Supporting Information for

Promotion Effect of Ag on Syngas Transformation to Long-chain Alcohols over CuFe Catalysts

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Experimental section

1. Catalysts synthesis

The $CuFeM_1$-LDH precursors with eight different elements of Mo, In, Ag, Cr, Ga, Mn, Nb and Re were prepared by using nucleation and aging separation method. This method was modified by using KOH and K_2CO_3 as precipitating agents and changing the colloid mill rotating to 4000 rpm. The $CuFeM_1$-LDHs precursors were directly reduced in syngas atmosphere consisting of 25% CO + 25% H_2 + 50% CO_2 with a two-step-process: 300 ºC for 2 h and 350 ºC for 1 h at a heating rate of 2 ºC min^{-1} (denoted as $Cu_4Fe_1M_1$, respectively).

$CuFeAg_x$ samples with other three Ag loadings (x=0.5, 0.1 and 0.05) and three control samples (Cu_4Fe_1, $Cu_4Ag_{0.5}$ and $Fe_1Ag_{0.5}$) were prepared by the same above method.

2. Catalytic evaluation

The catalytic evaluation was carried out in a fixed-bed stainless steel reactor. 0.5 g of catalyst was loaded in 10 mm inner diameter quartz tube inside. Before reaction, the LDHs precursors was activated *in situ* as mentioned above with a flow rate of 20 mL min^{-1}. After the reactor was cooled to room temperature, syngas with a flow rate of 20 mL min^{-1} (32% CO + 64% H_2 + 4% Ar) was introduced to reach the required pressure with argon as an internal standard gas. The reaction was conducted at 260 ºC. The modulation of reaction conditions was based on above criteria.

The outlet gas components (CO, H_2, CH_4, CO_2 and Ar) after passing through a hot trap (120 ºC) and a cold trap (5 ºC) were determined using Agilent 7890A gas chromatography with TCD detector (5A molecular sieve column and Plot Q column) and FID detector (Al_2O_3 capillary column) using He as carrier gas. The liquid products were collected from the hot trap and cold trap, followed by determination offline with FID detector (Heavy hydrocarbons were analyzed by HP-5 column and oxygenates were quantified by HP-INNOWAX column). 1,4-dioxane was used as internal standard for the aqueous products; and decalin was used as internal standard for the oily products.

CO conversion was defined as: $$\text{CO conversion (\%)} = \frac{F_{CO,in} - F_{CO,out}}{F_{CO,in}} \times 100 \quad (1)$$

Product selectivity was defined as: $$\text{Selectivity (mol \%)} = \frac{F_{Ci} \times i}{F_{CO,in} - F_{CO,out}} \times 100 \quad (2)$$

Where F is the moles of CO and product Ci (CO_2, hydrocarbon or alcohols) containing i

carbon atoms. The mass balance and carbon balance have been calculated at each product and kept between 90% and 93%.

3. Characterizations of catalysts

Powder XRD measurements were performed on a Rigaku XRD-6000 diffractometer, using Cu Kα radiation (λ= 0.15418 nm) at 40 kv and 30 mA, with a scanning rate of 5° min^{-1} and a 2θ angle ranging from 3° to 90°. Scanning electron microscope (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV was performed. The phases of components were identified based on JCPDS standard cards. The scanning transmission electron microscopy (STEM) and EDX mapping measurements were performed on a FEI Tecnai G2 F20 microscope with an accelerating voltage of 120 kV. The specific surface area determination and pore volume analysis were performed by Brunauer-Emmett-Teller (BET) and Barret-Joyner-Halenda (BJH) methods using a Quantachrome Autosorb-1C-VP Analyzer. Elemental analysis for Cu and Fe was performed using a Shimadzu ICPS-75000 inductively coupled plasma atomic emission spectrometer (ICP-AES).

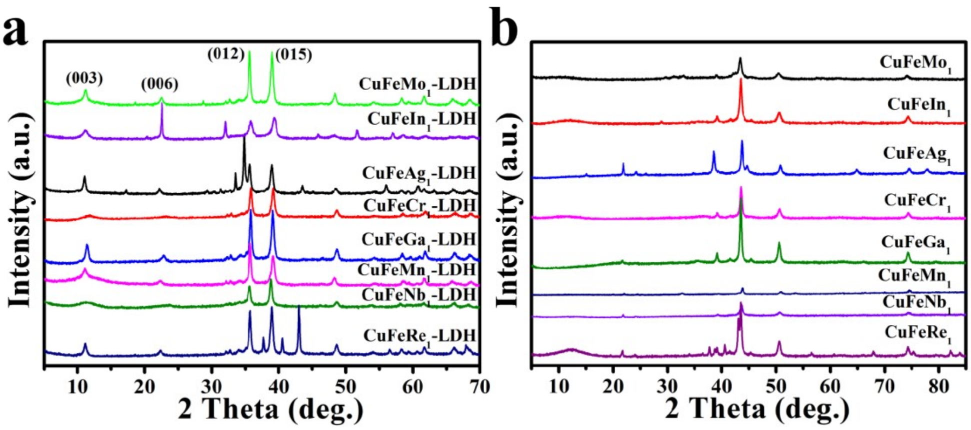

Figure S1. XRD patterns of (a) $CuFeM_1$-LDH precursors and (b) $CuFeM_1$ catalysts with different elements.

