Supplementary Information

for

Titania-supported molybdenum oxide combined with Au nanoparticles as a hydrogen-driven deoxydehydration catalyst of diol compounds

Schanth Hacatrjan,[a] Lujie Liu,[a] Jianxing Gan,[a] Yoshinao Nakagawa,[ab]* Ji Cao,[a] Mizuho Yabushita,[ab] Masazumi Tamura,[c] Keiichi Tomishige[ab]*

*Corresponding authors.

E-mail: yoshinao@erec.che.tohoku.ac.jp, tomi@erec.che.tohoku.ac.jp

[a] Department of Applied Chemistry, School of Engineering, Tohoku University, Aoba 6-6-07, Aramaki, Aoba-ku, Sendai, 980-8579, Japan

[b] Research Center for Rare Metal and Green Innovation, Tohoku University, Aoba 468-1, Aramaki, Aoba-ku, Sendai, 980-0845, Japan

[c] Research Center for Artificial Photosynthesis, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka, 558-8585, Japan

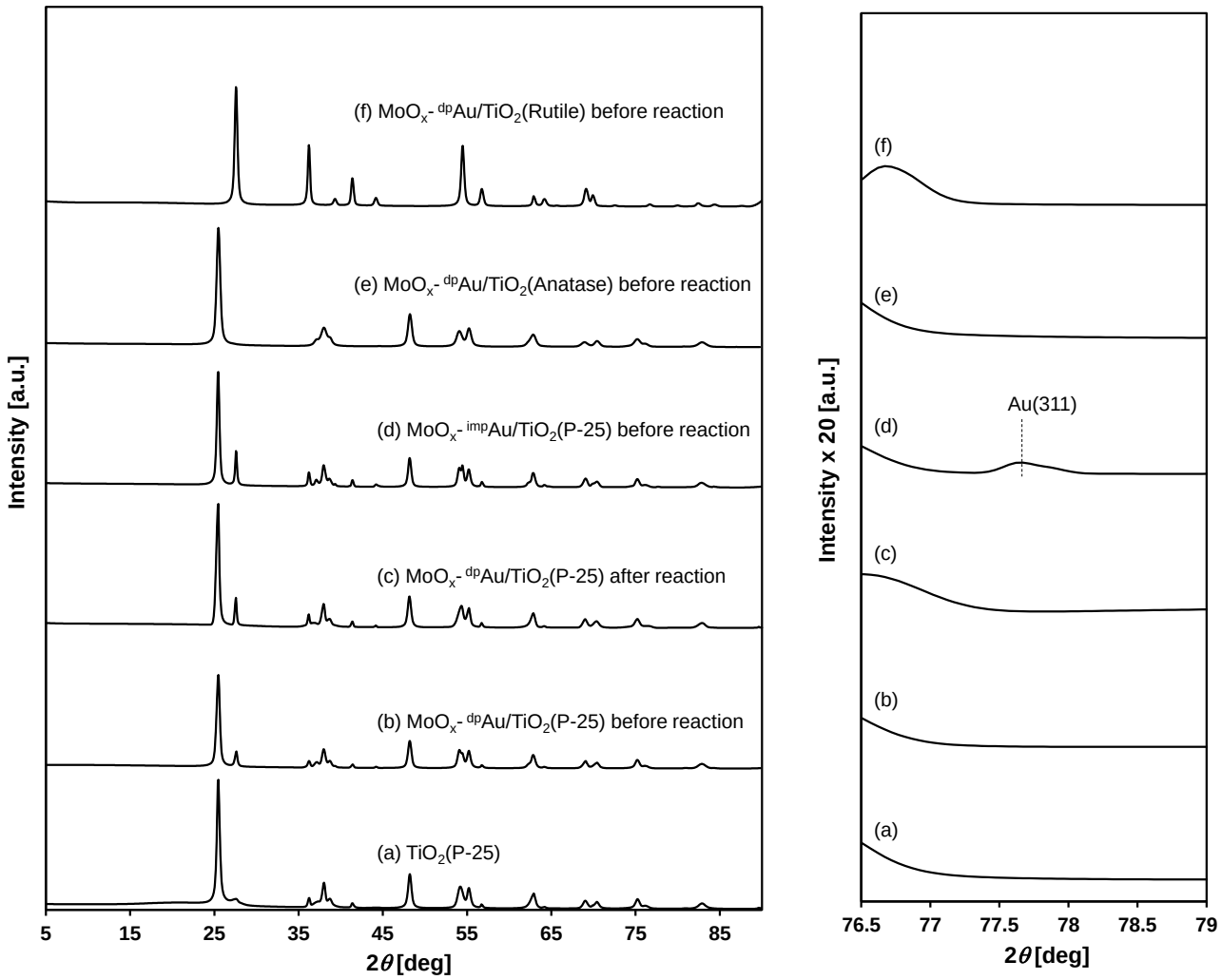

Figure S1. XRD patterns of MoO_x-Au/TiO_2 catalysts (Au 0.3 wt%, Mo 1 wt%).

Reaction conditions for the "after reaction" sample: MoO_x-$^{dp}Au/TiO_2$(P-25) = 0.15 g, 1,4-anhydroerythritol = 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K, t = 24 h.

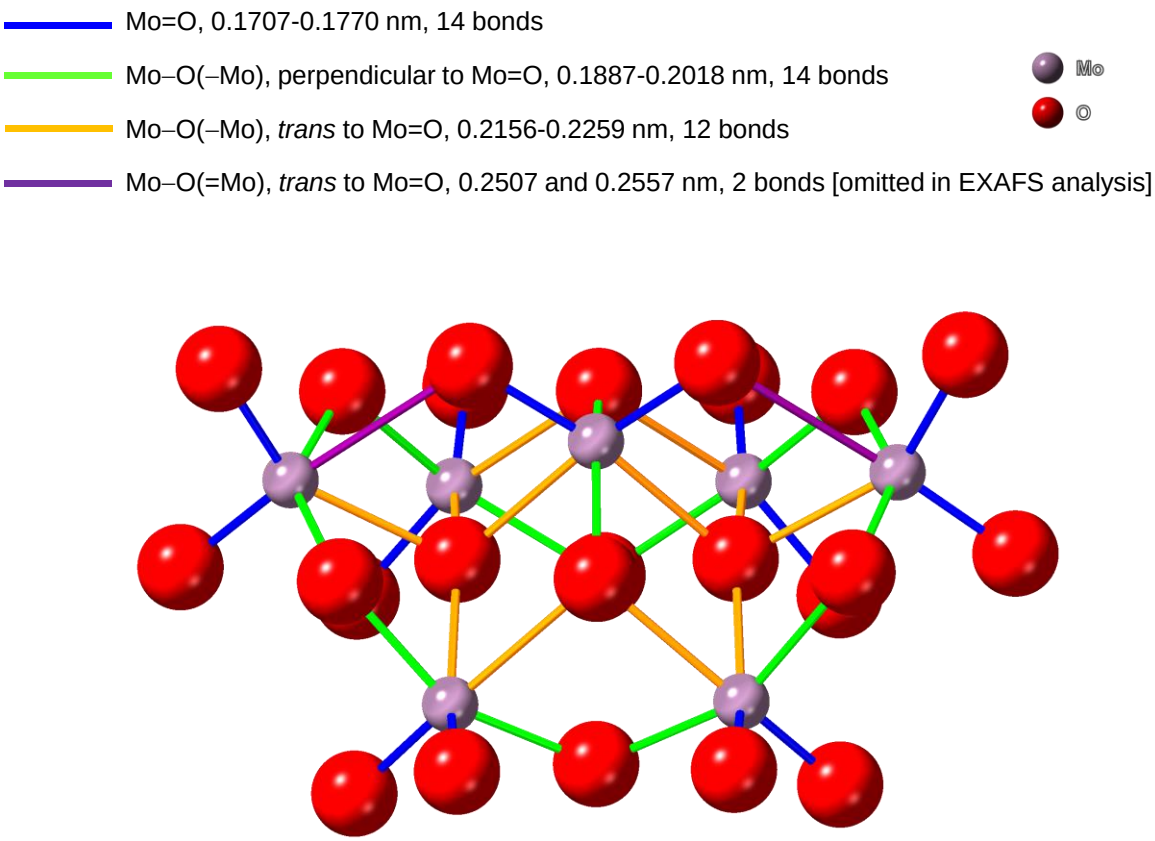

Figure S2. Bond types and lengths in $Mo_7O_{24}^{4-}$ polyoxomolybdate anion. Structure was taken from database, ICSD 4153 for ammonium heptamolybdate tetrahydrate.

