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

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Keywords: Hydrogenation, Levulinic acid, 1,4-Pentanediol, Hydroxyapatite, Pt-Mo bimetallic catalyst

Abstract: Hydroxyapatite-supported Pt-Mo bimetallic nanoparticles (Pt-Mo/HAP) catalyze the selective transformation of levulinic acid to 1,4-pentanediol under aqueous conditions. A concerted effect between Pt nanoparticles and molybdenum oxides facilely promotes the hydrogenation of the intermediates 4-hydroxypentanoic acid and γ-valerolactone to 1,4-pentanediol. The Pt-Mo/HAP catalyst is recoverable and reusable while maintaining its high activity and selectivity.

Recent requirements to decrease carbon dioxide emissions have led to utilization of renewable resources such as plant biomass as a carbon-neutral feedstock for commodity chemicals.[1] Levulinic acid (LA), produced from lignocellulose, is a well-known biogenic chemical that is a useful C_5 resource.[2,3] Many efforts have been devoted to the development of catalytic transformations of LA into highly valuable chemicals such as γ-valerolactone (GVL).[4-9] However, there are few catalytic systems for the selective transformation of levulinic acid to 1,4-pentanediol (1,4-PeD) despite its importance as a useful monomer for the production of polyesters.[6,9] Existing homogeneous catalytic methods for the synthesis of 1,4-PeD from LA suffer from the requirement of organic solvents or severe reaction conditions.[9,10] Heterogeneous catalysts such as $Cu\text{-}CrO_3$,[11] Ru-Re/C,[12] $Rh\text{-}MoO_x/SiO_2$,[13] and

Ir-MoO_x/SiO_2 [14] have potential advantages of catalyst recovery and operational simplicity. However, they give moderate to good yields of 1,4-PeD. In this context, an ideal process for the above hydrogenation should involve a highly selective and recyclable catalyst working under mild conditions without organic solvents. Therefore, the development of a more efficient heterogeneous catalyst system for the *green* synthesis of 1,4-PeD from LA is still a challenging issue.

Herein, we developed a hydroxyapatite-supported platinum-molybdenum bimetallic catalyst (Pt-Mo/HAP) for the selective hydrogenation of LA to 1,4-PeD under mild conditions using water solvent. The present catalyst system provides the highest yield of 1,4-PeD among the reported heterogeneous catalyst systems.[11-14] Furthermore, the Pt-Mo/HAP catalyst was easily separated from the reaction mixture and was reusable without appreciable loss of its activity or selectivity.

Pt/MoO_3 was prepared by an impregnation method with an aqueous solution of H_2PtCl_6 and MoO_3 (see Supporting Information for experimental details). Other metal oxide-supported monometallic catalysts used in Table 1 were prepared in a similar way. The bimetallic Pt-Mo catalysts supported on HAP, SiO_2, TiO_2, Al_2O_3, CeO_2, and MgO were prepared by a co-impregnation method. For example, the co-impregnation of hydroxyapatite with the aqueous solution of H_2PtCl_6 and $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, followed by calcination afforded Pt-Mo/HAP. Pt *L*-edge X-ray absorption near-edge structure (XANES) analysis of Pt-Mo/HAP showed the formation of partly reduced Pt species, whereas Mo *K*-edge XANES analysis revealed that the oxidation state of the Mo species was Mo^{6+}, similar to the precursor $(NH_4)_6Mo_7O_{24}$ (Fig. S1). The X-ray diffraction (XRD) pattern for Pt-Mo/HAP did not show any peaks derived from Pt or Mo oxides species, demonstrating that the Pt NPs and Mo oxides were well-dispersed over the surface of the HAP (Fig. S2). Transmission electron microscopy (TEM) of Pt-Mo/HAP also confirmed that the Pt NPs exhibited a high degree of dispersion, with a mean diameter of 3.2 nm (Fig. S3).

