Topotactic Transformation of Metal–Organic Frameworks to Iron-based Catalysts for the Direct Hydrogenation of CO_2 to Olefins

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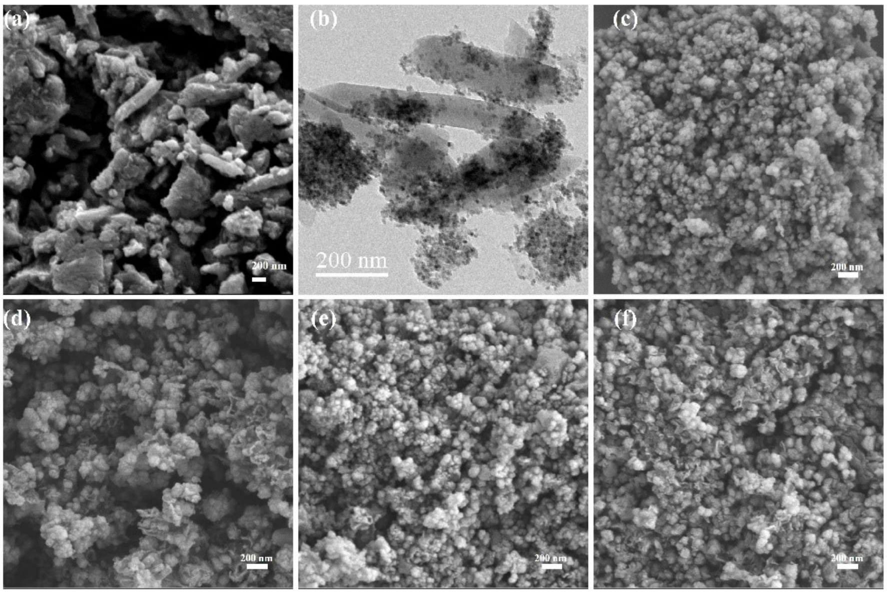

Figure S1 The (a) SEM and (b) TEM images of Fe-MIL-88; and the SEM images of (c) Fe/C, (d) NiFe/C, (e) ZnFe/C and (f) MnFe/C.

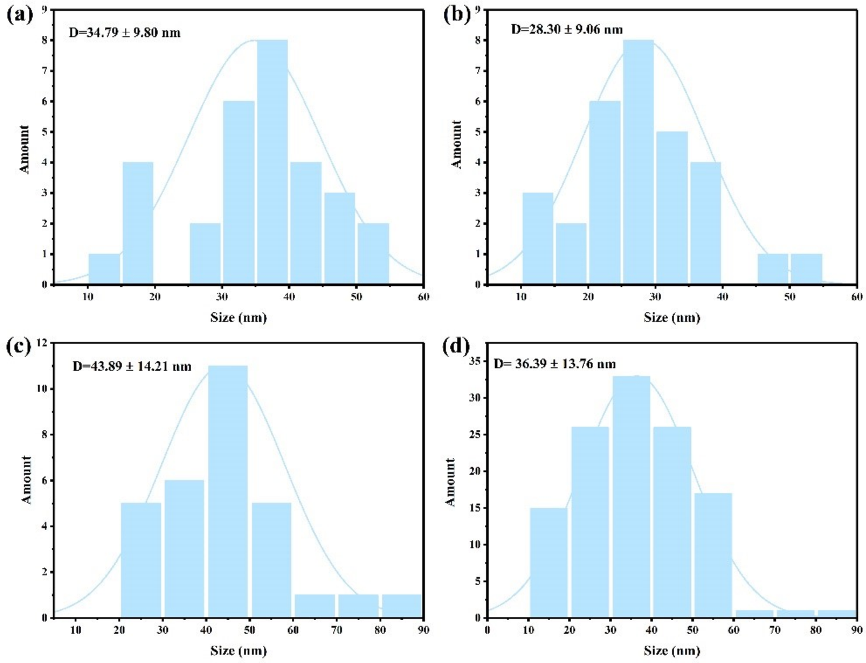

Figure S2 Particle distribution of the fresh MFe/C catalysts. (a) Fe/C, (b) NiFe/C, (c) ZnFe/C and (d) MnFe/C.

