.

Supporting information

Formic acid enabled selectivity boosting in transfer hydrogenation of 5-hydroxymethylfurfural to 2,5-furandimethanol on highly dispersed Co-N$_x$ sites

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Experimental Procedures

Materials

1,10-phenanthroline (99%) was purchased from Innochem, China. Poly(enthylene glycol)-block-poly(propylene glycol)-block-poly(enthylene glycol) (P123, Mn~5800) was purchased from Sigma-Aldrich. FAL (99%), FOL (98%), Co(OAc)$_2$·4H$_2$O (99.9%), Ni(OAc)$_2$·4H$_2$O (99.9%), Cu(OAc)$_2$·H$_2$O (99%), Fe(OAc)$_2$ (99%), Pt/C (5 wt%), Pd/C (5 wt%), Ru/C (5 wt%), laevulinic acid (99%) were purchased from Aladdin Chemicals. FA (98%), 5-hydroxymethylfurfural (97%), 2,5-furandimethanol (98%), 2,5-dimethylfuran (99%) were purchased from Macklin, China. Tetraethyl orthosilicate (AR), HCl (36.0-38.0%), HF (≥40%), NaOH (AR), 1,4-dioxane (≥99.5%), methanol (≥99.5%), isopropanol (≥99.5%), ethanol (≥99.5%)，ethyl acetate (≥99.5%), dichloromethane (≥99.5%), cyclohexane (≥99.5%), DMF (≥99.5%) were purchased from Sinopharm Chemical Reagent Co. Ltd, China. All chemicals were used without any further treatment.

Catalyst preparation

Preparation of SBA-15

Pluronic polymer surfactant P123 was used as structure-directing agent. First, 6 g P123 was dissolved in the 200 g 1.6 M HCl aqueous solution, the resulting solution was stirred at 40°C until the

solution became clear. Then, 12.75 g TEOS was added dropwise into this solution under stirring. The mixture was kept under stirring at 40°C for 12 h. This mixed solution was then transferred into a Teflon-lined autoclave and heated to and kept at 100°C for 24 h. Finally, white precipitates were collected, filtered and washed with water, dried, and calcined at 550°C for 6 h at a heating rate of 4°C/min in a tube furnace to remove the organic template.

Preparation of Co-MNC catalysts

Co-NC-A catalyst was prepared via pyrolysis of the mixture of $Co(phen)_2(OAc)_2$ and SBA-15 in nitrogen atmosphere. Typically, $Co(OAc)_2 \cdot 4H_2O$ (124 mg) and 1,10-phenanthroline monohydrate (198 mg) were added into 25 mL ethanol to form a transparent solution. After that, SBA-15 (0.2495 g) was added and the suspension was sonicated for 10 min. The mixture was stirred at 60 °C overnight. After ethanol was removed by rotary evaporation, the solid was dried, and heated to a 700 °C in N_2 atmosphere at a heating rate of 2 °C /min and kept for 2 h. The calcinated solid was treated by HF and HCl solution in order to completely remove SBA-15 and soluble cobalt species. The resulting sample was thoroughly washed with DI water until free of Co^{2+}, dried and named as Co-NC-A. For comparison, the calcinated solid was soaked with NaOH to remove SBA-15 to give a catalyst abbreviated as Co-NC-B. Replacing cobalt acetate with nickel acetate, ferric acetate or copper acetate gave rise to Ni- NC-A, Fe- NC-A or Cu-NC-A, respectively.

Adsorption test

10 mg of Co-NC-A was added into a 10 mL of HMF dioxane solution with an initial concentration of 4.6μg/mL and stirred for 1h. The supernatant was then obtained by centrifugation and analyzed by a Agilent 8453 Ultraviolet-visible Spectrophotometer. The amount of adsorbed HMF was calculated according to the equation: the amount of adsorbed HMF = $(c_0-c_r) \times V_0/m_c$. Here c_0 is the initial concentration of HMF, c_r is the residual HMF concentration after adsorption, V_0 is the volume of solution, and m_c is the mass of catalyst. Replacing HMF with FDM gave rise to the adsorption test of FDM.

Characterizations

Powder X-ray diffraction (XRD) was carried out with Ni-filtered Cu Kα (λ=0.154 nm) operating

at 40 kV and 30 mA on a Bruker D8 diffractometer. N_2 adsorption was carried out at 77 K using an auto-adsorption analyzer (Micromeritics, 3Flex). Transmission electron microscope (TEM) images were obtained using an accelerating voltage of 200 kV on a JEOL 2100F Transmission Electron Microscope. X-ray photoelectron spectra (XPS) were recorded on a Thermo Scientific ESCALab 250Xi employing a 200 W monochromatic Al Kα radiation (hv=1486.6 eV). C1s at 284.6 eV was used for calibrating the XPS spectra. H_2-TPD was measured by a FineSorb-3010 equipped with a thermal conductivity detector (TCD, Zhejiang Finetec Instruments Co., Ltd) in the temperature range of 50-500 °C at a ramping rate of 10 °C /min.

