Supporting Information

Multicomponent Metal-Organic Frameworks Derivatives for Optimizing the Selective Catalytic Performance of Styrene Epoxidation Reaction

Junfeng. Hui[a#], Huimin Chu[a#], Wenlei Zhang[c], Yu Shen[b], Wanzheng Chen[b], Yu Hu[b], Wan Liu[a], Cong Gao[b], Shaohua Guo[b], Gengwu Xiao[b], Sheng Li[b], Yu Fu[c], Daidi Fan[a], Weina Zhang[b*], and Fengwei Huo[b*]*

[a] Shaanxi Key Laboratory of Degradable Biomedical Materials, Shaanxi R&D Center of Biomaterials and Fermentation Engineering, School of Chemical Engineering, Northwest University, Xi'an 710069, Shaanxi, PR China.

[b] Key Laboratory of Flexible Electronics (KLOFE) & Institute of Advanced Materials (IAM), Nanjing Tech University (NanjingTech), 30 South Puzhu Road, Nanjing 211800, China.

[c] College of Science, Northeastern University, Shenyang 100819, China.

E-mail addresses: fandaidi@nwu.edu.cn (D. Fan), iamwnzhang@njtech.edu.cn (W. Zhang), iamfwhuo@njtech.edu.cn (F. Huo)

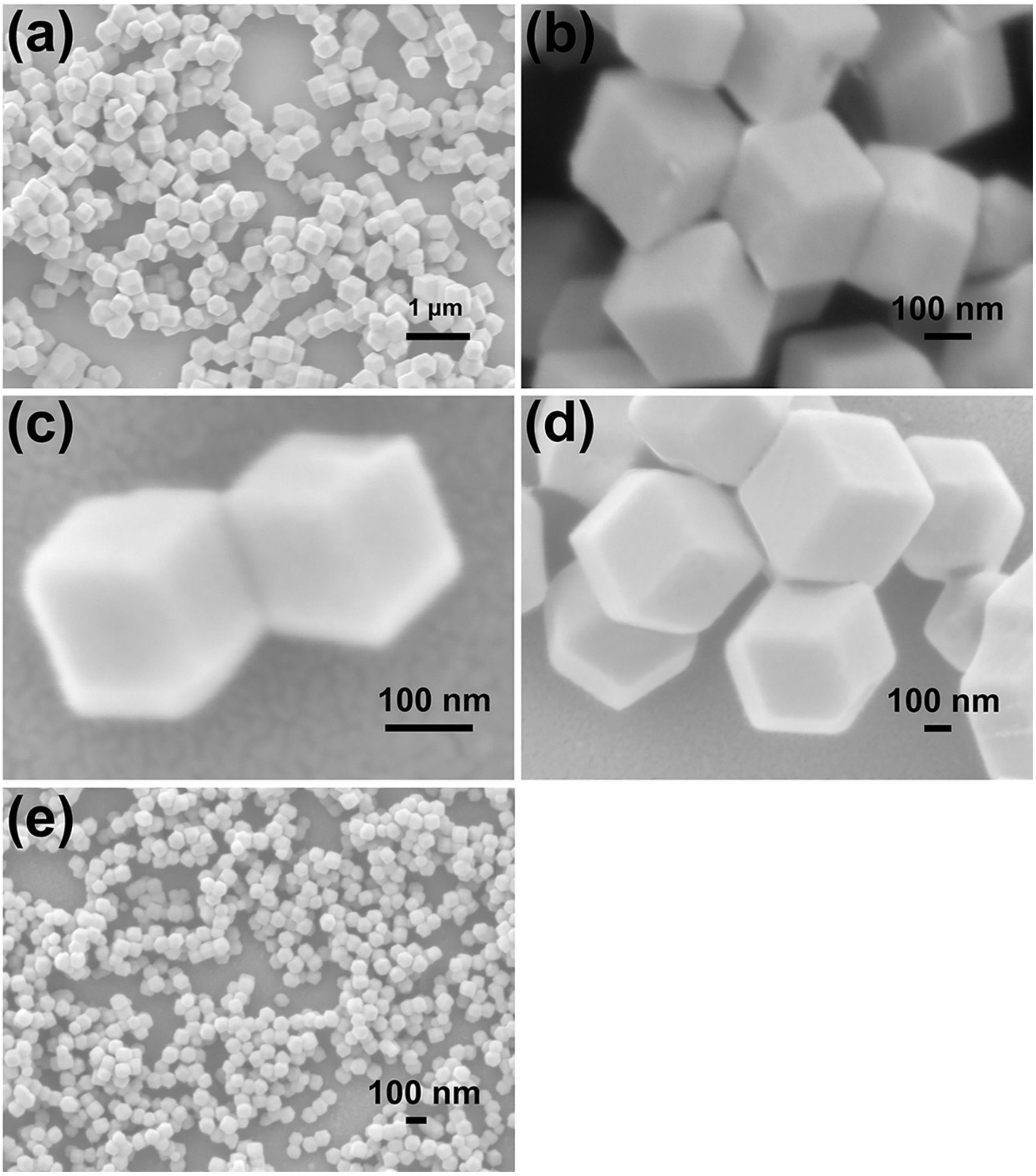

Fig. S1 The SEM images of the multicomponent MOFs. (a) $Zn_{0.5}Co_1$-ZIF, (b) $Zn_{1.5}Co_1$-ZIF, (c) Zn_2Co_1-ZIF, (d) ZIF-67, (e) ZIF-8.

