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Supplementary Materials for

High performance of a cobalt–nitrogen complex for the reduction and reductive coupling of nitro compounds into amines and their derivatives

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- table S1. The content of Co and N in the as-prepared catalysts.
- table S2. Recycling results for the Co–N_x/C-800-AT catalyst.

General

All of the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemicals were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). LUDOX® HS-40 colloidal silica (40 wt % in H_2O) was purchased from Sigma-Aldrich (St Louis, USA). Cobalt phthalocyanine (Fig. 1) was purchased from Tuopu Chemicals Co. Ltd. (Wuhan, China).

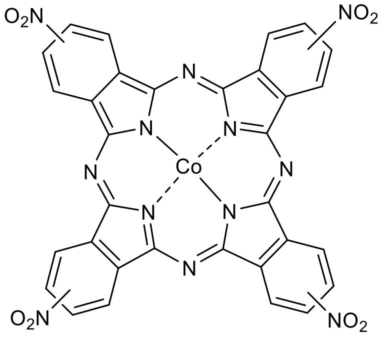


fig. S1. Structure of cobalt phthalocyanine.

Catalyst characterization

Transmission electron microscope (TEM) was performed on an FEI Tecnai G^2-20 instrument. X-ray powder diffraction (XRD) measurements were conducted on a Bruker advanced D8 powder diffractometer (Cu Kα), operating with 2θ range of 10–80° at a scanning rate of 0.016 °/s. X-ray photoelectron spectroscopy (XPS) experiments were carried out on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV. The cobalt content was determined by inductively coupled plasma atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation). Raman spectra were measured on a confocal laser micro-Raman spectrometer (Thermo Fischer DXR) equipped with a diode laser of excitation of 532 nm (laser serial number: AJC1200566). Spectra were obtained at a laser output power of 1 mW (532 nm), and a 0.2 s acquisition time with 900 lines/mm grating (Grating serial number: AJG1200531). UV–Visible absorption spectra were recorded on a Shimadzu UV-2550 spectrophotometer (Kyoto, Japan). Thermogravimetric (TG) analysis was performed with a thermogravimetric analyzer (NETZSCH TG209) at a heating rate of 10 $K \cdot min^{-1}$ and a nitrogen flow of 20 $mL \cdot min^{-1}$. Nitrogen physisorption measurements were conducted at 77 K on a quantachrome Autosorb-1-C-MS instrument.

Analytic methods

Analysis of the products was performed by a gas chromatography (GC) on a agilent 7890A instrument with a crosslinked capillary HP-5 column (30 m×0.32 mm×0.4 mm) equipped with a flame ionization detector. Operating conditions were as follows: The flow rate of the N_2 carrier gas was 40 $mL\cdot min^{-1}$, the injection port temperature was 300 °C. The GC oven temperature program was as follows: 50 °C ramp 10 °C/min to 280 °C and the detector temperature was 300 °C. The peaks were identified by comparison of the retention time of the unknown compounds with those of standard compounds and quantified based on the internal standard method using 4-chlorotoluene as the internal standard.

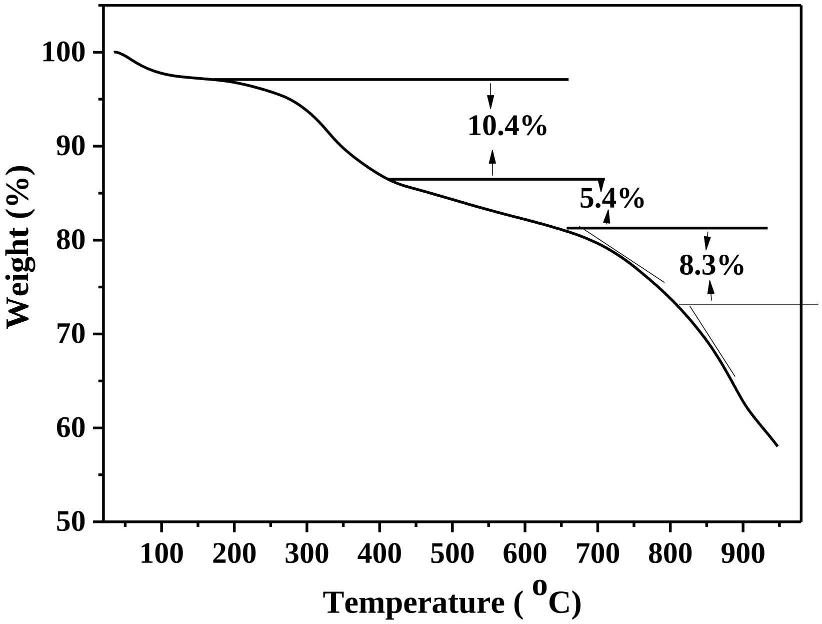


fig. S2. TGA of the cobalt phthalocyanine/silica composite under a N_2 atmosphere.

