

Supporting Information

Synthesis of Fe/M (M=Mn, Co, Ni) bimetallic metal organic frameworks and their catalytic activity for phenol degradation at mild conditions

Qiao Sun^a, Min Liu^a, Keyan Li^a, Yitong Han^a, Yi Zuo^a, Fanfan Chai^a, Chunshan

Song^{*a,b}, Guoliang Zhang^c, and Xinwen Guo^{*a}

^aState Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy

Research, School of Chemical Engineering, Dalian University of Technology, Dalian

116024, People's Republic of China

^bEMS Energy Institute, PSU-DUT Joint Center for Energy Research and Department

of Energy & Mineral Engineering, Pennsylvania State University, University Park,

Pennsylvania 16802, United States

^cCollege of Biological and Environmental Engineering, Zhejiang University of

Technology, Hangzhou 310014, People's Republic of China

*X. Guo. E-mail: guoxw@dlut.edu.cn; Fax: +86-0411-84986134; Tel: +86-0411-

84986133

*C. Song. E-mail: csong@psu.edu; Fax: +1-814-863-4466; Tel: +1-814-865-3573

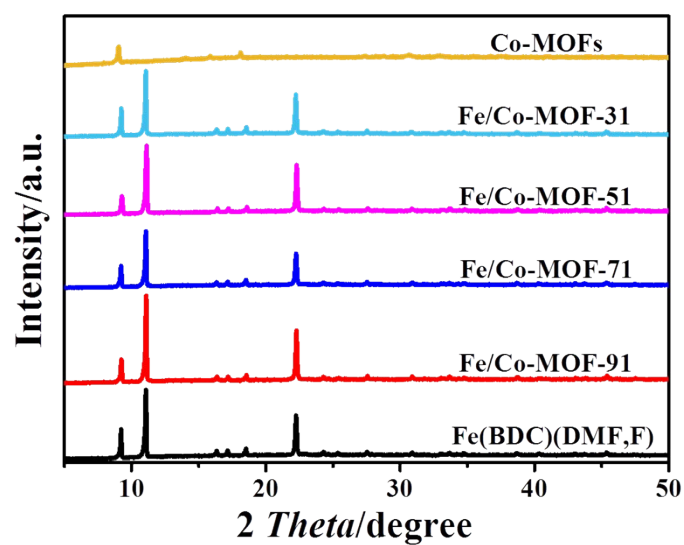


