Supporting Information

Transfer Hydrogenation of Unsaturated Bonds in the Absence of Base Additives Catalyzed by a Cobalt-Based Heterogeneous Catalyst

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1. General

All chemicals were purchased from commercial sources and used without further treatments. All solvents were analytical grade and distilled prior to use.

2. Experimental

2.1 *Synthesis of Co-MOF ($[Co(bdc)(ted)_{0.5}]\cdot 2\ DMF\cdot 0.2\ H_2O$)*

The Co-MOF was synthesized according to the literature reports.[1-3] Typically, a mixture of $Co(NO)_3.6H_2O$ (0.9 mmol), H_2bdc (1,4-benzenedicarboxylic acid, 0.72 mmol), ted (triethylenediamine, 0.58 mmol), and 15 mL DMF were transferred to a Teflon-lined autoclave, which was heated at 130 °C for 2 days. The resulting powder was washed by DMF and methanol, and then dried under vacuum at 150 °C. The powder X-ray diffraction (PXRD) patterns of as-synthesized Co-MOF (Fig. S1) matched well with the published XRD patterns, confirming the formation of Co-MOF.[1-3]

2.2 *Synthesis of Co@C-N-X-T*

The thermolysis temperatures were selected on the basis of the thermo stability of Co-MOF (Fig. S2). The thermolysis of Co-MOF was carried out under argon atmosphere. The sample was heated at a heating rate of 1 °C/min from room temperature to 200 °C and kept at this temperature for 2 h. Then, the temperature was increased to the target temperature (i.e., 500°C, 600°C, 700°C, 800°C, or 900°C). After calcined for 8 h or 15 h, the sample was cooled to room temperature. The obtained black powder was denoted as Co@C-N-X-T (where X and T represent the thermolysis temperature and time, respectively). The samples were heated at 200 °C in H_2 for 2 h prior to use as catalyst owing to the easy oxidation character of metallic cobalt.

2.3 *Characterization*

Powder X-ray diffraction patterns of the Co-MOF and Co@C-N-X-T were recorded on a Rigaku diffractometer (D/MAX-IIIA, 3 kW) using Cu Kα radiation (40 kV, 30 mA, 0.1543 nm). BET surface area and pore sizes were obtained from N_2 adsorption/desorption isotherms at 77 K with a Micromeritics ASAP 2020M instrument. Prior to the measurements, the samples were degassed at 150 °C for 12 h. The Co contents of the Co@C-N-X-T samples were measured by atomic absorption spectroscopy (AAS) with a Hitachi Z-2300 instrument. The stability of Co-MOF was evaluated by (TGA-DSC). The surface topography of Co-MOF and Co@C-N-X-T as well as the elemental mapping were investigated by scanning electron microscope (SEM, MERLIN of ZEISS) and transmission electron microscope (TEM, JEOL, JEM-2010HR) with energy-dispersive X-ray spectroscopy (EDS) analysis. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Kratos Axis Ultra DLD system with a base pressure of 10^{-9} Torr. The basic property of samples was determined by CO_2-TPD measured by the pulse technique on a Micromeritics AutoChem II 2920 instrument. Typically, 50 mg of activated sample was heated at 700 °C for 2 h under a He flow (50 mL min^{-1}). After adsorption of CO_2 at 100 °C, the sample was purged with He at 100 °C. The TPD data were collected from 100 °C to

700 °C at a heating rate of 20 °C min^{-1} in a flow of He.

2.4 *Catalytic reactions*

The transfer hydrogenation of acetophenone was carried out in a 25 mL Schlenk tube. The tube was degassed and purged several times with pure N_2 to remove the air after the addition of acetophenone, isopropanol, and catalyst. Then the tube was loaded into an oil bath that was preheated to 80 °C. The conversion and identity of the products were determined by GC–MS with diglyme as an internal standard.

For the recyclability test, after reaction, a magnet was placed close to the Schlenk tube. Very quickly, the powders were adsorbed on the wall of the tube (Fig. S13). After removing the solution from the reaction mixture, the powders were washed with isopropanol for several times, dried at 100 °C, and the reduced by H_2 at 200 °C for 2 h before being reused for the next run under identical reaction conditions.

