Supporting Information

Alloying palladium with copper on zirconium dioxide for accelerating the sellective catalytic transfer hydrogenation of furfural to furfuryl alcohol

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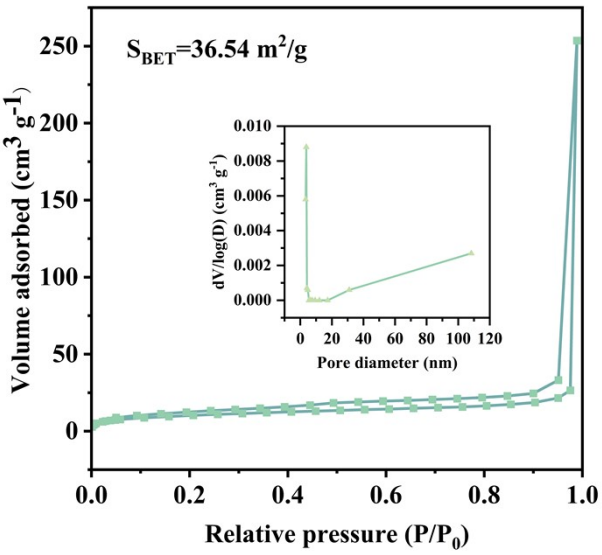

Fig. S1. N_2 adsorption/desorption isotherms and Barrett-Joyner-Halenda pore size distributions of Pd_5Cu_5-ZrO_2 catalyst.

Table S1 Physicochemical characteristics of Pd_5Cu_5-ZrO_2 catalyst.

Sample	S_{BET} (m^2/g)	V_{pore} (cm^3/g)	Pore diameter (nm)
Pd_5Cu_5-ZrO_2	36.54	0.38	3.77

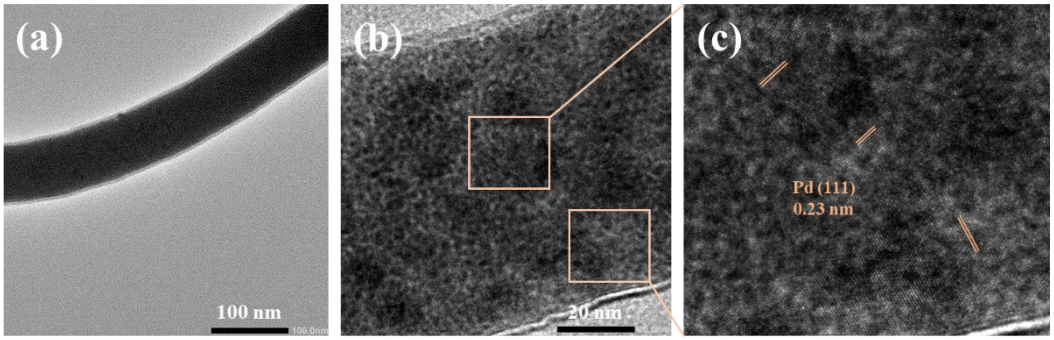

Fig. S2. TEM images of Pd_1Cu_9-ZrO_2 catalyst.

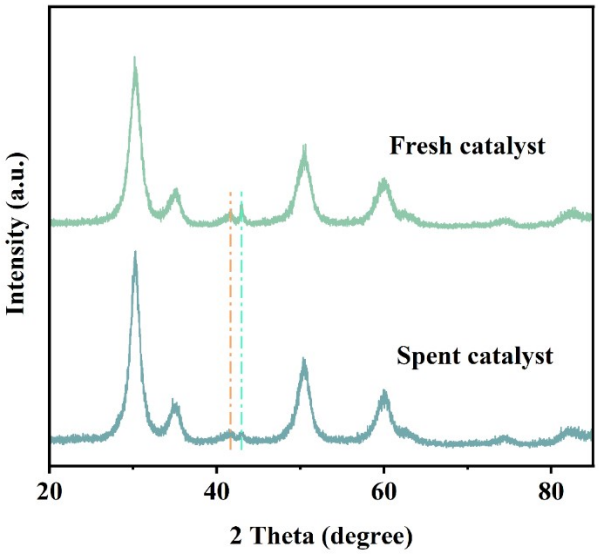

Fig. S3. XRD pattern of Pd_5Cu_5-ZrO_2 catalysts after cycling.

