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Electronic Supplementary Information

A MOF-Derived Co-CoO@N-doped Porous Carbon for Efficient Tandem Catalysis: Dehydrogenation of Ammonia Borane and Hydrogenation of Nitro Compounds

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S1. Materials and Instrumentation.

All chemicals were from commercial and used without further purification: cobaltous nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, 99.99%, Energy Chemical), 2-methylimidazole (98%, Macklin Inc.), ammonia borane (90%, Aldrich), methanol (≥99.5%, Sinopharm Chemical Reagent Co., Ltd.), nitrobenzene (≥98.5%, Sinopharm Chemical Reagent Co., Ltd.), *p*-fluoronitrobenzene (99%, Energy Chemical), *p*-chloronitrobenzene (≥99.5%, Aladdin), *p*-bromonitrobenzene (98%, Energy Chemical), *p*-nitrotoluene (cp, Sinopharm Chemical Reagent Co., Ltd.), *m*-nitrotoluene (98%, Aladdin) *o*-nitrotoluene (98%, Aladdin), *p*-nitrophenol (99%, Energy Chemical), *p*-nitrobenzyl alcohol (99%, Energy Chemical), *p*-nitroanisole (98%, Aladdin), *p*-nitroaniline (≥99%, Aladdin), *m*-nitroaniline (98%, Aladdin), dimethyl nitroterephthalate (98.0%, Energy Chemical), 1,3-dinitrobenzene (98%, Aladdin), *p*-nitrobenzaldehyde (98.0%, Energy Chemical), *p*-nitrobenzonitrile (98%, Energy Chemical), *m*-nitroacetophenone (98%, Energy Chemical), nitromethane (AR, Aladdin), nitroethane (AR, Aladdin).

Deionized water with the specific resistance of 18.25 MΩ·cm was acquired by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction patterns (XRD) were carried out on a Japan Rigaku SmartLab^{TM} rotation anode X-ray diffractometer equipped or Holland X'Pert PRO fixed anode X-ray diffractometer equipped with graphite monochromatized Cu Kα radiation (λ = 1.54 Å). Raman spectra were recorded on a Renishaw System 2000 spectrometer by using Ar^+ for excitation (λ= 514.5 nm). Field-emission scanning electron microscopy (FE-SEM) was carried out with a field emission scanning electron microanalyzer (Zeiss Supra 40 scanning electron microscope at an acceleration voltage of 5 kV). The transmission electron microscopy (TEM) and high-resolution TEM observation was acquired on JEOL-2011 with an electron acceleration energy of 200 kV. The selected area electron diffraction (SAED) was conducted on a JEOL-2100F with an electron acceleration energy of 200 kV. The content of Co in the catalysts was determined by an Optima 7300 DV inductively coupled plasma atomic emission spectrometer (ICP-AES). The X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250 high-performance electron spectrometer using monochromatized Al Kα (hν =1486.7 eV) as the excitation source. The conversion, purity and relative yields of the final products were determined by using a Shimadzu gas chromatograph (GC-2010 Plus with a 0.25 mm × 30 m Rtx®-5 capillary column) with an FID detector and high purity nitrogen as the carrier gas. The nitrogen sorption isotherms were measured by using an automatic volumetric adsorption equipment (Micrometritics ASAP 2020). Prior to nitrogen adsorption/desorption measurements, the samples were dried overnight at 150 ^{o}C (ZIF-67) or 120 ^{o}C (Co-based catalysts).

S2. Experimental Section

2.1 Preparation of catalysts

Synthesis of ZIF-67: Cobalt nitrate hexahydrate (0.45 g) was dissolved in 3 mL of deionized water, and 2-methylimidazole (Hmim, 5.50 g) was dissolved in 20 mL of deionized water. The above two solutions were mixed together and stirred for 6 h at room temperature. The resulting purple precipitates were harvested by centrifuging, washing with water and methanol, and finally being dried in vacuum at 50 ^{o}C overnight. Prior to use, ZIF-67 powder was activated at 150 ^{o}C for 24 h.

Preparation of Co-CoO/N-doped porous carbon by pyrolysis of ZIF-67: A 500 mg of activated ZIF-67 sample was placed into a porcelain boat, which was charged into the middle of a quartz tube in a furnace in a nitrogen gas atmosphere with a continuous nitrogen flow of ~80 mL/min. The furnace was heated from room temperature to the targeted temperature (500 ^{o}C~700 ^{o}C) with a programmed heating rate of 5 ^{o}C/min. After the pyrolysis under the targeted temperature for desired time, the sample was naturally cooled down to room temperature. The resultant samples were denoted as Co-T-t (T denotes as pyrolysis temperature and t represents pyrolysis time length).

