Electronic Supplementary Information

Selective hydrogenation of succinic acid to gamma-butyrolactone with PVP-capped CuPd catalysts

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Table S1: List of chemicals

Chemical name	Formula	Mw /g mol^{-1}	Supplier
Butyric acid	$C_4H_8O_2$	88.11	Aldrich
Copper (II) acetate monohydrate	$Cu(CO_2CH_3)_2 \cdot H_2O$	199.65	Wako
γ-Butyrolactone	$C_4H_6O_2$	86.09	Aldrich
Hydroxyapatite (HAP)	$Ca_{10}(PO_4)_6(OH)_2$	502.31	Kanto
Palladium acetate	$Pd(CH_3COO)_2$	224.51	Wako
Polyvinyl alcohol (PVA)	$(C_2H_4O)_n$	3500	Wako
Polyvinylpyrrolidone (PVP, K12)	$(C_6H_9NO)_n$	3500	Acros Org.
PVP (K16–18)	$(C_6H_9NO)_n$	8000	Acros Org.
PVP (K30)	$(C_6H_9NO)_n$	40000	Kanto
PVP (K29–32)	$(C_6H_9NO)_n$	58000	Acros Org.
PVP (K90)	$(C_6H_9NO)_n$	360000	Acros Org.
Starch, soluble	$(C_6H_{10}O_5)_n$	-	Kanto
Succinic acid	$C_4H_6O_4$	118.09	Kanto
1,4-Butanediol	$C_4H_{10}O_2$	90.12	Wako
1,4-Dioxane	$C_4H_8O_2$	88.11	Wako
1-Ethyl-2-pyrrolidone	$C_6H_{11}NO$	113.16	Acros Org.
1-Vinyl-2-pyrrolidone	C_6H_9NO	111.14	Aldrich
2-Ethoxyethanol	$C_4H_{10}O_2$	90.12	Wako

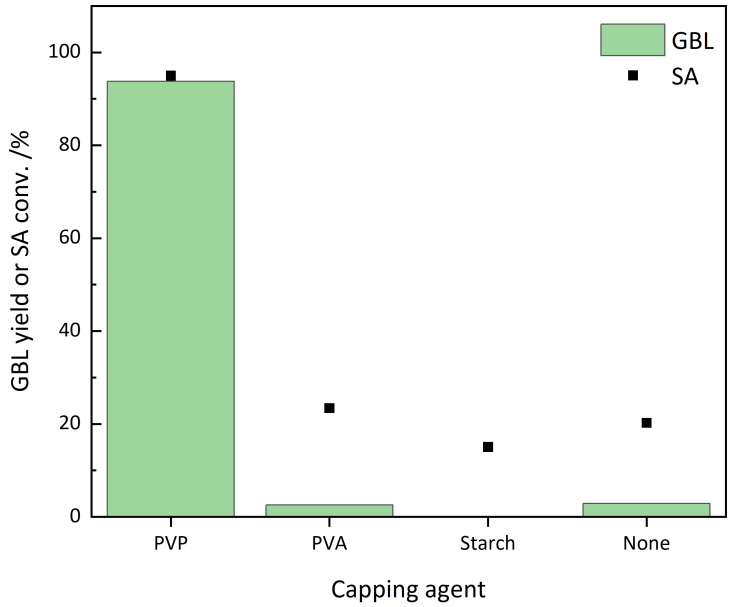

Fig. S1: Influence of difference capping agent on the catalytic performance of HAP supported $Cu_{40}Pd_{60}$ catalyst. Reaction conditions: SA (0.1 g), $Cu_{40}Pd_{60}$−Polymer/HAP (0.1 g), 1,4-dioxane (10 mL), temperature (200 °C), H_2 pressure (8 MPa), reaction time (48 h).

