Supplementary Information

Silicalite-1 zeolite encapsulated Cu-ZnO nanoparticles for selective CO_2 hydrogenation to oxygenates

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Figure Captions

Fig. S1 Pore size distribution of CZ(x)@S-t catalysts and CZ@Si precursor via N_2-sorption analysis.

Fig. S2 NH_3-TPD profiles of Cu@S-48 and CZ(0.4)@S-48 catalyst.

Fig. S3 H_2-TPR profiles of Cu@S-48 and CZ(0.4)@S-48 catalyst.

Fig. S4 Catalytic activity with time on stream (TOS) on CZ@Si for CO_2 hydrogenation to methanol. Catalytic reaction condition: T = 250 ^oC, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction.

Fig. S5 Catalytic activity with time on stream (TOS) on CZ(0.9)@S-t catalysts for CO_2 hydrogenation to form DME and methanol oxygenates at the reaction condition of T = 250 ^oC, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction; (a) CZ(0.9)@S-12, (b) CZ(0.9)@S-24, (c) CZ(0.9)@S-48, (d) CZ(0.9)@S-72 .

Fig. S6 Catalytic activity with time on stream (TOS) on CZ(0.9)@S-t catalysts for CO_2 hydrogenation to form DME and methanol oxygenates at the reaction condition of T = 250 ^oC, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction; (a) Cu@S-48, (b) CZ(0.4)@S-48.

Fig. S7 in situ DRIFTS analysis results of CZ(0.9)@S-12 under the reaction condition of T = 250 ^oC, P = 2.0 MPa, H_2/CO_2 molar ratio of 3/1.

Table S1 Chemical compositions of CZ(x)@S-t catalysts measured by XRF analysis

Table S2 Previously reported zeolite-encapsulated Cu-based catalysts for CO_2 hydrogenation activity to oxygenates.

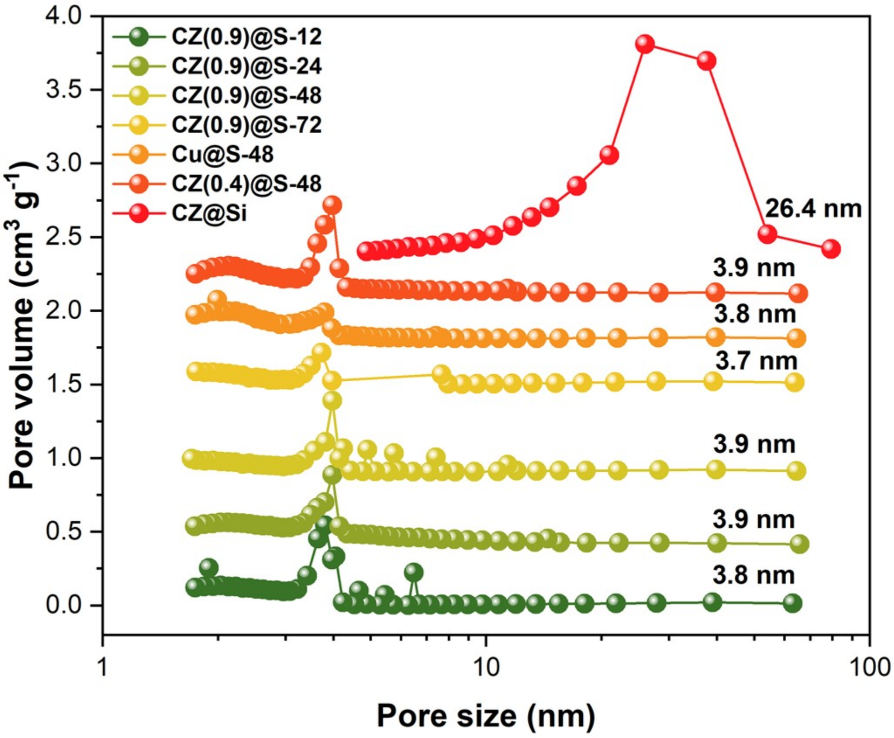

Fig. S1 Pore size distribution of CZ(x)@S-t catalysts and CZ@Si precursor via N_2-sorption analysis.

