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Electronic Supplementary Information

Amine-functionalized metal-organic framework-based Pd nanoparticles: Highly efficient multifunctional catalysts for base-free aerobic oxidation of different alcohols

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1. General remarks

All chemicals were purchased from Sigma-Aldrich and used as received, unless otherwise specified. ^{1}H NMR spectra were recorded on a Bruker AM 400 (400 MHz) using a solution prepared by digesting 10 mg of sample in mixture of DMSO-d_6 (600 μL) and dilute DCl (1.500 μL, 35% DCl). The FTIR spectra were obtained on a Nicolet iS10 FTIR spectrometer. All products were isolated by short chromatography on a silica gel (200-300 mesh) column, unless otherwise noted. X-ray powder diffraction patterns were recorded on a Rigaku diffractometer using CuKα (λ=1.54 Å). XPS measurements were carried out on a K-Alpha (Thermo Scientific). Nitrogen adsorption/desorption isotherms were measured on a Micromeritics ASAP 2020 surface analyzer at -196°C. Thermogravimetric analyses were carried out on a TGA (Scinco S-1000) system under a N_2 flow. Digital microscopic images were recorded with a Deno-Lite digital microscope (DinoLite_DNC-P-Ver.3.3.0.16). Metal contents in MOFs were evaluated using inductively coupled plasma spectrometry (ICP-OES, Optima 7300DV). Metal contents in the filtrate after catalysis reactions were determined using inductively coupled plasma-mass spectrometry (ICP-MS, Perkin-Elmer élan 6100). C, H, and N analyses were performed using a FLASH EA 1112 elemental analyzer (Thermo Electron Corporation). The samples were dried at 85°C under vacuum for 24 h prior to XPS, elemental, and metal analyses. GC/GCMS analyses were performed on an Agilent 6890 N GC coupled to an Agilent 5975 Network Mass Selective Detector.

2. Effect of catalyst loading (mol %)

We performed the oxidation of benzyl alcohol with various amounts of catalyst for screening the loading. As shown in Fig. S9, the yield of product gradually increased with an increase of loading amount of catalyst (0-1.4 mol %). Although the yield of reaction almost reached 100% with 0.8 mol % of catalyst **2B**, but 1.0 mol% and 1.4 mol% gave a 100% yield for benzyl alcohol at 80 °C. So, we determined 1.0 mol % loading of **2B** as an optimized loading under reaction conditions.

3. EA and ICP analysis for compound 1 and 2B

Table S1 Analytical data (wt %) for compound **1** and **2B** by EA & ICP analysis [a]

Compound	C	H	N	Zn	Pd
1	56.38 (56.59)	3.75 (3.89)	5.74 (6.00)	18.42 (18.67)	-
2B	45.23 (45.17)	3.48 (3.50)	4.01 (4.05)	12.70 (12.61)	8.33

[a] Calculated values are shown in parentheses. The material was dried at 80°C under vacuum for 24 h.

4. The color of the catalyst, 2B and its precursor

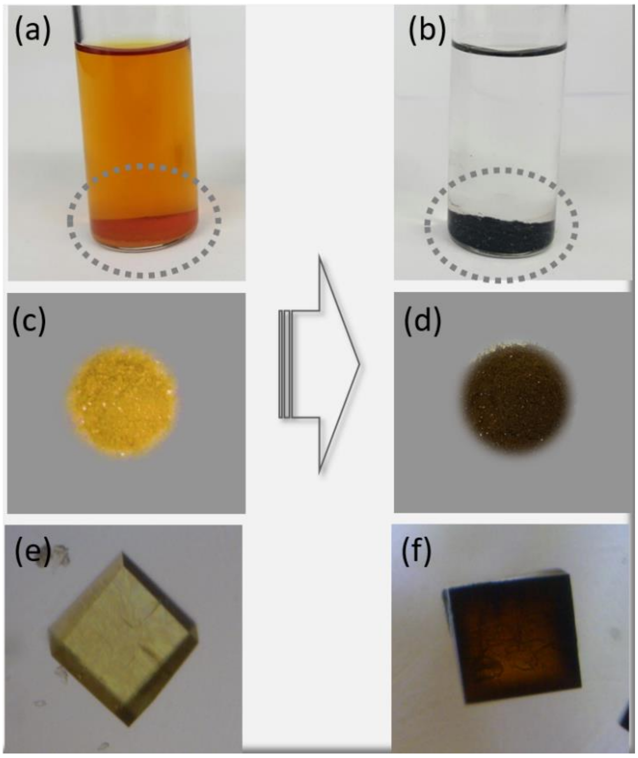


Fig. S1 The color of the catalyst, **2B** and its precursor; (a) before reaction in solution of palladium(II) acetate, (b) after reaction in solution; solid powder (c) compound **1**, (d) catalyst, **2B**; digital microscopic images (e) compound **1** (f) catalyst, **2B**, respectively.