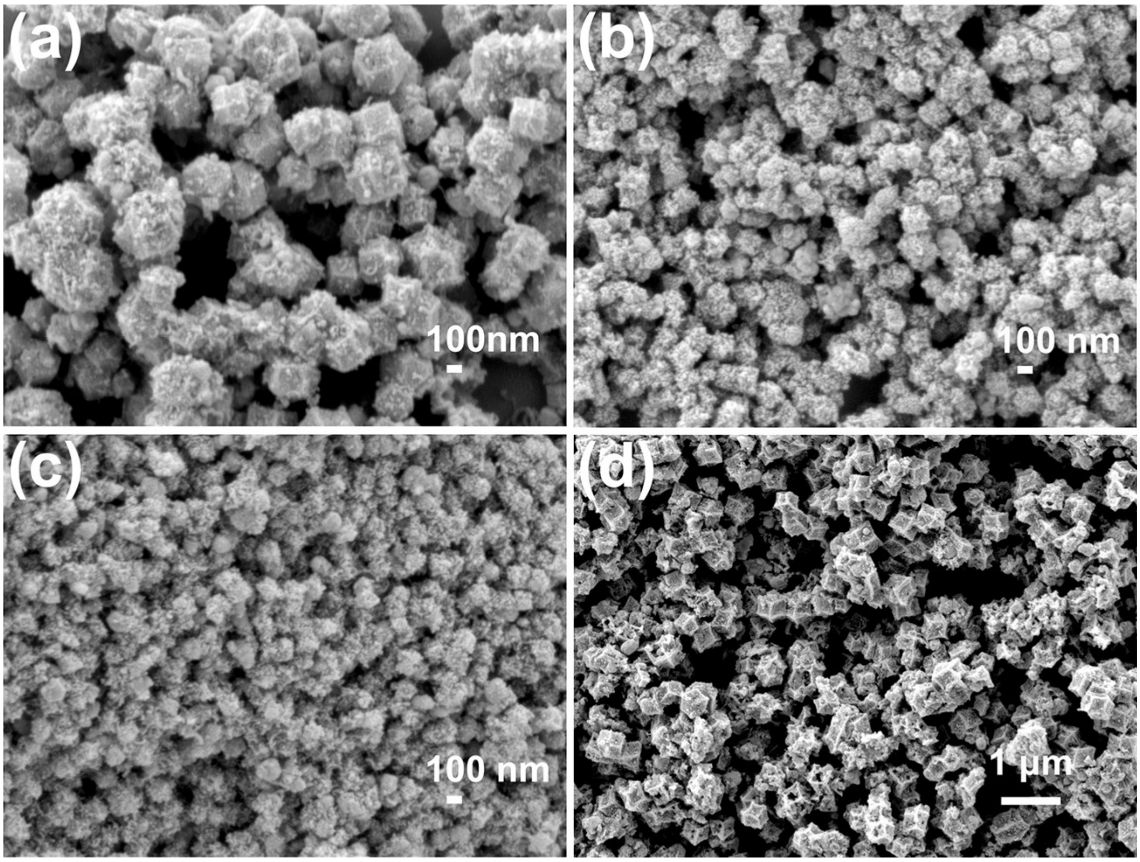

Fig. S2 The SEM images of the MOFs derivatives. (a) $Zn_{0.5}Co_1$-ZIF, (b) $Zn_{1.5}Co_1$-ZIF, (c) Zn_2Co_1-ZIF, (d) ZIF-67.

