Supplementary Information

Tungsten-zirconia-supported rhenium catalyst combined with deoxydehydration catalyst for the one-pot synthesis of 1,4-butanediol from 1,4-anhydroerythritol

Tianmiao Wang,[a] Yoshinao Nakagawa,*,[a],[b] Masazumi Tamura,[a],[b],† Kazu Okumura,[c] Keiichi Tomishige *,[a],[b]

[a] Department of Applied Chemistry, School of Engineering, Tohoku University, 6-6-07 Aoba, Aramaki, Aoba-ku, Sendai, 980-8579, Japan
[b] Research center for Rare Metal and Green Innovation, Tohoku University, 468-1 Aoba, Aramaki, Aoba-ku, Sendai, 980-0845, Japan
[c] Department of Applied Chemistry, Faculty of Engineering, Kogakuin University, 2665-1 Nakano-machi, Hachioji, Tokyo 192-0015, Japan

* Corresponding Authors: Yoshinao Nakagawa and Keiichi Tomishige
*E-mail: tomi@erec.che.tohoku.ac.jp and yoshinao@erec.che.tohoku.ac.jp

† Current address: Research Center for Artificial Photosynthesis, The Advanced Research Institute for Natural Science and Technology, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan

Table S1. Detailed data of Figure 3 (b). (Effect of hydrogen pressure on the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 catalyst)

Entry	H_2 Pressure /MPa	Reaction time /h	Conv. /%	Selectivity /%									
				1,4-BuD	THF	2,3-DHF	1-BuOH	GBL	Furan	2-HTHF	Acetal A	Acetal B	Others
1	2	0	2	0	26	0	0	0	74	0	0	0	0
2	2	1	10	0	31	0	0	0	69	0	0	0	0
3	2	2	19	16	33	3	2	10	12	0	0	16	2
4	4	0	15	0	44	0	0	0	56	0	0	0	0
5	4	1	32	15	32	2	2	8	17	4	0	16	2
6	4	2	44	18	39	2	3	7	9	2	0	17	2
7	8	0	44	15	52	5	4	7	10	0	0	8	0
8	8	0.5	60	29	48	2	4	4	5	0	0	8	0
9	8	1	75	31	45	0	4	6	3	1	0	8	1

Reaction conditions: 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 = 0.15 g (Re = 1 wt%, WO_3 = 10 wt%), 1,4-dioxane = 4 g, P_{H_2} = 2 or 4 or 8 MPa, T = 413 K, t = 0-2 h.

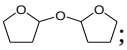
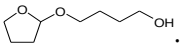
DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A:  ; Acetal B:  .

Table S2. Time course of reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 (detailed data of Figure 4)

Entry	Reaction time /h	Conv. /%	Selectivity /%								
			1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal B	Acetal C	Others
1	1	45	7	22	0	1	26	1	1	37	4
2	4	90	18	25	1	1	25	2	3	23	3
3	12	100	42	33	2	1	6	1	3	11	1
4	24	100	53	35	1	2	3	0	1	6	0
5	32	100	55	35	0	2	1	0	0	5	1
6	48	100	54	40	0	2	0	0	0	3	0

Reaction conditions: 1,4-AHERY = 0.3 g, ReO_x-Au/CeO_2 = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), ReO_x/WO_3-ZrO_2 = 0.15 g (Re = 1 wt%, WO_3 = 10 wt%), 1,4-dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 1-48 h.

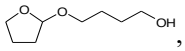
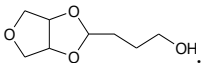
AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol, GBL: γ-butyrolactone, Acetal B:  , Acetal C:  .

