Supporting information

Transfer hydrogenation of phenol over Co-CoO_x/N-doped carbon: boosted catalyst performance enabled by synergistic catalysis between Co^0 and $Co^{\delta+}$

Yunqing Nie, [a] *Wei Lin,* [a] *Yongsheng Zhang,* Yi Chen, Renfeng Nie**

College of Chemical Engineering, Zhengzhou University, Zhengzhou 450001, China

[a] These authors contributed equally
Email address: rnie@zzu.edu.cn; yzhang@zzu.edu.cn

1. Experimental section

1.1 Materials

Cobalt nitrate hexahydrate, iron nitrate nonahydrate, nickel nitrate hexahydrate, copper nitrate trihydrate, resorcinol, hexamethylentetramine (HMT) and ethylenediamine (EDA) were purchased from Aladdin Co. Ltd., China. Pluronic F127 was purchased from Sigma Aldrich Co. Ltd., USA. Phenol and it's all derivatives were purchased from Aladdin Co. Ltd., China. All the chemicals were used without further purification and addition.

1.2 Catalyst preparation

Synthesis of mesoporous N-doped carbon sphere (NCS) polymer: Typically, 2 g of resorcinol, 0.386 g of EDA, 0.6 g of HMT and 5 g of Pluronic F127 were dissolved in 80 mL of H_2O. The solution was transferred into a Teflon-lined stainless-steel autoclave and kept at 160 °C for 8 h. Afterwards, the autoclave was cooled down, the polymer gel product was washed three times with deionized water, dried at 80 °C overnight and denoted as NCS polymer.

Synthesis of Co-CoO_x supported on mesoporous N-doped carbon sphere (Co-

CoO_x/NCS-x): 5.78 g NCS polymer was re-dispersed in 120 mL of solution (96 mL of H_2O and 24 mL of ammonium hydroxide solution (28.0-30.0%)) containing 4.62 mmol (1.345 g) of $Co(NO_3)_2 \cdot 6H_2O$, stirred at 50 °C for 6 h. Afterwards, the solid was collected by filtration, washed three times with deionized water and dried at 60 °C under vacuum for 8 h, which was named as $Co^{\delta+}$/NCS polymer. Then, $Co^{\delta+}$/NCS polymer was heated to 360 °C under N_2 with a rate of 2 °C min^{-1} and kept at that temperature for 3 h, then heated to 400-700 °C with a rate of 2 °C min^{-1} and kept at that temperature for 2 h. the product was named as Co-CoO_x/NCS-x. Replacing cobalt with nickel, copper and iron could give rise to Ni/NCS-x, Cu/NCS-x and Fe/NCS-x, respectively.

Synthesis of Co_3O_4 supported on mesoporous N-doped carbon sphere (Co_3O_4/NCS-x): Co_3O_4/NCS-x was obtained by heating Co-CoO_x/NCS-x at 200 ^{o}C in air for 12 h.

Synthesis of mesoporous N-doped carbon sphere (NCS-x): NCS-x was obtained by directly pyrolyzing NCS polymer at 400-700 °C like the procedure of Co-CoO_x/NCS-x.

1.3 Characterizations

Powder X-ray diffraction (XRD) was performed on a Bruker D8A25 diffractometer with CuKα radiation (λ = 1.54184 Å) operating at 30 kV and 25 mA. Fourier transform infrared (FTIR) spectra were analyzed on an OPUS Fourier Transform Infrared Spectrophotometer in the range of 400–4000 cm^{-1}. Raman spectra were collected at room temperature from 100 to 4000 cm^{-1} with a 514.5 nm argon ion laser (Renishaw Instruments, England). N_2 physisorption measurements were performed with a Micromeritics TriStar II surface characterization analyzer at 77 K. All samples were activated at 200 °C for 10 h under a vacuum ($< 10^{-5}$ torr) before the measurements. Transmission electron microscopy (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL-135 2010F Transmission Electron Microscope. X-ray photo-electron spectra (XPS) were recorded on a PerkinElmer PHI ESCA system.

The temperature-programmed reduction (TPR) was performed on FineSorb-3010 equipped with a thermal conductivity detector (TCD). In a typical test, a certain amount of catalyst was pretreated at 100 °C for 60 min in an Ar flow of 20 mL/min and then cooled down to 60 °C. Subsequently, the sample was heated to 600 °C with the heating rate of 10 °C/min under 10% H_2/Ar (15 mL/min).