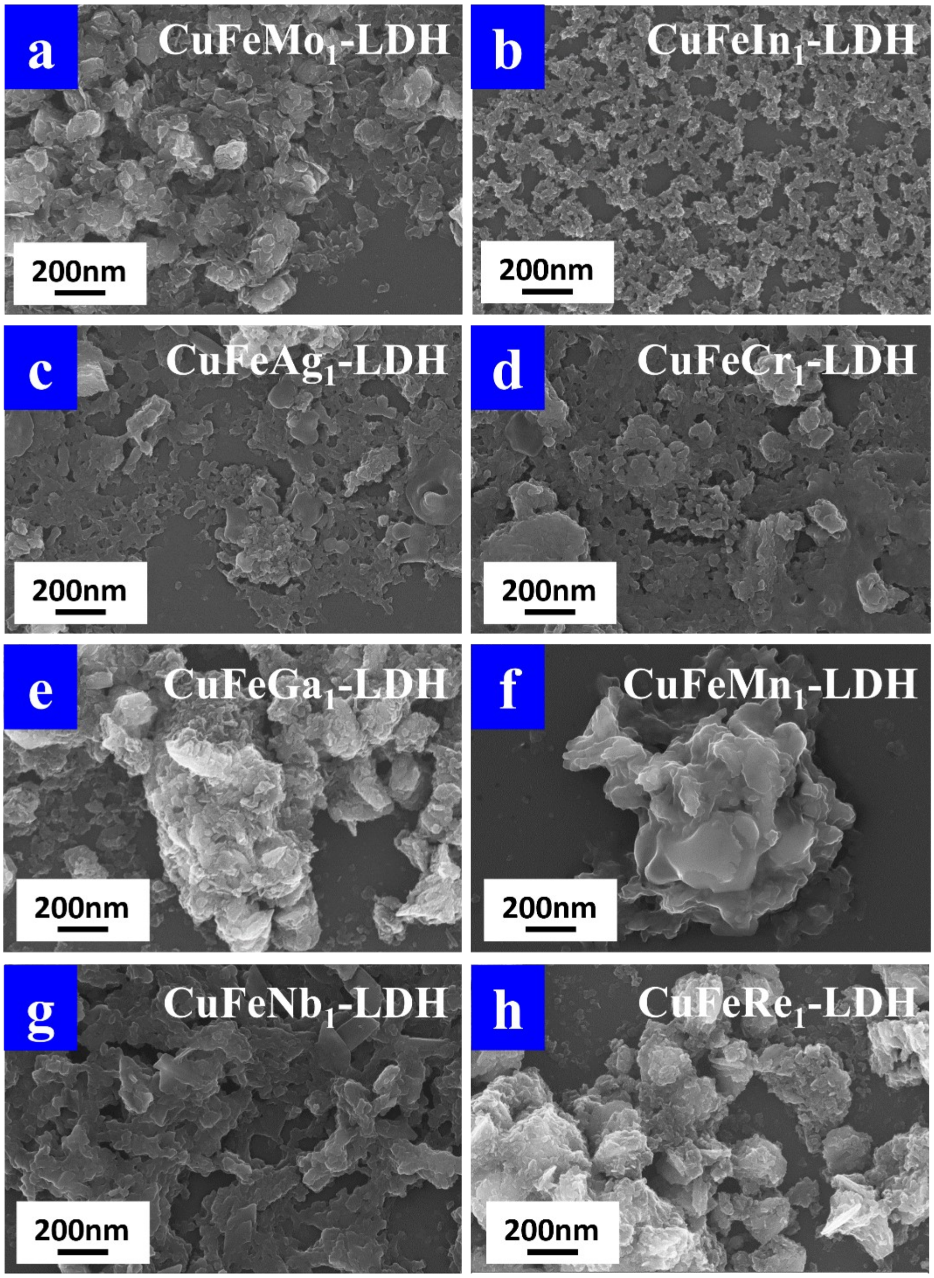

Figure S2. SEM images of $CuFeM_1$-LDH with different promoter elements.