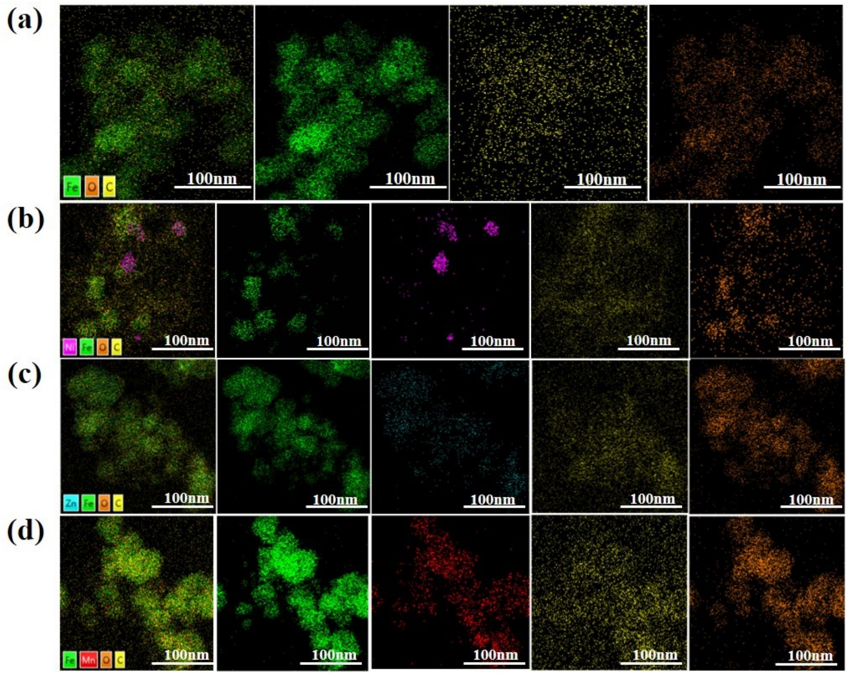

Figure S3 The EDS elemental mapping of the fresh MFe/C catalysts. (a) Fe/C, (b) NiFe/C, (c) ZnFe/C and (d) MnFe/C.