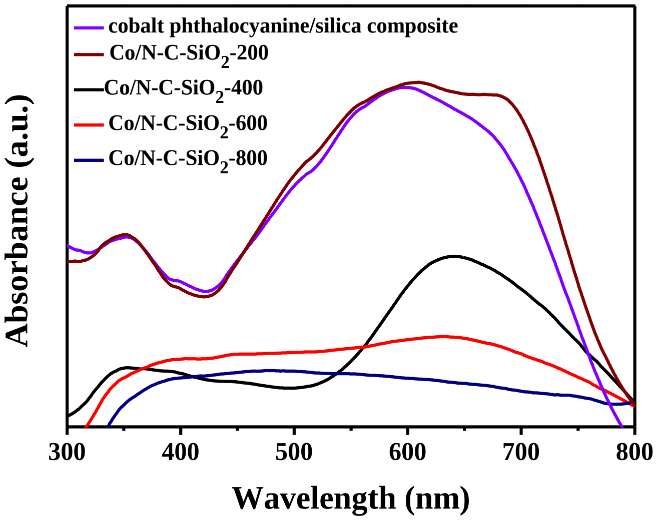


fig. S3. Solid UV-Vis spectra of the samples after the pyrolysis of the cobalt phthalocyanine/silica composite at different temperatures.

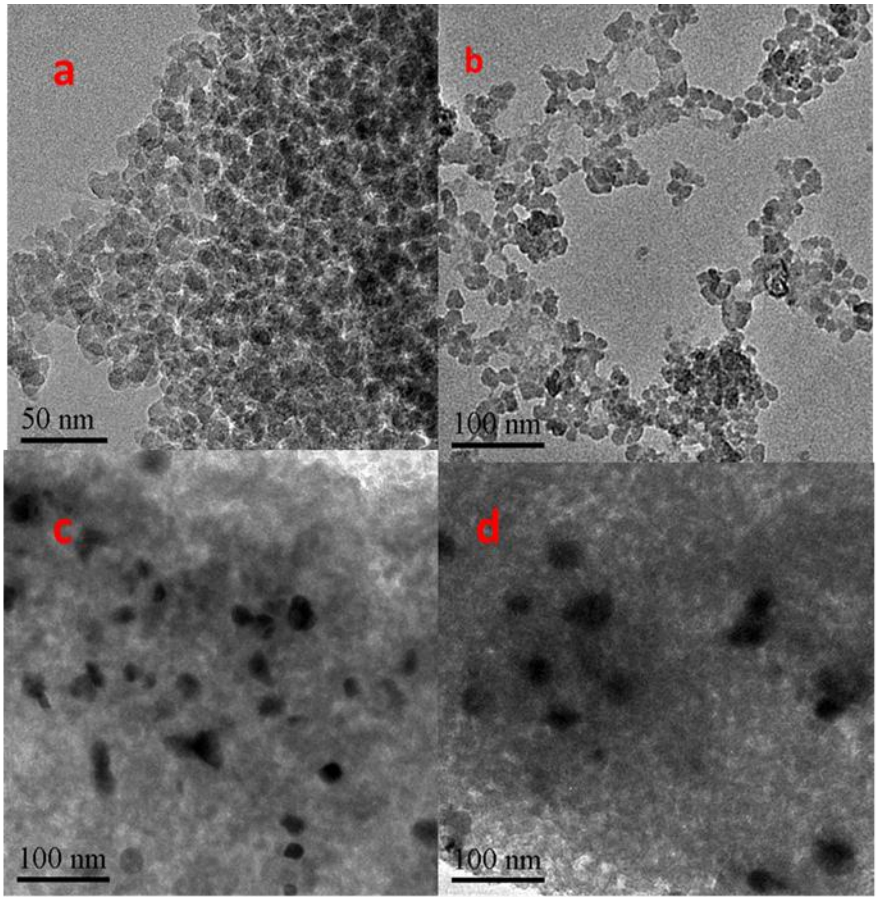
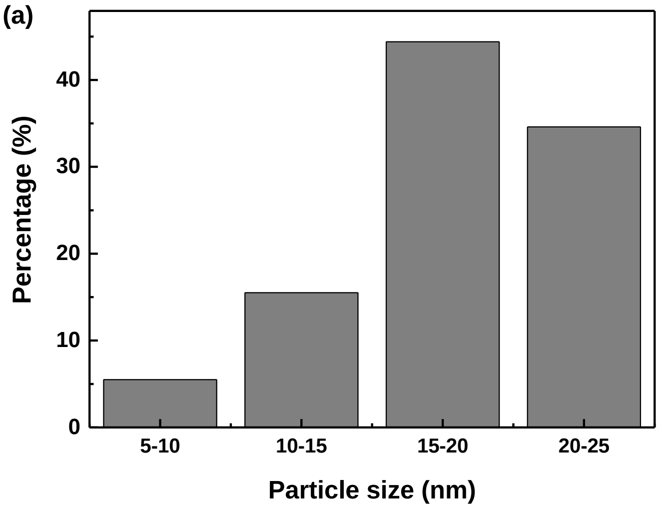


