Electronic Supplementary Information

Highly Efficient Hydrogenation Reduction of Aromatic Nitro Compounds using MOF Derivative Co-N/C Catalyst

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Content

Table S1. The preparation method for the reported catalyst and the reaction condition for the hydrogenation reduction of nitrobenzoamide derivatives

Examples for the similar Co@C catalysts	Preparation method for the catalyst	The reaction time and H_2 pressure for the hydrogenation reduction of nitrobenzoamide derivatives	Conversation
Co^0-Co_3O_4/N-Doped Carbon Nanotubes Hybrids[22]	A solid mixture of GAH, melamine, and $Co(NO_3)_2 \cdot 6H_2O$ was grinded into powder; Then, the powder was subjected to pyrolysis.	3-15 h, 3 MPa H_2	99%
Co catalyst[23]	The mixture of polysilazane HTT, bisamidinatocobalt(II) complex and dicumylperoxid was crossed linked at 110 ℃ for 24 h; Then, the solid powder was subjected to pyrolysis.	15 h, 5 MPa H_2	82-99%
Co–Co_3O_4/NGr@C-catalyst[24]	A mixture of $Co(OAc)_2 \cdot 4H_2O$ and Phen was stirred at 60 ℃ for 2 h. Next, Vulcan® XC 72R carbon was added and the suspension was stirred for 18 h. Then, the solid power was subjected to pyrolysis.	13-20 h, 2 MPa H_2	85-99%
Co-Co_3O_4@carbon-700 catalyst[25]	A mixture of cobalt (II) acetate tetrahydrate and chitosan was refluxed at 70 ℃ for 20 h. Then, the solid power was subjected to pyrolysis.	6 h, 4 MPa H_2	99%
Co@C NPs[21]	The purple solution of $Co(NO_3)_2$, Na_2EDTA, and NaOH in H_2O was transferred into stainless steel autoclave, followed by hydrothermal processing at 200 ℃ for 24 h. Then Co@C NPs was prepared by reduction of Co-EDTA in H_2 (50 mL/min) at 450 ℃ for 2 h.	6-15 h, 1 MPa H_2	93-99%
Co@NC catalyst[26]	The carbon nitride g-C_3N_4 was prepared by heating the melamine at 550 ℃ for 8 h; The cobalt nitrate hexahydrate, triethylene diamine and g-C_3N_4 were mixture in deionized water； Then, the solid power was subjected to pyrolysis.	3 h, 1 MPa H_2	97%-99%
Our prepared Co-N/C-800 catalysts	ZIF-67 powder was prepared by the reaction of $Co(NO_3)_2 \cdot 6H_2O$ and methylimizale in deionized water for 8 h at normal temperature. Then, the solid power was subjected to	4-8 h, 1.5 MPa H_2	97-99%

	pyrolysis.		

Table S2. Elemental analysis of Co-N/C-800 reused of 10 runs.

entry	Co[a] (wt%)	C[b] (wt%)	H[b] (wt%)	N[b] (wt%)
Fresh	23.9	56.9	1.1	3.1
Reused	20.4	58.8	1.0	2.7