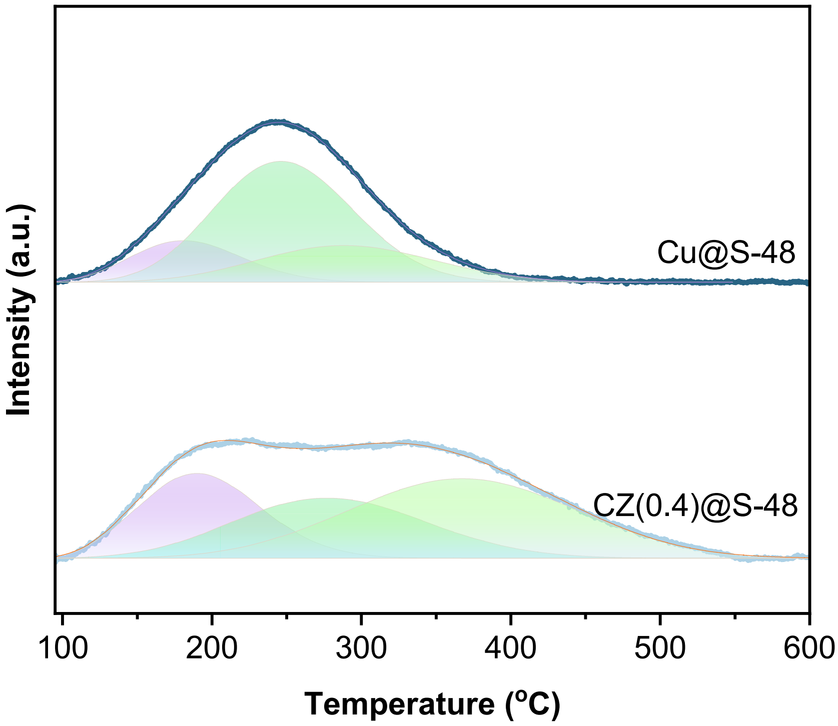

Fig. S2 NH_3-TPD profiles of Cu@S-48 and CZ(0.4)@S-48 catalyst.

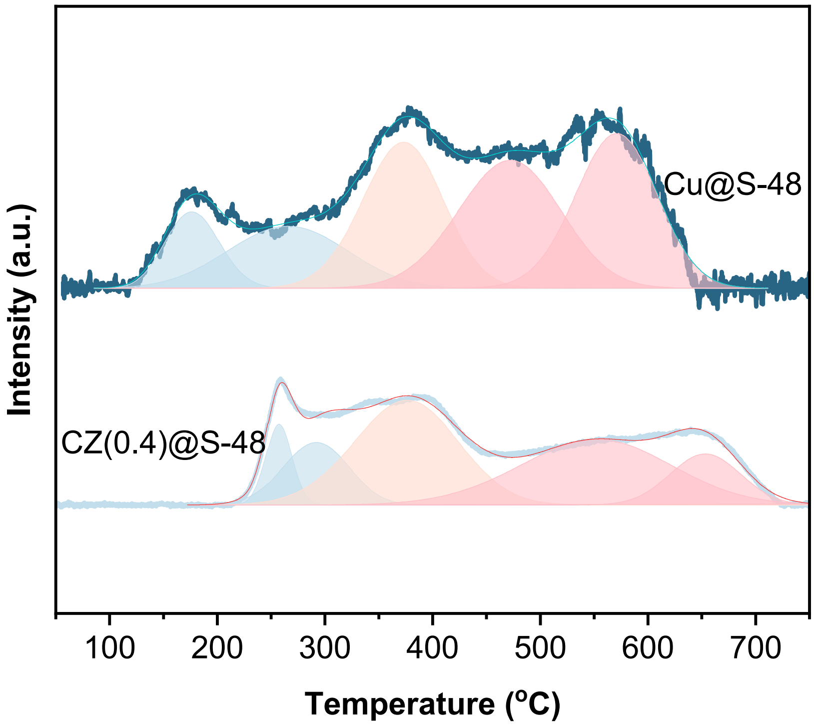

Fig. S3 H_2-TPR profiles of Cu@S-48 and CZ(0.4)@S-48 catalyst.