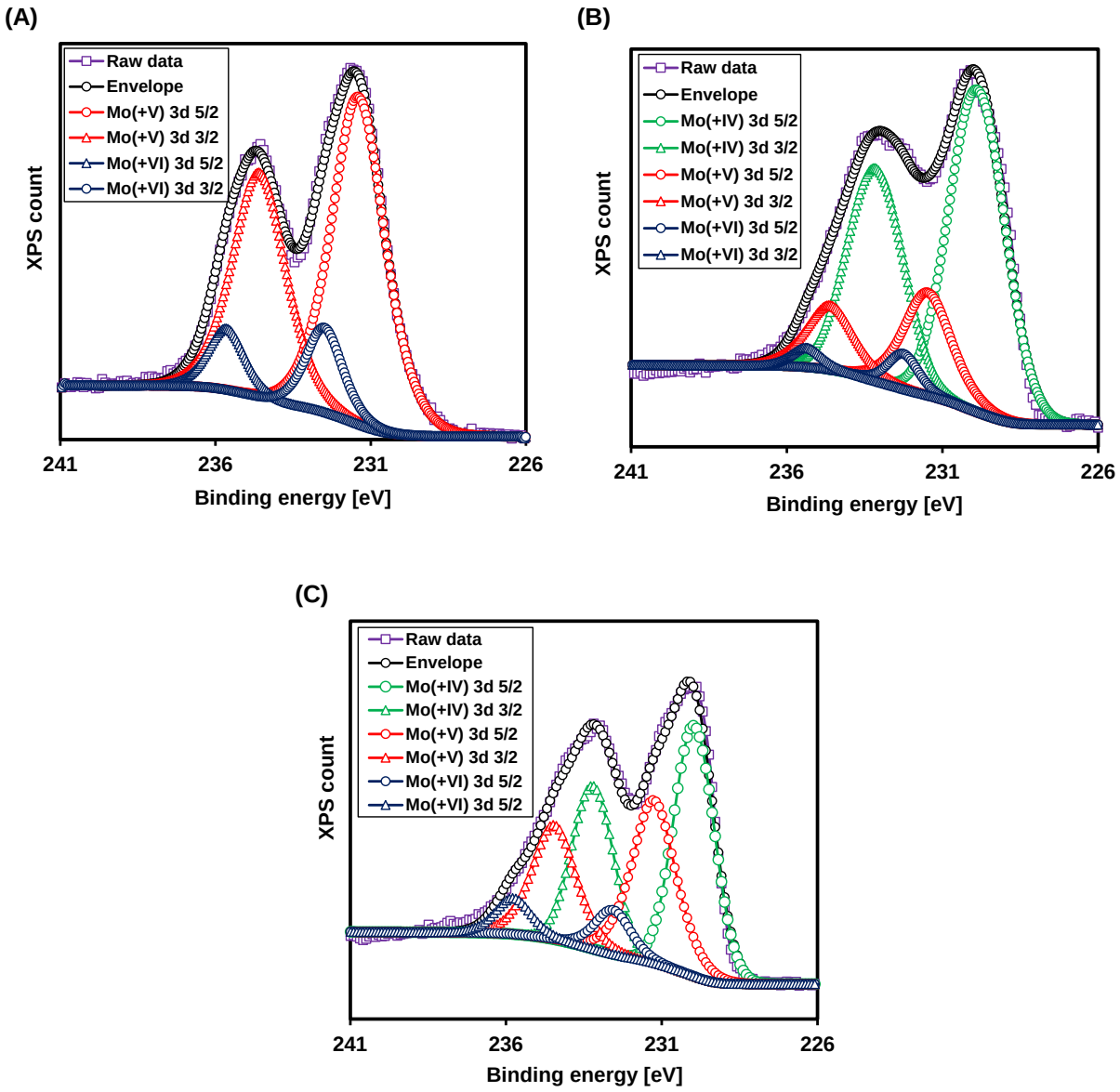

Figure S3. XPS data of MoO_x-$^{dp}Au/TiO_2$(P-25; Au 0.3 wt%, Mo 1 wt%) catalysts. (A) Before reaction, (B) after 0 h reaction (heating up to reaction temperature of 463 K under 8 MPa of H_2), and (C) after 24 h reaction. Reaction conditions: catalyst 0.15 g, 1,4-anhydroerythritol = 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K.