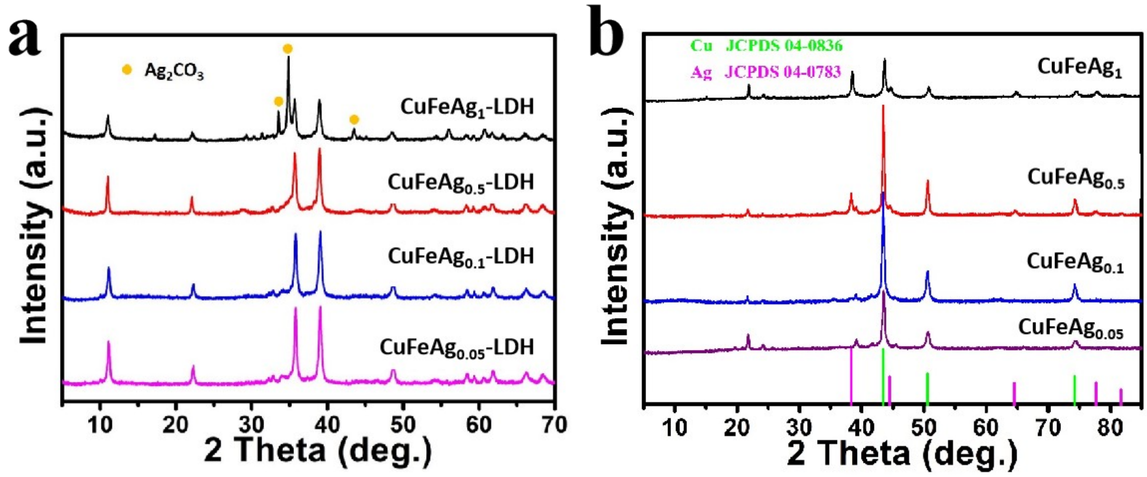

Figure S3. XRD patterns of (a) CuFeAg$_x$-LDH precursors and (b) CuFeAg$_x$ catalysts with different Ag/(Cu + Fe) ratios.

Table S1. Catalytic performances of samples with various promoters

Catalysts[a,b]	Conv. [%]	Selectivity[%]					Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
$CuFeMo_1$	21.4	33.2	7.7	7.9	11.8	39.4	45.7(5.4)	36.3(4.3)	10.4(1.2)	4.8(0.6)	2.8(0.3)
$CuFeIn_1$	1.8	58.1	8.3	11.0	–	22.6	–	–	–	–	–
$CuFeAg_1$	40.1	8.1	28.6	18.4	18.9	26.9	9.9(1.9)	28.3(5.3)	10.8(2.0)	8.5(1.6)	42.5(8.1)
$CuFeCr_1$	6.1	5.7	25.3	13.0	10.6	45.4	69.8(7.4)	21.7(2.3)	8.5(0.9)	–	–
$CuFeGa_1$	15.8	10.9	20.4	27.7	12.8	28.2	34.6(4.4)	44.8(5.7)	12.9(1.7)	5.3(0.7)	2.4(0.3)
$CuFeMn_1$	20.1	6.7	19.7	30.3	13.8	29.5	8.9(1.2)	46.4(6.4)	8.1(1.1)	5.5(0.8)	31.1(4.3)
$CuFeNb_1$	15.4	2.8	25.7	29.6	13.3	28.6	26.3(3.5)	46.3(6.2)	14.2(1.9)	8.2(1.1)	5.0(0.6)
$CuFeRe_1$	28.6	9.8	30.7	17.7	11.7	30.1	23.6(2.8)	26.9(3.1)	13.9(1.6)	12.1(1.4)	23.5(2.8)

[a] Activation conditions: 0.5 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: 2 MPa, 260 ºC, H_2/CO=2, 3000 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S2. Catalytic performances of samples with various Ag loadings

Catalysts[a,b]	Conv. [%]	Selectivity[mol%]					Alcohols distribution[%][c]				
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	C_{5+}OH
$CuFeAg_1$	40.1	8.1	28.6	18.4	18.9	26.9	9.9(1.9)	28.3(5.3)	10.8(2.0)	8.5(1.6)	42.5(8.1)
$CuFeAg_{0.5}$	70.1	4.7	25.3	12.8	25.4	31.8	12.7(3.2)	25.1(6.4)	12.5(3.2)	5.6(1.4)	44.1(11.2)
$CuFeAg_{0.1}$	54.8	6.7	32.9	17.1	11.4	31.9	18.1(2.1)	31.1(3.5)	9.9(1.1)	4.9(0.6)	36.0(4.1)
$CuFeAg_{0.05}$	31.7	9.0	28.7	18.2	11.5	32.6	15.0(1.7)	27.3(3.1)	9.6(1.1)	4.7(0.6)	43.4(5.0)

[a] Activation conditions: 0.5 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 °C min^{-1}, 300 °C 2 h + 350 °C 1 h.
[b] Reaction conditions: 2 MPa, 260 °C, H_2/CO=2, 3000 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S3. Catalytic performances of control samples

