# Electronic Supplementary Information

## Conversion of Metal−Organic Framework to N-doped Porous Carbon Incorporating Co and CoO Nanoparticles: Direct Oxidation of Alcohols to Esters

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## Section 1. Materials and Instrumentation

All chemicals were from commercial and used without further purification: cobaltous nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%, Sigma-Aldrich), 2-methylimidazole (99.0%, Sinopharm Chemical Reagent Co., Ltd.), benzyl alcohol (98%, Energy Chemical), $K_2CO_3$ (Sinopharm Chemical Reagent Co., Ltd., >99%), 1-heptane (99.0%, Sinopharm Chemical Reagent Co., Ltd.), 4-nitrobenaylalcohol (99.5%, Energy Chemical), (4-bromophenyl)methanol (98%, Energy Chemical), 4-methoxybenzyl alcohol (99%, Energy Chemical), 1,4-benzenedimethanol (99%, Aladdin), p-tolylmethanol (98%, Energy Chemical), 4-methoxybenzyl alcohol (99%, Energy Chemical), 2-phenylethanol (99%, Energy Chemical), 2-thiophenemethanol (>99.0%, TCI), furfuryl alcohol (98%, Energy Chemical), methyl benzoate (99.7%, Sigma-Aldrich), ethyl benzoate (99.7%, Sigma-Aldrich), methyl 4-bromobenzoate (99%, Sigma-Aldrich), dodecane (99.9%, Sigma-Aldrich), methanol ($CH_3OH$, Sinopharm Chemical Reagent Co., Ltd., >99%) and ethanol ($C_2H_5OH$, Sinopharm Chemical Reagent Co., Ltd., >99%), 1-propanol (Sinopharm Chemical Reagent Co., Ltd., AR) and 1-butanol (Sinopharm Chemical Reagent Co., Ltd., AR) were used as received. De-ionized water with the specific resistance of 18.25 MΩ·cm was obtained by reversed osmosis followed by ion-exchange and filtration (Cleaned Water Treatment Co., Ltd., Hefei). Powder X-ray diffraction patterns (PXRD) 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 ($\lambda$ = 1.54 Å). 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), high-resolution TEM, energy-dispersive X-ray spectroscopy (EDS) and elemental mapping were acquired on JEOL-2011 and 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 content of nitrogen was measured by using a VarioELIII Elemental analyzer. The X-ray photoelectron spectroscopy (XPS) measurements were performed by using an ESCALAB 250Xi high-performance electron spectrometer using monochromatized AlKa (hν =1486.7 eV) as the excitation source. The temperature programmed reduction (TPR) was performed by micromeritics AutoChem Π 2920. The hydrogen consumption in the experiment was monitored by a thermal conductivity detector (TCD) upon raising the sample temperature from room temperature to 700 °C at a constant rate of 5 °C $min^{-1}$. The percentages of conversion and selectivity of catalytic products were determined by using a Shimadzu gas chromatograph (GC-2010 Plus with a 0.25 mm × 30 m Rtx®-5 capillary column and GC-MS System 7890A insert XL MSD 5975C) 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 measurement, the samples were dried overnight at 150 $^{o}$C (ZIF-67) and 160 °C (Co-CoO@N-doped porous carbon) under vacuum.

# Section 2. Experimental Section

## 2.1 Preparation of Catalysts

**Synthesis of ZIF-67:** In a typical synthesis, 0.45 g cobalt nitrate hexahydrate was dissolved in 3 mL of deionized (DI) water, then 5.50 g 2-methylimidazole (Hmim) was dissolved in 20 mL of DI water. The two solutions were mixed ($Co^{2+}$ : Hmim: $H_2O$ = 1: 58: 1100) and stirred for 6 h at room temperature, then the resulting purple precipitates were collected by centrifuging, washing with water and methanol subsequently for 3 times, and finally being dried in vacuum at 50 °C overnight. The activated ZIF-67 powder was obtained by activated at 150 °C for 24 h.

**Introducing dicyandiamide as additional nitrogen source into ZIF-67:** In a typical procedure, the activated ZIF-67 sample (500 mg) was immersed into 20 mL aqueous solution containing dicyandiamide (DCDA, 750 mg). Then, the suspension was put into a glass container at room temperature under reduced pressure for accelerating the introduction of DCDA molecules into the nanopores in ZIF-67. Once the completion of the solvent evaporation, the procedure was terminated, and the excess of DCDA was removed by thorough washing with water. Finally, the sample was dried at 80 °C overnight.

**Preparation of Co-CoO@N-doped porous carbon via pyrolysis of ZIF-67:** The activated ZIF-67 (500 mg) was placed into a porcelain boat, which was put in the middle of a quartz tube in a furnace and its one-end was charged with nitrogen gas. After air in the quartz tube was drained, the furnace was gradually heated from room temperature to the target temperature (500 °C~800 °C) with a heating rate of 5 °C/min under a continuous nitrogen flow of ~50 mL/min. After the calcination under the target temperature for desired time, followed by natural cooling down to room temperature, the resultant catalysts were obtained and denoted as NC-T-t (NC is denoted as nanocomposite, T refers to carbonization temperature and t represents carbonization time). The NC-700-3h-250-3h means that the NC-700-3h sample was further oxidized in air at 250 °C for 3 hours.

