Supporting Information

Efficient Co/NSPC Catalyst for Selective Hydrogenation of Halonitrobenzenes and Mechanistic Insight

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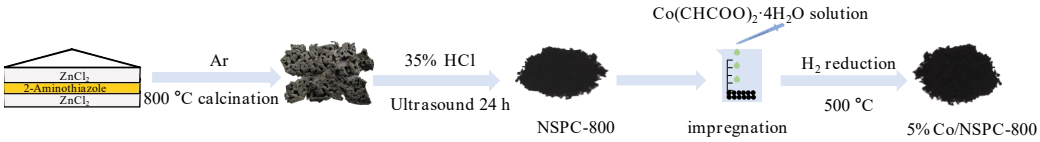
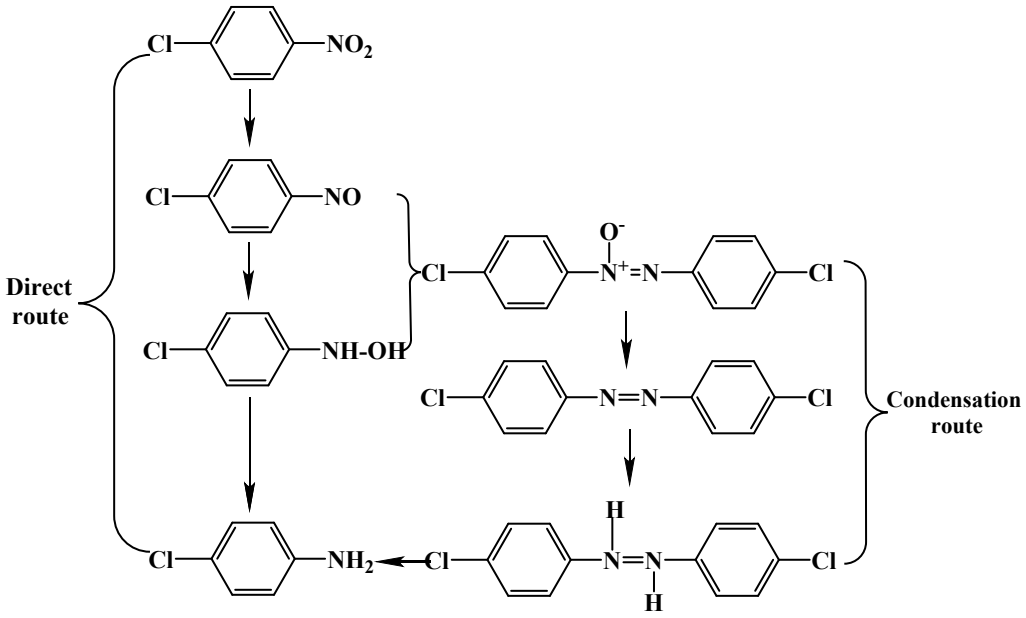
Supporting Figures and Tables



Scheme S1. The schematic illustration of the preparation of 5%Co/NSPC-800.



Scheme S2. The possible reaction pathway for *p*-CNB hydrogenation.

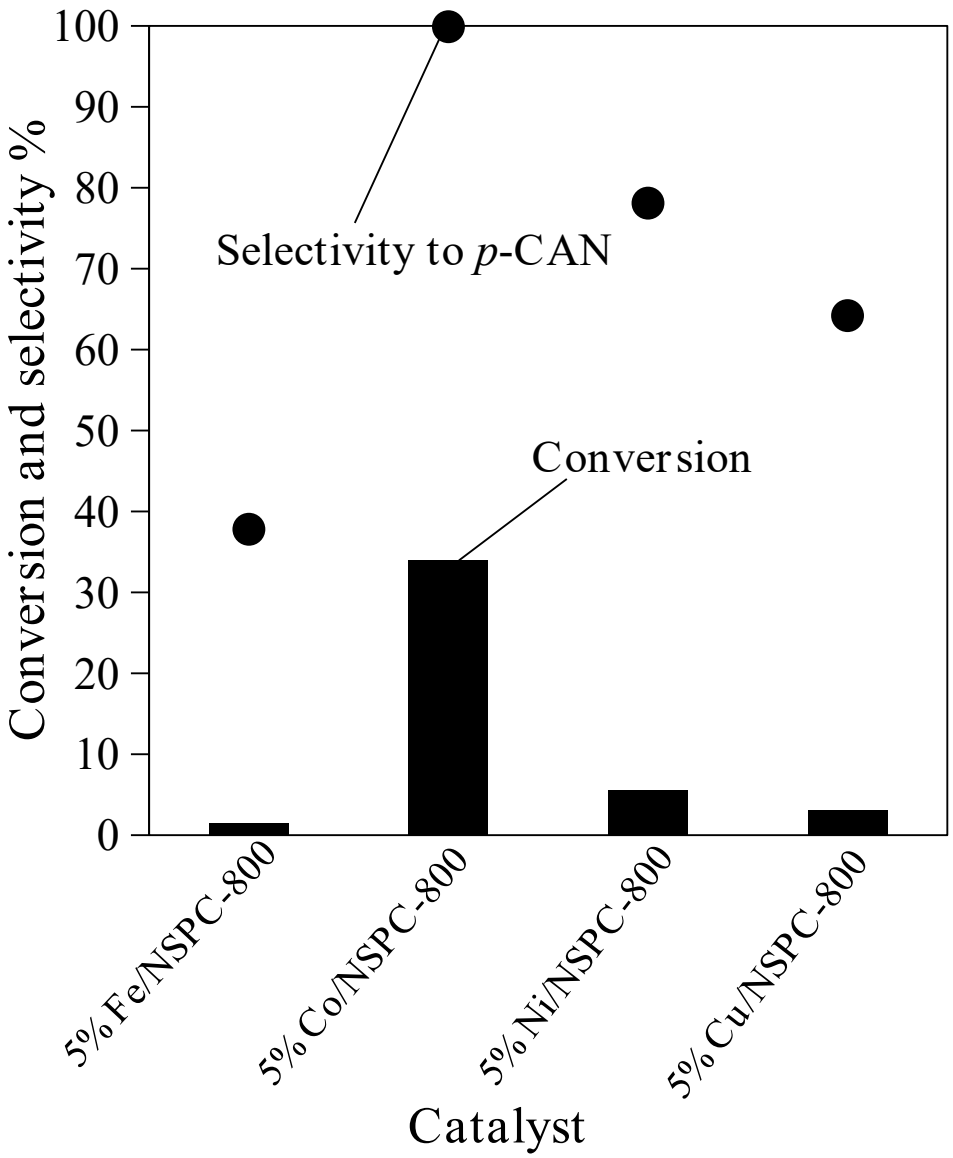


Figure S1. The effect of non-noble metal on the catalytic performance for *p*-CNB hydrogenation. Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