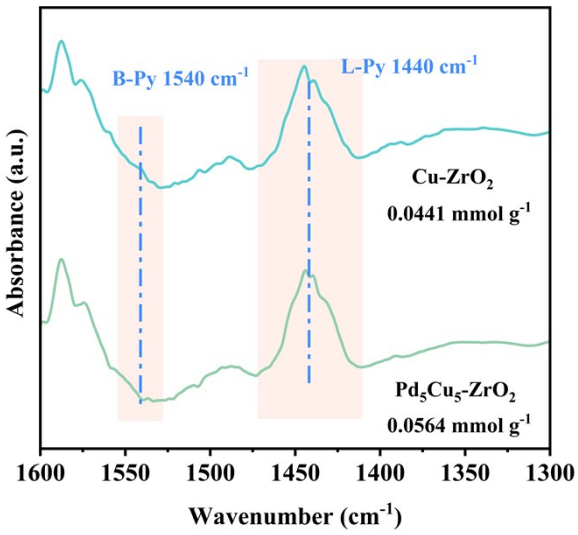

Figure S4 Py-IR spectra of various samples

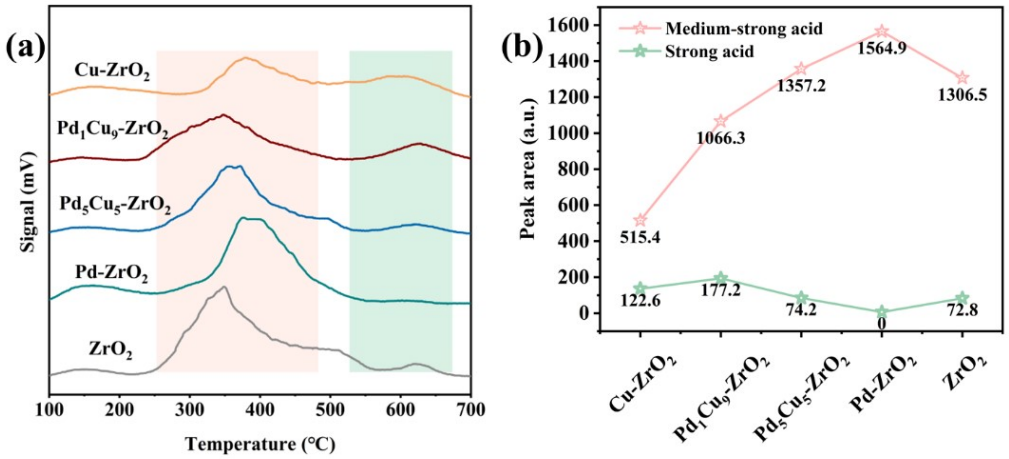

Fig. S5. (a) NH_3-TPD profiles and (b) peak area curve for the ZrO_2, Pd-ZrO_2, Pd_5Cu_5-ZrO_2, Pd_1Cu_9-ZrO_2, and Cu-ZrO_2 catalysts.

Table S2 The hydrogenation of furfural over catalysts in isopropanol.

Catalysts	FAL Conversion (%)	FOL Selectivity (%)	TOF (h^{-1})
No catalyst	12.8	90.3	-
ZrO_2	58.2	93	-
Pd-ZrO_2	99.5	92.9	4.47
Pd_5Cu_5-ZrO_2	95.6	91.5	4.06
Pd_1Cu9-ZrO_2	84.3	93.4	3.57
Cu-ZrO_2	71.5	91.3	2.94

Reaction conditions: furfural 2 mmol, isopropanol 10 mL, 2 MPa N_2, 12 h, catalyst 0.05 g.