Catalytic reactions

The reactions were carried out in an autoclave (8 mL) purchased from Zhengxin, China. In a typical run, 30 mg HMF, 20 mg catalyst, a certain amount of FA and 3.5 mL solvent were added into the autoclave. The sealed autoclave was purged, pressurized with N_2 to 0.5 MPa and heated to the treatment temperature under magnetic stirring (500 rpm). After the completion of reaction, the autoclave was quickly soaked within cold water. The liquid was diluted with methanol. The products and substrate were analyzed by high performance liquid chromatography (HPLC). The catalyst was successively washed by methanol for 3 times and then dried at 60°C for 12 h. The recovered catalyst was submitted to the next batch of reaction.

Analysis method

HMF, FDM, FA and other by-products were quantitatively analyzed via high performance liquid chromatography (HPLC, Agilent 1100) with a colum (Aminex HPX-87H, 300 mm×7.8 mm I.D., Bio-Rad Laboratories, Inc.). The flow rate of mobile phase (5 mmol/L H_2SO_4) was 0.4 mL/min. The temperature of the column and the RID were 60 °C and 35 °C, respectively. Reactant mole conversions were obtained as the number of moles of reactant consumed divided by the initial number of moles of reactant added to the reactor. Selectivity was calculated by the number of moles of product recovered divided by the number of moles of reactant reacted. A quantitative analysis was performed using calibration curves for every compound in the mixture. All data were calculated by the average of three replicate experiments.
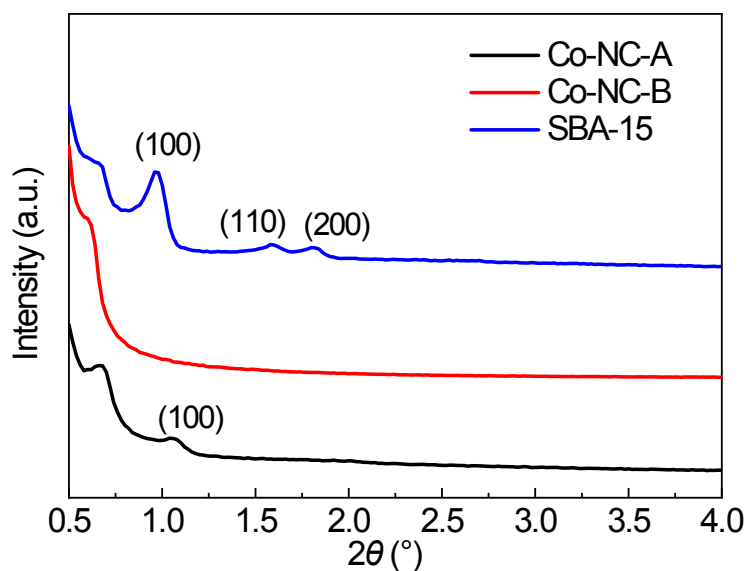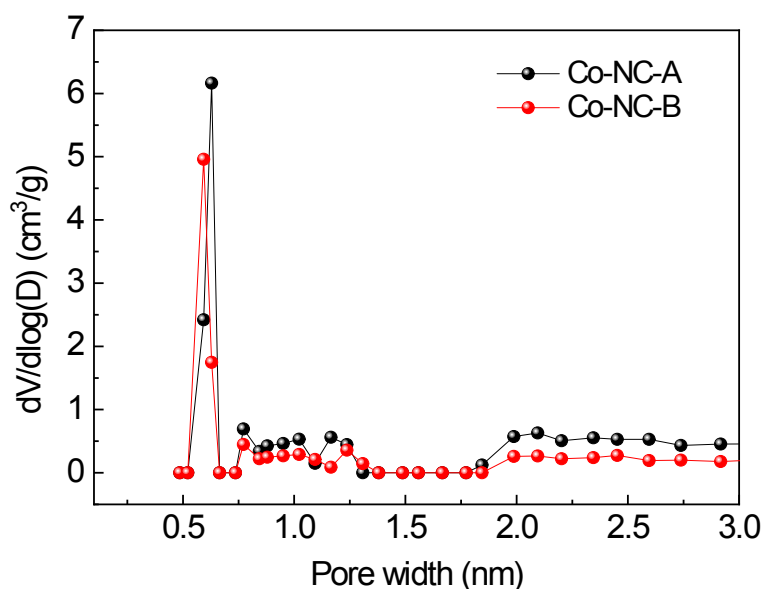
Fig. S1 SAXRD patterns of Co-NCs.

