Supplementary Information for

Interfacial Fe_5C_2-Cu catalysts toward Low-Pressure Syngas Conversion to Long-Chain Alcohols

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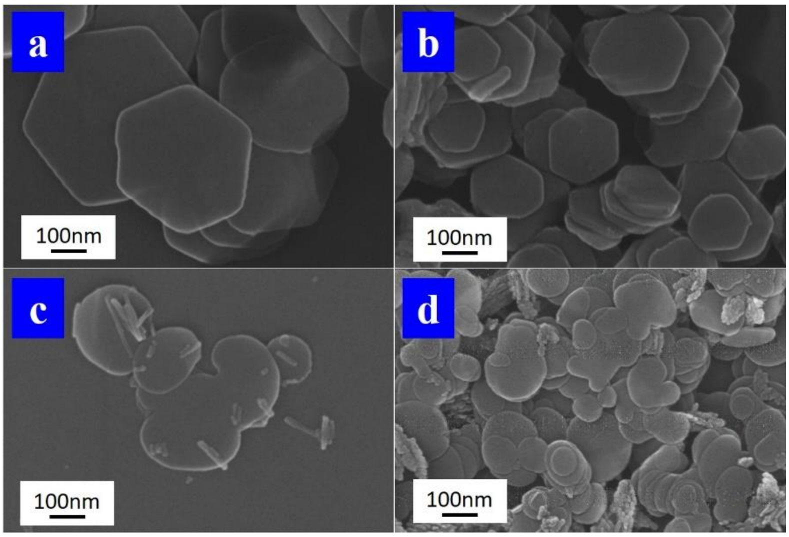
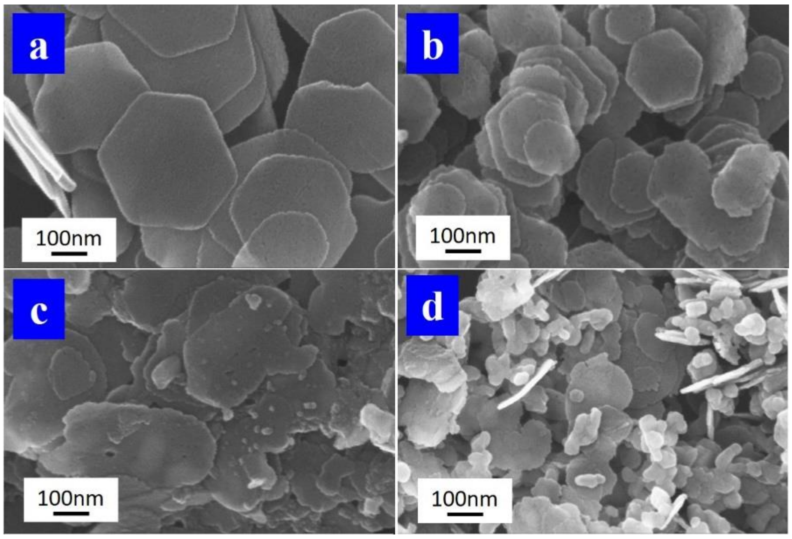
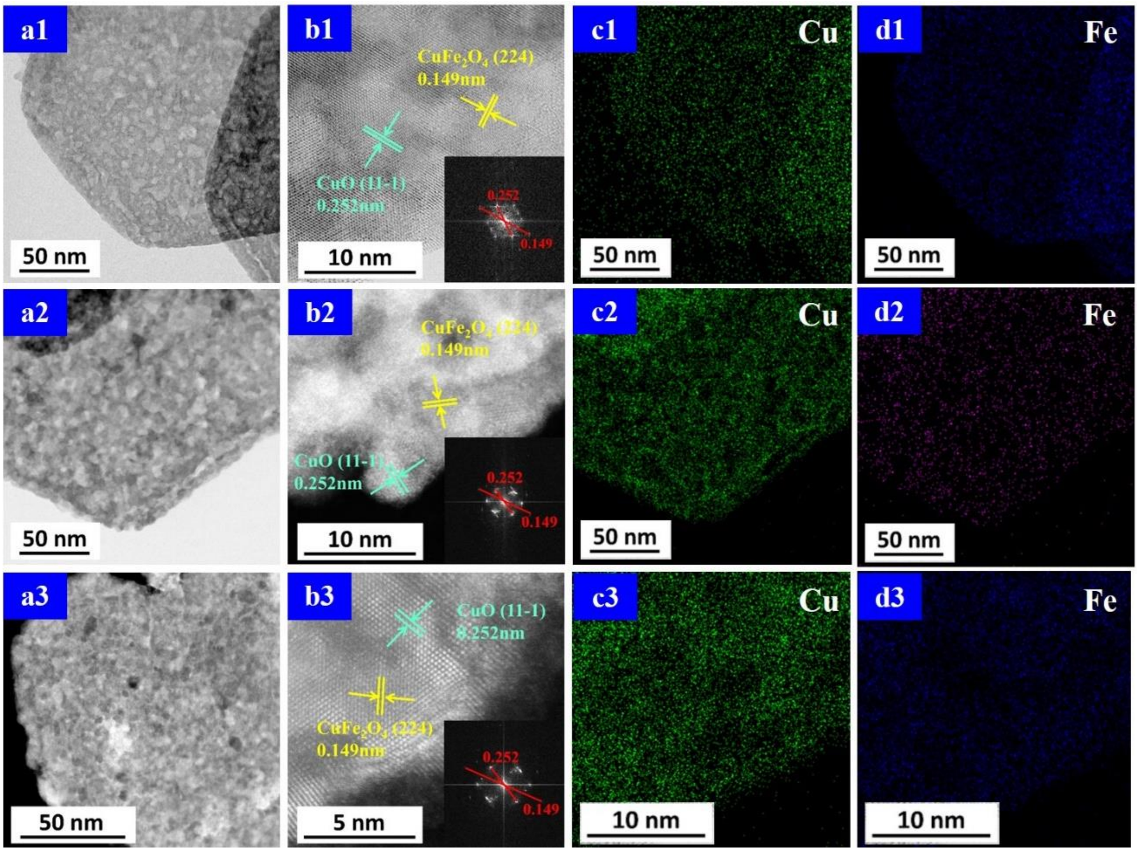
Supplementary Figures and Tables



Supplementary Figure 1. Morphology of $Cu_xFe_yMg_4$-LDH. SEM images of (a) $Cu_1Fe_1Mg_4$-LDH, (b) $Cu_2Fe_1Mg_4$-LDH, (c) $Cu_4Fe_1Mg_4$-LDH and (d) $Cu_6Fe_1Mg_4$-LDH.