Fig. S1 XRD patterns of the samples synthesized with FeCl_2 and CoCl_2

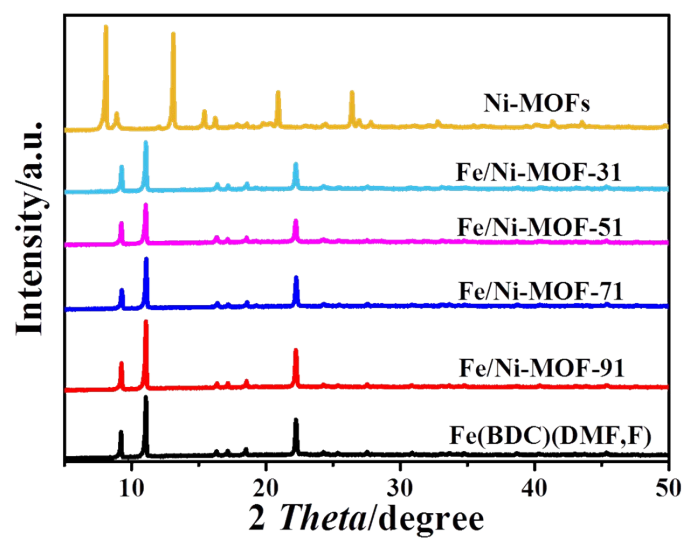


Fig. S2 XRD patterns of the samples synthesized with FeCl_2 and NiCl_2

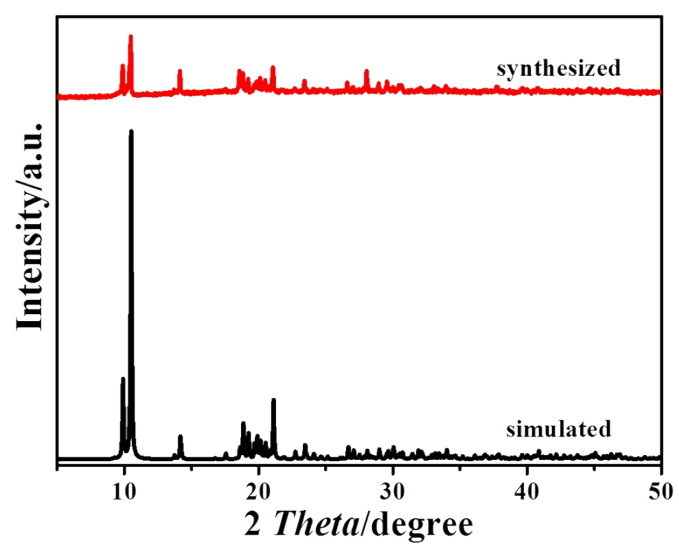


Fig. S3. XRD patterns of the sample synthesized with MnCl_2

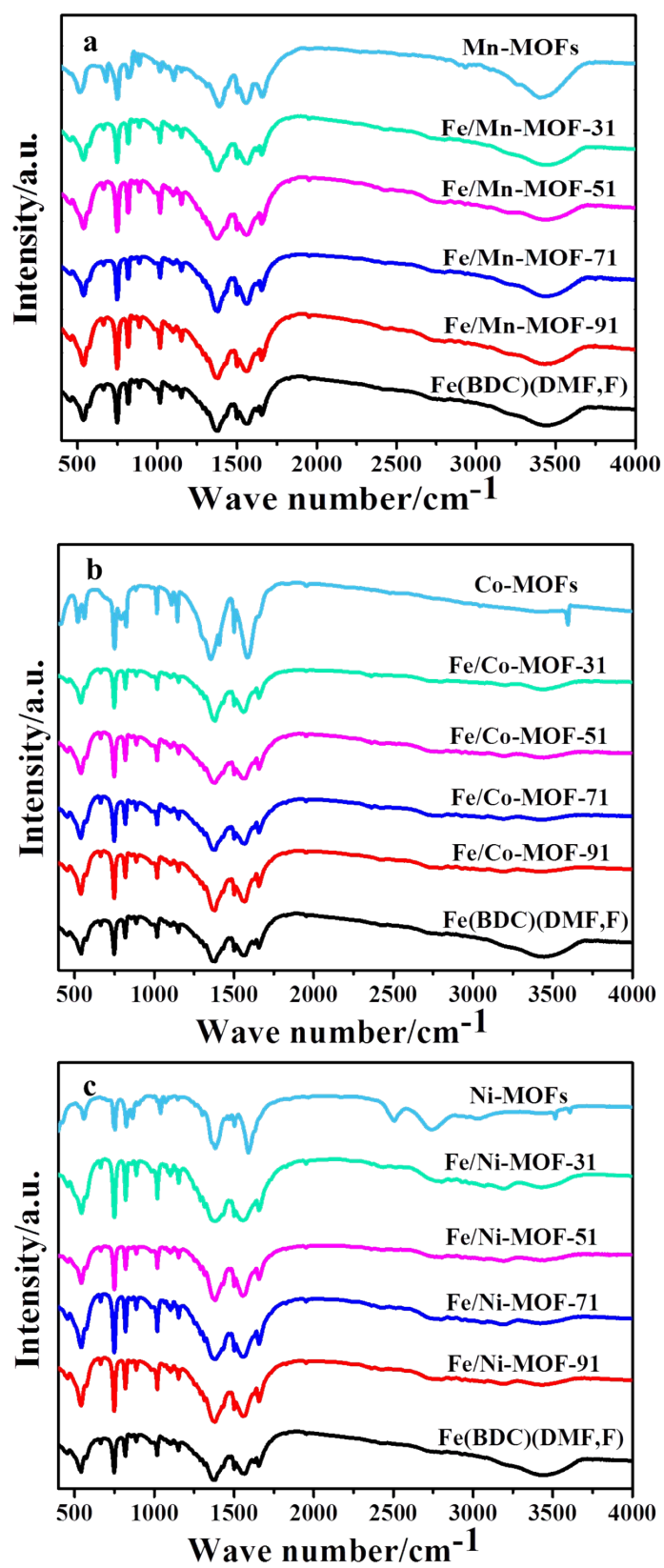


Fig. S4 FT-IR spectra of the Fe/Mn-MOFs, Fe/Co-MOFs and Fe/Ni-MOFs

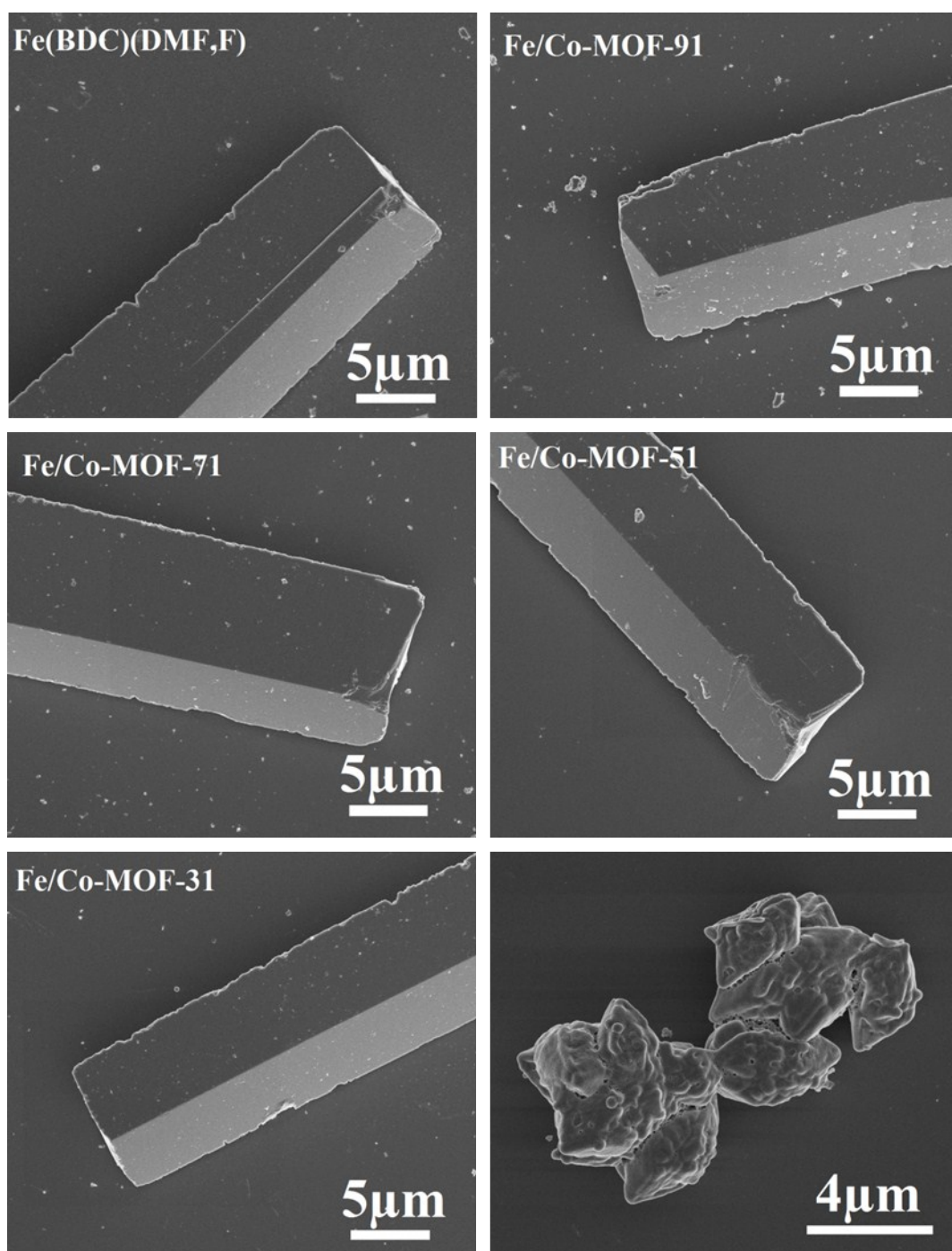


Fig. S5 SEM images of the Fe/Co-MOFs