fig. S4. TEM images of the Co/N-C-SiO$_2$-X samples. (**a**) Co/N-C-SiO$_2$-400; (**b**) Co/N-C-SiO$_2$-600; (**c**) Co/N-C-SiO$_2$-800; (**d**) Co/N-C-SiO$_2$-900.



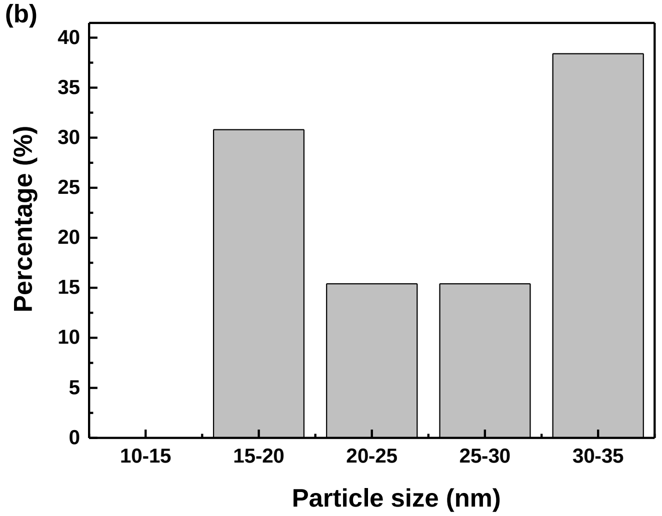


fig. S5. Particle size distribution of Co nanoparticles. (**a**) Co/N-C-SiO_2-800; (**b**) Co/N-C-SiO_2-900.

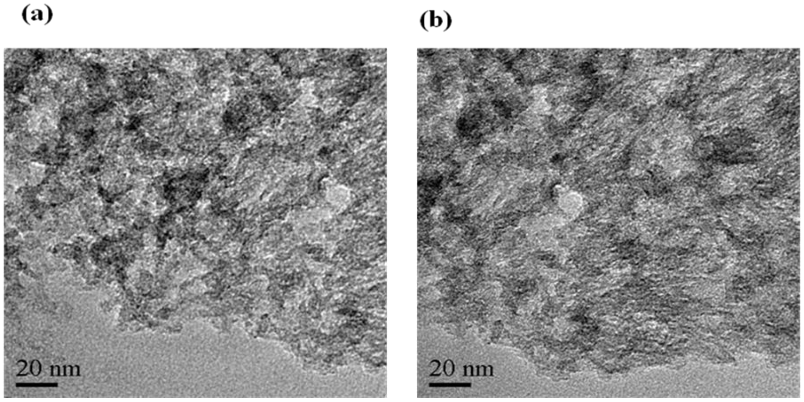


fig. S6. Higher-resolution TEM images of the Co/N-C-AT-*X* samples. (**a**) Co-N_x/C-800-AT; (**b**) Co-N_x/C-900-AT.