Fig. S2 Pore size distribution of Co-NCs.

Table S1 Physical properties of the Co-NCs.

Catalyst	Loading (wt%)[a]	S_{BET} (m^2/g)[b]	V (cm^3/g)[b]	D (nm)[b]
Co-NC-A	2.8	883.5	0.3	2.56
Co-NC-B	21.5	610.6	0.2	2.77
Co-NC-A(H)	2.4	-	-	-

[a] Detected by ICP-OES analysis.

[b] Detected by N_2 adsorption/desorption.

Table S2 Fitting parameters of Co 2p and N1s spectra for the Co-NCs.

Catalyst	Co^0	Co^{3+}	Co^{2+}	Pyridinic N	Pyridinic N-Co + pyrrolic N	Graphitic N	Pyridinic N oxide
Co-NC-A	7.6	42.6	38.7	33.3	41.9	16.6	8.1
Co-NC-B	0.6	58.8	40.6	31.7	52.3	9.0	7.0
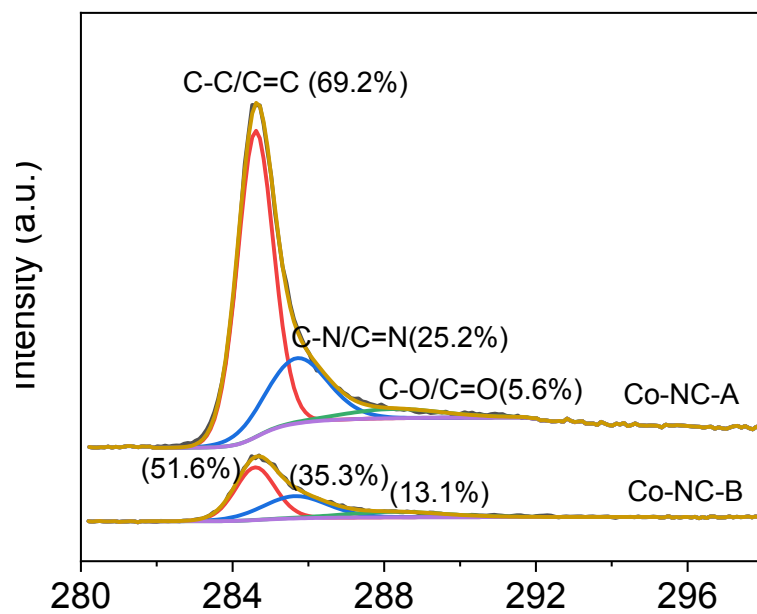
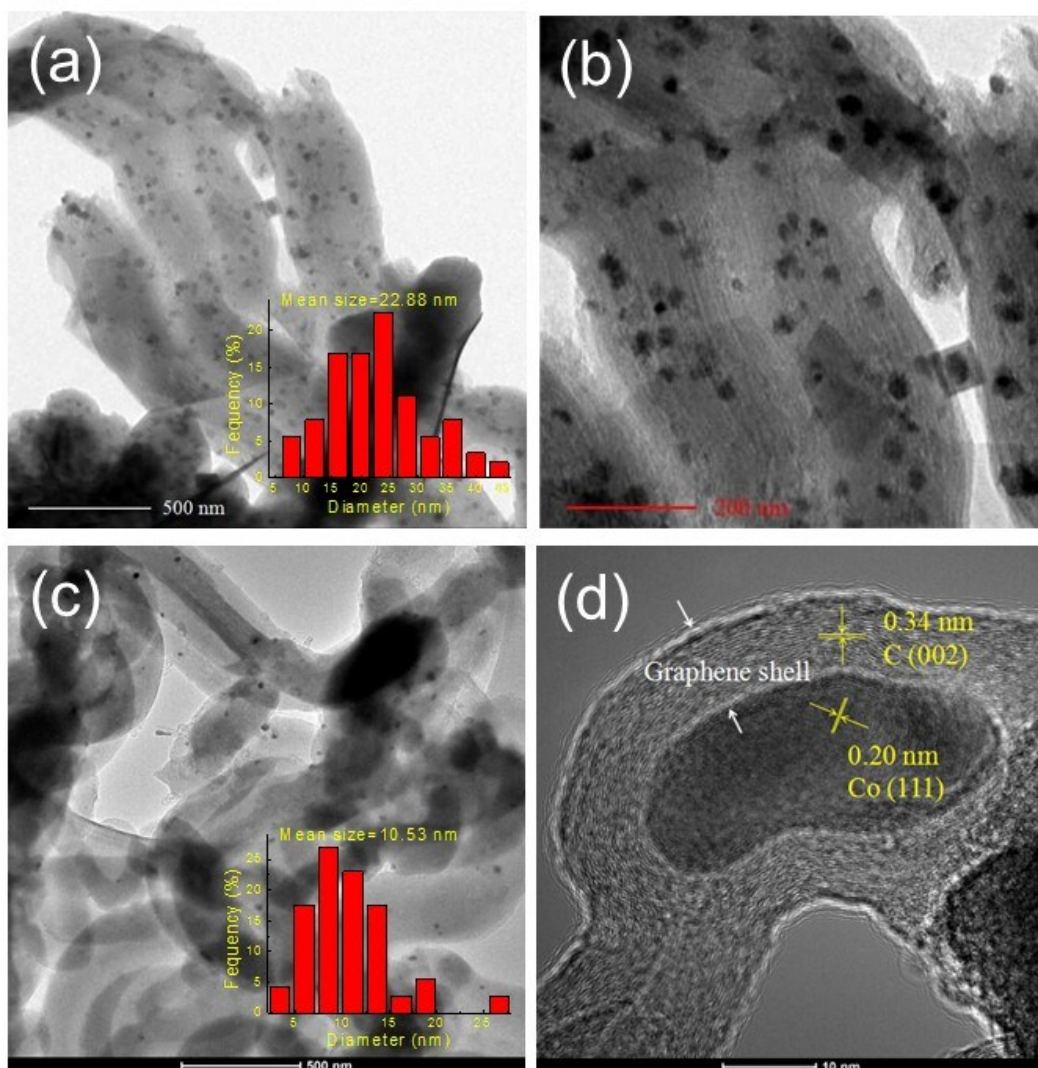**Fig. S3** C1s specta of Co-NC-A and Co-NC-B catalysts.