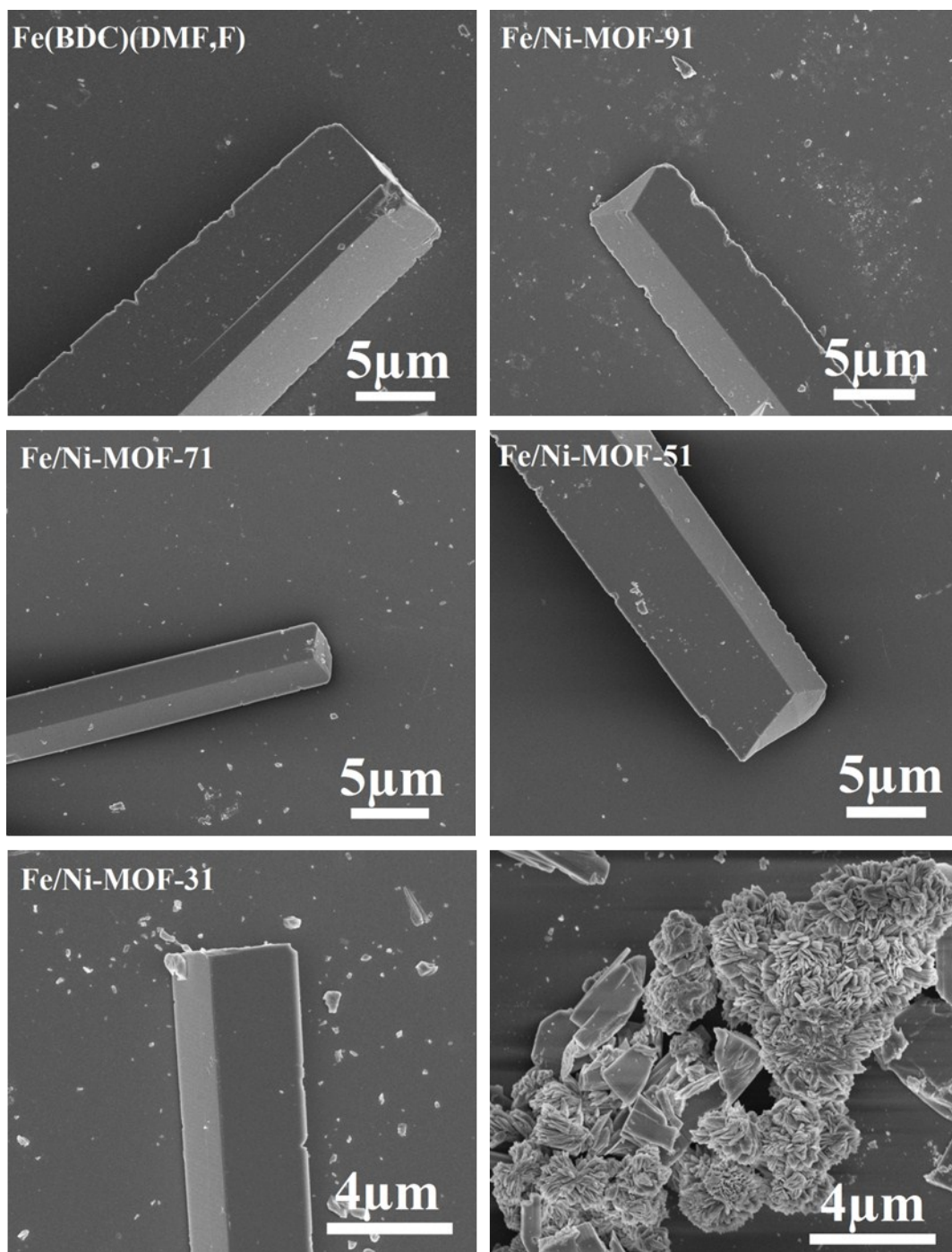


Fig. S6 SEM images of the Fe/Ni-MOFs

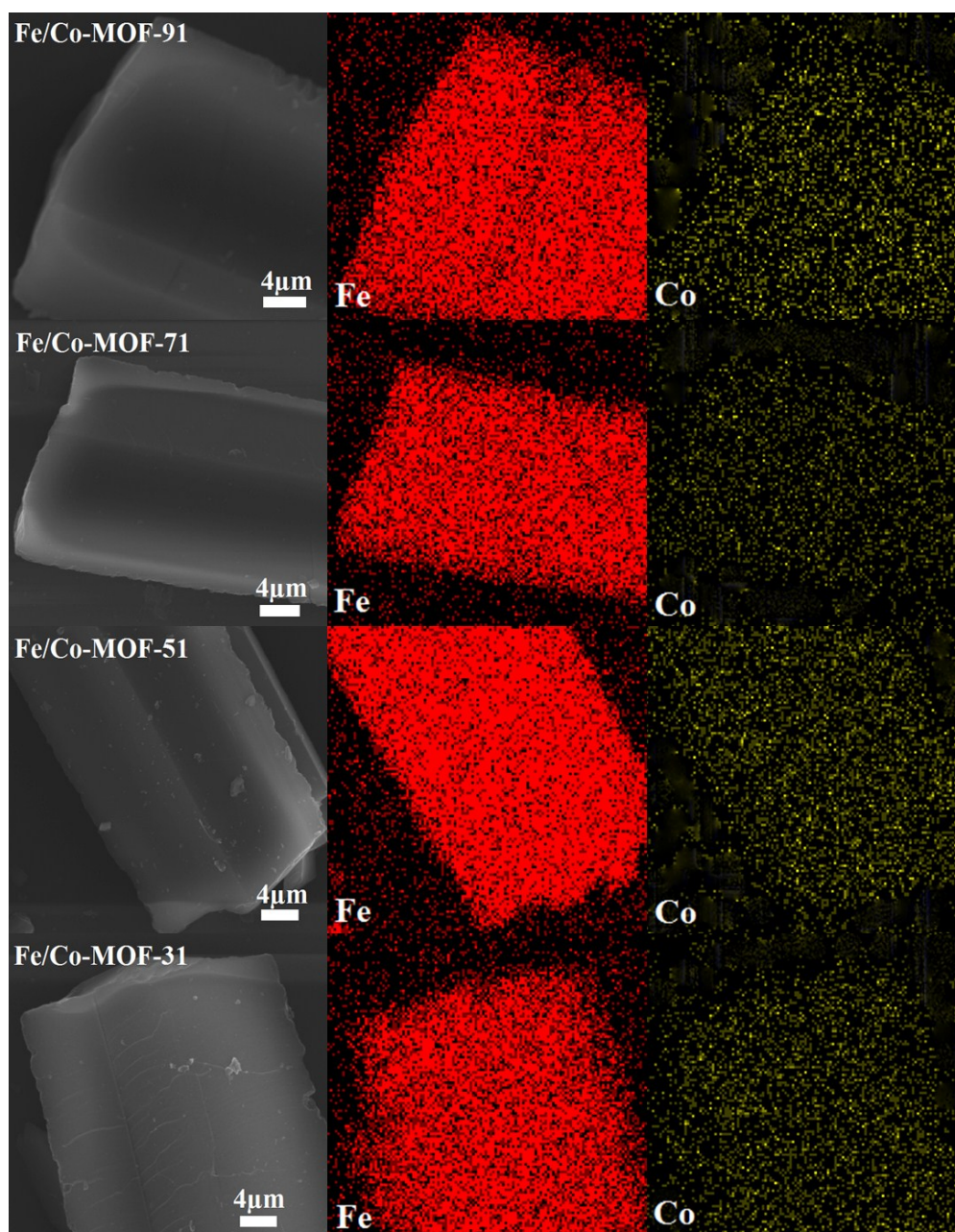


Fig. S7 EDS mapping of metal elements of the Fe/Co-MOFs

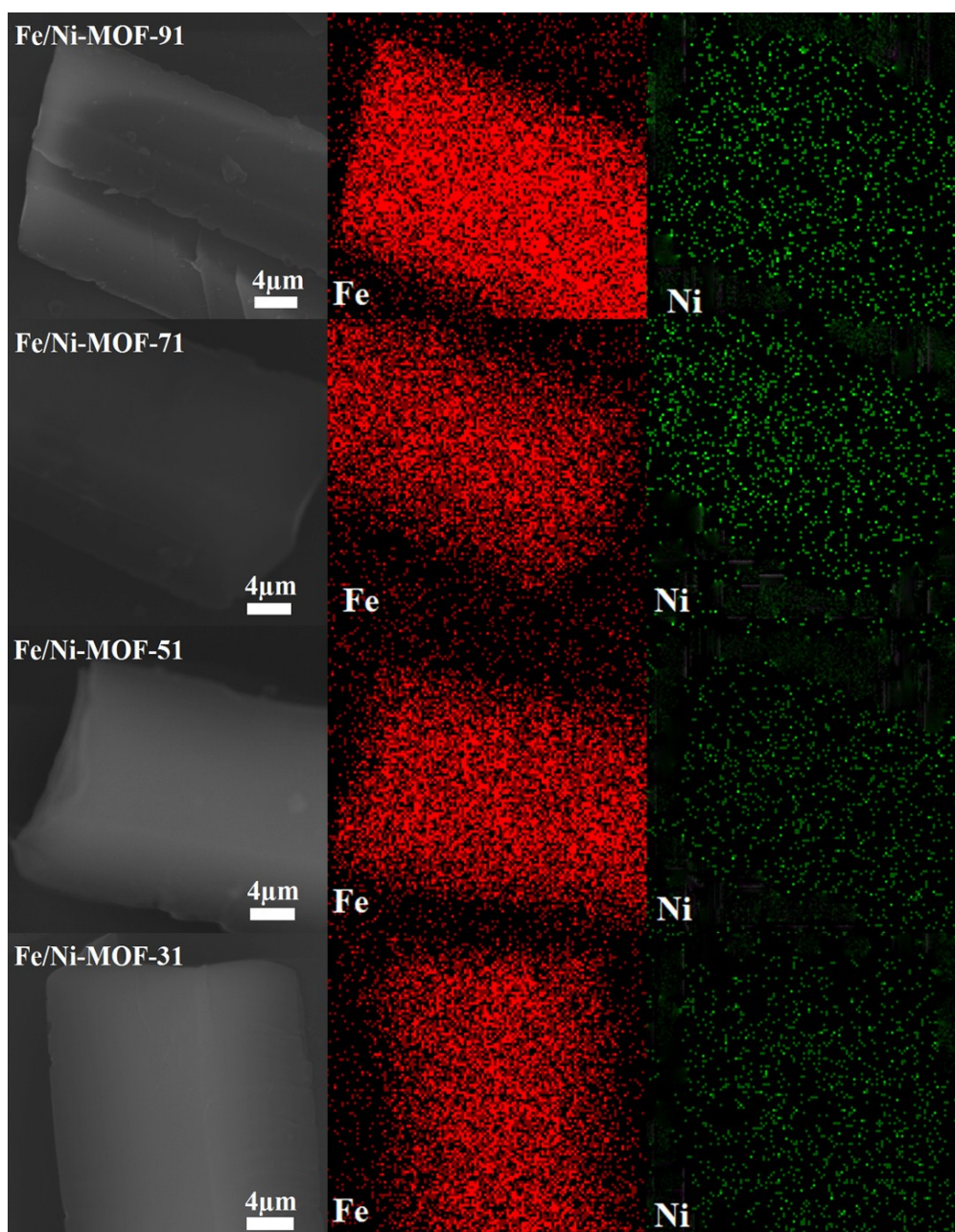


Fig. S8 EDS mapping of metal elements of the Fe/Ni-MOFs

Table S1 The contents of Fe and Co and the real ratio of $n(\text{Fe})/n(\text{Co})$ in these Fe/Co-MOFs

Sample	Fe/Co-MOF-91	Fe/Co-MOF-71	Fe/Co-MOF-51	Fe/Co-MOF-31
Fe/wt%	18.16	16.72	17.48	16.48
Co/wt%	0.63	0.60	1.19	1.90
