

## **Supporting Information**

### **CoPd nanoalloy embedded N-doped porous carbon catalyst for the selective reduction and reductive amination of levulinic acid using formic acid in water**

Ashish Kumar Kar, Arzoo Chauhan, and Rajendra Srivastava\*

Catalysis Research Laboratory, Department of Chemistry, Indian Institute of Technology  
Ropar, Rupnagar, Punjab-140001, India

---

\*Email: [rajendra@iitrpr.ac.in](mailto:rajendra@iitrpr.ac.in); Phone: +91-1881-232064

## Materials and reagents

Levulinic acid (98%), melamine (99 %), benzyl amine (99 %) and metal salts were purchased from Sigma-Aldrich. Formic acid (>98%), paraformaldehyde (96%), were purchased from Tokyo Chemical Industry Co., Ltd., S D Fine-Chem Limited, and Spectrochem Pvt. Ltd., respectively. All other solvents were obtained from Merck. All the chemicals were used without any further purification.

## Catalyst characterization

Powder X-ray diffraction (XRD) patterns were recorded on Rigaku Mini flex III diffractometer (30 kV and 10 mA). The surface area of the catalyst was determined by Nitrogen sorption measurements performed at 77 K by Quantachrome Instruments, Autosorb-iQ volumetric adsorption analyzer. The sample was degassed at 200 °C for 3 h in the degassing port of the adsorption apparatus. The surface area of the catalyst was calculated from the adsorption data points obtained for P/P<sub>0</sub> between 0.05-0.3 using the Branauer-Emmette-Teller (BET) equation. The metal content in the catalyst was determined by Agilent's microwave-plasma atomic emission spectrometer (MP-AES). High-resolution transmission electron microscopy (HRTEM) images were taken on a JEOL-2010 transmission electron microscope operating at 200 kV. The surface composition of the catalyst was investigated by X-ray photoelectron spectroscopy (XPS) analysis by an XPS system PHI 5000 VersaProbeII (ULVAC– PHI, INC, Japan) with a microfocus (100 μm, 25 W, 15 KV) monochromatic Al-K $\alpha$  source ( $h\nu = 1486.6$  eV), a hemispherical analyzer and a multichannel detector. The CO<sub>2</sub> temperature-programmed desorption (CO<sub>2</sub>-TPD) technique was used for the total acidity measurements on a Quantachrome, CHEMBETMTPR/TPD instrument. The samples were preheated at 200 °C at a heating rate of 10 deg/min under continuous He flow for 30 min. Similarly, H<sub>2</sub> temperature-programmed desorption (H<sub>2</sub>-TPD) technique was used for the extent of hydrogen consumption efficiency of all the carbonized catalyst. The samples were preheated at 200 °C at a heating rate of 10 deg/min under continuous He flow for 30 min. Then, the sample cell was cooled to 50 °C and the either CO<sub>2</sub> or H<sub>2</sub> gas was adsorbed by flowing the gas for one h in the sample cell with a flow rate of 10 mL/min. The excess or physically adsorbed gas was removed by He flow (50 mL/min) for 30 min. Finally, the amount of desorbed gas was monitored by a temperature-controlled device (TCD) as the function of temperature. The DRIFT FT-IR was conducted using a Thermofisher instrument using acetone as the probe molecule.

## Experimental

### Procedure for LA to GVL transformation using FA as a hydrogen source

The catalytic activity was investigated using formic acid as a hydrogen source via a catalytic transfer hydrogenation pathway. In a typical reaction, 1 mmol LA, 5 mmol formic acid, 30 mg catalyst, and 3 mL H<sub>2</sub>O (as a solvent) were charged into a 10 mL Teflon liner and secured with a stainless-steel jacket. The reaction proceeded in an oil bath maintained at 160 °C with a stirring rate of 400 rpm. After the reaction, the reaction mixture was filtered and centrifuged to separate the catalyst. The organic phase of the reaction was carefully extracted with ethyl acetate, and reactant conversion & product selectivity was monitored using a gas chromatograph (GC, Yonglin 6100; BP-5; 30 m × 0.25 mm × 0.25 mm). The product was confirmed using GC-MS (Shimadzu GCMS-QP 2010 Ultra Rtx-5 Sil Ms; 30 m × 0.25 mm × 0.25 mm).

