

Electronic Supplementary Information

Selective Hydrogenation of Levulinic Acid to 1,4-Pentanediol in Water Using a Hydroxyapatite-supported Pt-Mo Bimetallic Catalyst

T. Mizugaki,^a Y. Nagatsu,^a K. Togo,^a Z. Maeno,^a T. Mitsudome,^a K. Jitsukawa^a and
K. Kaneda^{*a,b}

^a Department of Materials Engineering Science, Graduate School of Engineering Science, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

^b Research Center for Solar Energy Chemistry, Osaka University, 1-3 Machikaneyama, Toyonaka, Osaka 560-8531, Japan

* E-mail: kaneda@cheng.es.osaka-u.ac.jp

Experimental

1) General

Levulinic acid, 1,4-pentanediol (1,4-PeD), γ -valerolactone (GVL), 2-methyltetrahydrofuran (MTHF), 1-pentanol (1-PeOH), 2-pentanol (2-PeOH), and hydroxyapatite (HAP) were purchased from Wako Pure Chemicals Co. and Tokyo Chemical Industry (TCI), and purified appropriately prior to use. H_2PtCl_6 (N. E. Chemcat), RhCl_3 hydrate (N. E. Chemcat), H_2IrCl_6 hydrate (N. E. Chemcat), PdCl_2 (N. E. Chemcat), $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (Nacalai Tesque), MoO_3 (Wako Pure Chemicals), Nb_2O_5 (Wako Pure Chemicals), V_2O_5 (Wako Pure Chemicals), γ -alumina (JRC-ALO-2), silica (CALiAct Q-3, Fuji Silicia), TiO_2 (Aeroxide R TiO_2 P-25, Aerosil), CeO_2 (JRC-CEO-3), and MgO (JRC-MGO-3) were used as received.

Gas chromatography-mass spectrometry (GC-MS) analyses were performed on a Shimadzu QP-2010SE instrument equipped with a capillary column (InertCap WAX-HT, GL Science, 30 m \times 0.25 mm i.d., 0.25 μm), using diethyleneglycol dimethylether (diglyme) as an internal standard. ^1H NMR spectra were obtained on JEOL GSX-270 spectrometer with TMS as the internal standard. Pt L_3 -edge and Mo K -edge X-ray absorption spectra were recorded at room temperature in the transmittance and fluorescence modes using a Si (311) monochromator on the 14B2 and 01B1 beam line stations at Spring-8, Japan Atomic Energy Research Institute (JASRI), Harima, Japan. Data analysis was performed using Demeter ver. 0.9.21 (B. Ravel, M. Newville, *J. Synchrotron Rad.* 2005, **12**, 537–541). Powder X-ray diffraction (XRD) patterns were acquired using a Philips X'Pert-MPD instrument with $\text{Cu-K}\alpha$ radiation. Transmission electron microscopy (TEM) images were obtained using a Hitachi HF-2000 type microscope,

operating at 200 kV, at the Research Center for Ultra-High Voltage Electron Microscopy, Osaka University. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) data were obtained using a SII Nano Technology SPS7800.

2) Catalyst preparation

Pt-Mo/HAP: 4 mL of an aqueous solution of H_2PtCl_6 (50 mM) and 2 mL of an aqueous solution of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (25 mM) were added to 50 mL of distilled water at 298 K. Then, hydroxyapatite (1 g) was added to the solution and the mixture was stirred magnetically while maintaining the same temperature for 4 h. Water was removed by rotary evaporation under reduced pressure to give the solid product. The obtained powder was dried at 383 K for 5 h, then calcined at 773 K for 3 h under a static air atmosphere to obtain Pt-Mo/HAP as a dark gray powder. ICP-AES analysis determined that the HAP had been impregnated with Pt and Mo at concentrations of 4 wt% and 0.49 wt%, respectively.