Supplementary Figure 2. Morphology of $Cu_xFe_yMg_4$-MMO. SEM images of Calcined sample: (a) $Cu_1Fe_1Mg_4$-MMO, (b) $Cu_2Fe_1Mg_4$-MMO, (c) $Cu_4Fe_1Mg_4$-MMO and (d) $Cu_6Fe_1Mg_4$-MMO.



Supplementary Figure 3. Morphology of $Cu_xFe_yMg_4$-MMO. TEM images of Calcined sample: (a1–a3) $Cu_1Fe_1Mg_4$-MMO, $Cu_2Fe_1Mg_4$-MMO and $Cu_4Fe_1Mg_4$-MMO. (b1–b3) HRTEM images selected from (a1–a3) and their Fourier transform patterns of the selected region (inset), respectively. (c1–c3) and (d1–d3) EDS mapping of elemental distribution for Cu and Fe.

Supplementary Table 1. Physicochemical properties of various catalysts

Sample	BET surface area (m^2 g^{-1})	Surface C content (%)	Cu/Fe ratio [a]	Cu/Fe ratio [b]	Cu Crystallite size [c] (nm)	Mean Cu particle size [d] (nm)
Cu_1Fe_1	32.49	33.53	0.63	0.99	15.7	13.4
Cu_2Fe_1	22.07	36.39	1.24	1.96	18.4	17.9
Cu_4Fe_1	15.96	35.43	2.37	3.84	21.7	21.0
Cu_6Fe_1	10.38	29.99	4.47	5.67	25.1	-

[a] Cu/Fe ratio was determined by XPS.

[b] Cu/Fe ratio was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES).

[c] Crystallite size was determined by XRD with the Scherrer equation.

[d] Mean Cu particle size was determined by TEM images.

Supplementary Table 2. Catalytic performances of samples with various calcination temperatures

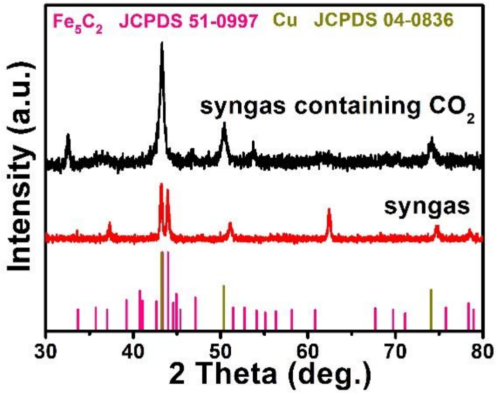
Catalysts[a,b,c]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][d]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
$Cu_4Fe_1Mg_4$-MMO(800)	17.3	11.3	44.7	5.2	38.8	21.3(1.1)	59.2(3.1)	12.0(0.6)	5.7(0.3)	1.8(0.1)
$Cu_4Fe_1Mg_4$-MMO(500)	48.7	2.8	48.0	15.6	33.6	6.0(0.9)	31.7(4.9)	5.8(0.9)	2.5(0.4)	54.0(8.5)
$Cu_4Fe_1Mg_4$-MMO(400)	43.2	4.3	47.8	19.0	28.9	10.9(2.1)	43.5(8.3)	10.6(2.0)	5.2(1.0)	30.8(5.6)
$Cu_4Fe_1Mg_4$-MMO(350)	44.9	3.1	43.4	18.8	34.7	5.9(1.0)	49.8(9.3)	9.2(1.7)	4.3(0.8)	31.8(6.0)
$Cu_4Fe_1Mg_4$-LDH	42.1	9.8	50.3	18.7	21.2	26.6(4.9)	45.3(8.4)	14.1(2.6)	6.2(1.2)	7.8(1.6)

[a] Activation conditions: 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 3 MPa, 260 ºC, H_2/CO=2，2400 mL g_{cat}^{-1} h^{-1}.
[c] Various calcination temperatures of $Cu_4Fe_1Mg_4$-LDH in brackets.
[d] Normalized data to S_{ROH}, mol% in brackets.

Supplementary Table 3. Catalytic performances of samples with various activation steps

Entry[a,b]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
500℃ 20h	4.8	5.6	41.8	45.2	7.4	85.4(38.6)	1.9(0.8)	1.5(0.7)	0.8(0.4)	10.4(4.7)
350℃ 2h	33.1	1.7	64.2	7.2	26.9	8.4(0.6)	18.4(1.3)	7.2(0.5)	1.3(0.1)	64.7(4.7)
350℃ 10h (H_2:CO:CO_2:N_2=1:1:2:8, 100 ml min^{-1})	12.8	2.3	63.9	13.2	20.6	20.8(2.7)	25.3(3.3)	5.4(0.7)	1.2(0.2)	47.3(6.3)
300℃ 2h + 350℃ 1h	48.7	2.8	48.0	15.6	33.6	6.0(0.9)	31.7(4.9)	5.8(0.9)	2.5(0.4)	54.0(8.5)

[a] Activation conditions : $Cu_4Fe_1Mg_4$-MMO, 1 g precursor, H_2:CO:CO_2=1:1:2 (40 ml min^{-1}), 2 ºC min^{-1}.
[b] Reaction conditions: 3 MPa, 260 ºC, H_2/CO=2，2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.



Supplementary Figure 4. XRD patterns of the reduced and passivated samples in syngas or syngas containing CO_2 of $Cu_4Fe_1Mg_4$-MMO.