Fig. S4 TEM images of (a, b) Co-NC-B and (c, d) Co-NC-A.

Table S3 Representative works for FDA production from HMF.

| Catalysts	Hydrogen donor	Reaction conditions	Yield (%)	Ref.
Co-NC-A	Formic acid	HMF (30 mg), catalyst (20 mg), $n_{FA/HMF}$=7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N_2, **160 °C**, 10 h, 500 rpm	86.0%	This study
Pd/C	Formic acid	HMF (0.25 g, 2 mmol), formic acid (0.31 mL, 8 mmol), 0.2 g catalyst, 15 mL THF, heated at reflux for 4 h.	94%	1
Homogeneous Ir catalyst	Formic acid	Formic acid (0.088 mL, 2.0 mmol), HMF (0.25 g, 2.0 mmol), 3 mL THF, **40°C**.	94%	2
Au/Al_2O_3	H_2	0.4 mmol HMF, 10 mg catalyst, 6.5 MPa H_2, 2 mL water, **140°C**, 2 h.	>96.0%	3
Ru(OH)$_x$/ZrO_2	H_2	HMF (100 μL, 0.97 mmol), catalyst (15 mg, 0.3 mol%), 15 bar H_2, 3 mL 1-butanol, **120°C**, 6 h.	>99%	4
Ru/C	H_2	**140-170°C**, H_2 (0.69-2.07 MPa), water, HMF concentration (19.8-59.5 mM), catalyst loading (0.3-0.7 kg/m^3).	n.a.(the study of reaction kinetics)	5
Sn-β	Isopropanol	160 mg HMF, 80 mg catalyst, 16 mL isopropanol, **180°C**, 6 h, 20.4 bar N_2.	>80%（2,5-bis(alkoxymethyl)furan）	6
ZrBa(3)-SBA	Isopropanol	0.2 g HMF, 19.8 g isopropanol, **150°C**, 2.5 h, 500 rpm, 1 atm N_2.	90.6%	7
Ru/Co_3O_4	Isopropanol	0.5 wt % HMF, 0.25 wt % Ru/Co_3O_4 and 20 mL isopropanol, **190°C**, 6 h.	82%	8
ZrO(OH)$_2$	Ethanol	1 g HMF, 0.5 g catalyst, 39 g ethanol, **150°C**, 2.5 h, 1 atm N_2.	83.7%	9
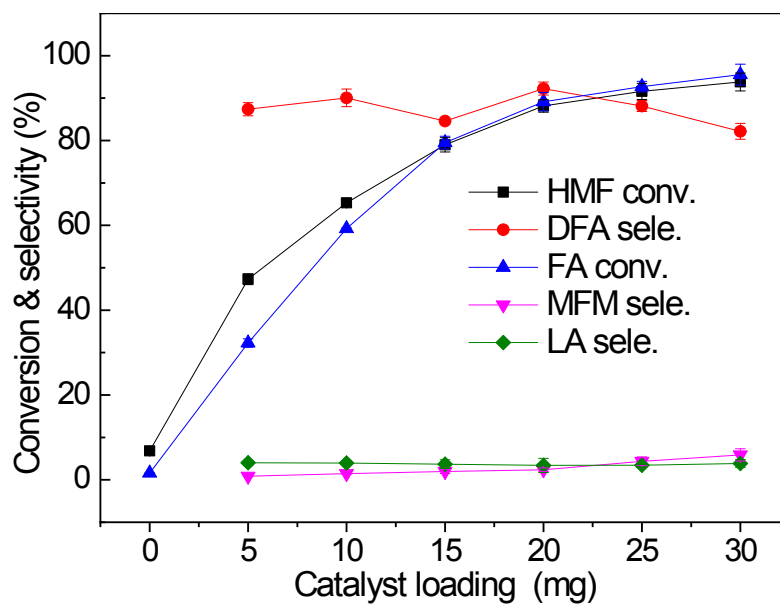
Fig. S5 Effect of catalyst loading on CTH of HMF over Co-NC-A. Reaction conditions: HMF (30 mg), $n_{FA/HMF}$=7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N_2, 160 °C, 5 h, 500 rpm.

