Frontiers of Materials Science

Electronic Supplementary Material

Blazing fast MOF magic: carbon nanotubes derived from MOFs for catalysis

Chuan Xu*, Junge Zhang*, Jiaxin Liu*, Weiqiang Zhou (✉), Xianghai Song, Xin Liu, Yangyang Yang, Qian Yang, Yi Guo, Yuqiao Zhang, Jisheng Zhang, Pengwei Huo (✉), and Long Zhang (✉)

Institute of Green Chemistry and Chemical Technology, School of Chemistry and Chemical Engineering, Jiangsu University, Zhenjiang 212013, China

E-mails: wqzhou@ujs.edu.cn (W.Z.), huopw@ujs.edu.cn (P.H.), longzhang@ujs.edu.cn (L.Z.)

* C.X., J.Z., and J.L. contributed equally to this work.

Experimental

Preparation of ZIF-67. First, cobalt nitrate hexahydrate ($Co(NO_3)_2·6H_2O$, 1.455 g, 5 mmol) and 2-methylimidazole (2-mlm, 1.642 g, 20 mmol) were separately dissolved in 80 mL methanol. Such two solutions were placed in an ultrasonic cleaning machine and sonicated for 5–10 min. After they were completely clear and uniform, the cobalt nitrate solution was poured into the 2-mlm solution, shaken vigorously for 30 s to mix evenly, and let stand at room temperature for 24 h. The as-synthesized sample was collected by centrifugation at 8500 $r·min^{-1}$ for 5 min and washed with methanol. Finally, the obtained ZIF-67 sample was dried at 60 ℃ under vacuum for 24 h.

Preparation of Ni_xCo_{1-x}-ZIF-67. Ni_xCo_{1-x}-ZIF-67 was synthesized using a similar synthesis procedure of ZIF-67 with some modifications. As for the synthesis of typical Ni_5Co_5-ZIF-67, $Co(NO_3)_2·6H_2O$ (0.7275 g, 2.5 mmol) and $Ni(NO_3)_2·6H_2O$ (0.7269 g, 2.5 mmol) were dissolved in 80 mL of methanol. 2-mlm (1.642 g, 20 mmol) was dissolved in 80 mL methanol separately. The two solutions were placed in an ultrasonic cleaning machine and sonicated for 5–10 min. After the solutions were completely clear and uniform, the cobalt nitrate solution was poured into the 2-mlm solution, shaken vigorously for 30 s to mix evenly, and let stand at room temperature for 24 h. The subsequent separation, washing, and drying procedures were the same with the synthesis of ZIF-67.

Similarly, the synthesis of Ni_7Co_3-ZIF-67 was performed by using the same synthesis procedure of Ni_5Co_5-ZIF-67 except for the variance of feed amounts of both $Co(NO_3)_2·6H_2O$ and $Ni(NO_3)_2·6H_2O$. In detail, the amounts of $Co(NO_3)_2·6H_2O$ and $Ni(NO_3)_2·6H_2O$ were 1.25 and 3.75 mmol for Ni_7Co_3-ZIF-67, respectively.

Preparation of C-CoNi. Previously prepared Ni_xCo_{1-x}-ZIF-67 was transferred into a specially designed 1 cm quartz vessel, and then the quartz vessel was placed into rapid thermal processing. The machine was set to be heated up to 1000 ℃ within 20 s and then held for 1 min. The product could be collected when it was cooled down to room temperature. After the samples of ZIF-67, Ni_5Co_5-ZIF-67, and Ni_7Co_3-ZIF-67 were treated by RTP, the as-prepared catalysts were marked as C-CoNi-10, C-CoNi-55, and C-CoNi-37, respectively.