Supplementary Table 4. Catalytic performances of samples with various activation atmosphere

Activation atmosphere[a,b]	Pressure [MPa]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
			CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
50.0% CO_2	1	53.2	3.7	36.5	29.8	30.0	8.7(2.6)	28.8(8.5)	8.2(2.4)	5.2(1.5)	49.1(14.8)
	2	39.9	2.8	60.3	17.9	19.4	10.4(1.8)	41.7(7.4)	9.9(1.7)	9.1(1.6)	28.9(5.4)
	3	48.7	2.8	48.0	15.6	33.6	6.0(0.9)	31.7(4.9)	5.8(0.9)	2.5(0.4)	54.0(8.5)
Pure syngas	1	39.3	7.6	46.6	20.7	25.1	21.6(4.4)	45.1(9.3)	14.2(2.9)	7.3(1.5)	11.8(2.6)
	2	39.7	7.8	44.8	23.0	24.4	19.2(4.4)	43.1(9.9)	13.4(3.1)	10.2(2.3)	14.1(3.3)
	3	48.9	7.8	48.7	19.2	24.3	15.0(2.9)	36.5(7.0)	10.0(1.9)	5.2(1.0)	33.3(6.4)

[a] Activation conditions: $Cu_4Fe_1Mg_4$-MMO, 1 g precursor, 40 mL min^{-1}, 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 260 ºC, $H_2/CO=2$，2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Supplementary Table 5. Catalytic performances of samples with various H_2/CO ratios in reaction gas

H_2/CO ratio[a,b]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
1/1	26.5	4.8	34.8	12.6	47.8	12.4(1.6)	38.3(4.8)	11.2(1.4)	11.4(1.4)	26.7(3.4)
2/1	48.7	2.8	48.0	15.6	33.6	6.0(0.9)	31.7(4.9)	5.8(0.9)	2.5(0.4)	54.0(8.5)

[a] Activation conditions: $Cu_4Fe_1Mg_4$-MMO, 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 3 MPa, 260 ºC, 2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Supplementary Table 6. Catalytic performances of samples with various reaction temperatures

Reaction temperature[a,b]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
220	4.6	4.7	39.9	53.8	1.6	12.2(6.6)	16.1(8.7)	10.7(5.7)	5.4(2.9)	55.6(29.9)
260	48.7	2.8	48.0	15.6	33.6	6.0(0.9)	31.7(4.9)	5.8(0.9)	2.5(0.4)	54.0(8.5)
300	55.4	7.4	57.3	13.7	21.6	80.3(11.0)	5.0(0.7)	3.6(0.5)	1.7(0.2)	9.4(1.3)

[a] Activation conditions: $Cu_4Fe_1Mg_4$-MMO, 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 3 MPa, H_2/CO=2， 2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

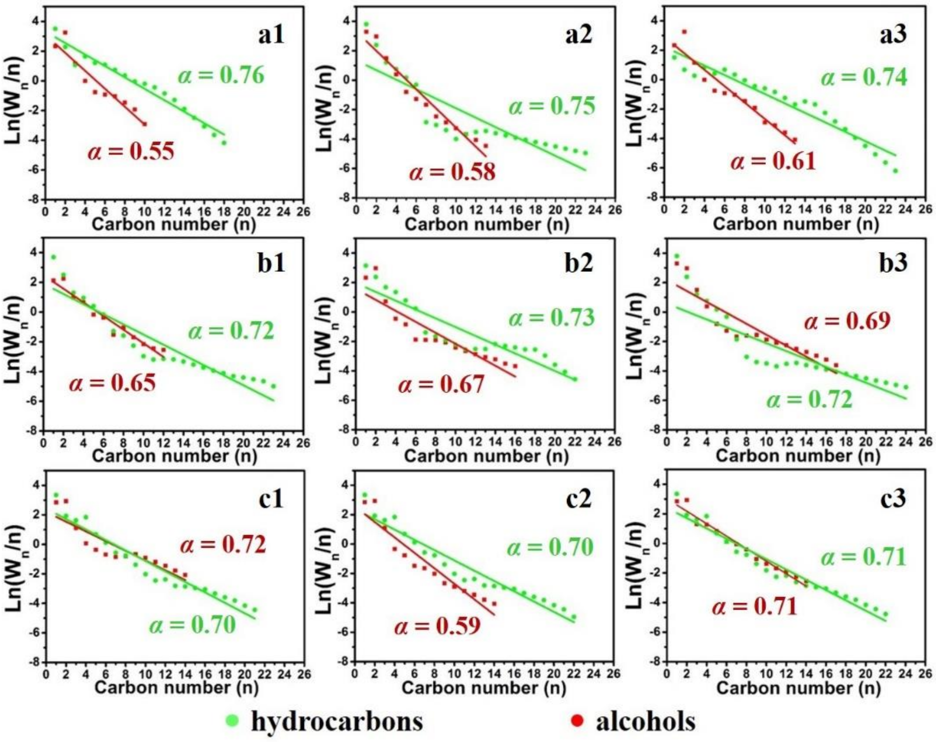
Supplementary Table 7. Catalytic performances of samples with various reaction pressure

Catalysts[a,b]	Pressure [MPa]	Conv. [%]	Selectivity[mol%]				Alcohols distribution [%][d]				
			CH_4	$C_{2+}H$	ROH [c]	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
Cu_1Fe_1	1	28.1	6.7	50.8	25.4 (30.6)	17.1	19.0 (4.8)	38.5 (9.8)	15.1 (3.8)	7.3 (1.8)	20.1 (5.2)
	2	33.5	3.8	59.1	21.8 (25.7)	15.3	12.8 (2.8)	44.1 (9.6)	14.2 (3.1)	7.5 (1.6)	21.4 (4.7)
	3	58.2	3.3	52.3	12.9 (18.8)	31.5	6.8 (0.9)	47.6 (6.1)	10.1 (1.3)	4.6 (0.6)	30.9 (4.0)
Cu_2Fe_1	1	28.8	2.1	44.8	23.6 (33.5)	29.5	10.9 (2.6)	31.0 (7.3)	13.4 (3.2)	8.8 (2.1)	35.9 (8.4)
	2	32.1	5.8	48.4	23.0 (29.7)	22.7	20.6 (4.7)	20.8 (4.8)	12.4 (2.8)	7.5 (1.7)	38.7 (9.0)
	3	38.4	2.4	60.9	16.8 (21.0)	19.9	21.4 (3.6)	21.6 (3.6)	9.3 (0.9)	5.3 (0.4)	43.4 (7.3)
Cu_4Fe_1	1	53.2	3.7	36.5	29.8 (42.6)	30.0	8.7 (2.6)	28.8 (8.5)	8.2 (2.4)	5.2 (1.5)	49.1 (14.8)
	1 [e]	31.6	8.4	47.3	20.2 (26.6)	24.1	15.1 (3.1)	22.5 (4.5)	13.2 (2.6)	10.6 (2.1)	38.6 (7.9)
	2	39.9	2.8	60.3	17.9 (22.2)	19.4	10.4 (1.8)	41.7 (7.4)	9.9 (1.7)	9.1 (1.6)	28.9 (5.4)
	3	48.7	2.8	48.0	15.6 (23.5)	33.6	6.0 (0.9)	31.7 (4.9)	5.8 (0.9)	2.5 (0.4)	54.0 (8.5)
Cu_6Fe_1	1	17.2	5.7	43.6	7.1 (12.6)	43.6	4.1(0.3)	14.7(1.0)	3.9(0.3)	2.1(0.1)	75.2(5.4)
	1 [f]	30.5	6.4	46.3	3.2 (5.7)	44.1	10.1 (0.3)	15.5 (0.5)	9.2 (0.3)	5.6 (0.2)	59.6 (1.9)
	2	27.5	3.1	45.2	9.8 (16.8)	41.9	9.1(0.9)	19.8(1.9)	6.8(0.6)	3.5(0.3)	60.8(6.1)
	3	61.5	10.7	38.0	8.9 (15.4)	42.4	9.7(0.9)	29.6(2.6)	8.2(0.7)	4.2(0.3)	48.3(4.4)