$n(\text{Fe})/n(\text{Co})$	30.37	29.36	15.48	9.14

Table S2 The contents of Fe and Ni and the real ratio of $n(\text{Fe})/n(\text{Ni})$ in these Fe/Ni-MOFs

Sample	Fe/Ni-MOF-91	Fe/Ni-MOF-71	Fe/Ni-MOF-51	Fe/Ni-MOF-31
Fe/wt%	14.34	15.38	13.92	13.10
Ni/wt%	1.57	2.11	2.89	3.90
$n(\text{Fe})/n(\text{Ni})$	9.62	7.68	5.07	3.54

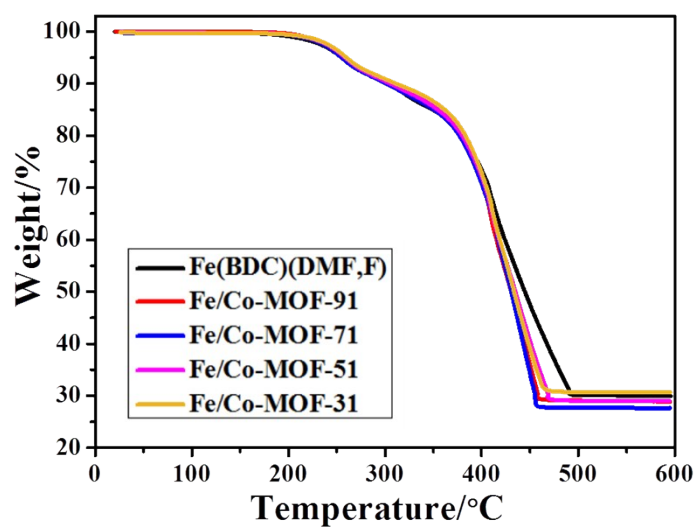


Fig. S9. TG curves of the Fe/Co-MOFs

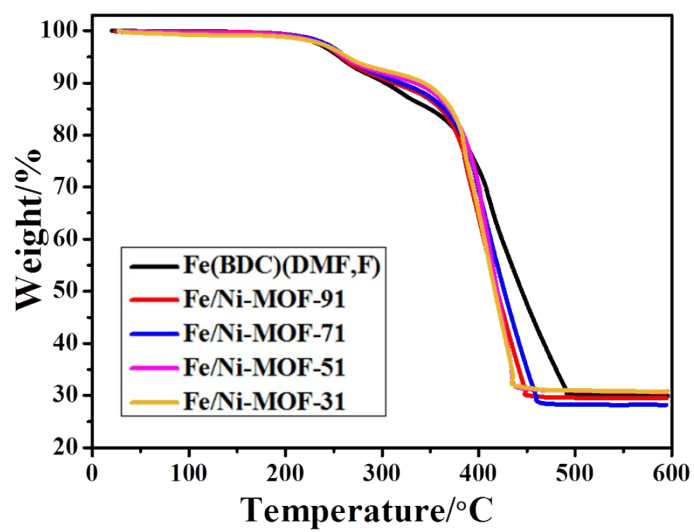


Fig. S10. TG curves of the Fe/Ni-MOFs

Table S3 Results of several blank experiments

Catalyst	Conv.(phenol)/ %	Conv.(H ₂ O ₂)/%	Conv.(COD)/ %
None	<1	<2	<1
Fe(BDC)(DMF,F)	<2	–	<1
Fe/Mn-MOF-31	<3	–	<2
Fe/Mn-MOF-51	<2	–	<2
Fe/Mn-MOF-71	<2	–	<2
Fe/Mn-MOF-91	<2	–	<1
Fe/Co-MOF-31	<2	–	<1
Fe/Co-MOF-51	<2	–	<2
Fe/Co-MOF-71	<2	–	<3
Fe/Co-MOF-91	<2	–	<2
Fe/Ni-MOF-31	<1	–	<3
Fe/Ni-MOF-51	<2	–	<2
Fe/Ni-MOF-71	<2	–	<1
Fe/Ni-MOF-91	<3	–	<2

Reaction conditions: 35 °C, 1 atm, cat 0.064 g L⁻¹, $n(\text{H}_2\text{O}_2):n(\text{phenol})=14$, $[\text{phenol}]_0$

1000 mg L⁻¹, 3 h, initial pH 6.2.