Catalytic measurements. Styrene epoxidation was carried out in acetonitrile solution, heated at 80 ℃ for 24 h with a reflux condenser. In a typical experiment, the catalyst (20 mg of C-CoNi) was loaded into a 25 mL round-bottom flask. Subsequently, a solution of acetonitrile (10 mL), styrene (4.35 mmol, 0.5 mL), and tert-butyl hydroperoxide (8.7 mmol, 1.2 mL) was added to the flask, and the mixture was sonicated for 5 min. After the catalytic reaction, the catalyst was separated from the reaction solution by centrifugation at 10000 $r \cdot min^{-1}$ for 6 min, thoroughly washed with ethanol, and then placed in a vacuum-drying oven at 60 ℃ for 24 h. The liquid substrates and products were filtrated and analyzed by gas chromatography (Shimadzu GC-2022). As a control, catalytic reactions were also conducted without any catalyst under the same conditions.

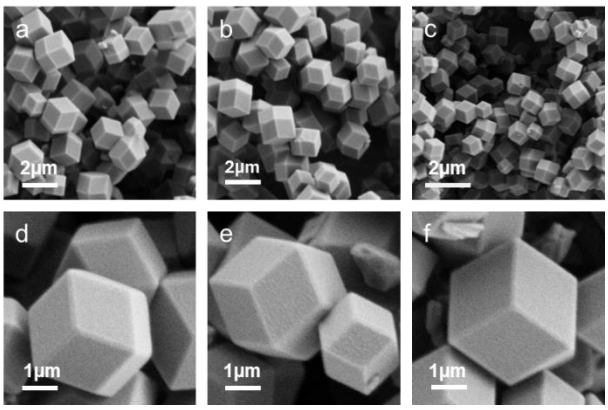

Fig. S1 The field emission-scanning electron microscopy (FESEM) images of ZIF-67 synthesized with varying Co/Ni ratios: **(a)(d)** ZIF-67 Co/Ni 1:0; **(b)(e)** ZIF-67 Co/Ni 5:5; **(c)(f)** ZIF-67 Co/Ni 3:7.

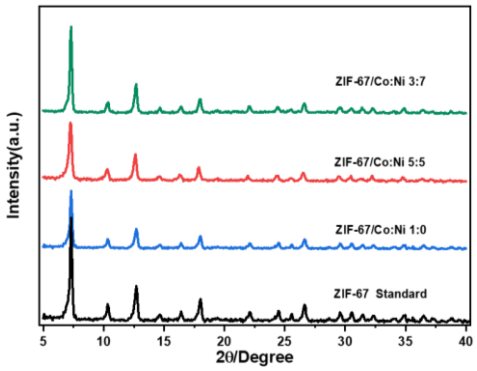

Fig. S2 Powder XRD patterns of ZIF-67 synthesized with various Co/Ni ratios.

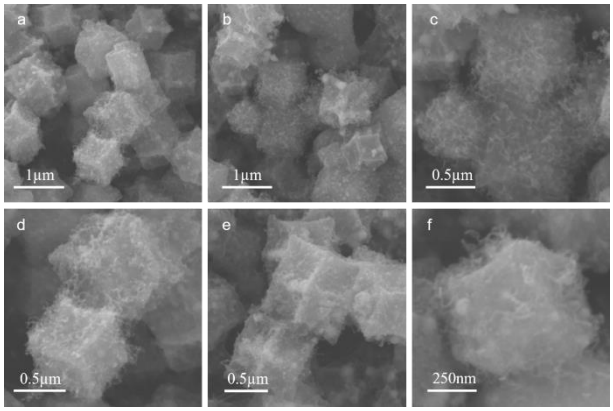

Fig. S3 FESEM images of C-CoNi with various Co/Ni ratios: **(a)(d)** C-CoNi-10; **(b)(e)** C-CoNi-55; **(c)(f)** C-CoNi-37.

