Electronic Supplementary Material (ESI) for Catalysis Science & Technology.
This journal is © The Royal Society of Chemistry 2022

Supporting Information

CoZn/N-doped porous carbon derived from bimetallic zeolite imidazolate framework/g-C_3N_4 for efficient hydrodeoxygenation of vanillin

Zegang Qiu,*[a] Xiaoxia He,[a] Zhiqin Li,[a] Qichen Guan,[b] Liang Ding,[a] Yanan Zhu[a] and Yueling Cao *[b,c]

[a] Xi'an Shiyou University, Xi'an 710065, PR China.

[b] Xi'an Key Laboratory of Functional Organic Porous Materials, School of Chemistry and Chemical Engineering, Northwestern Polytechnical University, Xi'an 710129, PR China.

[c] Chongqing Science and Technology Innovation Center of Northwestern Polytechnical University, Chongqing 401135, PR China

*Corresponding Authors: qiuzegang@xsyu.edu.cn; yuelingcao@nwpu.edu.cn

Table S1 Hydrodeoxygenation (HDO) of vanillin to 2-methoxy-4-methylphenol (MMP) over various catalysts in literatures and this work

Catalysts	Reaction conditions				Vanillin conversion/ %	MMP Selectivity /%	Reference	Date
	T/°C	p/MPa	t/h	Solvent				
Pd@BC-KFe-800	65	1	2	n-butanol	92.4	57.5	[6]	2021
Pd@NH_2-UiO-66	100	0.5	1	water	100	100	[7]	2016
[a]Pd-POP	140	1	18	isopropyl alcohol	96.5	98.2	[8]	2017
Pd/HHT	50	0.5	4	isopropyl alcohol	100	> 99.5	[9]	2021
$Pd_1/WO_{2.72}$	40	0.1	0.25	ethanol	99	99	[10]	2021
Ru-PEEK-WC	75	1.8	--	water	32.8	0	[11]	2021
Pd Rh/Al_2O_3	45	5.6	0.5	isopropyl alcohol	100	100	[12]	2021
Pd/$C_{vin}ZnCl_2$ CO_2	100	3	3	water	100	92	[13]	2020
Pd/Ru @GO	room	1	24	methanol	100	92.3	[14]	2020
[b]Cu_3Pd@BBA-1	140	1	8	isopropyl alcohol	99.3	93.6	[15]	2018
Co/N-C-600	150	1	8	isopropyl alcohol	100	99	[17]	2017
Co/Ce@NC	170	1	6	ethanol	> 99	> 99	[18]	2021
Cu/HNZY	160	1	2	methanol/water	100	99	[19]	2018
Cu/AC-600	180	2	5	isopropyl alcohol	99.9	99.1	[20]	2018
Cu/Zn15Al4Sn1-LDH	180	2	4	isopropyl alcohol	100	98.5	[21]	2019
[c]4Co-1Zn/NPC	100	1	2	water	100	> 99	This work	

[a]BBA-1: N-rich Porous Organic Polymer
[b]POP: Porous Organic Polymer
[c]HDO of vanillin to MMP over 4Co-1Zn/NPC catalyst in this work is presented for comparison