The 2-PrOH-TPSR was measured using an Autochem 2910 apparatus. The sample (50 mg) was pretreated at 200 °C for 2 h with an Ar flow rate of 80 mL/min. After that, the sample was cooled to 60 °C and absorbed with 2-PrOH/Ar flow (80 mL/min) for 2 h. Then the sample was purged by Ar flow (80 mL/min) for 3 h to remove the physically absorbed 2-PrOH. The 2-PrOH-TPSR was carried out with a heating rate of 10 °C/min to 600 °C. The signal of isopropanol, acetone and H_2 (m/z = 60, 58, 2) during desorption was recorded by MS-online (MS, Dycor LC-D, Ametek Process Instruments, Newark, DE).

1.4 Typical experiment and product analysis

The transfer hydrogenation of phenol was carried out in a 25 mL stainless steel high-pressure reactor. In a typical run, 5 mL 2-PrOH, 0.1 mmol phenol and 20 mg catalyst were added into the reactor. Then the reactor was sealed, purged with N_2, pressurized to 1 MPa and heated to 200 °C. After the reaction, the reactor was quenched in cold water to quickly stop the reaction. The solid catalyst and liquid products were separated by centrifugation. The liquid was diluted with EtOH and analyzed by GC (Agilent 7890A) with a 30 m capillary column (HP-5) using a flame ionization detector (FID). All the products were confirmed by GC-MS (Agilent 5977A MSD).

1.5 General procedure for catalytic dehydrogenation of 2-PrOH

The catalytic dehydrogenation of 2-PrOH was carried out in a 25 mL stainless steel high-pressure reactor. In a typical run, 5 mL 2-PrOH and 20 mg catalyst were added into the reactor. Then the reactor was sealed, purged with N_2 for five times. The solution was heated at 180 °C with stirring. After the reaction, the reactor was quenched in cold water to quickly stop the reaction. The gas was collected and measured by dewatering method.

Table S1 Pore parameters of Co/NCS-600 and NCS-600.

Catalyst	S_{BET} (m^2g^{-1})[a]	V_{total} (cm^3g^{-1})[b]	Average pore size (nm)[c]
Co-CoO_x/NCS-600	420.3	0.136	2.7
CN-600	477.6	0.335	3.7

[a] Obtained from Brunuaer-Emmett-Teller calculation.

[b] Calculated by single-point adsorption at relative pressure of 0.98.

[c] Calculated by BJH method from desorption isotherm linear plot.

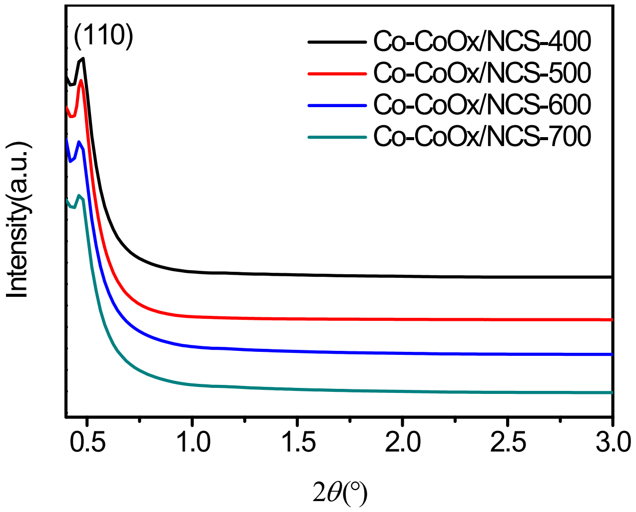


Fig. S1 Small angle XRD patterns of Co-CoO$_x$/NCS-400, Co-CoO$_x$/NCS-500, Co-CoO$_x$/NCS-600 and Co-CoO$_x$/NCS-700.

