Electronic supplementary information (ESI) for

One-pot synthesis of 1,3-butanediol by 1,4-anhydroerythritol hydrogenolysis over tungsten modified platinum on silica catalyst

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Fig. S3 Effect of support on the glycerol hydrogenolysis over the 4 wt% Pt-WO_x based catalysts (W/Pt = 0.25). Reaction conditions: Glycerol = 1 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K, t = 8 h.

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References

Experimental Section

Catalysts preparation. NM-MO_x/S (NM represents group 8 noble metals: Rh, Ru, Ir, Pt, Pd; M represents oxophilic metals: Mo, Re, W; S represents support: SiO_2, MgO, CeO_2, γ-Al_2O_3, ZrO_2, activated carbon, H-ZSM-5, rutile TiO_2, and P25 TiO_2) catalysts were prepared by sequential impregnation method. The preparation procedure for the typical Pt-WO_x/SiO_2 catalyst was shown as described below. Pt/SiO_2 was prepared by the impregnation of SiO_2 with an aqueous solution of $Pt(NH_3)_4(NO_3)_2$. After drying at 383 K for 12 h, the Pt-WO_x/SiO_2 sample was prepared by impregnation of Pt/SiO_2 with $(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$ solution. Typically, the loading amount of Pt was 4 wt%, and W/Pt molar ratio was 0.25. The sample was subsequently calcined in air at 773 K for 3 h after drying at 383 K for 12 h except activated carbon supported catalysts (no calcination treatment). All the precursors and supports as well as regents were summarized in Table S8.

Activity test. A stainless steel autoclave (190 ml) was used for activity test. First, the catalyst and water solvent were added to glass inner vessel. The vessel was set to the reactor, and then the reactor was purged with 1 MPa H_2 three times. After that, 8 MPa H_2 was introduced into the autoclave and temperature was increased to 473 K for reduction pretreatment for 1 h. After cooling down and depressurizing, a desired amount of substrate was quickly added into the autoclave. Once the temperature was increased to 413 K (reaction temperature), the reactor was pressurized with H_2 rapidly to 8 MPa and defined as 0 h. The mass transfer effects were eliminated at fixed stirring rate of 250 rpm. In the case of Ir-ReO_x/rutile catalyst, it was reduced by H_2 flow at 573 K for 1 h because it was the optimized conditions.[S1] The Ir-ReO_x/rutile catalyst was introduced into the reactor under N_2 atmosphere to avoid exposure to air, and same procedure was employed to conduct reaction. After reaction, a gas bag was used to collect gas-phase products for analysis using gas chromatograph (Shimadzu GC-2025). Liquid-phase products for GC test and HPLC (Shimadzu Prominence) with RID and a UV−vis detector were collected after separation from the rest of the reaction mixture. GC–MS (QP5050, Shimadzu) was further used to identify all the products. Others include THF, butanone, alkanes (C_1-C_4 alkanes), propanols and 1,4-anhydrothreitol (1,4-AHTRE). The carbon balance in each result was within the experimental error (±10%). The standard reaction was carried out in the following conditions: initial hydrogen pressure at 8.0 MPa, reaction temperature at 413 K, reaction time for 24 h, 0.5 g (4.8 mmol) of 1,4-anhydroerythritol, 4 g of water, and 200 mg of 4 wt% Pt-WO_x/SiO_2 (41 μmol Pt, W/Pt = 0.25). Some of the parameters were adjusted to optimize catalytic performance, and the details can be found in each figure or table. For the reuse test, catalyst was reduced in liquid phase (L, 473). After reaction, separated catalyst by decantation was directly introduced to the autoclave for the next test under N_2 atmosphere without further reduction treatment. The amount of 1,4-anhydroerythritol and water solvent in each reuse was adjusted to keep the 1,4-anhydroerythritol/water/catalyst ratio.

Catalyst characterization. Inductively-coupled plasma atomic emission spectrometry (ICP-AES, ThermoFisher iCAP6500) was used to determine the leached amount after liquid-phase reduction and reuse test by filtration of samples under N_2 atmosphere. X-ray diffraction (XRD) patterns were obtained on a Rigaku MiniFlex600 diffractometer. The X-ray absorption near edge structure (XANES) spectra were measured with the approval of Japan Synchrotron Radiation Research Institute (JASRI; Proposal No. 2019A1825). The sample preparation method was as follows: In the case of catalyst after calcination at 773 K, the powder was directly filled into a plastic bag for measurement. For the reduced catalyst (L, 473), sample was collected under N_2 atmosphere, dried after washing with methanol, and then placed into a plastic bag. The thickness of all the samples was about 2 mm, which gave the edge jump for Pt L_2-edge at 0.14–0.18 (transmission mode) and W L_3-edge at 0.19–0.20 (fluorescence mode), respectively. Analyses of XANES data were performed using a computer program (REX2000, ver. 2.6; Rigaku Corp.).