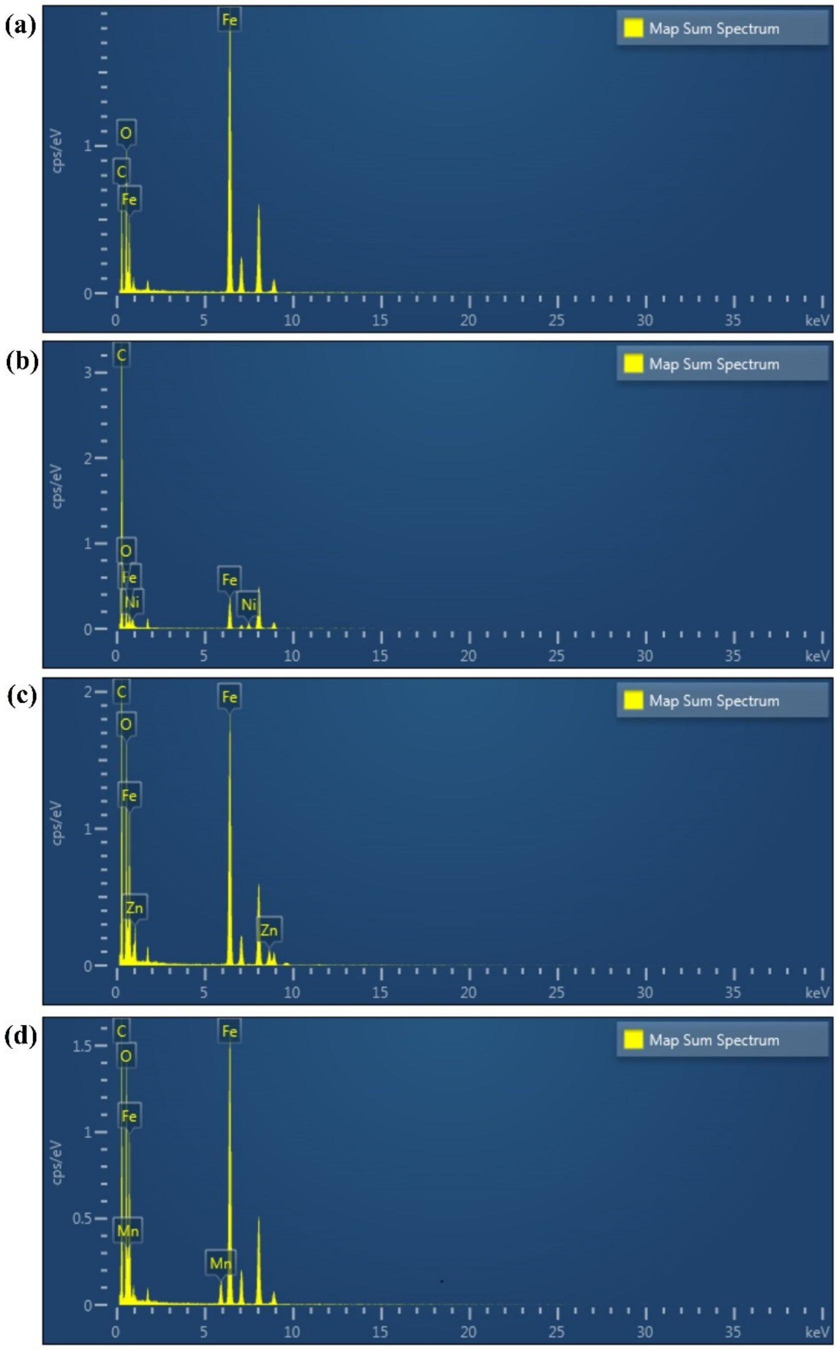

Figure S4 The EDS of the fresh MFe/C catalysts. (a) Fe/C, (b) NiFe/C, (c) ZnFe/C and (d) MnFe/C.