### Catalytic reaction procedure for the reductive amination of LA to pyrrolidone using HCOOH

The reductive amination of LA with benzylamine was carried in the same manner as it was done for LA. In a typical reaction, 1 mmol LA, 1 mmol amine, 3 mmol formic acid, 30 mg catalyst, and 3 mL H<sub>2</sub>O were charged into a 10 mL Teflon liner, with a stainless-steel jacket. The reaction was conducted in an oil bath maintained at 160 °C with a stirring rate of 400 rpm. After the reaction, the reaction mixture was filtered and centrifuged to separate the catalyst. The organic phase of the reaction was carefully extracted with ethyl acetate, and reactant conversion and product selectivity were monitored using gas chromatograph, and the product was confirmed using GC-MS.

$$\text{LA conversion (\%)} = \frac{\text{moles of LA}_{(\text{initial})} - \text{moles of LA}_{(\text{final})}}{\text{moles of LA}_{(\text{initial})}} \times 100$$

$$\text{Product yield (\%)} = \frac{\text{moles of product formed}}{\text{moles of LA}_{(\text{initial})}} \times 100$$

$$\text{Product selectivity (\%)} = \frac{\text{Product yield}}{\text{LA conversion}} \times 100$$

The reactions were conducted initially at different stirring speeds (100 rpm to 400 rpm). The reactant conversions were increased with an increase in the stirring rate up to 600 rpm. Above that rate, no increase in the reactant conversion was recorded. It suggests that above and equal to 600 rpm, the mass transfer was overcome, and only the kinetic and thermodynamic parameters will influence the reaction.

**Table S1. (a) Metal contents determined from MP-AES.**

Catalyst	Co (Wt %)	Pd (Wt %)
Co <sub>8</sub> Pd <sub>2</sub> @N-C	7.1	1.6
Co <sub>9</sub> Pd <sub>1</sub> @N-C	8.0	0.85
Co <sub>7</sub> Pd <sub>3</sub> @N-C	6.2	2.1
Co@N-C	8.9	-
Pd@N-C	-	7.8
Co <sub>8</sub> Pd <sub>2</sub> /AC	7.2	1.7
Co <sub>8</sub> Pd <sub>2</sub> /N-C	7.3	1.7

**(b) Surface elemental composition determined from XPS.**

Catalyst	C (%)	N (%)	O (%)	Co (%)	Pd (%)
Co <sub>8</sub> Pd <sub>2</sub> @N-C	<sup>a</sup> 90.1, <sup>b</sup> 88.7	<sup>a</sup> 3.1, <sup>b</sup> 3.1	<sup>a</sup> 3.7, <sup>b</sup> 8.2	<sup>a</sup> 2.6	<sup>b</sup> 0.5
Co@N-C	<sup>a</sup> 88.9	<sup>a</sup> 3.2	<sup>a</sup> 4.1	<sup>a</sup> 3.8	-
Pd@N-C	<sup>a</sup> 90.6	<sup>a</sup> 2.8	<sup>a</sup> 3.3	-	3.3

**Table S2.** Physicochemical properties of the catalysts.

<b>Catalyst</b>	<b>S<sub>BET</sub> (m<sup>2</sup>g<sup>-1</sup>)</b>	<b>Total pore vol. (cm<sup>3</sup>g<sup>-1</sup>)</b>	<b>Avg. pore size (nm)</b>
Co <sub>8</sub> Pd <sub>2</sub> @N-C	473	0.59	20.1
Co <sub>8</sub> Pd <sub>2</sub> @N-C <sub>no TMB</sub>	311	0.32	16.1
<sup>a</sup> Co <sub>8</sub> Pd <sub>2</sub> @N-C	<sup>a</sup> 452	<sup>a</sup> 0.54	<sup>a</sup> 20.0