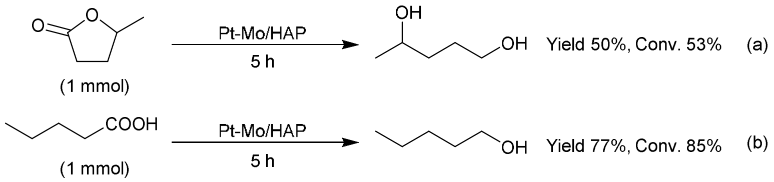
Using the various supported noble metal catalysts, the hydrogenation of LA was conducted in water solvent under 5 MPa of H_2 at 403 K (Table 1). Interestingly, Pt/MoO_3 gave 1,4-PeD as a major product in 74% yield along with GVL, 2-pentanol (2-PeOH), and 1-pentanol (1-PeOH) in 16 %, 3%, and 2% yields, respectively for 6 h (entry 1). Extending the reaction time to 12 h, the 1,4-PeD yield reached to 83% for the Pt-Mo/HAP catalyst (entry 2). Use of WO_3, Nb_2O_3, V_2O_5, and SiO_2 instead of MoO_3 resulted in low yields of 1,4-PeD where a shift of the major product from 1,4-PeD to GVL was observed (entries 3-6). When comparing the performances of noble metal/MoO_3 catalysts, only Pt gave a high yield of 1,4-PeD. Rh, Ir, and Pd resulted in the formation of GVL in 87, 96, and 99% yields, respectively (entry 1 vs. entries 7-9). These results clearly show that the combination of PtNPs and MoO_3 is uniquely effective for the synthesis of 1,4-PeD from LA under aqueous conditions.

In order to design more efficient bimetallic Pt-Mo catalysts for the 1,4-PeD synthesis, both PtNPs and Mo species dispersed on various inorganic matrices were prepared and tested in the hydrogenation of LA (Table 2). Interestingly, HAP was found to be an excellent support for PtNPs and Mo oxides, giving 1,4-PeD in 93% yield upon complete conversion of LA (entry 3). On the other hand, other solid supports such as SiO_2, TiO_2 and Al_2O_3 resulted in the moderate 1,4-PeD yields of 44%, 39% and 32%, respectively (entries 8-10). CeO_2 and MgO were less effective for the selective hydrogenation of LA to 1,4-PeD (entries 11 and 12).[15] Additionally, in the absence of Mo species, Pt/HAP exhibited high catalytic performance for GVL production giving a quantitative yield (entry 6), while Mo/HAP without Pt did not have any hydrogenation activity (entry 7).

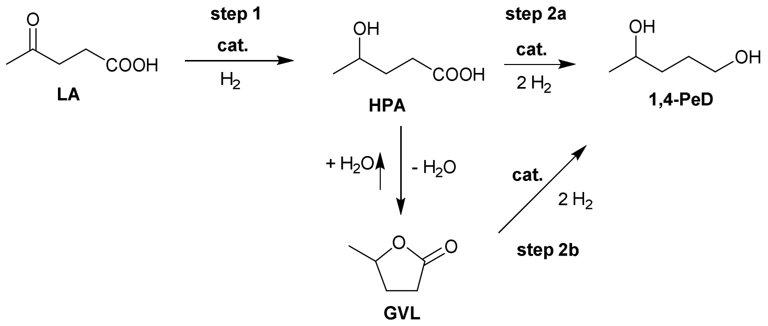
The Pt/Mo ratio in the Pt-Mo/HAP catalyst significantly affected the product selectivity showing a volcano type dependency of 1,4-PeD selectivity (Fig. S4). Among the catalysts with Pt/Mo = 1 – 20, the highest yield of 1,4-PeD (93%) was obtained at Pt/Mo =4. As for the solvents, water gave the best result among the solvents used (Table S2). Other organic solvents, ethanol, 2-propanol, *n*-dodecane, 1,4-dioxane, and methanol were found to be poor solvents for the 1,4-PeD synthesis. Conclusively, the combination of Pt-Mo/HAP having Pt/Mo = 4 and water solvent was the best catalyst system for the selective formation of 1,4-PeD. This catalyst system achieved the highest yield of 1,4-PeD even under lower H_2 pressures among the previously reported heterogeneous catalyst systems such as Rh-MoO_x/SiO_2, Ir-MoO_x/SiO_2, Ru-Re/C, and Cu-CrO_3 (Table S1).[11-14]

Following the hydrogenation of LA, the Pt-Mo/HAP catalyst was easily separated from the reaction mixture by centrifugation and could be reused two times without appreciable loss of activity or selectivity for 1,4-PeD (Table 2, entry 4).[16] Furthermore, the Pt-Mo/HAP catalyst was applicable to preparative scale reaction; 10 g of LA afforded 7.2 g of 1,4-PeD in 80 % isolated yield (see Supporting Information for experimental details).