[a] Activation conditions: 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions : 260 ºC, H_2/CO=2, 2400 mL g_{cat}^{-1} h^{-1}.
[c] S_{ROH} excluding CO_2 in brackets.
[d] Normalized data to S_{ROH}, mol% in brackets.
[e] WHSV = 4800 mL g_{cat}^{-1} h^{-1}
[f] WHSV = 1200 mL g_{cat}^{-1} h^{-1}

Supplementary Table 8. Space time yield of various products calculated from Table S7

Catalysts	Pressure [MPa]	Space time yield [g g_{cat}^{-1} h^{-1}]					
		CH_4	$C_{2+}H$	CO_2	ROH	MeOH	$C_{5+}OH$
Cu_1Fe_1	1	0.017	0.116	0.122	0.130	0.025	0.026
	2	0.012	0.166	0.135	0.141	0.018	0.030
	3	0.018	0.254	0.481	0.141	0.010	0.040
Cu_2Fe_1	1	0.006	0.106	0.218	0.111	0.014	0.042
	2	0.014	0.109	0.159	0.122	0.024	0.045
	3	0.009	0.200	0.205	0.131	0.027	0.053
Cu_4Fe_1	1	0.012	0.111	0.285	0.201	0.018	0.101
	2	0.010	0.205	0.207	0.140	0.014	0.040
	3	0.014	0.210	0.462	0.141	0.009	0.076



Supplementary Figure 5. Anderson-Schulz-Flory (A-S-F) plots for the distribution of alcohols and hydrocarbons. (a) Cu_1Fe_1, (b) Cu_2Fe_1 and (c) Cu_4Fe_1. (a1–c1) at 1 MPa, (a2–c2) at 2 MPa, (a3–c3) at 3 MPa.

Supplementary Table 9. Catalytic performance data for a variety of modified F−T catalysts used in LAS

Catalyst	H_2/CO ratio	Temperature /℃	Pressure /MPa	GHSV	CO conversion/%	Total alcohol Selectivity/%	Long-chain alcohol selectivity/%	Total alcohols STY[a]	Long-chain alcohols STY[a]	reference
Cu_4Fe_1	2	260	1	2400 mL g_{cat}^{-1} h^{-1}	53.2	29.8	49.1	0.201	0.101	This work
CuZnFeMn	2	260	4	6000 h^{-1}	52.62	31.04	3.65	0.24	0.016	*Catal. Commun.* **2008**, *9*, 1869-1873
3DOM Cu_2Fe_1	1	260	4.8	2000 h^{-1}	57.5	33.6	52.4	0.20	0.100	*ChemCatChem* **2014**, *6*, 473-478
$CF_{0.5}$	2	260	4	5000 h^{-1}	17.99	20.77	2.5	0.05	0.001	*J. Colloid Interface Sci.* **2016**, *470*, 162-171
CNF-2-0.005	1.5	240	5	32000 mL g_{cat}^{-1} h^{-1}	11	39		0.53		*ACS Catal.* **2018**, *8*, 9604-9618
CuFe NPs	2	220	6	6000 h^{-1}	17.1	21.9	64	0.14	0.085	*J. Mol. Catal. A: Chem.* **2013**, *378*, 319-325
0.5%K-FeCuMnZnO	2	260	4	6000 h^{-1}	27.3	49.3	3	0.29		*Appl. Energy* **2015**, *138*, 584-589
CoGa-ZnAl-LDO/ Al_2O_3	2	260	3	2000 h^{-1}	43.5	59	37.7	0.24	0.091	*J. Catal.* **2016**, *340*, 236-247
CoMn | CuZnAlZr	2	230	6	2000 mL g_{cat}^{-1} h^{-1}	17.8	46.1	57.1	0.04	0.023	*Angew. Chem., Int. Ed.* **2019**, *58, 4627-4631*
CoCu/MoO_x	1	270	4	120000 mL g_{cat}^{-1} h^{-1}	<2	46		0.03		*Angew. Chem., Int. Ed.* **2014**, *53*, 6397-6401
$(Cu_1Co_2)_2$Al/CNT	2	230	3	3900 mL g_{cat}^{-1} h^{-1}	45	62	13.8	0.34	0.05	*J. Mater. Sci.* **2016**, *51*, 5216-5231
CuFeCo	2	350	5.5	6000 h^{-1}	72	12.5	6	0.25	0.015	*Appl. Catal. A* **2015**, *503*, 51-61