Table S3 The hydrogenation of furfural over Pd_5Cu_5-ZrO_2 catalyst in isopropanol.

Entry	Catalyst dosage (mg)	Reaction temperature (℃)	Reduction temperature (℃)	P (MPa)	t (h)	FAL Conversion (%)	FOL Selectivity (%)	TOF (h^{-1})
1	50	**130**	400	2	12	52.3	75.7	1.84
2	50	**150**	400	2	12	68.2	79.8	2.53
3	50	**170**	400	2	12	95.6	91.5	4.06
4	50	170	400	2	**3**	50.3	82.6	7.71
5	50	170	400	2	**6**	79.8	88.8	6.57
6	50	170	400	2	**9**	87.3	91	4.92
7	**10**	170	400	2	12	46.2	79	8.47
8	**30**	170	400	2	12	85	89.2	5.87
9	50	170	400	**0.1**	12	82.4	90.4	3.46
10	50	170	400	**1**	12	84.6	89.5	3.51
11	50	170	**100**	2	12	74.1	95.1	3.27
12	50	170	**200**	2	12	97.4	94	4.25
13	50	170	**300**	2	12	99	93.1	4.28

Reaction conditions: furfural 2 mmol, isopropanol 10 mL.

Table S4 Comparison with the literature on the FAL to FOL.

Entry	Cat.	Cat. (mg)	FAL (mmol)	H donor	T (℃)	t (h)	Con. (%)	Sel. (%)	Ref.
1	0.5%Pd-15%Cu/SiO_2	500	15	cyclohexanol	195	10	86.6	97.7	[1]
2	$Pd_3Cu_{20}/ZrP_{2.0}O$	10	2	IPA	180	4	49.7	95.4	[2]
3	Pd-Cu/MCM-41	60	1.8	IPA	160	4	97.4	98.3	[3]
4	Cu-Pd/C	40	3.6	FA	100	3	91.7	97.8	[4]
5	1/5 wt % PdCu/ZrO_2	200	15.57	5 MPa H_2	100	1.3	97.9	95.4	[5]
6	Pd_5Cu_5-ZrO_2	50	2	IPA	170	9	87.3	91	This work

Table S5 Catalytic performance for catalytic transfer hydrogenation reaction of other aldehyde substrates over Pd_5Cu_5-ZrO_2 catalyst

Entry	Substrate	Product	Con. (%)	Sel. (%)
1	Furfural	Furfuryl alcohol	95.6	91.5
2	Benzaldehyde	Benzyl alcohol	43.9	95.0
3	Cyclohexanone	Cyclohexanol	41.7	98.4
4	5-Hydroxymethylfurfural	2,5-dihydroxymethylfuran	8.9	>99

Reaction conditions: 2 mmol substrate, 10 mL IPA, 170℃, 2 MPa N_2, 12 h.

Reference

[1] Lan X, Wang S, Zhang H, Zhang Y, Zhang Y, Zhang Y, et al. Pd–Cu/SiO_2 catalyzed efficient hydrogen transfer of cyclohexanol and furfural platforms into cyclohexanone and furfuryl alcohol. Fuel 2024;366:131278.

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[3] Gao B, Zhang J, Zhang M, Li H, Yang J-H. Highly dispersed PdCu supported on MCM-41 for efficiently selective transfer hydrogenation of furfural into furfuryl alcohol. Appl Surf Sci 2023;619:156716.

[4] Du J, Zhang J, Sun Y, Jia W, Si Z, Gao H, et al. Catalytic transfer hydrogenation of biomass-derived furfural to furfuryl alcohol over in-situ prepared nano Cu-Pd/C catalyst using formic acid as hydrogen source. J Catal 2018;368:69-78.

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