$SiCl_4$-Modified Layered Double Hydroxides for Boosting CO Selectivity in CO_2 Hydrogenation: Achieving Nearly 100% from Baseline 20%

Yuhang Dong[a,†], Chengcheng Zhang [a,†], Shenghua Wang[a], Chuangwang Xing[a], Shichang Wang[a], Yi Xiao[a], Hailong Feng[a], Ye Wan[d,], Wei Sun[a,b,c]*and Deren Yang[a]*

a State Key Laboratory of Silicon Materials and Advanced Semiconductor Materials, and School of Materials Science and Engineering, Zhejiang University, Hangzhou, Zhejiang 310027, People's Republic of China.

Email: sunnyway423@zju.edu.cn

b Shangyu Institute of Semiconductor Materials, Zhejiang University, Shaoxing 212399, China

c Zhejiang Provincial Key Laboratory of Optoelectronic Functional Materials and Devices, Hangzhou, 311200, China

d China Silicon Corporation Ltd., Luoyang 471023, P. R. China.

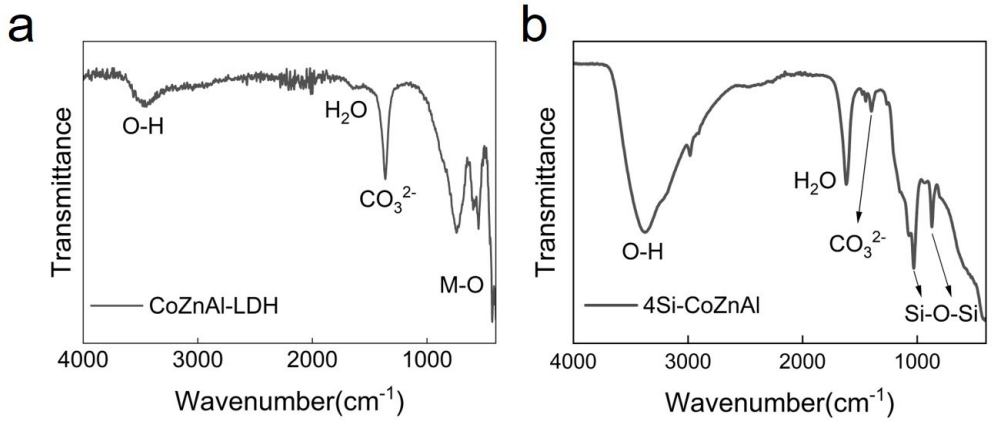

Fig. S1 FT-IR results of (a) CoZnAl-LDH and (b) 4Si-CoZnAl. A broad absorption band centered at ~3375 cm^{-1} is attributed to the O−H stretching vibrations associated with hydrogen-bonded hydroxyl groups[1]. The band observed at ~1618 cm^{-1} corresponds to the H−O−H bending vibration of interlayer water molecules[2]. The absorption peak at ~1398 cm^{-1} is assigned to the ν_3 asymmetric stretching mode of carbonate (CO_3^{2-}) species[3]. For the CoZnAl-LDH sample, the bands in the range of 500–800 cm^{-1} are attributed to the lattice vibrations of metal–oxygen bonds (M–O), such as Al–O[4]. In contrast, for the 4Si-CoZnAl sample, the newly emerged bands at ~1029 cm^{-1} and ~872 cm^{-1} are assigned to the asymmetric stretching vibrations of Si–O bonds, such as Si–O–Si[5]. Si–O–Si is formed by the condensation of Si–OH generated from the reaction of Si–Cl with H_2O.

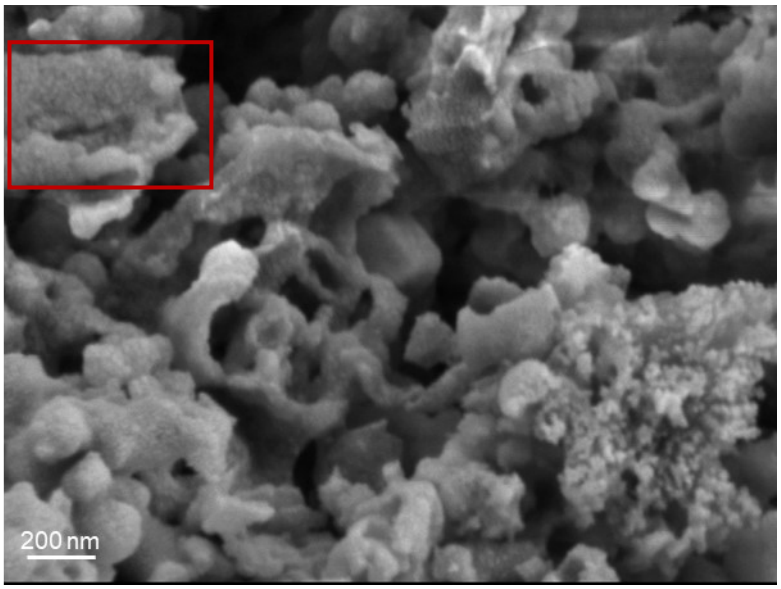

Fig. S2 SEM image of 4Si-CoZnAl. It can be observed that the surface is coated with nanospheres.