As for the reaction path from LA to 1,4-PeD, it is reported that the transformation of LA to 1,4-PeD might proceed via 1) the reduction of a keto group of LA to 4-hydroxypentanoic acid (HPA), 2) the facile cyclization of HPA to GVL as an intermediate, and 3) hydrogenation of GVL to 1,4-PeD.[12,13] In order to investigate the catalytic features of our Pt-Mo/HAP for the hydrogenation of LA, several control experiments were carried out as follows. ^{1}H NMR analysis of the reaction mixture after the hydrogenation of LA for 1 h revealed the formations of the intermediates of HPA and GVL in 9% and 58% yields, respectively, upon complete conversion of LA (Table 2, entry 1).[17] The hydrogenation of GVL as a starting material using Pt-Mo/HAP gave a 50% yield of 1,4-PeD for 5 h (Scheme 1a). Furthermore, the Pt-Mo/HAP catalyst possessed hydrogenation activity for carboxylic acids, e.g. the hydrogenation of 1-pentanoic acid afforded 77% yield of the corresponding primary alcohol of 1-pentanol while Pt/HAP was inactive for hydrogenation of both GVL and 1-pentanoic acid (Scheme 1b). In considering the above results, the selective 1,4-PeD synthesis from LA might involve three different types of hydrogenation with the Pt-Mo/HAP catalyst system. First, a keto group of LA is reduced to 4-hydroxypentanoic acid (HPA) (Scheme 2, step 1). HPA is facilely cyclized to an equilibrium product of GVL.[18] The final product of 1,4-PeD is derived from both hydrogenations of HPA and GVL. The outstanding performance of the present Pt-Mo/HAP catalyst is due to its high hydrogenation ability for two functional groups of a carboxylic acid and an ester by the concerted catalysis of Pt and Mo oxides (Scheme 2, steps **2a** and **2b**). It is known that Mo species in MoO_3-supported noble metals are partly reduced in the presence of molecular hydrogen by hydrogen spillover.[19-21] Our Mo *K*-edge XANES analysis of Pt-Mo/HAP after the hydrogenation confirms the formation of partly reduced species (Fig. S1). The reduced Mo species having oxygen vacancies act as Lewis acidic sites activating the carbonyl moieties of HPA and GVL, which promotes the above hydrogenation steps to 1,4-PeD.[22]



Scheme 1 Hydrogenation of (a) GVL and (b) 1-pentanoic acid using Pt-Mo/HAP. The reaction conditions were the same as those of entry 1 in Table 2 except for the substrate and the reaction time.



Scheme 2 Proposed reaction paths for the hydrogenation of LA to 1,4-PeD.

In conclusion, we have succeeded in the direct synthesis of 1,4-pentanediol from levulinic acid as a biomass-derived platform chemical using a Pt-Mo/HAP catalyst under the aqueous conditions. The cooperative catalysis of Pt NPs and MoO_x species on HAP drastically increased the selectivity to give 1,4-PeD in 93% yield. The Pt-Mo/HAP catalyst was recoverable and reusable without appreciable loss of either activity or selectivity.

Acknowledgements

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15 The high selectivity for 1,4-PeD might be attributed to the weak surface acidity and basicity of HAP. As shown in Table 2, entries 8-12, the acidic and basic supports cause the byproduct formation and/or the strong adsorption of an acidic intermediate, HPA.

16 The recovered catalyst was washed with water and calcined at 773 K in air prior to the reuse experiments.

17 Under our GC-MS analysis conditions, HPA was completely converted to the cyclized product of GVL.

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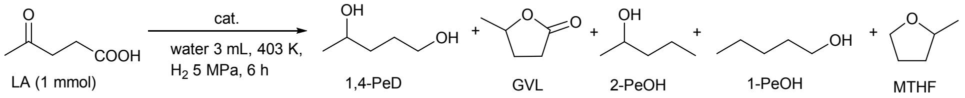
Table 1 Hydrogenation of levulinic acid using various supported metal catalysts



