Supporting Information (SI)

Siliceous mesocellular foam supported Cu catalysts for promoting non-thermal plasma activated CO_2 hydrogenation towards methanol synthesis

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Electronic Supplementary Material

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Table S1 ICP-OES analysis of the as-prepared catalysts

Catalysts	Theoretical loading / wt.%		Actual loading / wt.%	
	Cu	Zn	Cu	Zn
$Cu_{0.5}$/MCF	0.50	-	0.63	-
Cu_1/MCF	1.00	-	1.08	-
Cu_3/MCF	3.00	-	3.26	-
Cu_5/MCF	5.00	-	5.29	-
Cu_1Zn_1/MCF	1.00	1.01	0.87	0.72

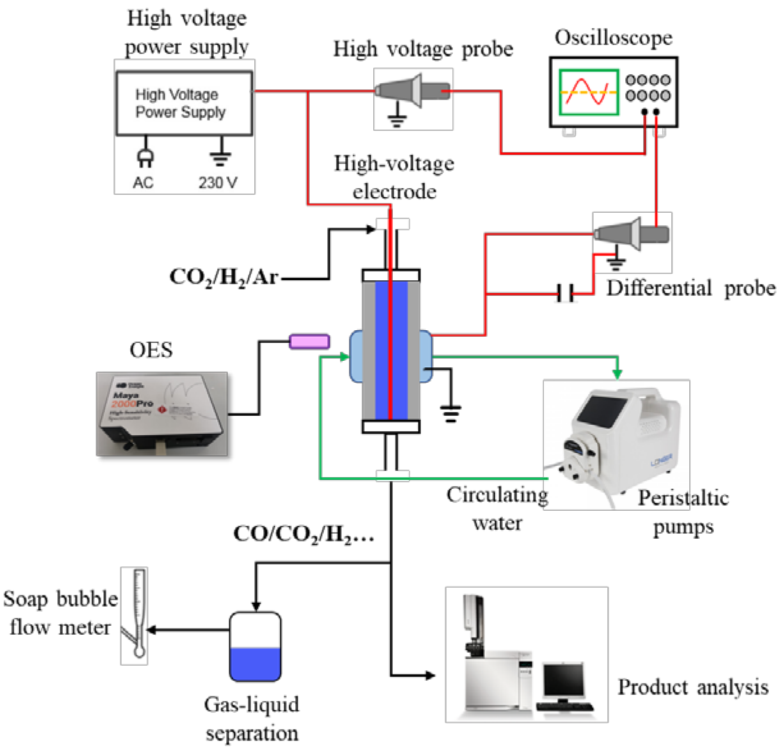

Fig. S1 Schematic of the plasma rig for CO_2 hydrogenation

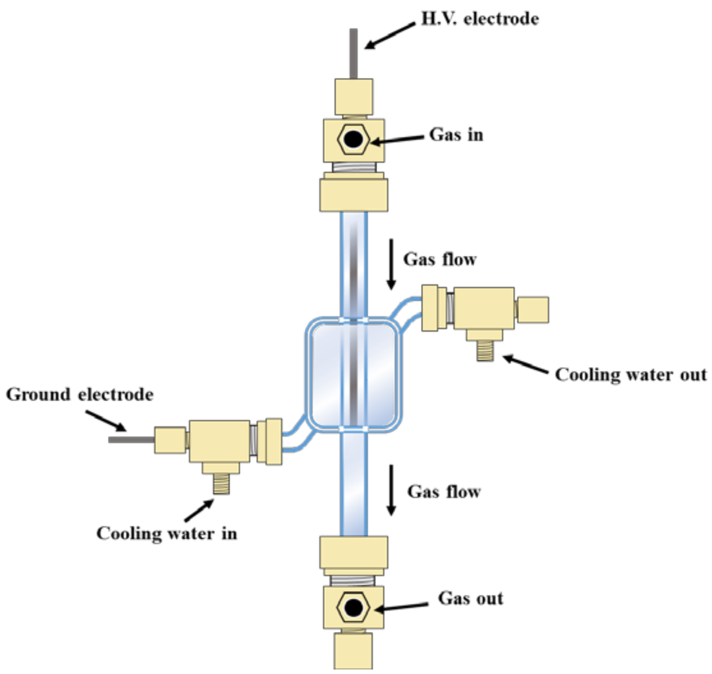

Fig. S2 Schematic of the DBD plasma reactor with the circulating cooling water as the ground electrode