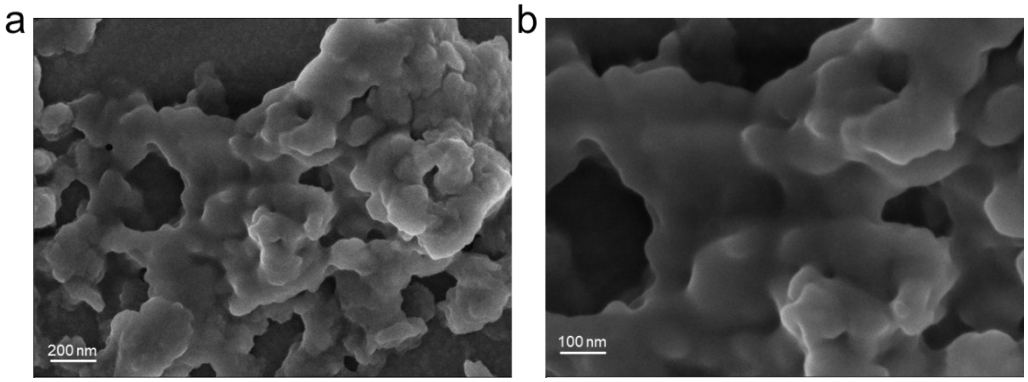

Fig. S3 SEM images of 2Si-CoZnAl. The CoZnAl-LDH treated with 2 mL of $SiCl_4$ did not exhibit SiO_2 nanospheres; the full coverage may not be guaranteed.