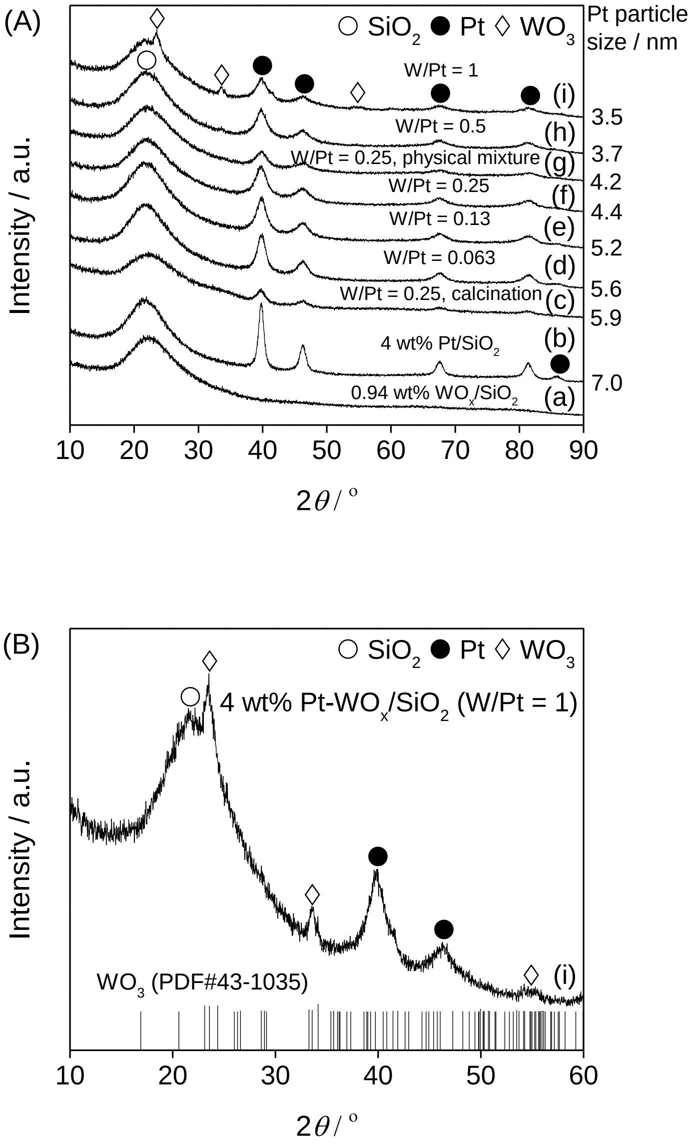

Fig. S1 XRD patterns of (A) the Pt-WO_x/SiO_2 with different molar ratio of W to Pt after reduction at 473 K (L, 473) and the catalytic use in 1,4-AHERY hydrogenolysis. (a) 0.94 wt% WO_x/SiO_2, (b) 4 wt% Pt/SiO_2, (c) 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) after calcination, (d) W/Pt = 0.063, (e) 0.13, (f) 0.25, (g) physical mixture sample (0.94 wt% WO_x/SiO_2 + 4 wt% Pt/SiO_2,), (h) 0.5, (i) 1, and (B) amplified XRD pattern of sample (i).