**Preparation of Co NPs supported on active carbon by impregnation method:**

Typically, 200 mg of active carbon (AC) was put in a porcelain crucible. Subsequently, 500 μL of hydrophilic aqueous $Co(NO_3)_2$ solution (2.50 M) was added dropwise and stirred with a glass rod for around 20 min until it became homogeneous. The resultant mash was dried at 80 °C for 12 h and then was treated in a stream of 20% $H_2$/Ar (40 mL/min) at 400 °C for 12 h to give Co/AC.

**Preparation of CoO NPs supported on Silica:** The $CoO/SiO_2$ nanocomposite catalyst was prepared by a three-step process. Typically, in the first step, 3 g of activated carbon was impregnated under magnetic stirring with 1.588 mL of tetraethoxysilane (TEOS, 3.52 mmol) diluted with 1.1 mL of 99% ethanol. The solution was completely absorbed by the activated carbon in 5 min under continuous stirring. Then the composite material was transferred into a muffle oven and annealed (heating rate 5 °C/min) at 350 °C for 30 min in air. During the heating process, the activated carbon was stable and no burn-off was observed. Black solid powder ($C\text{-}SiO_2$) was collected after the annealing process. In the second step, the above black solid powder ($C\text{-}SiO_2$) composite material was added to 1.90 mL of $Co(NO_3)_2$ aqueous solution (3.75 M) under magnetic stirring. The $Co(NO_3)_2$ solution was completely absorbed by the $C\text{-}SiO_2$ composite material during vigorous stirring for 15 min. The resulting solid was transferred into a muffle oven and calcined at 550 °C (heating rate 5 °C /min) for 90 min in air. Black solid powder ($Co_3O_4\text{-}SiO_2$) was collected after the annealing process. Finally, the above black solid powder ($Co_3O_4\text{-}SiO_2$) composite material was transferred into a muffle oven and calcined at 950 °C (heating rate 5 °C /min) for 3 h in $N_2$ atmosphere.

## 2.2 Catalytic Performance Investigations

**Methyl esterification of benzyl alcohol and methanol:** The Co-CoO@N-doped porous carbon catalyst (25 mg) or Co/AC (25 mg) or CoO (10 mg) and $K_2CO_3$ (27.6 mg, 0.2 mmol) were charged into a dried double-necked round bottom flask. Then, 8 mL $CH_3OH$ and 1 mmol benzyl alcohol were added sequentially. The reflux condenser was connected to the round bottom flask and the reaction was stirred violently and refluxed at 80 °C for 12 hours under $O_2$ bubbling. After cooling the reaction mixture to room temperature, 1 mmol dodecane as internal standard was added and the mixture was diluted with ethyl acetate. The reaction conversion and selectivity were determined by GC-FID and compared with authentic samples. In the comparative experiments of Co/AC and $CoO/SiO_2$ used as catalysts, the total amount of cobalt in the catalyst was kept consistent.

For methyl esterification of benzyl alcohol, the reaction was scaled up by factor 4 and the corresponding methyl benzoate was isolated. Upon the completion of the reaction, the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The solvent was evaporated and the reaction product was treated with water. The mixture was then extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$. After removing the solvent, the residue gives the ester as an oily liquid (yield: 525 mg, 96%). Methyl benzoate $^1$H NMR (400 MHz, $CDCl_3$): d 8.03 (d, 2H), d 7.49 (m, 3H), d 3.89 (s, 3H) (Fig. S11).

**The detection of benzoic acid:** The reaction of methyl esterification of benzyl alcohol was scaled up by factor 4. Upon the completion of the reaction, the solid catalyst was filtered off and washed thoroughly with water. The solvent was extracted by ethyl acetate for three times. The water phase solution was acidified (pH ≈ 2-3) with diluted HCl was detected. The mixture was then extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$. After removing the solvent, the product was detected by GC and that indicated the absence of benzoic acid.

**Recyclability investigation:** The reusability of NC-700-3h catalyst was tested for the methyl esterification of benzyl alcohol and methanol. Upon the completion of the reaction, the catalyst was collected by an external magnet. The recovered catalyst was washed with methanol for several times, and then reused for a consecutive reaction with fresh benzyl alcohol and methanol.

**Methyl esterification of the derivatives of benzyl alcohol and methanol:** The NC-700-3h catalyst (25 mg) and $K_2CO_3$ (27.6 mg, 0.2 mmol) were charged into a dried double-necked round bottom flask. Then, 8 mL $CH_3OH$ and 1 mmol the derivative of benzyl alcohol were added sequentially. The reflux condenser was connected to the round bottom flask and the reaction was stirred violently and refluxed at 80 °C for 24 hours under $O_2$ bubbling. After cooling the reaction mixture to room temperature, 1 mmol dodecane as internal standard was added and the mixture was diluted with ethyl acetate. The reaction conversion and selectivity were determined by GC-MS (in the absence of corresponding authentic products) or by GC-FID via comparing with authentic samples.