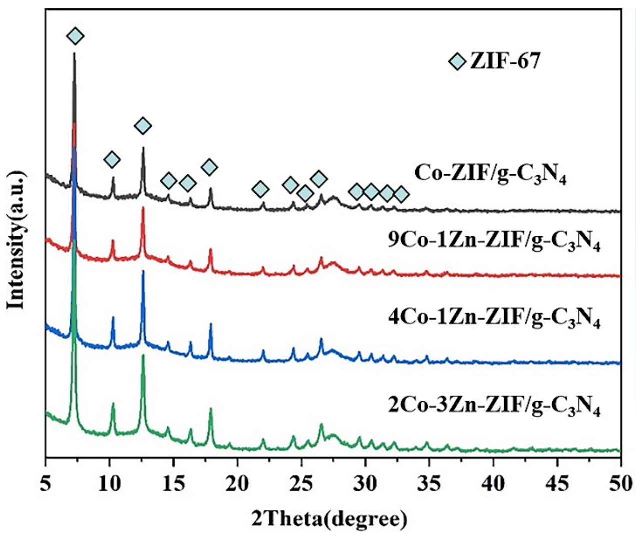

Fig. S1 XRD patterns of serial Co-Zn-ZIF/g-C_3N_4 with different ratios of Co/Zn

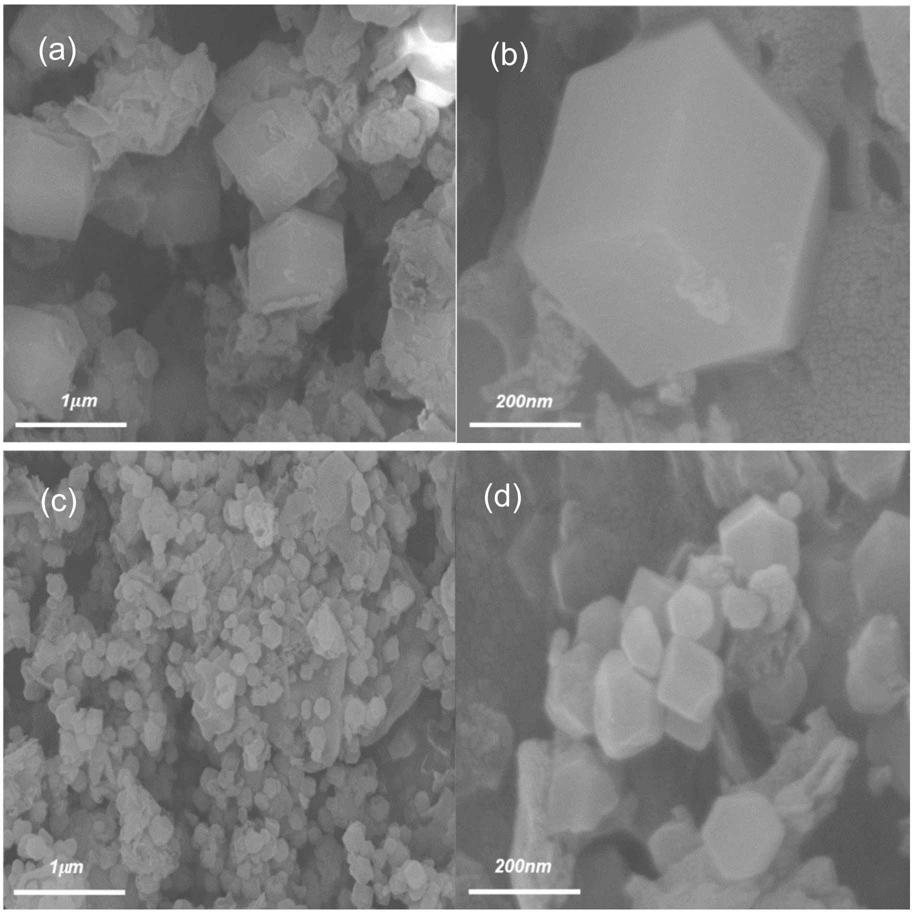

Fig. S2 SEM images of Co-ZIF/g-C_3N_4 (a and b) and 4Co-1Zn-ZIF/g-C_3N_4 (c and d)

