Supporting Information

Tuning the synthesis of polymetallic-doped ZIFs derived materials for efficient hydrogenation of furfural to furfuryl alcohol

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Contents

Synthesis of impregnation-CuCo/Zn@NPC and adsorption-CuCo/Zn@NPC.

I-CuCo/Zn@NPC-600:

The 0.25 g Co/Zn@NPC-600 was added to 20 ml of water and the ultrasound was performed for 30 minutes. 0.019 g $Cu(NO_3)_2$ was dissolved in 20 ml water and stirred for 10 minutes. Then mixed and stirred for 12 hours, heated and steamed to dry. Then the sample were dried in vacuum at 70 °C for overnight. The sample is reduced at 400 °C by 10% H_2/Ar.

A-CuCo/Zn@NPC-600:

Adsorption methods reported in the previous literature[1,2], the powder of BMZIFS (500 mg) was dispersed in n-hexane(10 ml) under ultrasound for 10 min at room temperature. After forming homogeneous solution, $Cu(NO_3)_2$ aqueous solution (100 mg ml^{-1}, 200 μL) was injected into the mixed solution slowly under ultrasound. Next, the mix solution was under vigorous stirring for 3 h at room temperature in order to make the salt solution be absorbed completely. Then the sample were centrifuged and dried in vacuum at 70 °C for 6 h. The pyrolysis process of the sample was consistent with that of CuCo/Zn@NPC-600.

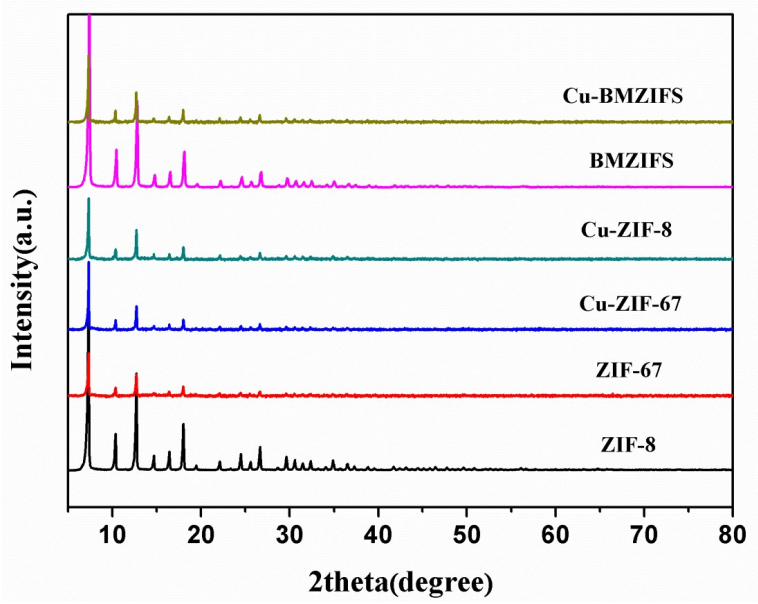

Figure S1. XRD patterns of a series of ZIF-8, ZIF-67 and BMZIFS.