5. **FETEM and HRSEM images of** fresh and used catalyst (after 5th run) at different magnifications.

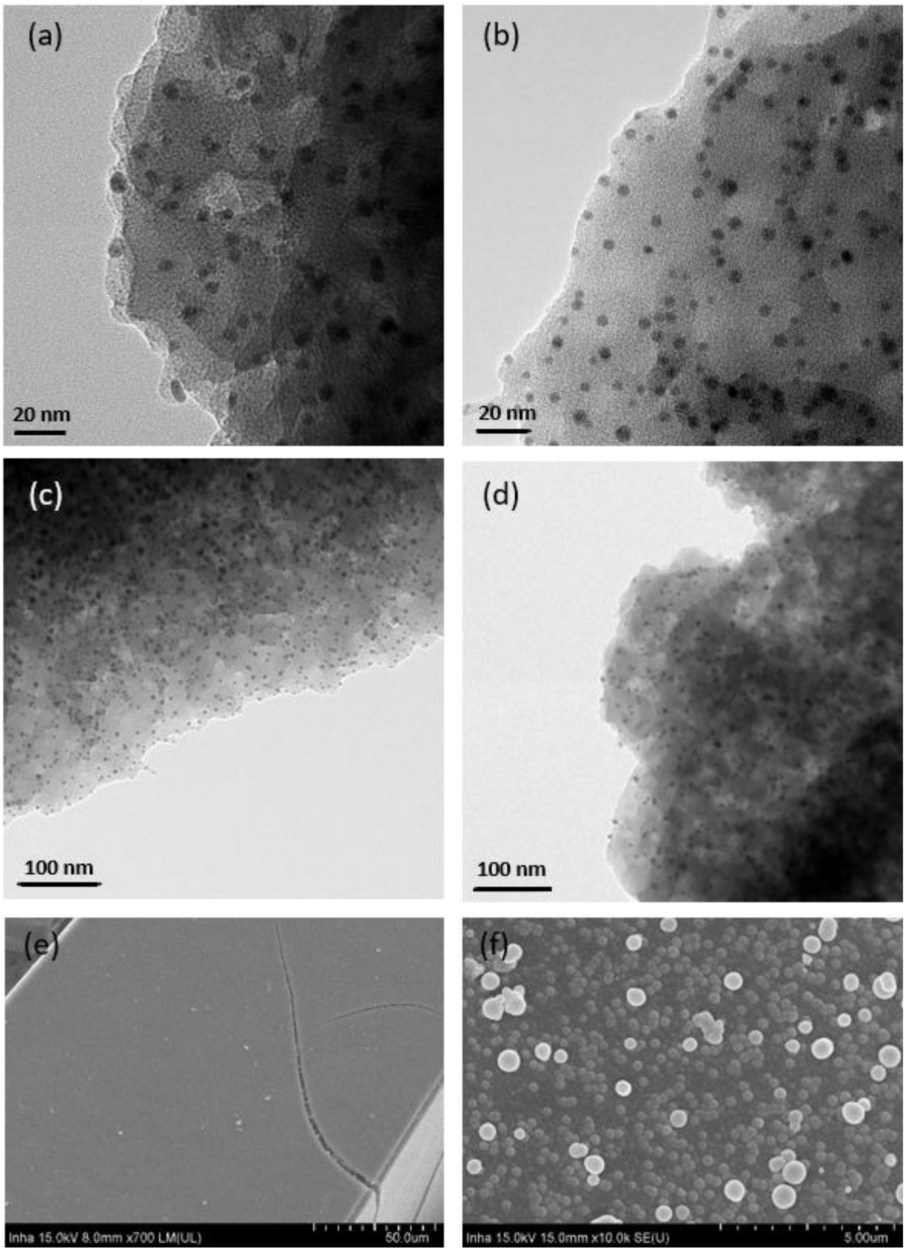


Fig. S2 FETEM images of catalyst **2B** fresh (a, c) and after 5th run (b, d) with different magnifications; (a, b) 20 nm and (c, d) 100 nm respectively. HRSEM images of the surface of used catalyst (after 5th run) at different magnifications (scale bars are shown at bottom) for 50 μm and 5 μm respectively (e & f).