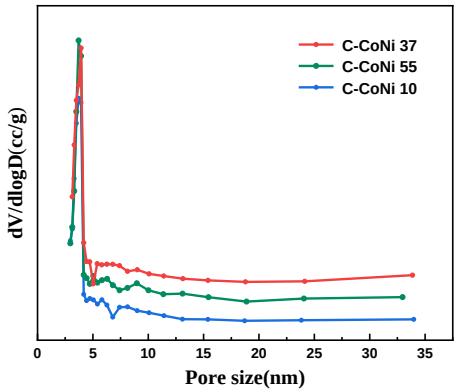

Fig. S4 The pore size distribution of C-CoNi.

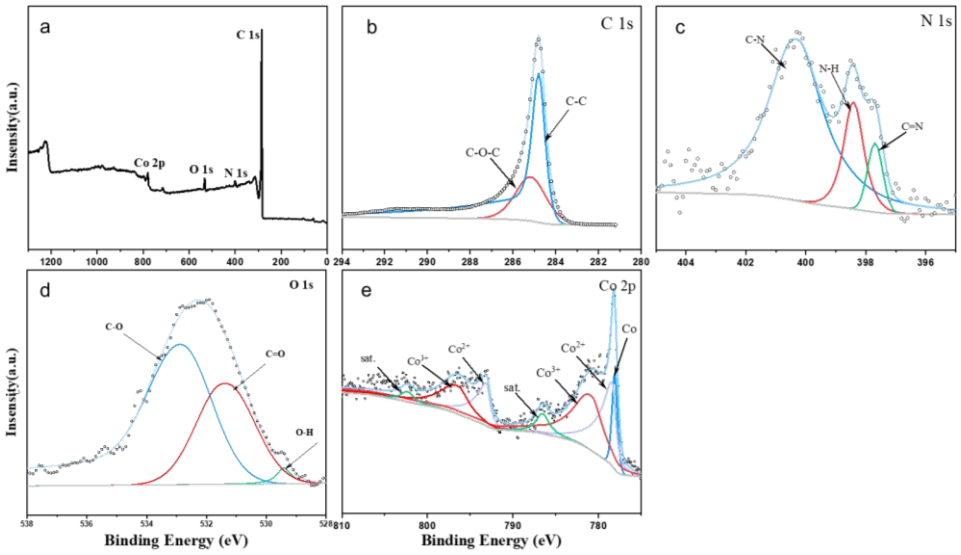

Fig. S5 XPS spectra of C-CoNi-10: **(a)** survey spectrum; **(b)** deconvolution of the C 1s spectrum; **(c)** deconvolution of the N 1s spectrum; **(d)** deconvolution of the O 1s spectrum; and **(e)** the Co 2p spectrum.

