Electronic Supplementary Material (ESI) for Dalton Transactions.
This journal is © The Royal Society of Chemistry 2019

Metal-Organic-Framework Derived Co-Pd Bond is Preferred over Fe-Pd for Reductive Upgrading of Furfural to Tetrahydrofurfuryl alcohol

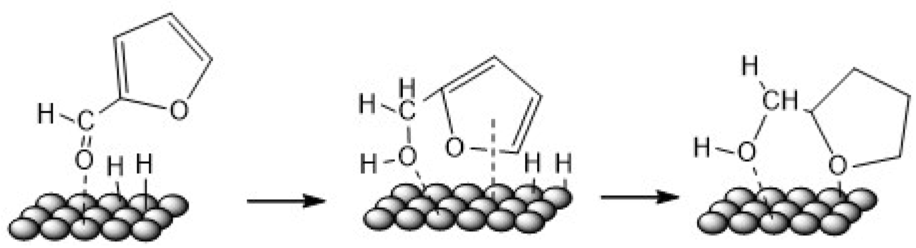
Saikiran Pendem,[a,b] Bolla Srinivasa Rao,[a,b] David J. Morgan[c] Digambar B. Shinde,[d] Zhiping Lai,[d] Nakka Lingaiah,[a,b] and John Mondal*[a,b]

[a]Catalysis and fine chemicals Division, CSIR-Indian Institute of Chemical Technology, Uppal Road, Hyderabad-500007, India, Email: johncuchem@gmail.com, johnmondal@iict.res.in

[b]AcSIR-Indian Institute of Chemical Technology, Hyderabad-500007 (India)

[c]Cardiff Catalysis Institute, School of Chemistry, Cardiff University, Park Place, Cardiff, CF10 3AT. UK

[d]Division of Physical Science and Engineering, King Abdullah University of Science and Technology (KAUST), Thuwal 23955-6900, Saudi Arabia.