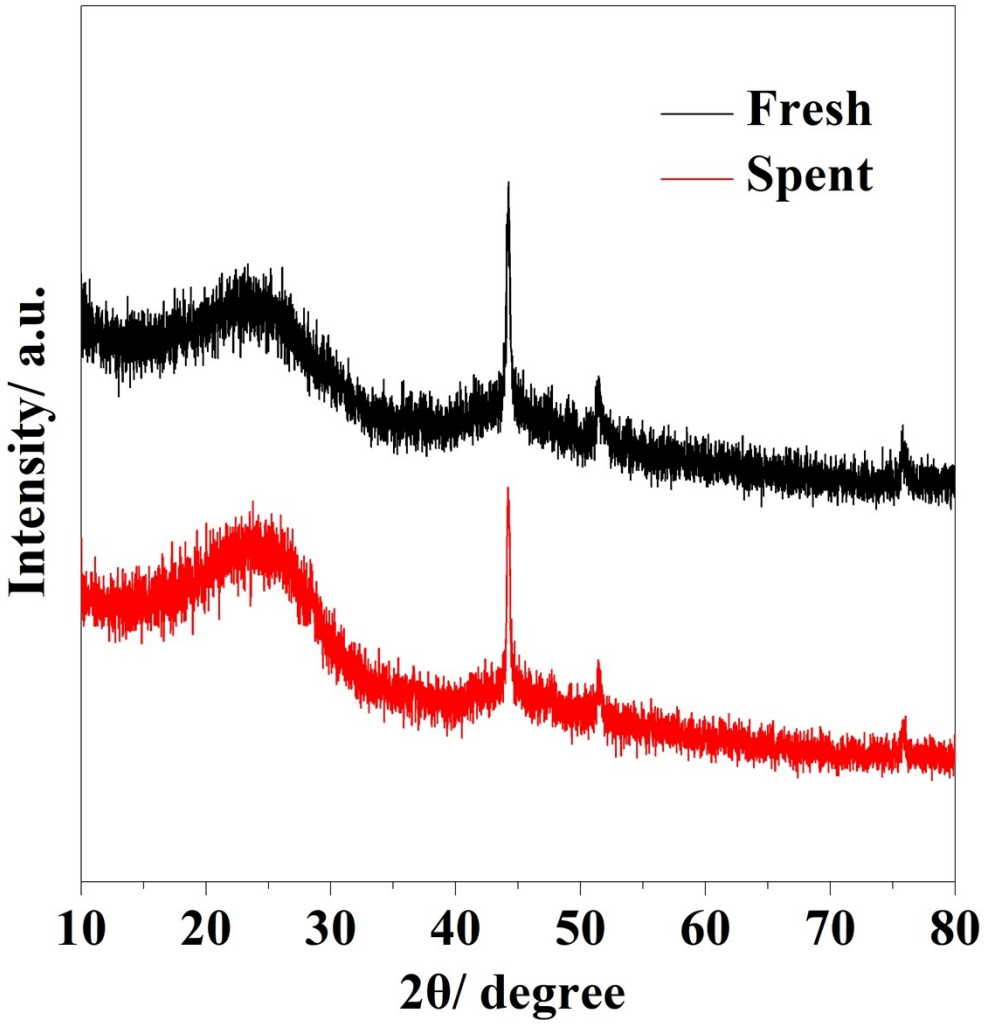


Figure S2. The XRD patterns of 5%Co/NSPC-800 before and after reaction.

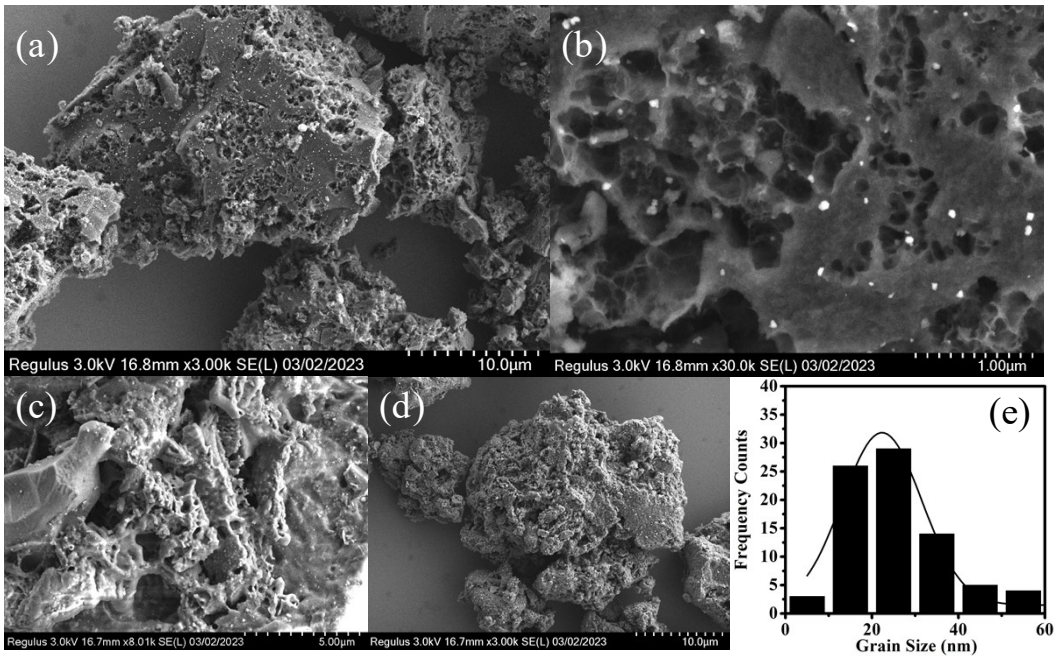


Figure S3. (a~b) The SEM images of 5%Co/NSPC-800, (c) 5%Co/NPC-800, (d) 5%Co/SPC-800 and (e) particle size distribution of 5%Co/NSPC-800.