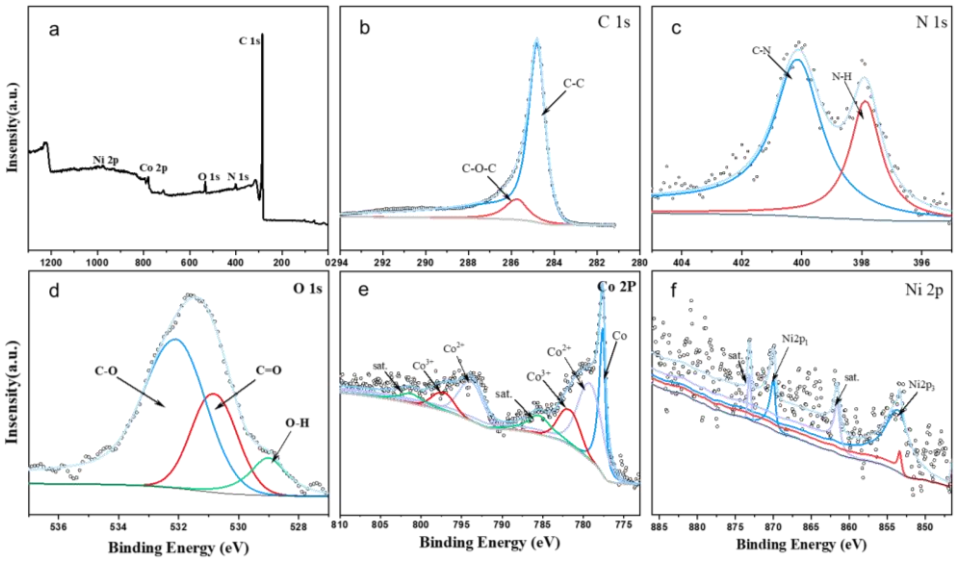

Fig. S6 XPS spectra of C-CoNi-55: **(a)** survey spectrum; **(b)** deconvolution of the C 1s spectrum; **(c)** deconvolution of the N 1s spectrum; **(d)** deconvolution of the O 1s spectrum; **(e)** deconvolution of the Co 2p spectrum; and **(f)** the Ni 2p spectrum.

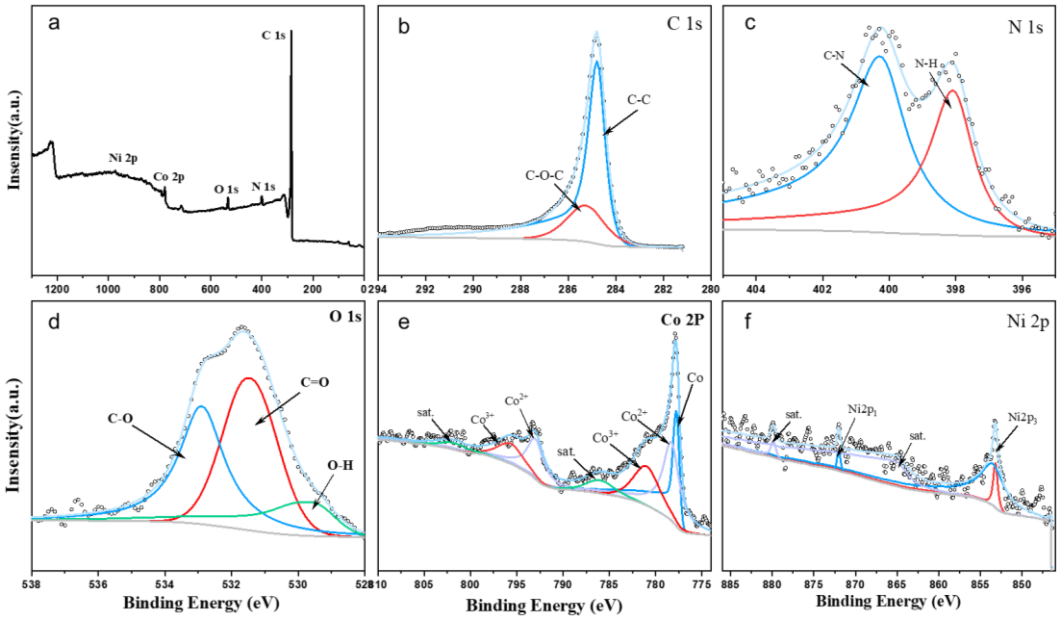

Fig. S7 XPS spectra of C-CoNi-37: **(a)** survey spectrum; **(b)** deconvolution of the C 1s spectrum; **(c)** deconvolution of the N 1s spectrum; **(d)** deconvolution of the O 1s spectrum; **(e)** deconvolution of the Co 2p spectrum; and **(f)** the Ni 2p spectrum.

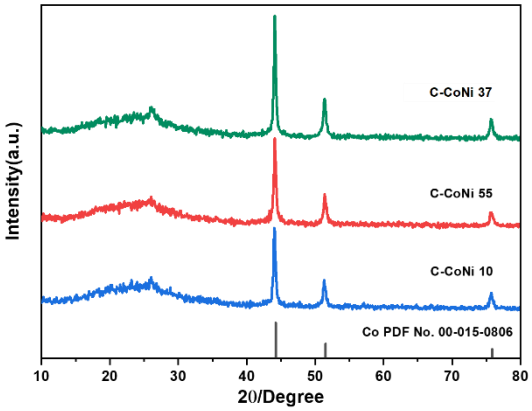

Fig. S8 Powder XRD patterns of C-CoNi after catalytic reactions.