6. SEM image of the catalyst, 2B with corresponding EDX

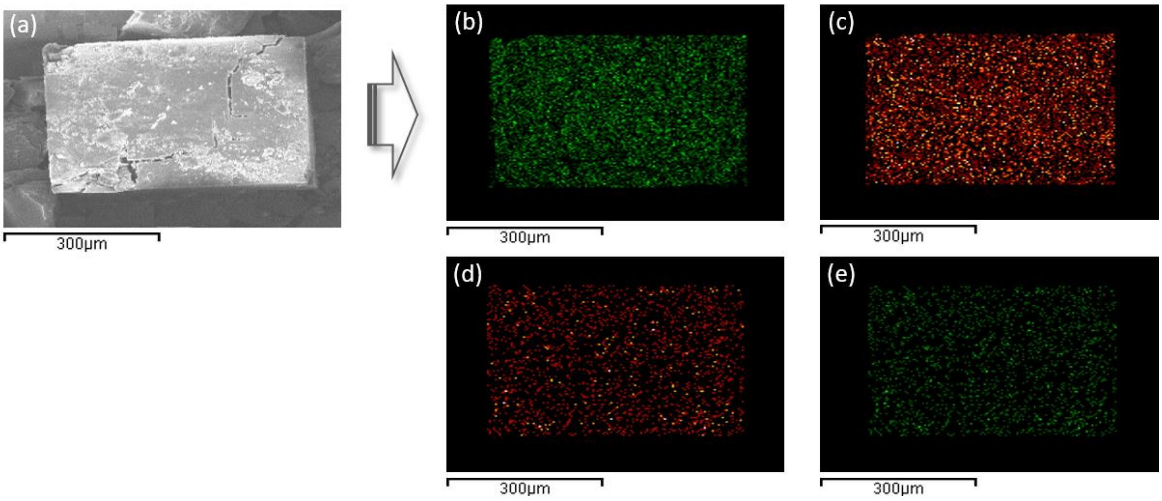


Fig. S3 A typical SEM image of the surface of **2B** (a) and its corresponding quantitative EDS mapping of C (b), Zn (c), Pd (d) and N (e) respectively.