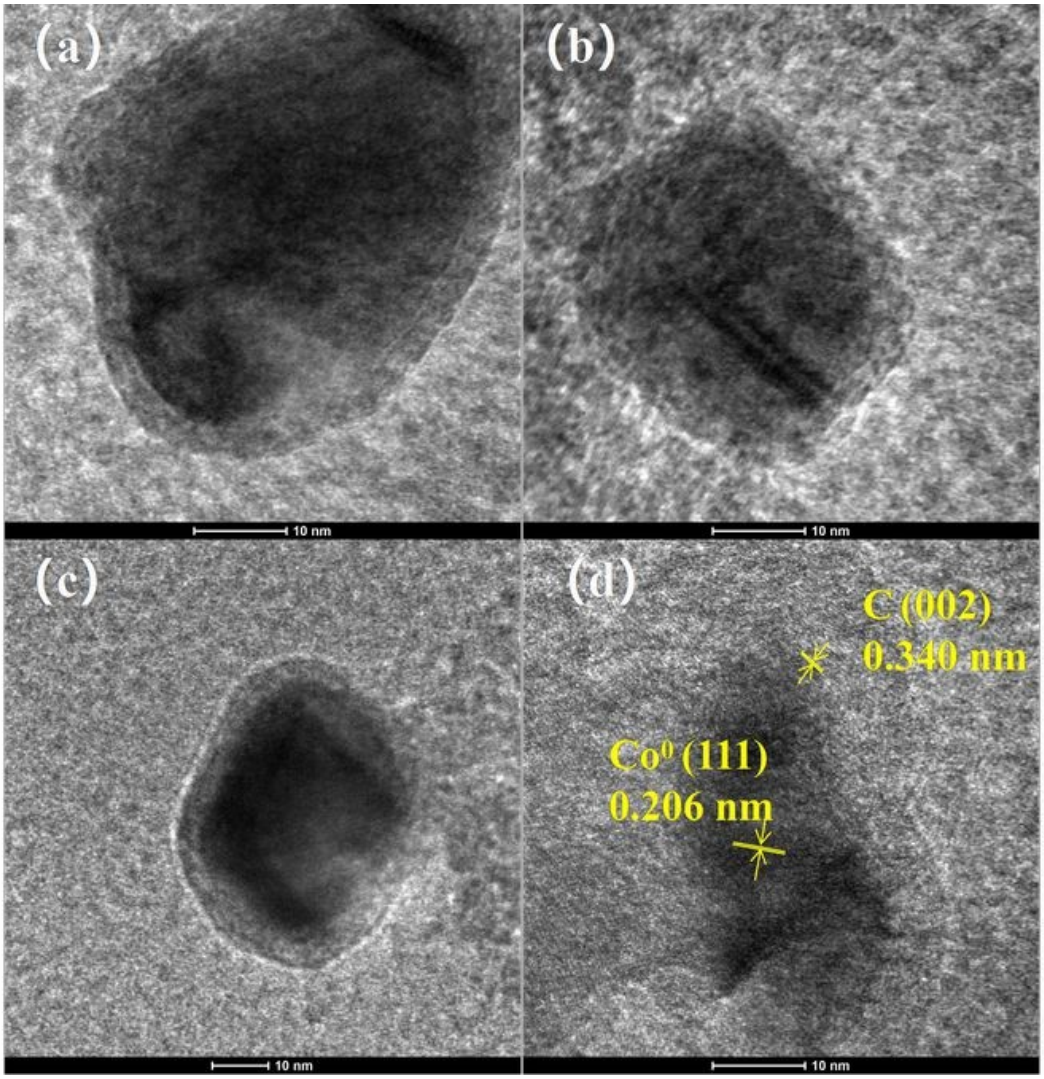


Figure S4. The HRTEM images of 5%Co/NSPC-800.

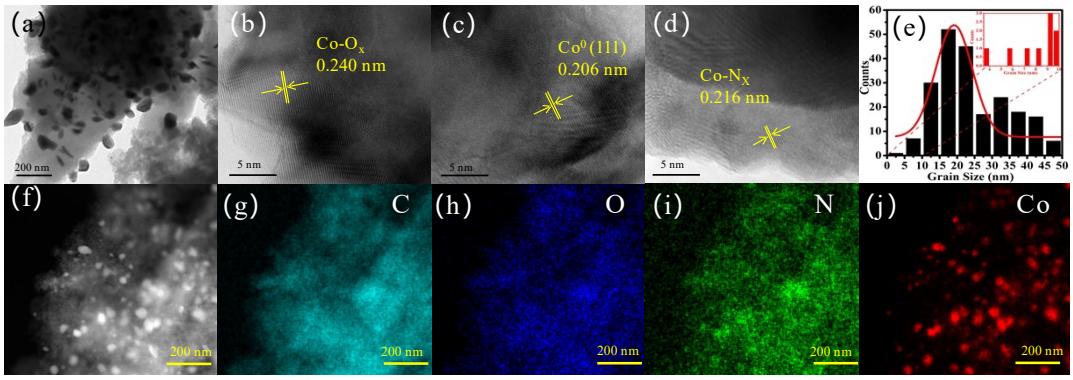


Figure S5. (a) The TEM images of 5%Co/NPC-800, (b~d) HRTEM images of 5%Co/NPC-800, (e) particle size distribution of 5%Co/NPC-800 and (f~j) EDX mapping of 5%Co/NPC-800, C, O, N and Co.

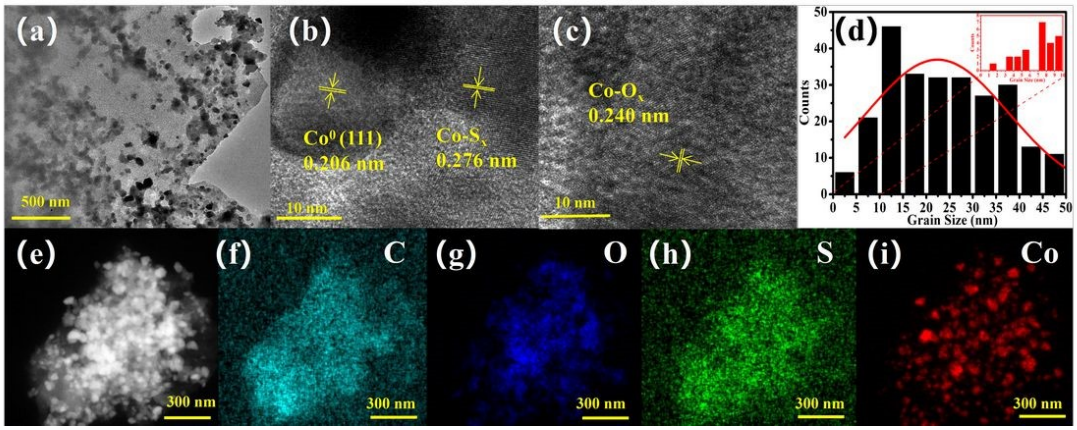


Figure S6. (a) The TEM images of 5%Co/SPC-800, (b~c) HRTEM images of 5%Co/SPC-800, (d) particle size distribution of 5%Co/SPC-800 and (e~i) EDX mapping of 5%Co/SPC-800, C, O, S and Co.

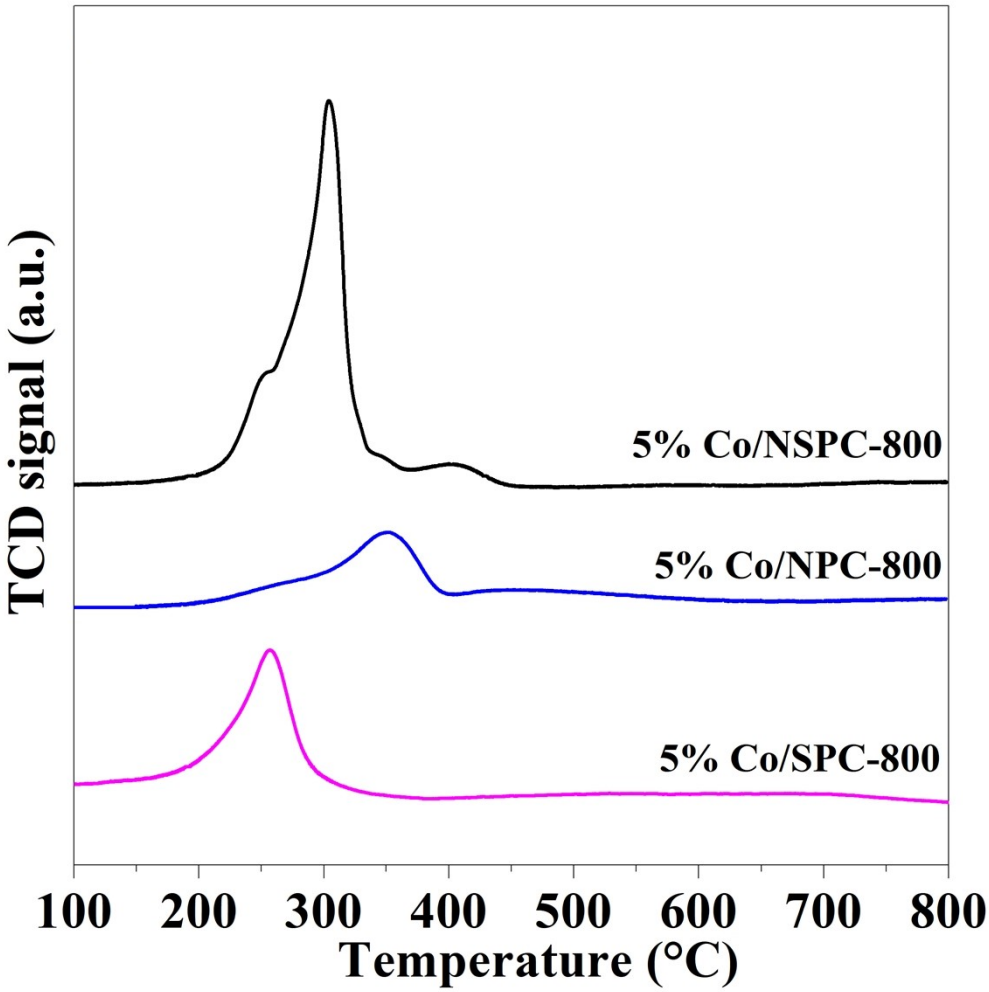


Figure S7. The H_2-TPR profile of 5%Co/NSPC-800, 5%Co/NPC-800 and 5%Co/SPC-800.