<sup>a</sup>Spent catalyst

**Table S3.** Comparative table HCOOH mediated LA to GVL.

	<b>Catalyst</b>	<b>Reaction conditions</b>	<b>Conversion (%)</b>	<b>Select. (%)</b>	<b>TOF (h<sup>-1</sup>)</b>	<b>Ref.</b>
1	2.5% Ru/ZrO <sub>2</sub>	LA (5 mmol), FA (2.5 mmol), PF (2.5 mmol) H <sub>2</sub> O (20 mL), catalyst (0.5g), He (1 atm), time (12 h), temp (150 °C).	73	>99	2.5	1
2	Ru/C	LA (1 g), FA (2 ml), H <sub>2</sub> O (30 mL), catalyst (0.6 g), time (5 h), temp (190 °C).	81	70.3	4.7	2
3	10% Pd/C	LA (2 mmol), FA (2 mmol), catalyst (0.02 g), H <sub>2</sub> O (1 mL), time (5 h), temp (150 °C).	9	17	1.9	3
4	Ru/U-C3N4	LA (1 mmol), catalyst (40 mg), 2-PrOH (5 mL), H <sub>2</sub> O (5 wt %), time (12 h), temp (100 °C), N <sub>2</sub> .	100	99.8	21.0	4
5	Mn <sub>2</sub> Co <sub>0.1</sub> O <sub>x</sub>	15 mL LA (0.1 mol/L) + FA (1.0 mol/L), catalyst (0.2 g), time (20 h), temp (230 °C), N <sub>2</sub> (1 MPa).	83.4	70.0	0.63	5
6	Ru(2%)NC nanoflakes	LA (1 mmol), FA (7 mmol) catalyst (20 mg), H <sub>2</sub> O (2 mL), time (20 h), temp (140 °C).	~100	~100	13.9	6
7.	Au-Ni nanoalloy/ $\gamma$ -	LA (1 g), formic acid (0.4 mL), catalyst (0.6 g), time	89	Yield=86	-	7

	Al <sub>2</sub> O <sub>3</sub>	(2 h), temperature (190 °C).				
8.	Pt/MP-ZrO <sub>2</sub>	LA (0.19 mmol cm <sup>-3</sup> ), FA (0.59 mmol cm <sup>-3</sup> ), catalyst (0.3 g), time (24 h), temperature (240 °C).	97	Yield=90	-	8
9.	ZnAl mixed oxide	FA/LA (5/1), time (6 h) temperature (140 °C).	87	Yield=90	-	9
10.	Co <sub>8</sub> Pd <sub>2</sub> @N-C	LA (1 mmol), formic acid (5 equiv.), catalyst (30 mg), H <sub>2</sub> O (3 mL), time (9 h), temperature (150 °C).	~100	99.3	2.71	This work

**Table S4.** Comparative table HCOOH mediated LA reductive amination for pyrrolidone synthesis.

S.N.	Catalyst	LA:Amine	Reaction conditions	Yield (%)	Ref.
1	Au/ZrO <sub>2</sub>	1:1	FA (2.5 mmol), H <sub>2</sub> O (0.35 mL), Au (0.05 mol %), time (12 h), temp (130 °C).	97	10
2	Ir catalyst-1a	1:2.7	LA (2 mmol), FA (2.5 mmol), catalyst (0.02 g), H <sub>2</sub> O (3 mL), time (12 h), temp (80 °C).	88	11
3	[Ru <sub>3</sub> (CO) <sub>12</sub> ]-derived Ru-NPs	1:2	FA (6.54 mmol), catalyst (0.2 g), time (12 h), temp (120 °C).	93	12
4	Ru@GOIL	1:1	FA (2 mmol), catalyst (0.02 g), MeOH (5 mL), time (18 h), temp (130 °C).	96	13
5	Chloro(p-cymene)	1:1	FA (1 equiv), catalyst (0.2	95	14

	ruthenium(II)dimer with PtBu <sub>3</sub> ligand		mol%), time (12 h), temp (120 °C).		
6	Fe <sub>3</sub> (CO) <sub>12</sub>	1:4	FA (4 eq), LA=1.65mmol, catalyst (4 mol%), temp (180 °C), time (15 h).	90	15
7	Co <sub>8</sub> Pd <sub>2</sub> @N-C	(1:1)	FA (3 equiv.) (catalyst (30 mg), H <sub>2</sub> O (3 mL), time (8 h), temperature (160 °C).	91.1	This work