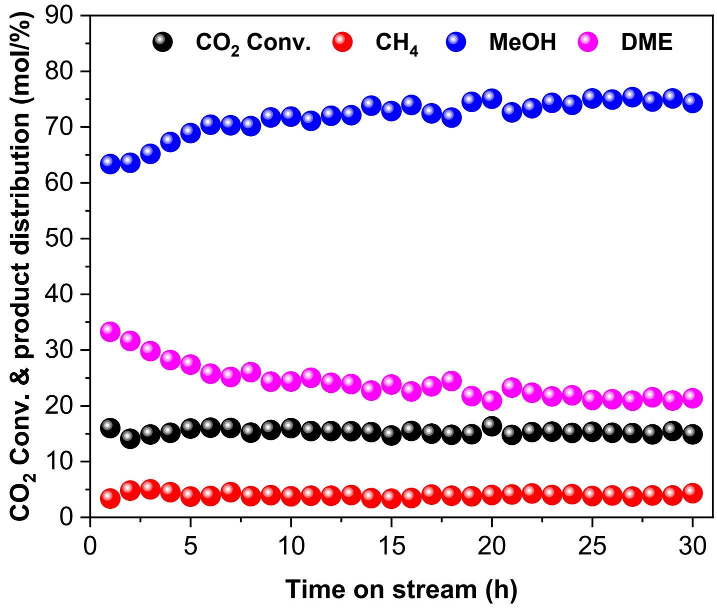

Fig. S4 Catalytic activity with time on stream (TOS) on CZ@Si for CO_2 hydrogenation to methanol. Catalytic reaction condition: T = 250 ^{o}C, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction.