Entry	Catalyst [a]	Conv. [%] [b]	Yield [%] [b]				
			1,4-PeD	GVL	2-PeOH	1-PeOH	MTHF
1[c]	Pt/MoO_3	>99	74	16	3	2	trace
2[c,d]	Pt/MoO_3	>99	83	0	4	1	trace
3	Pt/WO_3	>99	12	88	trace	trace	trace
4	Pt/Nb_2O_3	>99	3	97	trace	trace	trace
5	Pt/V_2O_5	>99	1	99	trace	trace	trace
6[e]	Pt/SiO_2	>99	trace	89	4	trace	trace
7	Rh/MoO_3	>99	13	87	trace	trace	trace
8	Ir/MoO_3	>99	2	96	2	0	trace
9	Pd/MoO_3	>99	1	99	trace	trace	trace

[a] Catalyst (0.1 g, noble metal 2 mol%). [b] Analyzed by GC-MS using an internal standard method.

[c] Catalyst (0.1 g, Pt 4 mol%). [d] 12 h. [e] 4 h.

Table 2 Effect of supports on the hydrogenation of levulinic acid using Pt-Mo catalysts [a]

Entry	Catalyst	H_2 [MPa]	Time [h]	Conv. [%] [b]	Yield [%] [b]				
					1,4-PeD	GVL	2-PeOH	1-PeOH	MTHF
1[c]	Pt-Mo/HAP	5	1	>99	24	67	2	trace	0
2	Pt-Mo/HAP	5	6	>99	72	23	3	2	trace
3	Pt-Mo/HAP	5	12	>99	93	trace	4	0	trace
4[d]	Pt-Mo/HAP	5	12	>99	91	4	4	1	0
5	Pt-Mo/HAP	3	24	>99	93	trace	5	0	trace
6	Pt/HAP	5	12	>99	trace	>99	0	0	0
7	MoO_x/HAP	5	12	trace	trace	trace	0	0	0
8	Pt-Mo/SiO_2	5	6	>99	44	0	26	8	18
9	Pt-Mo/TiO_2	5	6	>99	39	49	8	4	trace
10	Pt-Mo/Al_2O_3	5	6	>99	32	68	trace	trace	trace
11	Pt-Mo/CeO_2	5	6	>99	2	53	0	0	0
12	Pt-Mo/MgO	5	6	>99	trace	54	0	0	0

[a] Reaction conditions: LA 1 mmol, catalyst (0.1 g, Pt 2 mol%, Mo 0.5 mol%), water 3 mL, 403 K.

[b] Analyzed by GC-MS using an internal standard method.

[c] ^1H NMR analysis showed the formation of HPA in 9% yield, which transformed to GVL in GC-MS analysis (see ref. 17). [d] Reuse 2.

Supporting Information

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

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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), $(NH_4)_6Mo_7O_{24}\cdot4H_2O$ (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 × 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 Cu-Kα 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 $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (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/MoO_3, 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 H_2 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 H_2 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 H_2 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	*N*-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).

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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	*n*-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, H_2 5 MPa, 12 h. [b] Analyzed by GC-MS using an internal standard method.