Fe/K/ Mo_2C(Fe/Mo= 1/14)	2	320	7	4000 h^{-1}	50.25	22.69	0.62	0.14	0.001	*Catal. Lett.* **2010**, *136*, 9-13
S2-CuFeMg-Cat	2	300	4	2000 h^{-1}	56.89	49.07	11.25	0.28	0.032	*Catal. Sci. Technol.* **2013**, *3*, 1324-1332
CuFeK0.5M	2	320	5	6000 h^{-1}	53	61		0.32		*Fuel Process. Technol.* **2017**, *159*, 436-441
Fe-CuMnZrO_2(I)	2	310	8	8000 h^{-1}	45.5	26.2	3	0.45	0.014	*J. Mol. Catal. A: Chem.* **2004**, *221*, 51-58
Fe-Cu/Al_2O_3 (Al_2O_3 loading: 89.3%)	2.68	380	4	10000 h^{-1}		62.3		0.044		*J. Nat. Gas Chem.* **2008**, *17*, 327-331
Cu-Fe-K-M_{80}	2	320	5	6000 h^{-1}	56	63		0.35		*Energy Procedia* **2015**, *75*, 767-772
$Cu_{20}Fe_{30}K_1M$	2	320	5	6000 h^{-1}	46	53		0.35		*Catal. Today* **2014**, *234*, 278-284
K–$CoMoS_2$/Al_2O_3	2	300	5	5000 h^{-1}	9	47	47	0.30	0.141	*Energy Fuels* **2013,** *277*, 3769-3777
$Co_4Mn_1K_{0.1}$	5	220	4	3600 h^{-1}	34	44	22	0.20	0.044	*Nat Commun.* **2016**, *7*, 13058-13064
CoCuMn	2	200	6	3600 h^{-1}	3	52	65	0.12	0.078	*J. Am. Chem. Soc.* **2013**, *135*, 7114-7117
$Co_1Mo_1K_{0.05\text{-}12\%}$ (4.2% Co/MWCNT)	2	290	5	8000 mL g_{cat}^{-1} h^{-1}	21.1	85		0.33		*Appl. Catal. A* **2008**, *340*, 87-97

[a] **g g_{cat}^{-1} h^{-1}**

Supplementary Table 10. Catalytic performances of Cu_4Fe_1 with three runs

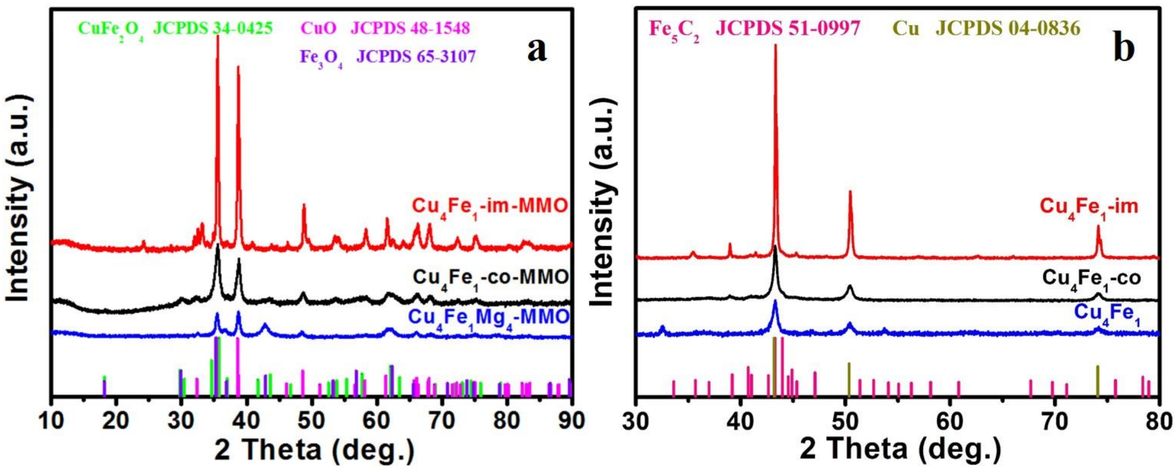
Entry[a,b]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
1	53.2	3.7	36.5	29.8	30.0	8.7(2.6)	28.8(8.5)	8.2(2.4)	5.2(1.5)	49.1(14.8)
2	50.1	3.4	34.3	31.2	30.1	9.6(3.0)	29.6(9.2)	8.7(2.7)	6.4(1.9)	45.7(14.4)
3	51.2	2.3	38.6	28.0	31.1	7.5(2.1)	28.0(7.8)	8.1(2.3)	6.0(1.7)	50.4(14.1)

[a] Activation conditions: 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 1 MPa, 260 ºC, H_2/CO=2, 2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

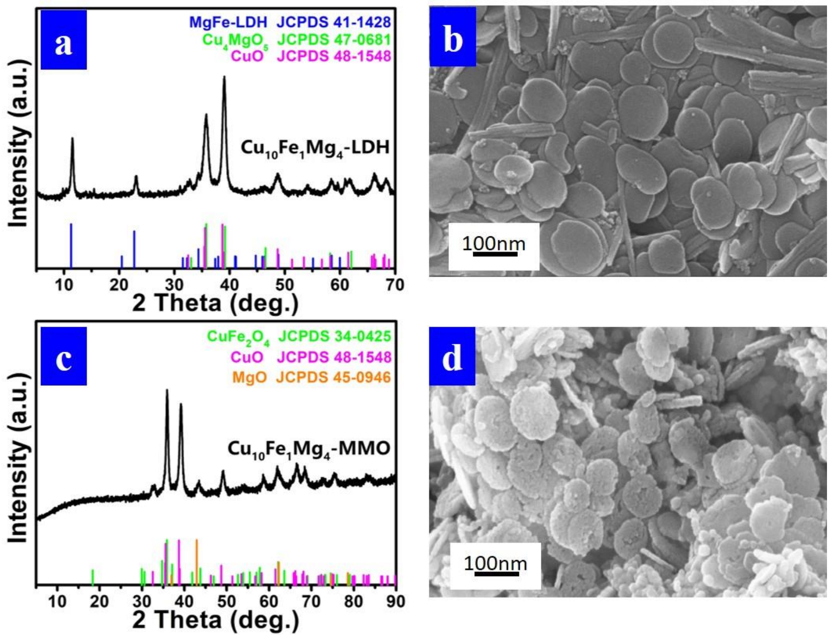
Supplementary Table 11. Catalytic performances of samples with different preparation methods and composition