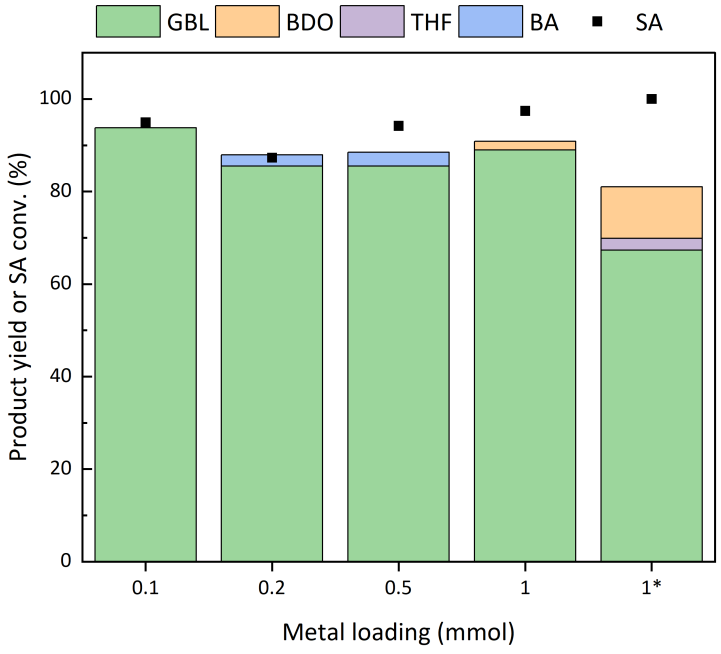

Fig. S2: Influence of metal loading on the activity of the $Cu_{40}Pd_{60}$−PVP/HAP catalyst. Reaction conditions: SA (0.1 g), catalyst (0.1 g), 1,4-dioxane (10 mL), temperature (200 °C), H_2 pressure (8 MPa), reaction time (48 h), *catalyst (0.2 g).

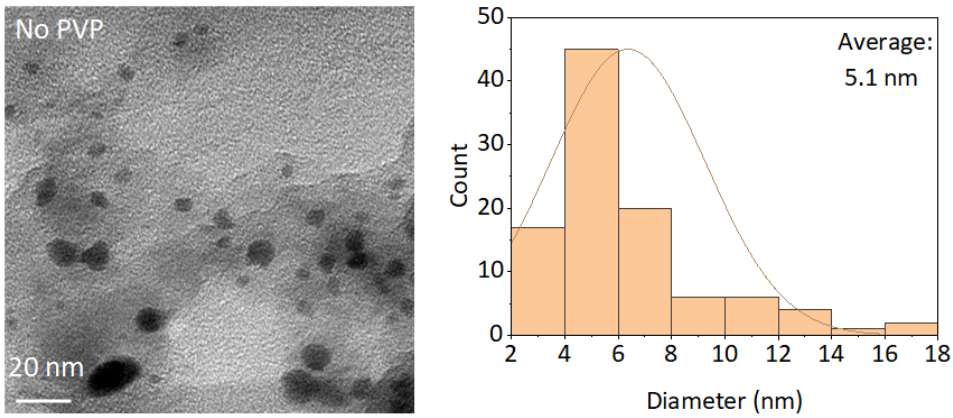

Fig. S3: TEM image of the $Cu_{40}Pd_{60}$/HAP catalyst (no capping agent)