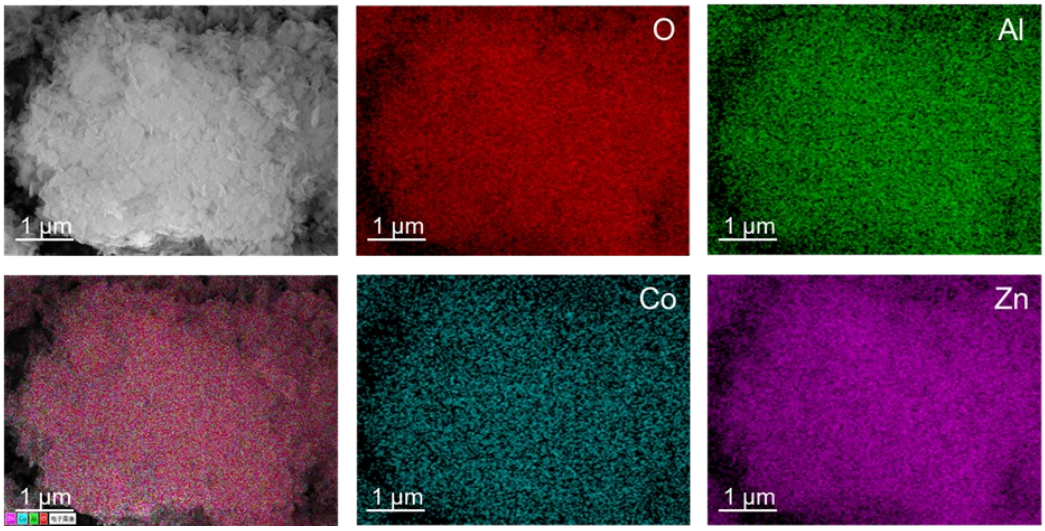

Fig. S4 EDS results of CoZnAl-LDH

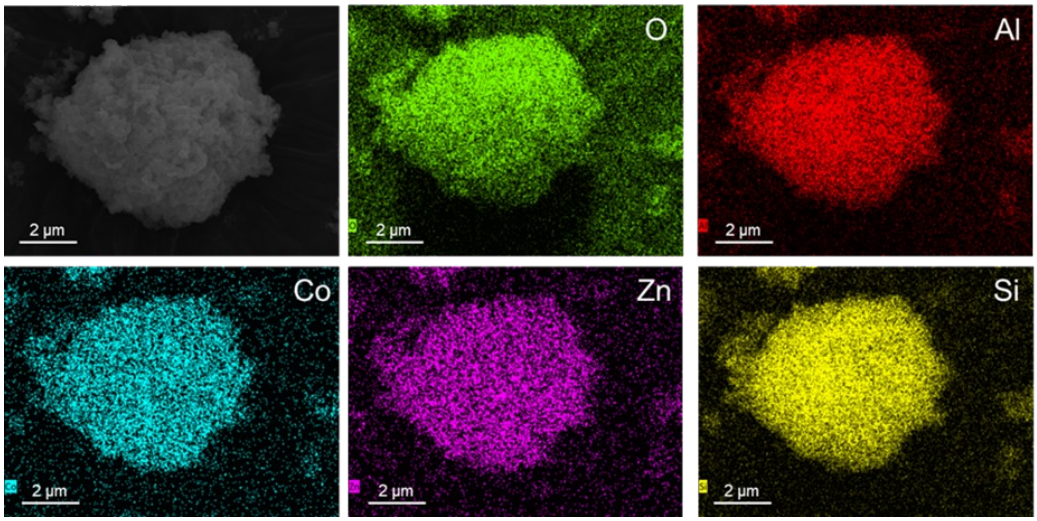

Fig. S5 EDS results of 4Si-CoZnAl

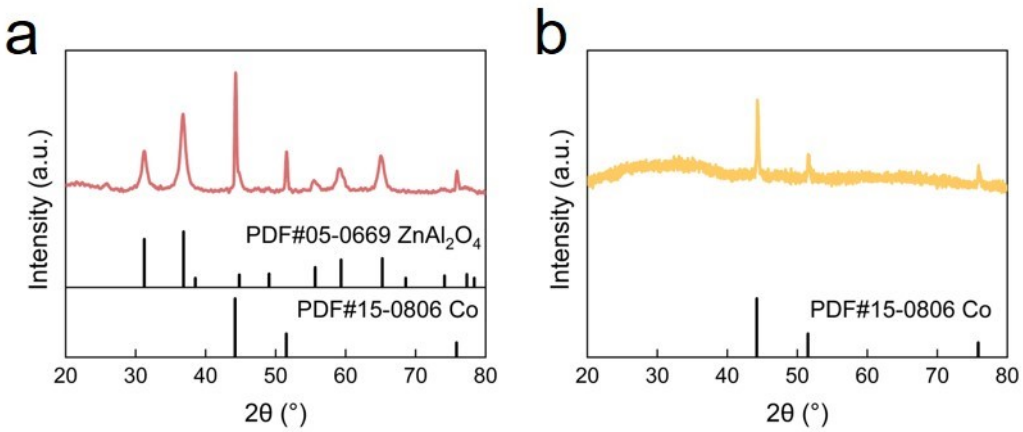

Fig. S6 XRD results of (a) CoZnAl-LDH and (b) 4Si-CoZnAl after reduction

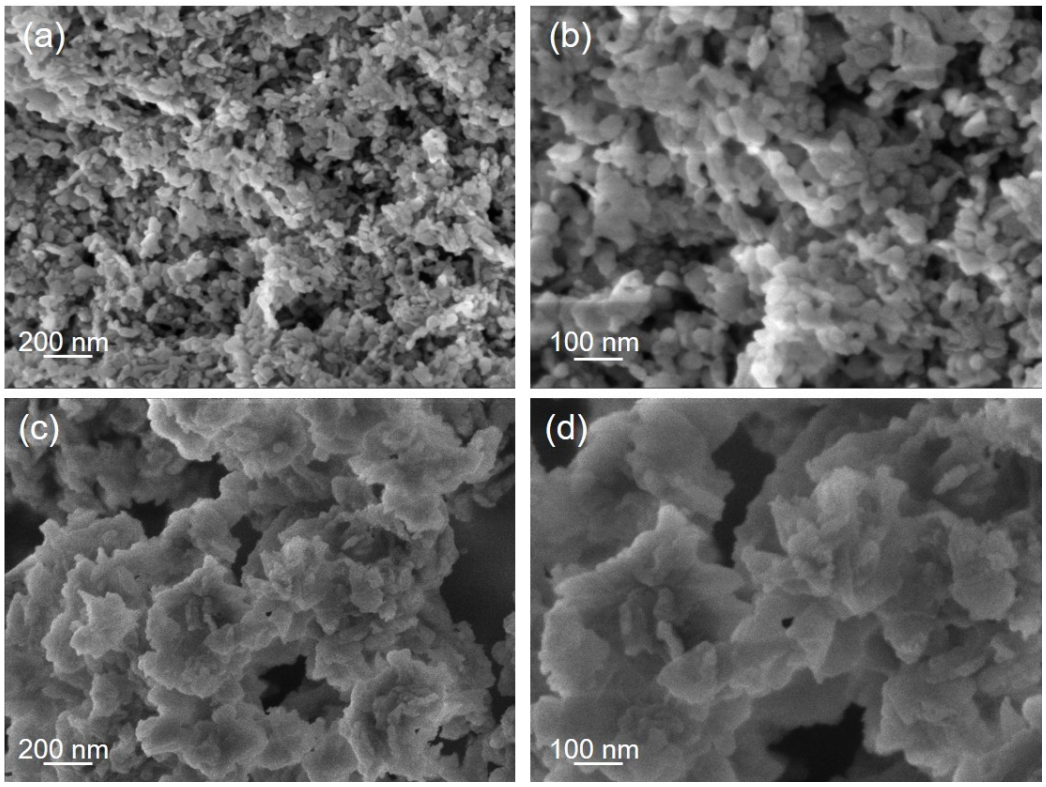

Fig. S7 SEM images of (a)(b) CoZnAl-LDH and (c)(d) 4Si-CoZnAl after reduction.

Specifically, CoZnAl-LDH transformed from a sheet-like structure into smaller spherical particles, which can be attributed to the collapse of the layered hydrotalcite structure and phase segregation