Scheme S1: Plausible mechanistic pathway

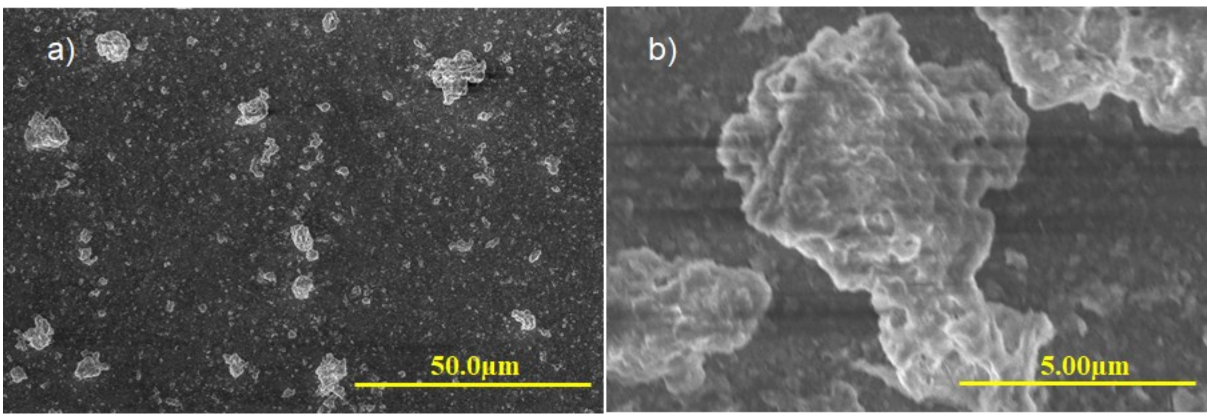


Figure S1: FE-SEM images (a & b) of PVP-Pd@ZIF-67

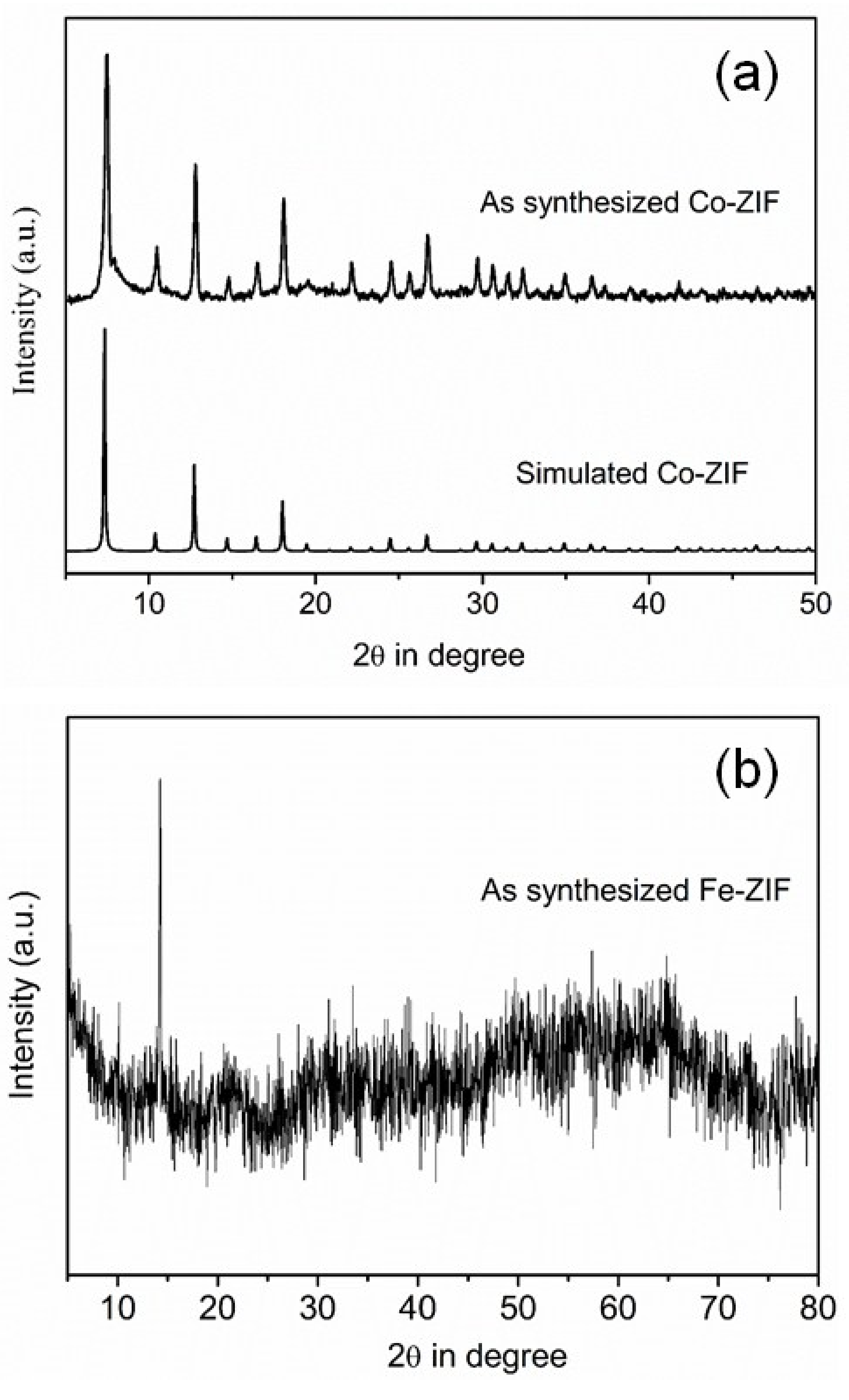


Figure S2: Wide angle powder XRD patterns and simulated pattern of Co-ZIF (a), and wide-angle powder XRD patterns of Fe-ZIF (b).

As shown in Figure S2b, The powder XRD patterns of Fe-ZIF are revealing that it has less crystalline nature.