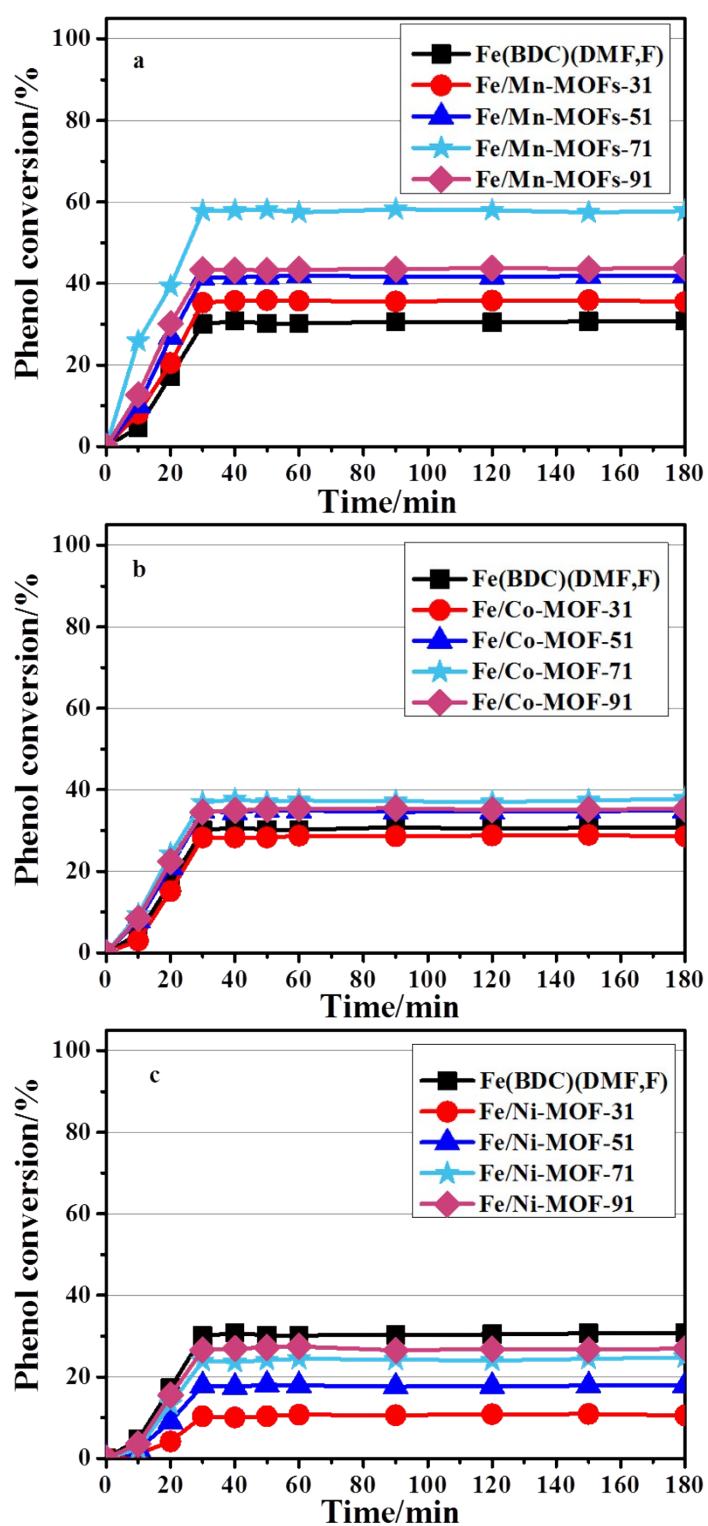


Fig. S11 Time conversion plot of phenol degradation with removal of catalysts after

30 minutes reaction (Conditions: initial phenol concentration, 1000 mg L⁻¹;

$n(\text{H}_2\text{O}_2):n(\text{phenol})=14$; initial pH 6.2; cat 0.064 g L⁻¹; 35 °C, 1 atm, 3 h)