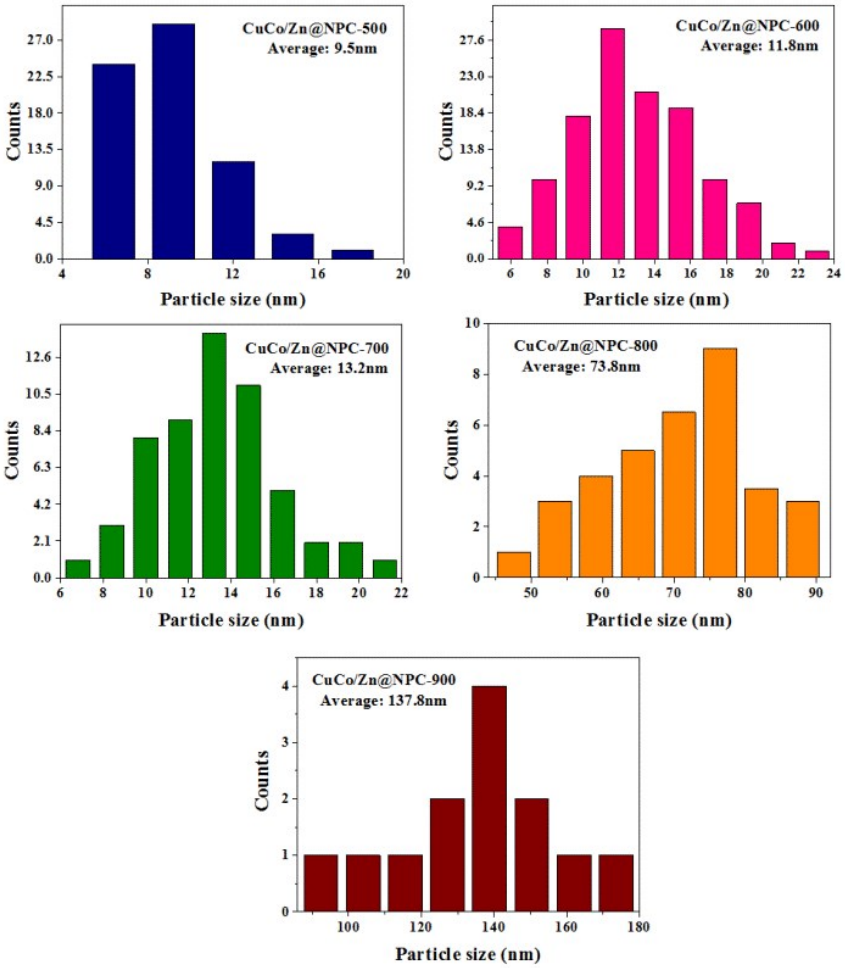

Figure S2. The particle sizes of materials at different calcination temperatures.

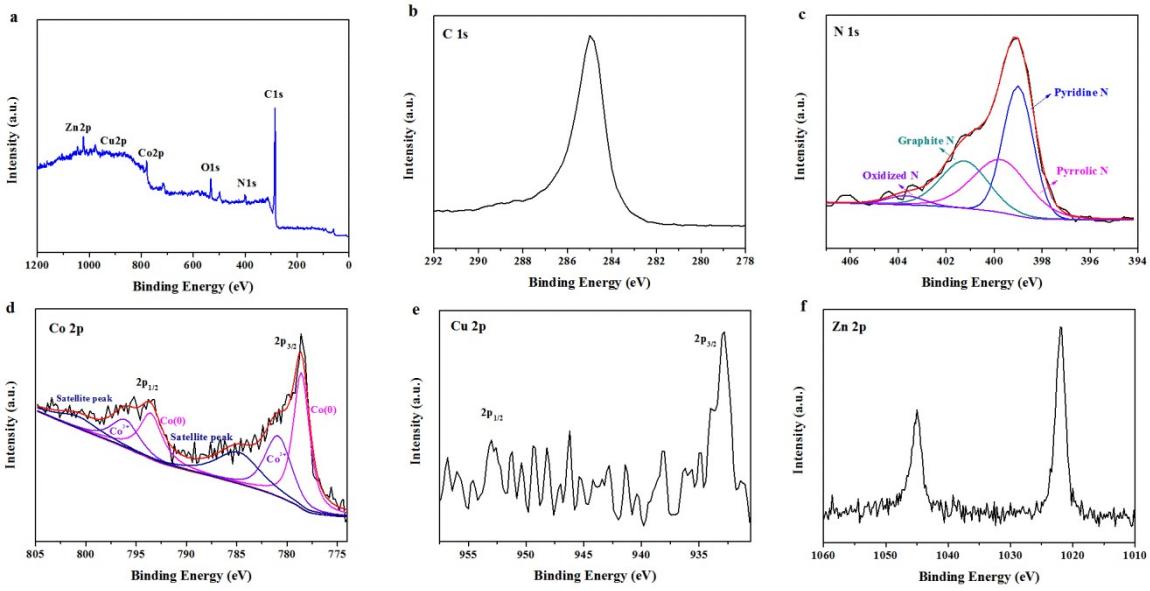

Figure S3. XPS spectra of CuCo/Zn@NPC-600 materials, (a) full spectrum, (b) C 1s, (c) N 1s, (d) Co 2p, (e) Cu 2p and (f) Zn 2p.

