Supplementary Information

Synergistic nanoalloy PdCu/TiO₂ catalyst for in situ hydrogenation of biomass-derived furfural at room temperature

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1. Experimental Section

1.1 Materials

All the reagents and chemicals were used as received. TiO₂ (anatase, Sigma Aldrich, 99.8%, trace metal basis), sodium hydroxide pellets (SRL Chemicals, 97%), palladium acetate (Sigma Aldrich, 99.98%, trace metal basis), copper nitrate trihydrate (Sigma Aldrich, 99%), ethylene glycol (SRL Chemicals, extra pure AR, 99%), hydrazine hydrate (Sigma Aldrich, reagent grade, 50-60%), polyvinylpyrrolidone (average mol. wt. 40000, Sigma Aldrich), nitric acid (SRL Chemicals, 70%), furfural (SRL Chemicals, extra pure AR, 99%), triethylsilane (BLD pharma, 99.98%), methanol (SRL Chemicals, HPLC grade), and dodecane (TCI Chemicals, >99%, GC grade). All the furfural derivatives are purchased from BLD pharma and used as received.

1.2 Catalyst synthesis

1.2.1 Preparation of TiO₂ nanomaterial

A hydrothermal method was used to synthesize TiO_2 nanomaterial (5 g scale) using anatase titania (Sigma Aldrich, 99.8%, trace metal basis). Briefly, 5 g of anatase titania was added to 5 mL of DI water, followed by sonication for 10 min. Freshly prepared 10 M NaOH (60 mL) was added dropwise for 10 min, and then stirred at room temperature for 30 min. The mixture was then transferred to a hydrothermal reactor and kept it in an oven at 140 °C for 20 h. The solid product was then collected by centrifugation and washed with DI water and 0.1 M nitric acid solution alternatively until the pH of the solution reached 7. The titania sample was oven-dried at 80 °C for 12 h and then calcined at 500 °C for 4 h to obtain TiO₂ nanomaterial.^{S1}

1.2.2 Preparation of PdCu/TiO₂ nanocatalyst

The PdCu/TiO₂ catalyst (2 wt% Pd and 3 wt% Cu w.r.t TiO₂) was prepared by a solvothermal method. Appropriate amounts of Pd precursor (palladium acetate, Sigma Aldrich, 99.98%, trace metal basis) and Cu precursor (copper nitrate trihydrate, Sigma Aldrich, 99%) were added to a 50 mL ethylene glycol (EG) solution and stirred for 10 min to completely dissolve the metal precursors. The required amount of hydrazine hydrate solution was added dropwise for 10 min, followed by the addition of 1.5 mol% of polyvinylpyrrolidone (PVP-40), and continued stirring for another 10 min. The TiO₂ nanorods were then added to the above mixture and stirred well for 1 h at room temperature. The resulting solution was transferred to a PPL-lined autoclave reactor and hydrothermally treated at 160 °C for 12 h in an oven. The solid sample was collected from the solution by centrifugation and washed with the mixture of DI water and methanol till the pH reached neutral. The PdCu/TiO₂ material was oven-dried at 80 °C for 12 h and then calcined at 400 °C for 4 h.^{S2}

1.3 Catalyst characterization

To estimate the crystalline nature and phases in TiO₂, Pd/TiO₂, Cu/TiO₂, and PdCu/TiO₂ catalysts, powder XRD analysis was carried out using a Malvern PANalytical non-ambient XRD Empyrean-DY2584 at 45 KW & 40 mA. Data were collected in the 20 range of 5–90° using Ni-filtered Cu K α radiation as the X-ray source. The BET surface area, average pore size, and pore volume of TiO₂, Pd/TiO₂, Cu/TiO₂, and PdCu/TiO₂ catalysts were estimated by N₂ adsorption-desorption analysis using the Autosorb iQ Station 1 instrument at liquid N₂ temperature (-196 °C). To obtain accurate data, the adsorbed species (water/gas molecules) were removed from the samples by drying them at ~180 °C for 12 h under vacuum conditions prior to N₂ adsorption-desorption. The oxidation states of the elements (Pd, Cu, Ti, and O) in the TiO₂, Pd/TiO₂, Cu/TiO₂, and PdCu/TiO₂ materials were estimated by XPS spectroscopy (AXIS Supra with AI K α) by charge-corrected binding energies using the adventitious C 1s peak at 284.6 eV. Particle size, shape, and elemental distribution in TiO₂ and PdCu/TiO₂ materials were analyzed using a JEOL instrument (JEM F200) at 200 kV electron beam accelerating voltage. A carbon-coated copper grid was used for TEM analysis.

