

Supplementary Data

MOF-derived metal oxide composite $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$ for efficient formaldehyde oxidation at low temperature

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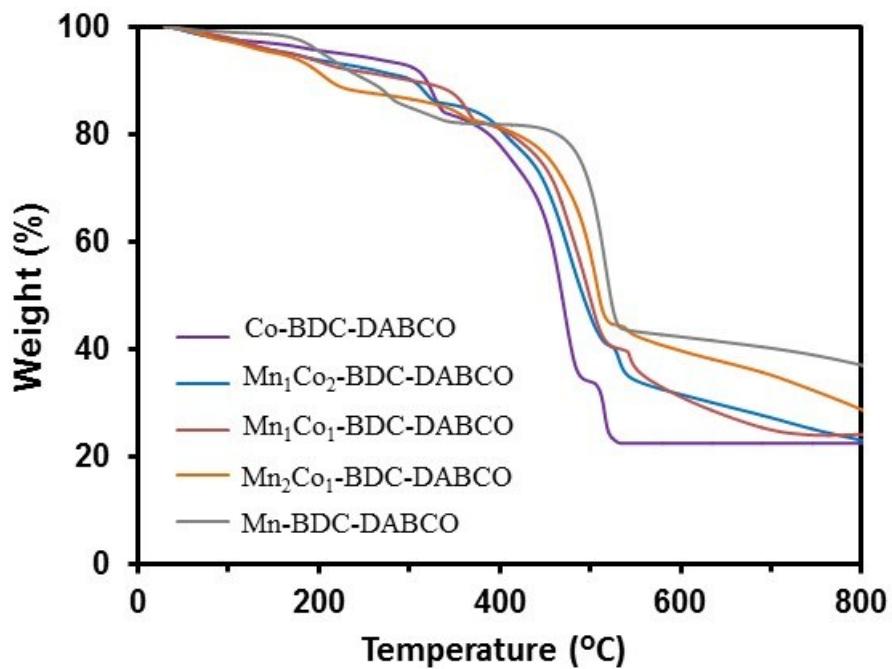


Figure S1. TGA curves of the MnCo-BDC-DABCO.