Catalysts[a,b]	Conv. [%]	Selectivity[%]					Alcohols distribution[%][c]					Total alcohols STY [g g_{cat}^{-1} h^{-1}]	LA STY [g g_{cat}^{-1} h^{-1}]
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$		
Cu_4Fe_1	47.6	8.8	24.2	22.1	19.7	25.2	11.6 (2.3)	30.3 (6.0)	14.1 (2.8)	6.2 (1.2)	37.8 (7.4)	0.14	0.051
$CuFeAg_{0.5}$	70.1	4.7	25.3	12.8	25.4	31.8	12.7 (3.2)	25.1 (6.4)	12.5 (3.2)	5.6 (1.4)	44.1 (11.2)	0.29	0.139
$Cu_4Ag_{0.5}$	9.9	26.0	6.2	-	61.5	6.3	91.0 (56.0)	4.3 (2.6)	1.3 (0.8)	1.0 (0.6)	2.4 (1.5)	0.09	0.002
$Fe_1Ag_{0.5}$	39.0	10.1	21.3	14.9	-	53.7	-	-	-	-	-	-	-

[a] Activation conditions: 0.5 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: 2 MPa, 260 ºC, H_2/CO=2, 3000 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S4. Catalytic performance data for a variety of modified FT catalysts used in LAS

Catalyst	H_2/CO ratio	Temperature /°C	Pressure /MPa	GHSV/WHSV	CO conversion/%	Total alcohol Selectivity/%	Long-chain alcohol selectivity/%	Total alcohols STY[a]	Long-chain alcohols STY[a]	reference
$CuFeAg_{0.5}$	2	260	2	3000 mL g_{cat}^{-1} h^{-1}	70.1	25.4	44.1	0.29	0.139	This work
Cu_4Fe_1	2	260	1	2400 mL g_{cat}^{-1} h^{-1}	53.2	29.8	49.1	0.20	0.101	*Nat Commun.* **2020**, *11*, 61 Previous work
CNF-2-0.005	2	270	5	16000 mL g_{cat}^{-1} h^{-1}	12	50		0.38		*ACS Catal.* **2018**, 8, 9604−9618
CuFeCo	2	350	5.5	6000 h^{-1}	72	12.5	6	0.25	0.015	*Appl. Catal. A* **2015**, *503*, 51-61
CuZnFeMn	2	280	4	6000 h^{-1}	59.37	31.04	3.65	0.26	0.016	*Catal. Commun.* **2008**, *9*, 1869-1873
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
3DOM Cu_2Fe_1	1	220	4.8	2000 h^{-1}	12.9	47.6	62.4	0.23	0.144	*ChemCatChem* **2014**, *6*, 473-478
CuFeK0.5M	2	320	5	6000 h^{-1}	53	61	NA	0.32	NA	*Fuel Process. Technol.* **2017**, *159*, 436-441
$CF_{0.5}$	2	260	4	5000 h^{-1}	17.99	20.77	2.5	0.05	0.001	*J. Colloid Interface Sci.* **2016**, *470*, 162-171
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
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
Fe-Cu/Al_2O_3 (Al_2O_3 loading: 89.3%)	2.68	380	4	10000 h^{-1}	NA	62.3	NA	0.044	NA	*J. Nat. Gas Chem.* **2008**, *17*, 327-331
CuFeCrNi/CNTs	2	400	4	5000 h^{-1}	44	46		0.021		*React. Kinet. Mech. Cat.* **2019**, *128*, 695-706
Cu-Fe@ HHSS	2	300	3	5000 h^{-1}	65.1	46.6		0.118		*Appl. Catal. A* **2020**, *608*, 117868
CoBa/AC	2	220	3	2000 h^{-1}	30.4	23.3	57			*Catal. Lett.* **2021**, 10.1007/s10562-021-03602-y
1.1Rh-CoMn	1	220	6	2000 mL g_{cat}^{-1} h^{-1}	33.1	40.9		0.071		*Appl. Catal. B* **2021**, *285*, 119840

$Co_4Mn_1K_{0.1}$	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
0.4Na-Co/AC	2	220	3	2000 mL g_{cat}^{-1} h^{-1}	15.8	29.2	45	0.34	0.153	*Appl. Catal. A* **2020**, *602*, 117704
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
Cu@(CuCo-alloy)/Al_2O_3	2	220	2	2000 mL g_{cat}^{-1} h^{-1}	21.5	50.6	48.9	0.21	0.103	*Green Chem.* **2015**, *17*, 1525-1534