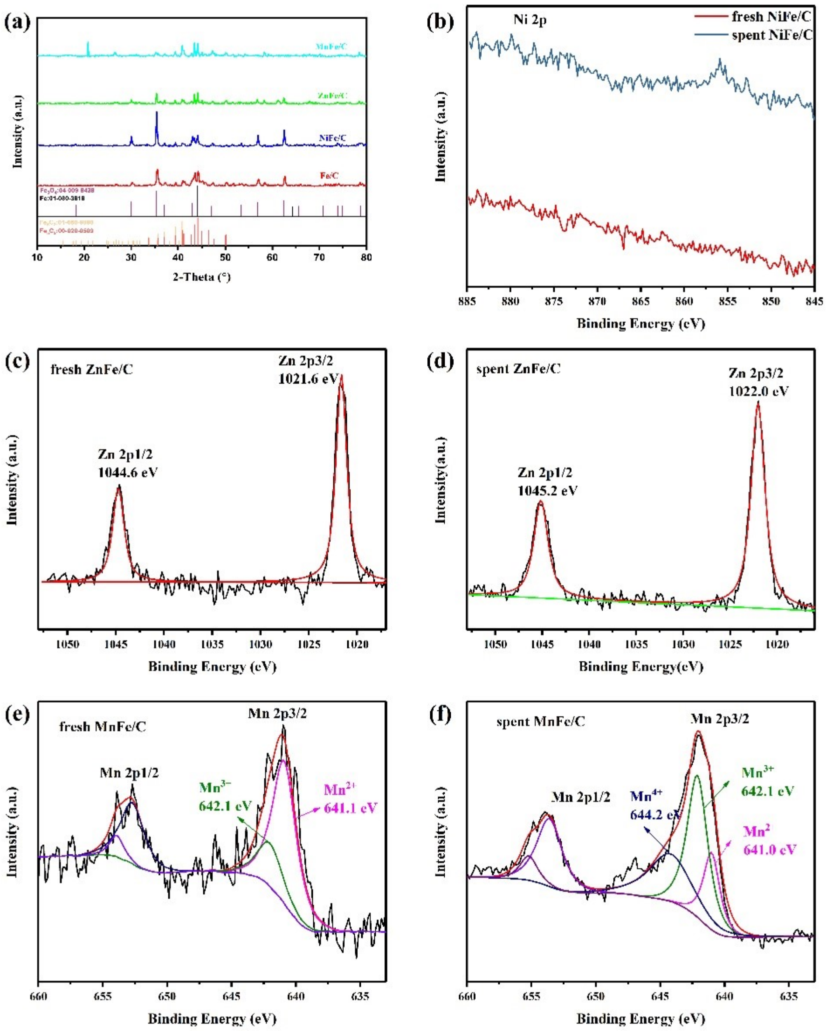

Figure S5 The physical and chemical properties of the MFe/C catalysts: (a) XRD patterns of spent MFe/C catalysts; (b) Ni 2p XPS spectra of fresh and spent NiFe/C; Zn 2p XPS spectra of (c) fresh and (d) spent ZnFe/C; Mn 2p XPS spectra of (e) fresh and (f) spent MnFe/C.

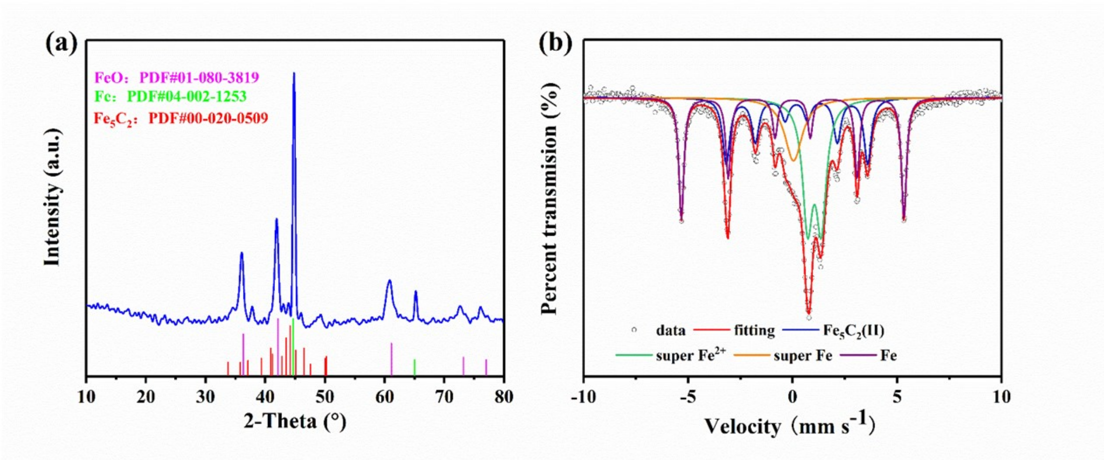

Figure S6 The XRD patterns (a) and Mössbauer spectra (b) of MnFe/C catalysts after H_2 reduction.

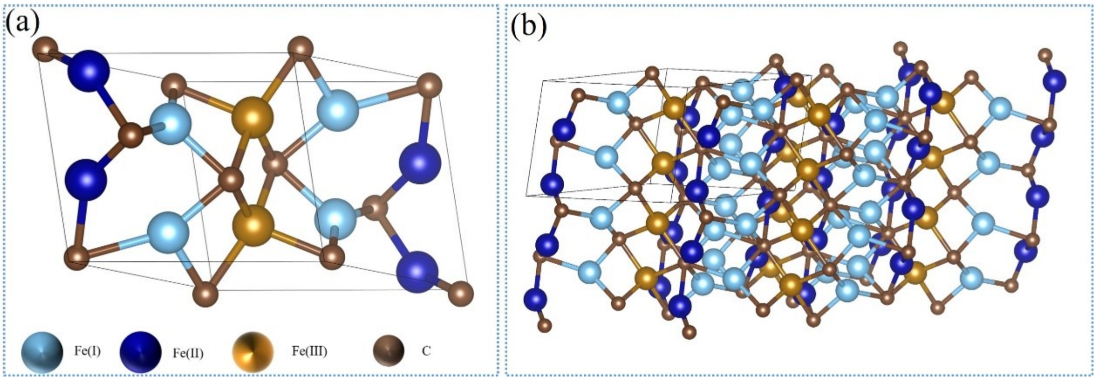

Figure S7 Unit cell structure of Fe at different sites in Fe_5C_2: The cell crystal structure (a) and 3x3x3 crystal structure (b) of Fe_5C_2。

Table S1 Textural properties of the MFe/C catalysts.