References:

1) J. Y. Lee, D. H. Olson,L. Pan, T. J. Emge, J. Li, *Adv. Funct. Mater.* 2007,17, 1255–1262;

2) K. Tan, N. Nijem, P. Canepa, Q. Gong, J. Li, T. Thonhauser, Y. J. Chabal, *Chem. Mater.* 2012, 24, 3153−3167;

3) D. N. Dybtsev, H. Chun, K. Kim, *Angew. Chem. Int. Ed.*2004, 43, 5033 –5036,

Table S1. Surface areas and pore distribution of the materials.

Catalyst	S_{BET} ($m^2\ g^{-1}$)	Pore volume ($cm^3\ g^{-1}$)	Pore size (nm)
Co-MOF	1160	0.64	5.6
Co@C-N-500-8h	121	0.12	4.8
Co@C-N-600-8h	120	0.12	5.5
Co@C-N-700-8h	151	0.16	3.6
Co@C-N-800-8h	131	0.13	4.3
Co@C-N-900-8h	116	0.11	5.6
Co@C-N-500-15h	165	0.20	3.6
Co@C-N-600-15h	149	0.16	3.7
Co@C-N-700-15h	119	0.12	6.4
Co@C-N-800-15h	139	0.14	4.2
Co@C-N-900-15h	128	0.13	4.7

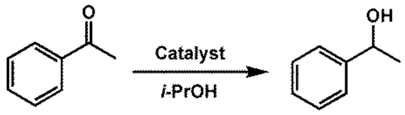
Table S2. Elements distribution of the materials

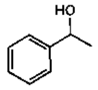
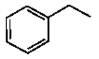
Catalyst	C content (wt%)[a]	N content (wt%)[a]	H content (wt%)[a]	Co content (wt%)[b]
Co-MOF	46.8	9.6	5.5	20.6
Co@C-N-500-8h	59.4	1.3	1.4	37.5
Co@C-N-600-8h	59.4	1.2	1.2	37.9
Co@C-N-700-8h	56.6	1.3	2.0	39.6
Co@C-N-800-8h	57.4	1.5	1.9	38.7
Co@C-N-900-8h	56.7	1.6	1.7	39.7
Co@C-N-500-15h	57.9	1.5	1.3	38.8
Co@C-N-600-15h	59.1	1.5	1.3	37.6
Co@C-N-700-15h	57.2	1.6	1.5	39.4
Co@C-N-800-15h	56.3	1.7	0.8	41.0
Co@C-N-900-15h	57.9	1.9	0.7	39.5

[a] Measured by elemental analysis.

[b] Measured by AAS.

Table S3. Transfer hydrogenation of acetophenone with isopropanol.[a]



Entry	Catalyst	Con. (%)	Sel. (%)	
				
1	-	-	-	-
2	Co@C-N-500-15h	90	81	19
3	Co@C-N-600-15h	92	84	16
4	Co@C-N-700-15h	92	85	15
5	Co@C-N-800-15h	94	89	11
6	**Co@C-N-900-15h**	**99**	**95**	**5**
7	Co@C-N-500-8h	33	62	38
8	Co@C-N-600-8h	64	76	24
9	Co@C-N-700-8h	80	78	22
10	Co@C-N-800-8h	84	83	17
11	Co@C-N-900-8h	84	90	10
12[b]	Co@C-N-900-15h	99	88	12
13[c]	Co@C-N-900-15h	95	95	5
14[d]	Co@C-N-900-15h	72	98	2
15	C-N	-	-	-
16	Co/C	<5	90	10

[a] Reaction condition: acetophenone (0.5 mmol), catalyst (Co 10 mol%), isopropanol (2 mL), 80 °C, 17 h. [b] Isopropanol, 1 mL. [c] Isopropanol, 3 mL. [d] Catalyst (Co 1 mol%), 96 h.

