Electronic Supplementary Information (ESI)

Intercalation of laminar Cu-Al LDH with molecular TCPP(M) (M=Zn, Co, Ni, Fe) towards high-performance CO_2 hydrogenation catalysts

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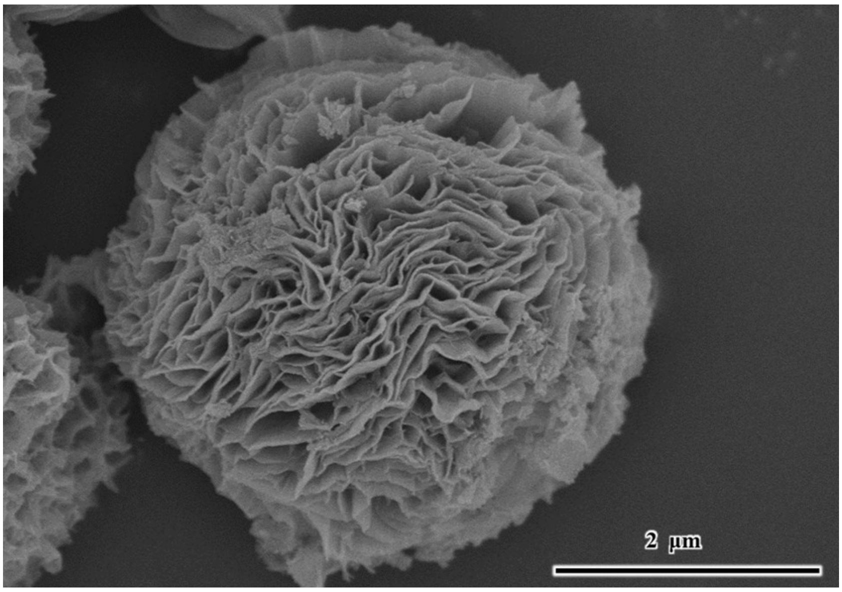

Fig. S1 Representative SEM image of CA-LDH sample.

Table S1 Metal contents in different catalyst samples determined by ICP-OES.

Sample	Metal composition [a] (wt%)	
	Cu	M[b]
TCPP(Zn)@CA-LDO	15.2	10.3
TCPP(Co)@CA-LDO	20.5	16.7
TCPP(Ni)@CA-LDO	18.4	13.7
TCPP(Fe)@CA-LDO	19.6	18.6

[a] Determined by ICP-OES, [b] M = Zn, Co, Ni, or Fe.

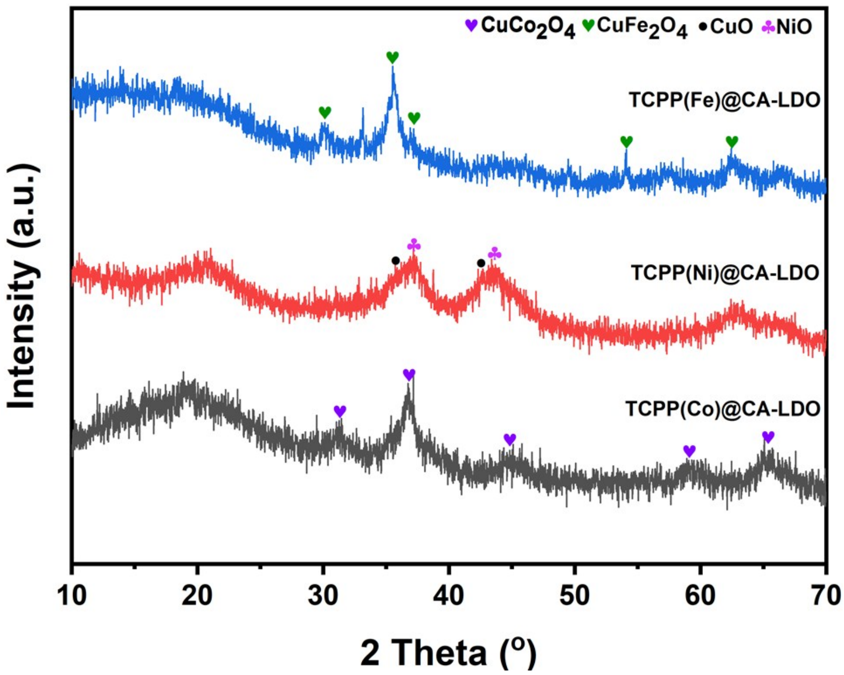

Fig. S2 XRD patterns of TCPP(Co)@CA-LDO, TCPP(Ni)@CA-LDO, and TCPP(Fe)@CA-LDO catalysts, which were all calcined at 500°C for 3 h.