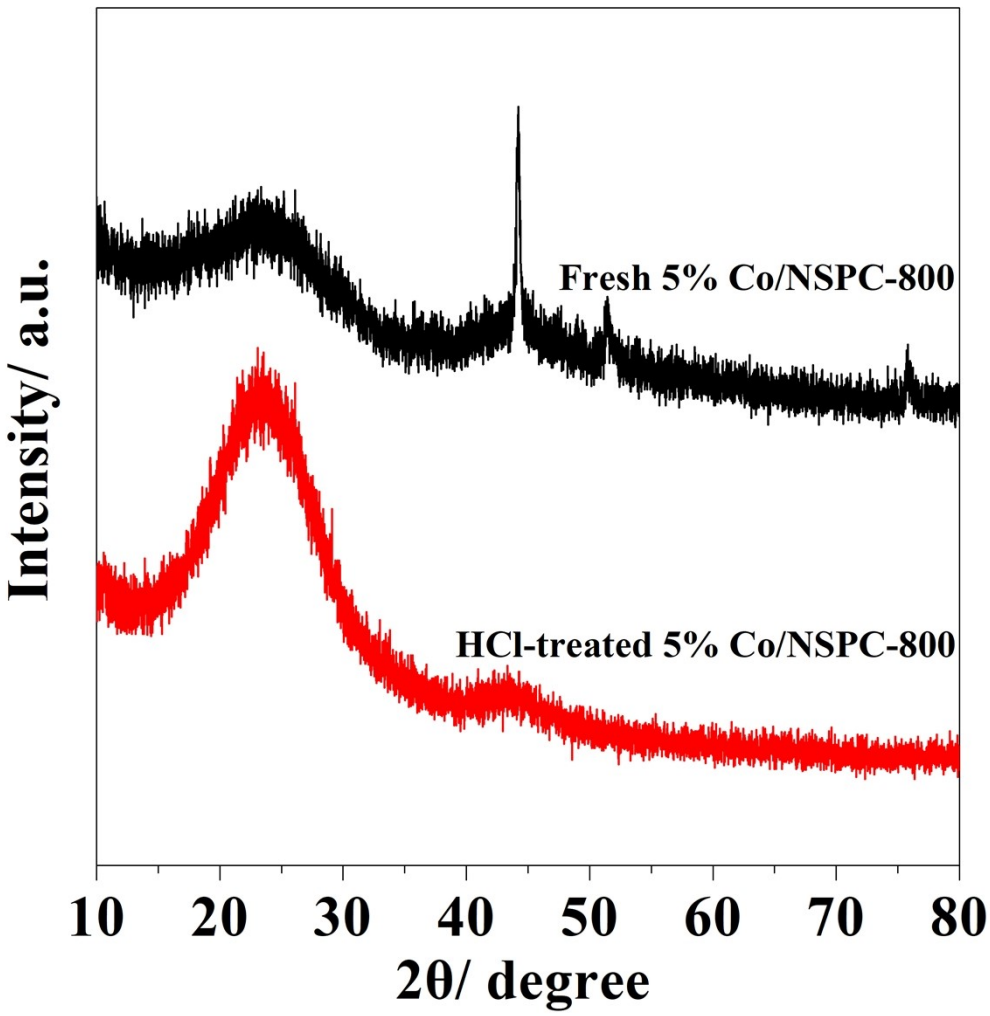


Figure S8. The XRD patterns of 5%Co/NSPC-800 before and after acid leaching.

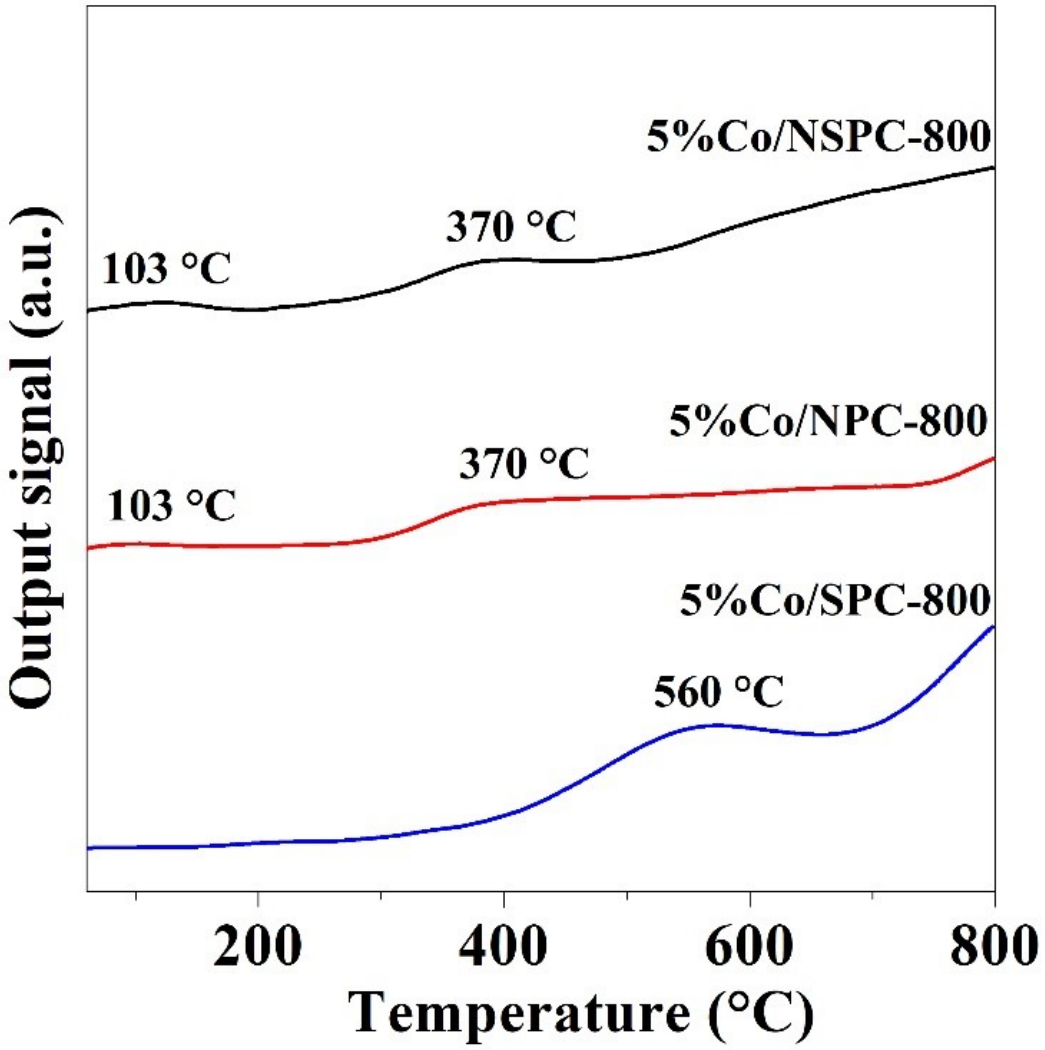


Figure S9. The H_2-TPD profile of 5%Co/NSPC-800, 5%Co/NPC-800 and 5%Co/SPC-800.