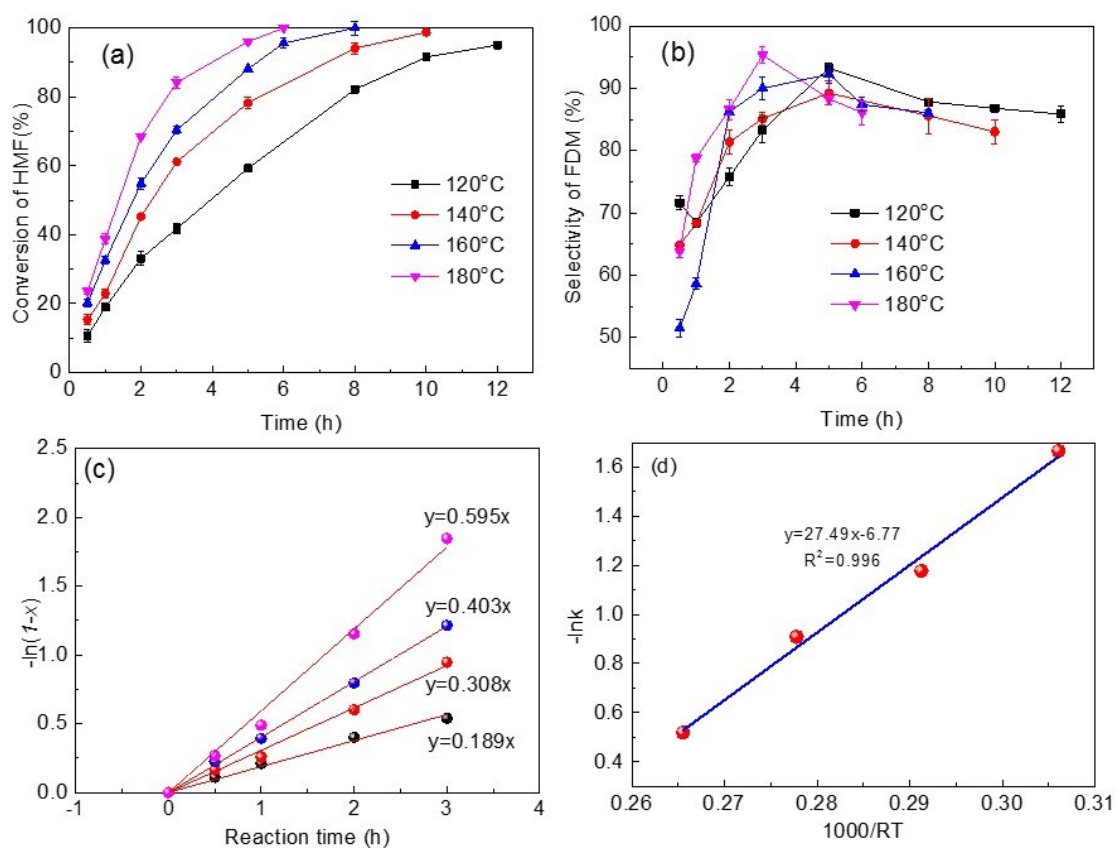**Fig. S6** Time-temperature-activity profiles for (a-d) HMF conversion. Reaction conditions: HMF (30 mg), Co-NC-A (20 mg), $n_{FA/HMF}$=7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N_2, 500 rpm.
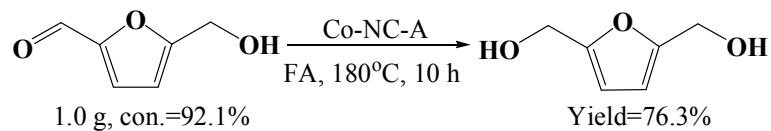
1.0 g, con.=92.1%   Yield=76.3%