S

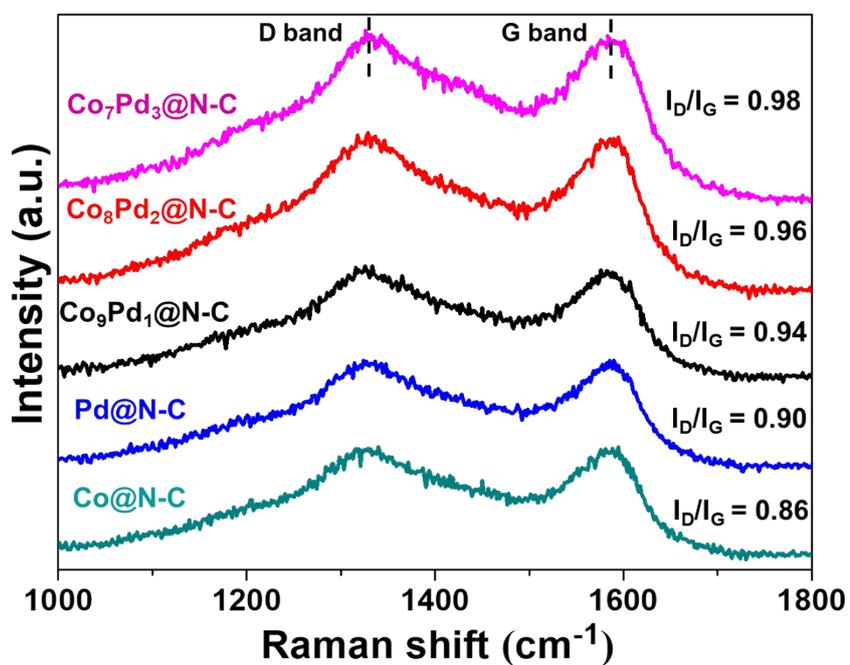


Fig. S1 Raman spectra of all the carbonized catalysts.

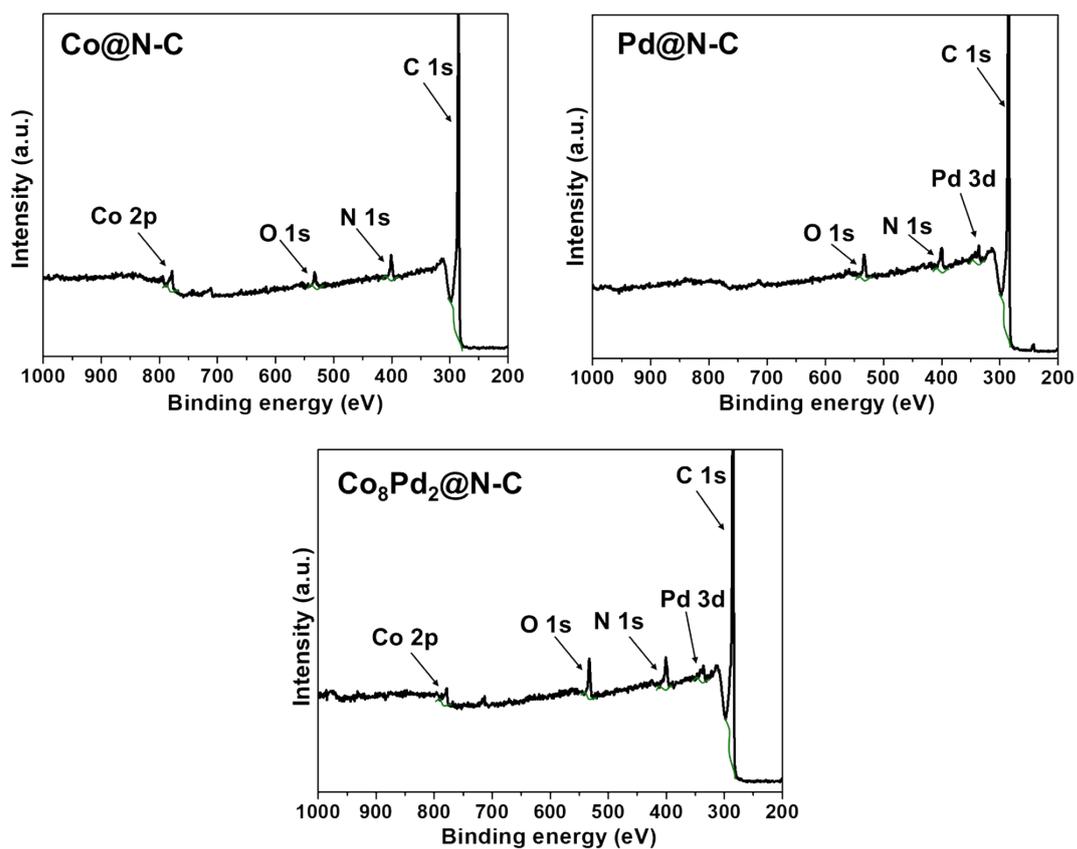


Fig. S2 XPS surface survey analysis of  $\text{Co}_8\text{Pd}_2@\text{N-C}$ ,  $\text{Co}@\text{N-C}$ , and  $\text{Pd}@\text{N-C}$ , respectively.