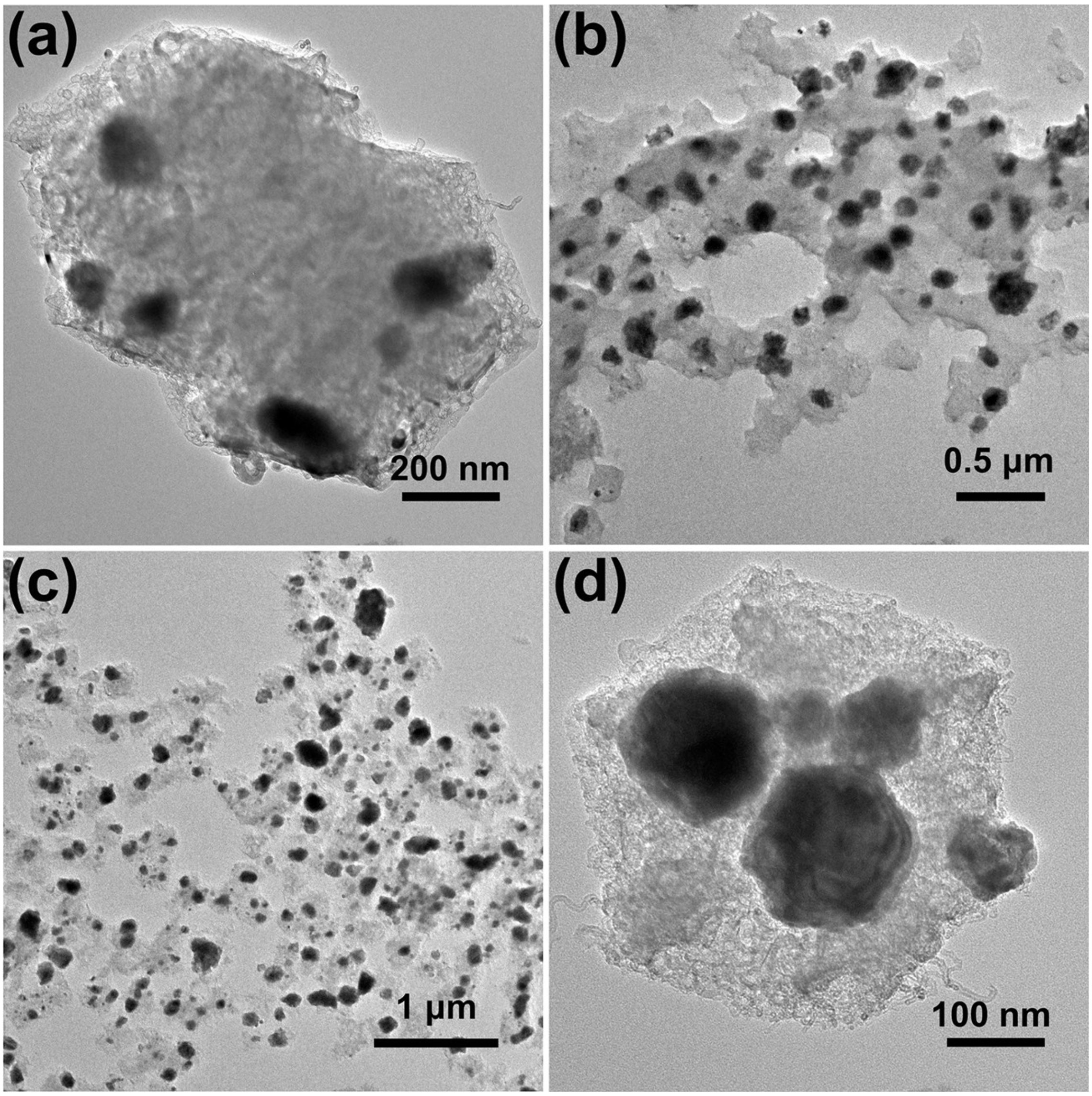

Fig. S3 The TEM images of the MOFs derivatives. (a) $Zn_{0.5}Co_1$-ZIF, (b) $Zn_{1.5}Co_1$-ZIF, (c) Zn_2Co_1-ZIF, (d) ZIF-67.

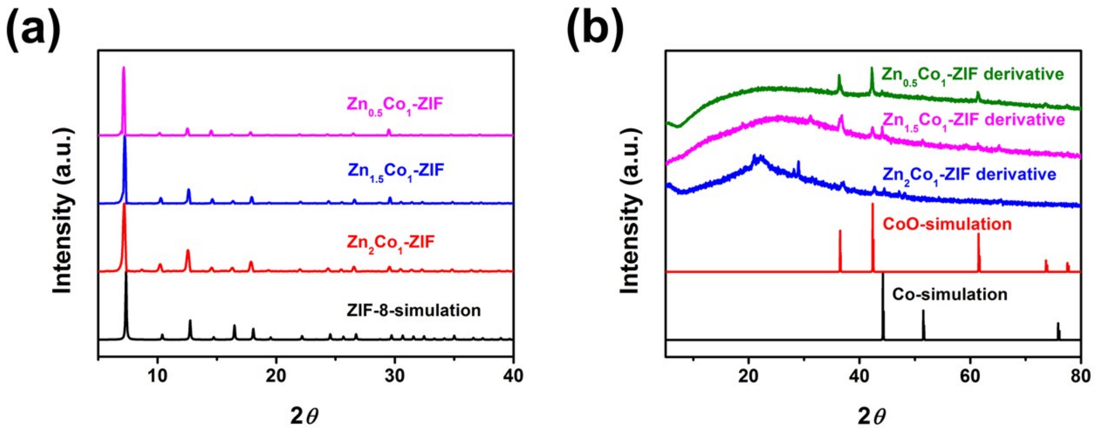

Fig. S4 The XRD of the multicomponent MOFs and their derivatives. (a) MOFs, (b) MOFs derivatives.

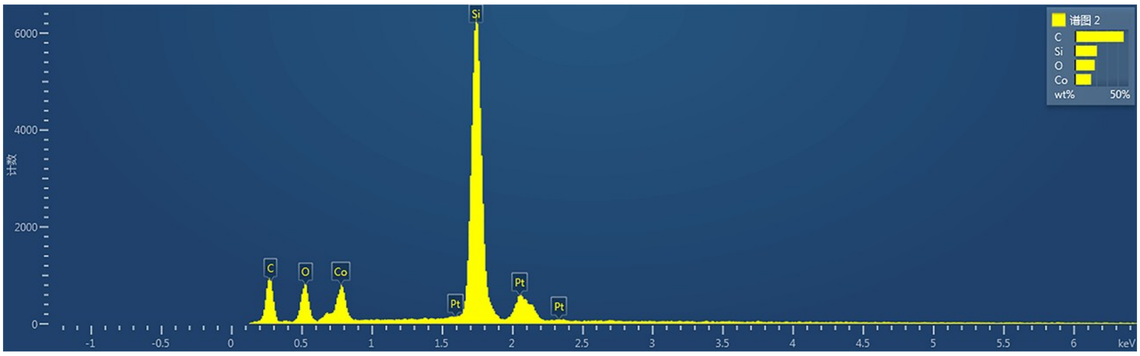

Fig. S5 The EDX image of Zn_1Co_1-MOF derivative.