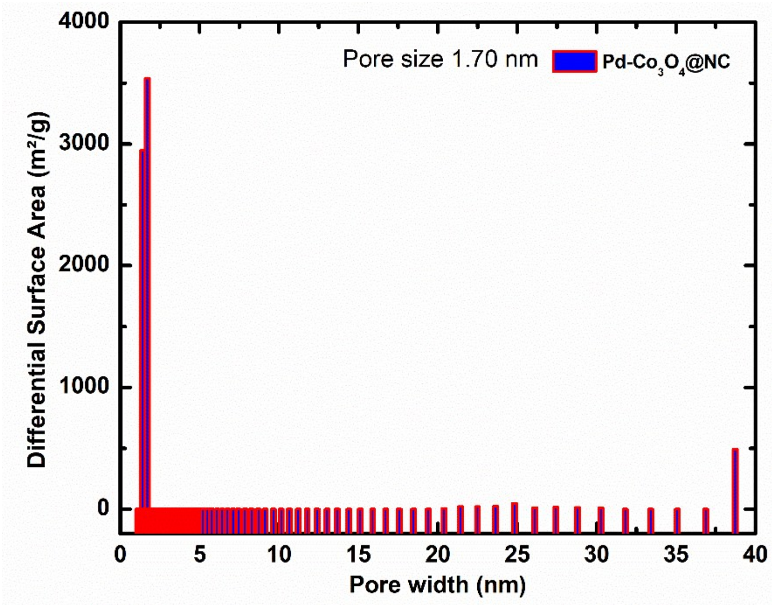


Figure S3: Pore-size distribution of $PdCo_3O_4$@NC catalyst

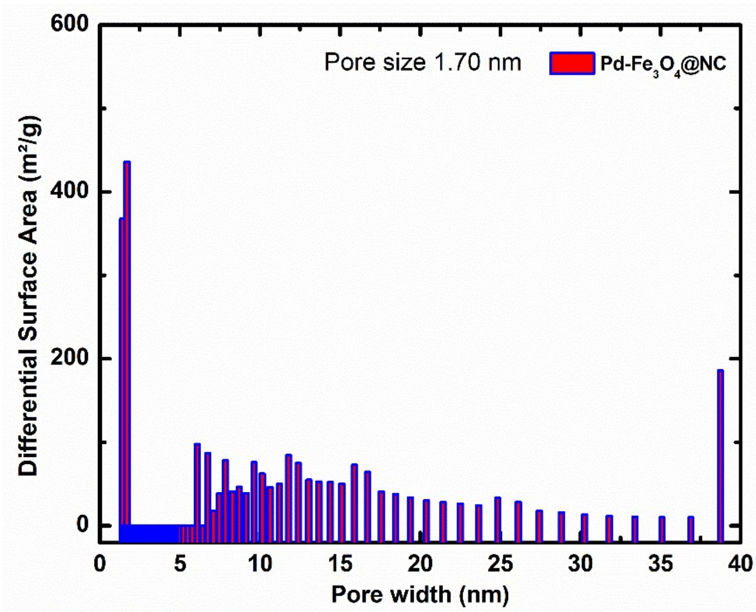


Figure S4: Pore-size distribution of $PdFe_3O_4$@NC catalyst.