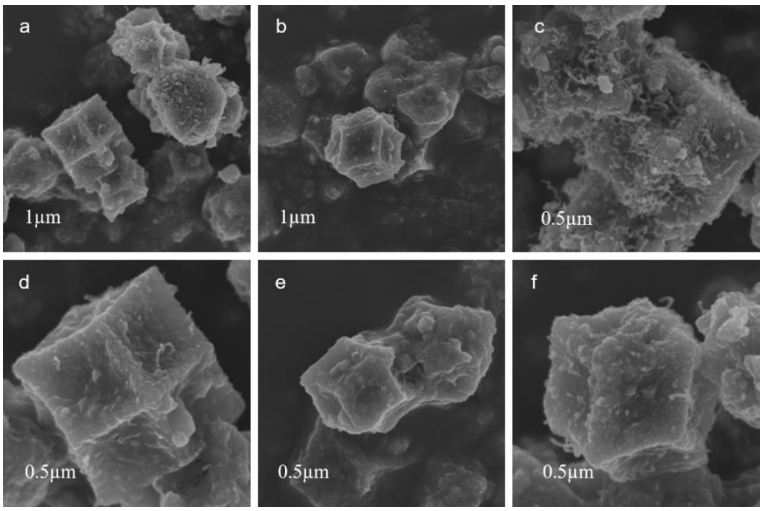

Fig. S9 FESEM images of C-CoNi with various Co/Ni ratios after reaction: **(a)(d)** C-CoNi-10; **(b)(e)** C-CoNi-55; **(c)(f)** C-CoNi-37.

Table S1 Comparison for the catalytic activity and selectivity of relevant catalysts

Catalyst	Oxidant	Styrene conversion/%	Styrene oxide selectively/%	Ref.
Au/CNTs	TBHP	6.9	61.4	[S1]
Zn_1Co_1-ZIF	TBHP	98.9	71.3	[S2]
Co/ZIF-1000	TBHP	99.9	71.0	[S3]
Fe-MIL-101	TBHP	19.7	64.2	[S4]
CoO_x/TiO_2/SBA-15	TBHP	80.5	67.5	[S5]
Ag-$Co_{0.79}Fe_{2.51}O$	TBHP	58.1	44.5	[S6]
C-CoNi-10	TBHP	82.1	52.4	This work
C-CoNi-55	TBHP	78.4	54.3	This work
C-CoNi-37	TBHP	79.4	58.5	This work

References

[S1] Liu J H, Wang F, Xu T, et al. Styrene Epoxidation over Carbon Nanotube-Supported Gold Catalysts. Catalysis Letters, 2010, 134: 51–55

[S2] Hui J F, Chu H M, Zhang W L, et al. Multicomponent metal–organic framework derivatives for optimizing the selective catalytic performance of styrene epoxidation reaction. Nanoscale, 2018, 10: 8772–8778

[S3] Jia B Q, Bai L, Han Z, et al. High-performance styrene epoxidation with vacancy-defect cobalt single-atom catalysts. ACS Applied Materials & Interfaces, 2022, 14(8): 10337–10343

[S4] Sun J, Yu G L, Huo Q S, et al. Epoxidation of styrene over Fe(Cr)-MIL-101 metal–organic frameworks. RSC Advances, 2014, 4(72): 38048–38054

[S5] Li Y Q, Zhao S C, Hu Q M, et al. Highly efficient CoO_x/SBA-15 catalysts prepared by atomic layer deposition for the epoxidation reaction of styrene. Catalysis Science & Technology, 2017, 7: 2032–2038

[S6] Zhang D H, Li H B, Li G D, et al. Magnetically recyclable Ag-ferrite catalysts: general synthesis and support effects in the epoxidation of styrene. Dalton Transactions, 2009, 32: 10527–10533