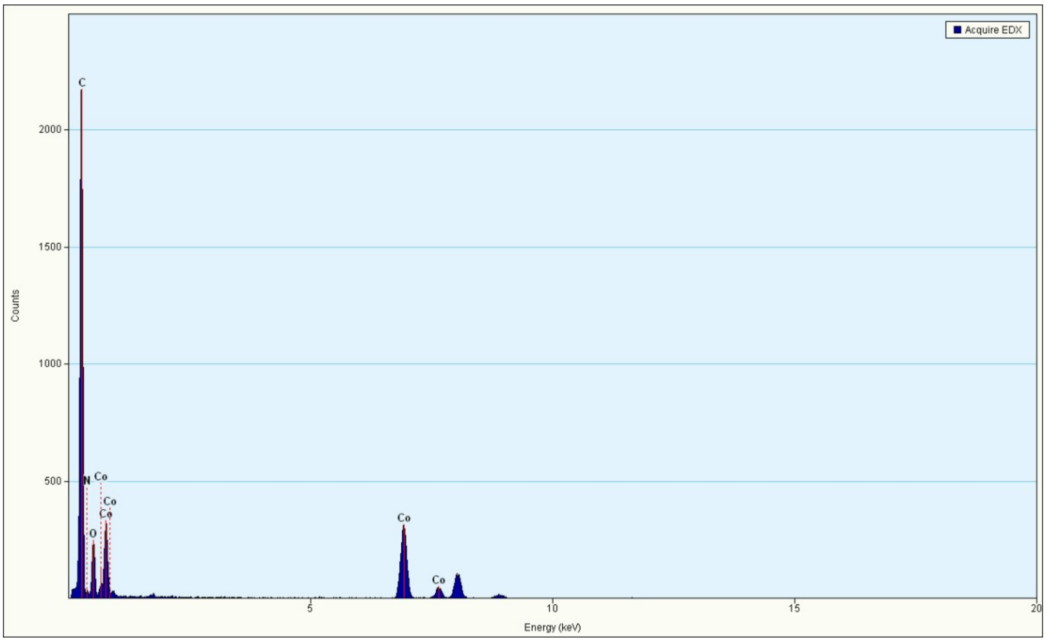


Fig. S2 EDX-mapping of Co-CoO$_x$/NCS-600.

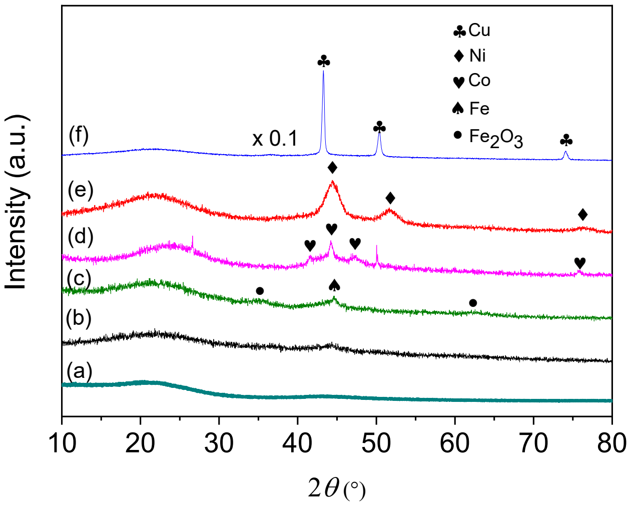


Fig. S3 XRD patterns of (a) NCS-600, (b) Co-CoO_x/NCS-600, (c) Ni/NCS-600, (d) Co/CB-600, (e) Fe/NCS-600 and (f) Cu/NCS-600.

Table S2 Chemical compositions of Co-CoO$_x$/NCS-*x* catalysts.[a]

Catalysts	Relative atomic percentage (%)			Atomic concentration (%)			
	Pyridinic N	Pyrrolic N	Graphitic N	C	N	O	Co
Co-CoO$_x$/NCS-400	99.9	0.1	0.1	73.4	5.2	19.6	1.76
Co-CoO$_x$/NCS-500	71.6	28.3	0.1	79.4	2.8	16.1	1.69
Co-CoO$_x$/NCS-600	44.1	44.7	11.2	80.8	1.7	15.6	1.89
Co-CoO$_x$/NCS-700	33.5	14.9	51.5	85.6	1.5	12.0	0.91

[a] Atomic concentrations were detected in XPS analysis.

Table S3 Influence of acetylacetone adding on transfer hydrogenation of phenol.

Catalyst	Acetylacetone /Co(mole ratio)	Con.%	Cyclohexanol selectivity (%)
Co-CoO$_x$/NCS-600	0	98.5	96.9
	0.2	37.2	96.5

Reaction conditions: phenol (0.1 mmol), catalyst (20 mg), 2-PrOH (5 mL), 200 °C, 3h, 1 MPa N_2.

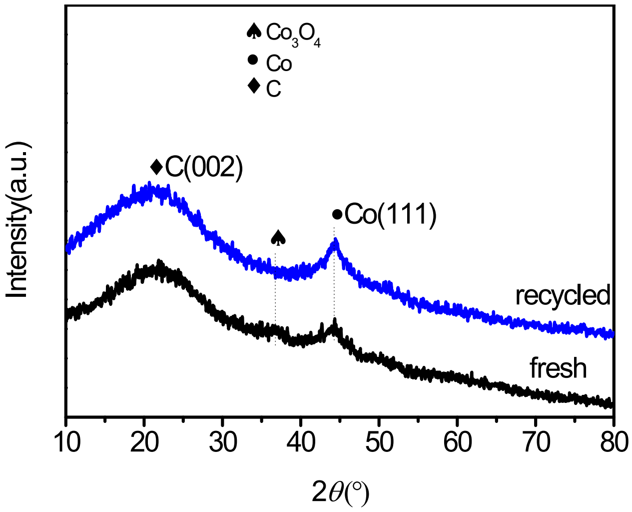


Fig. S4 XRD patterns of fresh and recycled Co-CoO_x/NCS-600.