As a representative, the methyl esterification of 4-bromobenzyl alcohol was scaled up by factor 4 and the corresponding methyl benzoate was isolated. Upon the completion of the reaction, the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The solvent was evaporated and the reaction product was treated with water. The mixture was then extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$. After removing the solvent, the residue was purified with column chromatography (silica gel, ethyl acetate : $CH_2Cl_2$ = 1:5) to give the ester as a white solid (yield: 658 mg, 77%). Methyl 4-bromobenzoate $^1H$ NMR (400 MHz, $CDCl_3$): d 7.88 (d, 2H), d 7.56 (d, 2H), d 3.90 (s, 3H) (Fig. S12).

**Oxidative alkyl esterification:** The NC-700-3h catalyst (25 mg) and $K_2CO_3$ (55.2 mg, 0.4 mmol) were charged into a dried double-necked round bottom flask. Then, 6 mL *n*-heptane, ethanol or other aliphatic alcohols (1.5 mL) and 1 mmol benzyl alcohol or its derivatives were added sequentially. The reflux condenser was connected to the round bottom flask and the reaction was stirred violently and refluxed at 100 $^{o}C$ for 24 hours (unless otherwise stated) under $O_2$ bubbling. After cooling the reaction mixture to room temperature, 1 mmol dodecane as internal standard was added and the mixture was diluted with ethyl acetate. The reaction conversion and selectivity were determined by GC-MS (in the absence of corresponding authentic products) or by GC-FID via comparing with authentic samples.

As a representative, the ethyl esterification of benzyl alcohol was scaled up by factor 4 and the corresponding methyl benzoate was isolated. Upon the completion of the reaction, the solid catalyst was filtered off and washed thoroughly with ethyl acetate. The solvent was evaporated and the reaction product was treated with water. The mixture was then extracted with ethyl acetate, the combined organic layers were dried over $MgSO_4$. After removing the solvent, the residue was purified with column chromatography (silica gel, ethyl acetate : $CH_2Cl_2$ = 1:10) to give the ester as an oil liquid (yield: 565 mg, 94%). Ethyl benzoate $^1$H NMR (400 MHz, $CDCl_3$): d 8.05 (m, 2H), d 7.56 (m, 3H), d 4.39 (q, 2H), d 1.38 (t, 3H) (Fig. S13).

**Oxidative self-esterification of aliphatic alcohols:** The NC-700-3h catalyst (60 mg) and $K_2CO_3$ (276 mg, 2 mmol) were charged into a dried double-necked round bottom flask. Then, 8 mL *n*-heptane and aliphatic alcohols (2 mmol) were added sequentially. The reflux condenser was connected to the round bottom flask and the reaction was stirred violently and refluxed at 100 $^oC$ for 24 hours (unless otherwise stated) under $O_2$ bubbling. The reaction conversion and selectivity were determined by GC-MS (in the absence of corresponding authentic products) or by GC-FID via comparing with authentic samples.

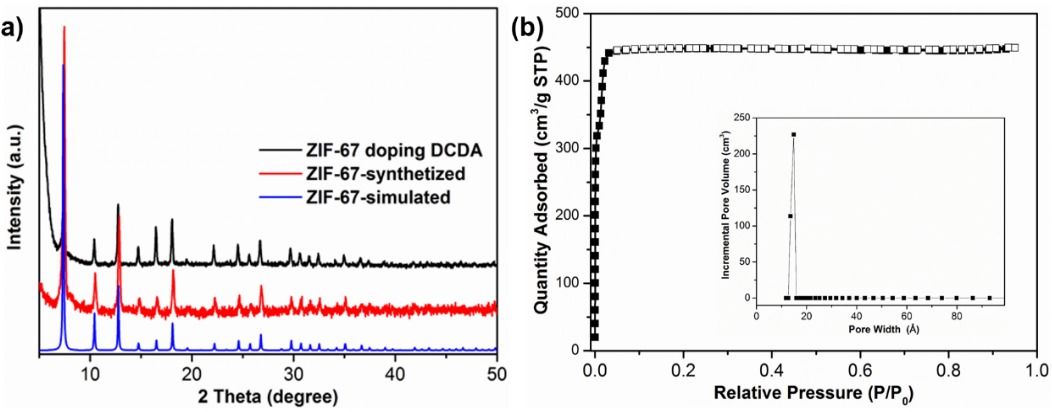


**Fig. S1** (a) Powder XRD patterns of as-prepared ZIF-67 and ZIF-67-DCDA, in good agreement with the simulated ones. (b) Nitrogen adsorption and desorption isotherms for ZIF-67 at 77 K. Inset: pore size distribution based on the DFT method.