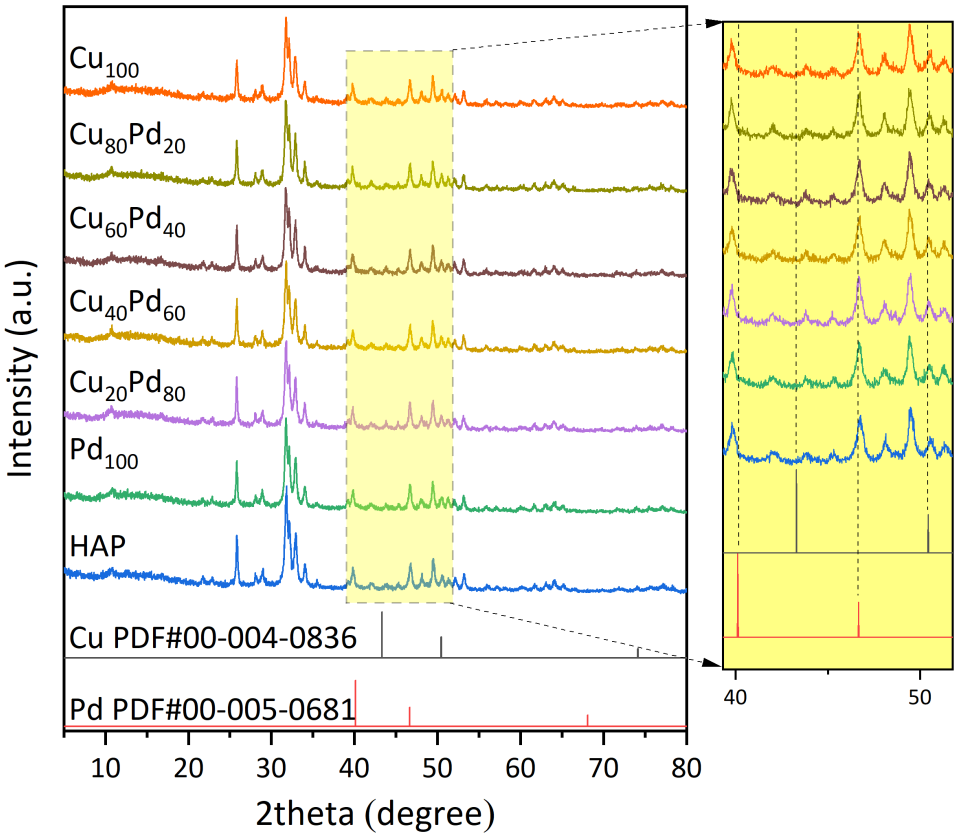

Fig. S4: XRD patterns of the Cu_xPd_y – PVP/HAP catalysts

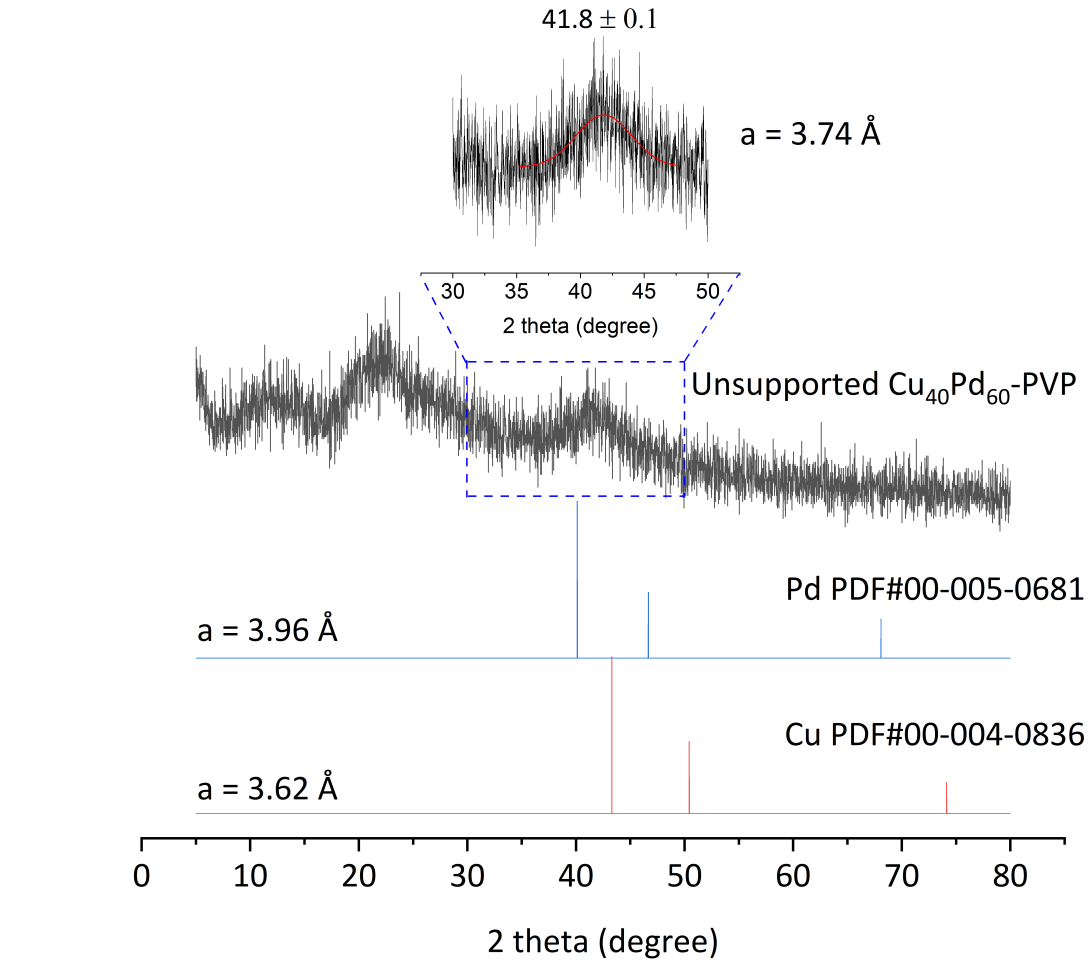

Fig. S5: XRD patterns of the unsupported PVP-capped $Cu_{40}Pd_{60}$ sample. The lattice parameter (a) was determined by using the Bragg's law.

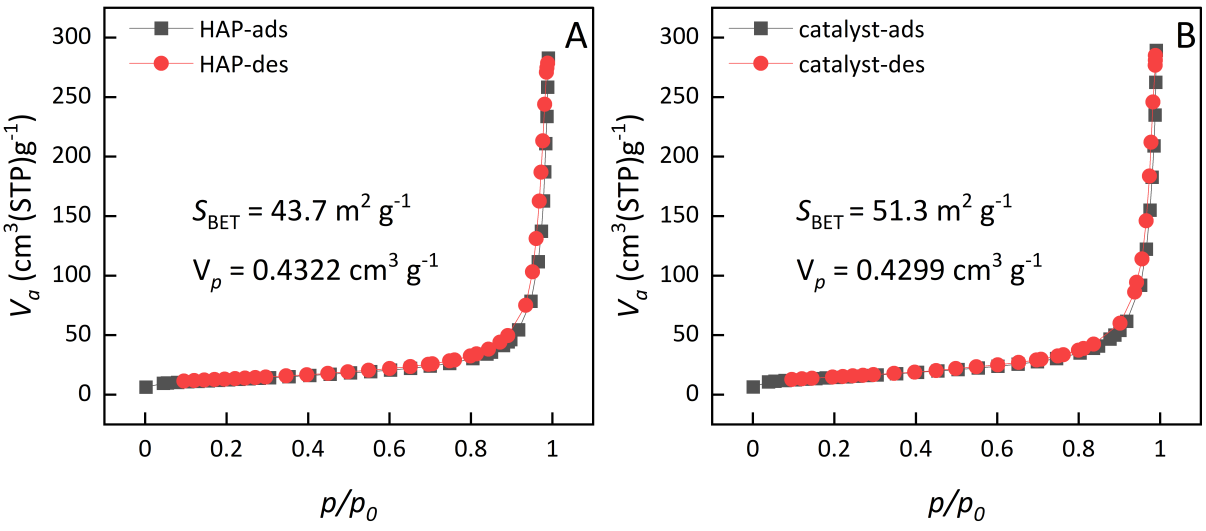

Fig. S6: N_2 adsorption/desorption isotherms of (A) the HAP support and (B) $Cu_{40}Pd_{60}$ – PVP/HAP catalyst.

Table S2: Binding energy of the Cu_xPd_y–PVP/HAP catalysts at Cu $2p_{3/2}$ and Pd $3d_{5/2}$ regions

Catalyst	Cu $2p_{3/2}$		Cu $2p_{1/2}$		Pd $3d_{5/2}$		Pd $3d_{3/2}$	
	Cu^0	Cu^{2+}	Cu^0	Cu^{2+}	Pd^0	Pd^{2+}	Pd^0	Pd^{2+}
Cu_{100}	933.2	935.1	952.9	955.3	-	-	-	-
$Cu_{80}Pd_{20}$	933.1	935.5	952.8	955.0	335.1	336.9	340.2	341.4
$Cu_{60}Pd_{40}$	933.0	935.8	952.8	955.6	334.9	336.2	340.1	341.2
$Cu_{40}Pd_{60}$	932.8	-	952.6	-	334.9	-	340.2	-
$Cu_{20}Pd_{80}$	933.2	-	953.5	-	335.0	336.6	340.3	341.5
Pd_{100}	-	-	-	-	334.6	335.7	339.9	340.9