Table S2. The specific BET surface area of different catalyst samples.

Sample	BET (m^2/g)
CA-LDO	184.6
TCPP@CA-LDO	206.5
TCPP(Zn)@CA-LDO	208.6
TCPP(Co)@CA-LDO	182.2
TCPP(Ni)@CA-LDO	236.3
TCPP(Fe)@CA-LDO	226.4

Note: the calcination temperature for the catalysts was fixed at 350^{o}C.

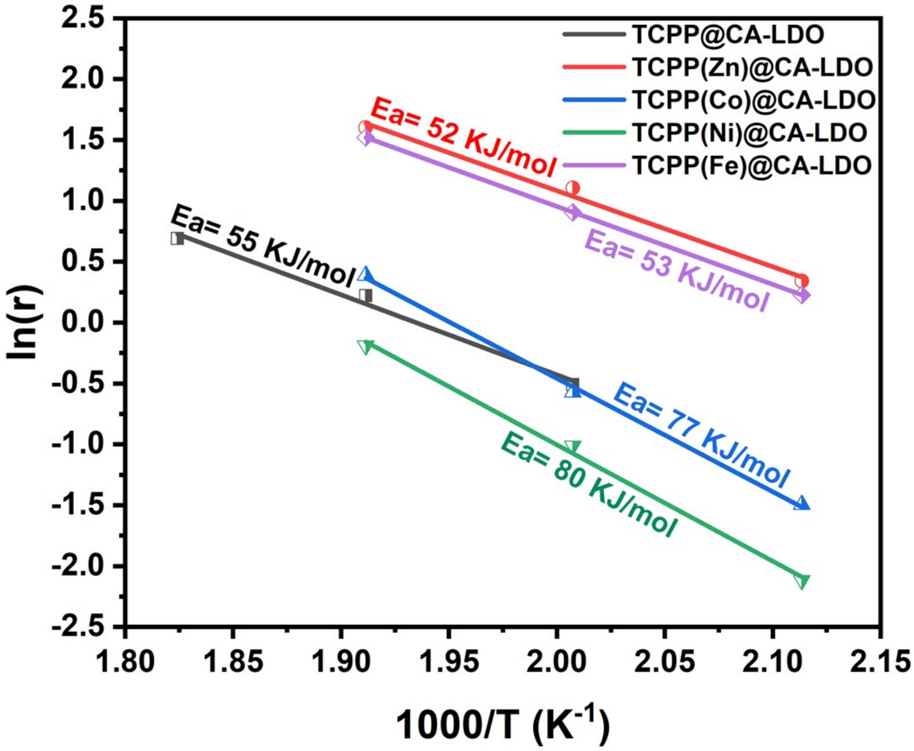

Fig. S3 The Arrhenius plots and activation energy of methanol formation reaction over the different catalyst samples.

Table S4. The specific BET surface area of catalyst samples prepared at 350 and 500℃, respectively.

Sample	BET (m^2/g)
TCPP(Zn)@CA-LDO-350	208.6
TCPP(Zn)@CA-LDO-500	170.2
TCPP(Zn)/CA-LDO-350	191.2
TCPP(Zn)/CA-LDO-500	175.6