7. EDX spectrum of catalyst, 2B and its corresponding TEM image

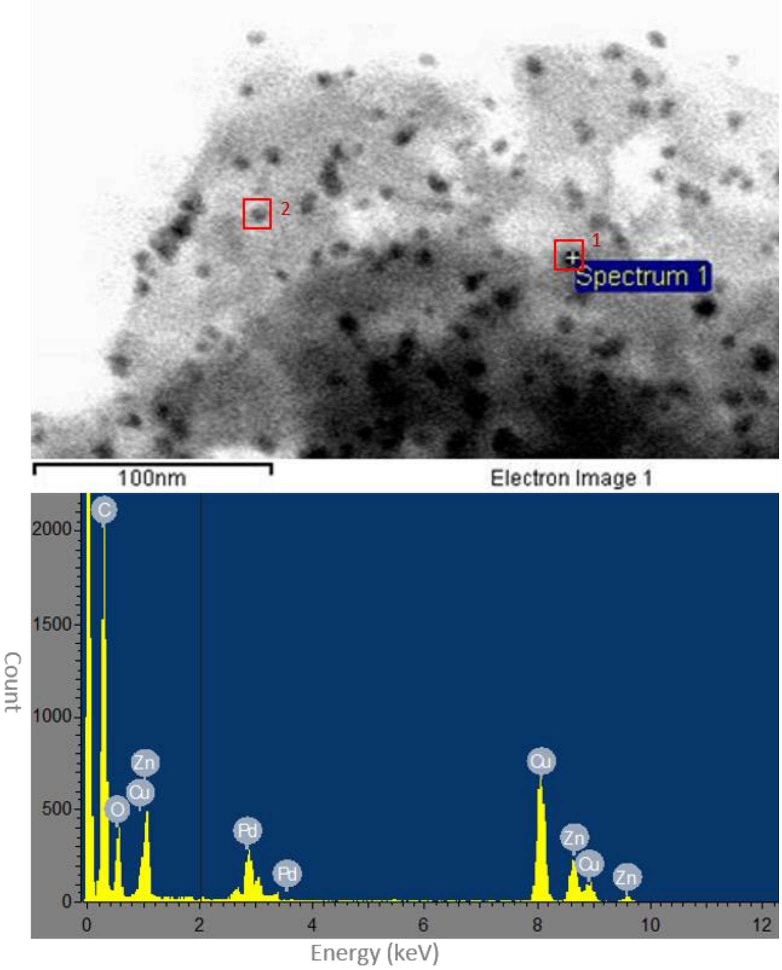


Fig. S4 EDX spectrum of catalyst, **2B** collected from area 1 as shown in the TEM measurement (note that the Cu peaks come from the copper grid).

8. XPS survey spectra of Compound 1 and 2B

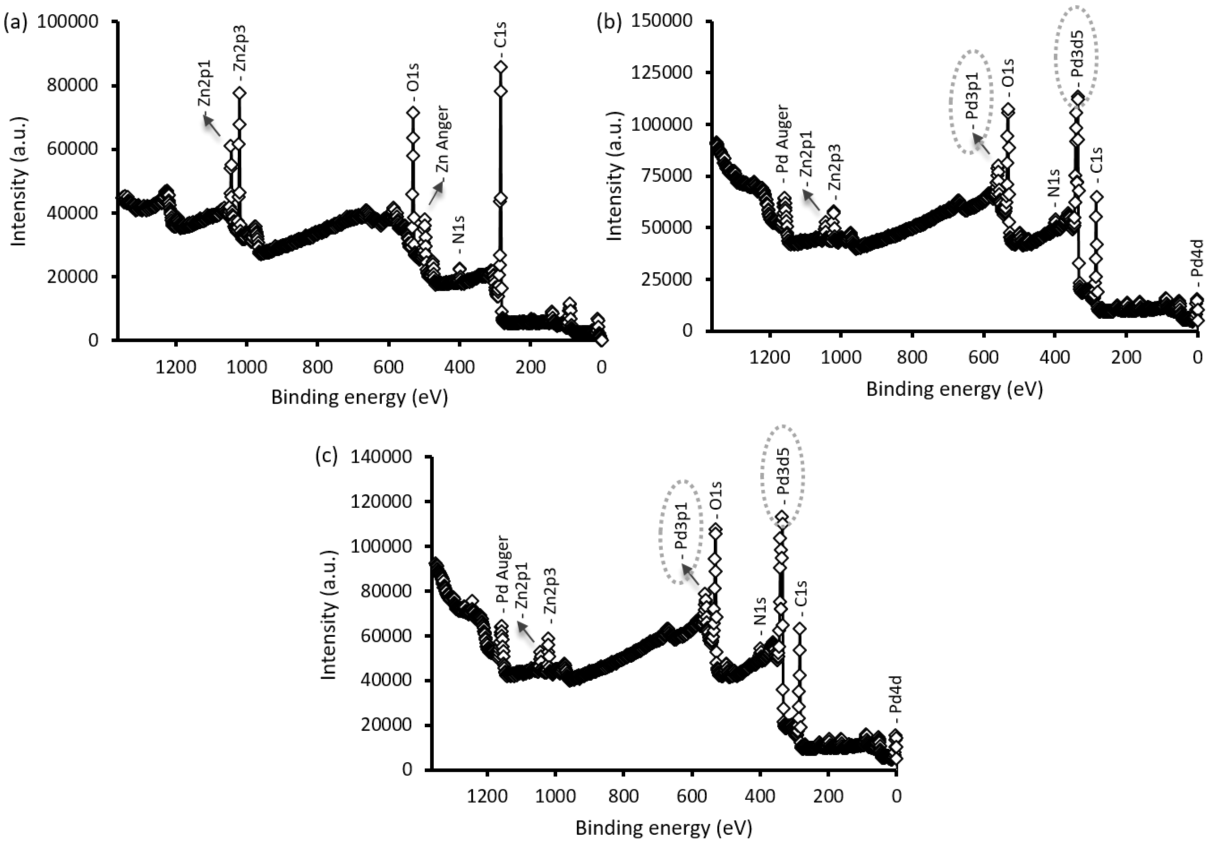


Fig. S5 XPS survey spectra of compound **1** (a), **2B** (b) and **2B** after 5th run (c), respectively.