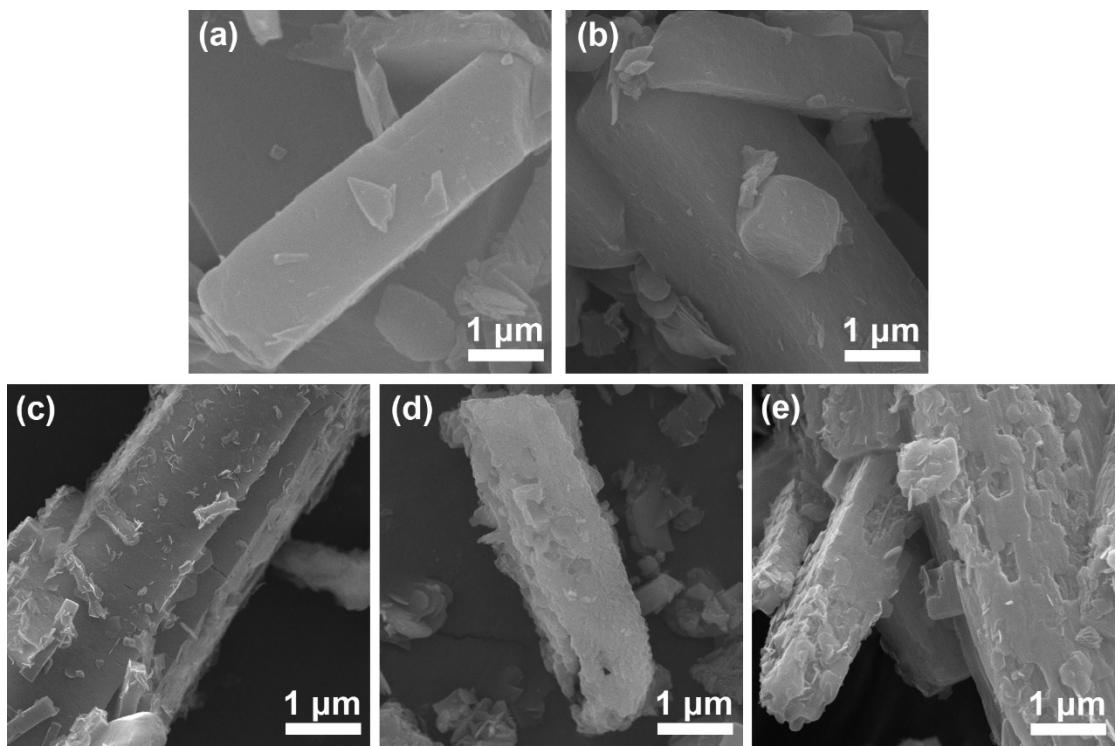


Figure S2. The SEM images of (a) Co-BDC-DABCO, (b) Mn₁Co₂-BDC-DABCO, (c) Mn₁Co₁-BDC-DABCO, (d) Mn₂Co₁-BDC-DABCO and (e) Mn-BDC-DABCO.

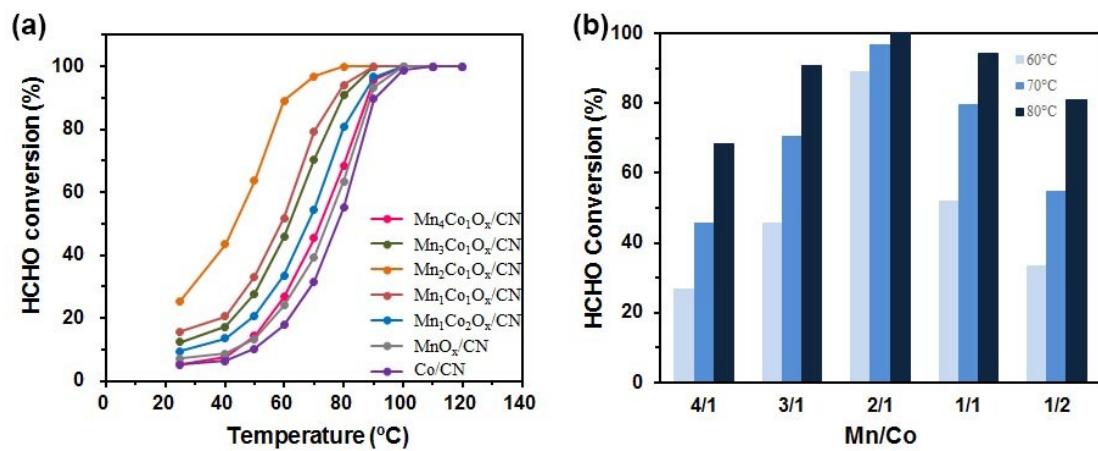


Figure S3. (a) Catalytic activity test for HCHO oxidation over MnCoO_x/CN catalysts.

(b) Effect of Mn/Co ratios on HCHO oxidation over MnCoO_x/CN catalysts.