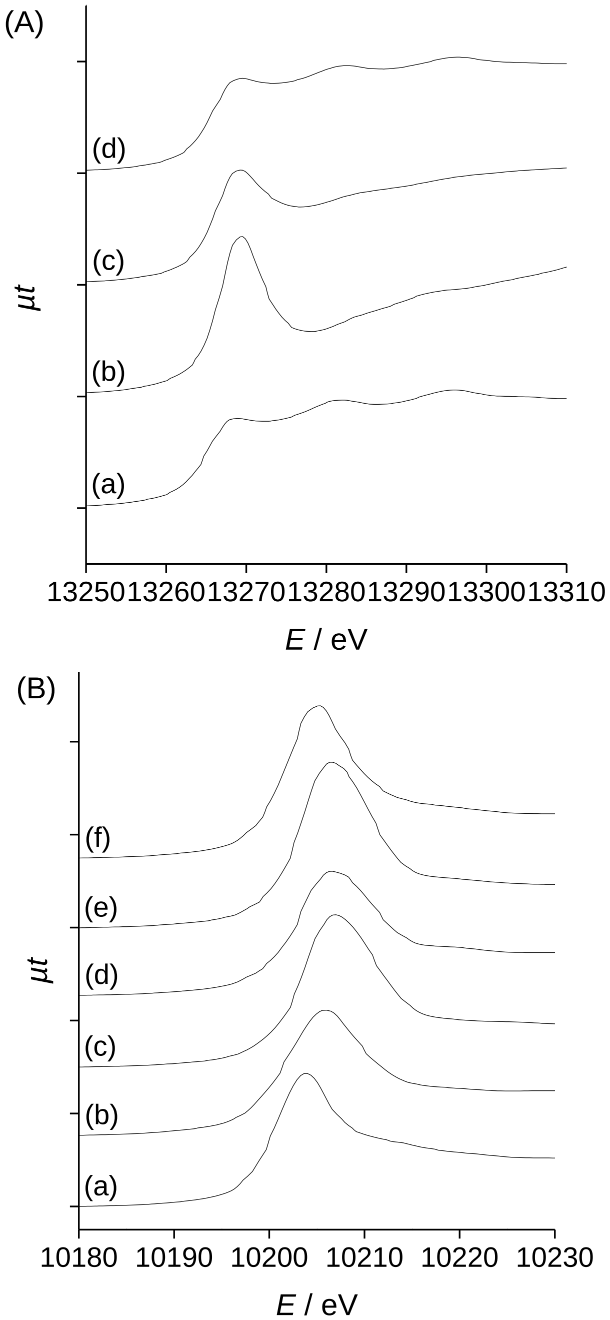

Fig. S2 The XANES spectra of (A) Pt L_2-edge, (a) Pt foil, (b) PtO_2, (c) 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) after calcination, (d) 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) after reduction (L, 473), and (B) W L_3-edge, (a) W foil, (b) WO_2, (c) WO_3, (d) $(NH_4)_6H_2W_{12}O_{40}{\cdot}nH_2O$, (e) 4 wt% Pt-$WO_x/SiO_2$ (W/Pt = 0.25) after calcination, (f) 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) after reduction (L, 473).

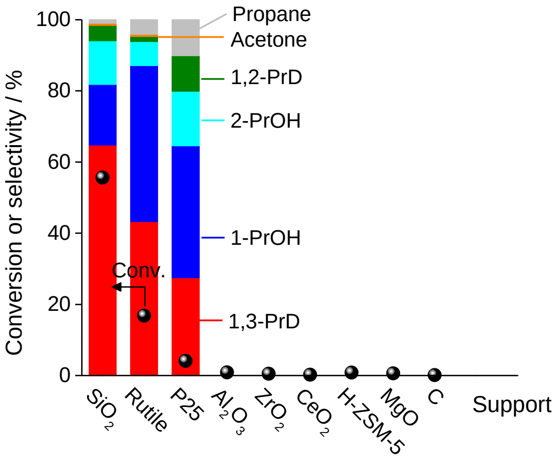

Fig. S3 Effect of support on the glycerol hydrogenolysis over the 4 wt% Pt-WO_x based catalysts (W/Pt = 0.25). Reaction conditions: Glycerol = 1 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K, t = 8 h.

Table S1 Summary of previous reports on hydrogenolysis of glycerol to 1,3-PrD over Pt-WO_x based and the present catalysts using water as solvent