Samples	**Fe Contents (wt%)**	**M^{2+}contents (wt%)**	**Fe/M ratio**	**Crystalline size (nm)[a]**
Fe/C	54.5	-	-	23.8
ZnFe/C	45.8	4.5	10.2	15.7
NiFe/C	48.7	5.8	8.4	21.4
MnFe/C	53.8	4.9	11.0	11.5

[a] The average crystalline sizes of Fe_3O_4 in MFe/C catalysts calculated by Scherrer equation.

Table S2 Properties of iron-based catalysts by EDS.

Sample	Fe Contents (wt%)	M^{2+}contents (wt%)
Fe/C	62.7	-
NiFe/C	10.2	1.8
ZnFe/C	38.2	2.9
MnFe/C	40.1	3.2

Table S3 Detailed Mössbauer parameters of the fresh catalysts.

Samples	Assignment	IS (mm s^{-1})	QS (mm s^{-1})	Line Width	Hhf (kOe)	Relative Abundance (%)
Fe/C	Fe_3O_4(A)	0.28	-0.01	0.41	489	51.1
	Fe_3O_4(B)	0.58	0.00	0.66	454	48.9
MnFe/C	Fe_2O_3	0.35	0.13	0.58	432	12.4
	Fe_5C_2(II)	0.19	0.03	0.43	209	32.9
	Fe^{2+}(super)[a]	1.04	0.62	0.58	-	29.6
	Fe(super)[a]	-0.00	0.00	0.90	-	11.9
	Fe	-0.02	-	0.58	329	13.3
ZnFe/C	Fe_5C_2(II)	0.20	0.02	0.88	200	61.8
	Fe^{2+}(super)[a]	1.08	0.53	0.52	-	16.6
	Fe^{3+}(super)[a]	0.28	0.77	0.86	-	21.6
NiFe/C	Fe_3O_4(A)	0.29	-0.01	0.32	491	42.9
	Fe_3O_4(B)	0.64	0.00	0.52	459	57.1

[a]superparamagnetic

Table S4 Comparison of the CO_2 hydrogenation performance of the MnFe/C catalyst in this work with the previously reported Fe-based catalysts.

Samples	P (MPa)	T (°C)	GHSV (mL h^{-1} $gcat^{-1}$)	CO_2 Con.（%）	S_{C5+}	STY (mol_{C5+} $g_{cat}^{-1}h^{-1}$)	Ref.
N-600-0	3	400	3600	46.0	22.2	0.05	1
N-K-600-0	3	400	3600	43.1	15.4	0.03	
5Mn-Na/Fe	3	320	2040	38.6	42.1	0.05	2
FeK/MPC	2.5	350	2000	52.4	33.2	0.05	3
0%Mn	-	290	20000	33.78	20.28	0.22	4
Fe-K	1.5	320	10000	35.1	21.9	0.11	5
$ZnFe_2Ox$	1.0	300	2400	34.6	20.4	0.02	6
$10Fe3Cu1K/Al_2O_3$	3	400	33600	41.7	13.8	0.27	7
FeZnNa/MWNTs	2	320	9000	36.5	37.2	0.17	8
FeK3/SWNTs	2	340	9000	53	56	0.38	9
Na-Zn-Fe	2.5	340	15000	39	40.5	0.34	10
MnFe/C	**2**	**400**	**12000**	**37.60**	**57.9**	**0.27**	**This work**

Table S5 Surface composition of the various catalysts calculated by XPS.

Element	fresh				spent			
	Fe/C	**NiFe/C**	**MnFe/C**	**ZnFe/C**	**Fe/C**	**NiFe/C**	**MnFe/C**	**ZnFe/C**
Fe	4.52	-	4.02	2.68	3.66	1.53	2.25	4.54
Na	1.56	0.77	-	4.86	3.27	2.94	3.14	3.44
O	21.21	11.46	19.98	23.33	16.79	13.59	14.7	17.19
C	72.71	84.74	75.99	69.13	76.27	81.94	79.91	70.55

Table S6 Detailed Mössbauer parameters of the spent catalysts.