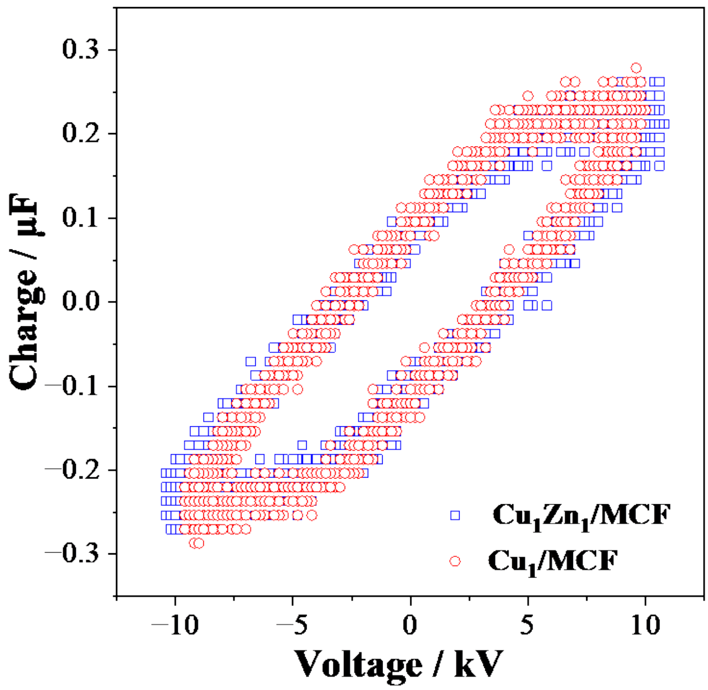

Fig. S3 The Q-V Lissajous plots of the NTP systems employing the Cu/MCF and Cu_1Zn_1/MCF catalysts. (Feed gas = 60 vol.%H_2/20 vol.%CO_2/20 vol.%Ar, total flow rate of 50 mL min^{-1}, applied peak voltage of 10.1 ± 0.4 kV, frequency of 7.7 kHz, input power of 20.9 ± 1.3 W)