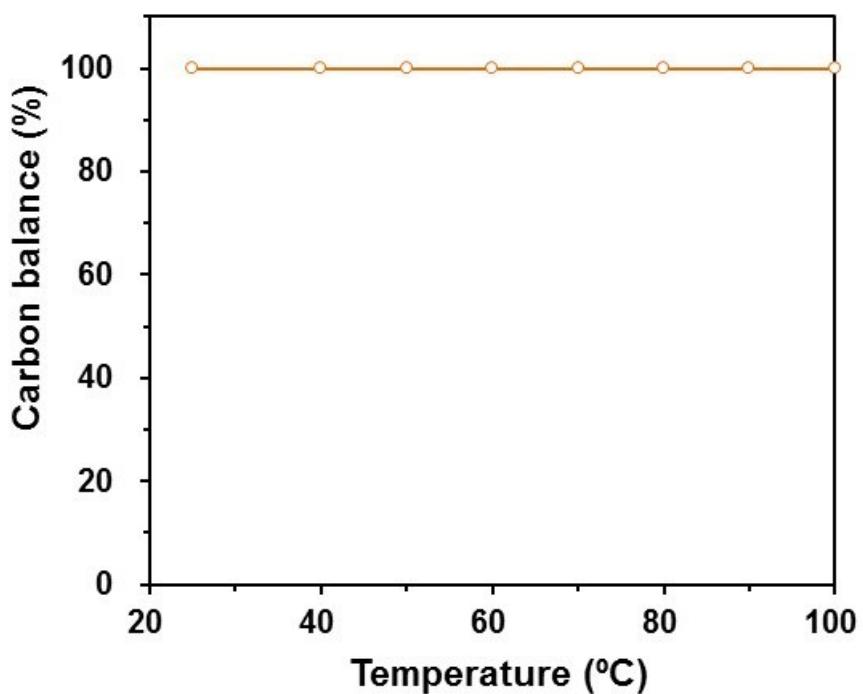


Figure S4. Carbon balance plotted as a function of the reaction temperature for $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$.

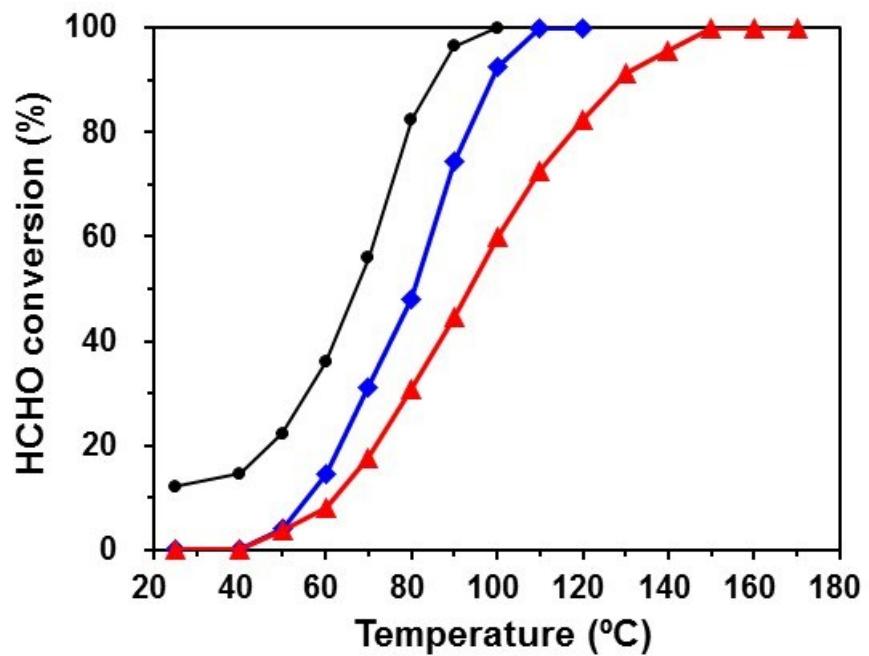


Figure S5. Activity profile of Mn₂Co₁O_x/C (black), Mn₂Co₁O_x/AC-N (blue) and Mn₂Co₁O_x (red).