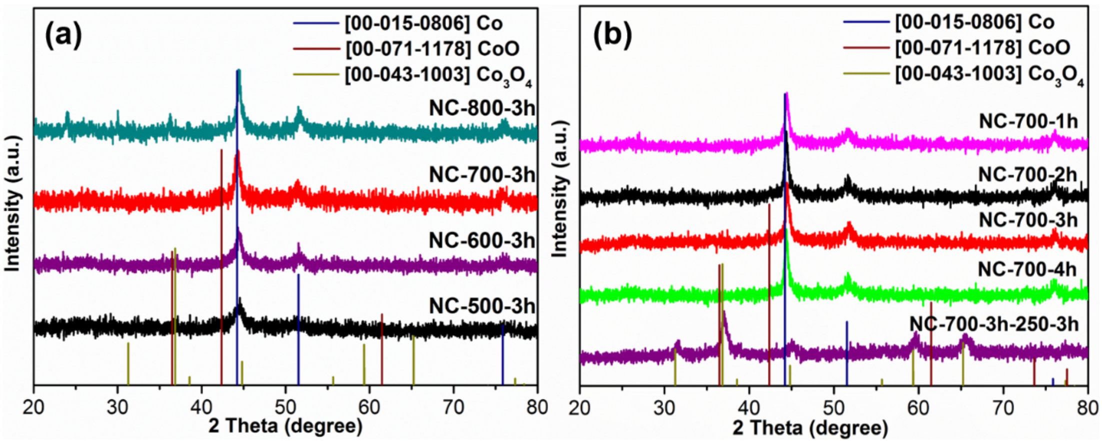


**Fig. S2** Powder XRD patterns for the samples after (a) pyrolysis of ZIF-67 in $N_2$ atmosphere at different temperatures for 3 h and (b) pyrolysis of ZIF-67 at 700 °C in $N_2$ atmosphere for different time, and further calcination treatment. All powder XRD patterns (except for NC-700-3h-250-3h) show weak broad peak at ~25° assigned to carbon from the organic moiety and three sharp characteristic peaks for metallic β-Co at $2\theta = 44.38°$ (111), 51.60° (200) and 75.68° (220) (associated with standard JCPDS card no. 00-043-0806), while no peak assignable to CoO (standard JCPDS card no. 00-071-1178) or $Co_3O_4$ species. In contrast, NC-700-3h-250-3h shows peaks well match to $Co_3O_4$ (standard JCPDS card no. 00-043-1003), while no peak assignable to Co species.

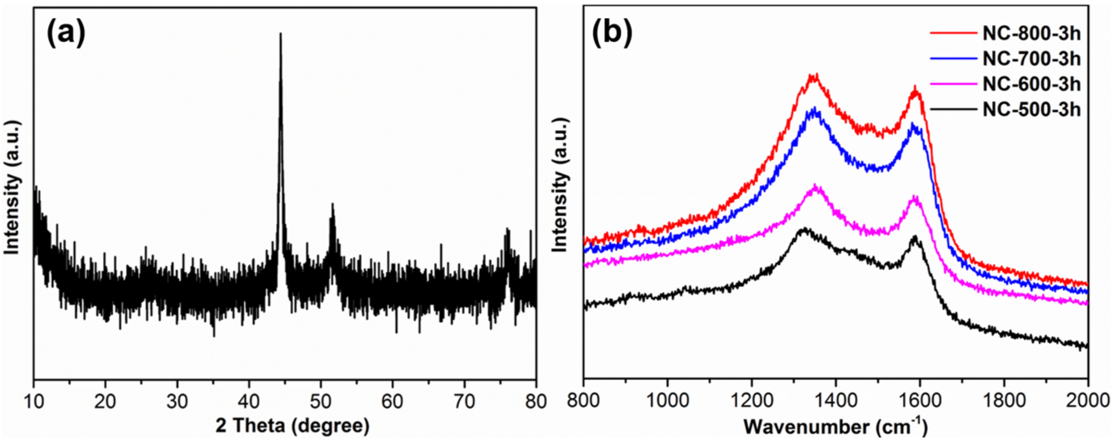


**Fig. S3** (a) Powder XRD pattern for NC-700-3h, clearly showing the weak broad peak at ~26° assigned to the typical (002) diffraction of graphitic carbon. (b) Raman spectra for the samples after pyrolysis of ZIF-67 in $N_2$ atmosphere at different temperatures for 3 h.

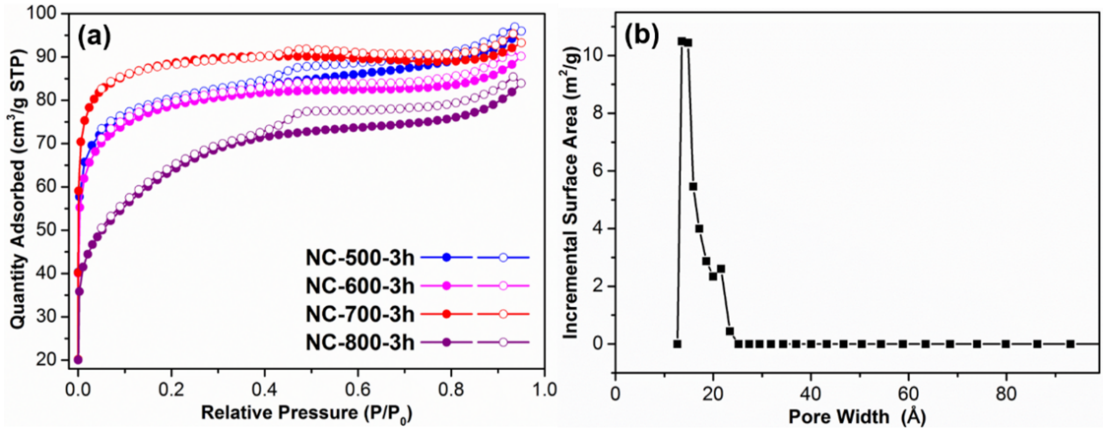


**Fig. S4** (a) Nitrogen adsorption and desorption isotherms for Co-CoO@N-doped porous carbon nanocomposites at 77 K. (b) Pore size distribution analysis for NC-700-3h (DFT method).