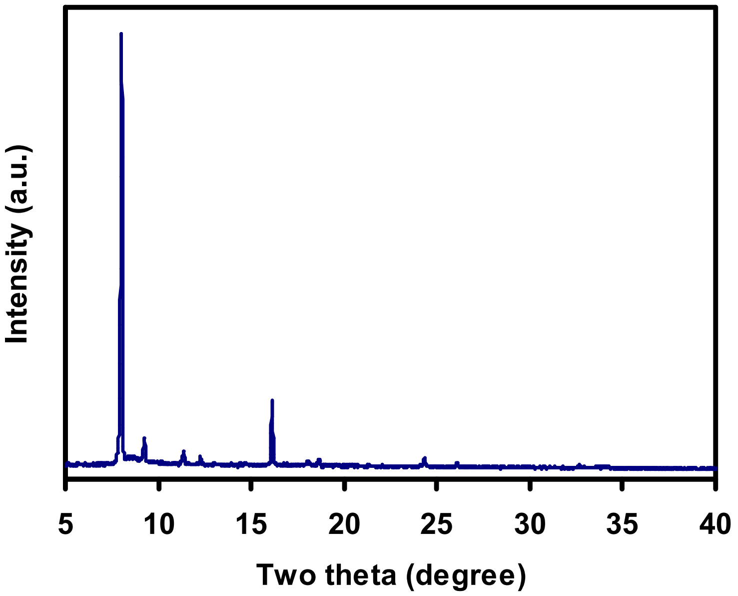


Figure S1. Powder XRD patterns of the as-synthesized Co-MOF.

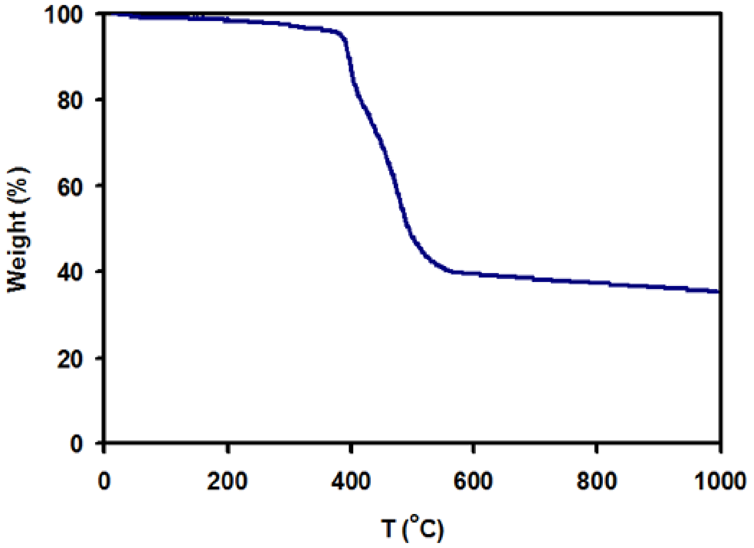


Figure S2. TGA-DSC curve of the Co-MOF.

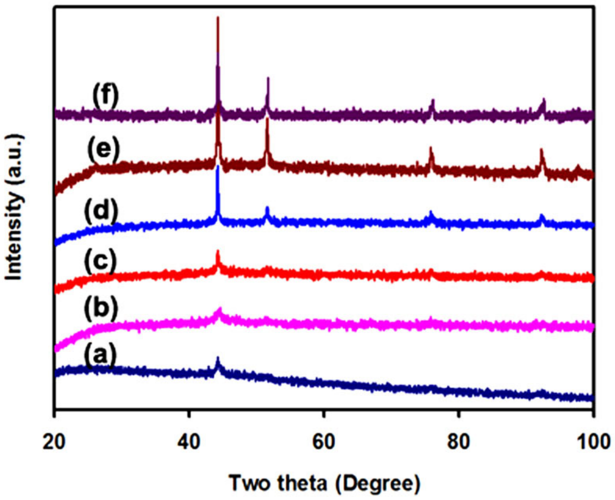


Figure S3. Powder XRD patterns of the Co@C-N samples: (a) Co@C-N-500-15h, (b) Co@C-N-600-15h, (c) Co@C-N-700-15h, (d) Co@C-N-800-15h, (e) Co@C-N-900-15h, and (f) Co@C-N-900-15h after reaction.