Note: The valence state of Mo species was probably changed during the XPS measurement, and thus the spectra should be only evaluated in the relative changes (see the main text).

Table S1. Dependence of catalytic performance on loading amounts of MoO_x-$^{dp}Au/TiO_2$(P-25) (detailed data of Figure 1).

Entry	Loading amount [wt%]		Conv.	Products (Selectivity [%])				
	Mo	Au	[%]	2,5-DHF	2,3-DHF	THF	1,4-BuD	Others
1	0	0.3	0.3a	>90	-	-	-	-
2	0.1	0.3	25	93	0.9	2.3	3.4	0.5
3	0.5	0.3	53	99	0.5	0.5	0.4	0.0
4	1.0	0.3	67	96	0.3	0.8	0.7	1.8
5	1.5	0.3	74	90	0.4	4.8	4.2	0.5
6	2.0	0.3	72	94	0.0	2.7	1.1	2.0
7	2.5	0.3	75	88	0.4	7.1	3.9	0.8
8	3.0	0.3	79	94	0.2	2.8	1.9	0.7
9	1.0	0	2.1	86	0.0	0.0	0.0	14
10	1.0	0.01	4.5	>99	0.0	0.0	0.0	0.0
11	1.0	0.1	50	94	0.0	1.7	1.1	2.8
12	1.0	0.2	62	97	0.0	0.6	0.4	2.1
(4)	1.0	0.3	67	96	0.3	0.8	0.7	1.8
13	1.0	0.4	68	96	0.0	1.0	0.3	2.7
14	1.0	0.5	68	92	0.0	4.8	1.9	1.1
15	1.0	0.6	58	94	0.0	3.0	0.6	3.0

Reaction conditions: MoO_x-$^{dp}Au/TiO_2$(P-25) catalyst = 0.15 g, 1,4-AHERY= 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran.

a Carbon balance = 63%.

Table S2. Dependence of catalytic performance MoO_x-$^{dp}Au/TiO_2$(P-25) on H_2 pressure (detailed data of Figure 2).

Entry	H_2 pressure [MPa]	Conv. [%]	Products (Selectivity [%])				
			2,5-DHF	2,3-DHF	THF	1,4-BuD	Others
1	0.15	22	93	1.3	0.8	0.8	4.3
2	1.45	45	93	0.6	2.1	2.1	4.1
3	2.9	59	93	0.0	4.3	1.6	1.1
4	4.4	65	95	0.3	1.8	0.9	1.9
5	5.8	71	96	0.3	1.8	0.0	0.9
6	8.0	67	96	0.3	0.8	0.7	1.8

Reaction conditions: MoO_x-$^{dp}Au/TiO_2$(P-25; Au 0.3 wt%, Mo 1.0 wt%) = 0.15 g, 1,4-AHERY= 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, T = 463 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran.

Table S3. Time course of 1,4-AHERY conversion (detailed data of Figure 3).

Entry	Reaction time [h]	Conv. [%]	Products (Yield [%])				
			2,5-DHF	2,3-DHF	THF	1,4-BuD	Others
Catalyst: MoO_x-$^{dp}Au/TiO_2$(P-25) (Figure 3a)							
1	0	18	17	0.0	0.0	0.0	0.1
2	4	35	35	0.0	0.0	0.0	0.1
3	8	45	45	0.0	0.0	0.0	0.2
4	14	54	54	0.0	0.2	0.0	0.4
5	24	67	64	0.2	0.6	0.0	1.2
6	48	84	77	0.0	6.0	0.0	0.5
Catalyst: MoO_x-$^{imp}Pd/TiO_2$(P-25) (Figure 3b)							
1	0	24	0.0	0.0	24	0.0	0.1
2	4	43	0.0	0.0	43	0.0	0.2
3	8	55	0.0	0.0	54	0.0	0.4
4	14	60	0.0	0.0	60	0.0	0.0
5	24	65	0.2	0.0	64	0.2	0.8
6	48	79	0.0	0.0	78	0.0	0.8

Reaction conditions: MoO_x-M/TiO_2(P-25; M 0.3 wt%, Mo 1.0 wt%) = 0.15 g, 1,4-AHERY= 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran.