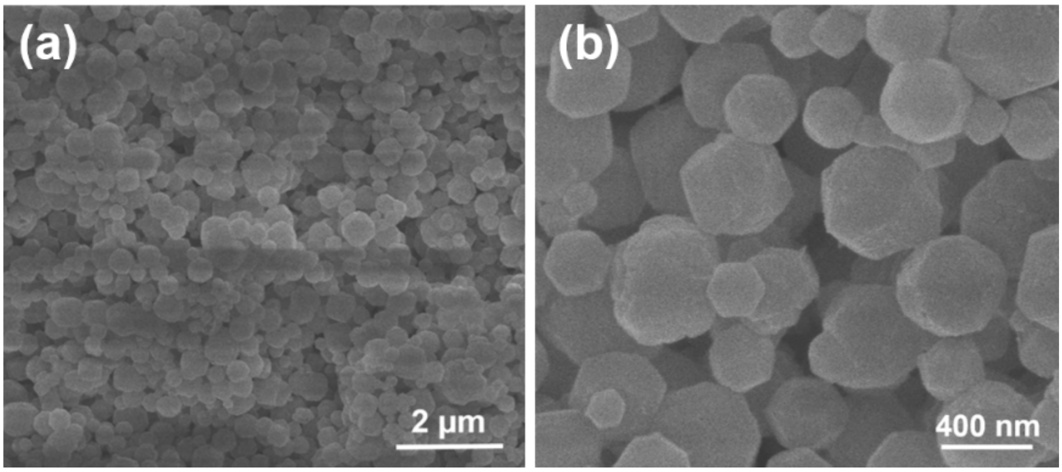


**Fig. S5** SEM images for monodisperse polyhedral nanocrystals of ZIF-67 showing their sizes of 200-500 nm.

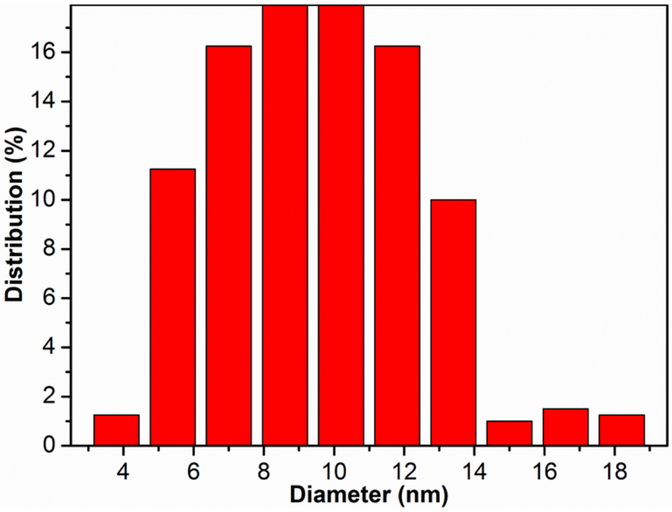


**Fig. S6** Size distributions of Co NPs with surface-oxidized CoO species in NC-700-3h.

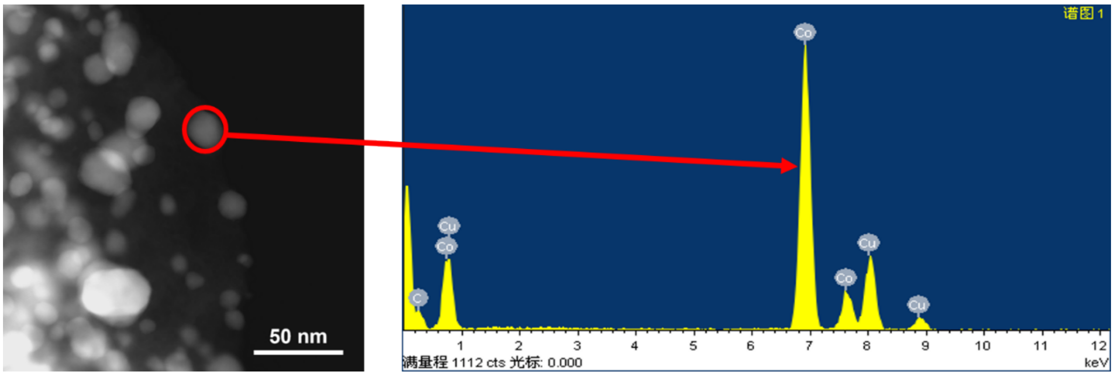


**Fig. S7** EDX analysis (right) for the particle indicated in the left image.

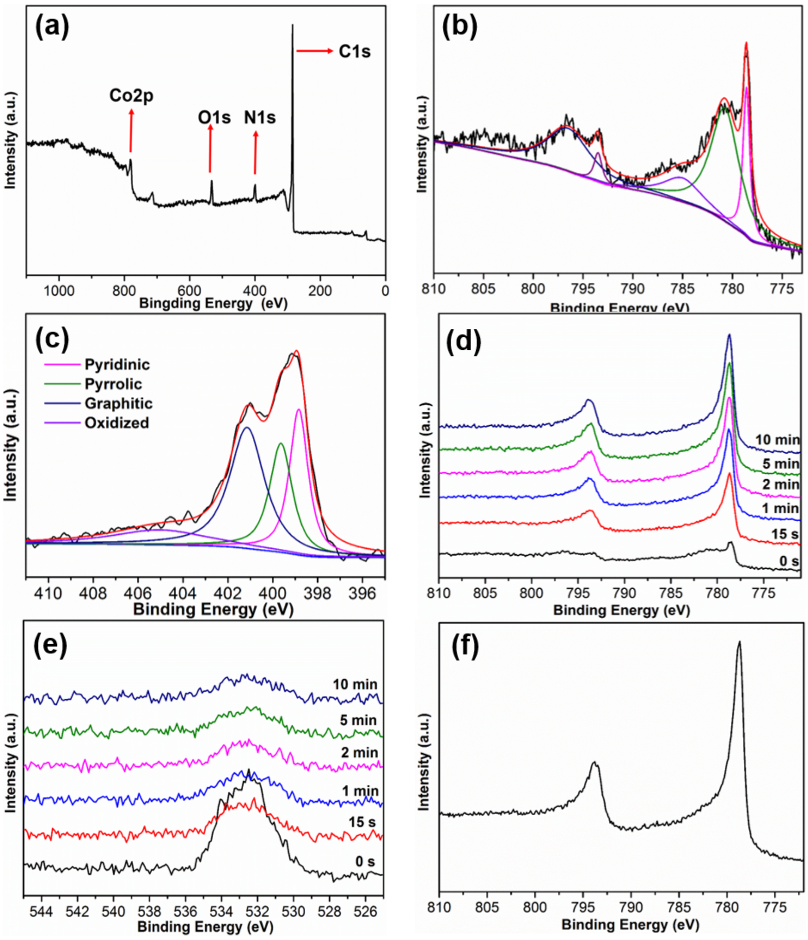


**Fig. S8** (a) XPS survey spectrum for NC-700-3h. High-resolution XPS survey spectra of (b) Co 2p and (c) N 1s for NC-700-3h without Ar ionic sputtering. High-resolution