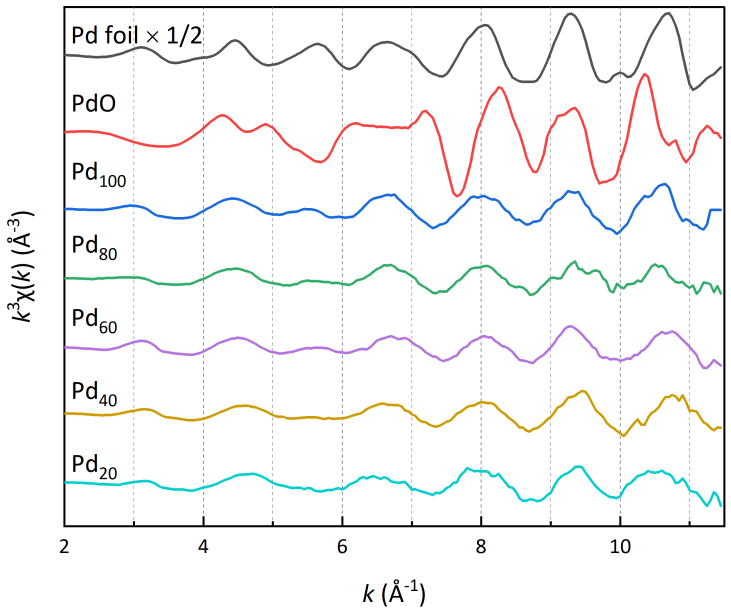

Fig. S7: k^3-weighted EXAFS spectra of the Cu_xPd_y–PVP/HAP catalysts and references at Pd K-edge

Table S3: EXAFS fitting results at Pd K-edge for the fresh and used $Cu_{40}Pd_{60}$–PVP/HAP catalysts

Sample	CN_{Pd-Pd}	CN_{Pd-Cu}	R_{Pd-Pd} (Å)	R_{Pd-Cu} (Å)
Fresh	4.7 ± 0.6	1.4 ± 0.5	2.7051 ± 0.0098	2.6612 ± 0.0295
Used	2.7 ± 0.6	2.2 ± 0.5	2.6844 ± 0.0111	2.6069 ± 0.0111