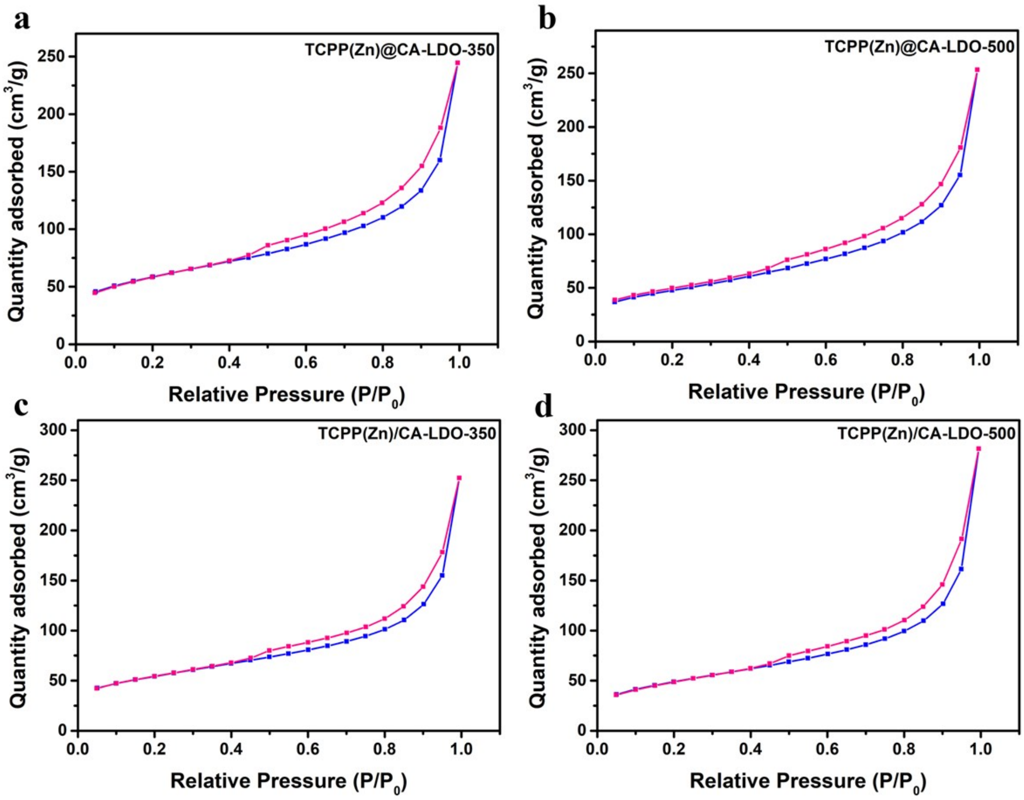

Fig. S4 N_2 physisorption isotherms of the intercalated and surface-supported catalysts calcined at different temperatures (350^{o}C and 500^{o}C).

Table S5. Comparison of CO_2 hydrogenation performance over different Cu-based catalysts in literature.

Catalysts	P (MPa)	T (°C)	CH_3OH Select. (%)	CO_2 Conv. (%)	GHSV ($mL/g_{cat}/h$)	Ref.
Cu/Zn/Al/Zr mixed oxides	5	250	61.3	25.6	4000	[1]
Cu/ZnO@*m*SiO_2	5	250	66.6	9.8	6000	[2]
CuO-ZnO/Al_2O_3	5	280	37	19.5	10000	[3]
$Cu_{0.5}Zn_{0.15}Ce_{0.35}$	2	200	83.1	4.3	2400	[4]
Cu-ZnO-Al_2O_3	3	250	73.4	6.0	2600	[5]
Cu/CeO_2/Al_2O_3	4	200	94	7.1	6000	[6]
Cu-ZnO-ZrO_2	3	220	80.2	18.2	6000	[7]
Cu/ZnO/C	4	230	80.7	2.92	6000	[8]
$Cu_{0.25}In_{0.75}Zr_{0.5}O$	2.5	250	79.7	1.48	18000	[9]
TCPP(Zn)@CA-LDO	3	200	99.5	1.41	24000	this work
TCPP(Zn)@CA-LDO	3	250	58.5	8.48	24000	this work

Note: GHSV: gas hourly space velocity.

Reference

[1]. P. Gao, R. Xie, H. Wang, L. Zhong, L. Xia, Z. Zhang, W. Wei and Y. Sun, Journal of CO_2 Utilization, 2015, 11, 41-48.

[2]. H. Yang, P. Gao, C. Zhang, L. Zhong, X. Li, S. Wang, H. Wang, W. Wei and Y. Sun, Catalysis Communications, 2016, 84, 56-60.

[3]. L. Angelo, K. Kobl, L. M. M. Tejada, Y. Zimmermann, K. Parkhomenko and A.-C. Roger, Comptes Rendus Chimie, 2015, 18, 250-260.

[4]. X. Hu, W. Qin, Q. Guan and W. Li, ChemCatChem, 2018, 10, 4438-4449.

[5]. X. Fang, Y. Men, F. Wu, Q. Zhao, R. Singh, P. Xiao, T. Du and P. A. Webley, Chemical Engineering Journal, 2019, 378, 122052.

[6]. S. Li, Y. Wang, B. Yang and L. Guo, Applied Catalysis A: General, 2019, 571, 51-60.

[7]. Y. Wang, S. Kattel, W. Gao, K. Li, P. Liu, J. G. Chen and H. Wang, Nature Communications, 2019, 10, 1166.

[8]. Z. Luo, S. Tian and Z. Wang, Industrial & Engineering Chemistry Research, 2020, 59, 5657-5663.

[9]. L. Yao, X. Shen, Y. Pan and Z. Peng, Journal of Catalysis, 2019, 372, 74-85.