Table S3. Time course of the reaction of 1,4-AHERY over ReO_x-Au/CeO_2 + ReO_x/WO_3-ZrO_2 for TOF calculation

Entry	Reaction time /h	Conv. /%	Selectivity (%)								
			1,4-BuD	THF	GBL	1-BuOH	2,5-DHF	2,3-DHF	Acetal B	Acetal C	Others
1	0	8	0	0	0	0	100	0	0	0	0
2	4	24	4	8	0	1	75	0	1	8	3

Reaction conditions: 1,4-AHERY = 0.5 g, ReO_x-Au/CeO_2 = 0.15 g (Re = 1 wt%, Au = 0.3 wt%), ReO_x/WO_3-ZrO_2 = 0.15 g (Re = 1 wt%, WO_3 = 10 wt%), 1,4-dioxane = 4 g, P_{H_2} = 8 MPa, T = 413 K, t = 0 or 4 h.

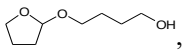
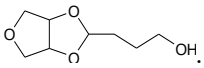
AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran, BuOH: butanol, GBL: γ-butyrolactone, Acetal B:  , Acetal C:  .

Table S4. Average valence of Re determined from white line intensity for each sample

Sample	Valence of Re	White line intensity
Re powder	0	15.70
ReO_2	4	19.41
ReO_3	6	21.55
Re_2O_7	7	22.08
ReO_x/WO_3-ZrO_2 after reaction	3.1	18.50

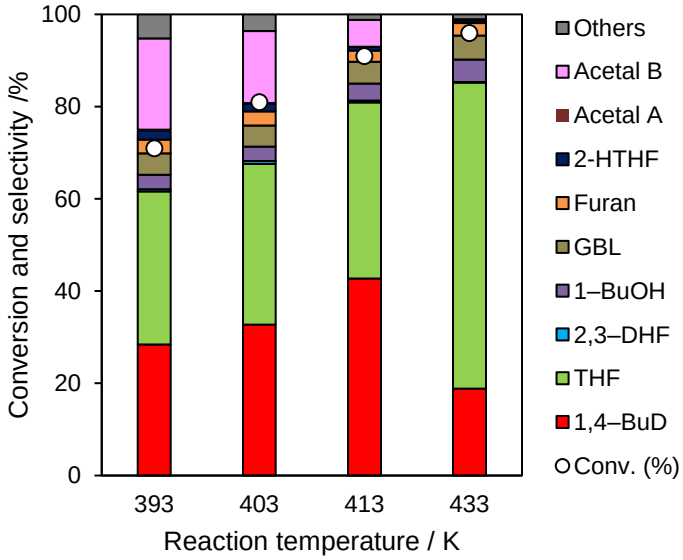
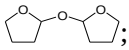
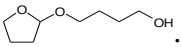


Figure S1. Effect of reaction temperature in the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2

Reaction conditions: 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 = 0.15 g (Re = 1 wt%, WO_3 = 10 wt%), 1,4-dioxane = 4 g, P_{H_2} = 8 MPa, T = 393 ~ 433 K, t = 4 h. DHF: dihydrofuran, BuD: butanediol, THF: tetrahydrofuran, BuOH: butanol, GBL: γ-butyrolactone, HTHF: hydroxytetrahydrofuran, Acetal A:  ; Acetal B: 

.

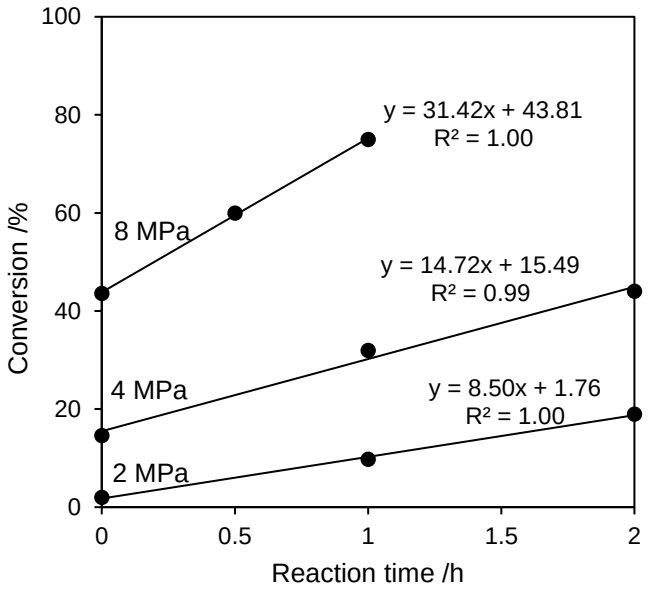


Figure S2. Detailed data of Figure 3 (b) (Effect of hydrogen pressure on the reaction of 2,5-DHF over ReO_x/WO_3-ZrO_2 catalyst)