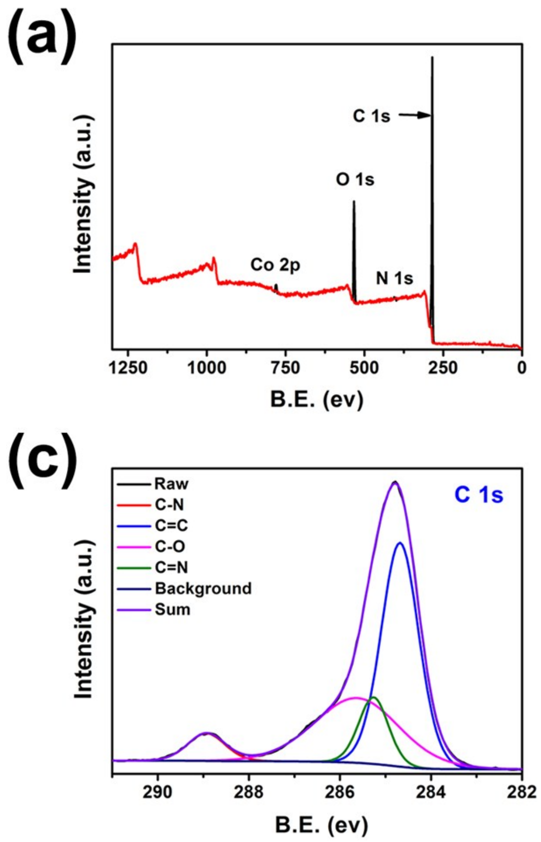

Fig. S6 The XPS spectra for (a) Survey scan, (b) N 1s, (c) C 1s, and (d) Co 2p of $Zn_{0.5}Co_1$-ZIF derivative.

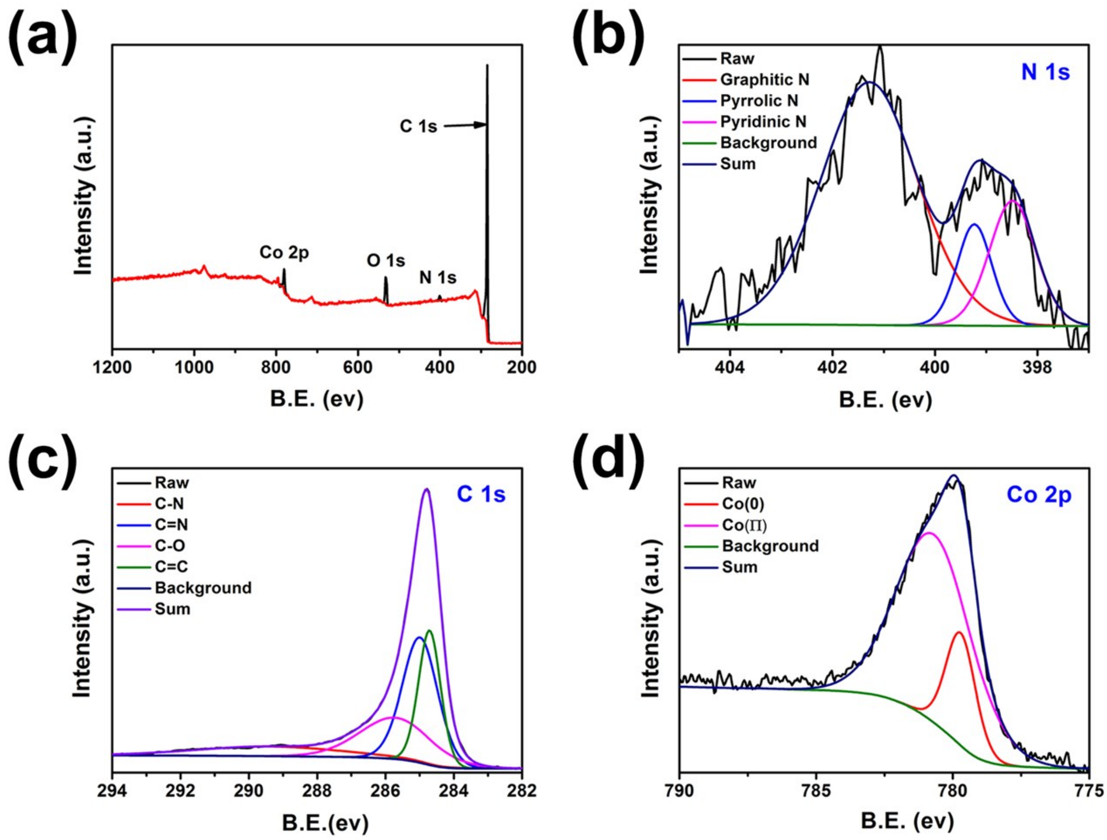

Fig. S7 The XPS spectra for (a) Survey scan, (b) N 1s, (c) C 1s, and (d) Co 2p of $Zn_{1.5}Co_1$-ZIF derivative.