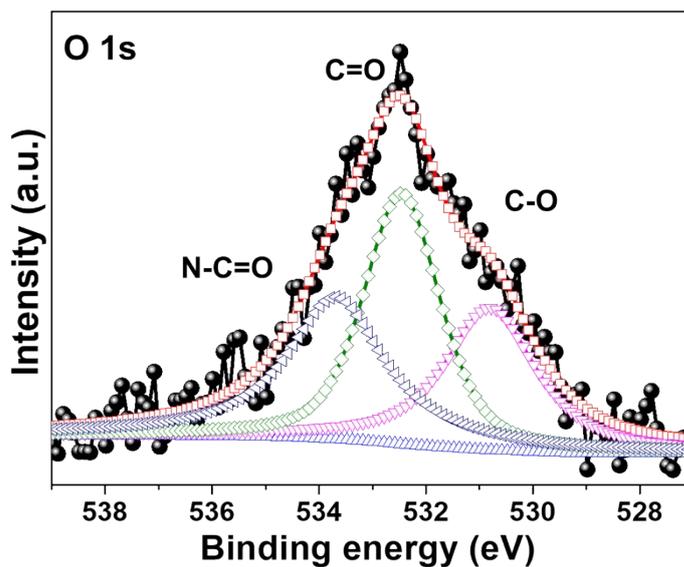
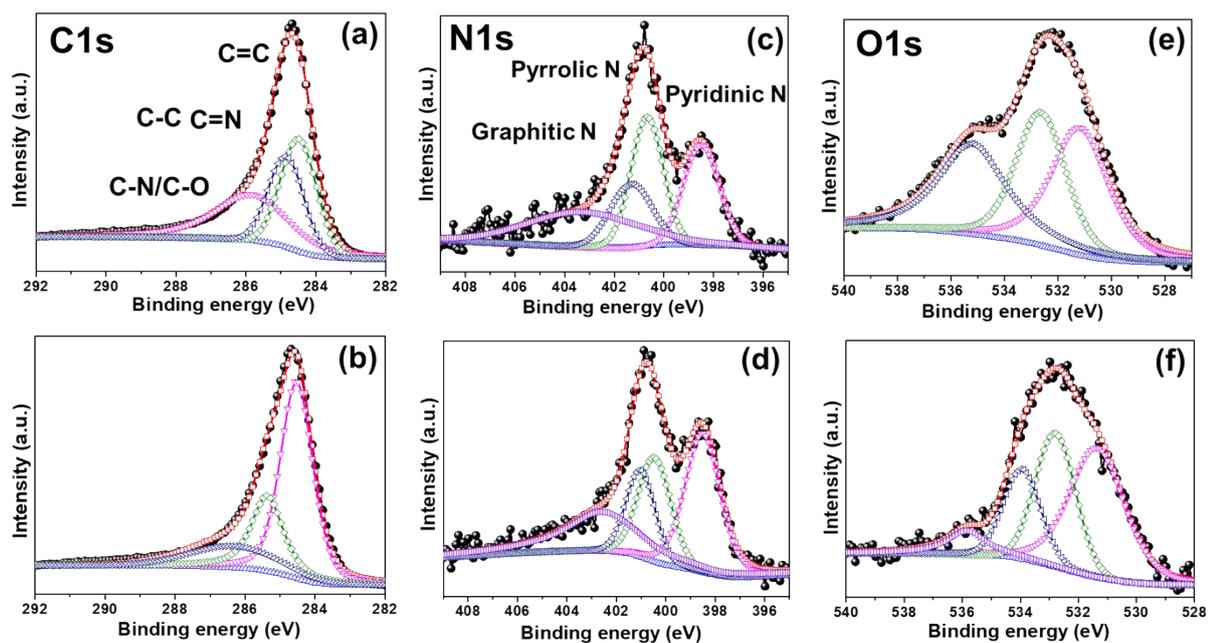
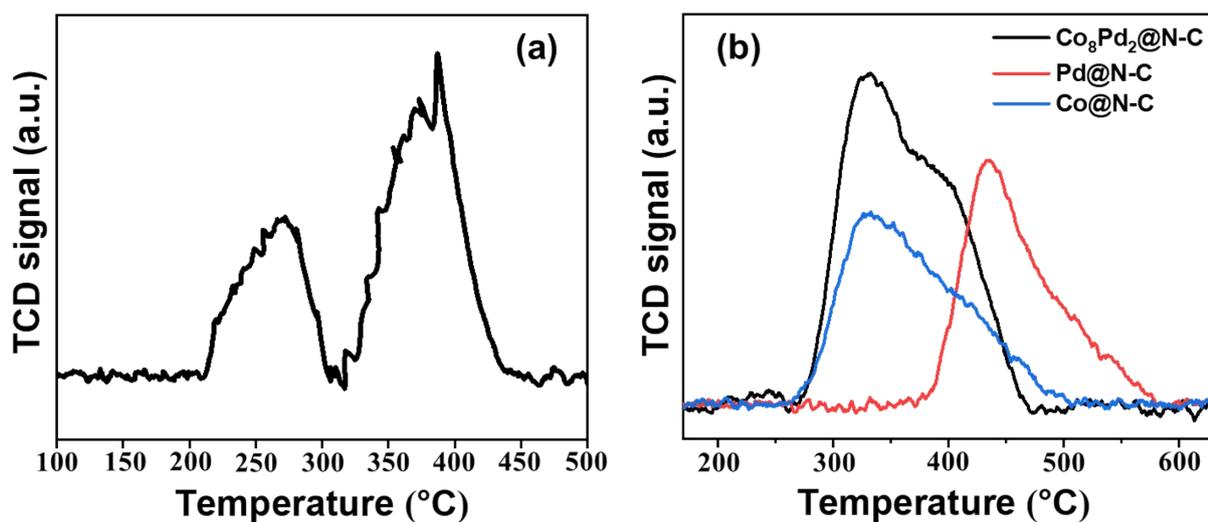