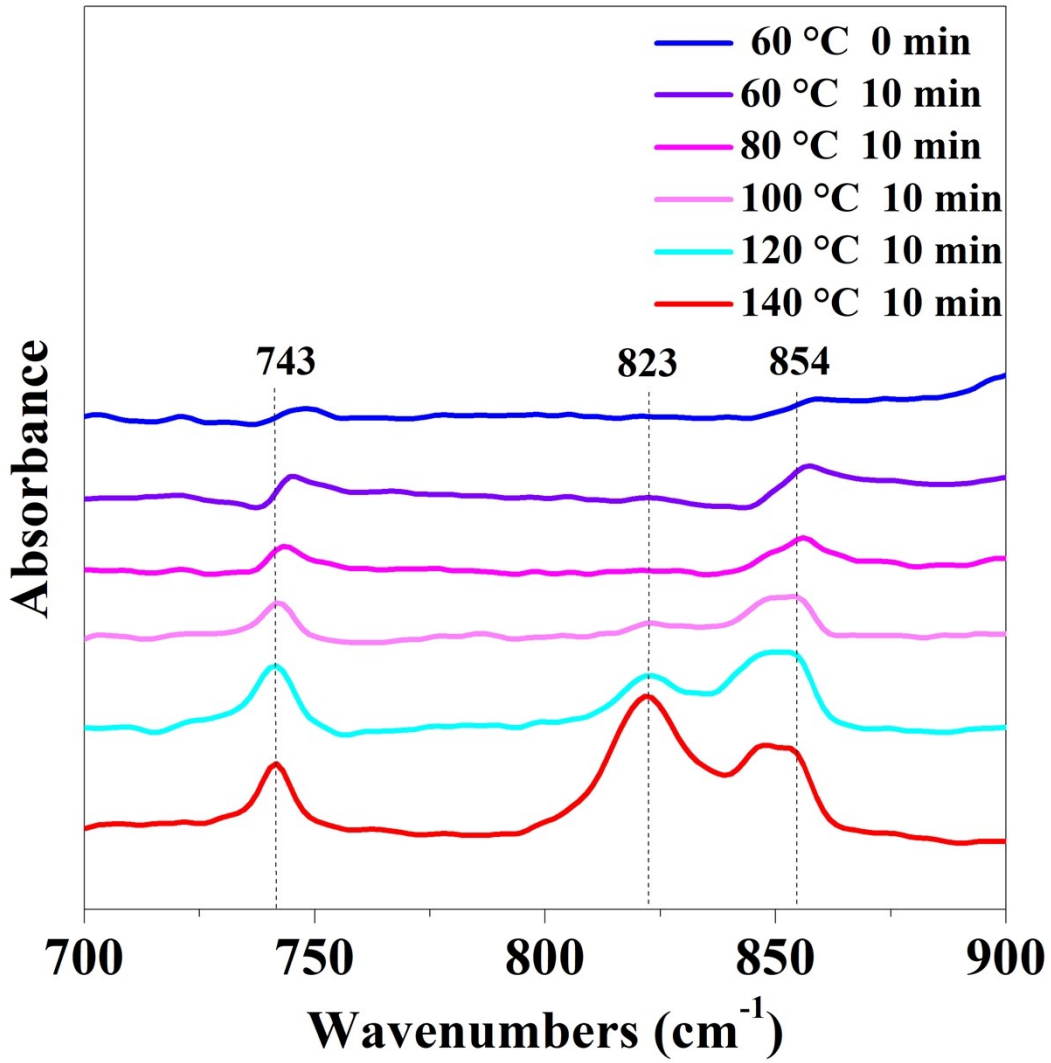
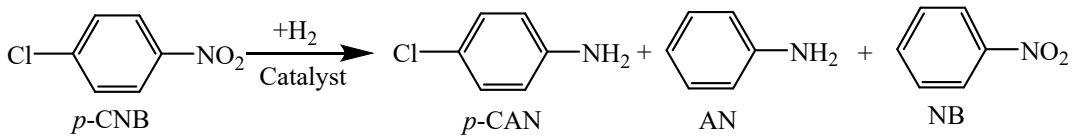
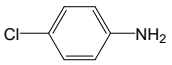
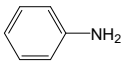
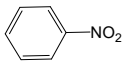


Figure S10. The *in-situ* DRIFTS of *p*-CNB over 5%/Co/NSPC-800 under 1 MPa H_2 and 60~140 °C.

Table S1. The effect of support on the catalytic performance for *p*-CNB hydrogenation.

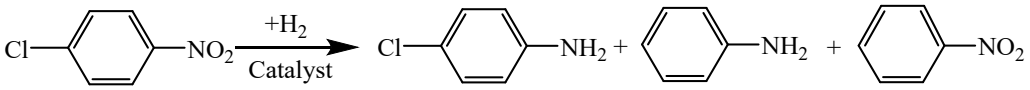


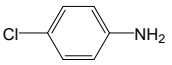
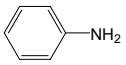
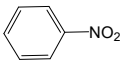
p-CNB *p*-CAN AN NB

Entry	Catalyst	Conversion /%	Selectivity /%		
					
1	SPC-800	0.71	6.8	93.2	＜0.1
2	NPC-800	0.88	74.1	＜0.1	25.9
3	NSPC-800	2.2	＞99.9	＜0.1	＜0.1
4	5%Co/NSPC-800	34.0	＞99.9	＜0.1	＜0.1
5	5%Co/NPC-800	17.8	86.9	＜0.1	13.1
6	5%Co/SPC-800	2.1	64.7	＜0.1	35.3
7	5%Co/PC-800	2.7	78.5	＜0.1	21.5
8	5%Co/SiO_2	5.2	3.1	79.4	17.5

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

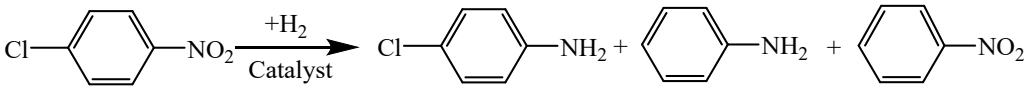
Table S2. The effect of Co loading amount on catalytic performance for *p*-CNB hydrogenation.

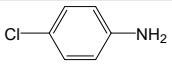
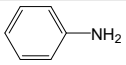
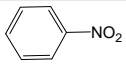


Entry	Catalyst	Conversion /%	Selectivity /%		
					
1	1%Co/NSPC-800	10.3	85.3	＜0.1	14.7
2	2%Co/NSPC-800	20.7	92.7	＜0.1	7.3
3	3.5%Co/NSPC-800	27.5	97.6	＜0.1	2.4
4	5%Co/NSPC-800	34.0	＞99.9	＜0.1	＜0.1
5	7.5%Co/NSPC-800	15.8	99.1	0.9	＜0.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

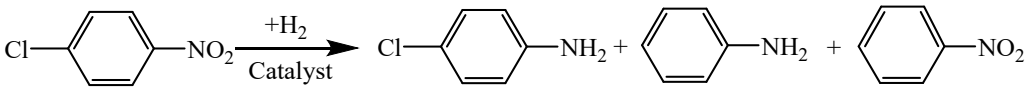
Table S3. The effect of different metal on catalytic performance for *p*-CNB hydrogenation.

