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 CO_2 and H_2O, which were detected by using mass spectrometer. In the TPD measurements, molar sensitivity of CO_2 was 1.64 times as large as that of NH_3 because of the difference of thermal conductivity of NH_3 and CO_2 gases. The detection of CO_2 and H_2O 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 date 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^{-2} m^{-2} at a conversion of 93.8 and 73.0 % (**Table 3** and **S2**), respectively.

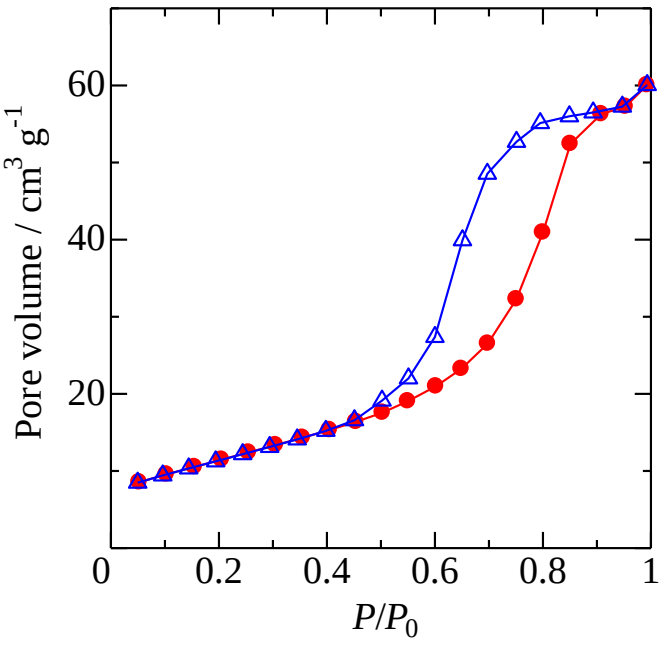

Figure S1 N_2 adsorption-desorption isotherm of YZrO calcined at 900 °C.

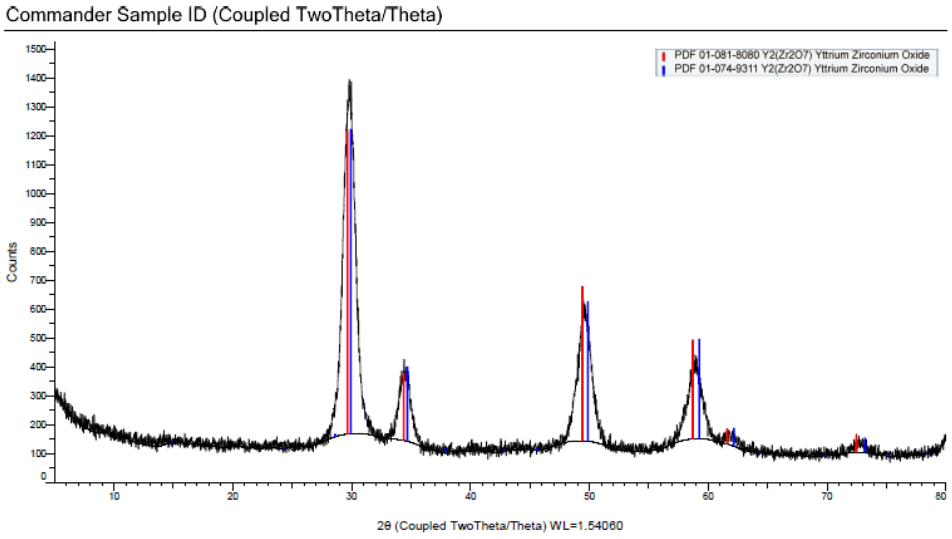

Figure S2 XRD pattern of YZrO calcined at 900 °C together with PDF data.

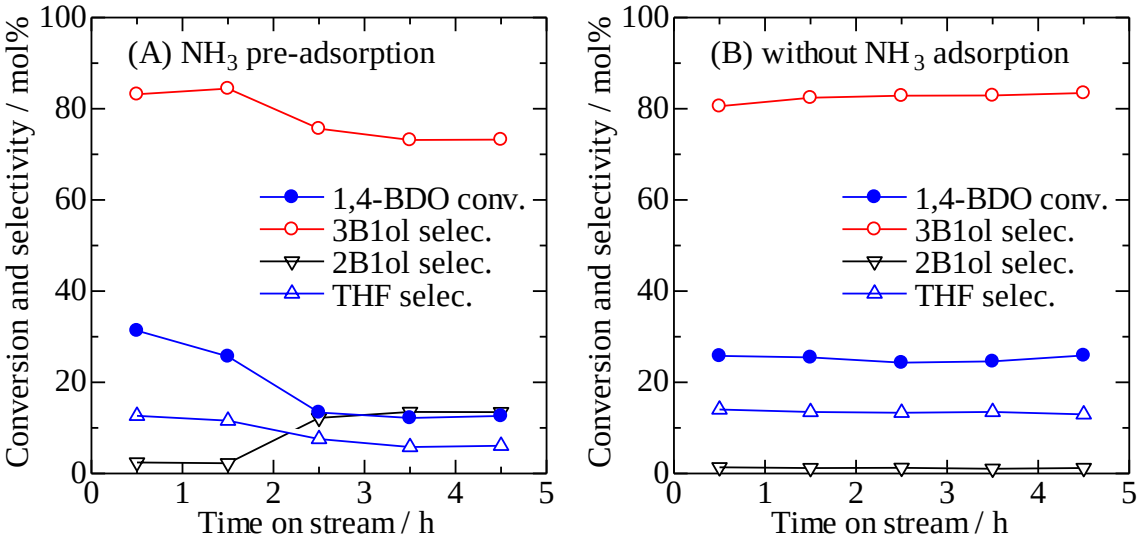

Figure S3 Changes in catalytic activity of YZrO calcined at 900 °C with TOS. NH_3 pre-adsorption prior to the reaction (A) and without NH_3 pre-adsorption (B). Reaction temperature, 300 °C; *W*/*F*, 0.31 h; N_2 carrier gas flow rate, 30 cm^3 min^{-1}.