9. N_2 adsorption-desorption isotherms of compound 1 and catalyst, 2B

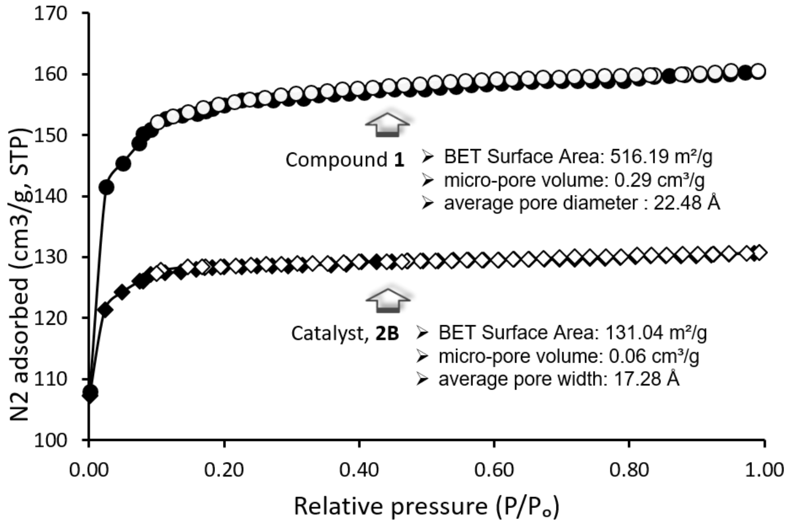


Fig. S6 N_2 adsorption-desorption isotherms of compound **1** (top) and catalyst, **2B** (bottom); filled mark represents the adsorption and unfilled mark represents the desorption, respectively.

10. Pore volume vs diameter curves for compound 1 and catalyst, 2B

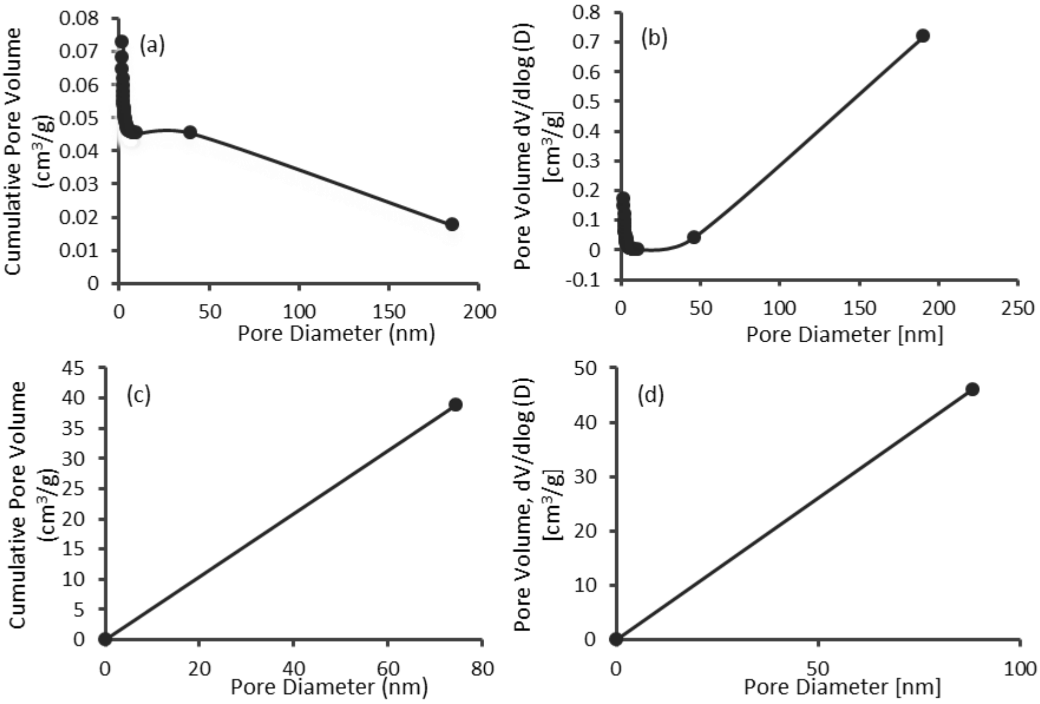


Fig. S7 BJH desorption cumulative pore volume vs diameter for **1** and **2B** (a, c); BJH desorption dV/dlog(D) pore volume vs diameter for **1** and **2B** (b, d)