XPS survey spectra of (d) Co 2p and (e) O1s for NC-700-3h after Ar ionic sputtering for different times. (f) A close look at the XPS spectrum of Co 2p in NC-700-3h after Ar ionic sputtering for only 15s.

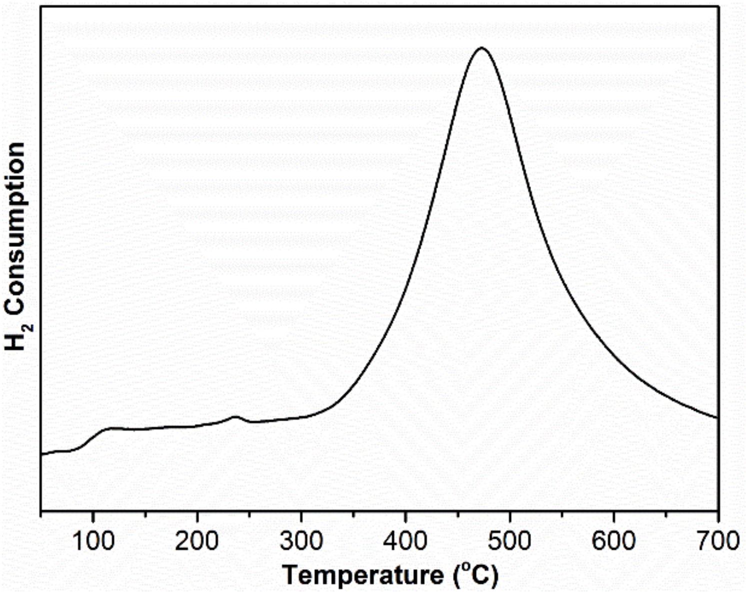


**Fig. S9** TPR profile of NC-700-3h showing the reduction of $Co^{2+}$ ions to metallic cobalt.

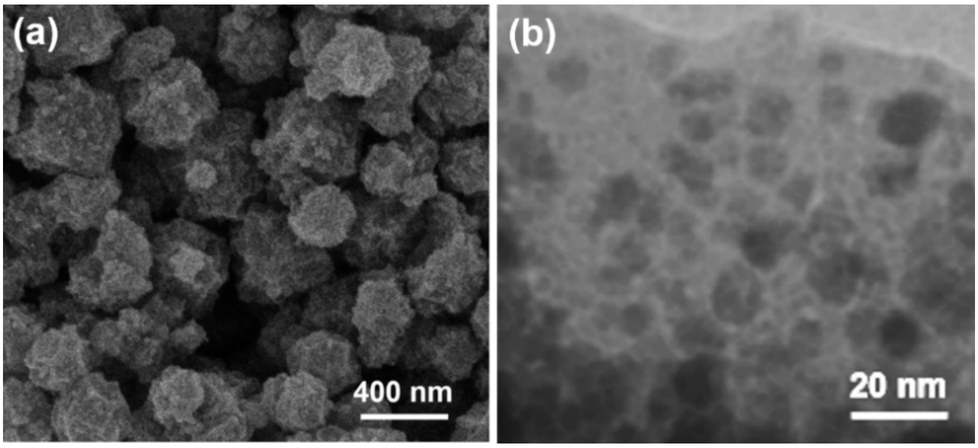


**Fig. S10** (a) SEM and (b) TEM images for NC-700-3h after catalysis, demonstrating (a) the retained monodispersion and shape of the whole particle, as well as (b) the absence of aggregation of metal (oxide) NPs after catalysis.