Fig. S7 Gram-scale CTH of HMF over Co-NC-A. Reaction conditions: HMF (1 g), Co-NC-A (500 mg), FA (1.5 ml), 1,4-dioxane (40 mL), 0.5 MPa N_2, 180 °C, 10 h, 500 rpm.
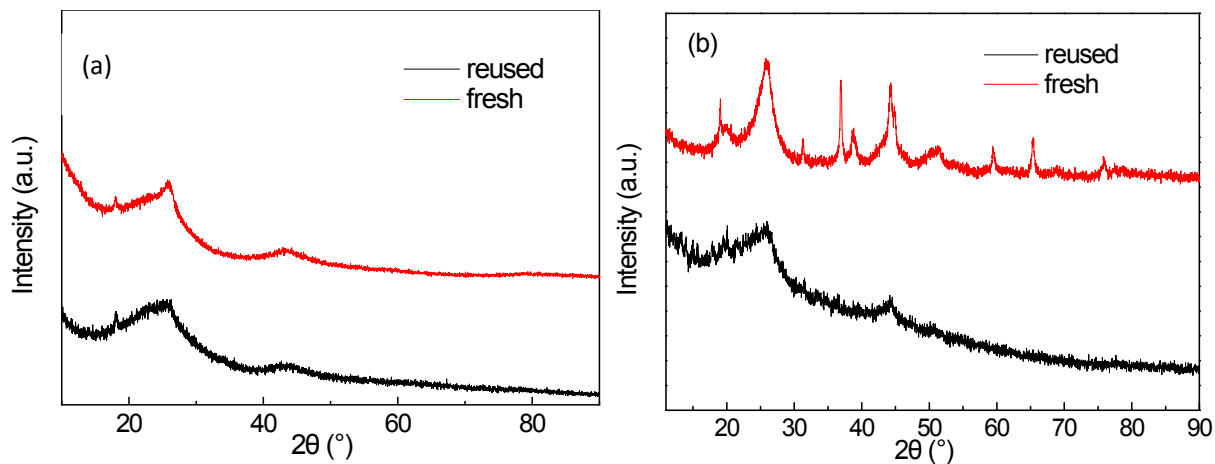
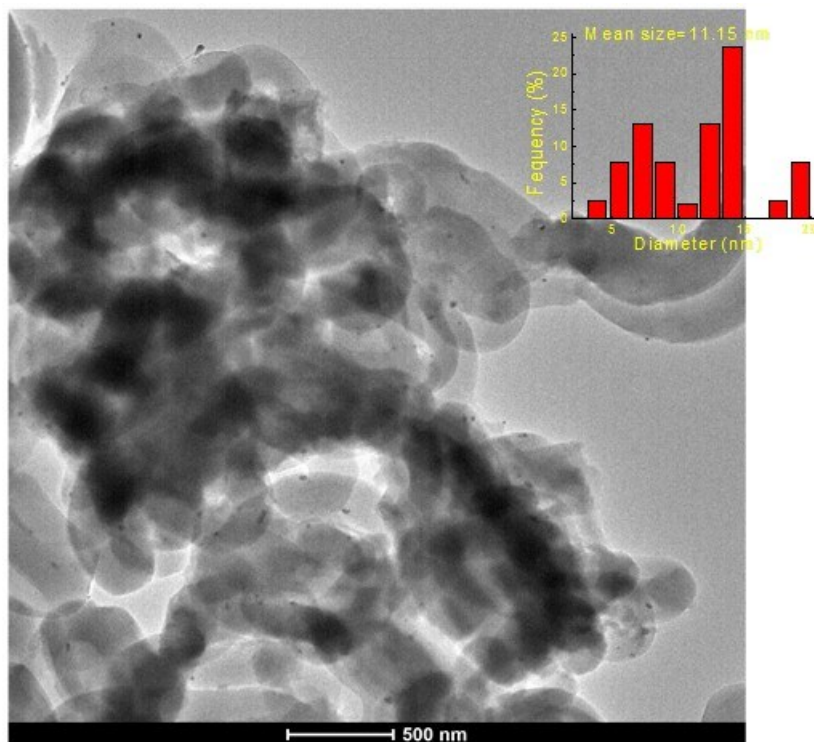**Fig. S8** XRD patterns of fresh and reused Co-NC-A(a) and Co-NC-B(b).
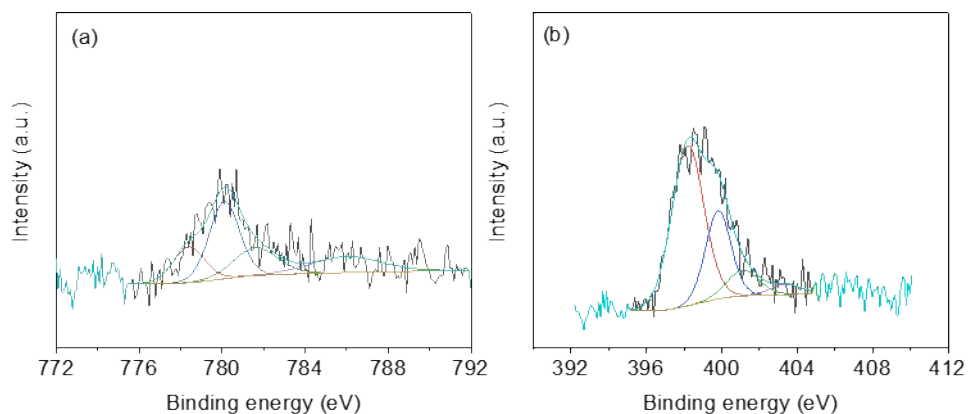