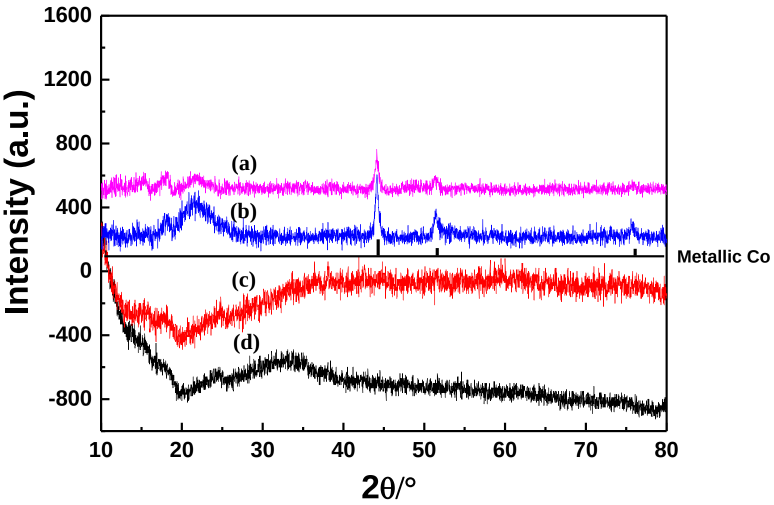


fig. S7. XRD patterns of the samples. (**a**) Co/N-C-SiO_2-900; (**b**) Co/N-C-SiO_2-800; (**c**) Co/N-C-SiO_2-600; (**d**) Co/N-C-SiO_2-400.

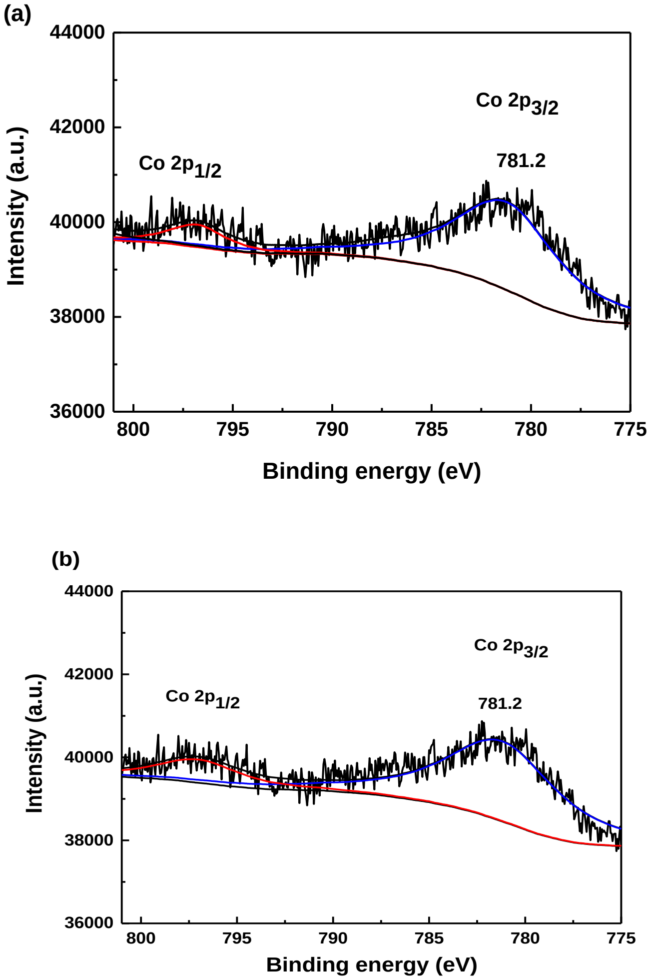


fig. S8. Higher-resolution Co 2p XPS spectra. (**a**) Co-N_x/C-800-AT; (**b**) Co-N_x/C-900-AT.