11. XRD patterns for fresh, after 5th run and run in water of catalyst, 2B

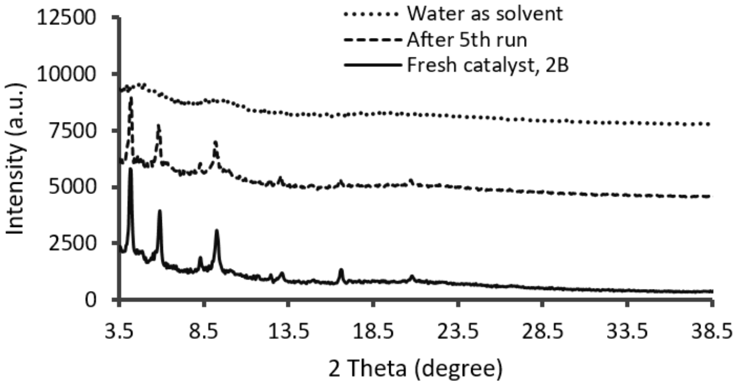


Fig. S8 X-ray powder diffraction patterns for fresh catalyst, after 5th run and run in water as solvent of the catalyst, **2B**.

12. Determining amount of catalyst using mol %

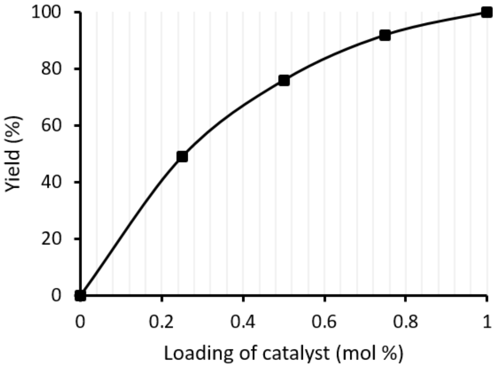


Fig. S9 Aerobic oxidation of benzyl alcohol with different loading of catalyst, **2B**. The reaction conditions are the same as Table 1 (entry 1).

13. FTIR spectra and XRD patterns of fresh catalyst 2B, and after 5th run

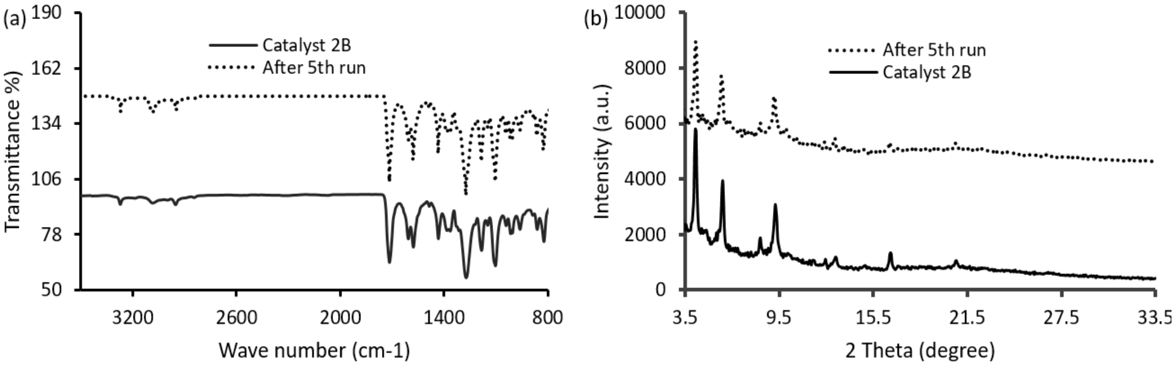
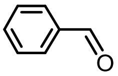


Fig. S10 FTIR spectra and XRD patterns of fresh catalyst, **2B** and catalyst after 5th run

14. Product characterization

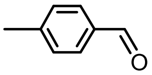
All products were characterized by ^{1}H NMR, ^{13}C NMR and HRMS, and their spectroscopic data were in good agreement with those reported in earlier reports (^{1}H and ^{13}C NMR).[1,2]

Benzaldehyde (Table 1, Entry 1)[1]



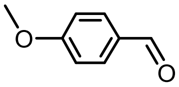
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.54 (2H, t, J = 7.8 Hz), 7.62-7.64 (1H, m), 7.87-7.91(2H, m), 10.03(1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 128.9, 129.6, 134.5, 136.4, 192.2; HRMS (EI) *m/z* calcd for C_7H_6O (M^+) 106.0418, found 106.0417.