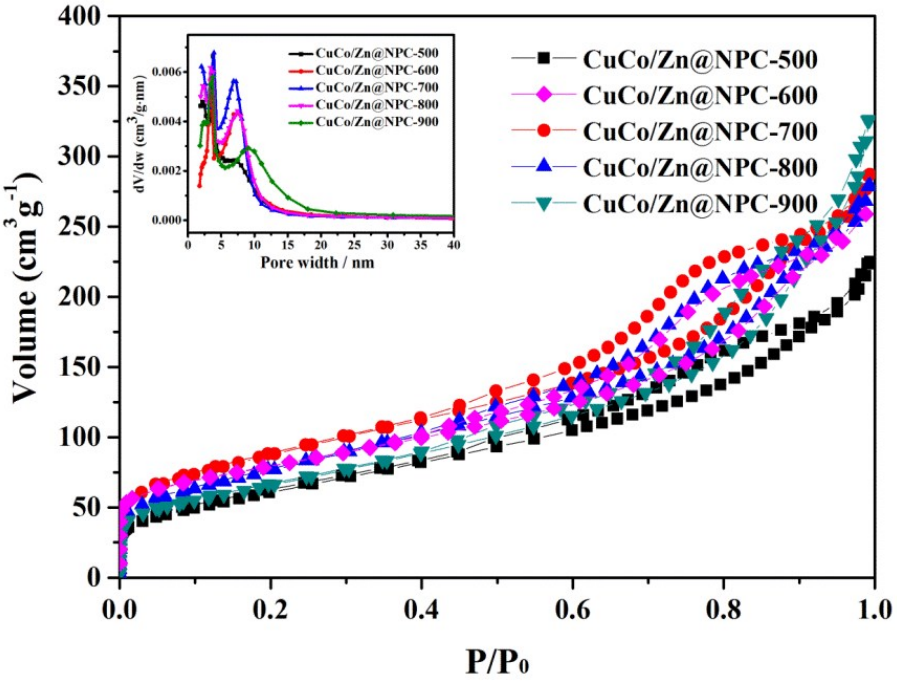

Figure S4. Nitrogen adsorption-desorption isotherms of the CuCo/Zn@NPC-T materials (inset is the pore size distribution).

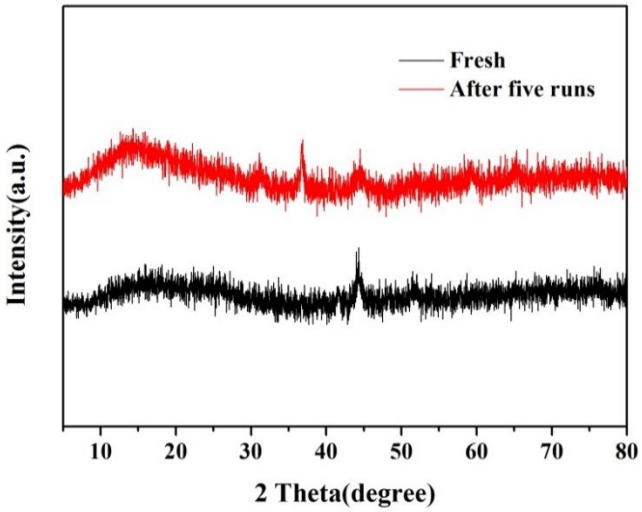

Figure S5. XRD patterns of the fresh and reused CuCo/Zn@NPC-600 catalysts.