Preparation of Co NPs supported on activated carbon by impregnation method: The activated carbon (AC, 200 mg) was placed into a porcelain crucible. Subsequently, a $Co(NO_3)_2$ aqueous solution (2.50 M, 500 μL) was added dropwise and stirred until the mixture became homogeneous. The resultant mash was dried at 80 ^{o}C for 12 h and then was treated in a 20% H_2/Ar (40 mL·min^{-1}) gas stream at 400

^{o}C for 12 h to afford Co/AC.

2.2 Catalytic Performance Evaluation

Catalytic dehydrogenation of ammonia borane over Co-500-3 h in water or water/methanol mixture: The Co-500-3 h (0.05 mmol, 20 mg) was dispersed into H_2O (10 mL) or a mixture of deionized water (6 mL) and methanol (4 mL) in a two-necked round-bottomed flask, which was placed in a constant temperature bath maintained at 25 ^{o}C. Then, a burette filled with water was connected to the reaction flask to measure the volume of hydrogen generated. Next, the reaction started when NH_3BH_3 (0.6 mmol, 20 mg) was added into the flask. The reaction was completed when there was no more gas generated. For the control experiment with different solvents, the same amount of NH_3BH_3 (0.6 mmol) was added into the flask to initiate the reaction. For the recycling experiments, the same amount of NH_3BH_3 (20 mg) was added into the reaction system to start a new cycle.

Catalytic activity evaluation for the tandem reaction: Typically, nitro compound (0.2 mmol) was charged into a dried round bottom flask with methanol (4 mL) and deionized water (6 mL). Then the ZIF-67-derived catalyst (0.05 mmol) or Co/AC (0.05 mmol) was introduced with ultrasonication in order to disperse the catalyst. After ammonia borane (0.6 mmol) was added, the round bottom flask was sealed immediately and the mixture was violently stirred at room temperature. The conversion and selectivity were decided by GC-FID and GC-MS using *n*-dodecane as a standard. In the control experiments by using Co/AC as a catalyst, the total amount of cobalt remains consistent with that in ZIF-67-derived catalysts.

Experimental procedure for recyclability investigation: After the reduction of nitrobenzene, the catalyst (Co-500-3 h) was separated out by an external magnet. Then the recovered catalyst was obtained by washing with methanol for several times. After that, the catalyst was used for the second run of tandem reaction. This procedure was repeated for three times to examine the recyclability of Co-500-3 h by using GC-FID and GC-MS using *n*-dodecane as a standard.

Filtration test for the tandem reaction over Co-500-3 h: The tandem reaction was conducted over Co-500-3 h (0.05 mmol) in two dried round flasks with a mixture of nitrobenzene (0.2 mmol), ammonia borane (0.6 mmol), methanol (4 mL) and deionized water (6 mL) at the same time. The conversion of these two reactions at every time interval in the total 180 minutes was determined by GC-FID and GC-MS using *n*-dodecane as standard. After 30 minutes of reaction, the catalyst in one of the flasks was separated out from the reaction for comparison.

S3. Discussions on the reduction of nitrobenzene

A possible mechanism for the reduction of nitrobenzene catalyzed by Co-CoO@N-doped porous carbon can be proposed (see Scheme S1).[S1] The reduction of nitrobenzene to aniline, *via* nitrosobenzene and phenylhydroxylamine, is considered to be a favorable pathway. At first, two fast steps take place, in which nitrobenzene is reduced to nitrosobenzene, subsequently the hydrogenation of nitrosobenzene results in phenylhydroxylamine, *via* active hydrogen from NH_3BH_3 or its derived H_2. Finally, the rate-determining step occurs by the transformation from the intermediate to aniline. During the process, the Co-500-3 h catalyst featuring hierarchical pores would benefit the transportation of the substrate, intermediates and product.

References:

S1. R. K. Rai, A. Mahata, S. Mukhopadhyay, S. Gupta, P.-Z. Li, K. T. Nguyen, Y. Zhao, B. Pathak and S. K. Singh, *Inorg. Chem.*, 2014, **53**, 2904.