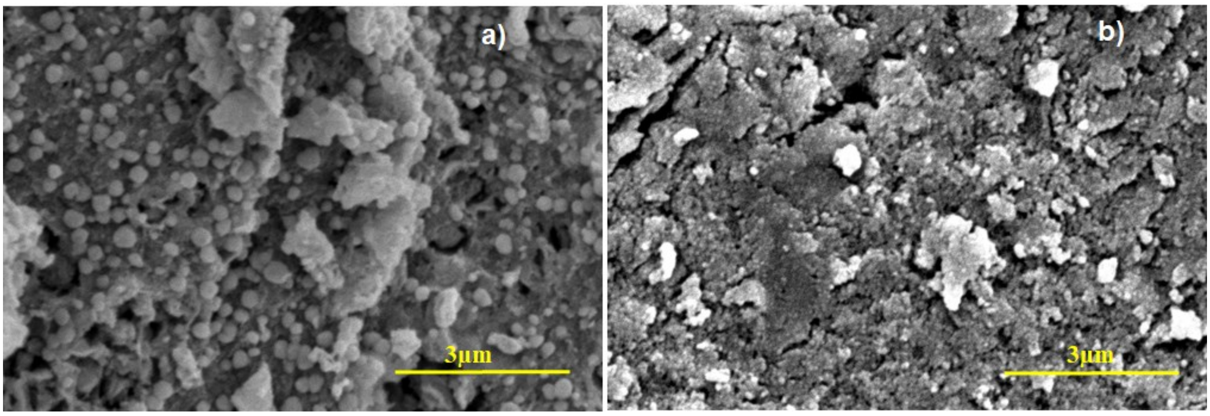


Figure S5: FE-SEM images (a) of Pd-Co_3O_4@NC, (b) of Pd-Fe_3O_4@NC, respectively.

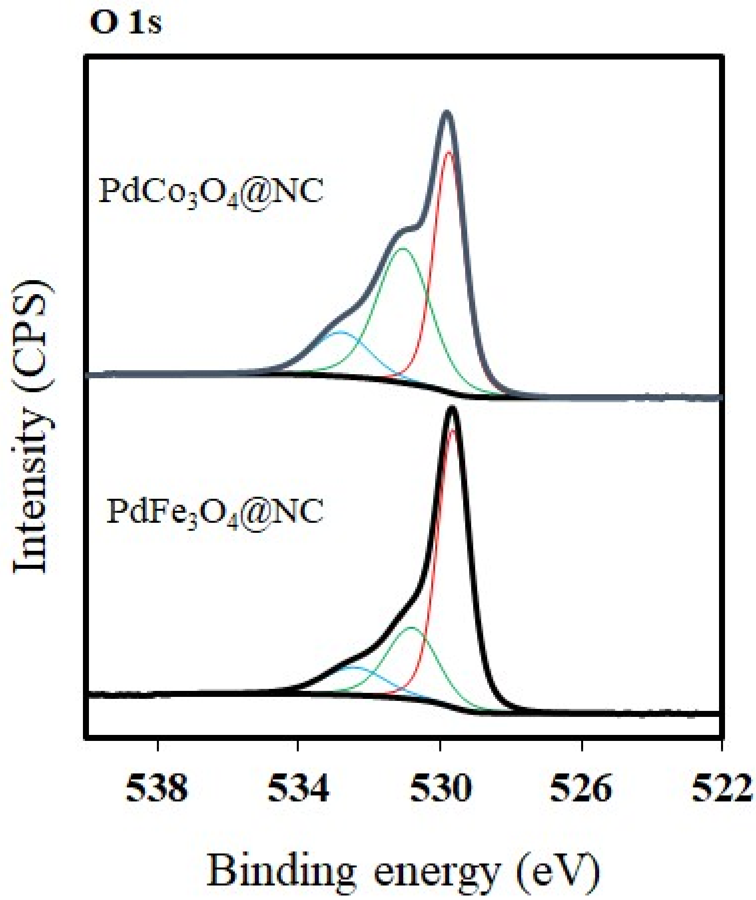


Figure S6: Fitted O-1s XPS spectra of Pd-Fe_3O_4@NC & Pd-Co_3O_4@NC.