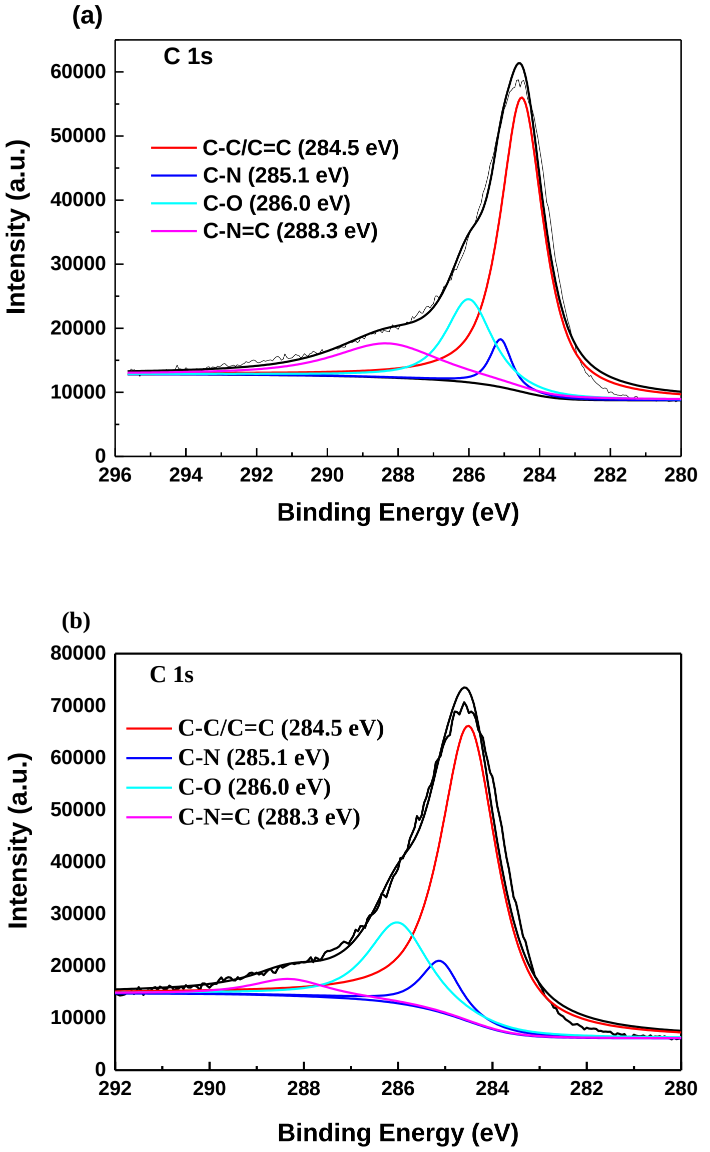


fig. S9. Higher-resolution C 1s XPS spectra. (**a**) Co/N-C-800-BT; (**b**) Co-N_x/C-800-AT.