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

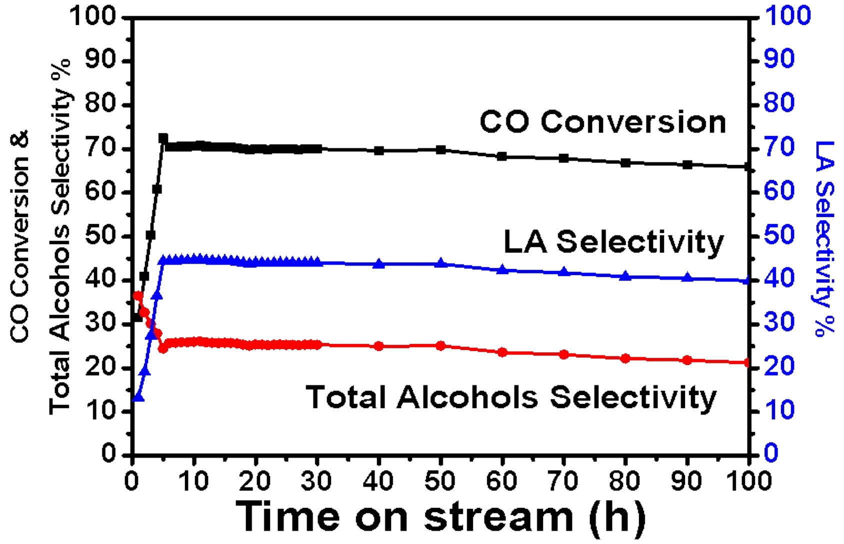

Figure S4. Time-on-stream (TOS) evolution of CO conversion, total alcohols selectivity and LA selectivity over the $CuFeAg_{0.5}$ catalyst within 100 h test.

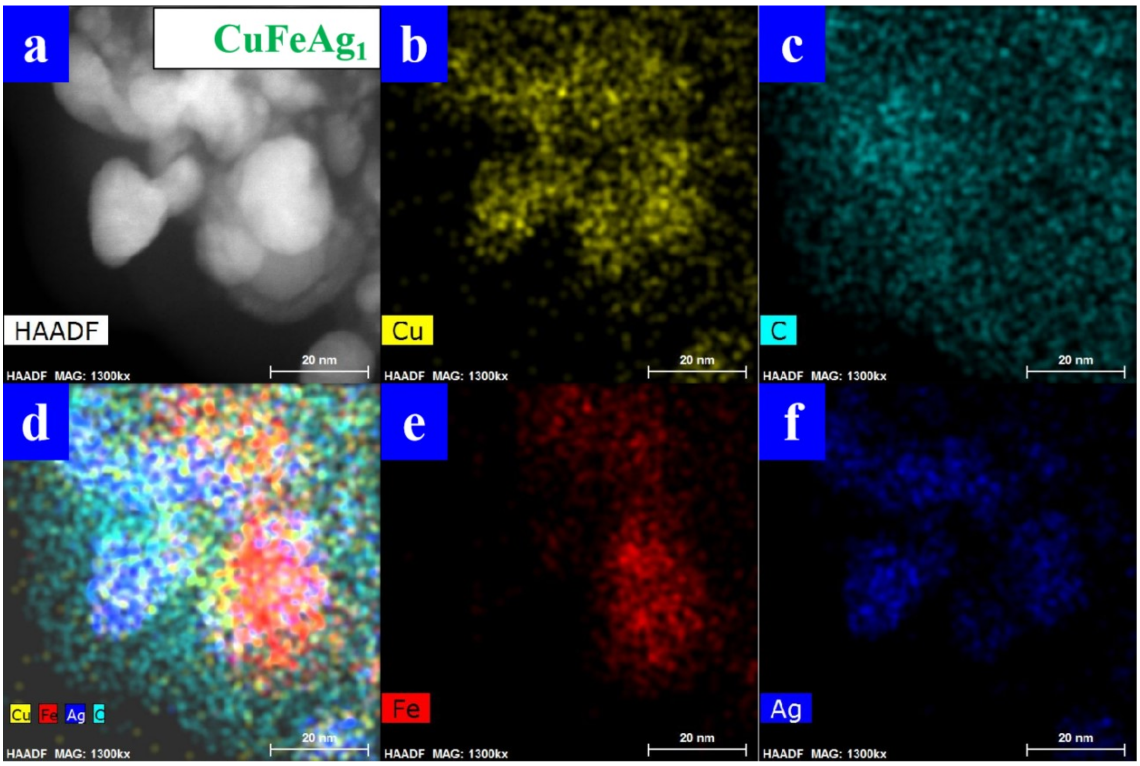

Figure S5. (a) HAADF-STEM images of $CuFeAg_1$ catalyst. (b, c, d, e and f) EDS mapping of elemental distribution for Cu, Fe, C and Ag, respectively.