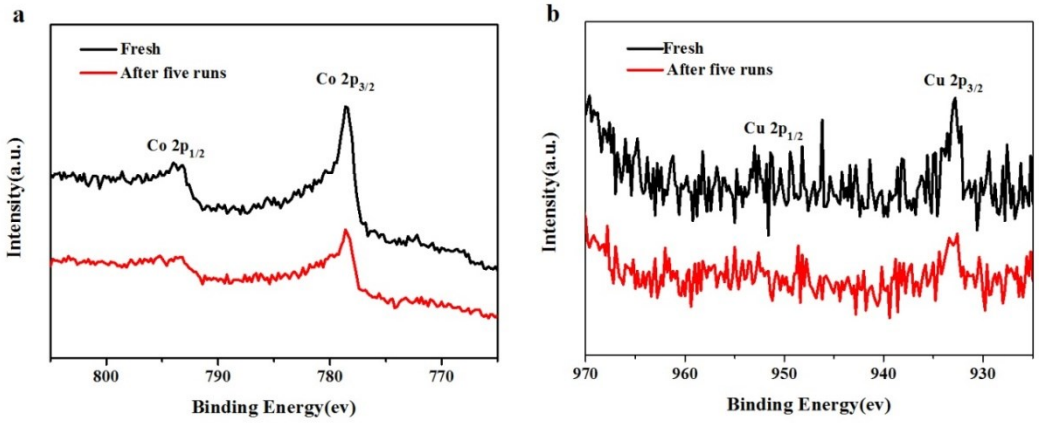

Figure S6. XPS spectra of Co 2p (a) and Cu 2p (b) for the fresh and reused CuCo/Zn@NPC-600 catalysts.

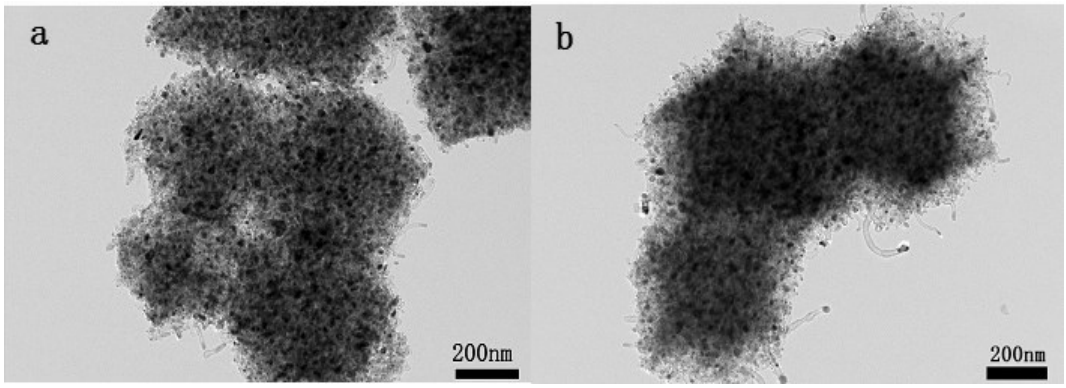

Figure S7. TEM images of the fresh (a) and reused (b) CuCo/Zn@NPC-600 catalysts.