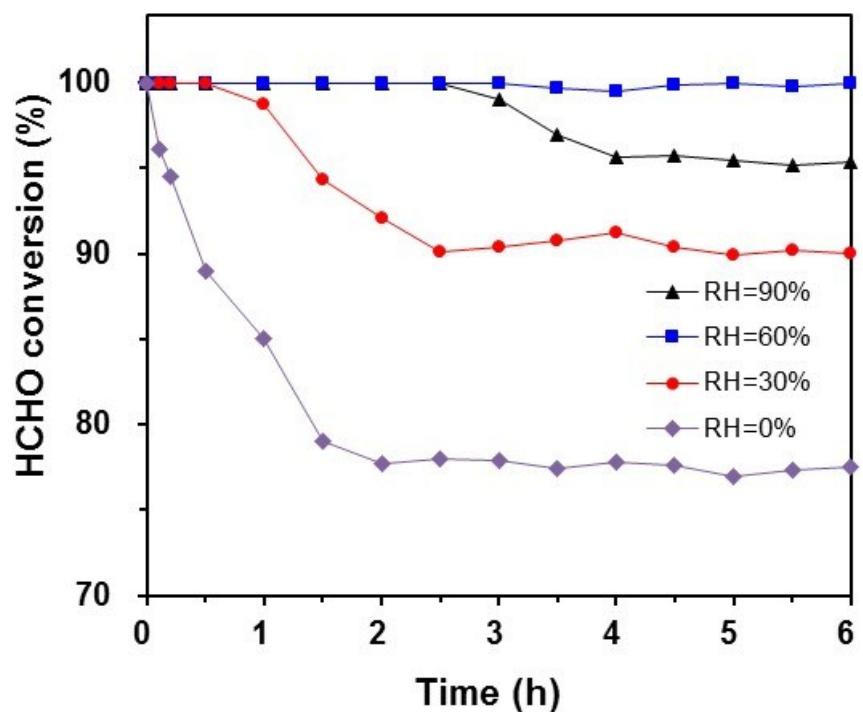


Figure S6. Effect of relative humidity on catalytic performance of $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$.

Reaction condition: HCHO concentration = 100 ppm, GHSV = 60000 mL/g_{cat}·h, T = 80°C.

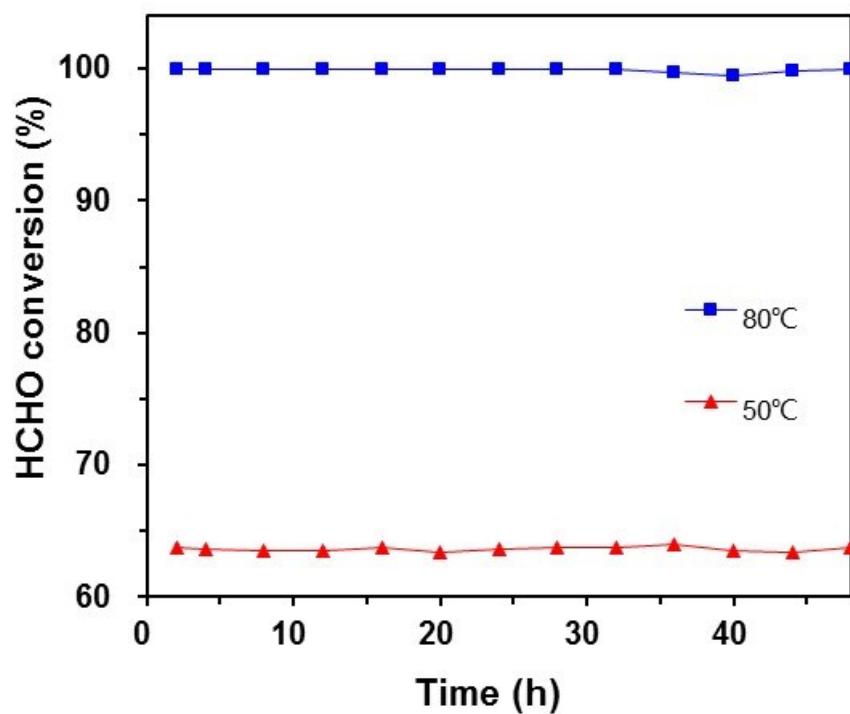


Figure S7. Catalytic stability test of $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$ at 80°C and 50°C . Reaction condition: HCHO concentration = 100 ppm, GHSV = $60000 \text{ mL/g}_{\text{cat}} \cdot \text{h}$, RH = 60%.