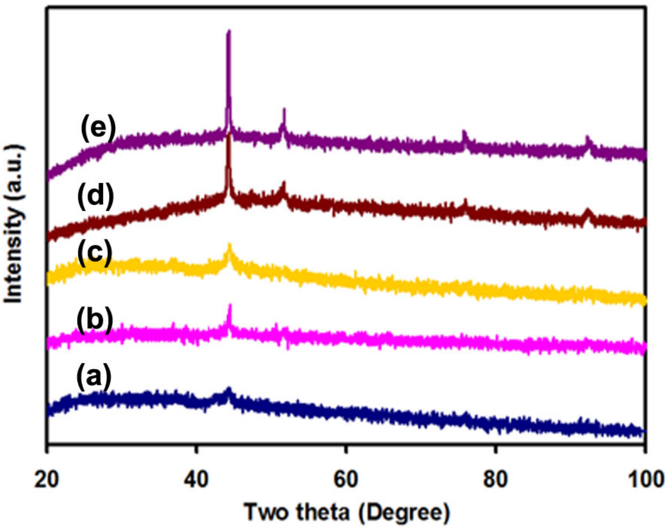


Figure S4. Powder XRD patterns of the Co@C-N-X-8h samples (a) Co@C-N-500-8h, (b) Co@C-N-600-8h, (c) Co@C-N-700-8h, (d) Co@C-N-800-8h, and (e) Co@C-N-900-8h.

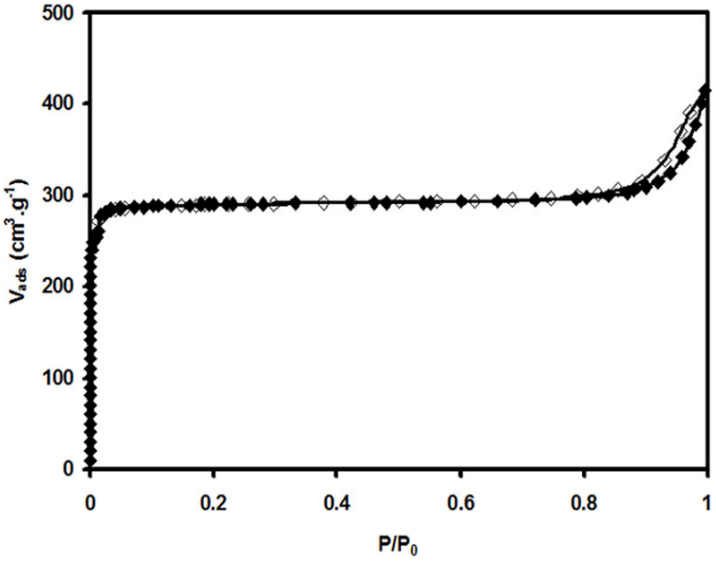


Figure S5. Nitrogen adsorption/desorption isotherms at 77 K for the as-synthesized Co-MOF.