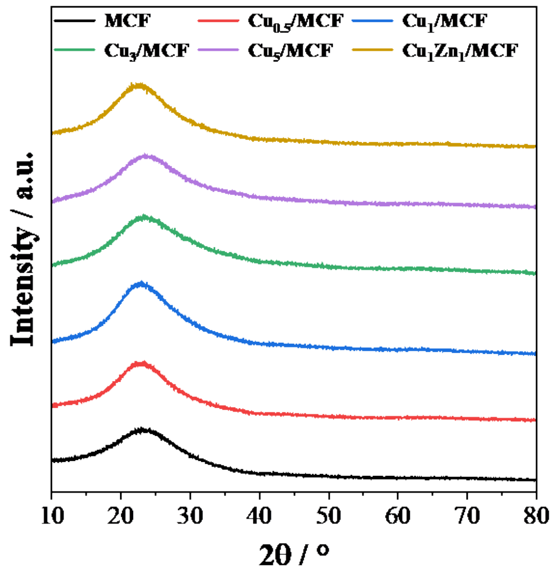

Fig. S4 XRD patterns of MCF and the MCF-supported Cu-based catalysts

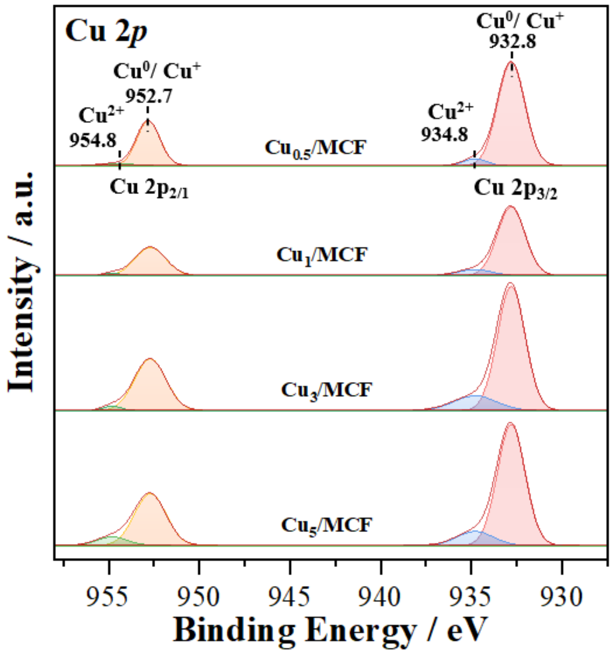

Fig. S5 Cu 2*p* XPS spectra of the MCF supported Cu-based catalysts

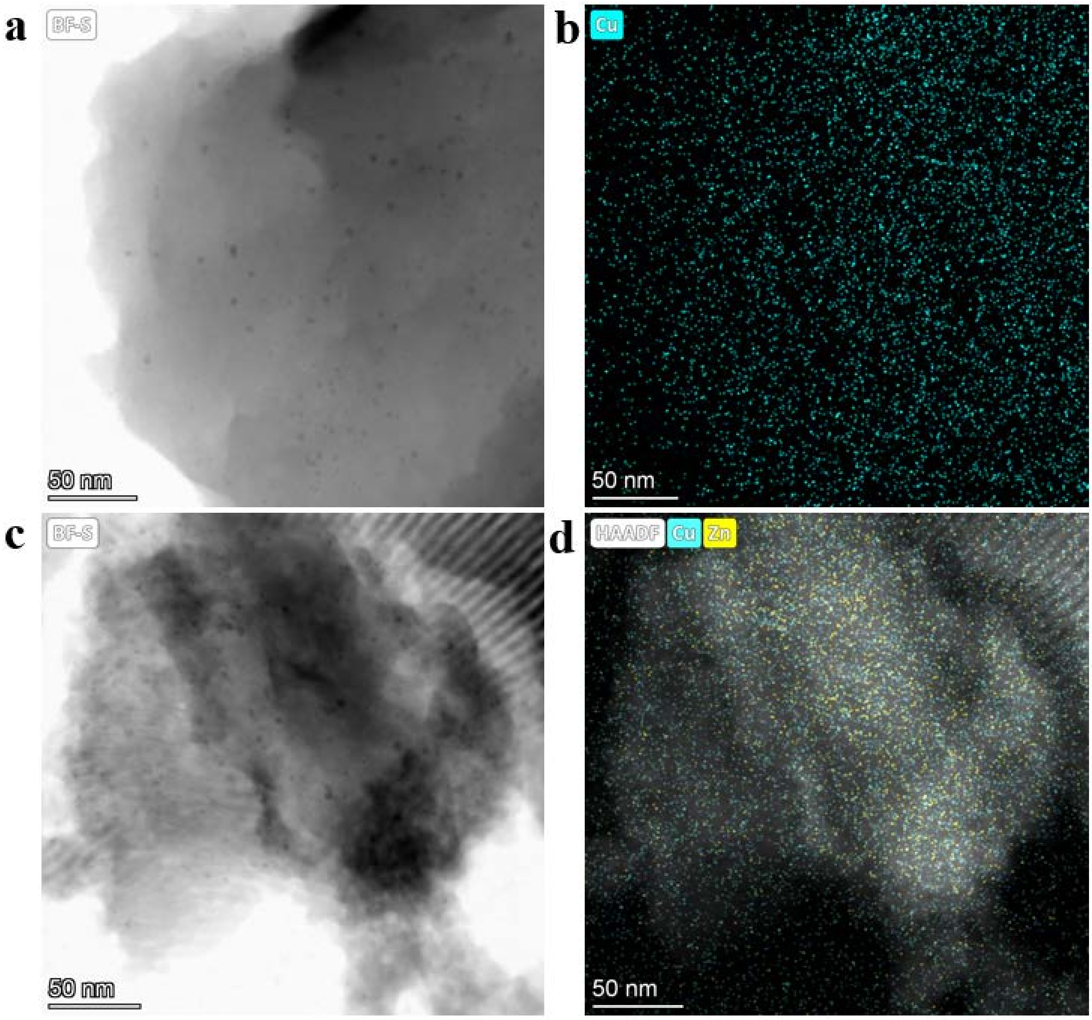

Fig. S6 HRTEM images and EDS mapping analysis of (a, b) Cu_1/MCF and (c, d) Cu_1Zn_1/MCF

For H_2-TPR measurements, ~50 mg of catalysts were loaded in the sample tube and pre-treated in a pure Ar with flow rate of 30 ml min^{-1} at 300 °C for 1 h, and then the temperature was cooled down to 60 °C in a pure Ar gas flow. After that, the H_2-TPR measurement was performed in a flow of 10 vol.% H_2/Ar with the temperature increasing from 60 to 800 °C (at 10 °C min^{-1}). For the TPD measurements, before CO_2/CO-TPD, ~100 mg of catalysts were *in situ* activated in pure H_2 (30 ml min^{-1}) for 2 h at 400 °C. After that, the system temperature was cooled down to 60 °C in a pure helium gas flow, and after 15 min the gas was switched to a flow of 10 vol.% CO_2/He or 10 vol.% CO/He gas mixture for 1 h at the same temperature. Finally, CO_2/CO-TPD profiles were collected in a flow of pure helium gas at temperature ramping from 60 to 800 °C (10 °C min^{-1}).

