | 1.0 | 0.75 |
| 0.25                | 74.9  | 85.1  | 3.0  | 88.1| 0.9 | 10.3| 0.4 | 0.3 | 0.81 |
| 0.31                | 77.6  | 87.7  | 2.8  | 90.5| 1.2 | 7.5 | 0.6 | 0.2 | 0.69 |
| 0.63                | 89.8  | 80.3  | 5.7  | 86.0| 3.5 | 9.4 | 0.3 | 0.8 | 0.38 |
| 0.94                | 99.4  | 76.9  | 7.5  | 84.4| 4.9 | 8.8 | 0.3 | 1.6 | 0.27 |

Conversion and selectivity are averaged between 1-5 h.

Reaction conditions: temperature, 325 °C; N₂ carrier gas flow rate, 30 cm³ min⁻¹.

3B1ol, 3-buten-1-ol; 2B1ol, 2-buten-1-ol; UOLs = 3B1ol + 2B1ol; BD, 1,3-butadiene; THF, tetrahydrofuran; GBL, γ-butyrolactone. Others include ethanol, 1-butanol, and some unidentified products.
## Table S3 Dehydration of 1,3-BDO over sixteen REZrO catalysts.

| Catalyst  | Conv. (mol%) | 3B2ol | 3B1ol | 2B1ol | UOLs | BD | MEK | MVK | others |
|-----------|--------------|-------|-------|-------|------|----|-----|-----|--------|
| LaZrO     | 40.2         | 44.9  | 1.2   | 35.1  | 81.2 | 1.7| 6.8 | 1.9 | 8.4    |
| PrZrO     | 40.9         | 50.0  | 1.0   | 41.9  | 92.9 | 1.6| 1.8 | 0.5 | 3.2    |
| NdZrO     | 46.2         | 50.3  | 1.1   | 41.2  | 92.6 | 0.4| 2.3 | 0.7 | 4.0    |
| CoZrO     | 64.7         | 55.8  | 1.0   | 35.1  | 91.9 | 1.9| 2.8 | 0.3 | 4.3    |
| SmZrO     | 61.9         | 51.3  | 1.1   | 41.9  | 91.6 | 2.2| 1.2 | 0.4 | 2.0    |
| EuZrO     | 63.8         | 51.5  | 1.0   | 41.8  | 94.3 | 1.9| 2.4 | 0.7 | 2.0    |
| GdZrO     | 61.6         | 50.2  | 1.3   | 44.1  | 95.6 | 1.2| 1.1 | 0.1 | 1.7    |
| TbZrO     | 53.8         | 50.5  | 1.2   | 44.4  | 96.1 | 0.6| 0.7 | 0.2 | 2.4    |
| DyZrO     | 61.0         | 52.2  | 1.1   | 42.0  | 95.3 | 1.0| 1.2 | 0.2 | 1.4    |
| HoZrO     | 59.9         | 51.7  | 1.2   | 41.8  | 94.7 | 3.7| 0.4 | 0.1 | 1.1    |
| YZrO      | 76.9         | 52.4  | 1.5   | 36.6  | 90.5 | 6.0| 1.2 | 0.3 | 2.0    |
| ErZrO     | 59.4         | 51.0  | 1.4   | 42.4  | 94.8 | 2.4| 1.0 | 0.2 | 1.6    |
| TmZrO     | 41.9         | 50.9  | 1.6   | 40.9  | 93.4 | 3.4| 0.9 | 0.3 | 2.0    |
| YbZrO     | 59.3         | 51.4  | 1.4   | 43.8  | 96.6 | 1.3| 0.7 | 0.1 | 1.3    |
| LuZrO     | 49.8         | 49.6  | 1.8   | 45.4  | 96.6 | 1.1| 0.6 | 0.2 | 1.5    |
| ScZrO     | 20.6         | 4.1   | 12.7  | 39.7  | 95.5 | 0  | 1.4 | 2.4 | 0.7    |

The catalyst samples are calcined at 900 °C. Conversion and selectivity are averaged at TOS between 1-5 h. Reaction conditions: reaction temperature, 325 °C; W/F, 0.31 h; N₂ carrier gas flow rate, 30 cm³ min⁻¹. 3B2O1, 3-buten-2-ol; 3B1O1, 3-buten-1-ol; 2B1O1, 2-buten-1-ol; UOLs = 3B2O1 + 3B1O1 + 2B1O1; BD, 1,3-butadiene; MEK, butanone; MVK, 3-buten-2-one. Others include ethanol, acetone, 1-butanol, and some unidentified products.

*W/F = 0.13 h.

## Table S4 Dehydration of 1,4-BDO over YZrO calcined at 900 °C.

| Temp. of cold trap (°C) | Conv. (%) | 3B1ol | 2B1ol | UOLs | BD | THF | GBL | Others | Formation rate of UOLs (mmol m² h⁻¹) |
|-------------------------|-----------|-------|-------|------|----|-----|-----|--------|-----------------------------------|
| -78                     | 77.6      | 87.7  | 28    | 90.5 | 12 | 7.5 | 0.6 | 0.2    | 0.69                              |
| 0                       | 74.4      | 85.9  | 29    | 88.8 | 13 | 5.7 | 0.5 | 3.7    | 0.65                              |

Conversion and selectivity are averaged between 1-5 h. Reaction conditions: temperature, 325 °C; W/F, 0.31 h; N₂ carrier gas flow rate, 30 cm³ min⁻¹. 3B1O1, 3-buten-1-ol; 2B1O1, 2-buten-1-ol; UOLs = 3B1O1 + 2B1O1; BD, 1,3-butadiene; THF, tetrahydrofuran; GBL, γ-butyro lactone. Others include ethanol, 1-butanol, and unrecovered products.