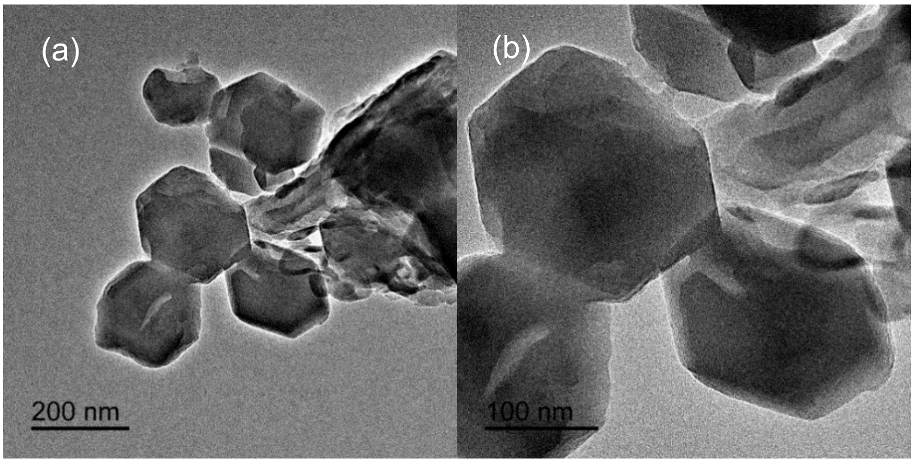

Fig. S3 TEM images of 4Co-1Zn-ZIF/g-C_3N_4

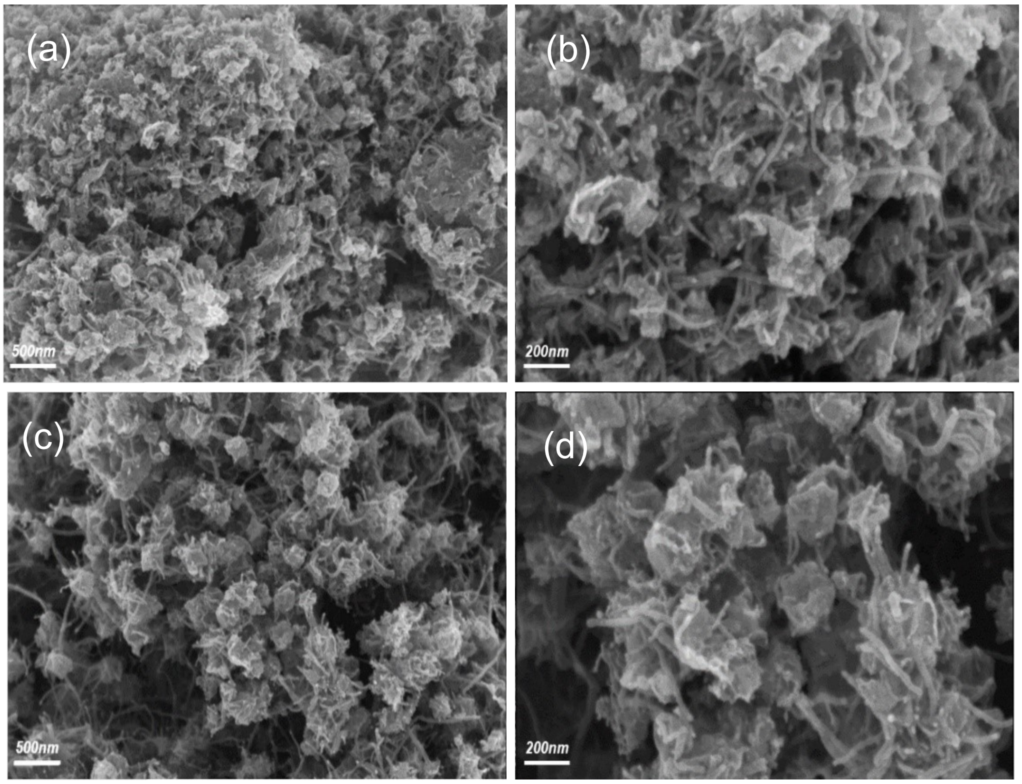

Fig. S4 SEM images of 9Co-1Zn/NPC (a and b) and 2Co-3Zn/NPC (c and d)

