Engineering active sites at hydrotalcite-derived Cu-ZnO interaction for promoting CO_2 hydrogenation to methanol

Ying Yang[1], Peixiang Shi[1,*], Zhiqiang Yan[1], Zhaohui Liu[1], Yanchun Li[1], Hongyan Ban[1], Congming Li[1,*]

[1] State Key Laboratory of Clean and Efficient Coal Utilization, College of Chemistry and Chemical Engineering, Taiyuan University of Technology, Taiyuan 030024, China.

Corresponding authors: Peixiang Shi; Congming Li

Email address: frankshi926@126.com; licongming0523@163.com

Catalytic tests:

Calculation formula for CO_2 conversion (X_{CO2}) rate:

$$X_{CO_2} = \left(1 - \frac{A_{out(CO_2)}/A_{out(Ar)}}{A_{in(CO_2)}/A_{in(Ar)}}\right) \times 100\%$$

where $A_{in(CO_2)}$ and $A_{in(Ar)}$ are the TCD peak area of CO_2 and Ar before reaction, $A_{out(CO_2)}$ and $A_{out(Ar)}$ are the TCD peak area of CO_2 and Ar after reaction.

The formula for calculating the selectivity of CO and CH_3OH:

$$S_{CO} = \frac{A_{out(CO)}/A_{out(Ar)} \times f_{CO/Ar}}{\left(A_{in(CO_2)}/A_{in(Ar)} - A_{out(CO_2)}/A_{out(Ar)}\right) \times f_{CO_2/Ar}} \times 100\%$$

$$S_{CH_3OH} = \left(\frac{A_{CH_3OH} \times f_{CH_3OH}}{\left(A_{in(CO_2)}/A_{in(Ar)} - A_{out(CO_2)}/A_{out(Ar)}\right) \times f_{CO_2/Ar}}\right) \times 100\%$$

where $A_{out(CO)}$ and A_{CH_3OH} is the peak area of CO and CH_3OH, respectively. $f_{CO/Ar}$, $f_{CO_2/Ar}$, and f_{CH_3OH} are the calibration factor of CO, CO_2, and CH_3OH.