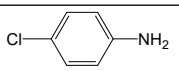
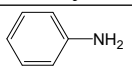
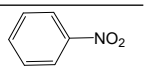


Entry	Catalyst	Conversion /%	Selectivity /%		
					
1	5%Fe/NSPC-800	1.5	37.8	＜0.1	61.2
2	5%Co/NSPC-800	34.0	＞99.9	＜0.1	＜0.1
3	5%Ni/NSPC-800	5.6	78.1	0.9	21.0
4	5%Cu/NSPC-800	3.1	64.2	＜0.1	35.8

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

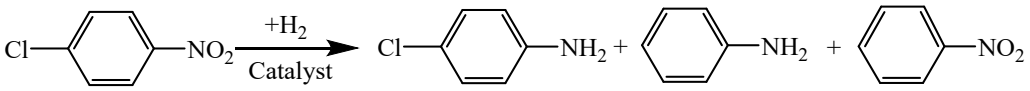
Table S4. The time course over 5%Co/NSPC-800 for *p*-CNB hydrogenation.



Entry	React time/ h	Conversion /%	Selectivity /%		
					
1	1.5	17.7	＞99.9	＜0.1	＜0.1
2	3	34.0	＞99.9	＜0.1	＜0.1
3	6	59.8	＞99.9	＜0.1	＜0.1
4	9	82.1	＞99.9	＜0.1	＜0.1
5	12	100	＞99.9	＜0.1	＜0.1
6	15	100	＞99.9	＜0.1	＜0.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 0-15 h.

Table S5. The time course over 5%Co/NPC-800 for *p*-CNB hydrogenation.



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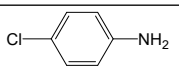
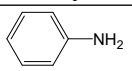
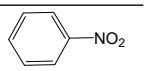
					
1	1.5	10.0	84.7	＜0.1	15.3
2	3	17.8	86.9	＜0.1	13.1
3	6	33.5	91.4	＜0.1	8.6
4	9	46.8	93.4	＜0.1	6.6
5	12	60.8	94.8	＜0.1	5.2
6	15	74.6	96.6	＜0.1	3.2
7	18	86.5	97.3	＜0.1	2.7
8	21	100	97.3	＜0.1	2.7
9	24	100	93.5	3.8	2.7

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 0-24 h.

Table S6. The elemental content of samples obtained by EA and ICP-OES.

Entry	Catalyst	EA				ICP-OES
		N(wt%)	C(wt%)	H(wt%)	S(wt%)	Co(wt%)
1	2%Co/NSPC-800	-	-	-	-	1.1
2	3.5%Co/NSPC-800	-	-	-	-	2.5
3	5%Co/NSPC-800	6.7	60.3	2.1	1.8	3.5
4	7.5%Co/NSPC-800	-	-	-	-	4.8
5	5%Co/NPC-800	4.7	71.3	1.9	0	3.0
6	5%Co/SPC-800	0	57.1	1.8	3.0	1.4

Table S7. The particle size and dispersion of catalysts.

Entry	Catalyst	Reduction temp./K	Particle size /nm		[b]Dispersion Co /%
			XRD	TEM	
1	2%Co/NSPC-800	773	26.5	-	-
2	3.5%Co/NSPC-800	773	26.8	-	-
3	5%Co/NSPC-800	773	24.5	22.4	6.0
4	7.5%Co/NSPC-800	773	25.7	-	-
5	5%Co/NPC-800	773	25.7	25.0	5.3
6	5%Co/SPC-800	773	26.0	25.2	4.3
7	[a]5%Co/NSPC-800	773	26.9	-	-

[a] After the reaction

[b] Determination by CO adsorption

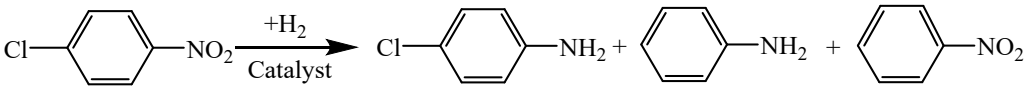
Table S8. The TOF and TOF_s values of reported effective Co-based catalysts.

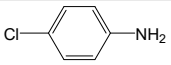
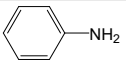
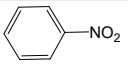
Catalyst	P_{H2} /MPa	T /K	TOF_s[a] /h^{-1}	TOF /h^{-1}	Ref.
Co-NSPC-N	1.5	393	123	7[b]	[1]
Co-NSPC-C	1.5	393	180	6[b]	[1]
Co-NSPC-S	1.5	393	154	3[b]	[1]
Co-NSPC-Cl	1.5	393	29	2[b]	[1]
$Co_1Cu_{0.30}$@CN/SiO_2	2	393	160	13[b]	[2]
Co@mesoNC	3	383	42	42	[3]
Co@CN-400	1	333	59	5	[4]
Co-N-C	3	353	36	36	[5]
Co-PC	1	353	108	10	[6]
Co-Phen	1	353	56	3	[6]
Co/N-C-600	1	373	45	5	[7]
Co-NSPC-800	3	353	84	84	[7]
Co/NMC-800	1	353	275	275	[8]
$Co800NH_3$	3	353	152	152	[9]
Co-N_x/C-800-ATc	0.35	383	392	392	[10]
Co_1@NC (SBA)	1	413	22	22	[11]
Co SAs/NC-800	0.5	393	110	110	[12]
Co SAs/NC	3	383	77	77	[13]
Co SAs/NHPCN	2	373	44	44	[14]
5%Co/SPC-800	3	353	44	2	This work
5%Co/NPC-800	3	353	140	7	This work
5%Co/NSPC-800	3	353	203	12	This work

[a] Calculated based on the amount of surface metal amount. TOF_s (h^{-1}) = (Converted *p*-CNB amount (mol))/(surface metal amount (mol))/(Time (h)). surface metal amount (mol) = (total metal amount (mol))·(1/particle size (nm)). The dispersion of single atom catalyst is considered to be 100%.

[b] Calculated based on the amount of total metal amount. TOF (h^{-1}) = (Converted *p*-CNB amount (mol))/(total metal amount (mol))/(Time (h))

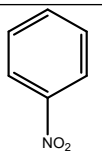
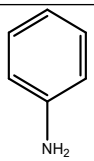
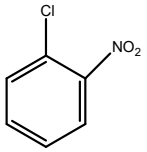
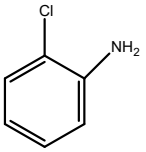
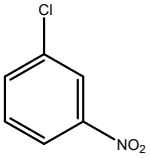
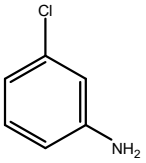
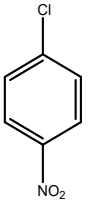
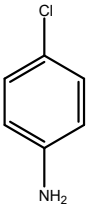
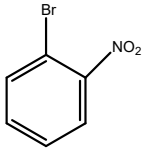
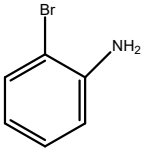
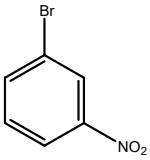
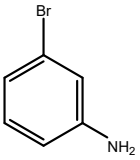
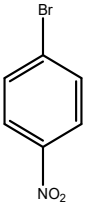
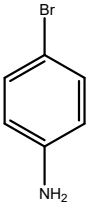
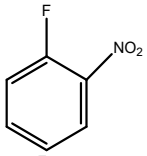
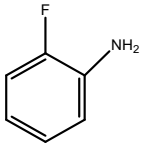
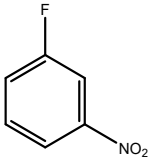
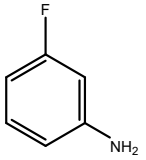
Table S9. The reusability experiment over 5%Co/NSPC-800 for *p*-CNB hydrogenation.