Fig. S9 TEM image of 5 times reused Co-NC-A.

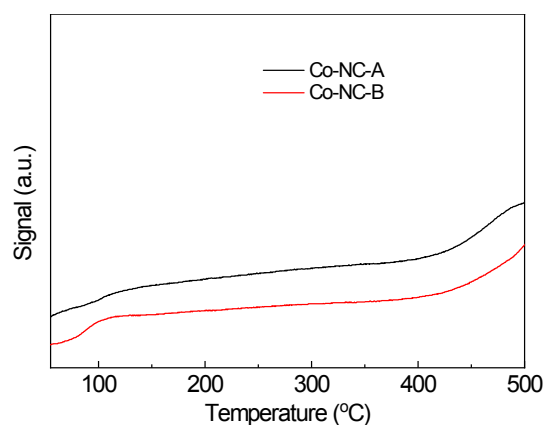**Fig. S10** (a) Co2p and (b) N1S spectra of reused Co-NC-A.

Fig. S11 HN$_3$-TPD profiles of Co-NC-A and   Co-NC-B.

Table S4 Comparison of CTH performance over Co-NC-A and Co-NC-B.

Catalysts	t(h)	Co species (mg)		Conversion /%	Selec. of FDM/%
		soluble	insoluble		
Co-NC-B	2	3.85	0.45	58.1	86.5
Co-NC-B	5			95.2	89.7
Co-NC-A	2	0	0.56	54.9	86.2
Co-NC-A	5			88.2	92.2