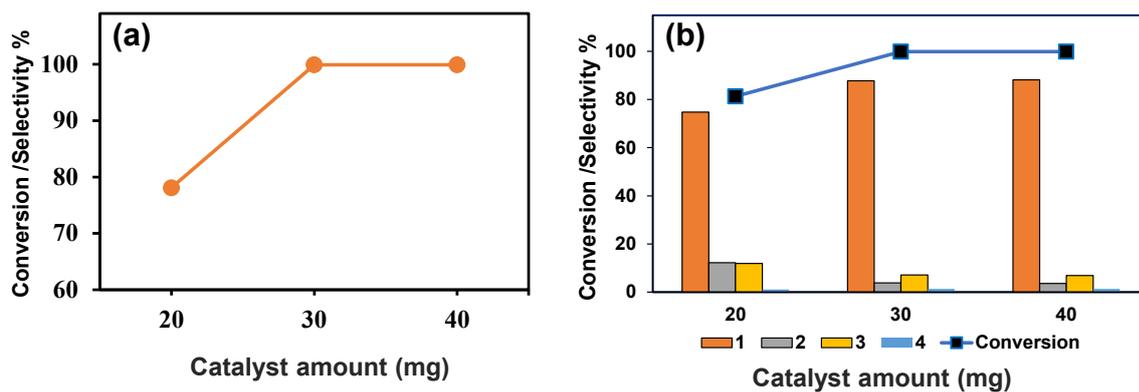
Fig. S3 High-resolution XPS spectra of O 1s of  $\text{Co}_8\text{Pd}_2@\text{N-C}$ .