Catalysts[a,b]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
Cu_4Fe_1	53.2	3.7	36.5	29.8	30.0	8.7(2.6)	28.8(8.5)	8.2(2.4)	5.2(1.5)	49.1(14.8)
Cu_4Fe_1-co	37.1	13.4	31.3	35.2	20.1	9.6(3.4)	79.6(28.0)	6.7(2.3)	2.4(0.8)	1.7(0.7)
Cu_4Fe_1-im	9.7	19.9	52.0	10.5	17.6	81.2(8.5)	9.6(1.0)	5.3(0.6)	3.9(0.4)	–
Cu_4	5.9	23.1	2.1	70.5	4.3	92.0(64.8)	3.9(2.7)	2.7(1.9)	1.4(1.1)	–
Fe_1	19.2	21.3	38.6	–	40.1	–	–	–	–	–
Cu_4/Fe_1[d]	7.8	25.5	21.7	27.6	25.2	85.6(23.6)	8.8(2.4)	5.6(1.6)	–	–
Cu_4+Fe_1[e]	6.2	21.7	47.8	15.0	15.5	89.1(13.3)	7.3(1.1)	3.6(0.6)		
Fe_1+Cu_4[f]	6.5	27.3	34.3	19.6	18.8	90.6(17.7)	7.6(1.5)	1.8(0.4)		

[a] Activation conditions: 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 1 MPa, 260 ºC, H_2/CO=2, 2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.
[d] Physical mixture of Cu_4 and Fe_1
[e] Fe_1 is located separately below Cu_4 by an inert layer of quartz wool.
[f] Cu_4 is located separately below Fe_1 by an inert layer of quartz wool.



Supplementary Figure 6. Structure of control samples. XRD patterns of the calcined samples (a) Cu_4Fe_1-im-MMO, Cu_4Fe_1-co-MMO, $Cu_4Fe_1Mg_4$-MMO and the reduced samples (b) Cu_4Fe_1-im, Cu_4Fe_1-co, Cu_4Fe_1.

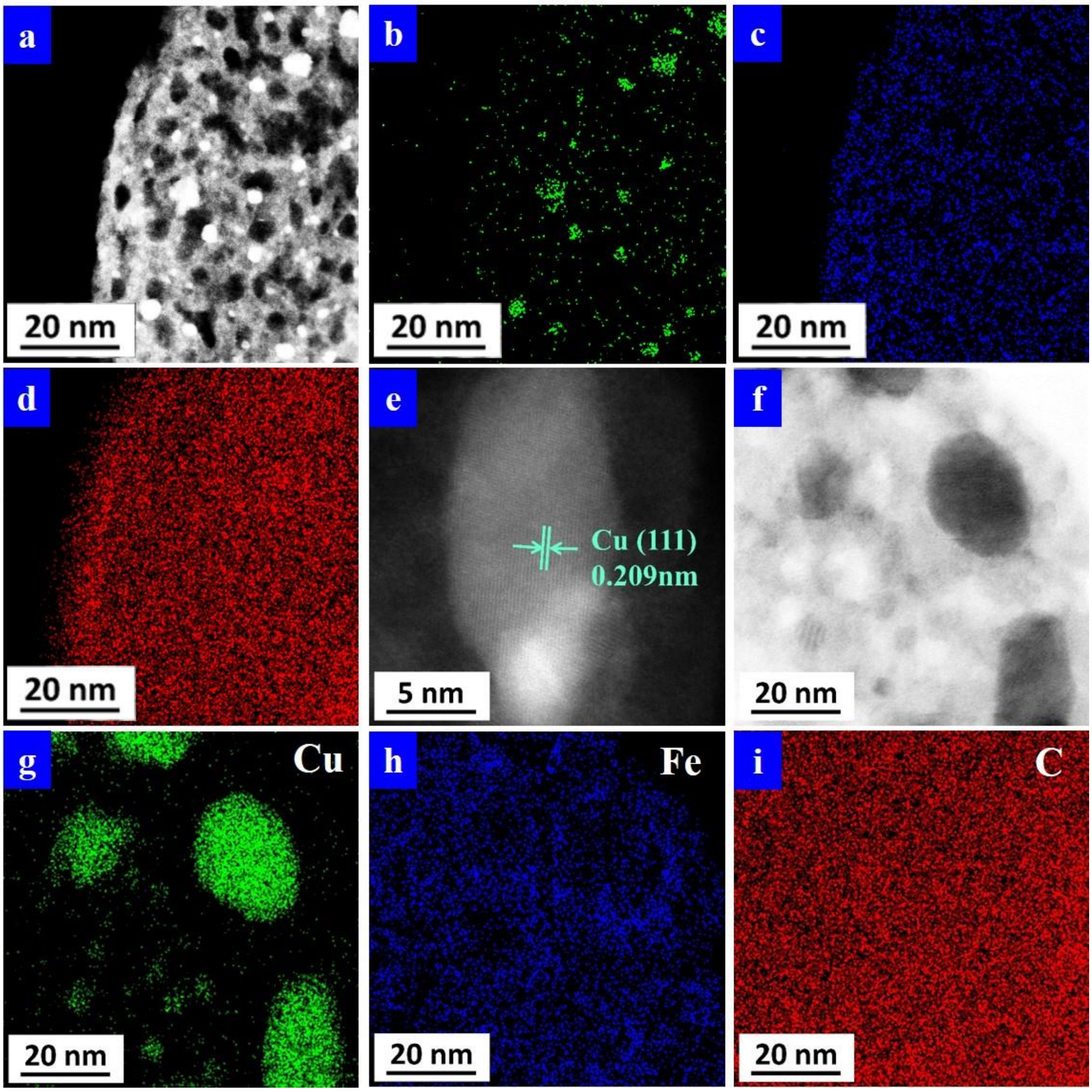


Supplementary Figure 7. Structure and morphology of $Cu_{10}Fe_1Mg_4$-LDH. XRD patterns of (a) $Cu_{10}Fe_1Mg_4$-LDH precursors and calcined (c) $Cu_{10}Fe_1Mg_4$-MMO precursors. SEM images: (b) $Cu_{10}Fe_1Mg_4$-LDH and (d) $Cu_{10}Fe_1Mg_4$-MMO.