Samples	Assignment	IS (mm s^{-1})	QS (mm s^{-1})	Line Width	Hhf (kOe)	Relative Abundance (%)
Fe/C	Fe_3O_4(A)	0.28	0.00	0.24	487	10.4
	Fe_3O_4(B)	0.67	0.00	0.45	457	23.7
	Fe_5C_2(I)	0.20	0.00	0.38	184	23.5
	Fe_5C_2(II)	0.26	0.12	0.32	215	23.1
	Fe_5C_2(III)	0.18	0.01	0.54	109	19.3
MnFe/C	Fe_5C_2(I)	0.22	-0.04	0.38	186	34.4
	Fe_5C_2(II)	0.24	0.11	0.32	216	33.1
	Fe_5C_2(III)	0.13	0.00	0.61	106	32.5
ZnFe/C	Fe_3O_4(A)	0.28	0.05	0.34	485	4.7
	Fe_3O_4(B)	0.67	-0.08	0.52	446	8.0
	Fe_5C_2(I)	0.16	0.09	0.40	185	30.4
	Fe_5C_2(II)	0.25	0.11	0.32	215	27.2
	Fe_5C_2(III)	0.22	0.11	0.30	110	16.5
	super	0.39	0.77	0.58	-	13.2
NiFe/C	Fe_3O_4(A)	0.28	0.00	0.28	488	20.4
	Fe_3O_4(B)	0.66	-0.01	0.35	459	28.6
	Fe_5C_2(I)	0.21	-0.03	0.56	182	23.8
	Fe_5C_2(II)	0.25	0.12	0.33	210	10.5
	Fe_5C_2(III)	0.18	-0.12	0.45	105	11.2
	super	0.21	0.94	0.39	-	5.5

[a]superparamagnetic

Table S7 Detailed Mössbauer parameters of MnFe/C catalysts after H_2 reduction.

Samples	Assignment	IS (mm s^{-1})	QS (mm s^{-1})	Line Width	Hhf (kOe)	Relative Abundance (%)
MnFe/C	Fe_5C_2(II)	0.19	0.03	0.42	210	24.3
	Fe^{2+}(super)[a]	1.04	0.65	0.58	-	31.0
	Fe(super)[a]	0.04	-8.46	1.02	-	14.2
	Fe	0.00	-	0.28	331	30.4

Table S8 Summary of olefin selectivity and O/P and Fe_5C_2 content of different catalysts in CO_2 hydrogenation reactions

References	Samples	Olefins selectivity	O/P	Fe_5C_2 (II)	Fe_5C_2 (II)
11	0Na/Fe	6.0	0.2	3.0	1.4
	0.01Na/Fe	11.8	0.3	3.7	1.9
	0.05Na/Fe	39.4	1.3	6.0	3.1
	0.1Na/Fe	56.8	3.1	10.0	4.7
	0.5Na/Fe	64.3	5.3	10.4	6.8
	1.0Na/Fe	64.1	5.3	11.3	5.0
	3.0Na/Fe	64.1	5.4	10.3	4.4
	5.0Na/Fe	63.6	5.3	9.9	5.3
2	1Na/Fe	23.4	11.0	11.3	5.0
	0.1Mn–Na/Fe	24.1	9.5	10.7	6.5
	1Mn–Na/Fe	25.1	8.2	12.7	7.3
	5Mn–Na/Fe	30.2	7.5	28.4	17.6
	10Mn–Na/Fe	29.2	6	14.9	7.8
8	FeZnNa/MWNTs	67.1	5.99	26.2	13.4
	FeZnK/MWNTs	66.8	6.42	22.8	19.0
	FeZnRb/MWNTs	62.7	5.35	18.1	16.8
9	Fe/SWNTs	5.4	0.6	14.6	2.7
	FeK1/SWNTs	12	0.8	17.6	8.7
	FeK3/SWNTs	23	0.6	20.1	9.7
	FeK5/SWNTs	25	1.6	22.4	10.8
	FeK7/SWNTs	27	1.8	20.2	5.3
10	Fe	5.9	0.13	1.5	0.6
	Zn-Fe	5.3	0.11	1.4	0.1
	Na-Fe	79	9.9	24	13
	Na-Zn-Fe	80	9.8	34	25

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