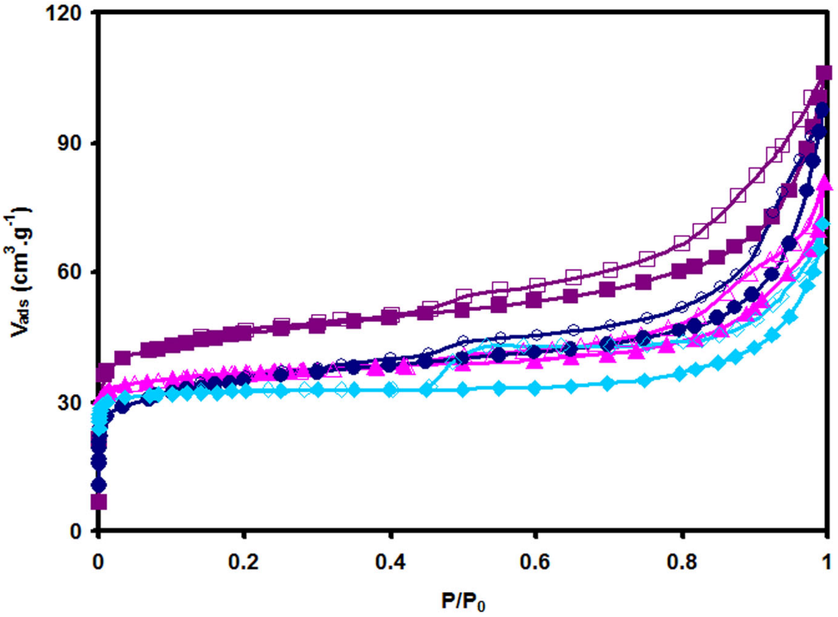


Figure S6. Nitrogen adsorption/desorption isotherms at 77 K for Co@C-N-600-8h (▲), Co@C-N-700-8h (■), Co@C-N-800-8h (●), and Co@C-N-900-8h (◆).

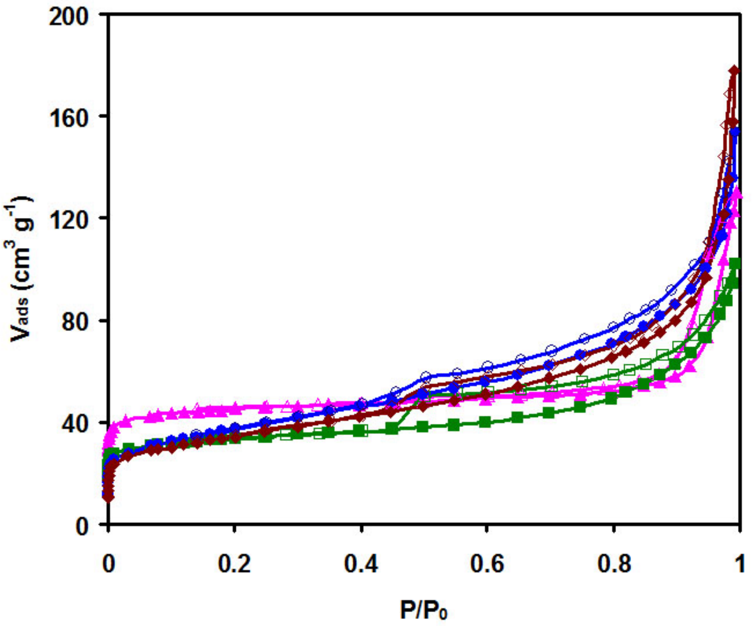


Figure S7. Nitrogen adsorption/desorption isotherms at 77 K for Co@C-N-600-15h (▲), Co@C-N-700-15h (■), Co@C-N-800-15h (●), and Co@C-N-900-15h (◆).

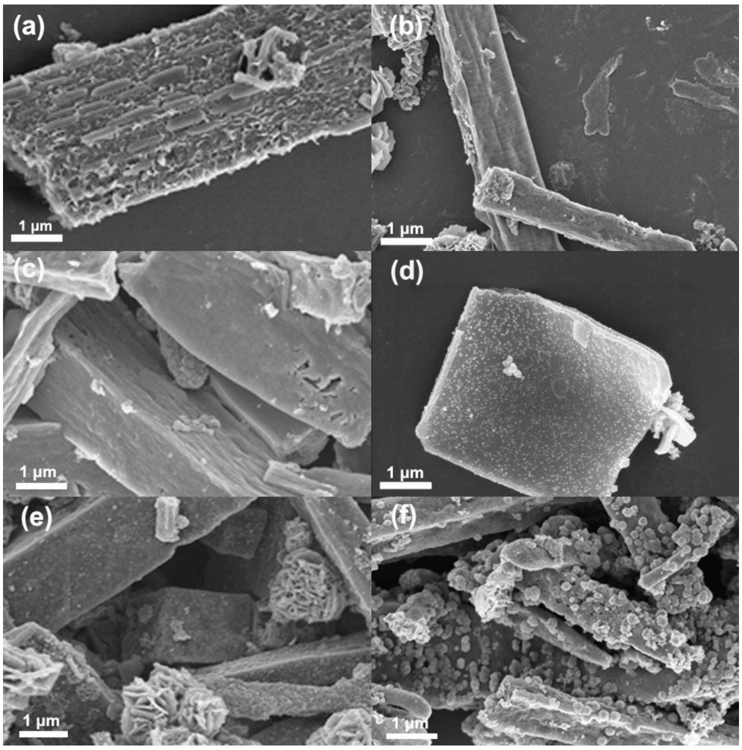


Figure S8. SEM images of (a) Co-MOF, (b) Co@C-N-500-8h, (c) Co@C-N-600-8h, (d) Co@C-N-700-8h, (e) Co@C-N-800-8h, and (f) Co@C-N-900-8h.