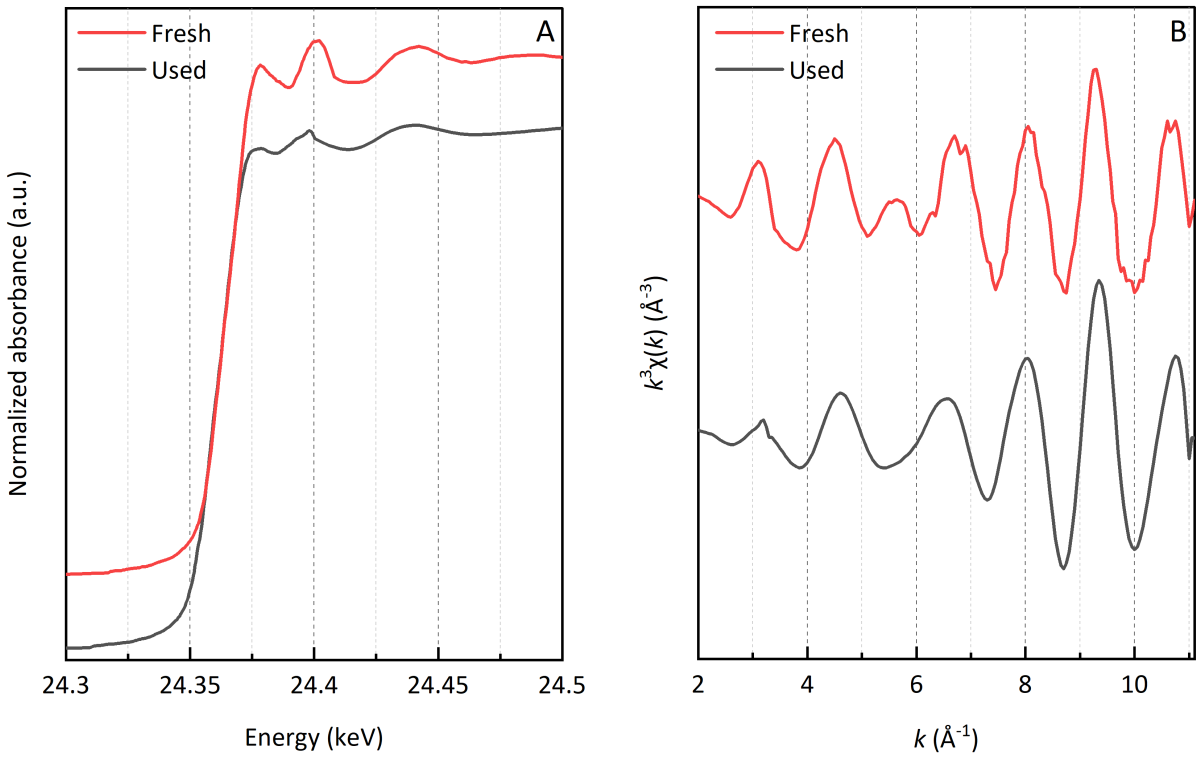

Fig. S8: (A) XANES features and (B) k^3-weighted EXAFS spectra at Pd K-edge of the fresh and used $Cu_{40}Pd_{60}$ – PVP/HAP catalysts

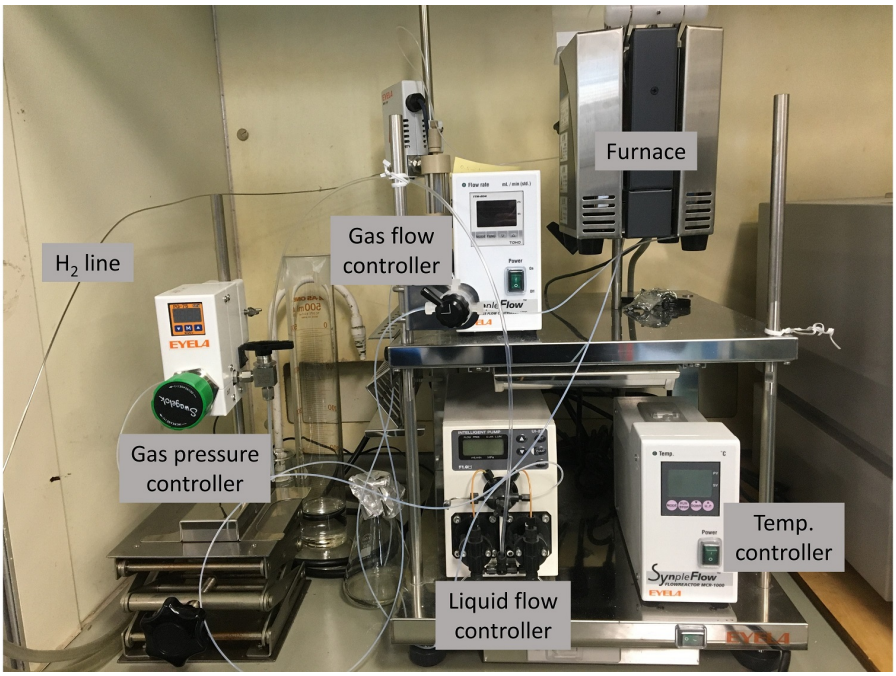

Fig. S9: Flow reactor system used in this study

Note: Continuous reactions were carried out in a down-flow fixed-bed reactor system (MCR-1000, EYELA, Tokyo, Japan). The catalyst (0.5 g) was loaded into a stainless steel tube (ϕ = 5 mm) and secured in place by bed filters at both ends. The liquid and hydrogen flow rates were set at 0.3 and 10 mL min^{-1}, respectively. The reactor was pressurized with pure H_2 (99.999%) to 0.5 MPa and then the temperature of the furnace was increased to 200 °C. The reaction mixture was collected at hourly intervals and analyzed by GC.