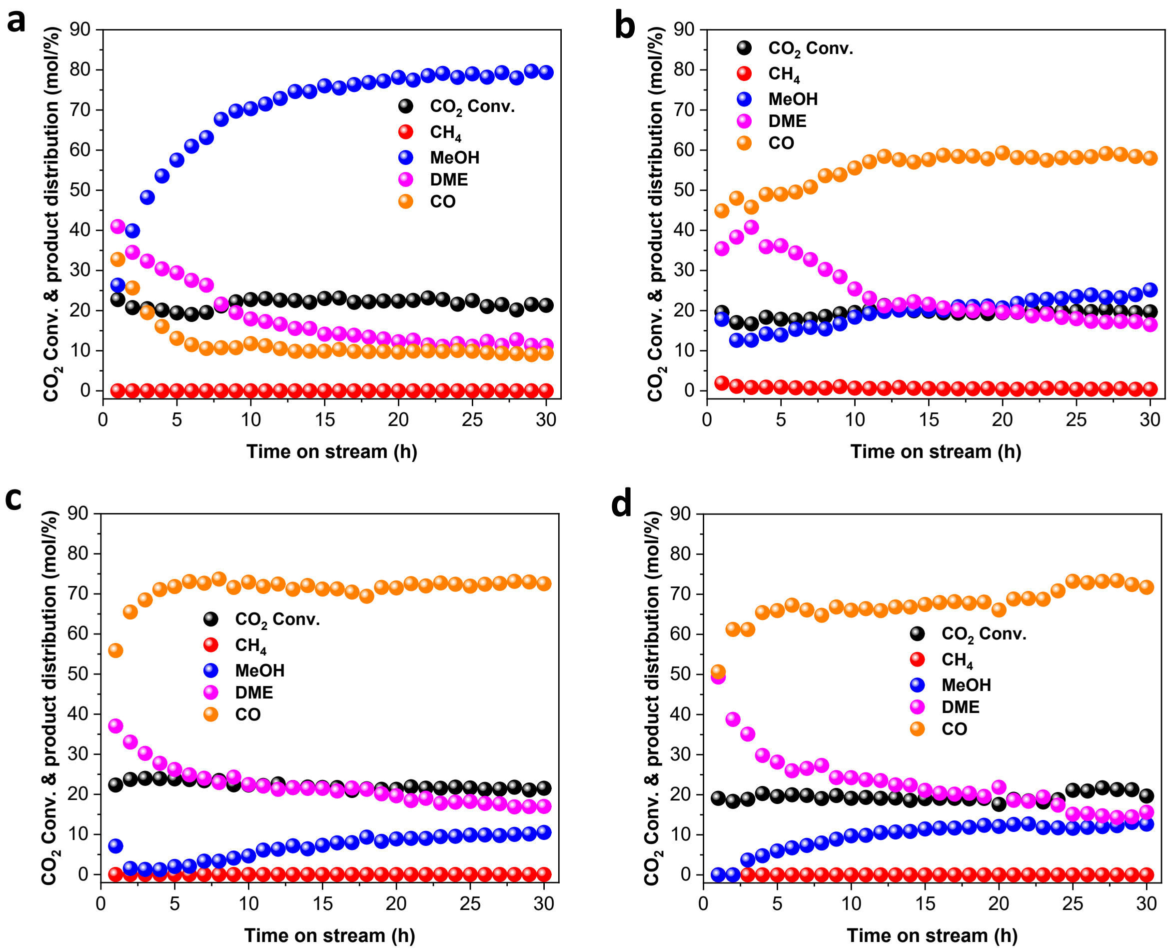

Fig. S5 Catalytic activity with time on stream (TOS) on CZ(0.9)@S-t catalysts for CO_2 hydrogenation to form DME and methanol oxygenates at the reaction condition of T = 250 °C, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction; (a) CZ(0.9)@S-12, (b) CZ(0.9)@S-24, (c) CZ(0.9)@S-48, (d) CZ(0.9)@S-72.