Entry	Catalyst	Composition		Reaction conditions		$P_{1,3\text{-PrD}}$ / (g g_{Pt}^{-1} h^{-1})	Highest 1,3-PrD yield / %	Ref.
		Pt / wt%	W/Pt molar ratio	T / K	$P(H_2)$ / MPa			
1	Pt-LiSiW/ZrO_2	1.0	(20 wt% HSiW) 18.3	453	5.0	0.2	23	[S2]
2	Pt/WO_x/Al_2O_3	9.0	(8 wt% W) 0.94	493	4.5	0.6	28	[S3]
3	Pt/WO_x/Al_2O_3	8.9	(8 wt% W) 0.95	493	4.5	1	39	[S4]
4	Pt/WO_3/TiO_2/SiO_2	2.0	(5 wt% WO_3) 2.1	453	5.5	1	14	[S5]
5	Pt/$Ti_{80}W_{20}$	2.0	(W/Ti = 20:80) -	453	5.5	1	15	[S6]
6	Pt/WO_x/SiO_2-ZrO_2	2.0	(15 wt% WO_3) 6.3	453	5.0	1	28	[S7]
7	Pt-WO_3/SBA-15	2.0	(10 wt% WO_3) 4.2	483	0.1	2	36	[S8]
8	Pt/W–SBA-15	3.0	(0.5 wt% W) 0.16	423	4	2	61	[S9]
9	Pt/WO_x/AlOOH	1.8	(8 wt% W) 4.7	453	5.0	2	66	[S10]
				413	1.0	0.5	-	
10	Pt/WO_3/ZrO_2	3.0	(10 wt% W) 3.5	403	4.0	2	32	[S11]
11	Pt/WO_x/Al_2O_3	6.0	(12.9 wt% W) 2.3	453	5.0	3	28	[S12]
12	Pt/*meso*-WO_x	2.0	-	433	1.0	4	14	[S13]
				413	1.0	2	22	
13	Pt/ZrW38Mn3	2.0	(38 wt% W) 20.2	453	8.0	4	26	[S14]
14	Pt-WO_x/*t*-ZrO_2	2.0	(7.7 wt% W) 4.1	413	8.0	5	49	[S15]
15	Pt-WO_x/SiO_2	4.0	(0.94 wt% W) 0.25	413	8.0	4.8	57	This work

Table S2 Catalytic performance of Pt-WO_x/SiO_2 related catalysts in the glycerol hydrogenolysis

Catalyst	W/Pt ratio	Conv. / %	Selectivity / %					
			1,3-PrD	1-PrOH	2-PrOH	1,2-PrD	Acetone	Propane
4wt% Pt-WO_x/SiO_2	0.063	<2	-	-	-	-	-	-
	0.13	9	56	6	21	14	2	<1
	0.25	56	65	17	12	4	1	1
	0.5	8	53	29	8	4	1	4
	1	<2	-	-	-	-	-	-

Reaction conditions: Glycerol = 1 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K, t = 8 h.

Table S3 Results of the 1,4-AHERY hydrogenolysis over 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) catalysts at same conversion level

W/Pt ratio	*t* / h	Conv. / %	Selectivity / %							
			1,3-BuD	1,2,3-BuT	1-BuOH	2-BuOH	1,2-BuD	2,3-BuD	3-HTHF	Others
0.063	144	22	19	69	<1	3	-	-	7	2
0.13	24	25	24	66	<1	4	1	1	3	1
0.25	4	26	17	74	1	5	-	-	3	<1
0.5	24	26	25	60	2	8	2	1	2	<1
1	144	26	19	57	3	15	-	1	3	2

Reaction conditions: 1,4-AHERY = 0.5 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K.

Table S4 Reusability of 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) catalyst in the 1,4-AHERY hydrogenolysis

1,4-AHERY amount / g	Water amount / g	Catalyst amount / g	Conv. / %	Selectivity / %							
				1,3-BuD	1,2,3-BuT	1-BuOH	2-BuOH	1,2-BuD	2,3-BuD	3-HTHF	Others
0.50^{1st}	4.00	0.20	34	18	71	1	6	<1	<1	3	<1
0.40^{2nd}	3.20	(0.16)[a]	38	19	72	2	5	<1	-	2	<1
0.31^{3rd}	2.56	(0.13)[a]	36	20	70	2	6	-	-	2	<1
0.25^{4th}	2.04	0.11	37	19	73	1	4	-	-	2	<1

Reaction conditions: 1,4-AHERY = 0.5 g, H_2O = 4 g, W_{cat} = 0.2 g, T = 413 K, t = 6 h.

[a] Estimated amount from the final catalyst amount.

Table S5 Leaching amount of Pt and W after reduction or reaction

Catalyst	Usage time	Conditions	Metal leached / %	
			Pt	W
4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25)	-	(L, 473), reduction	0.9	3.6
	1	Reaction	<0.1	1.8
	2	Reaction	<0.1	0.3
	3	Reaction	<0.1	<0.2

Note: The leached amount was on the basis of metal loading amount. (L, 473) means that catalyst was pre-reduced by H_2 in the presence of H_2O at 473 K for 1 h.