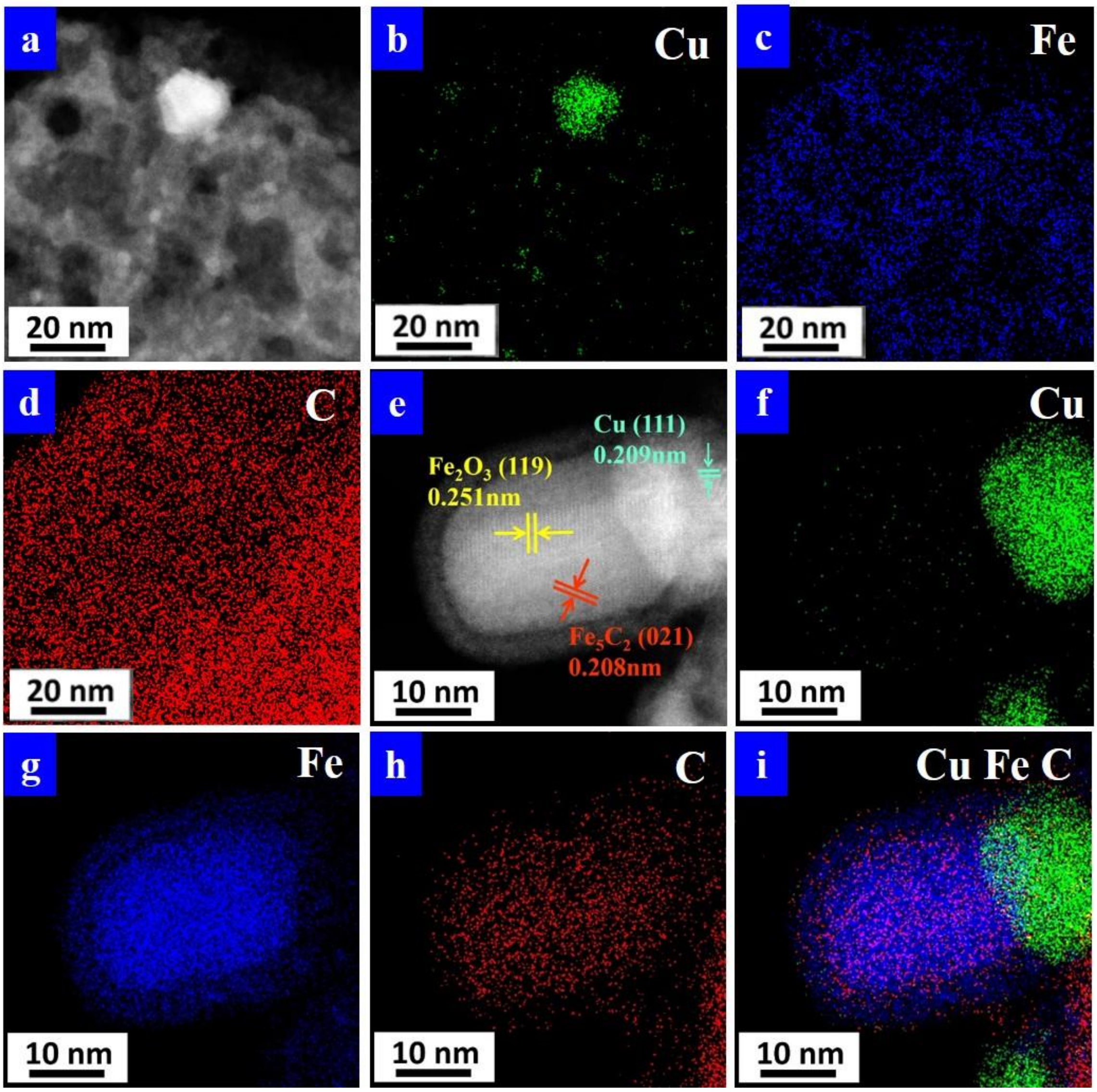
Supplementary Table 12. Catalytic performances of samples with Cu/Fe ratio 10/1

Catalysts[a,b]	Pressure [MPa]	Conv. [%]	Selectivity[mol%]				Alcohols distribution[%][c]				
			CH_4	$C_{2+}H$	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
$Cu_{10}Fe_1$	1	17.4	9.7	41.1	5.4	43.8	11.1(0.6)	21.2(1.1)	6.3(0.3)	3.2(0.2)	58.2(3.2)
	2	32.4	5.8	45.0	10.2	39.0	12.9(1.3)	25.5(2.6)	7.2(0.7)	3.6(0.4)	50.8(5.2)
	3	61.2	15.2	26.9	10.1	47.8	11.1(1.1)	24.0(2.4)	7.4(0.7)	4.1(0.4)	53.4(5.5)

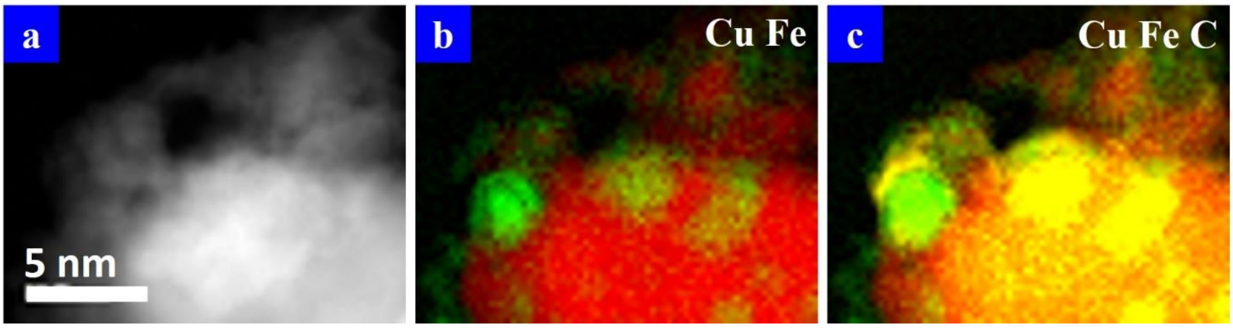
[a] Activation conditions: 1 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 ºC min^{-1}, 300 ºC 2 h + 350 ºC 1 h.
[b] Reaction conditions: 260 ºC, H_2/CO=2, 2400 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.