The nature of the acid sites (Lewis and Brønsted) in TiO₂, Pd/TiO₂, Cu/TiO₂, and PdCu/TiO₂ catalysts were investigated using in situ pyridine-adsorbed FT-IR spectroscopy. The experiments were carried out on Spectrum 3 (Perkin Elmer) coupled with a Harrick reaction chamber with a KBr window and DTGS detector. Before the analysis, all the aforementioned samples were treated thermally at 250 °C for 1 h under an N₂ atmosphere, followed by being allowed to reach room temperature. Then, the samples were exposed to pyridine vapors at a particular temperature in the range of 50-200 °C, and the FT-IR spectra were recorded in the absorbance mode. The redox sites were quantified by the H₂-temperature-programmed reduction (TPR)^{S3} using the Altamira AMI 300 instrument, which was equipped with the thermal conductivity detector (TCD). In TPR analysis, about 40 mg of the samples were loaded into the U-shaped quartz tube cell, which was placed in the high-temperature furnace. All the samples were degassed at 150 °C using 30 mL/min of Ar flow. The TPR analysis was performed by using a 30 mL/min flow of 10% H₂/Ar mixture gas, which is passed through the packed catalyst with the ramping of the temperature from 45 °C – 900 °C at the rate of 10 °C/min.

The nature of metal dispersion and quantification of active surface area were calculated by the CO-pulse chemisorption analysis using the Altamira AMI 300 instrument with the TCD detector. The samples were pretreated at 150 °C for 3 h under a He gas stream to remove the surface contaminants. Then, the samples were exposed to the 30 mL/min of 10% CO/He gaseous mixture, during which about 20 CO pulses were administered, followed by gas detection using a TCD detector. The saturation was attained within 20 CO pulses, beyond which no further adsorption was observed from the

TCD detector. Then, the concentration of the active sites, metal dispersion, and the active surface area of the metal components were evaluated through calibration.

1.4 Catalytic activity studies

The in situ hydrogenation of furfural to furfuryl alcohol was carried out at room temperature without the use of external high-pressure hydrogen. For a typical reaction, 1 mmol of furfural was taken into 10 mL of a sealed tube to which the catalyst, triethylsilane, and methanol were added. The catalyst screening was carried out at room temperature for 4 h. Using the best catalyst, the reaction conditions were optimized and then the in situ hydrogenation of different furfurals was carried out at room temperature. To determine the reusability efficiency of the PdCu/TiO₂ catalyst, the catalyst recovered from the reaction mixture by centrifugation was washed three times with methanol after each cycle, vacuum dried overnight at 60 °C and finally thermally treated at 400 °C in the presence of an H₂/Ar mixture (100 mL min⁻¹). A gas chromatograph (GC-2030, Shimadzu) equipped with an HP-5 column and a flame ionization detector was used to estimate furfural conversion and furfuryl alcohol selectivity (external standard: n-dodecane). The main product, furfuryl alcohol, was isolated by column chromatography and confirmed by the ¹H, ¹³C, and DEPT NMR spectroscopy (Fig. S4-S6), while the main byproduct (triethyl(methoxy)silane) formed from triethylsilane and methanol was confirmed by HR-MS analysis (Fig. S7). The HR-MS data of the products of the substrate scope studies (Table 3) are provided in Fig. S8-16.

 $Conversion of furfural (\%) = [mol_{furfural, initial} - mol_{furfural, final}] / mol_{furfural, initial}$

Selectivity of furfuryl alcohol (%) = mol_{furfuryl alcohol} / [mol_{furfural, initial} – mol_{furfural, final}]



Fig. S1. HR-TEM of TiO₂ nanorods.