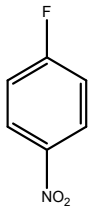
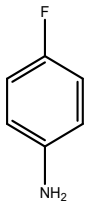
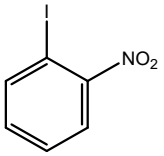
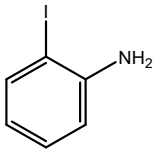
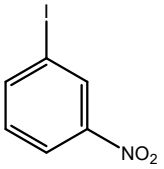
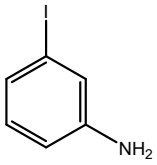
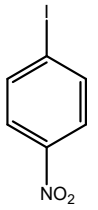
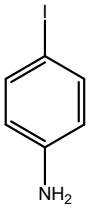


Usage time	Conversion /%	Selectivity /%		
				
1	16.6	＞99.9	＜0.1	＜0.1
2	16.0	＞99.9	＜0.1	＜0.1
3	14.9	＞99.9	＜0.1	＜0.1
4	14.6	＞99.9	＜0.1	＜0.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

Table S10. The substrate scope over 5%Co/NSPC-800.

Entry	reactant	Product	t/h	Conversion /%	Selectivity /%
1			3	40.2	＞99.9
			12	100	＞99.9
2			3	37.8	＞99.9
			12	100	＞99.9
3			3	38.1	＞99.9
			12	100	＞99.9
4			3	34.0	＞99.9
			12	100	＞99.9
5			3	33.8	＞99.9
			12	100	＞99.9
6			3	34.9	＞99.9
			12	100	＞99.9
7			3	35.2	＞99.9
			12	100	＞99.9
8			3	38.5	＞99.9
			12	100	＞99.9
9			3	35.8	＞99.9
			12	100	＞99.9

10			3 12	38.6 100	＞99.9 ＞99.9
11			3 20	17.4 100	93.0 96.2
12			3 20	15.8 100	98.7 96.3
13			3 20	16.0 100	97.5 97.3

Reaction conditions: HNBs 3.2 mmol, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3, 12 or 20 h.

Table S11. The relationship between Co^0 and Co-N_x XPS peak area and conversion.

Entry	Catalyst	Conversion /%	Peak area /(eV·Counts)	
			Co-N_x	Co^0
1	1%Co/NSPC-800	10.3	750	50
2	2%Co/NSPC-800	20.7	1370	100
3	3.5%Co/NSPC-800	27.5	1785	195
4	5%Co/NSPC-800	34.0	1900	400
5	7.5%Co/NSPC-800	15.8	1050	300
6	5%Co/NPC-800	17.8	1000	400
7	5%Co/SPC-800	2.1	0	280

Table S12. The binding energy and distribution of surface cobalt atomic chemical state based on XPS spectra.

Catalyst	Co $2p_{3/2}$ (eV)				Relative percentage (%)			
	Co^0	Co-O_x	Co-N_x	Co-S_x	Co^0	Co-O_x	Co-N_x	Co-S_x
1%Co/NSPC-800	778.6	780.5	782.5	778.1	2.0	66.0	31.2	0.8
2%Co/NSPC-800	778.6	780.5	782.5	778.1	2.4	64.3	32.1	1.2
3.5%Co/NSPC-800	778.6	780.5	782.5	778.1	4.0	58.8	36.2	1.0
5%Co/NSPC-800	778.6	780.5	782.5	778.1	7.5	54.9	35.7	1.9
7.5%Co/NSPC-800	778.6	780.5	782.5	778.1	7.6	64.6	26.6	1.2
5%Co/NPC-800	778.6	780.5	782.5	-	11.8	58.8	29.4	0
5%Co/SPC-800	778.6	780.5	-	778.1	12.6	80.7	0	6.7

Table S13. The Co content of 5%Co/NSPC-800, 5%Co/NPC-800 and 5%Co/SPC-800 measured by ICP-OES and XPS.

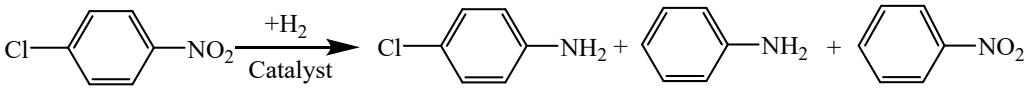
Entry	Catalyst	Co content (wt. %)	
		ICP-OES	XPS
1	5%Co/NSPC-800	3.5	0.9
2	5%Co/NPC-800	3.0	0.8
3	5%Co/SPC-800	1.4	0.5

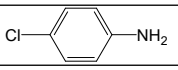
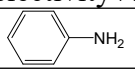
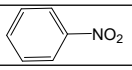
Table S14. The EXAFS fits parameters at the Co *K*-edge of various samples.

Catalyst	Shells	CN[a]	R^b / 10^{-1} nm	σ^c / 10^{-1} nm	$\Delta E_0{}^d$ / eV	$R_f{}^e$ / %
5%Co/NSPC-800	Co-Co	11.0	2.47	0.06	-2.7	0.028
	Co-N/O	2.0	2.04	0.06	3.5	
	Co-S	1.8	2.35	0.06	-2.7	
5%Co/NPC-800	Co-Co	11.5	2.49	0.07	-0.8	0.026
	Co-N/O	1.2	2.00	0.08	-7.6	
5%Co/SPC-800	Co-Co	11.6	2.50	0.06	-1.4	0.028
	Co-S	3.0	2.35	0.06	-0.7	
Co foil	Co-Co	12.0	2.50	0.07	0.5	0.003
CoPc	Co-N	4.0	1.91	0.06	-2.7	0.007
CoS	Co-S	6.0	2.28	0.06	1.8	0.002

[a]Coordination number. [b]Bond distance. [c]Debye-Waller factor. [d]Difference in the origin of photoelectron energy between the reference and the sample. [e]Residual factor. Fourier filtering range: 0.114-0.310 nm.

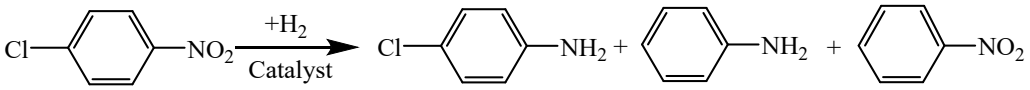
Table S15. The kinetic studies on the effect of *p*-CNB concentration over 5%Co/NSPC-800.

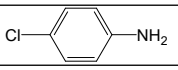
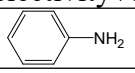
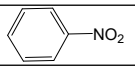


Entry	*p*-CNB mass /g	Conversion /%	Selectivity /%		
					
1	0.25	30.4	＞99.9	＜0.1	＜0.1
2	0.5	17.0	＞99.9	＜0.1	＜0.1
3	1	9.2	＞99.9	＜0.1	＜0.1

Reaction conditions: *p*-CNB 0.25-1 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 1.5 h.

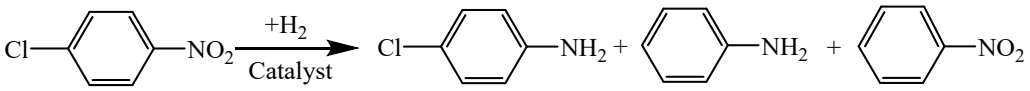
Table S16. The kinetic studies on the effect of *p*-CNB concentration over 5%Co/NPC-800.