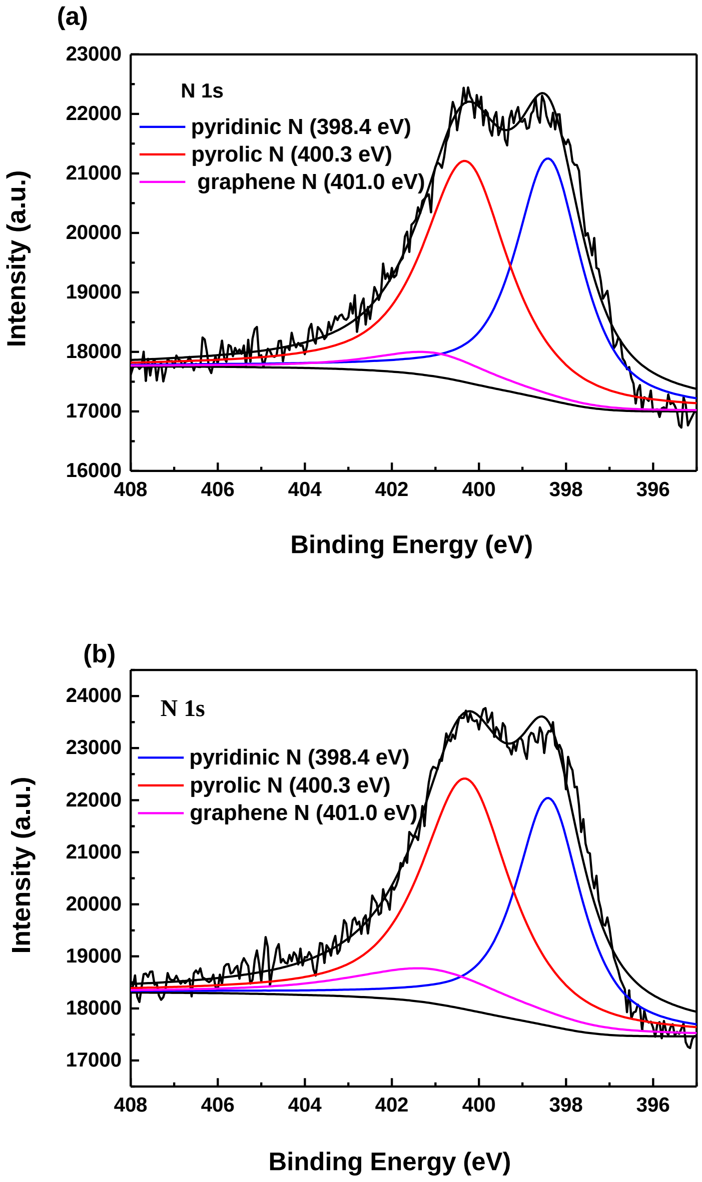


fig. S10. Higher-resolution N 1s XPS spectra. (**a**) Co/N-C-800-BT; (**b**) Co-N_x/C-800-AT.

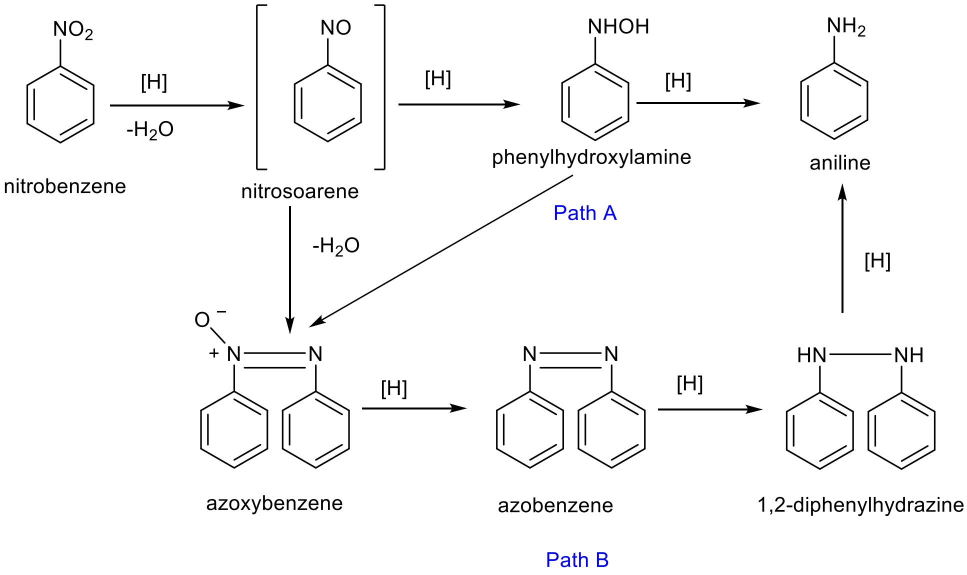


fig. S11. Reaction pathways of the reduction of nitrobenzene.

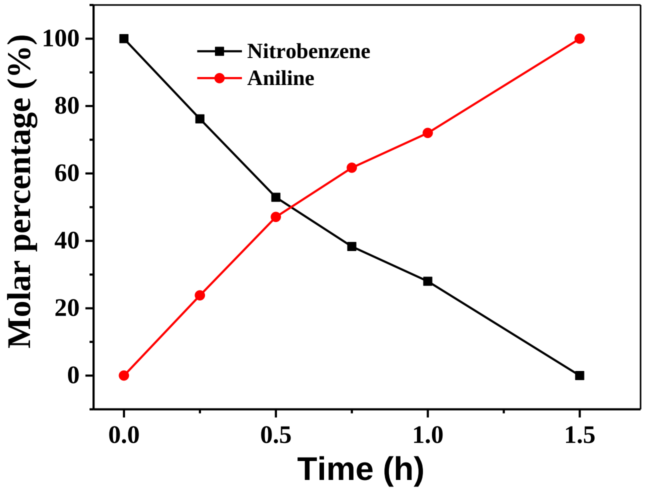


fig. S12. Time course of the molar percentage of each compound during the hydrogenation of the nitrobenzene process. Reaction conditions: Nitrobenzene (1 mmol), Co-N_x/C-800-AT catalyst (40 mg), H_2O (15 mL), H_2 pressure (3.5 bar), 110 °C.