Other Pt-Mo bimetallic catalysts were prepared in a similar way. Metal oxide-supported monometallic catalysts were prepared by the impregnation method using various supports and noble metal salts. The noble metal contents were adjusted to 0.2 mmol of noble metal/g catalyst. In the case of Pt/MoO₃, Pt content was 8 wt%.

3) Representative reaction procedure

The hydrogenation of levulinic acid was carried out in a 50 mL stainless steel autoclave equipped with a Teflon® vessel. The vessel was charged with 1 mmol of levulinic acid, 0.1 g of catalyst and 3 mL of water, and a Teflon®-coated magnetic stir bar was added. The reactor was sealed, purged three times with H₂ at 1 MPa, then pressurized to 5 MPa, heated to 403 K and stirred at 1100 rpm for 12 h. Following the reaction, the autoclave was cooled in an ice-water bath and the hydrogen gas was carefully released. The resulting reaction mixture was diluted with methanol and analyzed by GC-MS.

4) Catalyst reuse experiments

During reuse experiments, following each hydrogenation reaction, the catalyst was separated from the reaction mixture by centrifugation, washed with water and dried at 110 °C overnight. The recovered catalyst was subsequently calcined for 3 h at 773 K, after which it was reused for the next reaction.

5) A 10 g-scale reaction:

The 10g-scale hydrogenation of levulinic acid was carried out in a 100 mL stainless steel autoclave equipped with a Teflon® vessel. The vessel was charged with 10 g (86.1 mmol) of levulinic acid, 1.0 g of catalyst and 40 mL of water, and a Teflon®-coated magnetic stir bar was added. The reactor was purged three times with H₂ at 2 MPa, then pressurized to 7 MPa at room temperature, heated to 423 K and stirred at 1100 rpm for 48 h. During the period, the hydrogen pressure was kept constant by charging H₂ pressure.

After the reaction, the autoclave was cooled in an ice-water bath and the hydrogen gas was carefully released. The solid catalyst was removed by suction filtration and washed several times with water. The GC-MS analysis of the filtrate showed the complete conversion of LA and 1,4-PeD was formed in 87% yield and 2-PeOH and 1-PeOH were observed in 10% and 3% yields, respectively. Evaporation of the filtrate to remove water and the byproducts of 2-PeOH, 1-PeOH. Trace of water was removed as an azeotrope with toluene. Finally, evaporation of remaining toluene and distillation under reduced pressure gave 7.2 g of pure 1,4-PeD as a colorless oil (80% isolated yield).

Table S1 Reported catalyst system for hydrogenation of levulinic acid to 1,4-pentanediol

Entry	Catalyst	Temp. [K]	H ₂ [MPa]	LA/cat. [mol/mol]	Solvent	Conv. [%] ^b	Yield of 1,4-PeD [%] ^b	Ref.
1	Pt-Mo/HAP	403	3	50	water	>99	93	This work
2	Ru-Re/C	413	15	2290	water	>99	82	1S
3	Rh-MoO _x /SiO ₂	353	6	flow*	water	>99	70	2S
4	Cu-CrO ₃	463	20	11.6**	neat	>99	44	3S
5	Ir-MoO _x /SiO ₂	373	6	flow*	water	>99	42	4S
6	<i>N</i> -triphos Ru complex	423	6.5	200	THF	>99	99	5S
7	triphos Ru complex	433	10	1000	neat	>99	95	6S

* Hydrogenation was carried out under the fixed-bed flow conditions. ** LA/cat (g/g).

[1S] L. Corbel-Demilly, B. K. Ly, D. P. Minh, B. Tapin, C. Especel, F. Epron, A. Cabiac, E. Guillon, M. Besson and C. Pinel, *ChemSusChem*, 2013, **6**, 2388-2395.

[2S] M. Li, G. Li, N. Li, A. Wang, W. Dong, X. Wang and Y. Cong, *Chem. Commun.*, 2014, **50**, 1414-1416.

[3S] R. V. Christian, Jr., H. D. Brown and R. M. Hixon, *J. Am. Chem. Soc.*, 1947, **69**, 1961-1963.