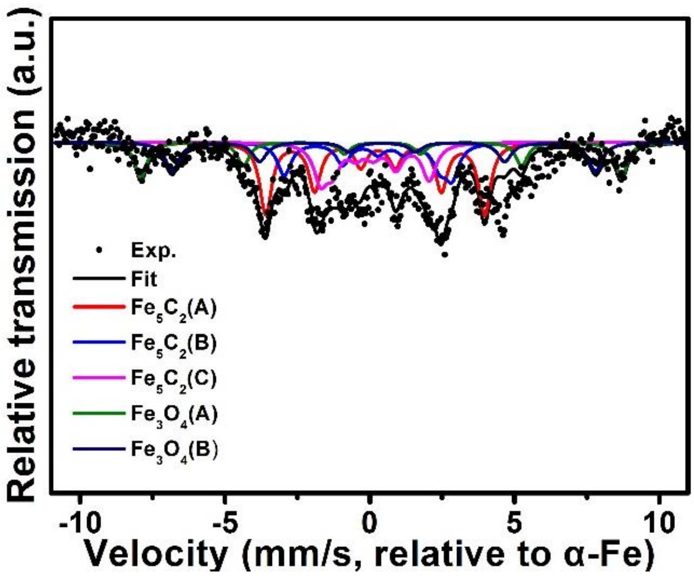
Supplementary Figure 8. Morphology of Cu_1Fe_1 catalyst. (a, e and f) TEM images of Cu_1Fe_1 catalyst (reduced and passivated). (b, c, d, g, h and i) EDS mapping of elemental distribution for Cu, Fe and C, respectively.



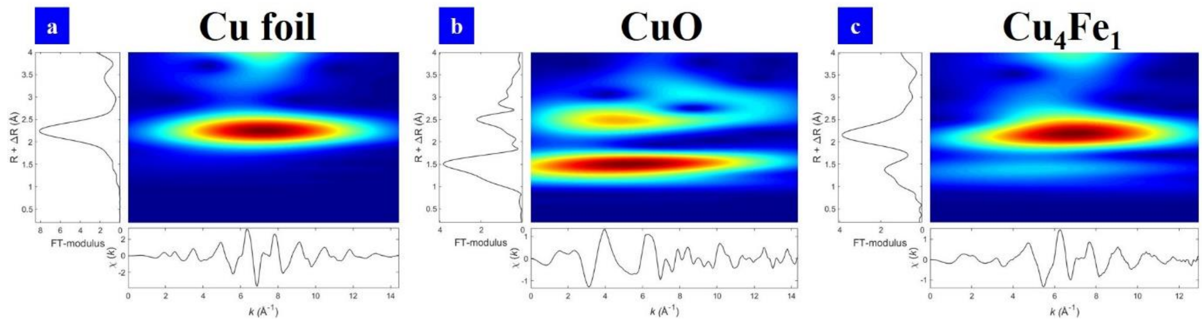
Supplementary Figure 9. Morphology of Cu_2Fe_1 catalyst. (a, e) TEM images of Cu_2Fe_1 catalyst (reduced and passivated). (b, c, d, f, g, h and i) EDS mapping of elemental distribution for Cu, Fe and C, respectively.



Supplementary Figure 10. Morphology of Cu_4Fe_1 catalyst. (a) HAADF-STEM image and (b, c) corresponding EELS mapping of Cu (red), Fe (green) and C (yellow).

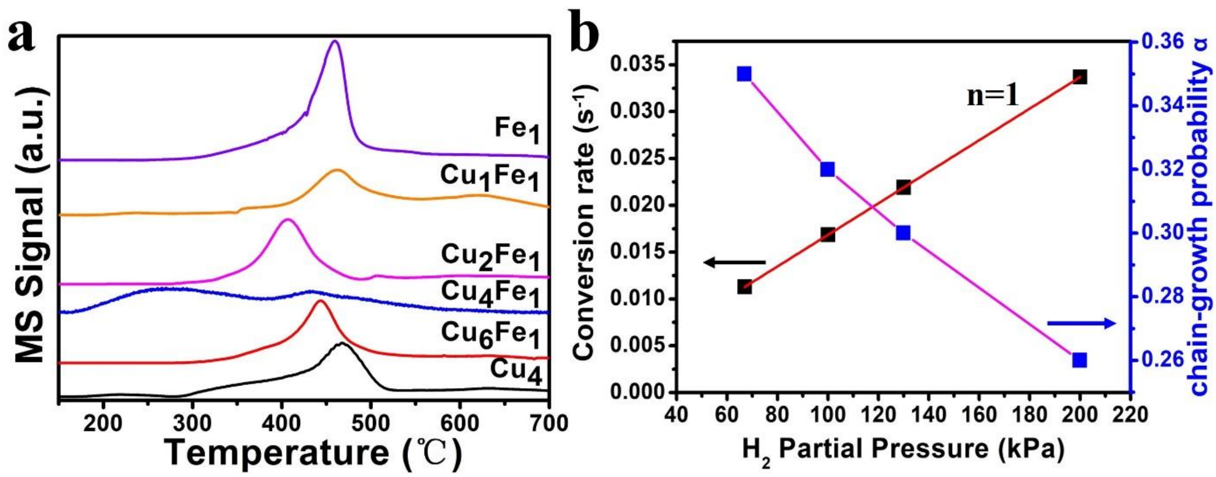


Supplementary Figure 11. Mössbauer spectrum of Cu_4Fe_1 sample (reduced and passivated) (Exp.: experimental data; Fit: fitting data).



Sample	Cu-Cu				Cu-O			
	C.N.	σ^2/*10^{-3}(Å^2)	E_0/eV	R/Å	C.N.	σ^2/*10^{-3}(Å^2)	E_0/eV	R/Å
Cu foil	12.0	8.5	4.38	2.544±0.002	-	-	-	-
CuO	-	-	-	-	4.0	3.4	-0.68	1.950±0.004
Cu_4Fe_1	4.6	5.2	-7.13	2.46±0.06	2.6	1.1	-7.13	1.82±0.03

Supplementary Figure 12. Structure of Cu_1Fe_1 catalyst. Wavelet transformation of (a) Cu foil, (b) CuO and (c) Cu_4Fe_1. The fitting results are listed in the table.



Supplementary Figure 13. H_2 activation of Fe_1, Cu_4 and Cu_xFe_y samples. (a) H_2-TPD profiles of Fe_1, Cu_4 and Cu_xFe_y samples. (b) Kinetic orders of H_2 and the corresponding chain-growth probability at various H_2 partial pressures over Cu_4Fe_1.