during calcination and reduction, accompanied by the formation of nanosized metal particles [6]. In contrast, 4Si-CoZnAl was still more intact, maintaining the sheet form, due to the protection of silica.These variations in particle size, together with the degree of silica coverage on the catalyst surface, result in differences in catalytic conversion, while silica modification further influences product selectivity.

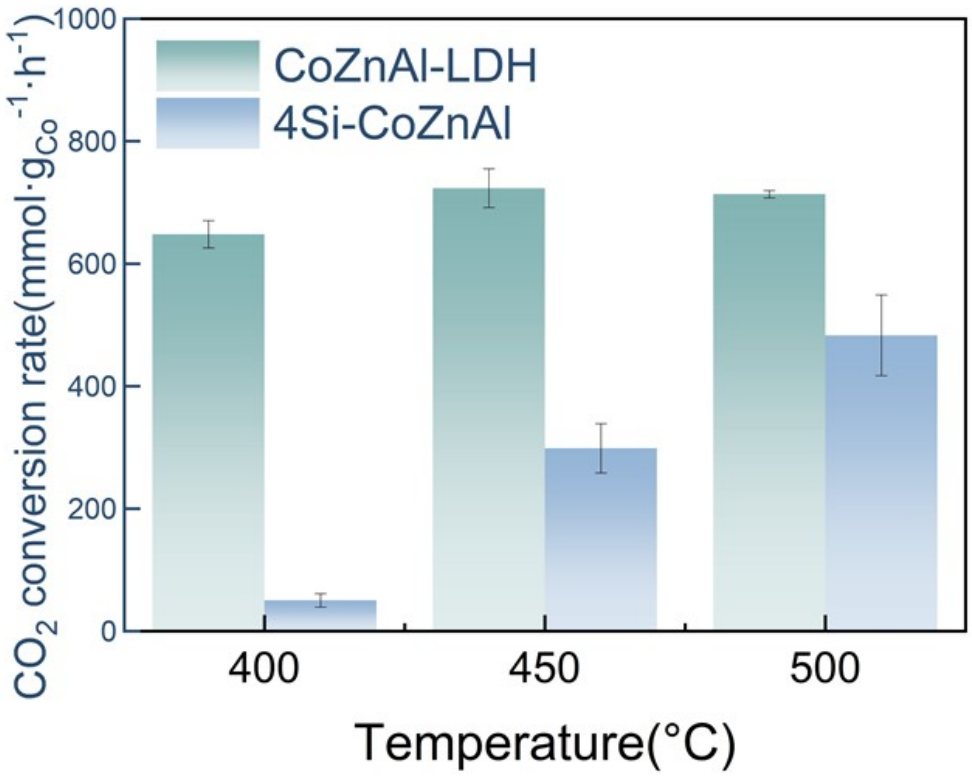

Fig. S8 Total conversion rate of CoZnAl-LDH and 4Si-CoZnAl normalized to mass of Co (CO_2: H_2: N_2 = 4:12:4 mL/min).