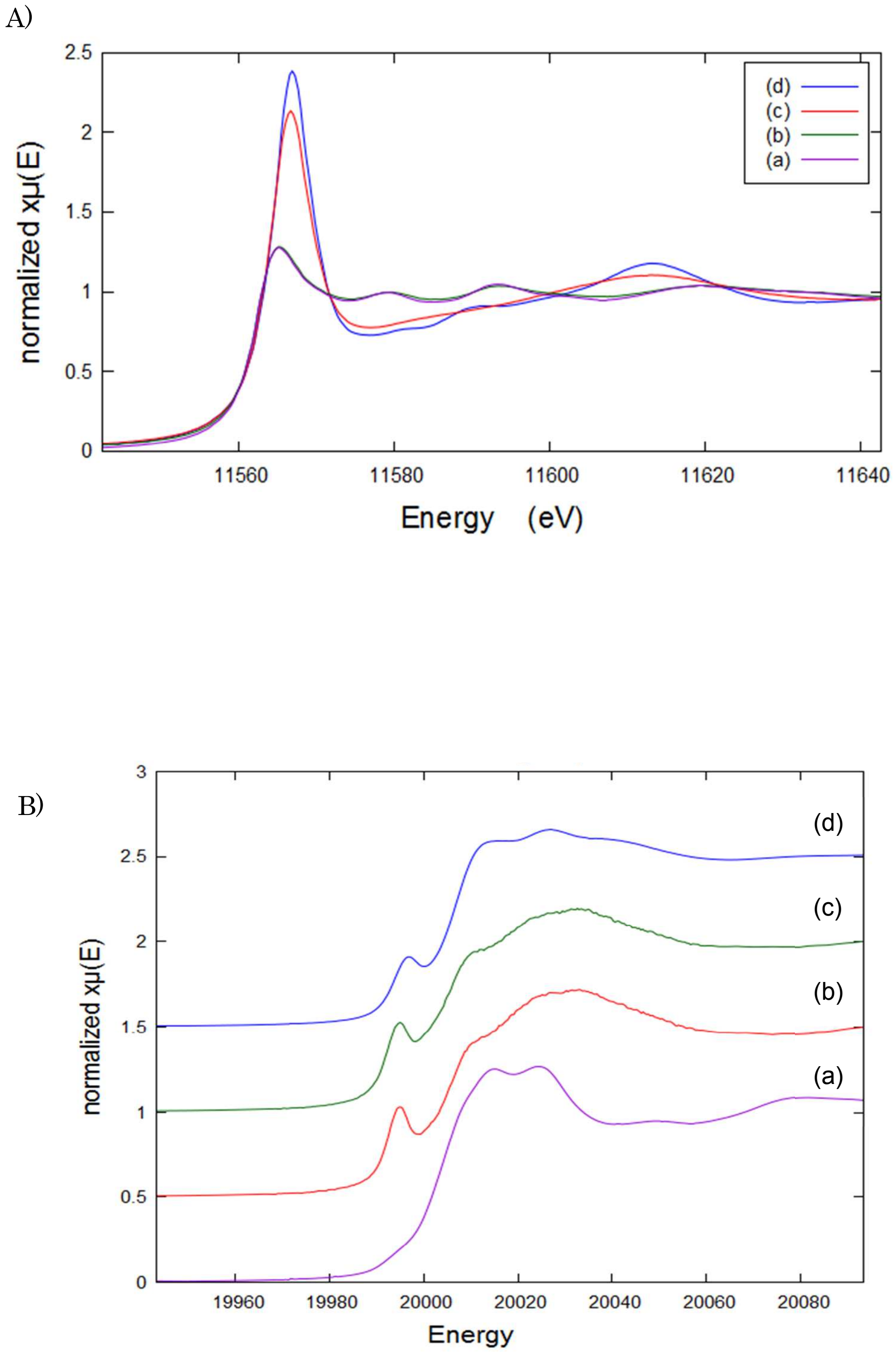

Fig. S1 A) Pt *L*-edge Xanes spectra of (a) Pt foil, (b) Pt-Mo/HAP after hydrogenation, (c) Pt-Mo/HAP fresh, and (d) PtO_2, and B) Mo *K*-edge XANES spectra of (a) MoO_2, (b) Pt-Mo/HAP after hydrogenation, (c) Pt-Mo/HAP fresh, and (d) $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$.