[4S] Z. Wang, G. Li, X. Liu, Y. Huang, A. Wang, W. Chu, X. Wang and N. Li, *Catal. Commun.*, 2014, **43**, 38-41.

[5S] A. Phanopoulos, A. J. P. White, N. J. Long and P. W. Miller, *ACS Catal.*, 2015, **5**, 2500-2512.

[6S] F. M. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer and W. Leitner, *Angew. Chem. Int. Ed.*, 2010, **49**, 5510-5514.

Table S2 Solvent effect on the hydrogenation of levulinic acid using Pt-Mo/HAP catalyst ^a

Entry	Solvent	Conv. [%] ^b	Yield [%] ^b				
			1,4-PeD	GVL	2-PeOH	1-PeOH	MTHF
1	water	>99	93	trace	4	0	trace
2	ethanol	>99	38	18	26	9	4
3	2-propanol	>99	31	1	45	10	10
4	<i>n</i> -dodecane	>99	28	0	33	14	7
5	1,4-dioxane	>99	16	15	39	8	9
6	methanol	>99	3	90	2	1	trace

^a Reaction conditions: LA 1 mmol, catalyst (0.1 g, Pt 2 mol%, Mo 0.5 mol%), solvent 3 mL, 403 K, H₂ 5 MPa, 12 h. ^b Analyzed by GC-MS using an internal standard method.

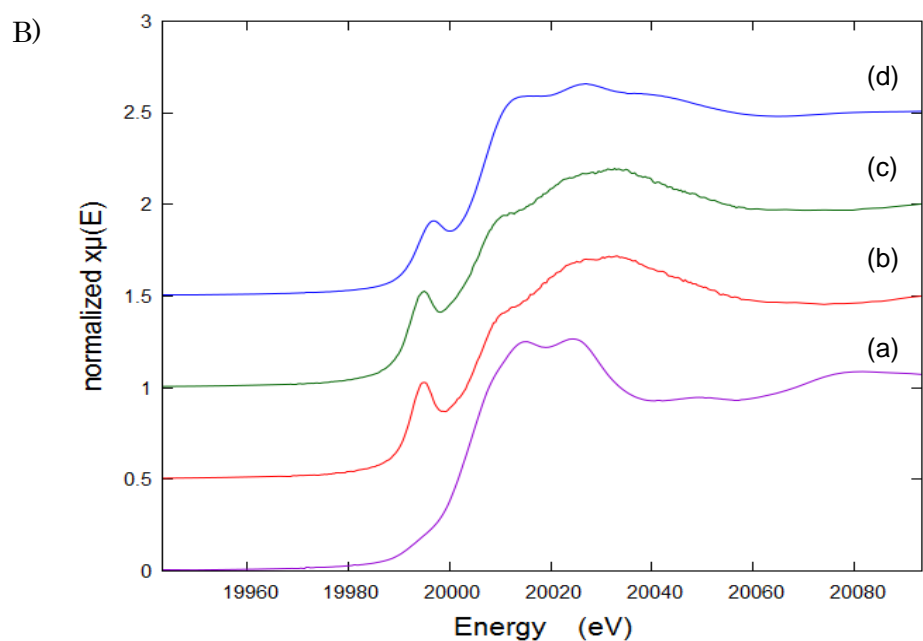
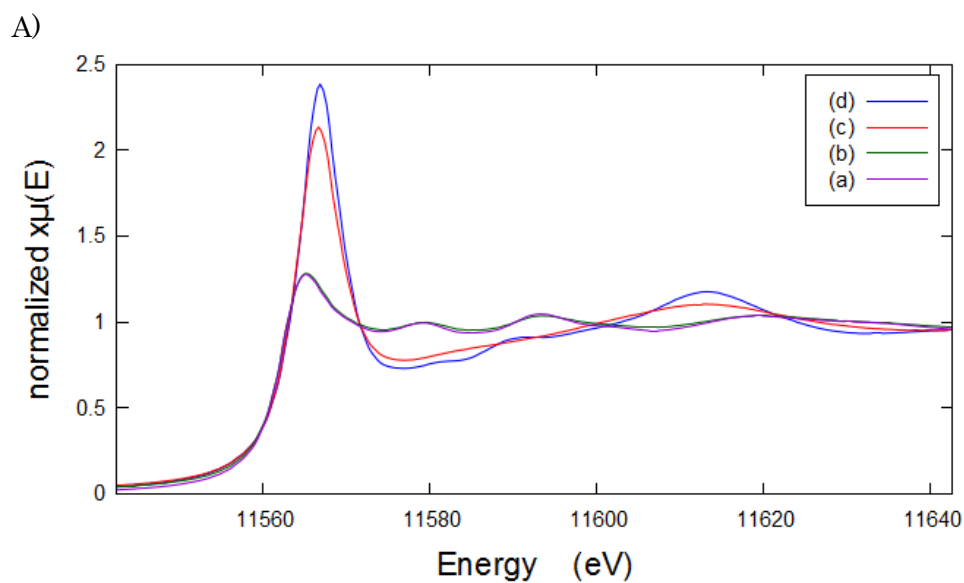