Table S4. Comparison of MoO_x-$^{dp}Au/TiO_2$(P-25) with homogeneous Mo catalysts in DODH of 1,2-alkanediol

Entry	Catalyst	Substrate (S), S/Mo ratio	Reductant	*T* [K]	*t* [h]	Conv. [%]	Alkene yield [%]	TON	Average TOF [h^{-1}]	Ref.
1	MoO_x-$^{dp}Au/TiO_2$(P-25)	1,2-PeD, 308	H_2	463	24	56	53	163	6.8	This work
2	MoO_x-$^{dp}Au/TiO_2$(P-25)	1,2-PrD, 422	H_2	463	24	45	44	184	7.7	This work
3	$Mo(CO)_4$(bipy)	1,2-C14diol, 20	substrate	468-493	1	100	40	8	8	S1
4	MoO_2Cl_2(bipy)	1,2-HexD, 200	substrate	468-493	16	n.d.	19	38	2	S1
5	$(NH_4)_6Mo_7O_{24}$	1,2-HexD, 20	iPrOH	515	13.3	n.d.	46	7.2	0.7	S2
6	$(NH_4)_6Mo_7O_{24}$	1,2-DeD, 19	PPh_3	473	24	100	42	8	0.3	S3
7	$MoO_2(acac)_2$	1,2-HexD, 10	PPh_3	473	2	21	15	1.5	0.8	S4
8	$MoO_2(acac)_2$ + dione ligand (4 eq. to alkene)	1,2-HexD, 10	PPh_3	473	2	n.d.	93	9.3	4.7	S4
9	$(NH_4)_6Mo_7O_{24}$	1,2-OcD, 20	Na_2SO_3	463	24	n.d.	13	2.6	0.1	S5
10	Mo ONO pincer complex	1,2-OcD, 10	PPh_3	423	48	n.d.	59	5.9	0.1	S6
11	Mo aminobisphenolate complex	1,2-DeD, 10	PPh_3	443	24	n.d.	5	0.5	<0.01	S7
12	$[Cp^*MoO_2]_2$	1,2-OcD, 25	PPh_3	463	15	62	24	6	0.4	S8

PrD = propanediol; PeD = pentanediol; HexD = hexanediol; OcD = octanediol; DeD = decanediol; C14diol = tetradecanediol; n.d. = no data. TON = (formation amount of alkene (mol))/(Mo amount (mol)). Average TOF = TON/(reaction time (h)).

Table S5. Reuse tests of MoO_x-$^{dp}Au/TiO_2$(P-25) (detailed data of Figure 4) and effect of high-temperature calcination.

Number of uses	Treatment before use	Conv. [%]	Products (Selectivity [%])				
			2,5-DHF	2,3-DHF	THF	1,4-BuD	Others
1	(Fresh)	67	96	0.3	0.8	0.7	1.8
2	Regenerated	67	94	0.0	1.9	2.5	2.1
2	Only washing	42	98	0.0	1.2	0.0	0.6
3	Regenerated	67	94	0.0	3.0	1.4	1.4
3	Only washing	35	99	0.0	0.0	0.0	0.8
4	Regenerated	65	90	0.0	1.8	6.9	1.9
4	Only washing	35	97	0.0	0.6	0.0	2.5
2[a]	Regenerated at 673 K	53	82	0.0	9.9	5.8	2.1
1	Fresh, calcined at 673 K before use	67[b]	54	0.0	13	19	13

Reaction conditions: MoO_x-$^{dp}Au/TiO_2$(P-25; Au 0.3 wt%, Mo 1.0 wt%) = 0.15 g, 1,4-AHERY = 0.5 g, 1,2-DME = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K, t = 24 h. AHERY: anhydroerythritol, BuD: butanediol, THF: tetrahydrofuran, DHF: dihydrofuran. DME: dimethoxyethane. Catalysts with "Only washing" were reused after washing 1,2-DME and drying at 383 K for 12 h. "Regenerated" catalysts were reused after washing with 1,2-DME and calcination at 573 K ([a] 673 K) for 3 h. [b] Carbon balance = 87%.