Reaction conditions: HMF (30 mg), catalyst (20 mg), n$_{FA/HMF}$=7.5, 1,4-dioxane (3.5 mL), 0.5 MPa N$_2$, 160 ^{o}C, 500 rpm
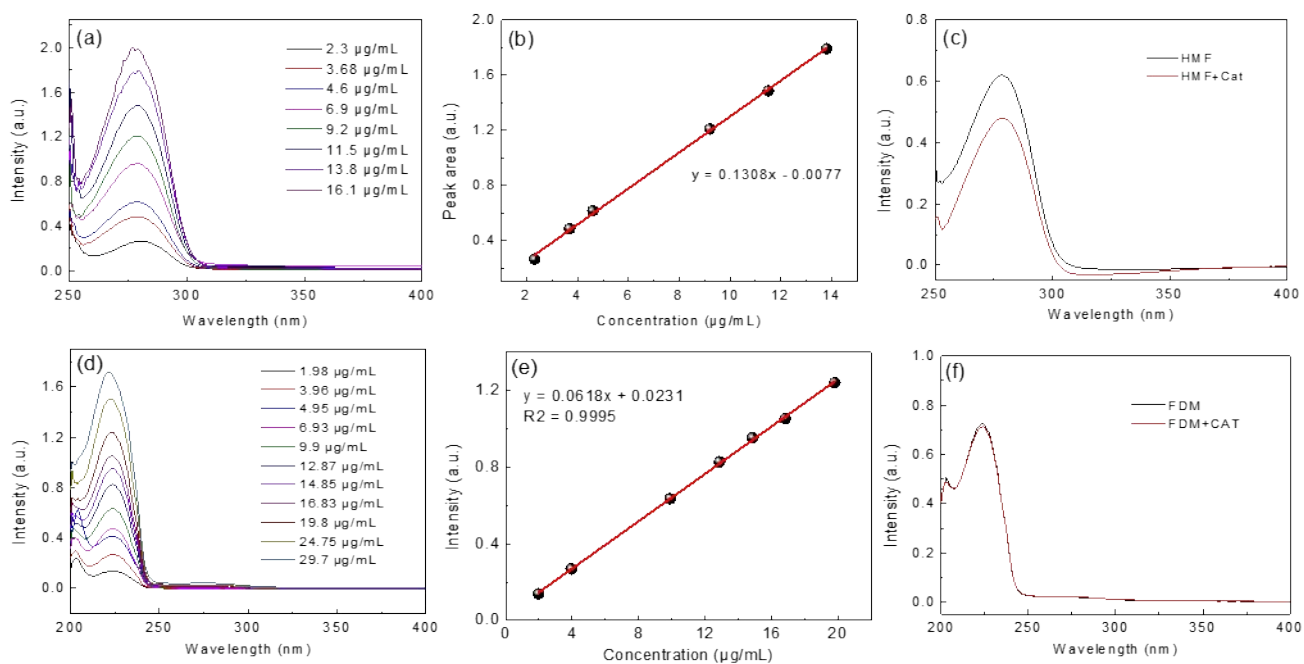
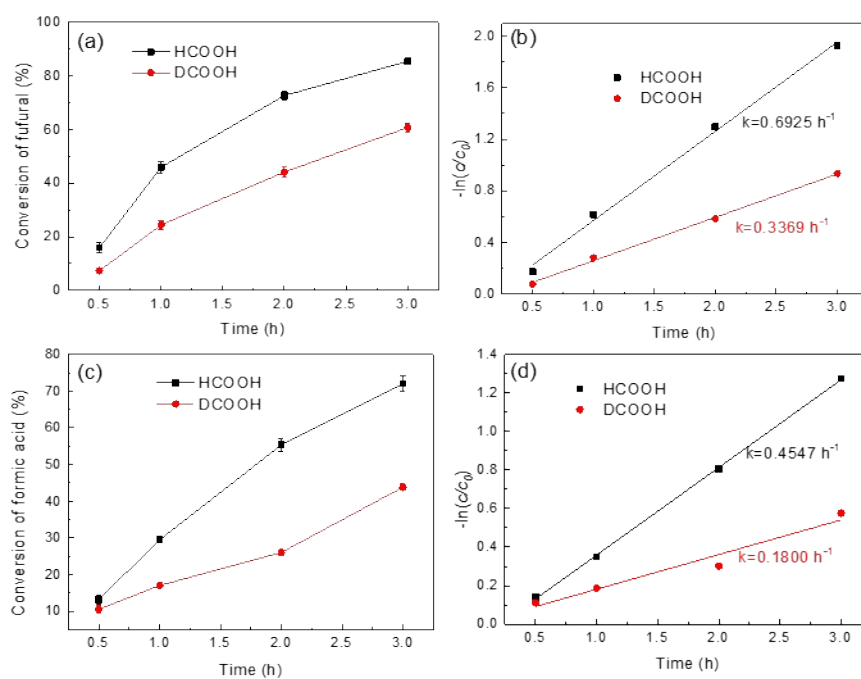**Fig. S12** (a-c) HMF and (d-f) FDM adsorption over Co-NC-A

Fig. S13 KIE studies of (a and b) furfural and (c and d) FA conversions over Co-NC-A. Reaction conditions: FAL (0.73 mmol), catalyst (25 mg), FA/FAL=3.5(mole ratio), 1,4-dioxane (3.5 mL), 0.5 MPa N_2, 150 ºC.
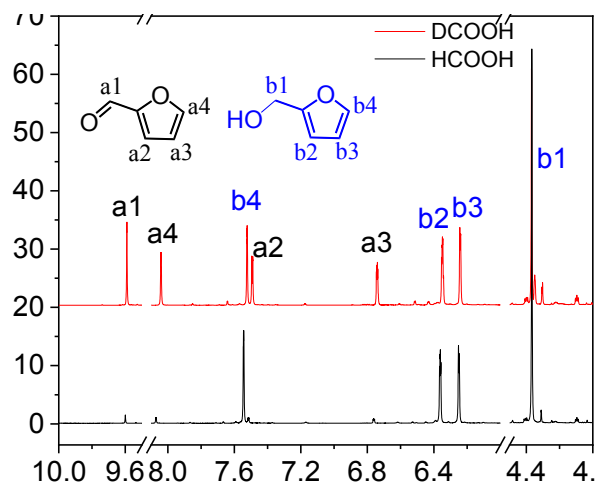
Fig. S14 ^{1}H-NMR spectra of reaction mixture using HCOOH and DCOOH as hydrogen donor.

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