Fig. S1 A) Pt *L*-edge Xanes spectra of (a) Pt foil, (b) Pt-Mo/HAP after hydrogenation, (c) Pt-Mo/HAP fresh, and (d) PtO₂, and B) Mo *K*-edge XANES spectra of (a) MoO₂, (b) Pt-Mo/HAP after hydrogenation, (c) Pt-Mo/HAP fresh, and (d) (NH₄)₆Mo₇O₂₄·4H₂O.

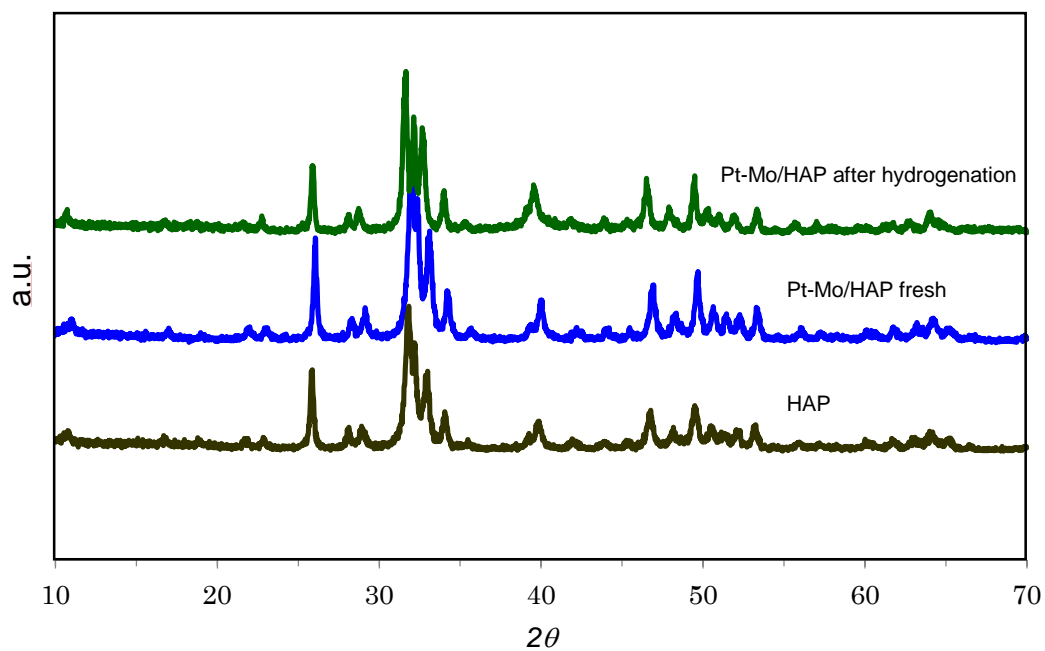


Fig. S2 XRD patterns for HAP, Pt-Mo/HAP fresh, and used Pt-Mo/HAP after hydrogenation.