4-methylbenzaldehyde (Table 1, Entry 2)[1]



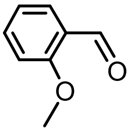
^{1}H NMR (500 MHz, CDCl$_3$): δ = 2.45 (3H, s), 7.35 (2H, d, J = 8.0 Hz), 7.79 (2H, d, J = 8.0 Hz,), 9.97 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 21.9, 129.8, 129.8, 134.3, 145.5, 191.8; HRMS (EI) *m/z* calcd for C_8H_8O (M^+) 120.0575, found 120.0576.

4-methoxybenzaldehyde (Table 1, Entry 3)[1]



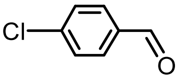
^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.91 (3H, s), 7.02-7.04 (2H, m), 7.84-7.87 (2H, m), 9.89 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 55.6, 114.3, 130.0, 131.9, 164.5, 190.8; HRMS (EI) *m/z* calcd for $C_8H_8O_2$ (M^+) 136.0524, found 136.0525.

2-methoxybenzaldehyde (Table 1, Entry 4)[1]



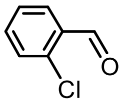
^{1}H NMR (500 MHz, CDCl$_3$): δ = 3.94 (3H, s), 7.01-7.06(2H, m), 7.56-7.60 (1H, m), 7.85-7.86 (1H, m), 10.50 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 55.6, 111.7, 120.6, 125.1, 128.6, 136.0, 161.9, 189.8; HRMS (EI) *m/z* calcd for $C_8H_8O_2$ (M^+) 136.0524, found 136.0524

4-chlorobenzaldehyde (Table 1, Entry 5)[1]



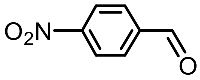
^{1}H NMR (500 MHz, CDCl$_3$): δ = 7.50-7.54 (2H, dt, J = 9.5, 7.2 Hz), 7.80-7.83 (2H, m, J = 13.0 Hz), 9.97 (1H, s); ^{13}C NMR (125 MHz, CDCl$_3$): δ = 129.5, 130.8, 134.6, 140.9, 190.9; HRMS (EI) *m/z* calcd for C_7H_5ClO (M^+) 140.0028, found 140.0027.

2-chlorobenzaldehyde (Table 1, Entry 6)[1]



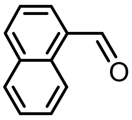
^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.48 (1H, t, *J* = 7.2 Hz), 7.56-7.61 (1H, m), 7.75-7.76 (1H, m), 7.85 (1H, t, *J* = 1.7 Hz), 9.98 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 128.0, 129.1, 130.4, 134.3, 135.5, 137.8, 190.8; HRMS (EI) *m/z* calcd for C_7H_5ClO (M^+) 140.0028, found 140.0029.

4-nitrobenzaldehyde (Table 1, Entry 7)[1]



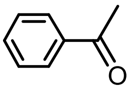
^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.10 (2H, dd, *J* = 7.2, 2.0 Hz), 8.42 (2H, d, *J* = 8.0 Hz), 10.18 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 124.4, 130.5, 140.1, 151.2, 190.1; HRMS (EI) *m/z* calcd for $C_7H_5NO_3$ (M^+) 151.0269, found 151.0268.

1-naphthaldehyde (Table 1, Entry 8)[1]



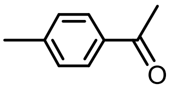
^{1}H NMR (500 MHz, CDCl3): δ 7.58 (t, J = 7.5 Hz, 2H), 7.66-7.71 (m, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.92 (dd, J = 8.0, 1.5 Hz, 1H), 9.25 (d, J = 9.0 Hz, 1H), 10.36 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 124.6, 126.7, 128.3, 128.8, 130.2, 131.2, 133.4, 135.1, 136.3, 193.2; HRMS (EI) *m/z* calcd for $C_{11}H_8O$ (M^+) 156.0601, found 156.0602.