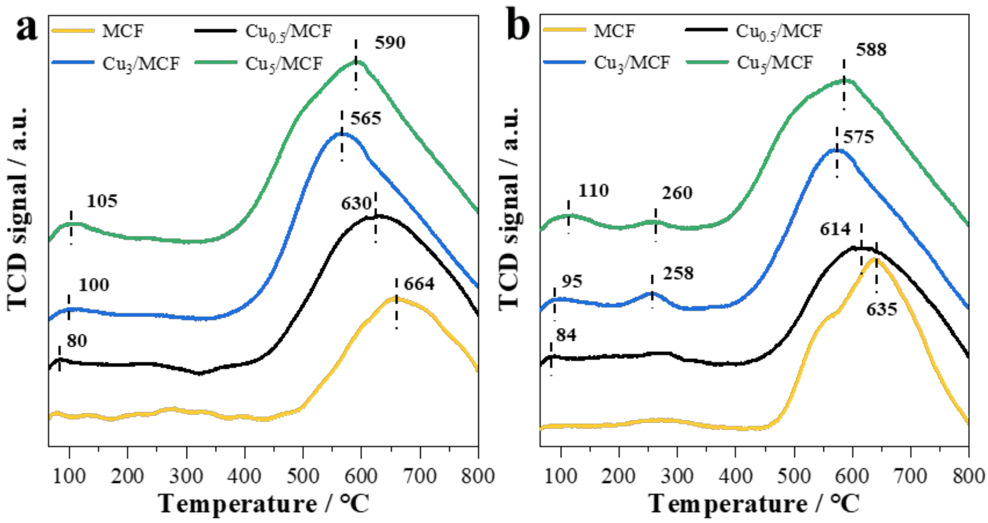

Fig. S7 (a) CO_2-TPD and (b) CO-TPD profiles of the MCF-supported Cu-based catalysts

Table S2 Total CO_2 and CO adsorption amount of the catalysts under investigation

Catalysts	Total CO_2 adsorption amount / mmol g_{cat}^{-1}	Total CO adsorption amount / mmol g_{cat}^{-1}
MCF	0.315	0.536
$Cu_{0.5}$/MCF	0.426	0.440
Cu_1/MCF	0.619	0.571
Cu_3/MCF	0.525	0.544
Cu_5/MCF	0.520	0.679
Cu_1Zn_1/MCF	0.602	0.691

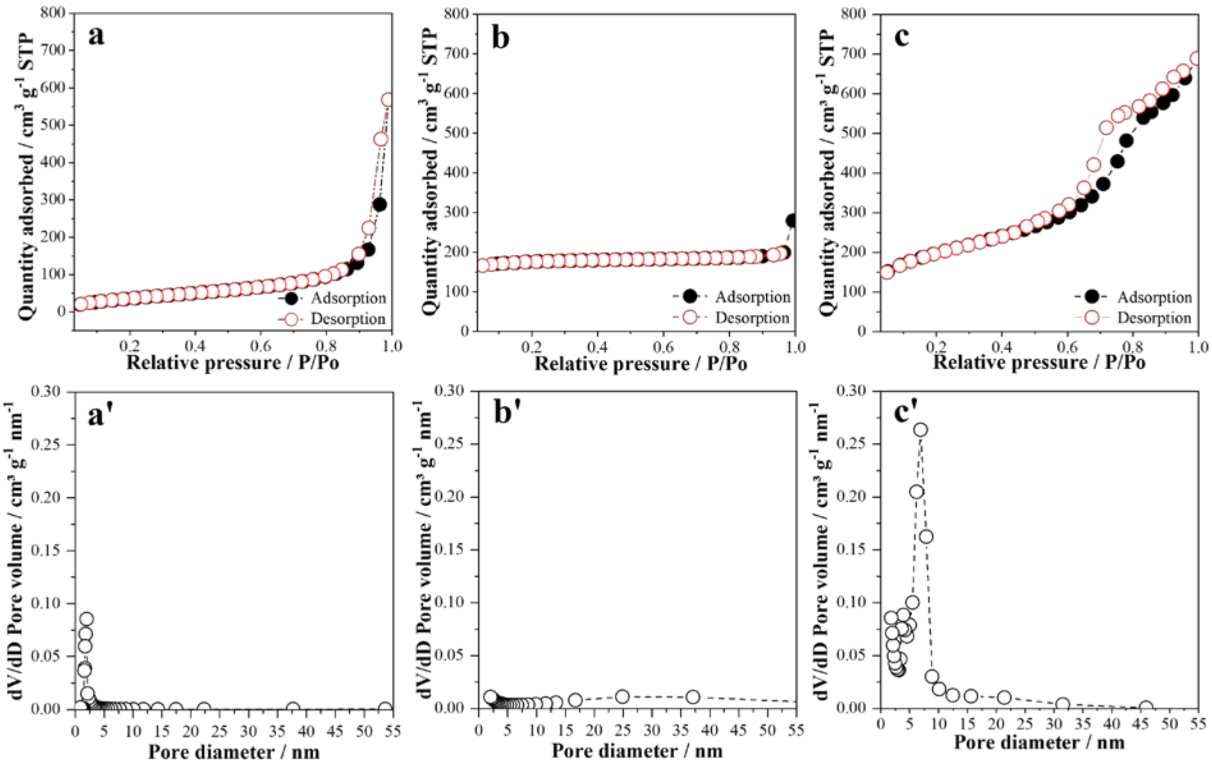

Fig. S8 N_2 adsorption/desorption isotherms and pore size distribution curves of bare porous materials: (a, a') S-1, (b, b') SiO_2, and (c, c') SBA-15