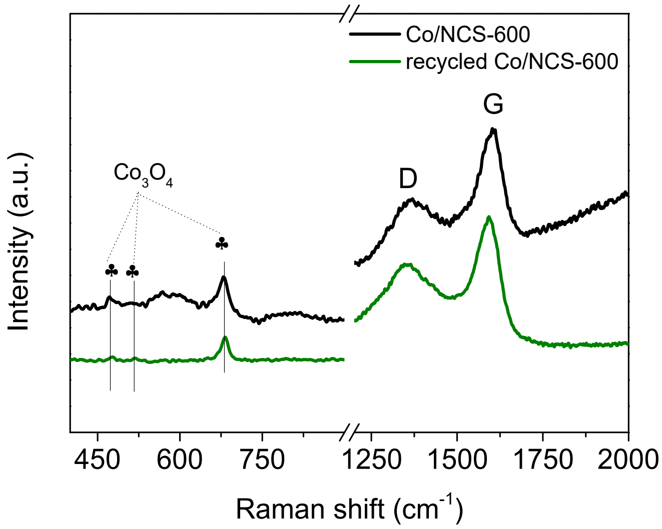
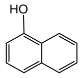
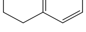
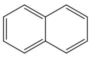
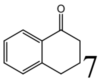
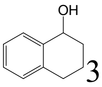
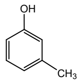
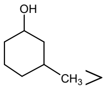
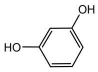
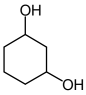
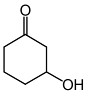
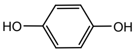
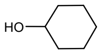
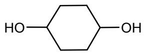


Fig. S5 Raman spectra of fresh and recycled Co-CoO$_x$/NCS-600.

Table S4 CTH of phenols over Co-CoO$_x$/NCS-600.

Substrate	t / h	Con./ %	Sel./ %
	5	93.5	 50.3  12.2  7.3  30.3
	5	92.4	 >99
	5	47.9	 95.2  4.8
	3	100	 34.6  65.4

Reaction conditions: substrate (0.1 mmol), Co-CoO$_x$/NCS-600 (80 mg), 2-PrOH (20 mL), 200 ^{o}C, 1 MPa N_2.

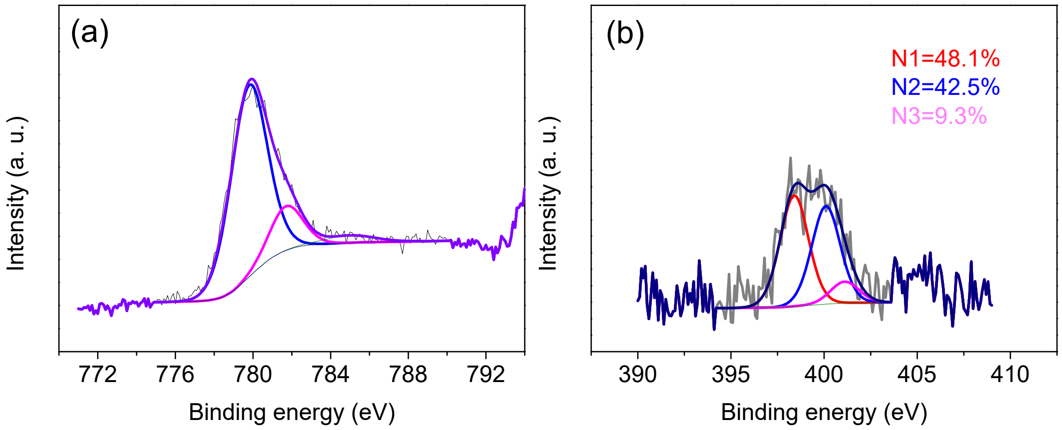


Fig. S6 (a) Co 2p and (b) N1s XPS spectra of Co_3O_4/NCS-600.