From O-1s spectrum of Pd-Co_3O_4@NC three peaks at binding energies of ~533.0 eV ~529.5 which can be attributed to trapped water/surface carbonates and lattice oxygen atoms respectively and ~531.5 corresponding to surface hydroxide or O-N/C bonds in the hybrid (Figure S6, ESI).[1]

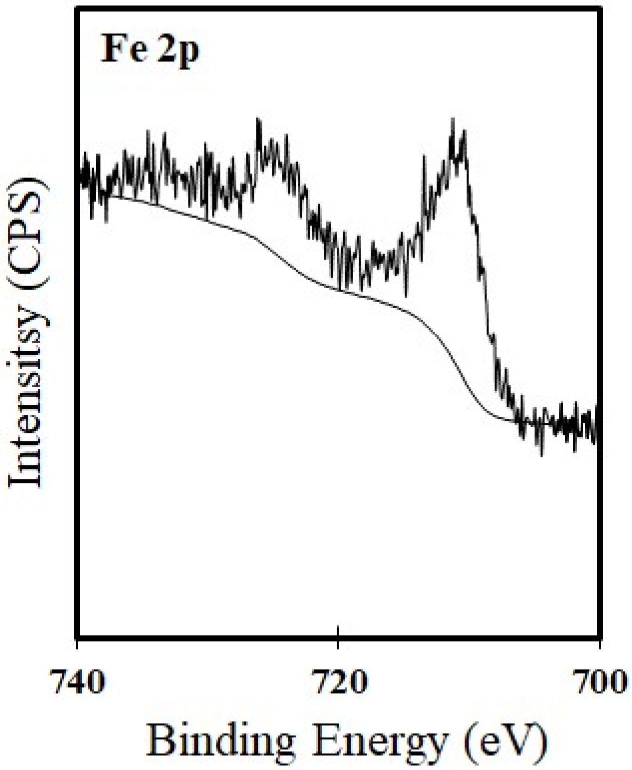


Figure S7: Fe-2p XP spectra of used Pd-Fe_3O_4@NC.