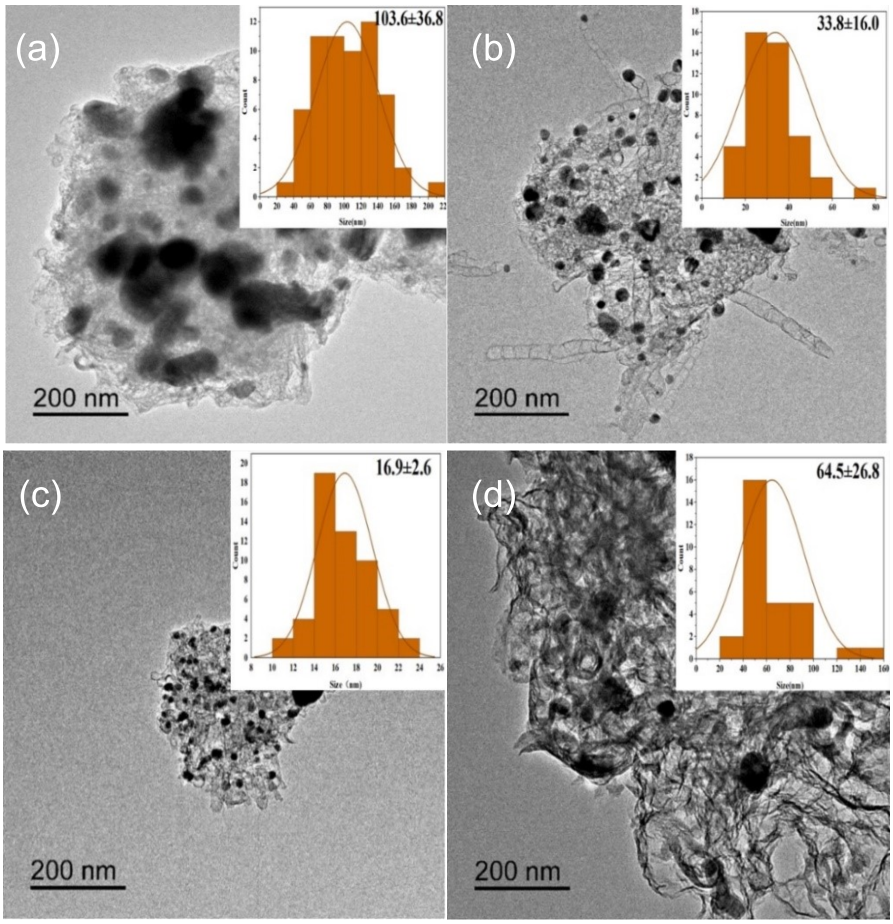

Fig. S5 TEM images of serial Co-Zn/ NPC catalysts with different ratios of Co/Zn

(a) Co/ NPC；(b) 9Co-1Zn/ NPC；(c) 4Co-1Zn/ NPC；(d) 2Co-3Zn/ NPC

Table S2 The content of Co and Zn measured via ICP-AES

Catalysts	Co wt./%	Zn wt./%
Co/NPC	0.48	--
9Co-1Zn/NPC	0.44	0.08
4Co-1Zn/NPC	0.40	0.29
2Co-3Zn/NPC	0.22	2.50