Table S6 Time course of the 1,4-AHERY hydrogenolysis over 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) catalyst

t / h	Conv. / %	Selectivity / %							
		1,3-BuD	1,2,3-BuT	1-BuOH	2-BuOH	1,2-BuD	2,3-BuD	3-HTHF	Others
0	<1	-	-	-	-	-	-	-	-
2	11	15	74	1	6	-	-	2	2
4	26	17	74	1	5	-	-	3	<1
6	34	18	71	1	6	<1	<1	3	<1
12	51	23	64	1	5	1	2	4	<1
24	60	38	41	2	7	2	5	5	<1
48	82	48	25	5	13	1	5	3	<1
80	100	54	3	11	26	-	4	<1	1
100	100	43	-	19	37	-	-	<1	1

Reaction conditions: 1,4-AHERY = 0.5 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K.

Table S7 Time course of the glycerol hydrogenolysis over 4 wt% Pt-WO_x/SiO_2 (W/Pt = 0.25) catalyst

t / h	Conv. / %	Selectivity / %					
		1,3-PrD	1-PrOH	2-PrOH	1,2-PrD	Acetone	Propane
0	<1	-	-	-	-	-	-
1	10	63	19	13	2	2	1
2	21	62	20	12	4	2	-
8	56	65	17	12	4	1	1
12	82	64	18	12	5	<1	1
24	100	57	28	12	1	-	2
30	100	50	35	13	<1	-	2

Reaction conditions: Glycerol = 1 g, H_2O = 4 g, W_{cat} = 0.2 g, $P(H_2)$ = 8 MPa, T = 413 K.

Table S8 Summary of precursors, gases, supports and reagent used in this work

Precursor or reagent	Manufacturer
$Pt(NH_3)_4(NO_3)_2$	Sigma Aldrich
$Pd(NO_3)_2$	N.E. Chemcat Co., Ltd.
$RhCl_3\cdot 3H_2O$	FUJIFILM Wako Pure Chemical Co.,
$Ru(NO)(NO_3)_{3-x}(OH)_x$	Sigma Aldrich
H_2IrCl_6	Furuya Metals Co., Ltd.
NH_4ReO_4	Soekawa Chemical Co., Ltd.
$(NH_4)_6H_2W_{12}O_{40}\cdot nH_2O$	FUJIFILM Wako Pure Chemical Co.,
$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$	FUJIFILM Wako Pure Chemical Co.,
H_2	Nippon Peroxide Co., Ltd., 99.99%
N_2	Nippon Peroxide Co., Ltd., >99%
SiO_2	G6, Fuji Silysia, calcined at 973 K for 1 h, S_{BET} 485 m^2 g^{-1}
MgO	Ube Industries, Ltd., 500A, 34 m^2 g^{-1}
CeO_2	Daiichi Kigenso Co., Ltd., HS, calcined at 873 K for 1 h, 84 m^2 g^{-1}
γ-Al_2O_3	Nippon Aerosil Co., Ltd., calcined at 973 K for 1 h, 100 m^2 g^{-1}
ZrO_2	Daiichi Kigenso Kogyo Co., Ltd., calcined at 773 K for 1 h, 62 m^2 g^{-1}
Activated carbon	Shirasagi FAC-10, Japan EnviroChemicals, Ltd., 851 m^2 g^{-1}
H-ZSM-5	JRC-Z5-90H(1), Süd-Chemie Catalysts and Catalysis Society of Japan, Si/Al_2 = 90, 270 m^2 g^{-1}
Rutile TiO_2	Wako Pure Chemical Industries, Ltd., 6 m^2 g^{-1}
P25 TiO_2	Nippon Aerosil, 50 m^2 g^{-1}
H_2	Nippon Peroxide Co., Ltd., 99.99%
N_2	Nippon Peroxide Co., Ltd., > 99%
CH_4	Japan Fine Products Corp., 22.1%, diluted with Ar, standard gas
$C_2H_6 + C_3H_8 + n\text{-}C_4H_{10}$	GL Sciences, C_2H_6 (0.997%) + C_3H_8 (1.00%) + C_3H_8 (1.02%), diluted with N_2, standard gas
Glycerol	FUJIFILM Wako Pure Chemical Co., >99%
Erythritol	FUJIFILM Wako Pure Chemical Co., >97%
1,4-Anhydroerythritol	Tokyo Chemical Industries, Ltd., >98%
1,2,3-Butanetriol	Tokyo Chemical Industries, Ltd., >90%
1,2,4-Butanetriol	FUJIFILM Wako Pure Chemical Co., >95%
1,3-Butanediol	FUJIFILM Wako Pure Chemical Co., >98%
1,4-Butanediol	FUJIFILM Wako Pure Chemical Co., >98%
1,2-Butanediol	FUJIFILM Wako Pure Chemical Co., >98%
2,3-Butanediol	Tokyo Chemical Industries, Ltd., >97%
3-Hydroxytetrahydrofuran	FUJIFILM Wako Pure Chemical Co., >97%
2-Butanol	FUJIFILM Wako Pure Chemical Co., >99.5%
1-Butanol	FUJIFILM Wako Pure Chemical Co., >99%
2-Butanone	Tokyo Chemical Industries, Ltd., >99%
1,3-Propanediol	FUJIFILM Wako Pure Chemical Co., > 97%
Acetone	Kanto Chemical Co., Inc., >99.5%
1,4-Dioxane	FUJIFILM Wako Pure Chemical Co., >99%, internal standard