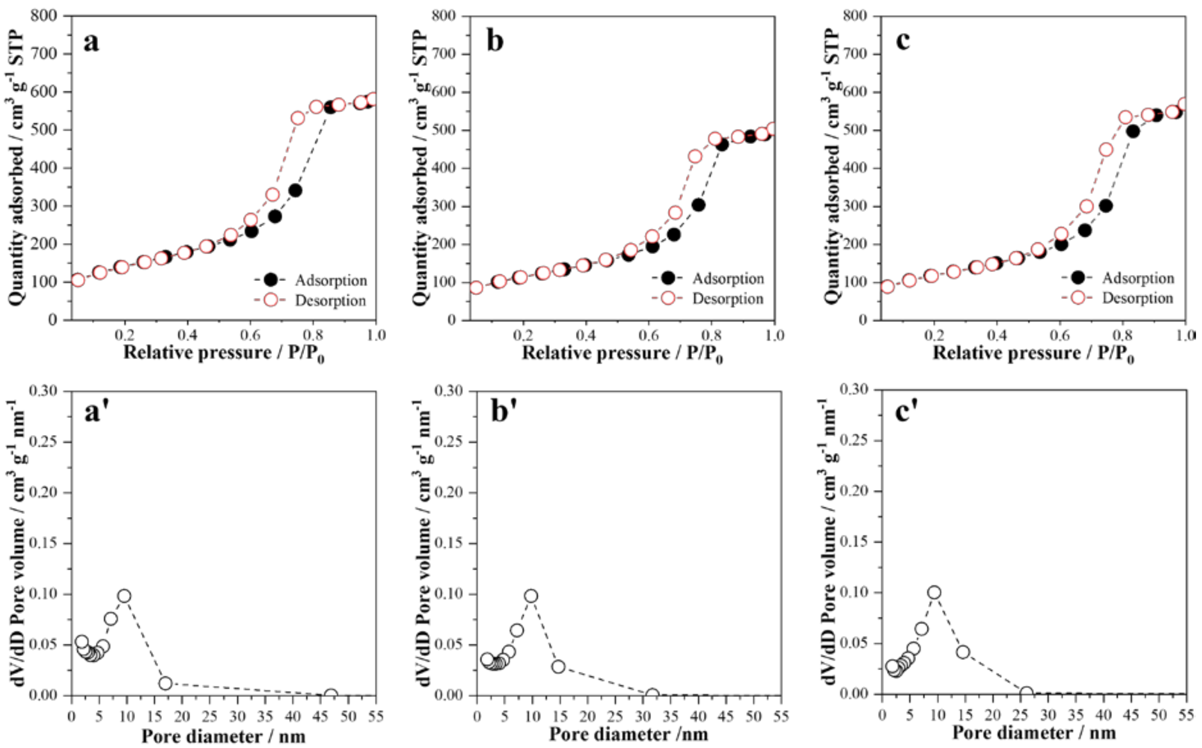

Fig. S9 N_2 adsorption/desorption isotherms and pore size distribution curves of the MCF-supported Cu catalysts: (a, a') $Cu_{0.5}$/MCF, (b, b') Cu_3/MCF, and (c, c') Cu_5/MCF