Reaction conditions: 2,5-DHF = 0.15 g, water = 0.04 g, ReO_x/WO_3-ZrO_2 = 0.15 g (Re = 1 wt%, WO_3 = 10 wt%), 1,4-dioxane = 4 g, P_{H_2} = 2, 4 or 8 MPa, T = 413 K, t = 0-2 h.

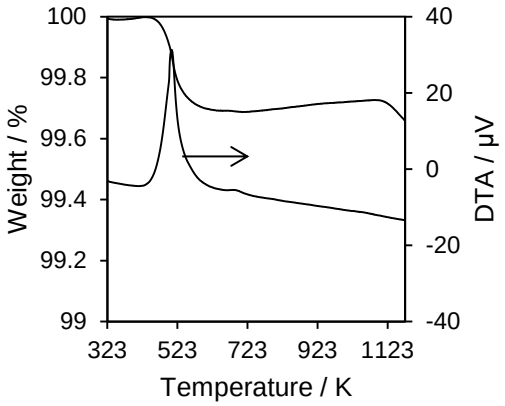


Figure S3. TG-DTA profile of the 1:1 mixture of ReO_x-Au/CeO_2 (Re = 1 wt%, Au = 0.3 wt%) and ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%) (after 1st use). Heating rate = 10 K/min, sample weight = 10 mg, under air.

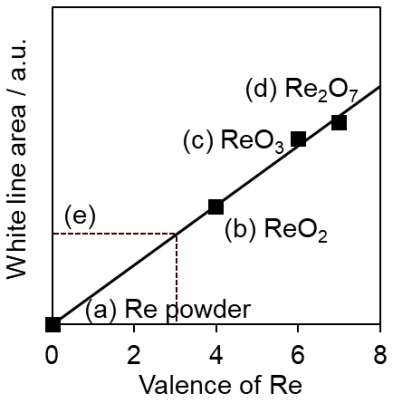


Figure S4. White line area of Re L_3-edge XANES vs. valence of Re plot in reference samples

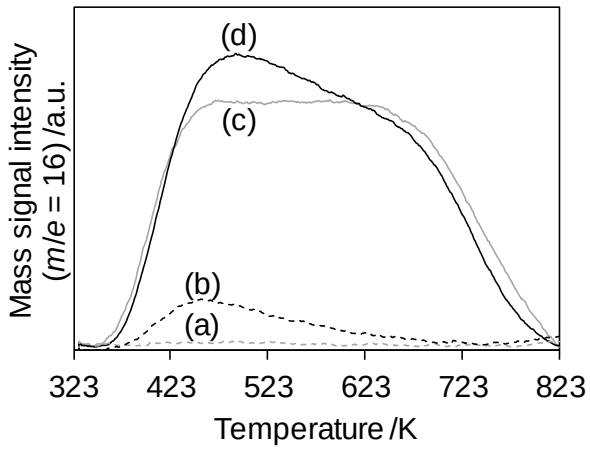


Figure S5. NH_3-TPD profiles of (a) C, (b) ReO_x/C (Re = 3 wt%), (c) WO_3-ZrO_2, (d) ReO_x/WO_3-ZrO_2 (Re = 1 wt%, WO_3 = 10 wt%). Samples were pretreated at 773 K under He, and adsorption of NH_3 was conducted at 323 K. The peak area corresponded to NH_3 desorption amount of (a) 0.004 mmol g^{-1}, (b) 0.028 mmol g^{-1}, (c) 0.22 mmol g^{-1} and (d) 0.22 mmol g^{-1}, while the Re and W amount in ReO_x/WO_3-ZrO_2 was 0.054 and 0.43 mmol g^{-1}, respectively.