S4. Characterization Section

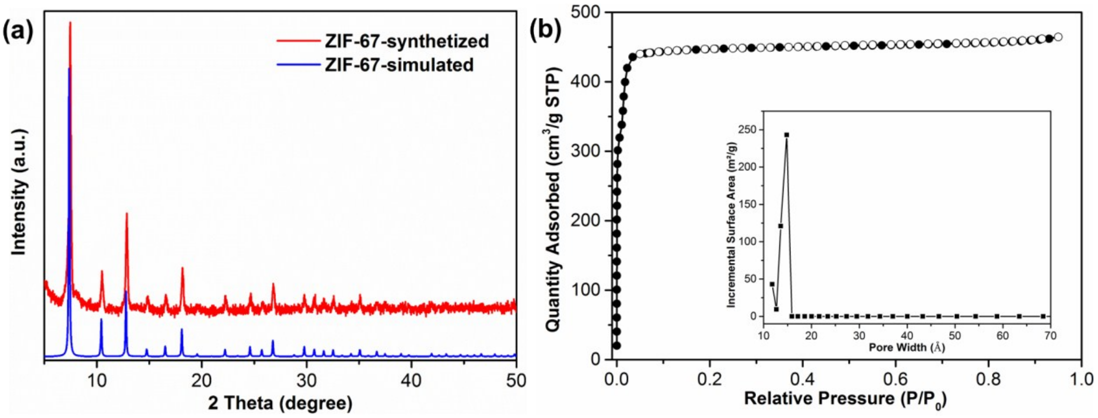


Fig. S1 (a) Powder XRD patterns of as-prepared and simulated ZIF-67. (b) Nitrogen adsorption and desorption isotherms for ZIF-67 at 77 K. Inset: pore size distribution based on the DFT model.

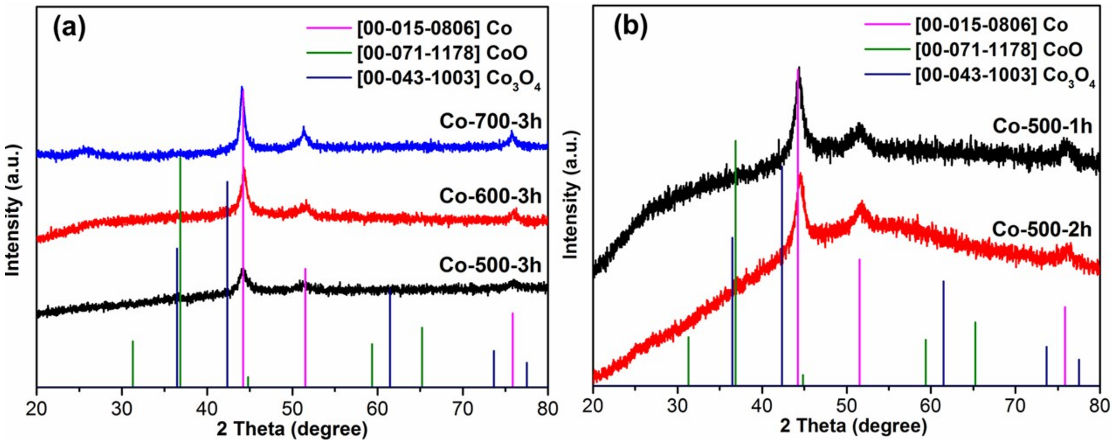


Fig. S2 Powder XRD patterns for the samples after pyrolysis of ZIF-67 in N_2 atmosphere (a) at different temperatures for 3 h and (b) at 500 °C for different time length. All powder XRD patterns show three sharp characteristic peaks for metallic β-Co at 2θ = 44.38° (111), 51.60° (200) and 75.68° (220) (associated with standard JCPDS card no. 00-015-0806), while no peak assignable to any cobalt oxide species.

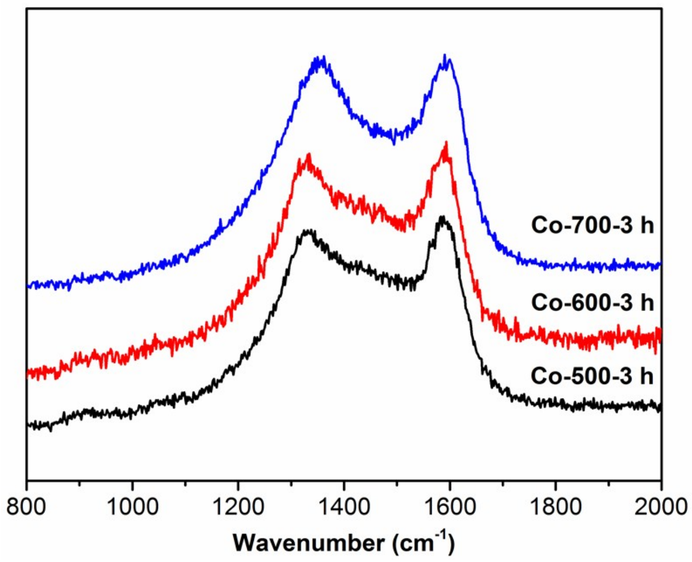


Fig. S3 Raman spectra of Co-500-3 h, Co-600-3 h and Co-700-3 h.