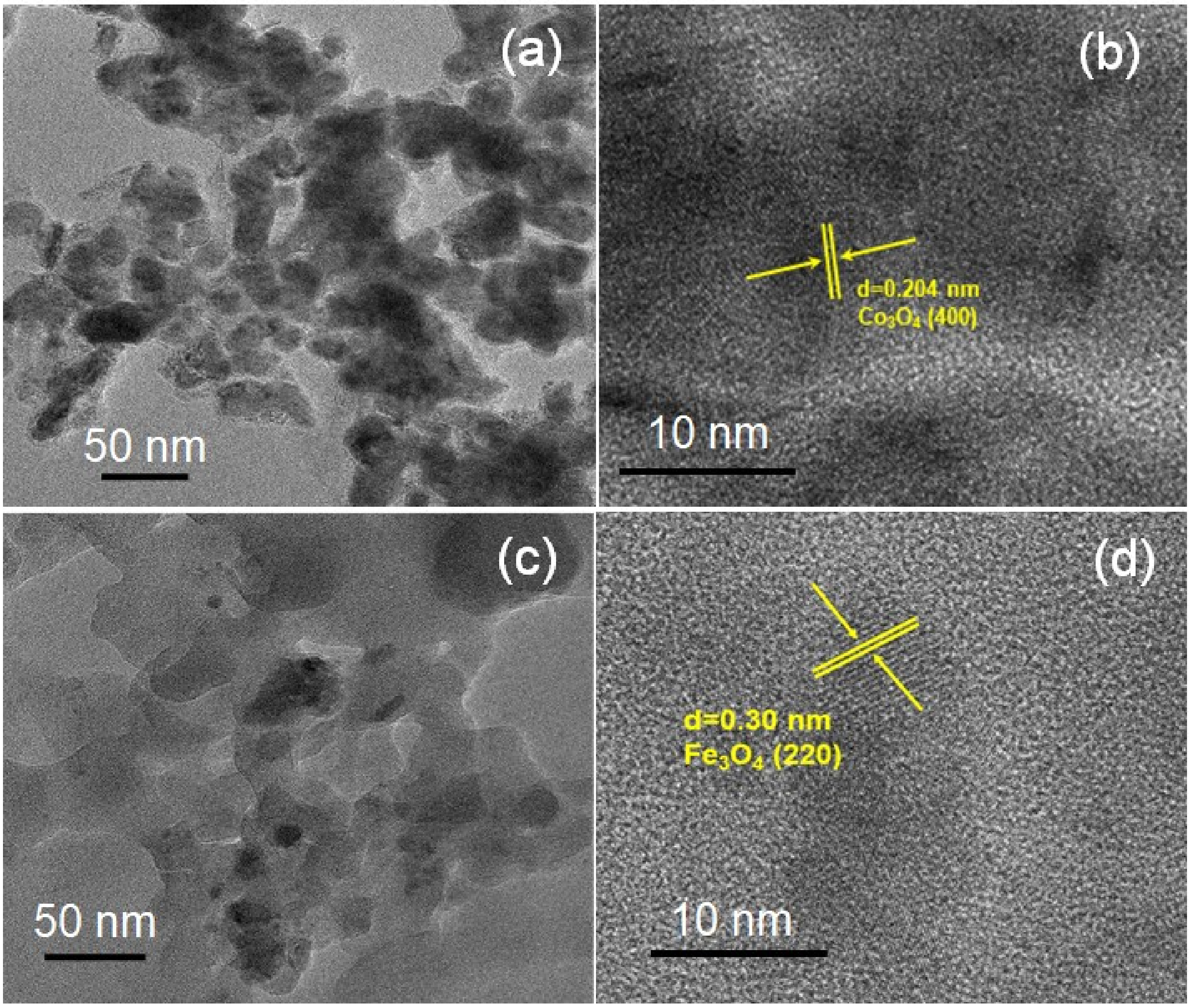


Figure S8: HR-TEM images (a, b) of used Pd-Co_3O_4@NC, (c, d) used Pd-Fe_3O_4@NC, respectively.