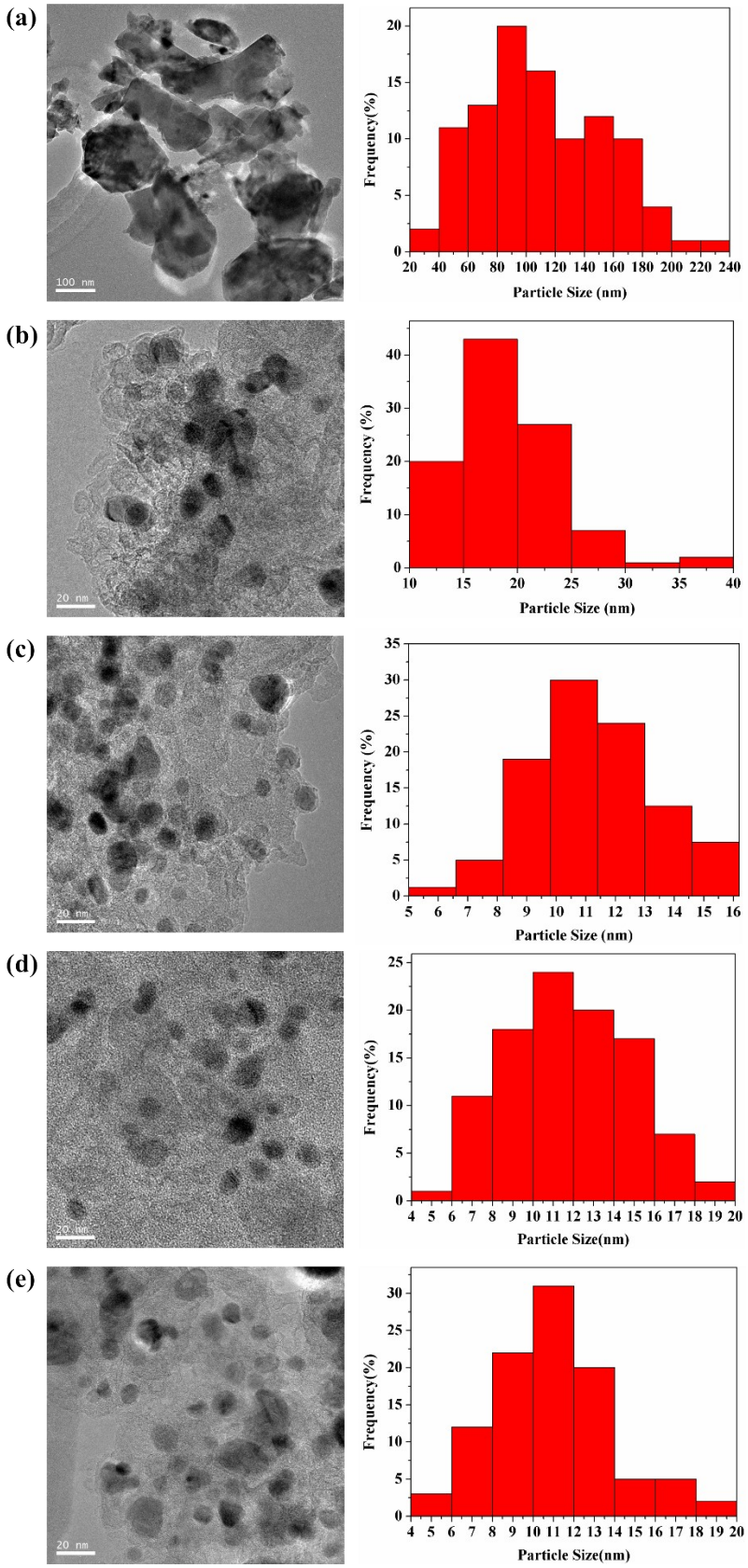


Figure S1. HR-TEM images (Left) and Particle size distribution statistics (right) of the as-prepared (a) Co-N/C-800-1, (b) Co-N/C-800-2, (c) Co-N/C-800, (d) Co-N/C-800-10, (e) Co-N/C-800-45.