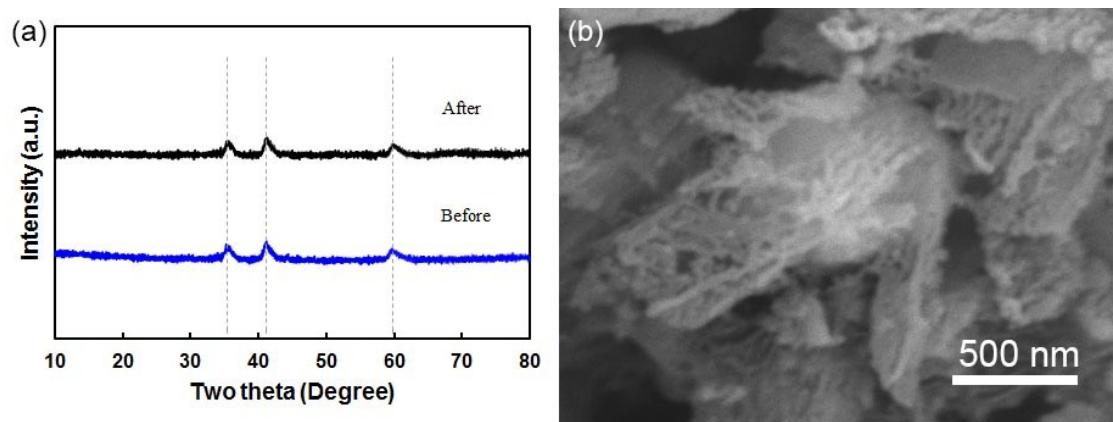


Figure S8. (a) XRD pattern of $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$ before and after the reaction at 80°C . (b) SEM images of $\text{Mn}_2\text{Co}_1\text{O}_x/\text{CN}$ after the reaction at 80°C .

Table S1. Surface areas and pore distribution of the materials.

Materials	S _{BET} (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
Mn-BDC-DABCO	1311	0.60	0.56
Mn ₂ Co ₁ - BDC-DABCO	1389	0.66	0.57
Mn ₁ Co ₁ - BDC-DABCO	1467	0.69	0.57
Mn ₁ Co ₂ - BDC-DABCO	1524	0.70	0.56
Co-BDC-DABCO	1585	0.71	0.56
MnO _x /CN	79	0.14	4.12
Mn ₂ Co ₁ O _x /CN	129	0.18	4.02
Mn ₁ Co ₁ O _x /CN	170	0.20	4.01
Mn ₁ Co ₂ O _x /CN	176	0.21	4.00
Co/CN	193	0.22	4.01

Table S2. Surface element molar ratios for MnCoO_x/CN catalysts.

Catalysts	Mn ³⁺ /Mn ⁴⁺	Co ³⁺ /Co ²⁺	O _{ads} /O _{total}
MnO _x /CN	0.45	-	0.28
Mn ₂ Co ₁ O _x /CN	0.53	0.67	0.42
Mn ₁ Co ₁ O _x /CN	0.49	0.63	0.39
Mn ₁ Co ₂ O _x /CN	0.46	0.60	0.33
Co/CN	-	0.59	0.31

Table S3. The main element contents of various MOFs and catalysts

Materials	C (wt%) ^a	N (wt%) ^a	H (wt%) ^a	Co (wt%) ^b	Mn (wt%) ^b
Mn-BDC-DABCO	46.4	9.5	5.8	/	20.5
Mn ₂ Co ₁ - BDC-DABCO	47.0	9.6	5.5	6.9	13.8
Mn ₁ Co ₁ - BDC-DABCO	46.5	9.8	5.6	10.5	10.2
Mn ₁ Co ₂ - BDC-DABCO	45.6	9.3	5.2	13.7	7.1
Co-BDC-DABCO	46.8	9.4	5.7	20.6	/
MnO _x /CN	42.6	0.9	0.8	/	40.3
Mn ₂ Co ₁ O _x /CN	43.5	1.0	0.9	13.5	27.1
Mn ₁ Co ₁ O _x /CN	44.4	1.2	0.9	20.3	19.9
Mn ₁ Co ₂ O _x /CN	45.9	1.3	1.0	26.7	13.8
Co/CN	51.1	1.5	1.0	41.4	/
Mn ₂ Co ₁ O _x /AC-N	44.1	1.5	0.4	13.7	25.2

^a Measured by elemental analysis.^b Measured by AAS.