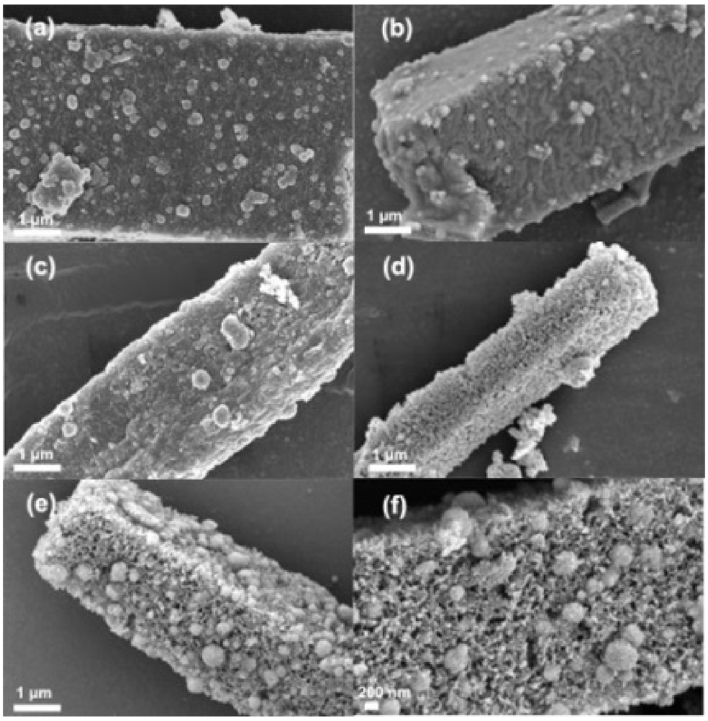


Figure S9. SEM images of the Co@C-N materials: (a) Co@C-N-500-15h, (b) Co@C-N-600-15h, (c) Co@C-N-700-15h, (d) Co@C-N-800-15h, and (e, f) Co@C-N-900-15h.

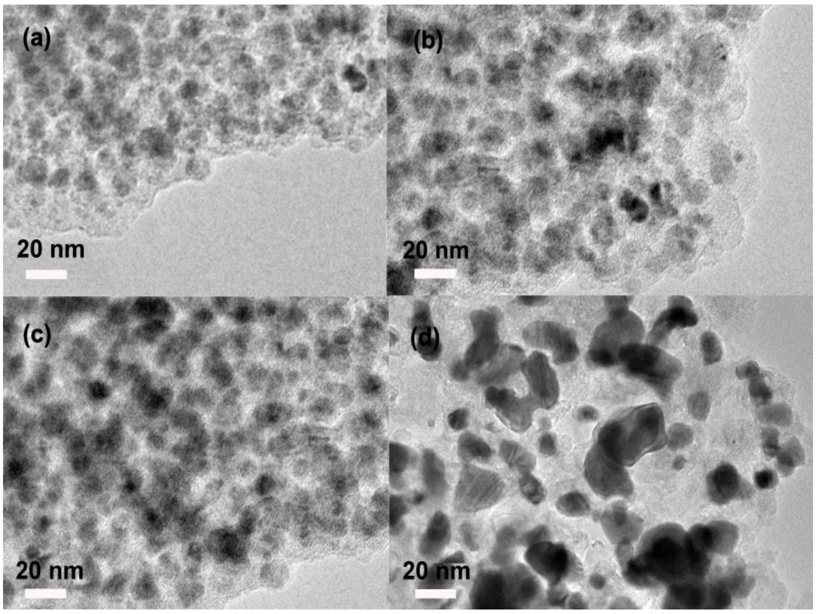


Figure S10. TEM images of Co@C-N-500-15h (a), Co@C-N-600-15h (b), Co@C-N-700-15h (c), and Co@C-N-800-15h (d).