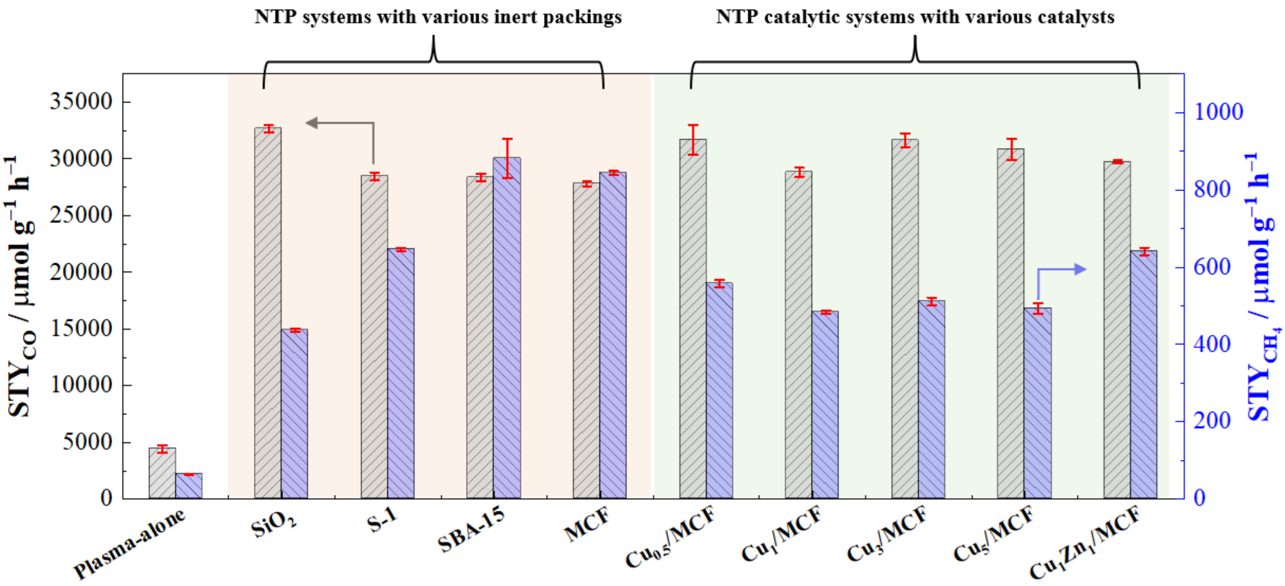

Fig. S10 NTP-assisted CO_2 hydrogenation performance (regarding CO and CH_4 STY) of the NTP-alone system (noted that the unit of CO and CH_4 STY for this system is μmol h^{-1}), NTP systems with the inert packing and NTP-catalytic systems with the Cu_x/MCF and Cu_1Zn_1/MCF catalysts. (Experimental conditions: feed gas composition = 60 vol.%H_2/20 vol.%CO_2/20 vol.%Ar, total flow rate = 50 mL min^{-1}, applied peak voltage = 10.1 ± 0.4 kV, frequency = 7.7 kHz, discharge power = 20.9 ± 1.3 W)

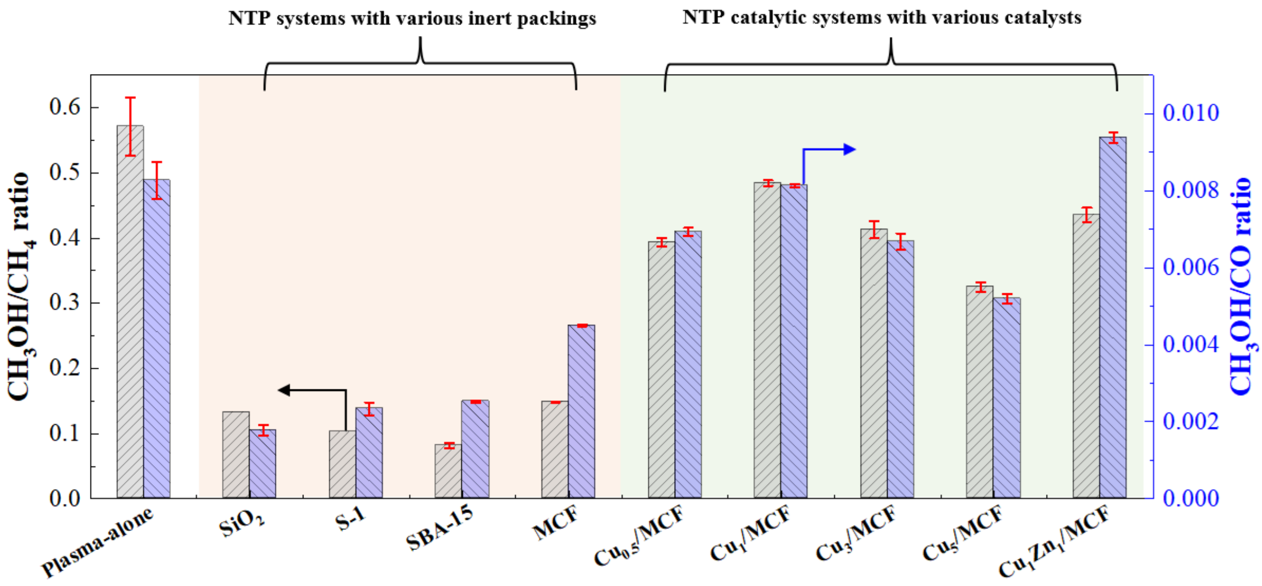

Fig. S11 NTP-assisted CO_2 hydrogenation performance (regarding CH_3OH/CH_4 and CH_3OH/CO product ratio) of the NTP-alone system, NTP systems with the inert packing and NTP-catalytic systems with the Cu_x/MCF and Cu_1Zn_1/MCF catalysts. (Experimental conditions: feed gas composition = 60 vol.%H_2/20 vol.%CO_2/20 vol.%Ar, total flow rate = 50 mL min^{-1}, applied peak voltage = 10.1 ± 0.4 kV, frequency = 7.7 kHz, discharge power = 20.9 ± 1.3 W)