Table S4. Survey of manganese oxides and cobalt oxides catalysts for the oxidation of formaldehyde

Catalysts	Mass (mg)	Reaction conditions	GHSV	T _{100%} (°C)	Ref.
Birnessite	100	460 ppm HCHO, purified air	30,000 ml/g·h	100	[1]
Birnessite	100	40 ppm HCHO, air, 80% RH	120,000 ml/g·h	100	[2]
Birnessite	100	200 ppm HCHO, air, 45% RH	120,000 ml/g·h	100	[3]
Todorokite	200	400 ppm HCHO, 10.0% O ₂	18,000 ml/g·h	160	[4]
K-OMS-2 nanorods	100	460 ppm HCHO, 21% O ₂	30,000 ml/g·h	200	[5]
OMS-2	200	500 ppm HCHO, 10% O ₂	30,000 ml/g·h	120	[6]
3D-MnO ₂ mesoporous	200	400 ppm HCHO, 20% O ₂	30,000 ml/g·h	130	[7]
Birnessite nanospheres	50	100 ppm HCHO, 20% O ₂	50,000/h	140	[8]
δ-MnO ₂	60	170 ppm HCHO, 20% O ₂ , 25% RH	100,000 ml/g·h	80	[9]
Spinel Co ₃ O ₄	100	100 ppm HCHO, 21% O ₂	69,000/h	90	[10]
3D- Co ₃ O ₄	200	400 ppm HCHO, 20% O ₂	30,000 ml/g·h	130	[11]
3D- Co ₃ O ₄	200	100 ppm HCHO, 20% O ₂	30,000/h	110	[12]
Co ₃ O ₄ nanofibers	100	400 ppm HCHO, 20% O ₂	30,000 ml/g·h	98	[13]
Co-Mn	150	80 ppm HCHO, 21% O ₂ , 50% RH	60,000/h	75	[14]
3D-Co-Mn	250	80 ppm HCHO, 21% O ₂ , 50% RH	36,000/h	70	[15]
MnO _x -Co ₃ O ₄ -CeO ₂	50	200 ppm HCHO, 21% O ₂	36,000 ml/g·h	100	[16]
Mn ₂ Co ₁ O _x /CN	100	100 ppm HCHO, air	60,000 ml/g·h	80	This work

References

- 1 H. Tian, J. He, L. Liu, D. Wang, Z. Hao and C. Ma, *Microporous Mesoporous Mater.*, 2012, **151**, 397-402.
- 2 J. Wang, J. Li, C. Jiang, P. Zhou, P. Zhang and J. Yu, *Appl. Catal. B: Environ.*, 2017, **204**, 147-155.
- 3 J. Wang, G. Zhang and P. Zhang, *J. Mater. Chem. A*, 2017, **5**, 5719-5725.
- 4 T. Chen, H. Dou, X. Li, X. Tang, J. Li and J. Hao, *Microporous Mesoporous Mater.*, 2009, **122**, 270-274.
- 5 H. Tian, J. He, L. Liu and D. Wang, *Ceram. Int.*, 2013, **39**, 315-321.
- 6 R. Wang and J. Li, *Catal. Lett.*, 2009, **131**, 500-505.
- 7 B. Bai, Q. Qiao, J. Li and J. Hao, *Chin. J. Catal.*, 2016, **37**, 27-31.
- 8 L. Zhou, J. Zhang, J. He, Y. Hu and H. Tian, *Mater. Res. Bull.*, 2011, **46**, 1714-1722.
- 9 J. Zhang, Y. Li, L. Wang, C. Zhang and H. He, *Catal. Sci. Technol.*, 2015, **5**, 2305-2313.
- 10 Z. Fan, Z. Zhang, W. Fang, X. Yao, G. Zou and W. Shangguan, *Chin. J. Catal.*, 2016, **37**, 947-954.
- 11 B. Bai, H. Arandiyan and J. Li, *Appl. Catal. B: Environ.*, 2013, **142-143**, 677-683.
- 12 B. Bai and J. Li, *ACS Catal.*, 2014, **4**, 2753-2762.
- 13 Y. Wu, M. Ma, B. Zhang, Y. Gao, W. Lu and Y. Guo, *RSC Adv.*, 2016, **6**, 102127-102133.
- 14 C. Shi, Y. Wang, A. Zhu, B. Chen and C. Au, *Catal. Commun.*, 2012, **28**, 18-22.
- 15 Y. Wang, K. Wang, J. Zhao, X. Liu, J. Bu, X. Yan and R. Huang, *J. Am. Chem. Soc.*, 2013, **135**, 4799-4804.
- 16 S. Lu, K. Li, F. Huang, C. Chen and B. Sun, *Appl. Surf. Sci.*, 2017, **400**, 277-282.