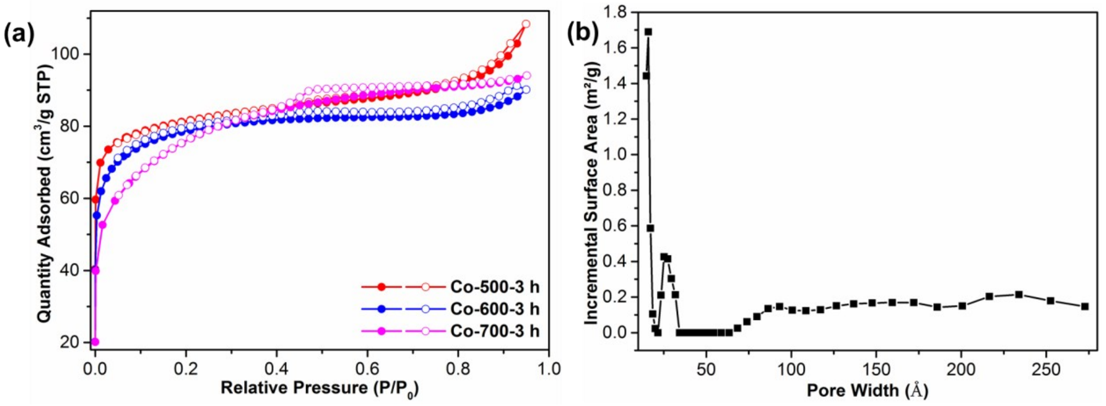


Fig. S4 (a) Nitrogen adsorption and desorption isotherms for Co-CoO/N-doped porous carbon nanocomposites at 77 K. (b) Pore size distribution analysis for Co-500-3 h (DFT method).

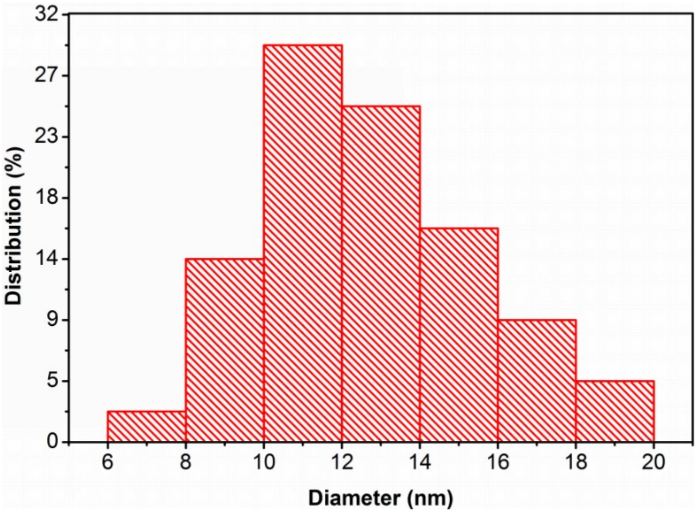


Fig. S5 Size distribution of Co NPs in Co-500-3 h, showing the average sizes of 6-20 nm.

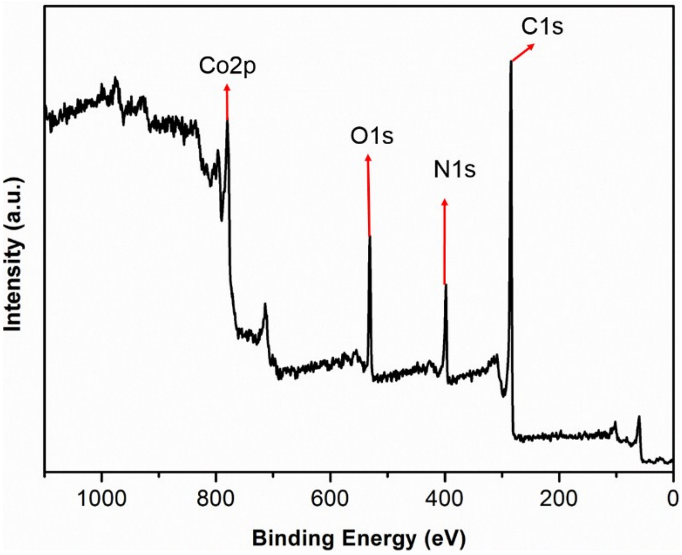


Fig. S6 XPS survey spectrum for Co-500-3 h.