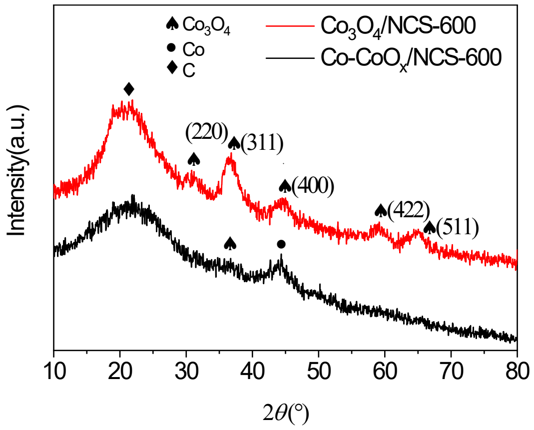


Fig. S7 (a) XRD patterns of Co-CoO$_x$/NCS-600 and Co$_3$O$_4$/NCS-600.

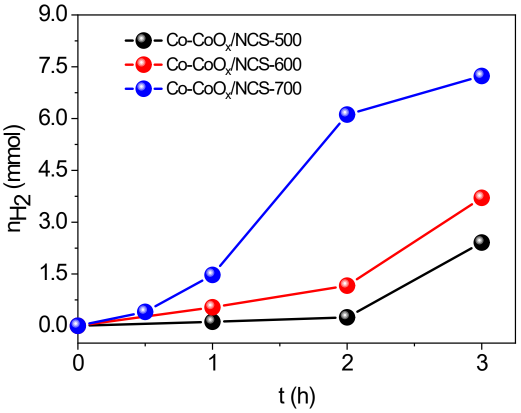


Fig. S8 The dehydrogenation activity towards 2-PrOH over different catalysts. Reaction conditions: catalyst (20 mg), 2-PrOH (5 mL), 200 °C, 3h, 1 atm N_2.

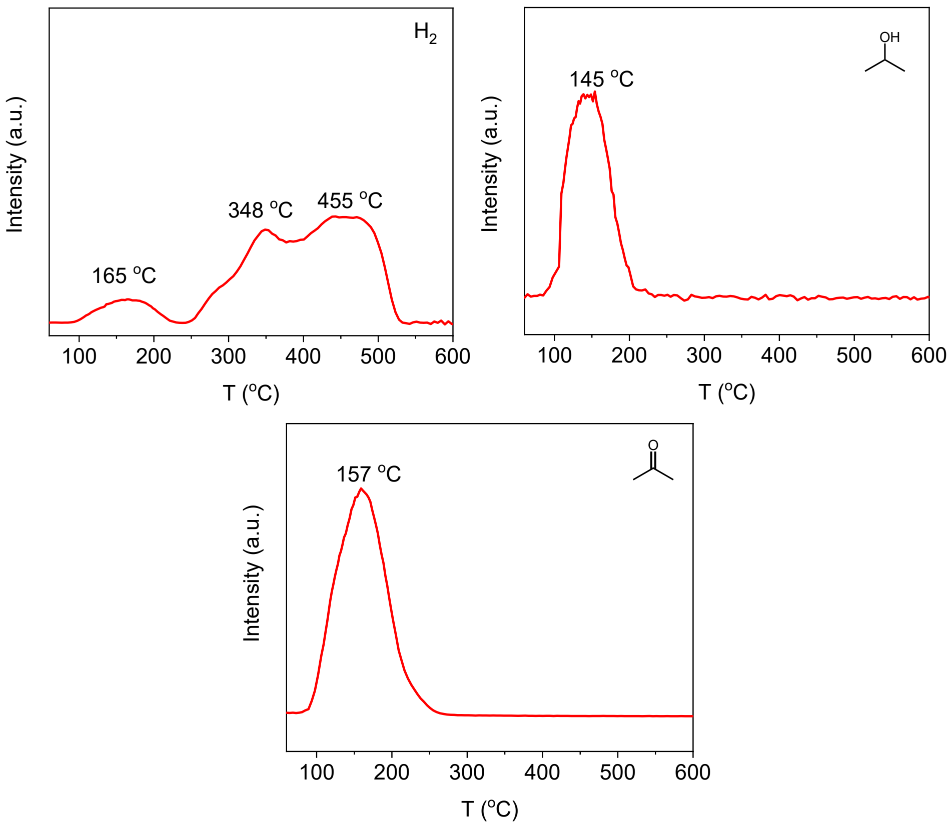


Fig. S9 TPSR-MS spectra of 2-PrOH over Co-CoO_x/NCS-600.

During the TPSR-MS procedure, apart from that unreacted 2-PrOH could be detected at 145 °C, 2-PrOH went through dehydrogenation and the corresponding desorption peaks were observed at 157 °C, which can be proved by the desorption signals of H_2. However, H_2 desorption peak was in range of 100-550 °C, which was wide and hysteretic than that of acetone desorption peak, suggesting the existence of intimate interaction between as-formed H_2 and catalyst.