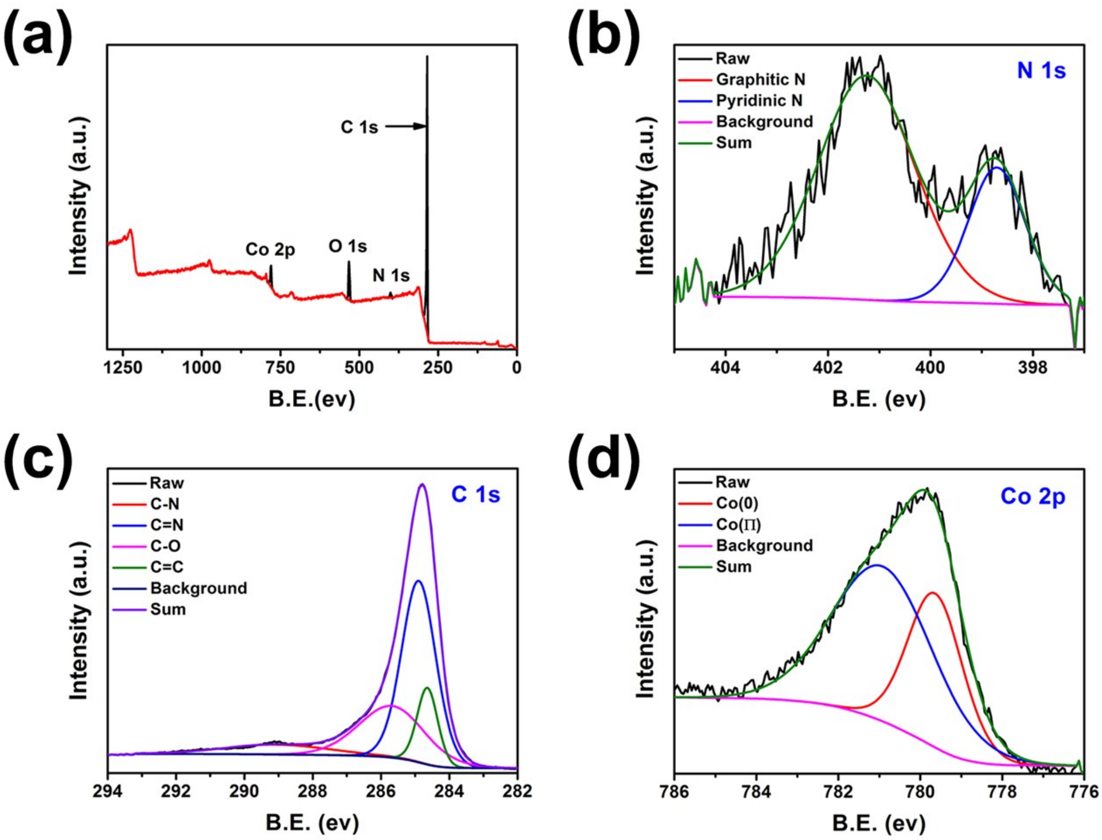

Fig. S8 The XPS spectra for (a) Survey scan, (b) N 1s, (c) C 1s, and (d) Co 2p of Zn_2Co_1-ZIF derivative.

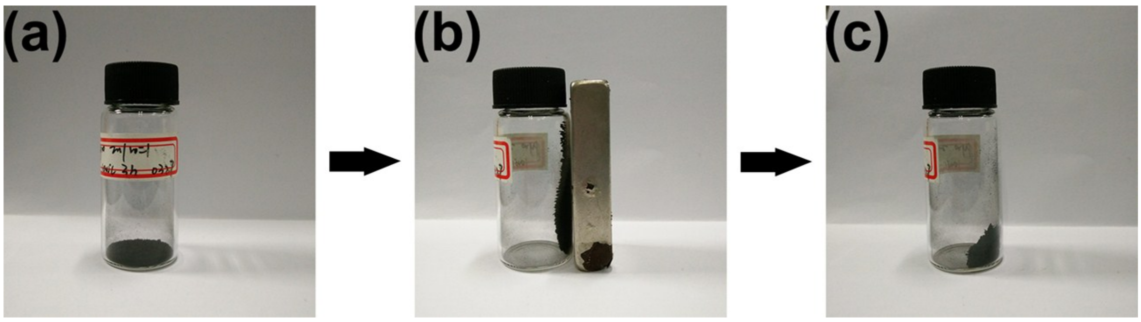

Fig. S9 The magnetic adsorption test of Zn_1Co_1-ZIF derivative.

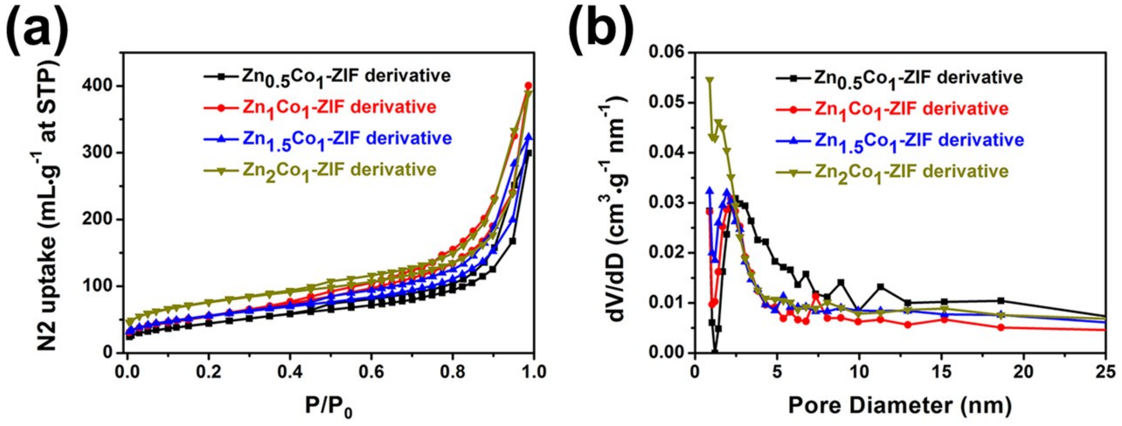

Fig. S10 (a) Nitrogen adsorption−desorption isotherm and (b) Pore size distribution of the multicomponent MOFs derivatives