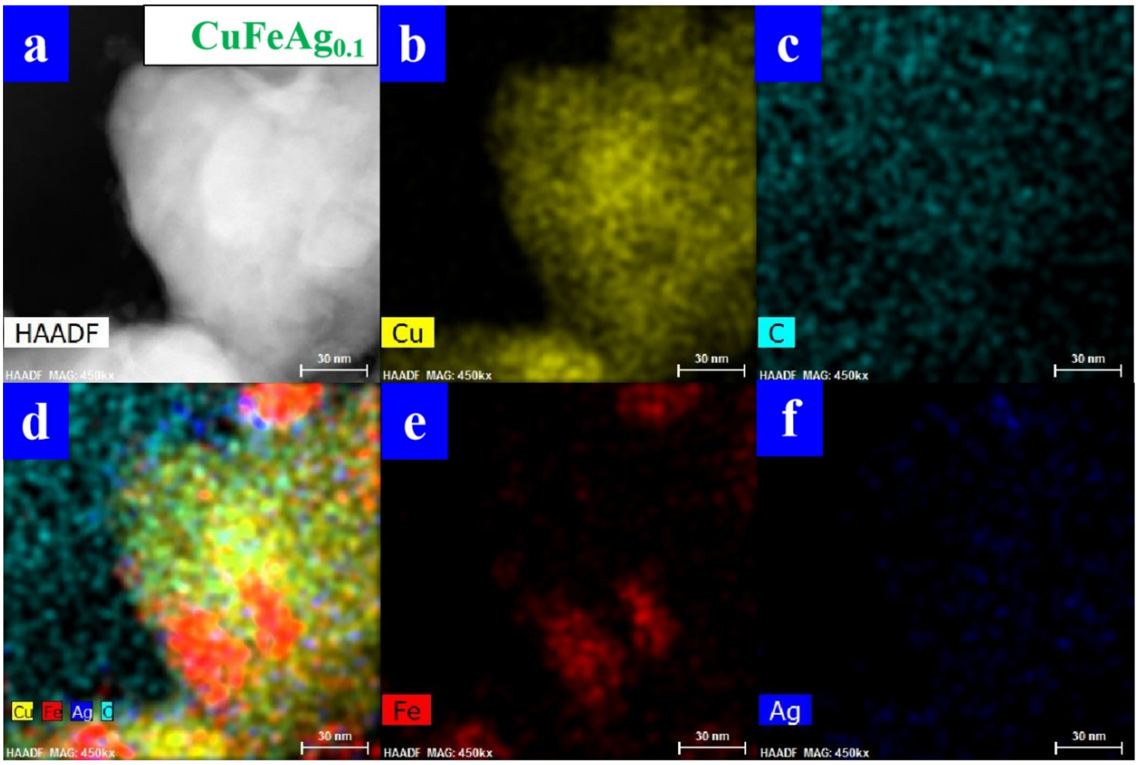

Figure S6. (a) HAADF-STEM images of $CuFeAg_{0.1}$ catalyst. (b, c, d, e and f) EDS mapping of elemental distribution for Cu, Fe, C and Ag, respectively.

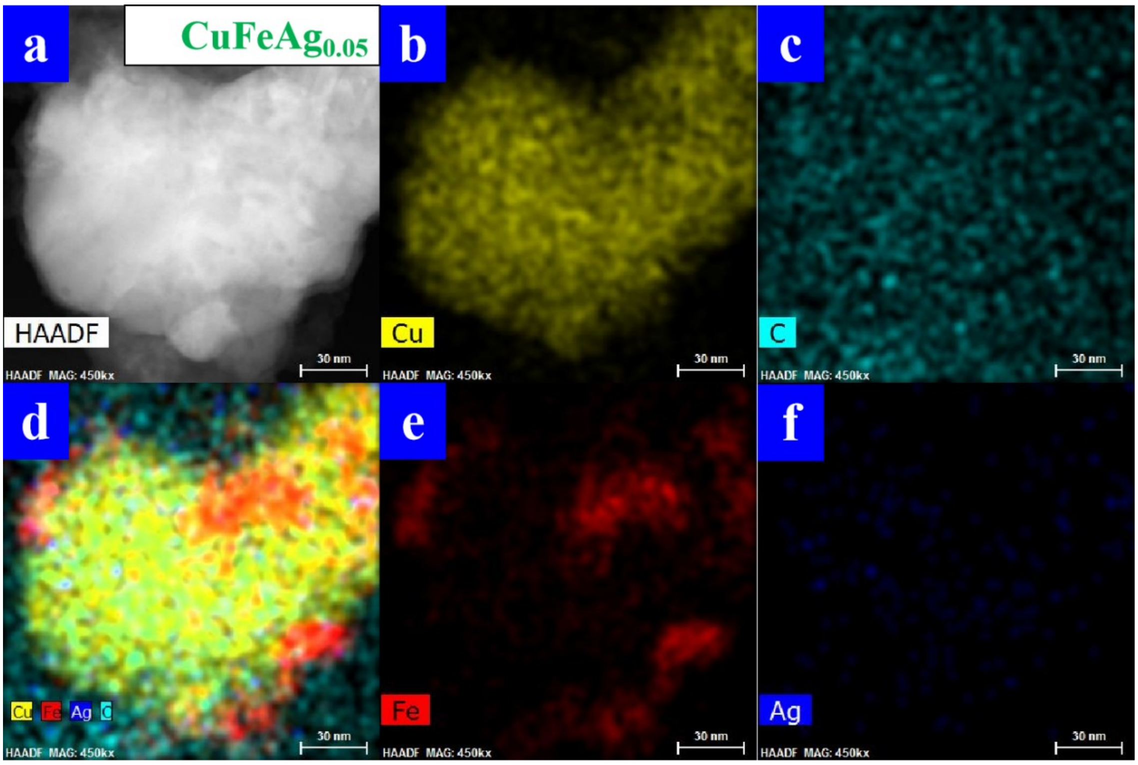

Figure S7. (a) HAADF-STEM images of $CuFeAg_{0.05}$ catalyst. (b, c, d, e and f) EDS mapping of elemental distribution for Cu, Fe, C and Ag, respectively.