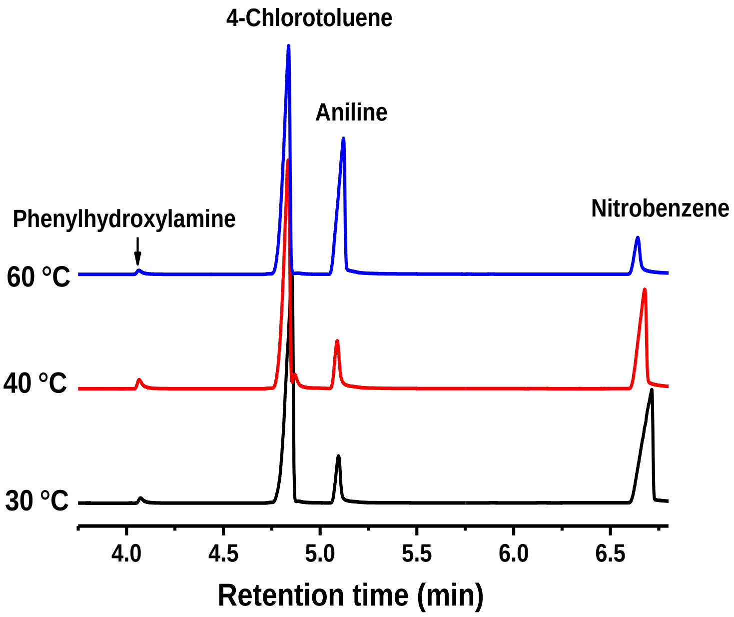


fig. S13. GC analysis of the hydrogenation of nitrobenzene over the Co/N*x*-C-800-AT catalyst at low reaction temperatures. Reaction conditions: Nitrobenzene (0.5 mmol), 4-Chlorotoluene (0.5mmol) as internal standard, Co-N_x/C-800-AT catalyst (20 mg), acetonitrile (15 mL), H_2 pressure (50 bar), 1 h.

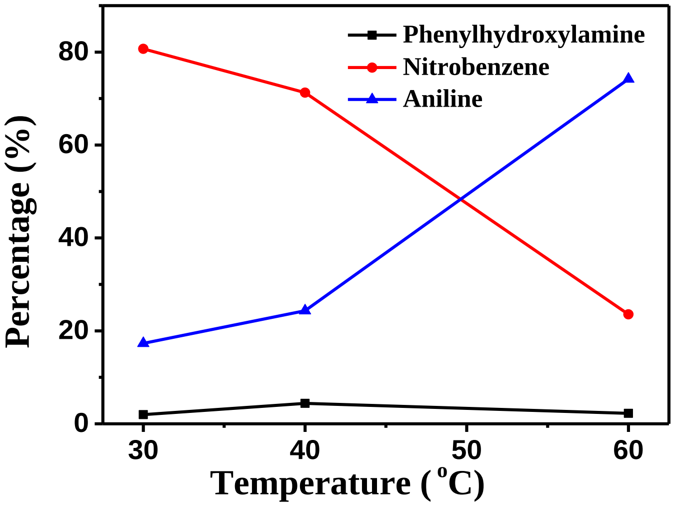


fig. S14. Molar percentage of the samples at three different temperatures. Reaction conditions: Nitrobenzene (0.5 mmol), 4-chlorotoluene (0.5mmol) as internal standard, Co-N_x/ C-800-AT catalyst (20 mg), acetonitrile (15 mL), H_2 pressure (50 bar), 1 h.