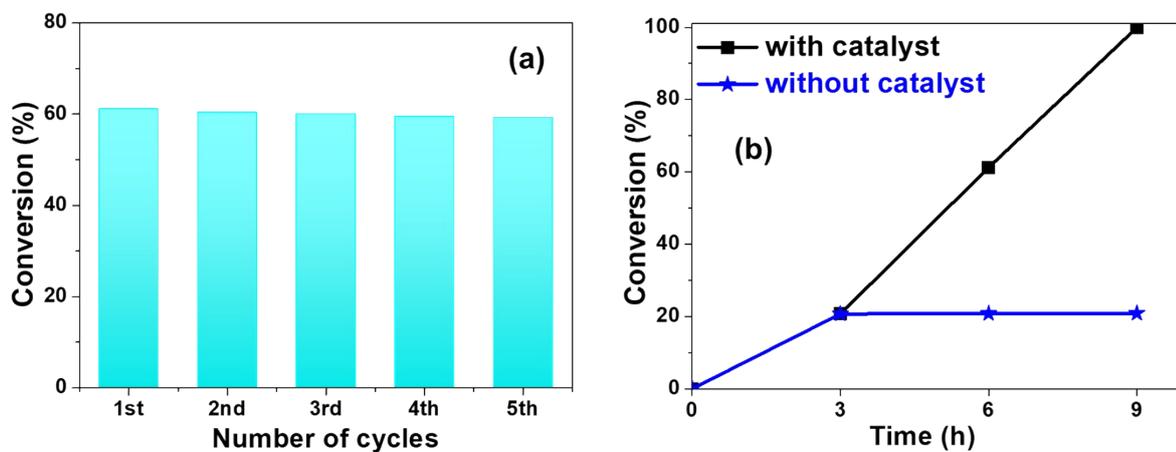
**Fig. S4** High-resolution XPS spectra of C 1s, N 1s, and O 1s of Co@N-C and Pd@N-C, respectively.



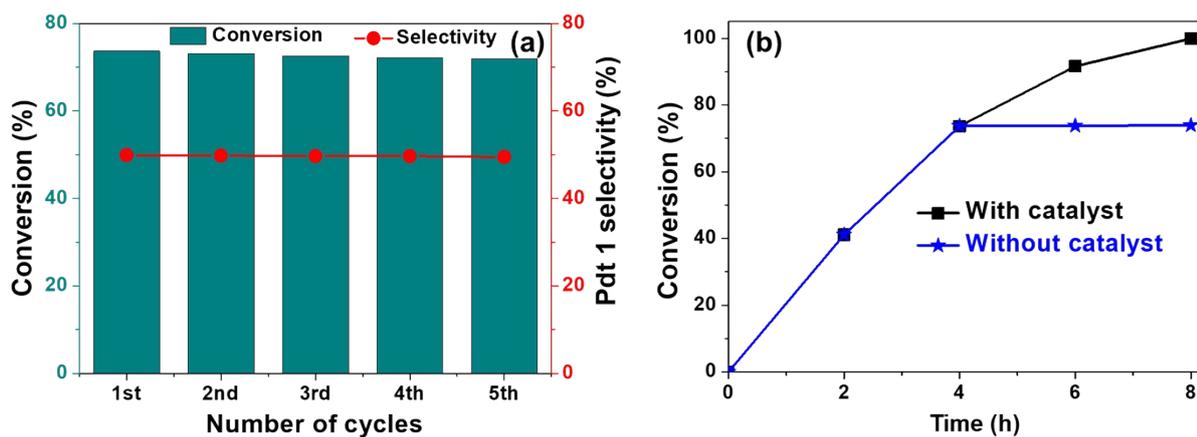
**Fig. S5** (a) CO<sub>2</sub>-TPD profiles of Co<sub>8</sub>Pd<sub>2</sub>@N-C, (b) H<sub>2</sub>-TPD profiles of Co<sub>8</sub>Pd<sub>2</sub>@N-C, Co@N-C and Pd@N-C respectively.