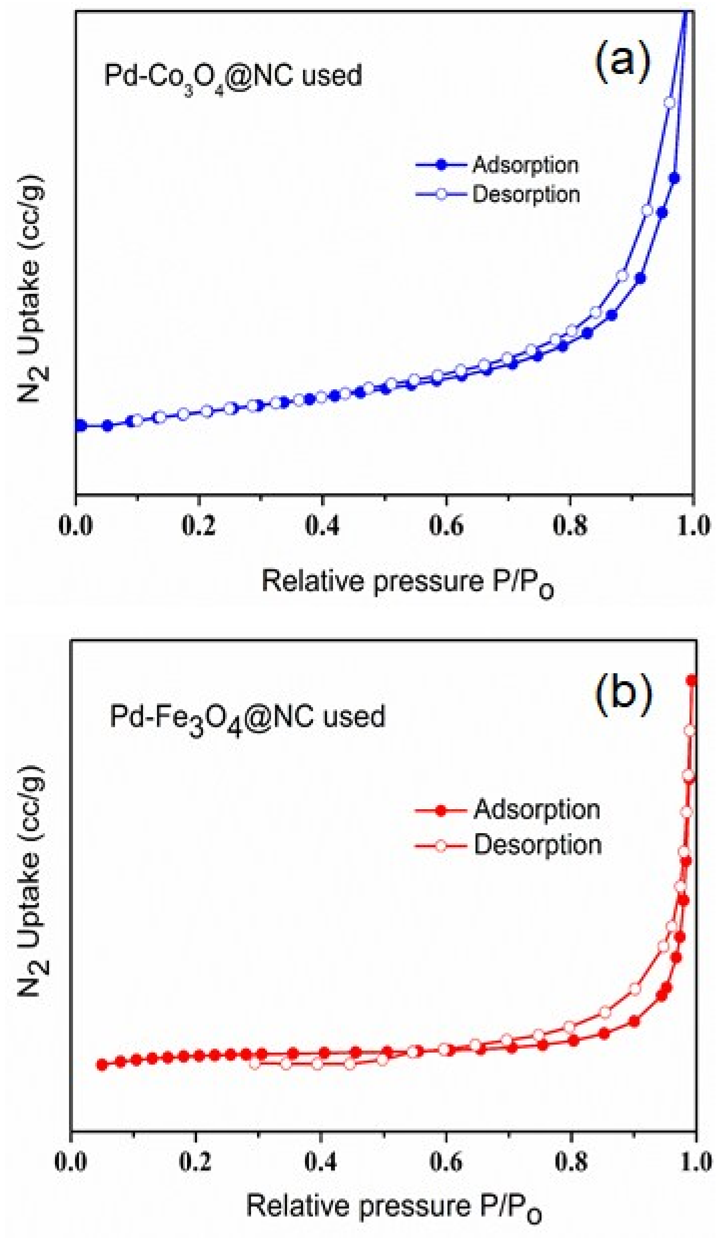


Figure S9: N_2 adsorption/desorption isotherms (a) and (b), of used Pd-Co_3O_4@NC and used Pd-Fe_3O_4@NC, respectively.

Table S1: Catalytic performances of Pd-Based heterogeneous catalysts for the conversion of Furfural to THFAL

Entry	Catalyst	FA feed (mmol)	T (°C)	P (bar)	t (h)	FA conv. (%)	THFAL yield (%)	Ref.
1	Pd/TiO_2	300	30	3	4	100	42	2
2	Pd–Pt/TiO_2	300	30	3	4	100	95	2
3	5 wt % Pd/C[a]	604	120	50	1	99	13	3
4	5 wt % Pd– 3[b] wt % Cu/Al_2O_3	2.5	90	20	2	99	51	4
5	5 wt % Pd/Al_2O_3 [b]	2.5	90	20	2	100	72	4
6	10 wt %[c]Pd/Al_2O_3	10.4	25	60	8	80.3	78.2	5
8	Ni/C	0.2	120	10	2	100	100	6
7	Ni–Pd/SiO_2 [b]	5	40	80	2	100	96	7

[a]methanol solvent, [b]H_2O solvent, [c]2-propanol

Table S2: ICP-AES metal analysis data chart for metallic catalysts.

Catalyst	Pd ($mmolg^{-1}$)	Fe ($mmolg^{-1}$)	Co ($mmolg^{-1}$)
Pd-Co_3O_4@NC (Fresh)	0.039	-	1.45
Pd-Fe_3O_4@NC (Fresh)	0.036	1.29	-
Pd-Co_3O_4@NC (Used)	0.027	-	1.37
Pd-Fe_3O_4@NC (Used)	0.002	1.15	-

Table S3: Catalytic performances of Pd-Co_3O_4@NC-400, 500 & 600 catalysts for the Conversion of furfural to THFAL.

Entry	Catalyst Used	FA Con (%)	THFAL Yield (%)
1.	PdCo_3O_4@NC-400	97	94
2.	PdCo_3O_4@NC-500	80	86
3.	PdCo_3O_4@NC-600	73	72

Reference:

1. S. Pendem, R. Singuru, C. Sarkar, B. Joseph, J. F. Lee, D.B. Shinde, Z. Lai, and J.Mondal, *ACS Appl. Nano Mater.,* 2018, **1** (9), 4836-4851.
2. R. Albilali, M. Douthwaite, Q. He and S. H. Taylor, *Catal. Sci. Technol*., 2018, **8**, 252-267.
3. N. Merat, C. Godawa and A. Gaset, *J. Chem. Technol. Biotechnol*., 1990, **48**, 145-159.
4. M. Lesiak, M. Binczarski, S. Karski, W. Maniukiewicz, J. Rogowski, E. Szubiakiewicz, J. Berlowska, P. Dziugan and I. Witońska, *J. Mol. Catal. A: Chem.,* 2014, **395**, 337-348.
5. S. Bhogeswararao and D. Srinivas, *J. Catal.,* 2015, **327**, 65-77.
6. Y. Su, C. Chen, X. Zhu, Y. Zhang, W. Gong, H. Zhang, H. Zhao and G. Wang, *Dalton Trans*., 2017, **46**, 6358-6365.
7. Y. Nakagawa and K. Tomishige, *Catal. Commun*., 2010, **12**, 154-156.