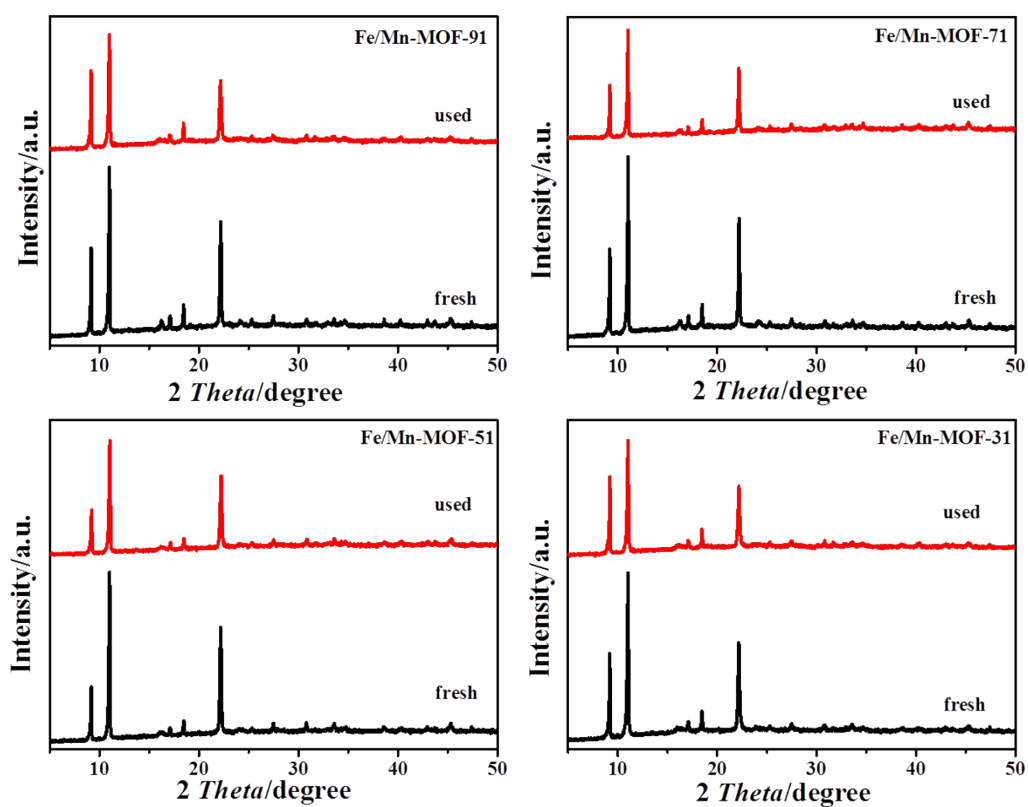


Fig. S12. XRD patterns of the four Fe/Mn-MOFs before and after catalysis

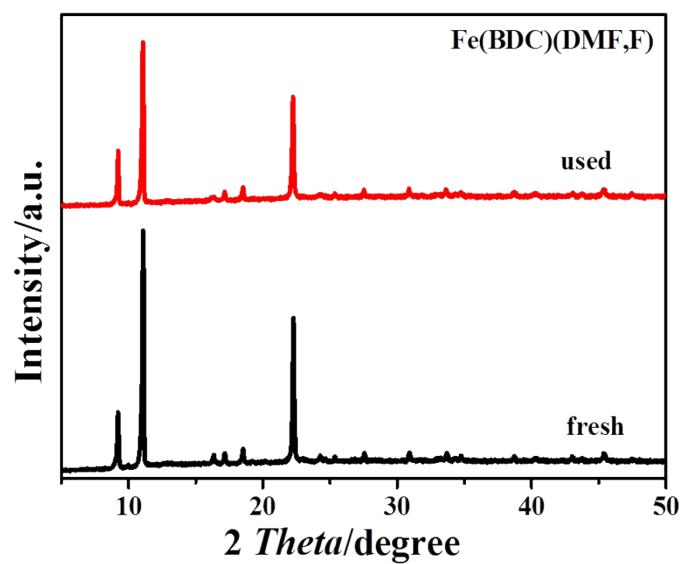


Fig. S13 XRD patterns of Fe(BDC)(DMF,F) before and after reactions

Table S4. Summary of Fe and Mn species leached in the solution after degradation

Catalyst	Fe/mg·L ⁻¹	Mn/mg·L ⁻¹
Fe(BDC)(DMF,F)	1.3	0
Fe/Mn-MOF-31	1.1	0.4
Fe/Mn-MOF-51	1.2	0.2
Fe/Mn-MOF-71	1.1	0.5
Fe/Mn-MOF-91	1.0	0.4

Reaction conditions: initial phenol concentration, 1000 mg L⁻¹; $n(\text{H}_2\text{O}_2):n(\text{phenol})=14$; initial pH 6.2; cat 0.32 g L⁻¹; 35 °C, 1 atm, 3 h.