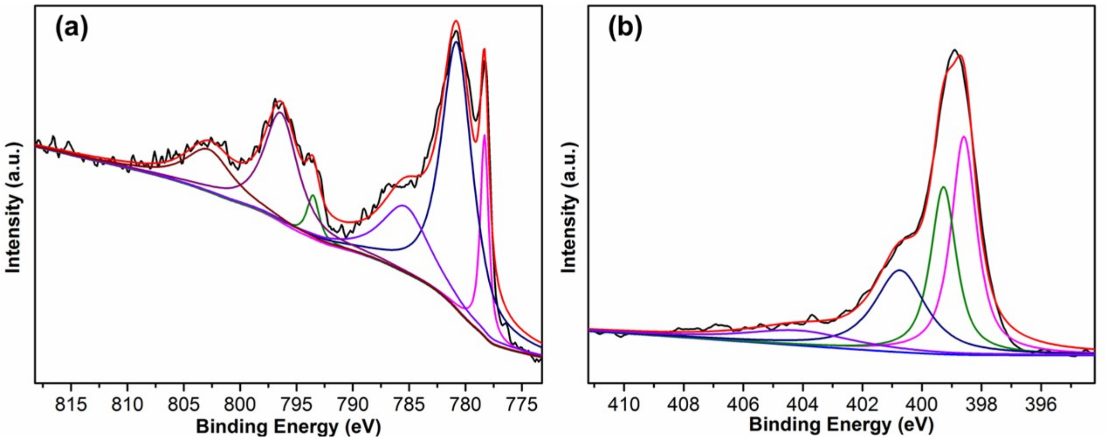


Fig. S7 High-resolution XPS survey spectra of (a) Co 2p and (b) N 1s for Co-500-3 h.

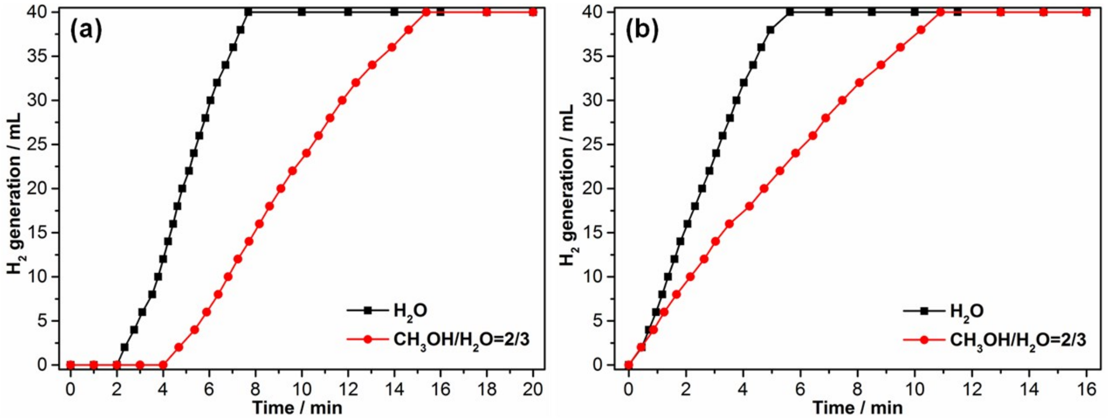


Fig. S8 Hydrogen generation *vs* time curves in the (a) 1st run and (b) 5th run for dehydrogenation of ammonia borane using Co-500-3 h catalyst. Reaction conditions: 20 mg catalyst, 20 mg NH_3BH_3, 10 mL H_2O or a mixture of 4 mL CH_3OH and 6 mL H_2O, room temperature. The induction time in the first run might be caused by the surface oxidation of Co species and that can be eliminated in the subsequent runs.