Acetophenone (Table 1, Entry 9)[1]



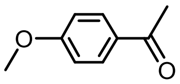
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.63 (3H, s), 7.48 (2H, t, *J* = 7.2 Hz), 7.58 (1H, t, *J* = 7.2 Hz), 7.98 (2H, d, *J* = 7.2 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.4, 128.3, 128.4, 133.1, 137.0, 198.1; HRMS (EI) *m/z* calcd for C_8H_8O (M^+) 120.0575, found 120.0575.

1-(p-tolyl)ethan-1-one (Table 1, Entry 10)[1]



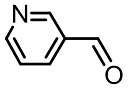
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.41 (3H, s), 2.56(3H, s), 7.24 (2H, d, *J* = 8.0 Hz), 7.86 (2H, d, *J* = 8.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 21.7, 26.3, 128.4, 129.3, 134.6, 143.6, 197.9; HRMS (EI) *m/z* calcd for $C_9H_{10}O$ (M^+) 134.0731, found 134.073166.

1-(4-methoxyphenyl)ethan-1-one (Table 1, Entry 11)[1]



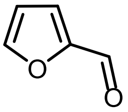
^{1}H NMR (500 MHz, $CDCl_3$): δ = 2.58 (3H, s), 3.87 (3H, s), 6.96 (2H, d, J = 8.5 Hz), 7.96 (2H, d, J = 9.0 Hz); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 26.2, 55.3, 113.7, 130.5, 130.5, 163.4, 196.7; HRMS (EI) *m/z* calcd for $C_9H_{10}O_2$ (M$^+$) 150.0680, found 150.0681.

Nicotinaldehyde (Table 1, Entry 12)[2]



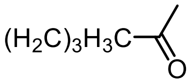
^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.01 (1H, s), 9.0 (1H, s), 8.75 (1H, d, J = 7.2 Hz), 8.02 (1H, d, J = 7.2 Hz), 7.45-7.41 (1H, m); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 192.2, 156.4, 150.2, 137.8, 135.0, 123.2; HRMS (EI) *m/z* calcd for C_6H_5NO (M$^+$) 107.0371, found 107.0372.

Furan-2-carbaldehyde (Table 1, Entry 13)[1]



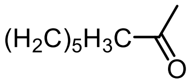
^{1}H NMR (500 MHz, $CDCl_3$): δ = 6.54-6.56 (1H, m), 7.21 (1H, t, J = 1.8 Hz), 7.64 (1H, d, J = 7.2 Hz), 9.59 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$): δ = 112.6, 121.3, 148.2, 153.0, 177.9; HRMS (EI) *m/z* calcd for $C_5H_4O_2$ (M$^+$) 96.0211, found 96.0211.

Hexan-2-one (Table 1, Entry 14)[2]



^{1}H NMR (400 MHz, $CDCl_3$): δ = 2.43 (2H, t, J = 7.2 Hz,), 2.14 (3H, s), 1.601-1.53 (2H, m), 1.36-1.30 (2H, m), 0.92 (3H, t, J = 7.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 43.4, 29.7, 25.9, 22.2, 13.7; HRMS (EI) *m/z* calcd for $C_6H_{12}O$ (M$^+$) 100.0888, found 100.0887.

Octan-2-one (Table 1, Entry 15)[2]



^{1}H NMR (400 MHz, $CDCl_3$): δ=2.43 (2H, t, J = 7.2 Hz), 2.14 (3H, s), 1.61-1.52 (2H, m), 1.34-1.27 (6H, m), 0.87 (3H, t, J = 6.8 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ = 209.3, 43.7, 31.5, 29.7, 28.8, 23.8, 22.4, 13.9; HRMS (EI) *m/z* calcd for $C_8H_{16}O$ (M$^+$) 128.1201, found 128.1201.

References

1. G. Zhang, X. Han, Y. Luan, Y. Wang, X. Wen and C. Ding, *Chem. Commun.*, 2013, **49**, 7908-7910.
2. C. Bai, A. Li, X. Yao, H. Liu and Y. Li, *Green Chem.*, 2016, **18**, 1061-1069.