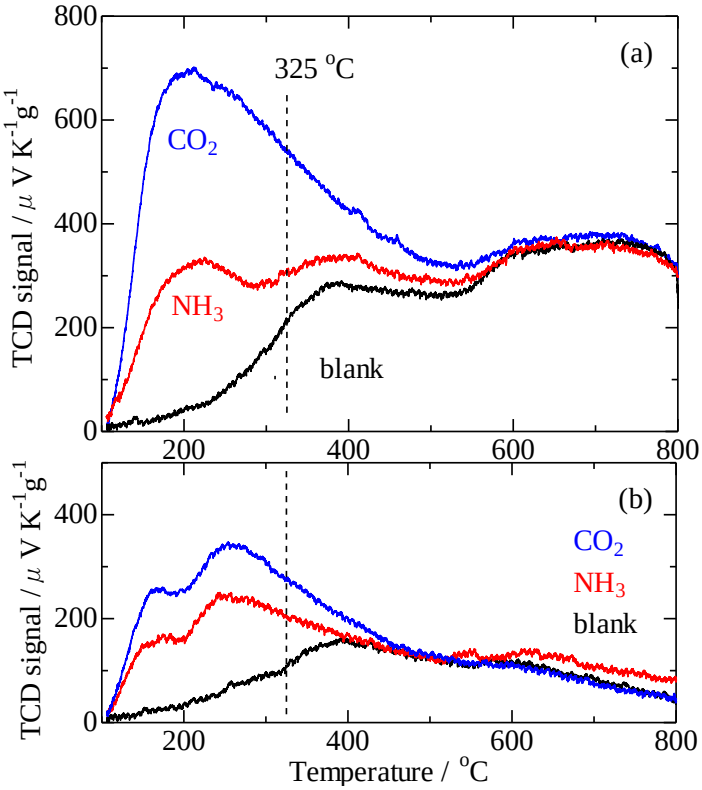

Figure S4 TCD signal profiles in the TPD measurement of NH_3 and CO_2 desorbed from YZrO calcined at 600 (a) and 900 °C (b).

Table S1 Dehydration of 1,4-BDO over YZrO calcined at different temperatures.

Calcination	Conv.	Selectivity (mol%)					Formation rate of UOLs
(°C)	(%)	3B1ol	2B1ol	UOLs	THF	Others	mmol m^{-2} h^{-1}
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; N_2 carrier gas flow rate, 30 cm^3 min^{-1}.

3B1ol, 3-buten-1-ol; 2B1ol, 2-buten-1-ol; UOLs = 3B1ol + 2B1ol; THF, tetrahydrofuran. Others include 1,3-butadine, 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*	Conv.	Selectivity (mol%)							Formation rate of UOLs
(h)	(%)	3B1ol	2B1ol	UOLs	BD	THF	GBL	Others	mmol m^{-2} h^{-1}
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; N_2 carrier gas flow rate, 30 cm^3 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.	Selectivity (mol%)							
	(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 [a]	50.0	1.0	41.9	92.9	1.6	1.8	0.5	3.2
NdZrO	46.2 [a]	50.3	1.1	41.2	92.6	0.4	2.3	0.7	4.0
CeZrO	64.7	55.8	1.0	35.1	91.9	2.8	0.7	0.3	4.3
SmZrO	61.9 [a]	51.3	1.1	41.9	94.2	2.2	1.2	0.4	2.0
EuZrO	63.8 [a]	51.5	1.0	41.8	94.3	2.4	1.0	0.2	2.0
GdZrO	61.6 [a]	50.2	1.3	44.1	95.6	1.2	1.1	0.4	1.7
TbZrO	53.8 [a]	50.5	1.2	44.4	96.1	0.6	0.7	0.2	2.4
DyZrO	61.0 [a]	52.2	1.1	42.0	95.3	2.4	0.7	0.2	1.4
HoZrO	59.9 [a]	51.7	1.2	41.8	94.7	3.7	0.4	0.1	1.1
YZrO	76.9 [a]	52.4	1.5	36.6	90.5	6.0	1.2	0.3	2.0
ErZrO	59.4 [a]	51.0	1.4	42.4	94.8	2.4	1.0	0.2	1.6
TmZrO	41.9 [a]	50.9	1.6	40.9	93.4	3.4	0.9	0.3	2.0
YbZrO	59.3 [a]	51.4	1.4	43.8	96.6	1.3	0.7	0.1	1.3
LuZrO	49.8 [a]	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; N_2 carrier gas flow rate, 30 cm^3 min^{-1}. 3B2OL, 3-buten-2-ol; 3B1OL, 3-buten-1-ol; 2B1OL, 2-buten-1-ol; UOLs= 3B2OL+3B1OL+2B1OL; BD, 1,3-butadiene; MEK, butanone; MVK, 3-buten-2-one. Others include ethanol, acetone, 1-butanol, and some unidentified products.

[a] *W/F* = 0.13 h.

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

Temp. of cold trap (°C)	Conv.	Selectivity (mol%)							Formation rate of UOLs
	(%)	3B1ol	2B1ol	UOLs	BD	THF	GBL	Others	mmol m^{-2} h^{-1}
-78	77.6	87.7	2.8	90.5	1.2	7.5	0.6	0.2	0.69
0	74.4	85.9	2.9	88.8	1.3	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; N_2 carrier gas flow rate, 30 cm^3 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 unrecovered products.