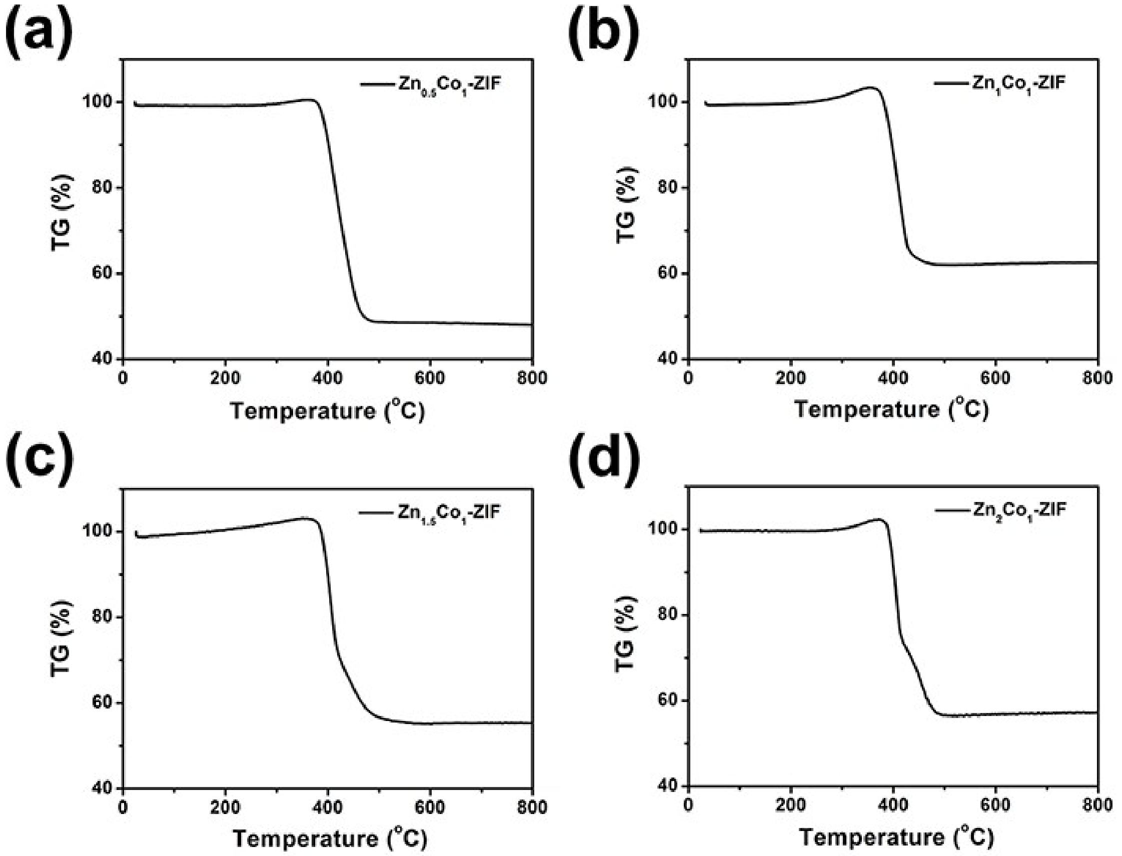

Fig. S11 The TGA images of the multicomponent MOFs derivatives with different Zn/Co ratios in air.