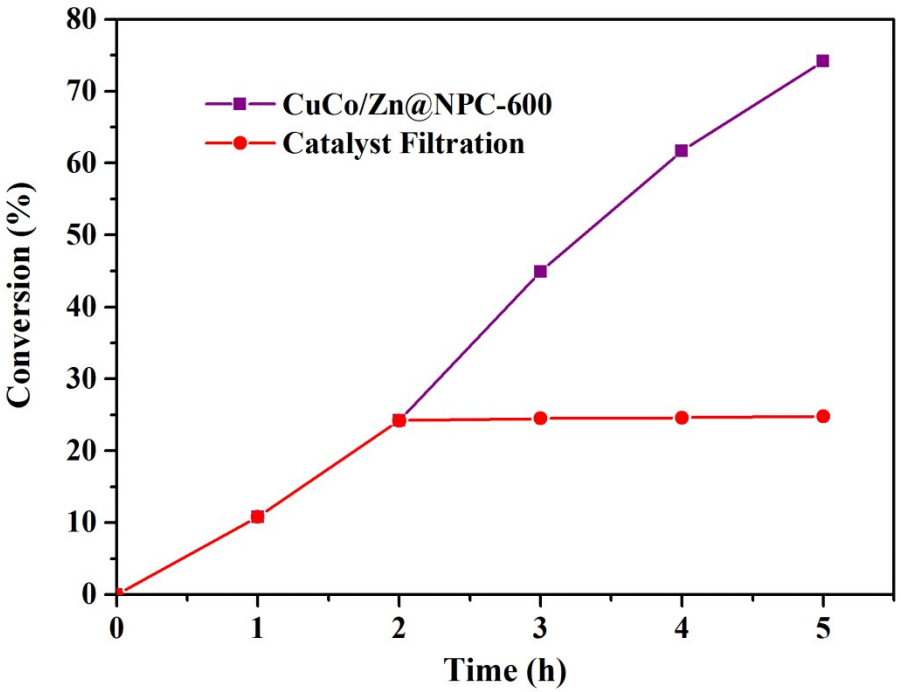

Figure S8. Leaching test with catalyst (purple) and with filtrate (red).

Table S1. N and Co (at.%) from XPS analysis for CuCo/Zn@NPC-T materials.

Sample	Pyridnic N 398.8 eV	Pyrrolic N 399.8 eV	Graphite N 401.1 eV	Oxidized N 403.0 eV	Co(0) 778.3 eV	Co^{2+} 780.4 eV
Co/Zn@NPC -600	68.23	17.40	11.86	2.51	32.27	67.73
CuCo@NPC -600	72.64	3.83	22.72	0.81	18.63	81.37
CuCo/Zn@NPC -500	61.51	17.94	20.55	0	14.08	85.92
CuCo/Zn@NPC -600	70.42	7.50	20.78	1.30	58.93	41.07
CuCo/Zn@NPC -700	53.11	7.13	32.63	7.13	44.57	55.43
CuCo/Zn@NPC -800	23.06	32.40	35.90	8.64	47.96	52.04
CuCo/Zn@NPC -900	18.42	32.65	39.30	9.63	31.51	68.49

Table S2. The XPS element analysis of different sampales.

Sample	% C	% N	% Co	% Zn
Co/Zn@NPC-600	85.63	17.40	3.48	3.65
CuCo@NPC-600	85.88	9.18	4.94	0
CuCo/Zn@NPC-500	79.60	13.14	3.74	3.52
CuCo/Zn@NPC-600	88.60	6.79	2.27	2.34
CuCo/Zn@NPC-700	91.47	5.44	2.03	1.06
CuCo/Zn@NPC-800	93.41	3.79	1.87	0.93
CuCo/Zn@NPC-900	97.63	2.09	0.61	-

Table S3. Comparison on hydrogenation of FF to FAL over different catalysts.

Catalysts	Reaction conditions	Conversion (%)	Selectivity (%)	Ref.
Co/SBA-15	150 °C, 2 MPa H_2, 1.5 h,	92	96	[3]
5 wt% Pt/C	185 °C, 8 MPa H_2, 0.5 h,	99.3	47.9	[4]
Cu-Fe	160 °C, 9 MPa H_2, 5 h	91	89.5	[5]
Pt/NC-BS-500	100 °C, 1 MPa H_2, 6 h	99	99	[6]
Cu/MgAlO	150 °C, 4 MPa H_2, 3 h	99	99	[7]
Fe-L1/C-800	160 °C, 15 h, 2-propanol	91.6	83	[8]
Pd/NPC	120 °C, 10 h, 2-butanol.	92	84	[9]
NiO	150 °C, 4 h, 2-propanol	84.6	95	[10]
Cu-Pd/C	170 °C, 3 h, formic acid	100	98.1	[11]
CuCo/Zn@NPC-600	140 °C, 4 h, 2 MPa H_2	>99	100	This work
CuCo/Zn@NPC-600	130 °C, 7 h, 2-propanol	95.8	99.1	This work

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