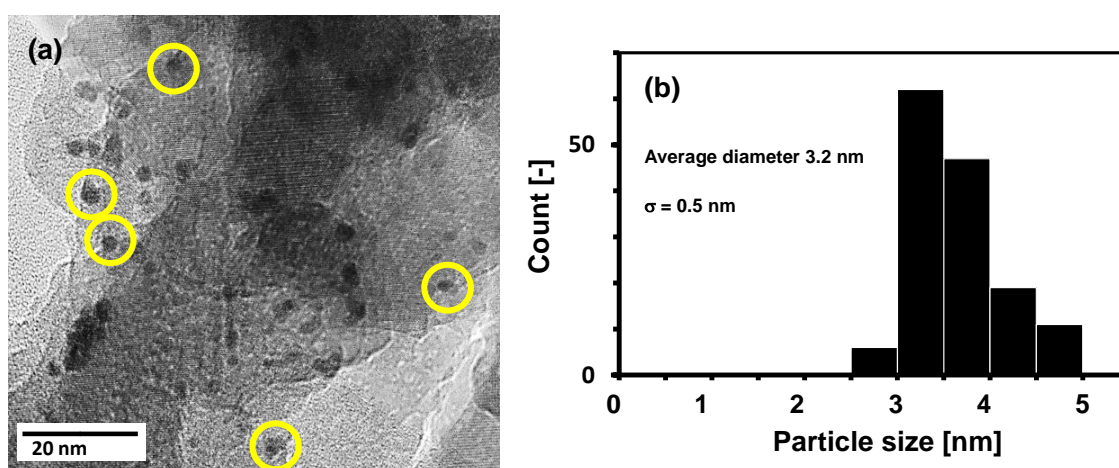


Fig. S3 TEM image (a) and the size distribution (b) of Pt-Mo/HAP.

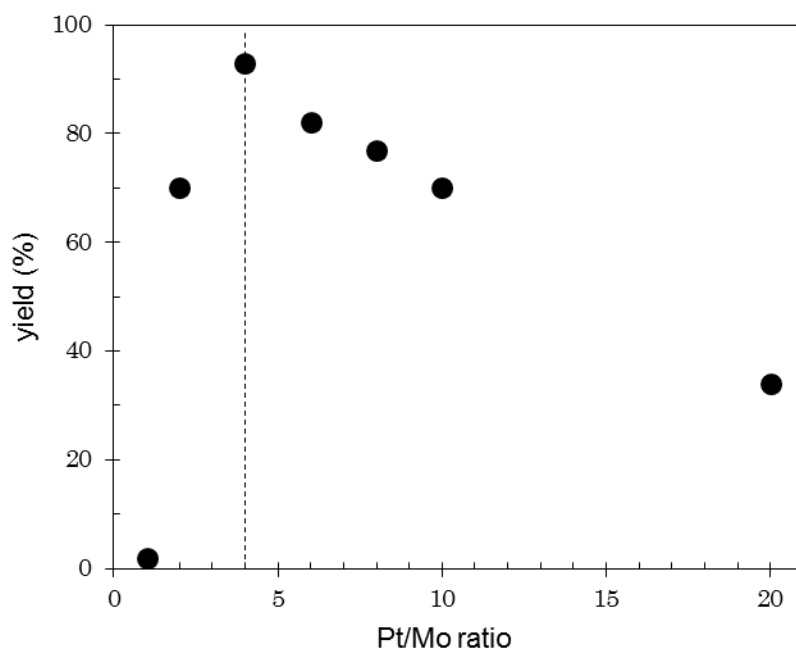


Fig. S4 Effect of Pt/Mo ratio in the Pt-Mo/HAP catalyst on the yield of 1,4-PeD. Reaction conditions were similar to those in Table 2, entry 3.