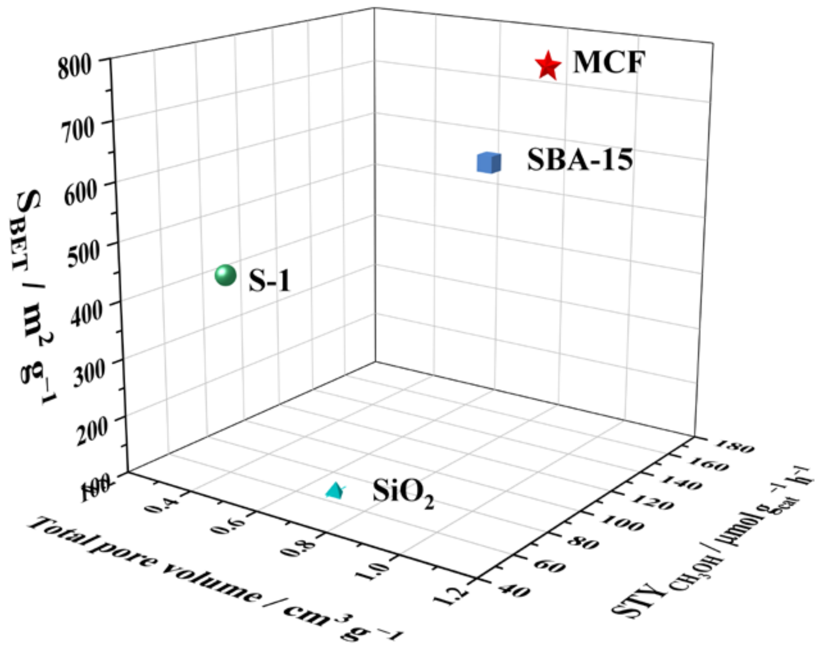

Fig. S12. The correlation between methanol STY and porous properties of the inert packing materials

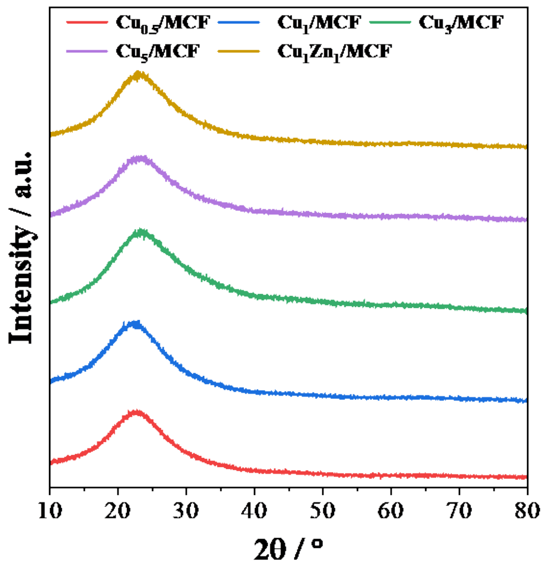

Fig. S13 XRD patterns of the used MCF-supported Cu-based catalysts after the NTP-catalytic experiments

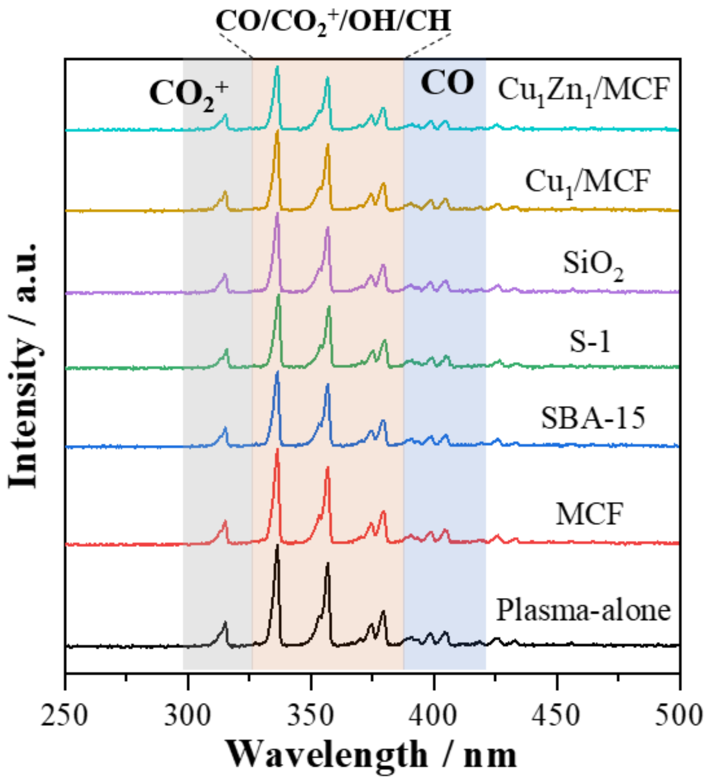

Fig. S14 (a) OES spectra of NTP-alone system and the NTP systems employing different materials and catalysts. (Feed gas = 60 vol.%H_2/20 vol.%CO_2/20 vol.%Ar, total flow rate of 50 mL min^{-1}, applied peak voltage of 10.1 ± 0.4 kV, frequency of 7.7 kHz, input power of 20.9 ± 1.3 W)