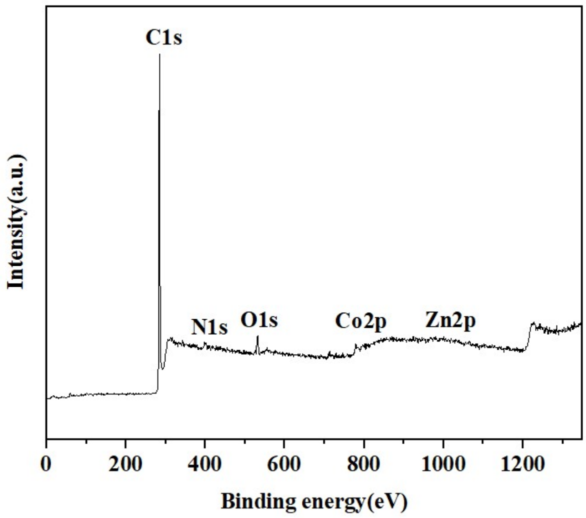

Fig. S6 XPS survey spectrum of 4Co-1Zn/NPC

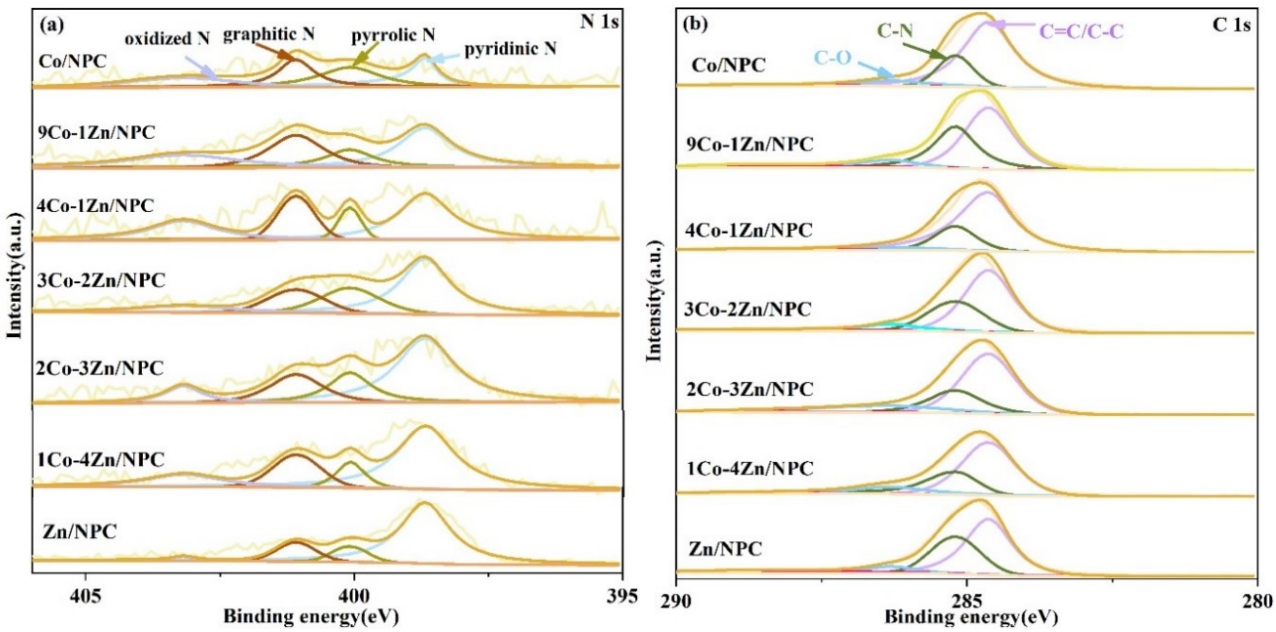

Fig. S7 XPS spectra of serial Co-Zn/ NPC catalysts with different ratios of Co/Zn

(a) N 1s; (b) C 1s

Table S3 The content of surface elements obtained from XPS

Catalysts	Co/%	Zn/%	C/%	N/%	O/%
Co/NPC	0.50	--	93.31	3.35	2.84
9Co-1Zn/NPC	0.44	0.13	91.77	2.52	5.14
4Co-1Zn/NPC	0.61	0.42	91.80	3.72	3.45
3Co-2Zn/ NPC	0.87	0.74	87.01	6.14	5.24
2Co-3Zn/NPC	0.64	0.40	89.19	4.57	5.20
1Co-4Zn/ NPC	0.76	0.56	88.19	5.98	4.51

Table S4 Hydrodeoxygenation of Vanillin to 2-methoxy-4-methylphenol (MMP) over different catalysts

Catalysts	Vanillin Conversion /%	MMP Selectivity /%	HMP Selectivity /%
Co/CN	100	36.1	63.9
Co/NPC	100	48.5	51.5
4Co-1Zn/CN	100	88.5	11.5
4Co-1Zn/NPC	100	99.0	1.0