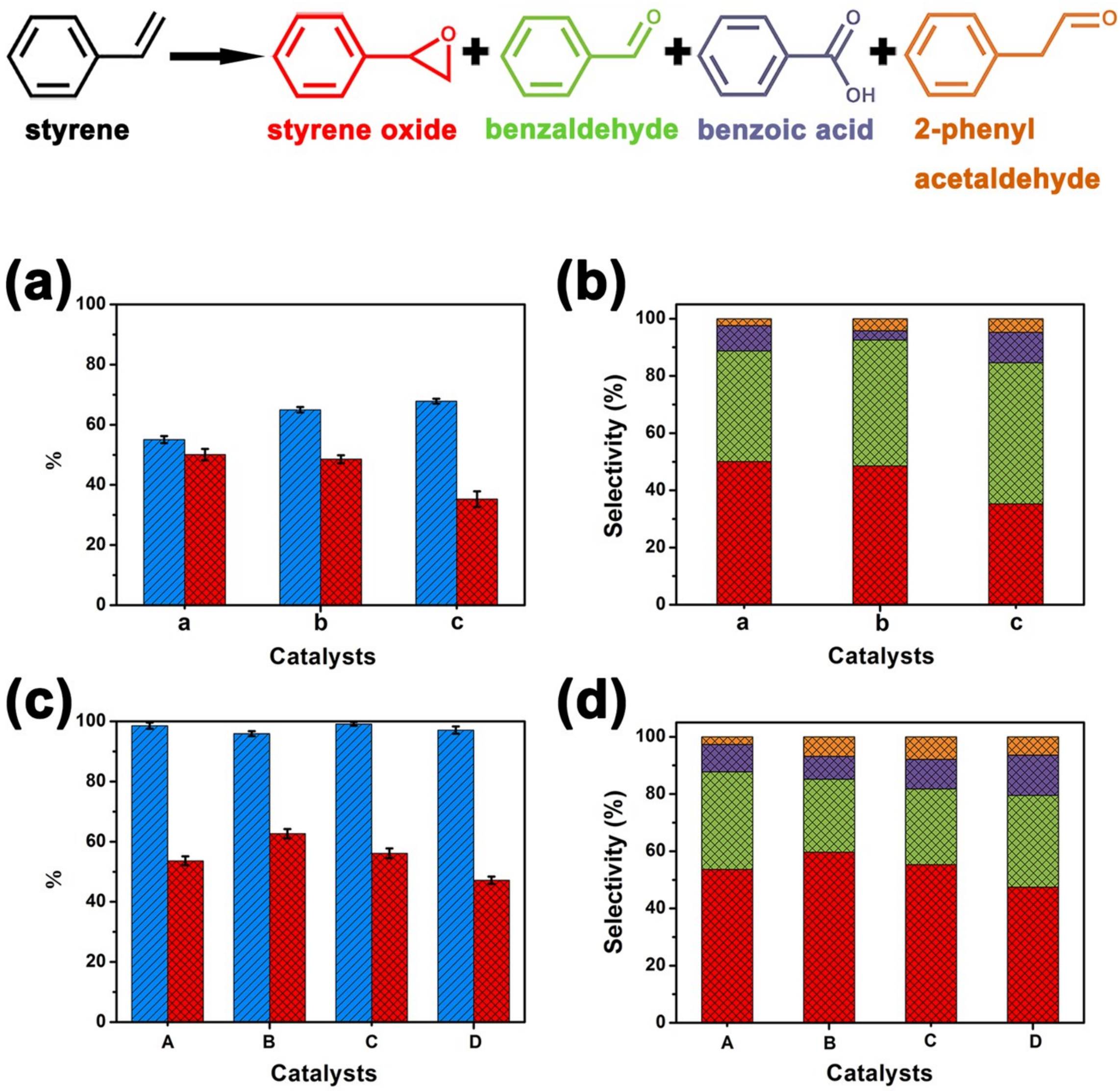

Fig. S12 The GC characterization of styrene epoxidation reaction with different catalysts in 24 h. (a) and (c) the conversion of styrene and the selectivity of styrene oxide (blue: conversion; red: selectivity). (b) and (d) the selectivity of different products (red: styrene oxide; green: benzaldehyde; purple: benzoic acid; orange: 2-phenyl acetaldehyde). a: $Zn_{0.5}Co_1$-ZIF; b: $Zn_{1.5}Co_1$-ZIF; c: Zn_2Co_1-ZIF; A: $Zn_{0.5}Co_1$-ZIF derivative; B: $Zn_{1.5}Co_1$-ZIF derivative; C: Zn_2Co_1-ZIF derivative; D: ZIF-67 derivative.

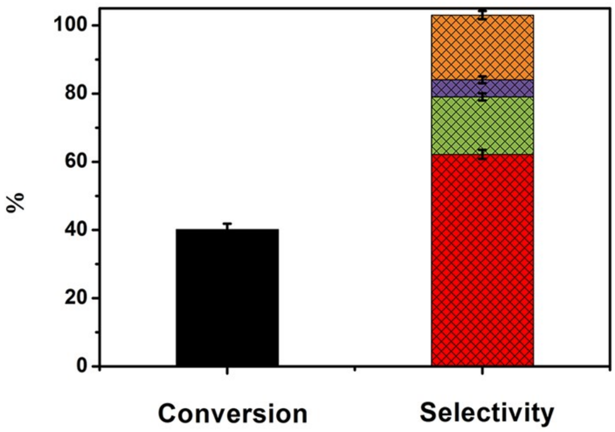

Fig. S13 The GC characterization of styrene epoxidation reaction with commercial CoO in 24 h. (red: styrene oxide; green: benzaldehyde; purple: benzoic acid; orange: 2-phenyl acetaldehyde)

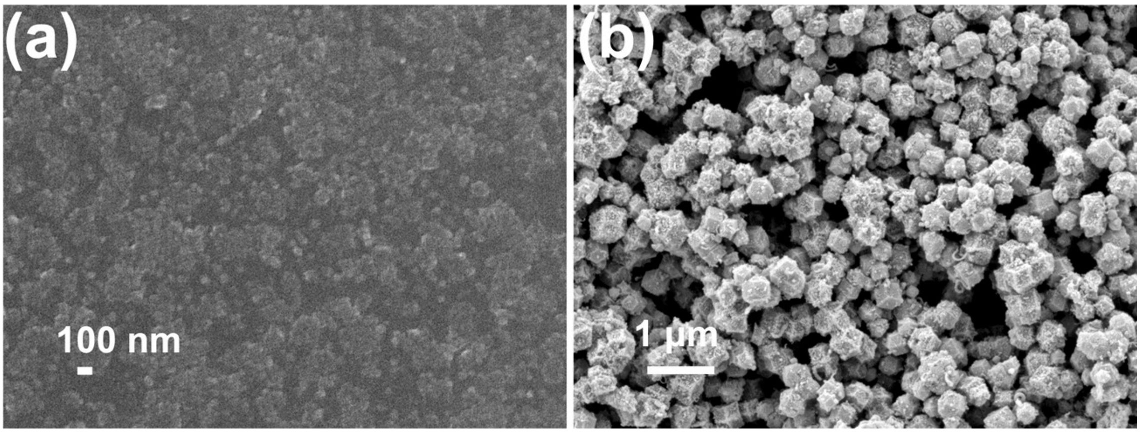

Fig. S14 The SEM images of the Zn_1Co_1-ZIF and its derivative after reaction. (a) Zn_1Co_1-ZIF; (b) Zn_1Co_1-ZIF derivative.

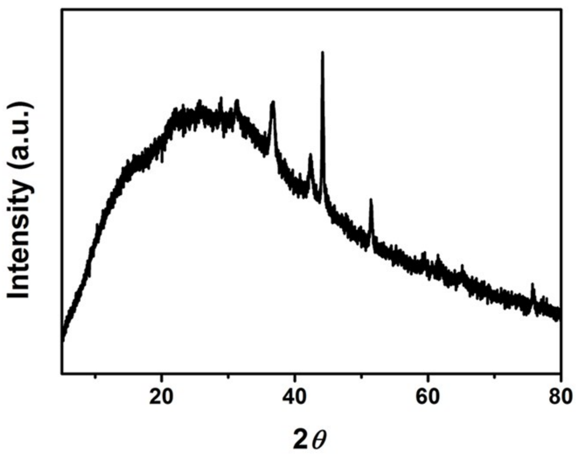

Fig. S15 The XRD spectra of the Zn_1Co_1-ZIF derivative after reaction.