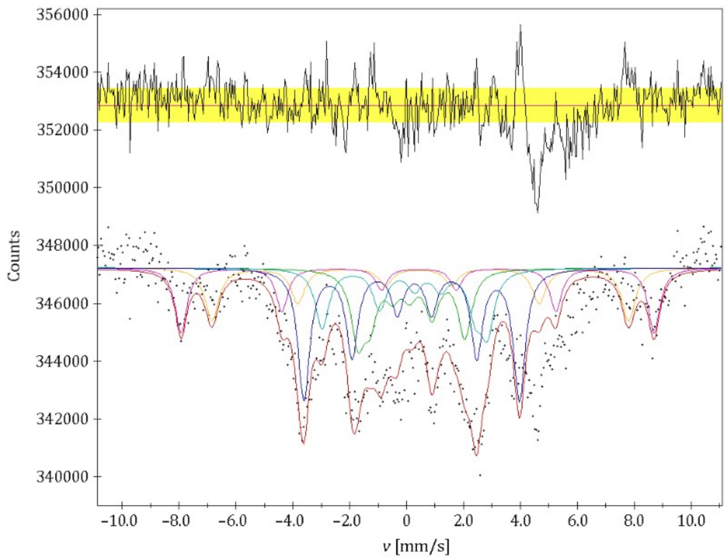

Figure S8. Mössbauer spectrum of $CuFeAg_{0.5}$ sample.

Table S5. Physicochemical properties of various catalysts

Sample	BET surface area ($m^2\ g^{-1}$)	Ag/(Cu + Fe) ratio [a]	Cu Crystallite size [b] (nm)	Mean Cu particle size [c] (nm)
$CuFeAg_1$	22.38	0.21	25.7	24.6
$CuFeAg_{0.5}$	20.07	0.10	46.4	44.8
$CuFeAg_{0.1}$	21.77	0.02	45.1	44.2
$CuFeAg_{0.05}$	25.96	0.01	33.6	32.9

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

[b] Crystallite size was determined by XRD with the Scherrer equation.
[c] Mean Cu particle size was determined by mapping images.

Table S6. Catalytic performances of $CuFeAg_{0.5}$ under various reaction temperature[a,b]

Temp. [ºC]	Conv. [%]	Selectivity[mol%]					Alcohols distribution[%][c]					Total alcohols STY [g g_{cat}^{-1} h^{-1}]	LA STY [g g_{cat}^{-1} h^{-1}]
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$		
220	12.2	14.6	21.3	18.6	-	45.5	-	-	-	-	-	-	-
240	21.6	5.9	9.0	7.7	35.6	41.8	18.7 (6.7)	41.7 (14.8)	14.9 (5.3)	11.3 (4.0)	13.4 (4.8)	0.11	0.016
260	70.1	4.7	25.3	12.8	25.4	31.8	12.7 (3.2)	25.1 (6.4)	12.5 (3.2)	5.6 (1.4)	44.1 (11.2)	0.29	0.139
280	82.9	9.5	18.8	14.8	10.7	46.2	7.8 (0.8)	28.7 (3.1)	7.7 (0.8)	4.2 (0.4)	51.6 (5.6)	0.14	0.074
300	96.6	18.7	22.5	20.5	3.6	34.7	12.2 (0.4)	54.3 (2.0)	14.1 (0.5)	6.5 (0.2)	12.9 (0.5)	0.05	0.008

[a] Activation conditions: 0.5 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 °C min^{-1}, 300 °C 2 h + 350 °C 1 h.
[b] Reaction conditions: 2 MPa, H_2/CO=2, 3000 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S7. Catalytic performances of $CuFeAg_{0.5}$ under various reaction pressure[a,b]

Press. [MPa]	Conv. [%]	Selectivity[%]					Alcohols distribution[%][c]					Total alcohols STY [g g_{cat}^{-1} h^{-1}]	LA STY [g g_{cat}^{-1} h^{-1}]
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$		
3.00	63.8	7.9	27.1	7.8	14.7	42.5	7.5 (1.1)	26.0 (3.8)	7.3 (1.1)	3.8 (0.6)	55.4 (8.1)	0.22	0.111
2.00	70.1	4.7	25.3	12.8	25.4	31.8	12.7 (3.2)	25.1 (6.4)	12.5 (3.2)	5.6 (1.4)	44.1 (11.2)	0.29	0.139
1.00	50.6	10.1	25.4	8.7	14.1	41.7	18.7 (2.6)	35.2 (5.0)	11.8 (1.7)	5.8 (0.8)	28.5 (4.0)	0.13	0.041
0.14	79.4	9.5	18.4	13.6	4.8	59.1	18.0 (0.9)	18.1 (0.9)	11.1 (0.5)	5.2 (0.2)	47.6 (2.3)	0.06	0.028