References

S1 L. J. Liu, T. Asano, Y. Nakagawa, M. Tamura, K. Okumura and K. Tomishige, *ACS Catal.*, 2019, **9**, 10913-10930.

S2 S. Zhu, X. Gao, Y. Zhu, Y. Zhu, X. Xiang, C. Hu and Y. Li, *Appl. Catal. B*, 2013, **140-141**, 60-67.

S3 S. García-Fernández, I. Gandarias, J. Requies, M. B. Güemez, S. Bennici, A. Auroux and P. L. Arias, *J. Catal.*, 2015, **323**, 65-75.

S4 S. García-Fernández, I. Gandarias, J. Requies, F. Soulimani, P. L. Arias and B. M. Weckhuysen, *Appl. Catal. B*, 2017, **204**, 260-272.

S5 L. Gong, Y. Lu, Y. Ding, R. Lin, J. Li, W. Dong, T. Wang and W. Chen, *Appl. Catal. A*, 2010, **390**, 119-126.

S6 Y. Zhang, X.-C. Zhao, Y. Wang, L. Zhou, J. Zhang, J. Wang, A. Wang and T. Zhang, *J. Mater. Chem. A*, 2013, **1**, 3724-3732.

S7 S. Zhu, X. Gao, Y. Zhu, J. Cui, H. Zheng and Y. Li, *Appl. Catal. B*, 2014, **158-159**, 391-399.

S8 S. S. Priya, V. P. Kumar, M. L. Kantam, S. K. Bhargava, A. Srikanth and K. V. R. Chary, *Ind. Engin. Chem. Res.*, 2015, **54**, 9104-9115.

S9 Y. Fan, S. Cheng, H. Wang, D. Ye, S. Xie, Y. Pei, H. Hu, W. Hua, Z. H. Li, M. Qiao and B. Zong, *Green Chem.*, 2017, **19**, 2174-2183.

S10 R. Arundhathi, T. Mizugaki, T. Mitsudome, K. Jitsukawa and K. Kaneda, *ChemSusChem*, 2013, **6**, 1345-1347.

S11 L.-Z. Qin, M.-J. Song and C.-L. Chen, *Green Chem.*, 2010, **12**, 1466-1472.

S12 N. Lei, X. Zhao, B. Hou, M. Yang, M. Zhou, F. Liu, A. Wang and T. Zhang, *ChemCatChem*, 2019, **11**, 3903-3912.

S13 J. Wang, X. Zhao, N. Lei, L. Li, L. Zhang, S. Xu, S. Miao, X. Pan, A. Wang and T. Zhang, *ChemSusChem*, 2016, **9**, 784-790.

S14 W. Zhou, J. Luo, Y. Wang, J. Liu, Y. Zhao, S. Wang and X. Ma, *Appl. Catal. B*, 2019, **242**, 410-421.

S15 Y. Fan, S. Cheng, H. Wang, J. Tian, S. Xie, Y. Pei, M. Qiao and B. Zong, *Appl. Catal. B*, 2017, **217**, 331-341.