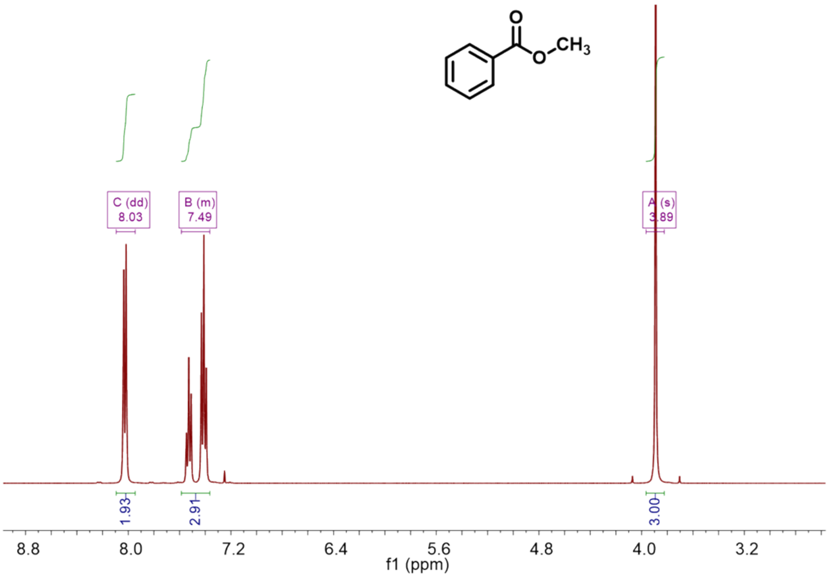


**Fig. S11** $^1$H NMR (400 MHz, CDCl$_3$) spectrum for isolated methyl benzoate: d 8.03 (d, 2H), d 7.49 (m, 3H), d 3.89 (s, 3H).

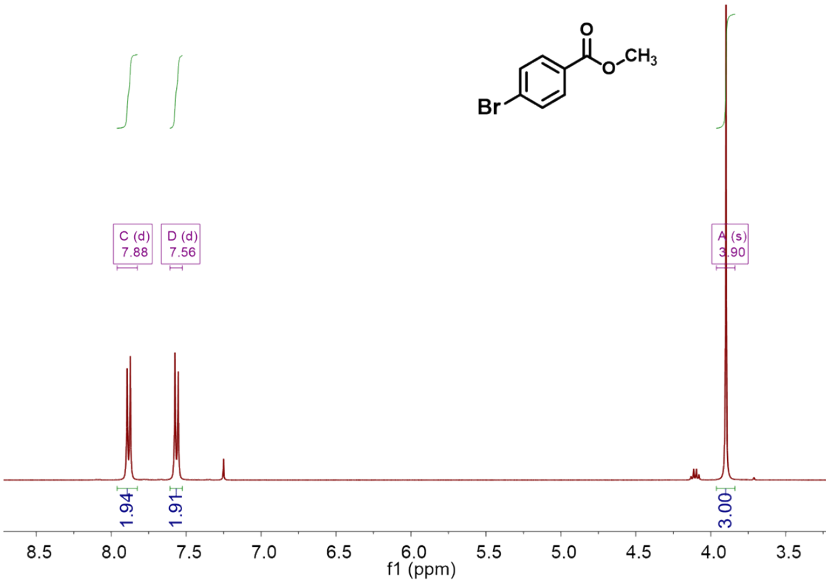


**Fig. S12** $^1$H NMR (400 MHz, CDCl$_3$) spectrum for isolated methyl 4-bromobenzoate: d 7.88 (d, 2H), d 7.56 (d, 2H), d 3.90 (s, 3H).