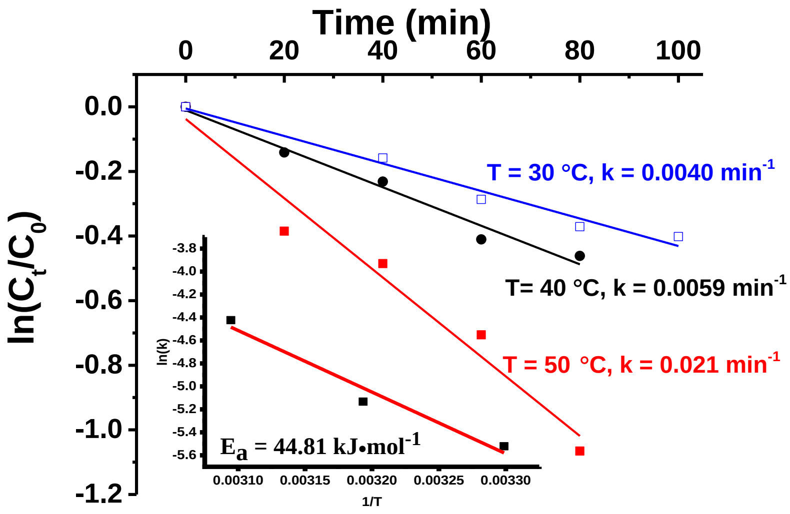


fig. S15. Plot of ln(C_t/C_0) versus time for the reduction of nitrobenzene over the Co–N_x/ C-800-AT catalyst at different temperatures. The inset shows the corresponding Arrhenius plot. Reaction conditions: nitrobenzene (1 mmol), Co-N_x/C-800-AT catalyst (40 mg), H_2O (15 mL), H_2 pressure (50 bar).

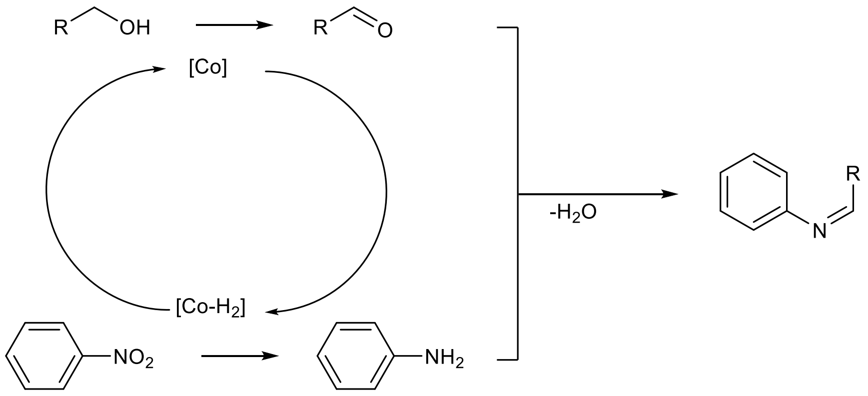
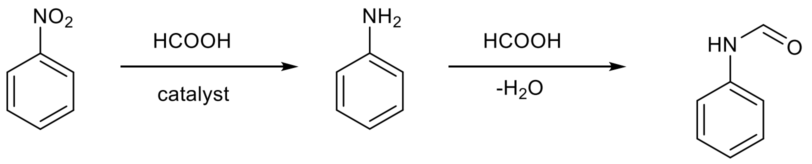


fig. S16. Tandem reaction of nitrobenzene with primary amines to produce imines.



Catalyst: Co-Nx/C-800-AT

fig. S17. Reductive N-formylation of nitrobenzene to *N*-phenylformamide by formic acid.

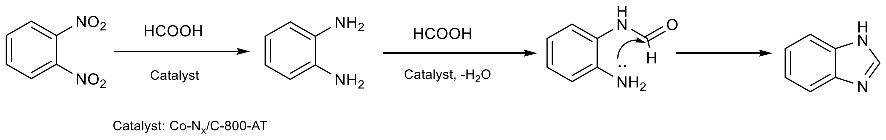


fig. S18. Synthesis of benzimidazole with *o*-dinitrobenzene and formic acid.

table S1. The content of Co and N in the as-prepared catalysts.

Catalysts	Co wt% by ICP	N at % by XPS
Co-N$_x$/C-600-AT	0.36	14.34
Co-N$_x$/C-800-AT	0.25	8.16
Co-N$_x$/C-900-AT	0.18	5.38
Co/N-C-800-BT	12.3	6.28

table S2. Recycling results for the Co–N$_x$/C-800-AT catalyst.

Run No.	Conversion (%)	Selectivity (%)
1	100	>99
2	100	>99
3	100	>99
4	100	>99
5	100	>99
6	100	>99
7	100	>99
8	100	>99

Reaction conditions: Nitrobenzene (1 mmol), Co-N$_x$/C-800-AT (40 mg), 3.5 bar H_2, H_2O (15 mL), 110 °C, 1.5 h.