Reaction conditions: catalyst 20 mg, vanillin 0.5 mmol, H_2O 5 mL, 110 °C, 1 MPa H_2, 2 h

Co/CN and 4Co-1Zn/CN: N-doped carbon catalysts without the adding of g-C_3N_4

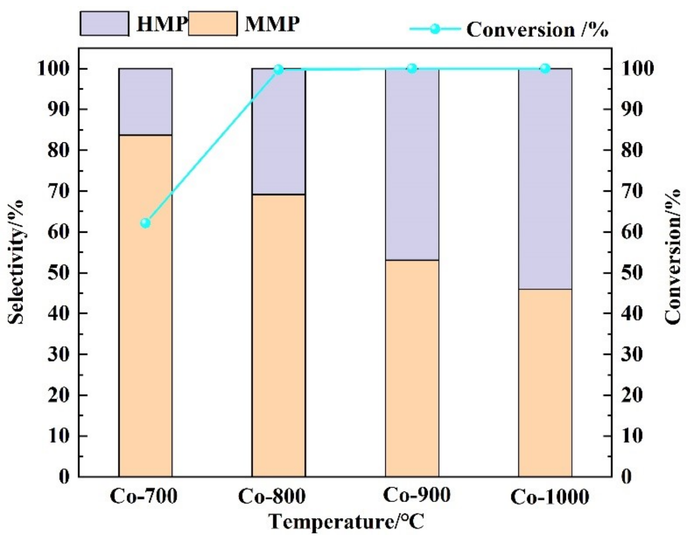

Fig. S8 Influence of pyrolyzing temperatures on hydrodeoxygenation reaction of vanillin over Co/NPC

Co-700, Co-800, Co-900, Co-1000: Co/NPC catalysts pyrolyzed at 700°C, 800°C, 900°C, 1000°C

MMP: 2-methoxy-4-methylphenol; HMP: 4-Hydroxy-3-methoxybenzyl alcohol

Reaction conditions: catalyst 20 mg, Vanillin 0.5 mmol, H_2O 5 mL, 110 °C, 1 MPa

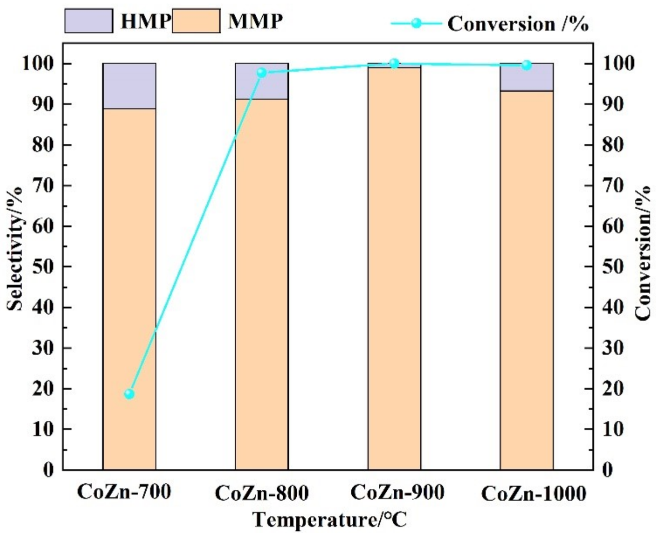

Fig. S9 Influence of pyrolyzing temperatures on hydrodeoxygenation reaction of vanillin over 4Co-1Zn/NPC

CoZn-700, CoZn-800, CoZn-900, CoZn-1000: 4Co-1Zn/NPC pyrolyzed at 700℃, 800℃, 900℃, 1000℃

MMP: 2-methoxy-4-methylphenol; HMP: 4-Hydroxy-3-methoxybenzyl alcohol

Reaction conditions: catalyst 20 mg, Vanillin 0.5 mmol, H_2O 5 mL, 110 ℃, 1 MPa