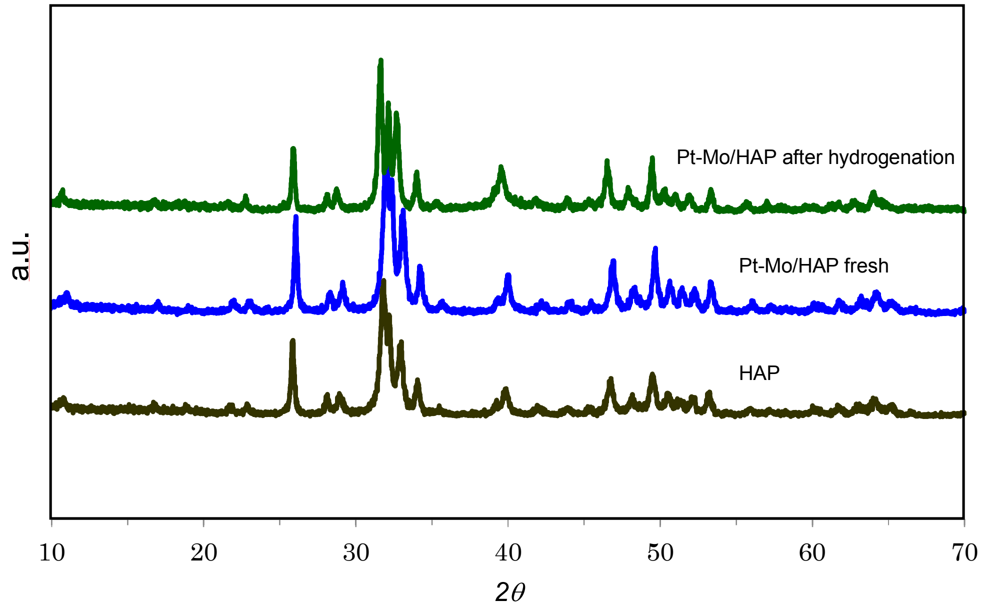

Fig. S2 XRD patterns for HAP, Pt-Mo/HAP fresh, and used Pt-Mo/HAP after hydrogenation.

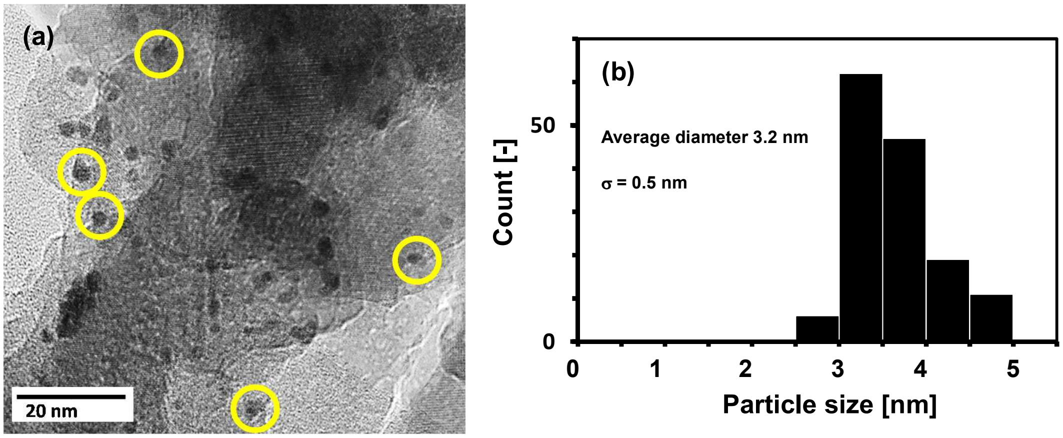

Fig. S3 TEM image (a) and the size distribution (b) of Pt-Mo/HAP.

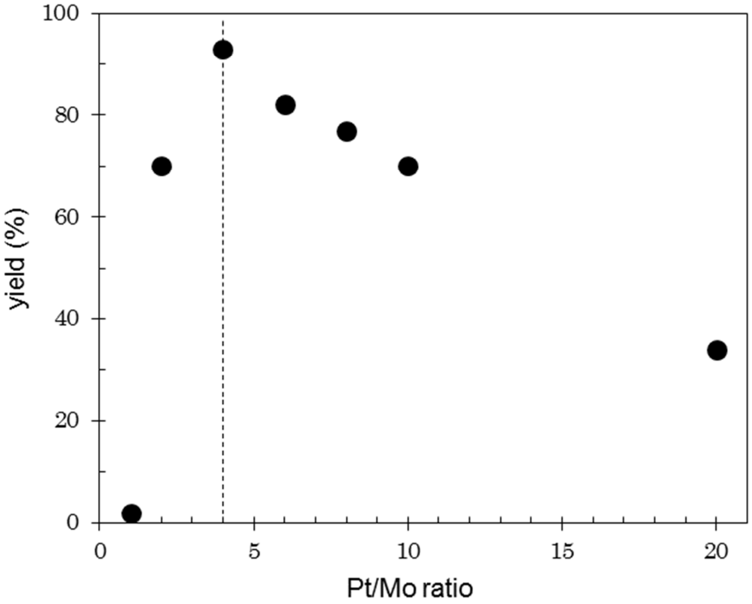

Fig. S4 Effect of Pt/Mo ratio in the Pt-Mo/HAP catalyst on the yield of 1,4-PeD. Reaction conditions were similar to those in Table 2, entry 3.

Graphical Abstract

Hydroxyapatite-supported Pt-Mo bimetallic nanoparticles (Pt-Mo/HAP) catalyze the selective transformation of levulinic acid to 1,4-pentanediol under aqueous conditions.