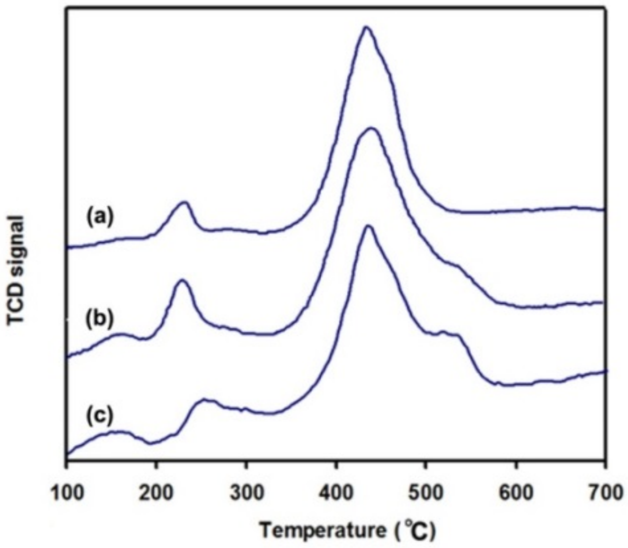


Figure S11. CO_2-TPD profile for (a) Co@C-N-700-15h, (b) Co@C-N-800-15h, and (c) Co@C-N-900-15h.

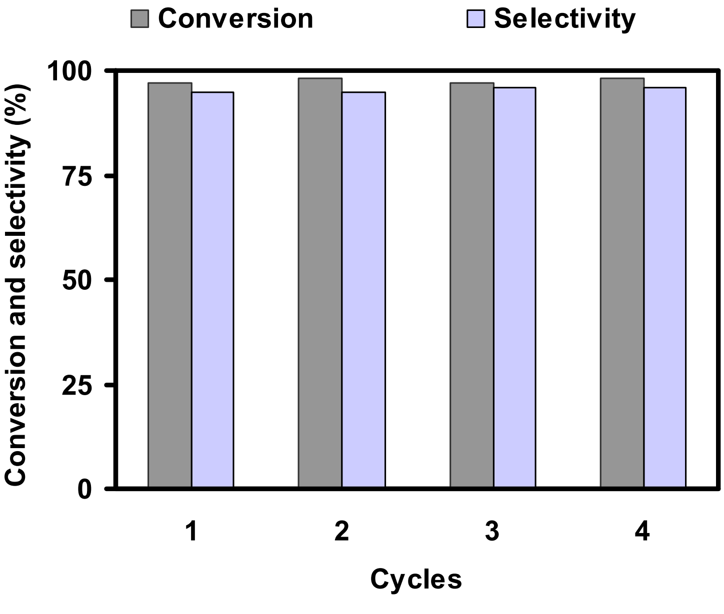


Figure S12. Reuse of the Co@C-N-900-15h catalyst in the transfer hydrogenation of acetophenone. Conditions: acetophenone (0.5 mmol), catalyst (Co, 10 mol%), isopropanol (2 mL), 80 ^{o}C, 17 h.

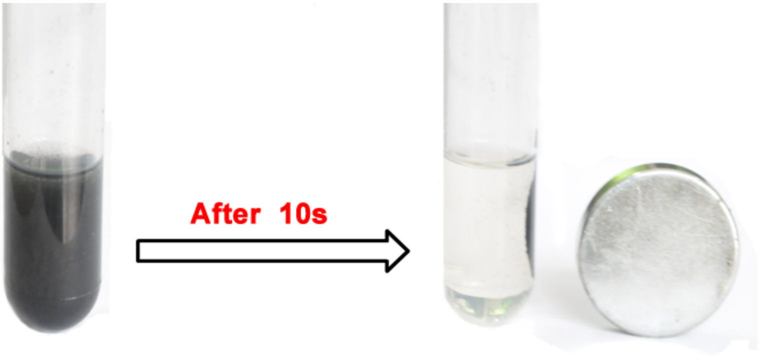


Figure S13. Magnetic separation of the Co@C-N catalyst after reaction.