Table S6. ICP-OES measurement of the reaction liquid of MoO_x-$^{dp}Au/TiO_2$ after each reuse cycle in the conversion of 1,4-AHERY.

Reuse times	Element (X)	Loss of X [%]
0 (Fresh)	Au	0.15
	Mo	0.67
	Ti	0.00
1	Au	0.19
	Mo	0.62
	Ti	0.00
2	Au	0.16
	Mo	0.67
	Ti	0.00
3	Au	0.14
	Mo	0.62
	Ti	0.00

Reaction conditions: MoO_x-$^{dp}Au/TiO_2$(P-25; Au 0.3 wt%, Mo 1 wt%) = 0.15 g, 1,4-AHERY= 0.5 g, 1,2-dimethoxyethane = 4 g, *n*-dodecane = 0.1 g, $P(H_2)$ = 8.0 MPa, T = 463 K, t = 24 h, AHERY: anhydroerythritol.

Table S7. Comparison of different heterogeneous catalysts and Mo-based catalysts in DODH of 1,4-anhydroerythritol (1,4-AHERY)

Entry	Catalyst	*T* [K]	*t* [h]	*P*(H_2) [MPa]	Conv. [%]	Products (Selectivity [%])					TON
						2,5-DHF	2,3-DHF	THF	1,4-BuD	Others	
1[a]	MoO_x-^{dp}Au/TiO_2(P-25)	463	24	8	67	96	0.3	0.8	0.7	2	197
2[a]	MoO_x-^{imp}Au/TiO_2(P-25)	463	24	8	51	96	0.0	2.0	1.1	1.3	151
3[a]	MoO_x/TiO_2(P-25)	463	24	8	2.0	93	0.0	0.0	0.0	7.4	6
4[S9]b	MoO_x/TiO_2(Anatase)	473	18	- (3-octanol)	94	59	-[j]	-[j]	-[j]	41	11
5[a]	MoO_x-^{imp}Pd/TiO_2(P-25)	463	24	8	65	0.4	0.0	98	0.0	1.0	192
6[S10]c	MoO_x-^{imp}Pd/CeO_2	413	4	8	0.6	0	0	26	0	74	0.2
7[a]	ReO_x-^{dp}Au/TiO_2(P-25)	463	24	8	29	1.8	0.0	51	36	11	153
8[S11]c	ReO_x-^{imp}Pd/TiO_2(P-25)	413	4	8	2	0	0	77	0	23	5
9[S11]c	ReO_x-^{imp}Pd/CeO_2	413	4	8	51.0	0.0	0.0	>99.9	0.0	0.0	152
10[S12]d	ReO_x-^{imp}Au/CeO_2	413	24	8	93	86	9	3	0	3	269
11[S13]e	ReO_x-^{dp}Au/CeO_2	413	24	8	64	89	6	1	0	4	183
12[S14]f	ReO_x/C	473	2	0.4	73.5	34.4 (2,5- and 2,3-)		0.1	0.4	65.1	9
13[S15]g	ReO_x/CeO_2 + ReO_x/C	413	24	8	97	0	0	7	86	7	134
Homogeneous Mo catalysts											
14[S16]h	Bis(phenolato) Mo complex	473	18	- (3-octanol)	81	70	-[j]	-[j]	-[j]	30	11
15[S4]i	$MoO_2(acac)_2$ + dione ligand	473	18	- (2-octanol)	-	72 (yield)	-	-	-	-	14

AHERY: anhydroerythritol, DME: dimethoxyethane, DHF: dihydrofuran, BuD: butanediol. TON: turnover number calculated by (produced DHF + THF + 1,4-BuD [mol])/(total Mo or Re [mol]).

[a] M'O_x-Au/TiO_2(P-25; Au 0.3 wt%, M'(Mo or Re) 1 wt%), MoO_x-^{imp}Pd/TiO_2(P-25; Pd 0.3 wt%, Mo 1 wt%) or MoO_x/TiO_2(P-25; Mo 1 wt%) = 0.15 g, 1,4-AHERY= 0.5 g, 1,2-DME = 4 g, dodecane = 0.1 g.

[b] MoO_x/TiO_2(Anatase; Mo 5 wt%) = 0.038 g, 1,4-AHERY= 0.042 g, 3-octanol= 0.52 g, Ar atmosphere, catalyst was pre-reduced in a hydrogen atmosphere at 573 K for 3 h.