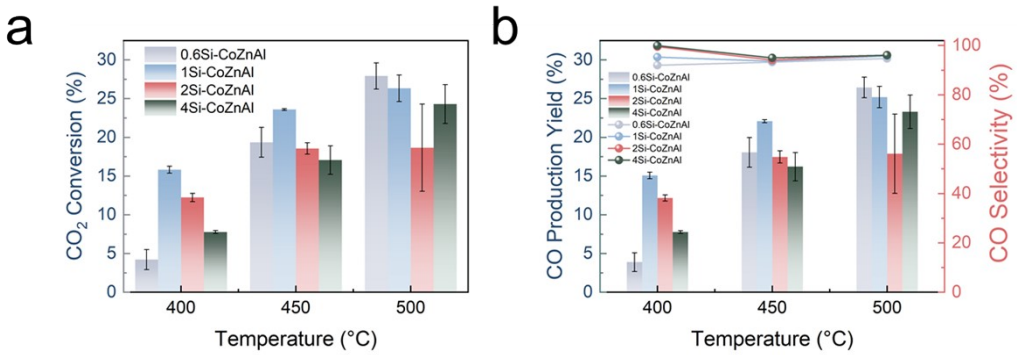

Fig. S9 Thermocatalytic performance of CO_2 hydrogenation over samples treated with different $SiCl_4$ ratios (a) CO_2 conversion (b) CO production and selectivity

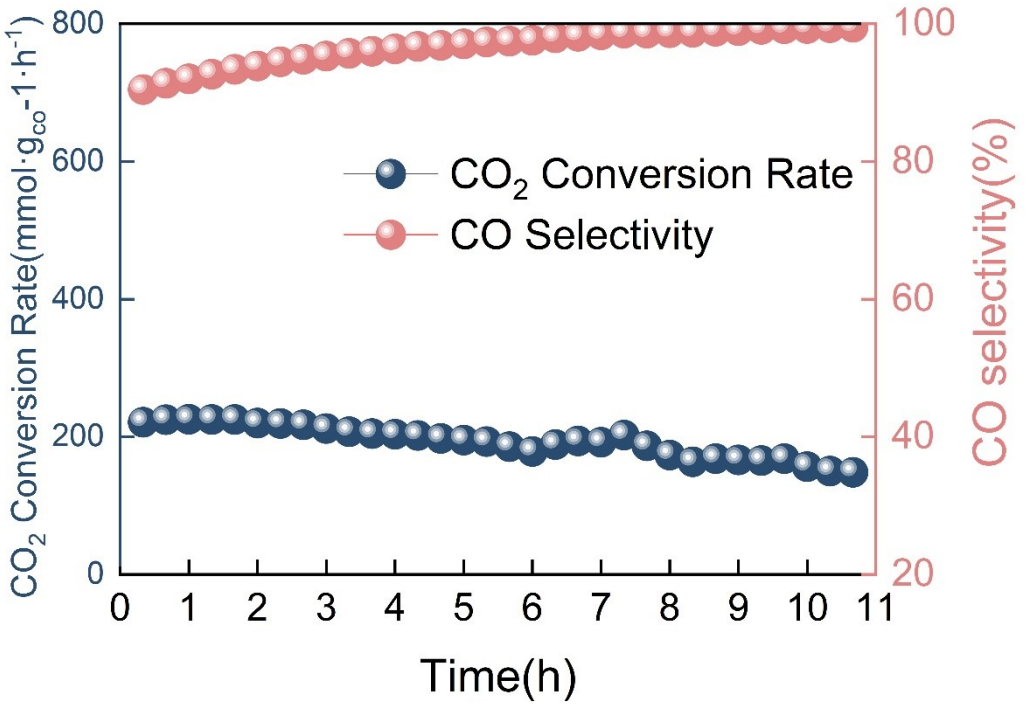

Fig. S10 Thermal catalytic stability results of 4Si-CoZnAl at 450°C.

Table S1 Crystallite sizes of CoZnAl-LDH and 4Si-CoZnAl determined via XRD

	K	λ (Å)	θ (°)	FWHM (°)	D (nm)
CoZnAl-LDH	0.89	1.54	44.29	0.29	29.2
4Si-CoZnAl	0.89	1.54	44.34	0.28	30.3

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2 Starukh, G., Rozovik, O. and Oranska, O. Organo/Zn-Al LDH Nanocomposites for Cationic Dye Removal from Aqueous Media, Nanoscale Res Lett, 2016, 11, 228.
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