[a] Activation conditions: 0.5 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, 3000 mL g_{cat}^{-1} h^{-1}.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S8. Catalytic performances of $CuFeAg_{0.5}$ under various WHSV[a,b]

WHSV [mL g_{cat}^{-1} h^{-1}]	Conv. [%]	Selectivity[%]					Alcohols distribution[%]					Total alcohols STY [g g_{cat}^{-1} h^{-1}]	LA STY [g g_{cat}^{-1} h^{-1}]
		CH_4	$C_{2+}H$	C_{2+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$		
1500	82.4	6.5	7.6	15.0	25.9	45.0	22.0 (5.7)	48.6 (12.6)	11.1 (2.9)	4.8 (1.2)	13.5 (3.5)	0.13	0.022
3000	70.1	4.7	25.3	12.8	25.4	31.8	12.7 (3.2)	25.1 (6.4)	12.5 (3.2)	5.6 (1.4)	44.1 (11.2)	0.29	0.139
4500	43.8	9.1	25.0	18.5	5.3	42.1	17.2 (0.9)	36.1 (1.9)	9.9 (0.5)	4.8 (0.3)	32.0 (1.7)	0.05	0.019
6000	26.5	11.7	20.3	25.2	1.1	41.7	19.6 (0.2)	35.6 (0.4)	9.4 (0.1)	7.8 (0.1)	27.6 (0.3)	0.01	0.004

[a] Activation conditions: 0.5 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: 2 MPa, 260 ºC, H_2/CO=2.
[c] Normalized data to S_{ROH}, mol% in brackets.

Table S9. Catalytic performances of Cu_4Fe_1 and $CuFeAg_x$ with addition of 8% C_2H_4[a,b]

Catalysts[a,b]	CO Conv. [%]	C_2H_4 Conv. [%]	Selectivity[%]					Alcohols distribution[%]				
			CH_4	$C_{2+}H$	C_{3+}=H	ROH	CO_2	MeOH	EtOH	PrOH	BuOH	$C_{5+}OH$
Cu_4Fe_1	16.3	26.7	0.1	7.8	11.1	36.3	44.7	13.5	33.3	46.3	1.9	5.0
$CuFeAg_1$	15.6	25.1	0.1	7.6	13.3	35.0	44.0	15.6	46.9	31.8	1.6	4.1
$CuFeAg_{0.5}$	33.9	72.9	0.1	5.7	3.4	45.1	45.7	38.3	6.6	52.1	1.4	1.6
$CuFeAg_{0.1}$	18.9	29.5	0.1	10.3	16.5	30.0	43.1	20.4	45.4	28.9	1.5	3.8
$CuFeAg_{0.05}$	10.7	19.8	0.1	14.0	15.7	26.6	43.6	22.3	44.4	27.7	1.4	4.2

[a] Activation conditions: 0.5 g precursor, H_2: CO: CO_2=1: 1: 2 (40 mL min^{-1}), 2 °C min^{-1}, 300 °C 2 h + 350 °C 1 h

[b] Reaction conditions: 2 MPa, 260 °C, H_2/CO=2, 3000 mL g_{cat}^{-1} h^{-1}

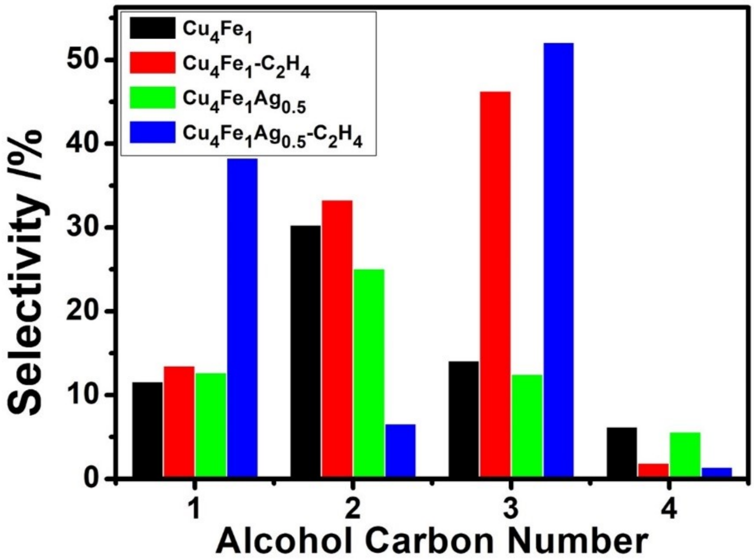

Figure S9. C_1-C_4 alcohols selectivity over the Cu_4Fe_1 and $CuFeAg_{0.5}$ catalysts before/after the addition of C_2H_4.