[c] M'O_x-^{imp}Pd/support (M' 2 wt%, Pd 0.3 wt% (M' = Re) or 0.5 wt% (M' = Mo)) = 0.15 g, 1,4-AHERY = 0.5 g, 1,4-dioxane = 4.0 g.

[d] ReO_x-^{dp}Au/CeO_2 (Au 0.3 wt%, Re 1 wt%) = 0.3 g, 1,4-AHERY = 0.5 g, 1,4-dioxane = 4.0 g, dodecane = 0.1 g.

[e] ReO_x-^{dp}Au/CeO_2 (Au 0.3 wt%, Re 1 wt%) = 0.15 g, 1,4-AHERY = 0.5 g, 1,4-dioxane = 4.0 g.

[f] ReO_x/Calgon C (Re 5 wt%) = 0.1 g, 1,4-AHERY = 0.1 g, no solvent.

[g] ReO_x/CeO_2 (Re 1 wt%) = 0.15 g, ReO_x/BP2000 carbon (Re 3 wt%) = 0.15 g, 1,4-AHERY = 0.5 g, 1,4-dioxane = 4 g.

[h] Di(oxo){1,5-dithiapentanediyl-2,20-bis(4,6-di-*t*-butylphenolato)}molybdenum = 0.01 mmol, 1,4-AHERY = 0.2 mmol (0.021 g), 3-octanol = 0.52 g.

[i] $MoO_2(acac)_2$ = 0.025 mmol, 2,2,6,6-tetramethylheptane-3,5-dione = 0.25 mmol, 1,4-AHERY = 0.5 mmol (0.052 g), 2-octanol = 2 mL, N_2 atmosphere.

[j] Included in "Others".

References

[S1] J. R. Dethlefsen, D. Lupp, B.-C. Oh and P. Fristrup, *ChemSusChem*, 2014, **7**, 425-428.

[S2] J. R. Dethlefsen, D. Lupp, A. Teshome, L. B. Nielsen and P. Fristrup, *ACS Catal.*, 2015, **5**, 3638-3647.

[S3] B. E. Sharkey, A. L. Denning, F. C. Jentoft, R. Gangadhara, T. V. Gopaladasu and K. M. Nicholas, *Catal. Today*, 2018, **310**, 86-93.

[S4] M. Stalpaert and D. De Vos, *ACS Sustainable Chem. Eng.*, 2018, **6**, 12197-12204.

[S5] C. A. Navarro and A. John, *Inorg. Chem. Commun.*, 2019, **99**, 145-148.

[S6] R. Tran and S. M. Kilyanek, *Dalton Trans.*, 2019, **48**, 16304-16311.

[S7] T. C. Siu, I. Silva, M. J. Lunn and A. John, *New J. Chem.*, 2020, **44**, 9933-9941.

[S8] J. Li, M. Lutz and R. J. M. K. Gebbink, *ChemCatChem*, 2020, **12**, 6356-6365.

[S9] L. Sandbrink, K. Beckerle, I. Meiners, R. Liffmann, K. Rahimi, J. Okuda and R. Palkovits, *ChemSusChem*, 2017, **10**, 1375-1379.

[S10] Y. Nakagawa, S. Tazawa, T. Wang, M. Tamura, N. Hiyoshi, K. Okumura and K. Tomishige, *ACS Catal.* 2018, **8**, 584-595.

[S11] N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *ACS Catal.*, 2016, **6**, 3213-3226.

[S12] S. Tazawa, N. Ota, M. Tamura, Y. Nakagawa, K. Okumura and K. Tomishige, *ACS Catal.*, 2016, **6**, 6393-6397.

[S13] T. Wang, S. Liu, M. Tamura, Y. Nakagawa, N. Hiyoshi and K. Tomishige, *Green Chem.*, 2018, **20**, 2547-2557.

[S14] L. E. Manzer (du Pont), US Patent 6593481B1, 2003.

[S15] T. Wang, M. Tamura, Y. Nakagawa and K. Tomishige, *ChemSusChem*, 2019, **12**, 3615-3626.

[S16] K. Beckerle, A. Sauer, T. P. Spaniol and J. Okuda, *Polyhedron*, 2016, **116**, 105-110.