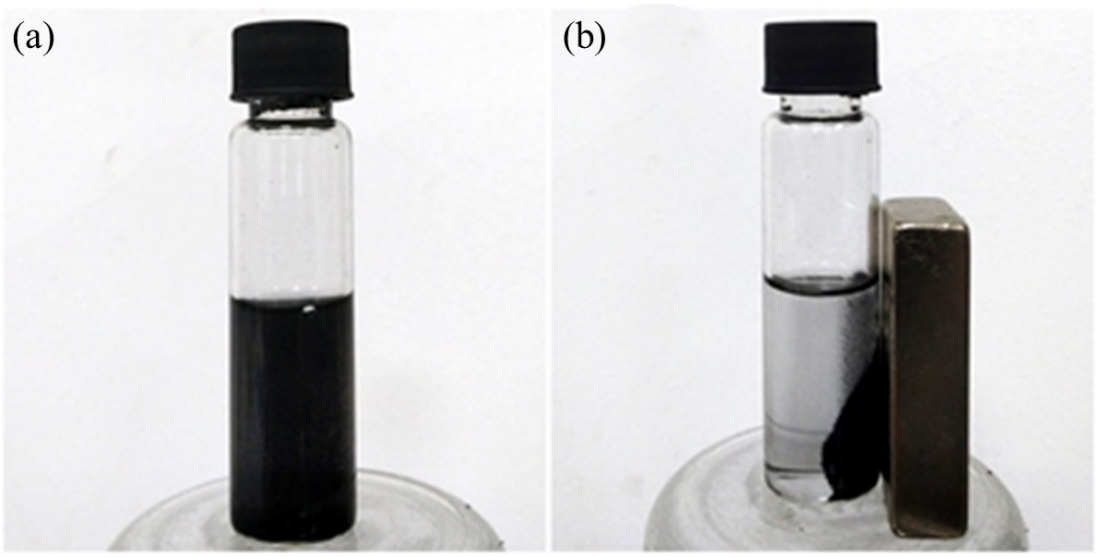


Figure S2. Collection of Co-N/C-800 catalyst

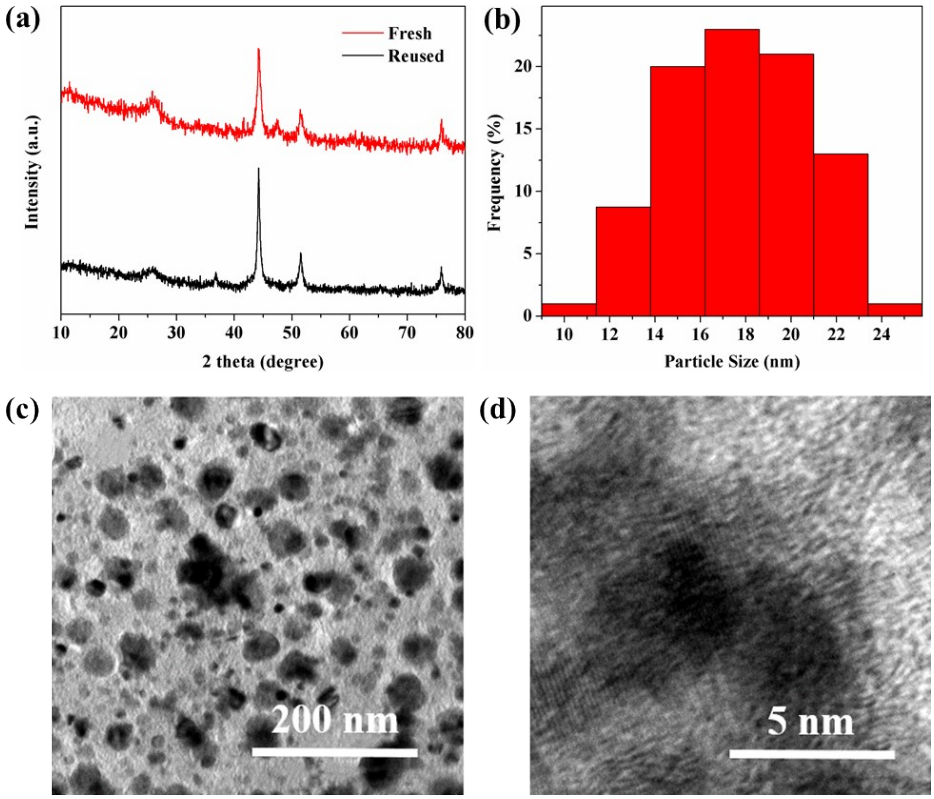
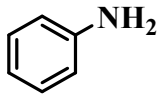


Figure S3 (a) XRD spectra of the reused Co-N/C-800 catalyst; (b) Particle size distribution statistics of deactivation Co-N/C-800 catalyst; TEM images of partial deactivation Co-N/C-800 catalyst (c) at 200 nm, (d) at 5 nm.

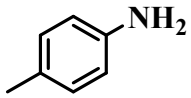
Characterization of the corresponding aromatic amines products for the aromatic nitro compounds in Table 4.



E1

Aniline

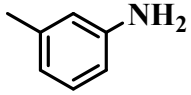
^{1}H NMR (500 MHz, DMSO-d6) δ 7.07 – 6.97 (m, 2H), 6.61 – 6.54 (m, 2H), 6.54 – 6.47 (m, 1H), 4.99 (s, 2H).



E2

p-Touidine

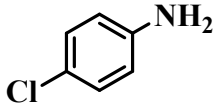
^{1}H NMR (500 MHz, DMSO-d6) δ 6.82 (d, J = 8.0 Hz, 2H), 6.49 – 6.44 (m, 2H), 4.77 (s, 2H), 2.12 (s, 3H).



E3

m-Toluidine

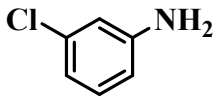
^{1}H NMR (500 MHz, DMSO-d6) δ 6.90 (t, J = 7.6 Hz, 1H), 6.42 – 6.35 (m, 2H), 6.33 (d, J = 7.3 Hz, 1H), 4.91 (s, 2H), 2.16 (s, 3H).