Tab. S1 ICP of the multicomponent MOFs

Multicomponent MOFs	Zn/wt%	Co/wt%	Zn/Co
$Zn_{0.5}Co_1$-ZIF	5.51	16.6	0.42
Zn_1Co_1-ZIF	11.2	12.2	0.65
$Zn_{1.5}Co_1$-ZIF	13.05	12.25	1.16
Zn_2Co_1-ZIF	17.8	12.65	1.59

Tab. S2 ICP of the multicomponent MOFs derivatives

Multicomponent MOFs derivatives	Co/wt%
$Zn_{0.5}Co_1$-ZIF derivative	20.62
Zn_1Co_1-ZIF derivative	18.93
$Zn_{1.5}Co_1$-ZIF derivative	18.89
Zn_2Co_1-ZIF derivative	18.86

Tab. S3 Epoxidation of styrene catalyzed by the multicomponent MOFs and the multicomponent MOFs derivatives

Entry	Catalysts	Styrene Conversion (%)	Selectivity (%)			
			Styrene oxide	Benzaldehyde	Benzoic acid	2-Phenyl acetaldehyde
1	$Zn_{0.5}Co_1$ -ZIF	55.08 ± 1.15	50.09 ± 1.91	38.67 ± 2.04	8.85 ± 0.66	2.39 ± 0.86
2	Zn_1Co_1 -ZIF	58.19 ± 1.05	49.35 ± 0.51	44.29 ± 1.69	2.88 ± 0.44	3.47 ± 1.10
3	$Zn_{1.5}Co_1$ -ZIF	64.99 ± 0.92	48.57 ± 1.30	43.99 ± 0.57	3.25 ± 0.82	4.18 ± 0.78
4	Zn_2Co_1 -ZIF	67.84 ± 0.80	35.27 ± 2.59	49.33 ± 0.89	10.65 ± 1.15	4.74 ± 0.65
5	ZIF-8	74.03 ± 1.42	30.65 ± 0.61	30.82 ± 0.94	27.63 ± 0.69	10.90 ± 0.89
6	Blank	31.38 ± 1.51	46.50 ± 0.58	46.32 ± 3.04	3.04 ± 0.46	4.13 ± 0.68
7	$Zn_{0.5}Co_1$ -ZIF derivative	98.57 ± 1.03	53.65 ± 1.48	34.12 ± 1.57	9.55 ± 0.68	2.67 ± 0.92
8	Zn_1Co_1 -ZIF derivative	99.16 ± 0.84	71.31 ± 2.29	24.07 ± 0.78	2.84 ±0.62	1.78 ± 0.83
9	$Zn_{1.5}Co_1$ -ZIF derivative	98.87 ± 0.82	59.67 ± 1.53	25.51 ± 1.95	8.01± 0.92	6.81 ± 1.66
10	Zn_2Co_1 -ZIF derivative	96.73 ± 0.63	55.34 ± 1.64	26.45 ± 1.38	10.31 ± 0.94	7.89 ± 0.54
11	ZIF-67 derivative	97.10 ± 1.19	47.46 ± 1.23	32.07 ± 0.99	14.05 ± 0.59	6.42 ± 0.73
12	commerci -al CoO	40.12 ± 1.70	59.18 ± 1.32	16.87 ± 1.06	5.01 ± 0.99	18.94 ± 1.21

Conditions: 10 mM styrene and 20 mM TBHP reacted with 20 mg catalysts in a three flask under 600 rpm, 100 °C, 24 h.

Tab. S4 Epoxidation of styrene catalyzed by the general catalysts

Entry	Catalysts	Oxidants	Styrene Conversion (%)	Styrene oxide Selectivity (%)	References
1	35 CoOx/5 TiO_2/SBA-15	TBHP	80.5	67.5	*Catal. Sci. Technol.*, 2017, **7**, 2032.
2	0.5Au_{25}-HAP	TBHP	21.8	36.4	*Chem.Commun.*, 2010, **46**, 550.
3	CuO	TBHP	56.9	81.1	*Catal. Commun.*, 2007, **8**, 1556.
4	Ag–$Co_{0.79}Fe_{2.51}O$	TBHP	58.1	44.5	*DaltonTrans.*, 2009, **32**, 10527.
5	Fe-MIL-101	TBHP	19.7	64.2	*RSC Adv.*, 2014, **4**, 38048.
6	Au/MgO	TBHP	44.6	36.1	*J. Catal.*, 2004, **223**, 236.
7	Au/CNTs	TBHP	6.9	61.4	*Catal. Lett.*, 2010, **134**, 51.
8	BaO	TBHP	40.7	78.7	*Green Chem.*, 2006, **8**, 689.
9	CuO-NR/LDH	TBHP	96	81	*Chem.Commun.*, 2015, **51**, 8817.
10	Ti(50)-FeTAPP	PhIO+Air	39.2	79.6	*Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal Chemistry*, 2012, **42**, 608.
11	Ti-MCM-41	H_2O_2	18.2	38.7	*Appl. Surf. Sci.*, 2008, **255**, 2632.
12	Zn_1Co_1-ZIF derivative	TBHP	98.87	71.31	This work