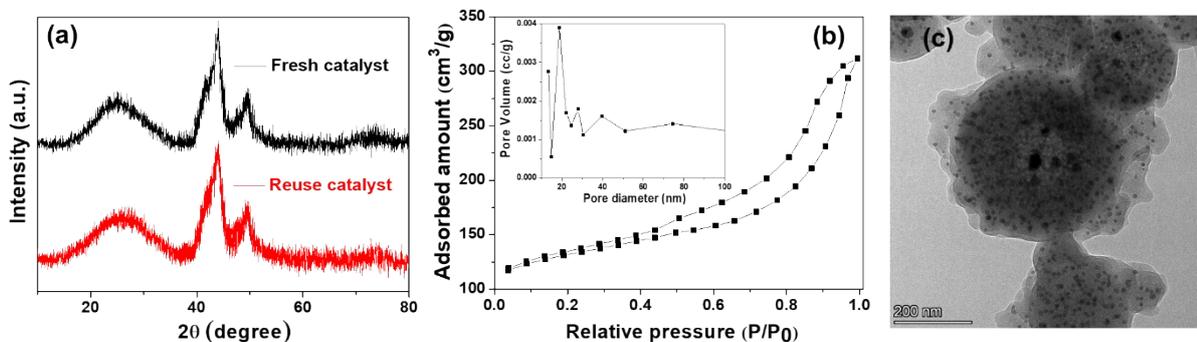
**Fig. S6** Influence of the catalyst amount in (a) LA to GVL transformation, and (b) reductive amination of LA.



**Fig. S7** (a) Recyclability test and (b) Hot-filtration for LA to GVL transformation using  $\text{Co}_8\text{Pd}_2@\text{N-C}$ .



**Fig. S8** (a) Recyclability test and (b) Hot-filtration for the reductive amination of LA using  $\text{Co}_8\text{Pd}_2@\text{N-C}$ .



**Fig. S9** (a) PXRD of fresh and reuse  $\text{Co}_8\text{Pd}_2@\text{N-C}$ , (b)  $\text{N}_2$  adsorption-desorption isotherms, and (c) TEM image of spent  $\text{Co}_8\text{Pd}_2@\text{N-C}$ .

## References

1. Y. Gao, H. Zhang, A. Han, J. H. Wang, R. E. -S. Tok, S. Jaenicke, and G. -K Chuah, *ChemistrySelect*, 2018, **3**, 1343–1351.
2. A. M. Ruppert, M. Jędrzejczyk, O. S. Płatek, N. Keller, A. S. Dumon, C. Michel, and P. Sautet, *Green Chem.*, 2016, **18**, 2014–2028.
3. P. A. Son, S. Nishimura, and K. Ebitani, *RSC Adv.*, 2014, **4**, 10525–10530.
4. B. Cai, Y. Zhang, and J. Feng, *Renew. Energy*, 2021, **177**, 652–662.
5. J. Wang, G. Zhang, M. Liu, Q. Xia, X. Yu, W. Zhang, J. Shen, C. Yang, X. Jin, *Chem. Eng. Sci.*, 2020, **222**, 1157215–1157225.
6. A. Chauhan, A. K. Kar, and R. Srivastava, *Appl. Catal. A: Gen.*, 2022, **636**, 118580–118591.
7. A. M. Ruppert, M. Jędrzejczyk, N. Potrzebowska, K. Kaźmierczak, M. Brzezińska, O. S.-Płatek, C. Michel and J. Gramsa, *Catal. Sci. Technol.*, 2018, **8**, 4318–4331.
8. M. Al-Naji, M. Popova, Z. Chen, N. Wilde, and R. Glaser, *ACS Sustainable Chem. Eng.*, 2020, **8**, 393–402.
9. M. N. E. H. Belguendouz, J. Gancedo, P. Rapado, D. Ursueguía, Y. Patino, L. Faba, A. Bahmani, E. Díaz, and S. Ordonez, *Chem. Eng. J.* 2021, **414**, 128902–128913.
10. X. Du, L. He, S. Zhao, Y. Liu, Y. Cao, and H. He, *Angew. Chem. Int. Ed.*, 2011, **50**, 7815–7824.
11. Y. Wei, C. Wang, X. Jiang, D. Xue, J. Li, and J. Xiao, *Chem. Commun.*, 2013, **49**, 5408–5410.
12. C. Ortiz-Cervantes, M. Flores-Alamo, and J. García, *Tetrahedron Lett.*, 2016, **57**, 766–771.
13. A. Raut, V. Shende, T. Sasaki, and B. Bhanage, *J. Catal.*, 2020, **383**, 206–214.
14. Y. Huang, J. Dai, X. Deng, Y. Qu, Q. Guo, and Y. Fu, *ChemSusChem*, 2011, **4**, 1578–1581.
15. G. Metzker, R. Dias, and A. Burtoloso, *ChemistrySelect*, 2018, **3**, 368–372.