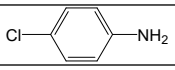
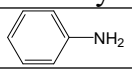
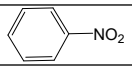


Entry	*p*-CNB mass /g	Conversion /%	Selectivity /%		
					
1	0.25	31.1	80.0	7.5	12.5
2	0.5	17.8	86.9	＜0.1	13.1
3	1	10.0	84.5	5.8	9.7

Reaction conditions: *p*-CNB 0.25-1 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

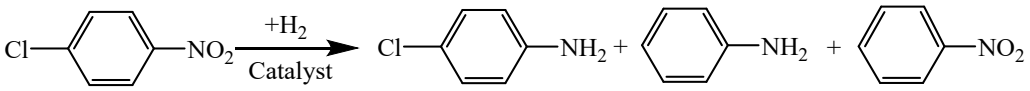
Table S17. The kinetic studies on the effect of H_2 pressure over 5%Co/NSPC-800.

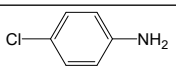
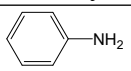
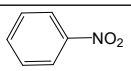


Entry	P_{H2} /MPa	Conversion /%	Selectivity /%		
					
1	0.5	4.2	＞99.9	＜0.1	＜0.1
2	1.5	11.4	＞99.9	＜0.1	＜0.1
3	3	34.0	＞99.9	＜0.1	＜0.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 0.5-3 MPa, temperature 353 K, reaction time 3 h.

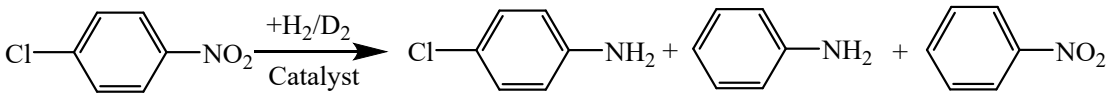
Table S18. The kinetic studies on the effect of H_2 pressure over 5%Co/NPC-800.



Entry	P_{H2} /MPa	Conversion /%	Selectivity /%		
					
1	0.5	2.8	＞99.9	＜0.1	＜0.1
2	1.5	11.2	92.7	＜0.1	7.3
3	3	17.8	86.9	＜0.1	13.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 0.5-3 MPa, temperature 353 K, reaction time 3 h.

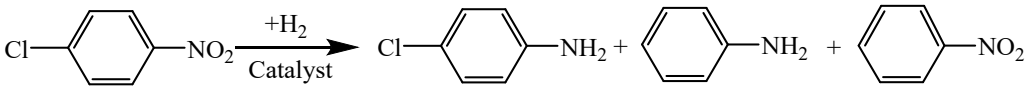
Table S19. The H_2-D_2 exchange kinetics experiment result over 5%Co/NPC-800.

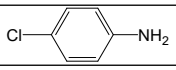
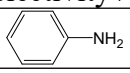
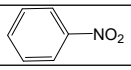


Entry	Reaction time	Conversion	
		H_2 atmosphere	D_2 atmosphere
1	0	0	0
2	1.5	0.055	0.012
3	3	0.117	0.025

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, pressure 1.5 MPa, temperature 353 K, reaction time 0-3 h.

Table S20. The effect of reaction temperature on the catalytic performance over 5%Co/NSPC-800.

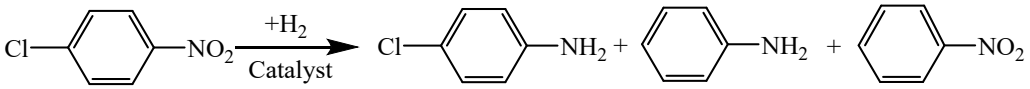


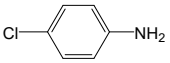
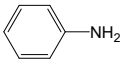
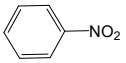
Entry	Temp. /K	Conversion /%	Selectivity /%		
					
1	333	14.2	＞99.9	＜0.1	＜0.1
2	353	34.0	＞99.9	＜0.1	＜0.1
3[a]	373	25.0	＞99.9	＜0.1	＜0.1

Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 333-373 K, reaction time 3 h.

[a] reaction time 1.5 h.

Table S21. The effect of reaction temperature on the catalytic performance over 5%Co/NPC-800.



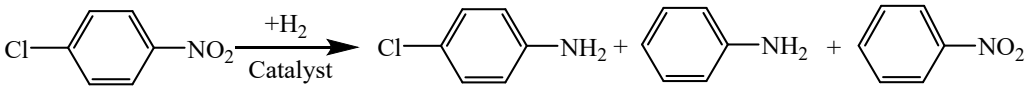
Entry	Temp. /K	Conversion /%	Selectivity /%		
					
1	333	7.5	88.1	＜0.1	11.9
2	353	17.8	86.9	＜0.1	13.1
3	373	49.7	48.7	51.3	＜0.1

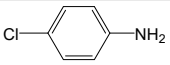
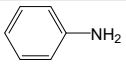
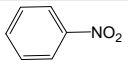
Reaction conditions: *p*-CNB 0.5 g, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 333-373 K, reaction time 3 h.

Table S22. The activation energy values of reported effective transition metal catalysts.

Catalyst	P_{H2} /MPa	T /K	E_a /KJ·mol^{-1}	Ref.
Co-NSPC-800	3	333-373	50	[7]
Co SAs/NHPCN	2	363-383	49	[14]
Co_1/NC	3	363-403	51	[15]
Co_1/NPC	3	363-403	22	[15]
Co/NMC-800	1	343-383	28	[16]
2Co-1Zn@NC-800	1	323-353	63	[17]
5%Co/NPC-800	3	333-373	48	This work
5%Co/NSPC-800	3	333-373	33	This work

Table S23. The hydrogenation of *p*-CNB over 5%Co/NSPC-800 under different reaction conditions.



Entry	Conversion /%	Selectivity /%		
				
1	33.8	＞99.9	＜0.1	＜0.1
2[a]	20.8	90.6	＜0.1	9.4
3[b]	19.7	90.5	＜0.1	9.5
4[c]	15.2	84.4	＜0.1	15.6
5[d]	15.0	81.7	＜0.1	18.3
6[e]	12.4	51.1	28.7	20.2

Reaction conditions: halogenated nitrobenzene 3.2 mmol, catalyst 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

[a] 0.03 mmol KSCN as catalyst inhibitor with SCN^- to cobalt molar ratio of 1.

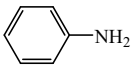
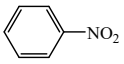
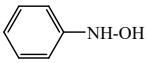
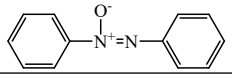
[b] 0.25 mmol KSCN as catalyst inhibitor with SCN^- to cobalt molar ratio of 8.5.

[c] 0.03 mmol EDTA as catalyst inhibitor with EDTA to cobalt molar ratio of 1.

[d] 0.25 mmol EDTA as catalyst inhibitor with EDTA to cobalt molar ratio of 8.5.

[e] The catalyst was treated with 35% hydrochloric acid for 12 h.

Table S24. The experimental results of hydrogenation of various intermediates.

Entry	Reactant	Conversion /%	Selectivity /% 
1		40.2	＞99.9
2		0	0
3		22.0	＞99.9

Reaction conditions: reactant 3.2 mmol, 5%Co/NSPC-800 50 mg, methanol 30 mL, H_2 pressure 3 MPa, temperature 353 K, reaction time 3 h.

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