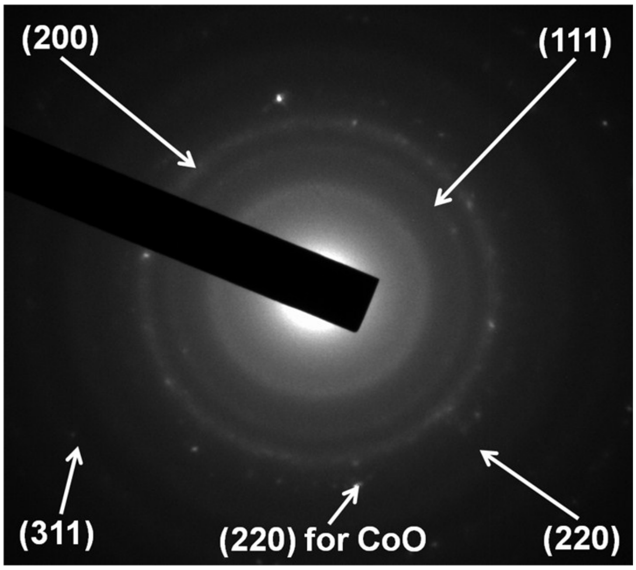


Fig. S9 The SAED pattern indexed to Co or CoO (if mentioned) for Co-500-3 h after catalysis.

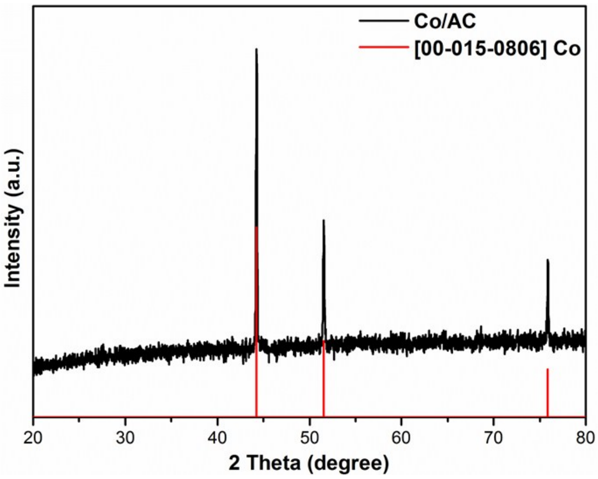
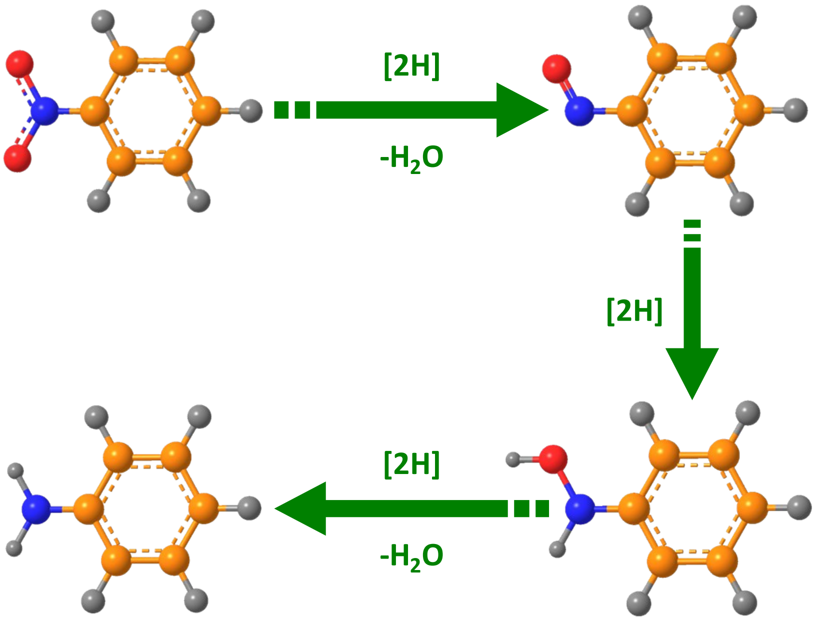


Fig. S10 The PXRD pattern of Co/AC shows three sharp peaks characteristic for metallic β-Co at $2\theta = 44.38°$ (111), 51.60° (200) and 75.68° (220) (associated with standard JCPDS card no. 00-015-0806).



Scheme S1. Proposed mechanism for the reduction of nitrobenzene to aniline using Co-500-3 h catalyst, in which nitrosobenzene and phenylhydroxylamine are reaction intermediates.

Table S1. ICP-AES analysis results for the Co contents in Co-CoO/N-doped carbon.

Co-CoO/N-doped carbon	The content of Co (%)
Co-500-3 h	21.6
Co-600-3 h	29.0
Co-700-3 h	32.7