E4

4-Chloroaniline

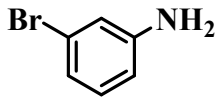
^{1}H NMR (500 MHz, DMSO) δ 7.05 – 6.98 (m, 2H), 6.60 – 6.52 (m, 2H), 5.22 (s, 2H).



E5

m-Chloroaniline

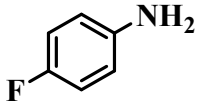
^{1}H NMR (500 MHz, DMSO-d6) δ 7.00 (dd, J = 10.4, 5.6 Hz, 1H), 6.58 (t, J = 1.5 Hz, 1H), 6.52 – 6.46 (m, 2H), 5.38 (s, 2H).



E6

3-Bromoaniline

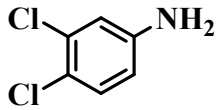
^{1}H NMR (500 MHz, DMSO-d6) δ 6.94 (t, J = 8.0 Hz, 1H), 6.74 (t, J = 1.8 Hz, 1H), 6.64 – 6.59 (m, 1H), 6.54 (dd, J = 8.1, 1.9 Hz, 1H), 5.37 (s, 2H).



E7

4-Fluoroaniline

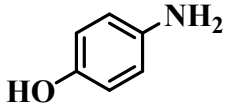
^{1}H NMR (500 MHz, DMSO-d6) δ 6.88 – 6.80 (m, 2H), 6.59 – 6.52 (m, 2H), 4.92 (s, 2H).



E8

3,4-Dichloroaniline

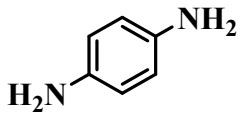
^{1}H NMR (500 MHz, DMSO-d6) δ 7.18 (dd, J = 8.7, 4.6 Hz, 1H), 6.77 – 6.71 (m, 1H), 6.56 – 6.48 (m, 1H), 5.54 (s, 2H).



E9

p-Aminophenol

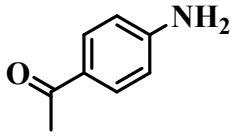
^{1}H NMR (500 MHz, DMSO-d6) δ 8.33 (s, 1H), 6.49 – 6.45 (m, 2H), 6.43 – 6.38 (m, 2H), 4.37 (s, 2H).



E10

p-Phenylenediamine

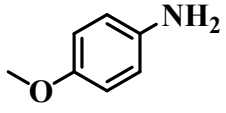
^{1}H NMR (500 MHz, DMSO-d6) δ 6.36 (s, 4H), 4.18 (s, 4H).



E11

4'-Aminoacetophenone

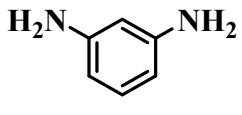
^{1}H NMR (500 MHz, DMSO-d6) δ 7.70 – 7.64 (m, 2H), 6.61 – 6.50 (m, 2H), 6.03 (s, 2H), 2.38 (s, 3H).



E12

p-Anisidine

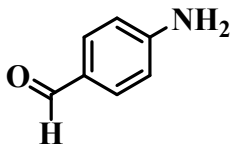
^{1}H NMR (500 MHz, DMSO-d6) δ 6.69 – 6.61 (m, 2H), 6.56 – 6.48 (m, 2H), 4.58 (s, 2H), 3.62 (s, 3H).



E13

m-Phenylenediamine

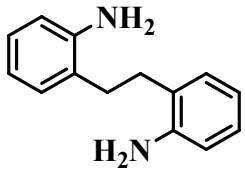
^{1}H NMR (500 MHz, DMSO-d6) δ 6.65 (t, J = 7.8 Hz, 1H), 5.81 (t, J = 2.0 Hz, 1H), 5.79 (d, J = 2.1 Hz, 1H), 5.77 (d, J = 2.1 Hz, 1H), 4.64 (s, 4H).



E14

4-Aminobenzaldehyde

^{1}H NMR (500 MHz, DMSO-d6) δ 9.57 (s, 1H), 7.60 – 7.46 (m, 2H), 6.72 – 6.54 (m, 2H), 6.29 (s, 2H).



E15

2, 2'-Ethylenedianiline

^{1}H NMR (500 MHz, DMSO-d6) δ 6.99 (d, J = 7.2 Hz, 2H), 6.89 (t, J = 7.3 Hz, 2H), 6.63 (d, J = 7.7 Hz, 2H), 6.50 (t, J = 7.1 Hz, 2H), 4.86 (s, J = 35.8 Hz, 4H), 2.67 (d, J = 14.7 Hz, 4H).