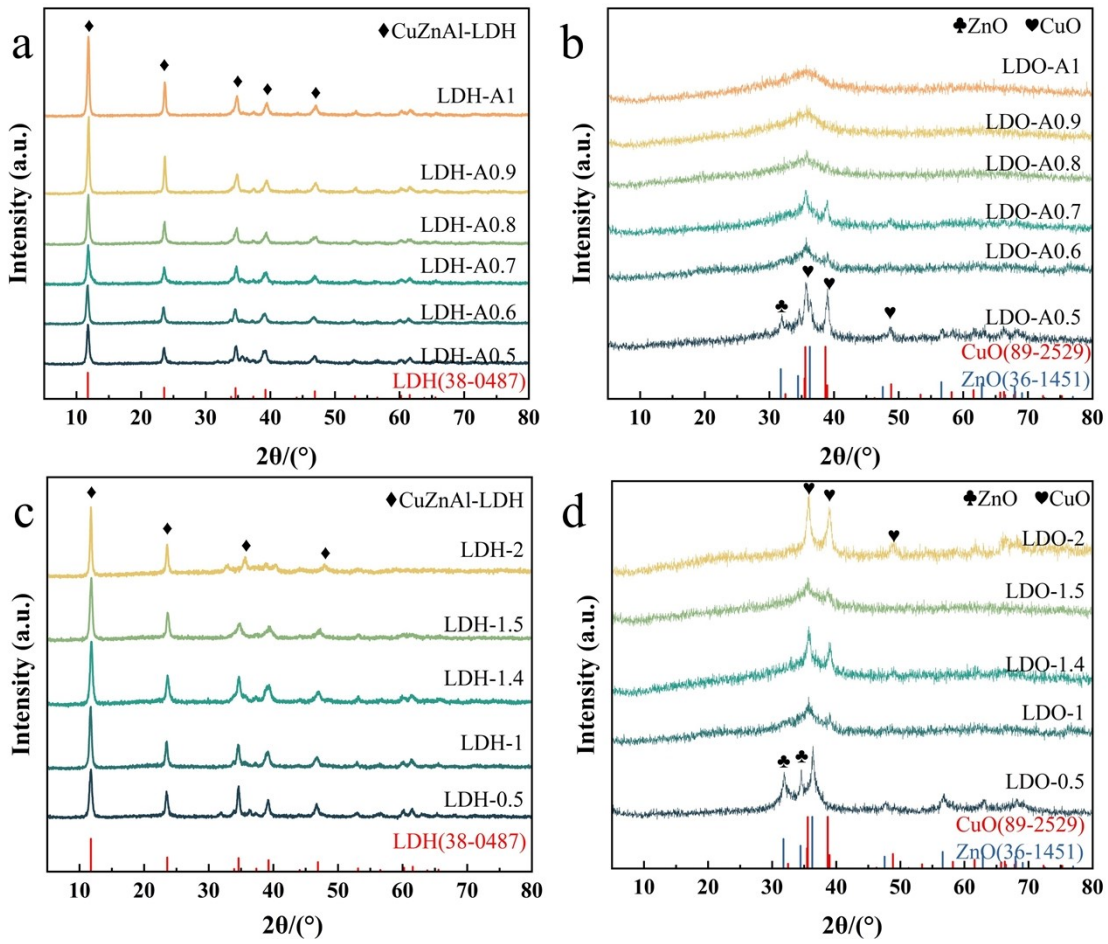

Fig. S1. XRD patterns of the (a) the precursor of LDH-Ax; (b) calcined LDO-Ax; (c) the precursor of LDH-y; (d) calcined LDO-y.

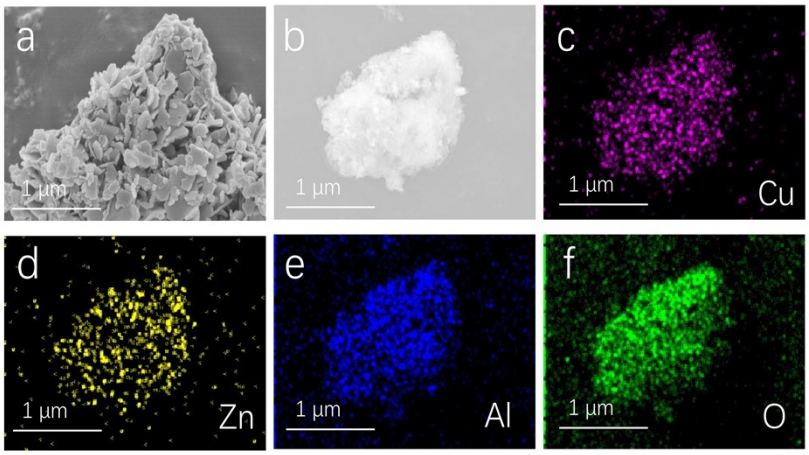

Fig. S2. (a) SEM images and (b-f) EDS element mapping of LDO-1.4.

Table S1. Actual catalyst compositions determined from ICP of the LDO-y and CZA-1.4 catalysts.

Catalyst	Cu(mol%)	Zn(mol%)	Al(mol%)	(Cu+Zn)/Al(mol%)	Cu:Zn:Al
LDO-0.5	18.44	58.54	23.02	3.34	0.481:1.527:0.6
LDO-1	38.13	40.11	21.76	3.59	1.051:1.106:0.6
LDO-1.4	52.91	24.46	22.63	3.42	1.403:0.649:0.6
LDO-1.5	58.03	19.61	22.36	3.47	1.527:0.526:0.6
LDO-2	78.07	0	21.93	3.56	2.136:0:0.6
CZA-1.4	52.11	24.89	22.31	3.45	1.401:0.669:0.6

Table S2. Summary of N_2-physisorption, crystallite size and average particle size of the LDO-1.4 and CZA-1.4 catalysts.

Catalyst	S_{BET}[a] (m^2/g)	Pore volume[b] (cm^3/g)	Pore diameter[c] (nm)
LDO-1.4	26.23	0.36	35.43
CZA-1.4	67.75	0.84	32.42

a Specific surface area was calculated using the BET method.

b Cumulative pore volume was determined from desorption branches via the BJH method.

c Pore size distribution was derived from desorption data based on the BJH method.

Table S3. Surface copper species content of prereduced LDO-1.4 and CZA-1.4.

Catalyst	Kintic energy and surface copper species percentage (eV/%)	
	Cu^+	Cu^0
LDO-1.4	914.3(57.5%)	917.4(42.5%)
CZA-1.4	914.5(66.9%)	917.7(33.1%)

Table S4. Surface zinc species content of prereduced LDO-1.4 and CZA-1.4.

Catalyst	Binding energy and surface zinc species percentage (eV/%)	
	Zn^{2+}	$Zn^{\delta+}$
LDO-1.4	499.1(68.4%)	495.9(31.6%)
CZA-1.4	498.8(68.3%)	495.7(31.7%)

Table S5. Surface oxygen species content of prereduced LDO-y and CZA-1.4.

Catalyst	Binding energy and surface oxygen species percentage (eV/%)	
	O_L	O_V
LDO-1.4	530.3(18.7%)	531.7(81.3%)
CZA-1.4	530.0(29.5%)	531.6(70.5%)

Table S6. The maximum temperature and amount of CO_2 and H_2 desorption over prereduced LDO-1.4 and CZA-1.4 catalysts.

Catalyst	CO_2-TPD(μmol/g)			H_2-TPD(μmol/g)
	Weak	Medium	Total	Total
LDO-1.4	10（123℃）	39（344℃）	49	62（307℃）
CZA-1.4	10（125℃）	51（339℃）	61	45（317℃）