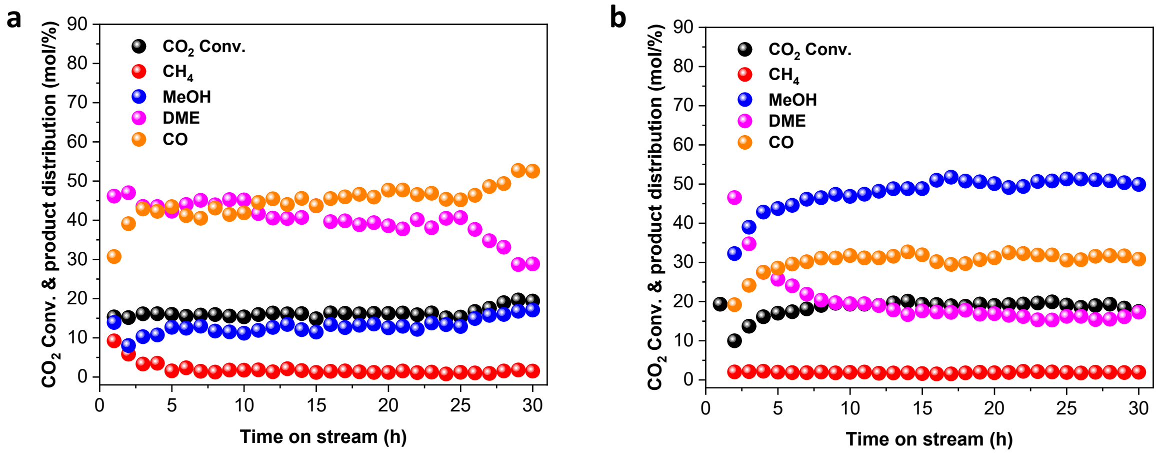

Fig. S6 Catalytic activity with time on stream (TOS) on CZ(0.9)@S-t catalysts for CO_2 hydrogenation to form DME and methanol oxygenates at the reaction condition of T = 250 °C, P = 5.0 MPa, H_2/CO_2 molar ratio = 3 (4% N_2 balance) at space velocity (SV) = 3000 mL g_{cat}^{-1} h^{-1} for 30 h reaction; (a) Cu@S-48, (b) CZ(0.4)@S-48.

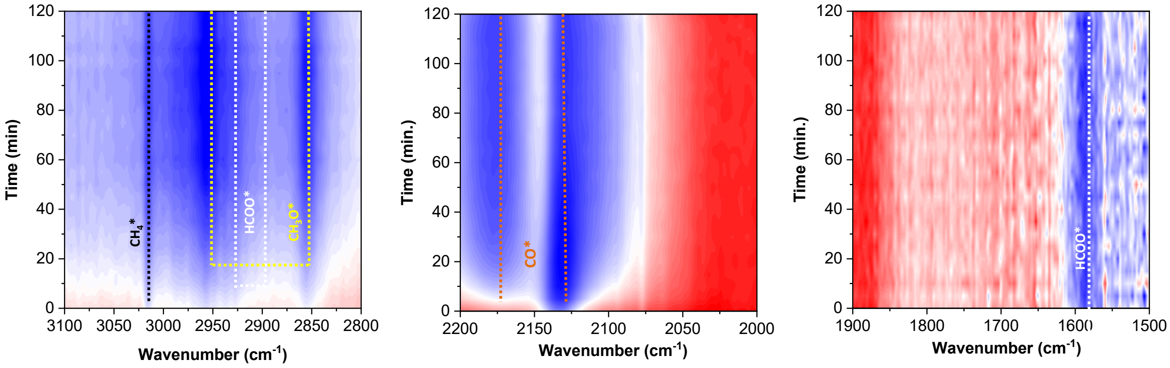

Fig. S7 *in situ* DRIFTS analysis results of CZ(0.9)@S-12 under the reaction condition of T = 250 °C, P = 2.0 MPa, H_2/CO_2 molar ratio of 3/1.

Table S1 Chemical compositions of CZ(x)@S-t catalysts measured by XRF analysis

Catalyst	XRF compound content (wt%)		
	CuO	ZnO	SiO_2
CZ(0.9)@S-12	3.9	4.2	91.9
CZ(0.9)@S-24	3.7	4.1	92.2
CZ(0.9)@S-48	3.7	4.3	92.0
CZ(0.9)@S-72	3.5	4.0	92.5
Cu@S-48	3.5	-	96.5
CZ(0.4)@S-48	1.6	4.1	94.3

Table S2 Previously reported zeolite-encapsulated Cu-based catalysts for CO_2 hydrogenation activity to oxygenates.

Catalysts	Temperature (°C)	CO_2 conversion (%)	Methanol selectivity (%)	DME selectivity (%)*	Ref.
ZnO/Cu@S-1	250	4.7	55.3	N	1
Cu/ZnO$_x$@Na-ZSM-5	250	6.3	77.8	N	2
CX-220	290	10.2	91.2	N	3
Cu0.2m-NaY	250	~0.5	~68	N	4
Cu@FAU	240	11.5	89.5	N	5
Cu-ZnOx/13X	290	~10	~83	N	6
CuO-ZnOx@H-S-1	250	~3	85	N	7
CuO-ZnO@Cu-MOR	240	~21	~97	N	8
mhZSM-5-AlCu	280	7.3	~24	20	9
CZ@Z	260	20.8	19.4	62.2	10
CZ(0.9)@S-48	250	21.5	10.5	72.5	This work

*N represents no DME formation reported.

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