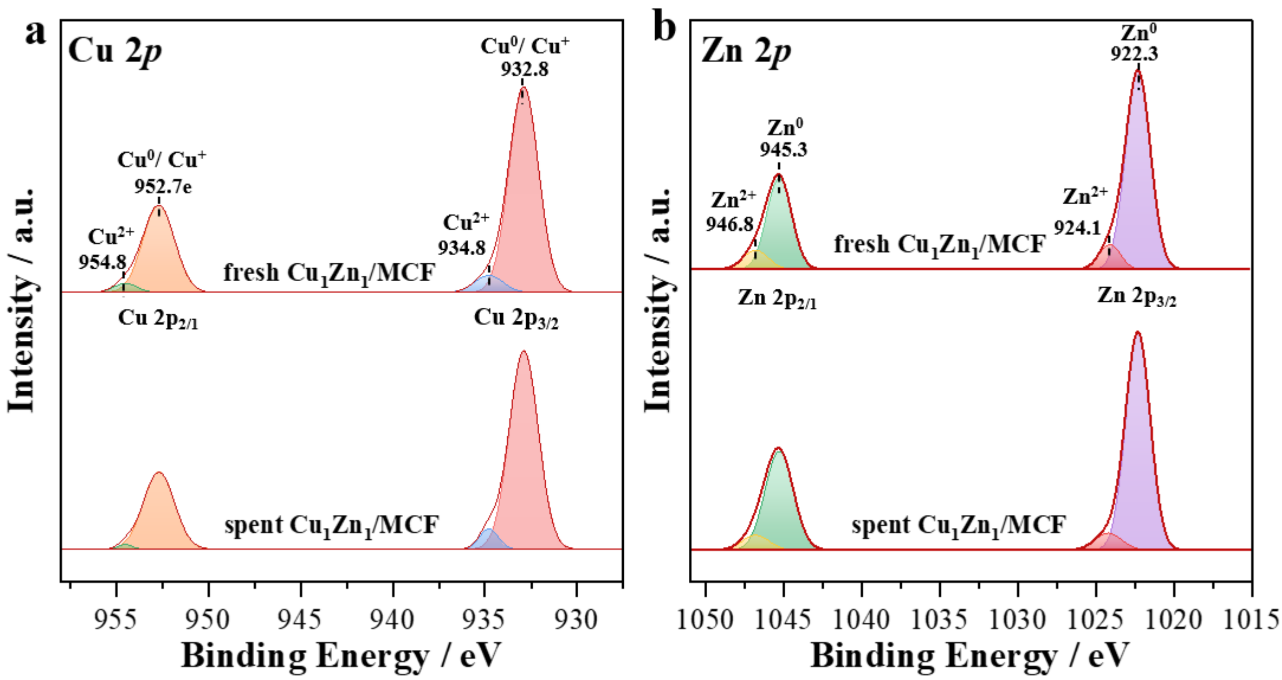

Fig. S15 XPS spectra of the fresh and used Cu_1Zn_1/MCF catalysts: (a) Cu 2*p*, and (b) Zn 2*p*

Table S3 Comparison of CO_2 hydrogenation to methanol over different catalysts under NTP conditions

Catalyst	Frequenc / kHz	Input power	Total flow rate / mL min^{-1}	CO_2 Conversio / %	Methanol production	Ref.
Cu/γ-Al_2O_3	9	10 W	40	21.2	11.3% (yield)	6
Cu/γ-Al_2O_3	9.5	26 W	72	10	65% (selectivity)	7
MnO_x/ZrO_2	/	10 W	30	11	4.5 mg_{MeOH} g_{cat}^{-1} h^{-1} (STY)	8
Fe_2O_3/γ-Al_2O_3	9	18 W	75	12	58% (selectivity)	9
CuO/Fe_2O_3/QW	0.05	2 W	100	7	32.7% (selectivity)	10
Co_xO_y/MgO	9.2	30 kV (Applied voltage)	28	35	10% (yield)	11
Pt/In_2O_3	20	/	40	37	62.6% (selectivity)	12
Cu_1Zn_1/MCF	7.7	21 W	50	16	275 μmol g_{cat}^{-1} h^{-1} (STY)	This work