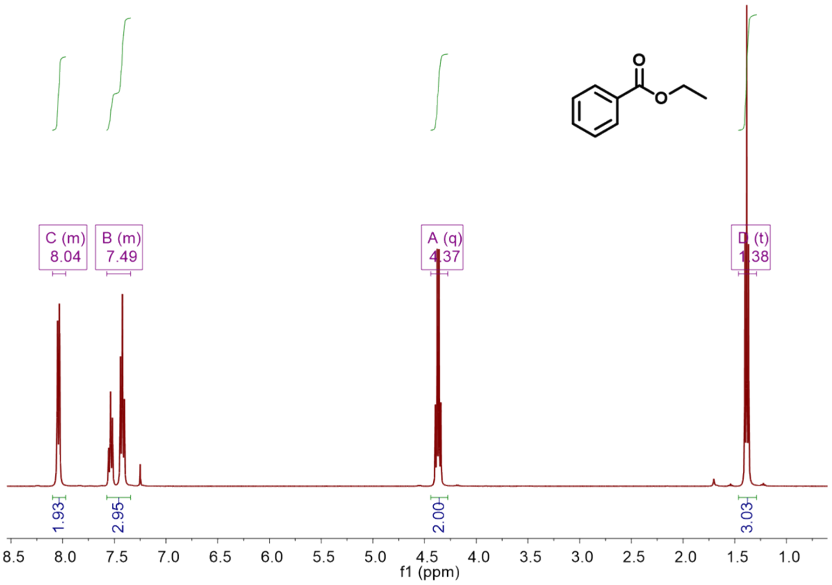
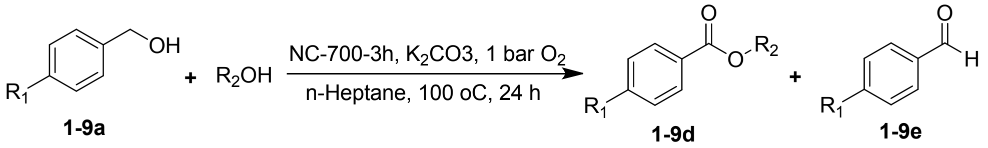


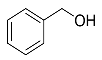
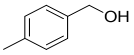
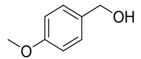
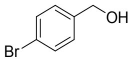
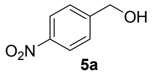
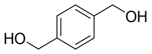
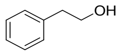
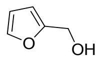
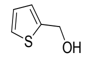
**Fig. S13** $^1$H NMR (400 MHz, $CDCl_3$) spectrum for isolated ethyl benzoate: d 8.05 (m, 2H), d 7.56 (m, 3H), d 4.39 (q, 2H), d 1.38 (t, 3H).

**Table S1** ICP-AES and elemental analysis results for the contents of Co and N in Co-CoO@N-doped porous carbon.

| Co-CoO@N-doped Carbon | Co content (%) | N content (%) |
|---|---|---|
| NC-500-3h | 21.6 | 9.23 |
| NC-600-3h | 29 | 6.22 |
| NC-700-3h | 32.89 | 5.01 |
| NC-700-3h with higher N contents | - | 7.02 |
| NC-800-3h | 39.69 | 3.10 |

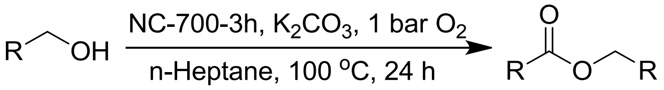
**Table S2** Catalytic synthesis of alkyl esters of benzyic alcohols over NC-700-3h.[a]



| Entry | R1 | Conversion (%)[b] | Selectivity (%)[b] | |
|---|---|---|---|---|
| | | | 1-9d | 1-9e |
| 1 |  <br>1a | 99 | 98 | 2 |
| 2[c] | | 99 | 95 | 5 |
| 3[d] | | 97.5 | 91 | 9 |
| 4[e] | | 77 | 100 | 0 |
| 5 |  <br>2a | 92 | 97 | 3 |
| 6 |  <br>3a | 91 | 97.6 | 2.4 |
| 7 |  <br>4a | 89 | 89 | 11 |
| 8 |  <br>5a | 79 | 90 | 10 |
| 9[f] |  <br>6a | 88 | 87 | 13 |
| 10 |  <br>7a | 89 | 88 | 12 |
| 11 |  <br>8a | 88 | 85 | 15 |
| 12 |  <br>9a | 79 | 79 | 21 |

[a]Reaction conditions: 1 mmol benzyl alcohol or its derivatives (**1a**), $R_2OH$ (1.5 mL): ethanol or [c]1-propanol or [d]1-butanol as aliphatic alcohol, NC-700-3h (25 mg), 0.4 mmol $K_2CO_3$, 6 mL *n*-Heptane otherwise mentioned, 1 mmol dodecane was added as an internal standard. [b]Determined by GC or GC-MS. [e]In the absence of $R_2OH$, self-esterification of benzyl alcohol and 1equiv. $K_2CO_3$ as base. [f]0.4 mmol $K_2CO_3$, and the product is diethyl terephthalate.

**Table S3** The oxidative esterification of aliphatic alcohols over NC-700-3h catalyst.[a]



| Entry | Aliphatic alcohol | Conversion (%)[b] |
|---|---|---|
| 1 | ethanol | 54.2 |
| 2 | 1-propanol | 57.6 |
| 3 | 1-butanol | 59.8 |

[a]Reagents and reaction conditions: 2 mmol ethanol, 2 mmol $K_2CO_3$, NC-700-3h (60 mg), 8 mL *n*-Heptane, 1 mmol dodecane was added as an internal standard. [b]Determined by GC or GC-MS.

## Reference

**Complete 5c:** P. Nugent, Y. Belmabkhout, S. D. Burd, A. J. Cairns, R. Luebke, K. Forrest, T. Pham, S. Ma, B. Space, L. Wojtas, M. Eddaoudi and M. J. Zaworotko, *Nature*, 2013, **495**, 80.