Fig. S2. TEM images of commercial TiO₂.

S. No.	Catalyst	BET surface area	Pore volume	Pore width
		(m²/g)	(cc/g)	(nm)
1	TiO ₂	78	0.038	15.278
2	Cu/TiO ₂	96	0.041	15.323
3	Pd/TiO ₂	92	0.050	15.306
4	PdCu/TiO ₂	83	0.044	15.334

Table S1: BET surface area, pore volume, and pore size of the catalysts.

Table S2: Quantitative measurements of H₂-TPR profiles.

S. No.	Catalyst	Peak maxima temp. (°C)	H ₂ uptake (μmol/g)	Total H ₂ Uptake (µmol/g)	
		531.5	2.09		
1	TiO ₂	690.3	4.89	6.98	
2	Pd/TiO ₂	79.6	1.20	10.40	
		668.7	9.20		
3	Cu/TiO ₂	239.6	13.76		
		664.8	8.78	22.54	
		93.4	5.31		
4	PdCu/TiO	662.8	7.11	12.42	
	2				

Table S3: Controlled reactions to elucidate the role of TES and MeOH on CTH of furfural.

S.	Catalyst	TES	MeOH	Triethyl(methoxy)silan	Furfuryl
No.		(mmol)	(mL)	e (%)	alcohol (%)
1	PdCu/TiO	1.5	-	-	-
2	PdCu/TiO	-	5	-	-
3	PdCu/TiO 2	1.5	5	99%	99%

Reaction conditions: furfural = 1 mmol, $PdCu/TiO_2 = 15$ mg, room temperature, and 4 h.



Fig. S3: (a) O 1s XPS (O_v : oxygen vacancies and O_L : lattice oxygen) and (b) Ti 2p XPS spectra of the catalysts.



Fig. S4: ¹H NMR spectrum of furfuryl alcohol.



Fig. S5: ¹³C NMR spectrum of furfuryl alcohol.



Fig. S6: (a) DEPT-135 and (b) DPET-90 NMR spectra of furfuryl alcohol.



Fig. S7: HR-MS spectrum of triethyl(methoxy)silane.



Fig. S8. HR-MS data of (5-chlorofuran-2-yl)methanol (entry 4, Table 3).



Fig. S9. HR-MS data of (5-bromofuran-2-yl)methanol (entry 5, Table 3).



Fig. S10. HR-MS data of (5-iodofuran-2-yl)methanol (entry 6, Table 3).







Fig. S13. HR-MS image of (5-phenylfuran-2-yl)methanol (entry 9, Table 3).



Fig. S14. HR-MS data of (5-(4-chlorophenyl)furan-2-yl)methanol (entry 10, Table 3).



Fig. S15. HR-MS data of (5-(4-bromophenyl)furan-2-yl)methanol (entry 11, Table 3).



Fig. S16. HR-MS data of (5-aminofuran-2-yl)methanol (entry 12, Table 3).



Fig. S17. (a) Conversion of furfural at different temperatures and time intervals (reaction conditions: furfural = 1 mmol, $PdCu/TiO_2 = 15$ mg, TES = 1.5 mmol, and methanol = 4 mL) and (b) Arrhenius plot of the CTH of furfural over the $PdCu/TiO_2$ catalyst.^{S4}

References

- S1 P. Sudarsanam, A. Köckritz, H. Atia, M. H. Amin and A. Brückner, *ChemCatChem*, 2021, **13**, 1990–1997.
- S2 K. Mandal, D. Bhattacharjee, P. S. Roy, S. K. Bhattacharya and S. Dasgupta, *Appl Catal A Gen*, 2015, **492**, 100–106.
- S3 N. W. Hurst, S. J. Gentry, A. Jones and B. D. McNicol, *Catalysis Reviews*, 1982, 24, 233–309.
- S4 C. Panzone, R. Philippe, C. Nikitine, L. Vanoye, A. Bengaouer, A. Chappaz and P. Fongarland, *Ind Eng Chem Res*, 2021, **60**, 16635–16652.