Supporting Information

Unravelling Proximity-Driven Synergetic Effect within CIZO-SAPO Bifunctional Catalyst for CO_2 Hydrogenation to DME

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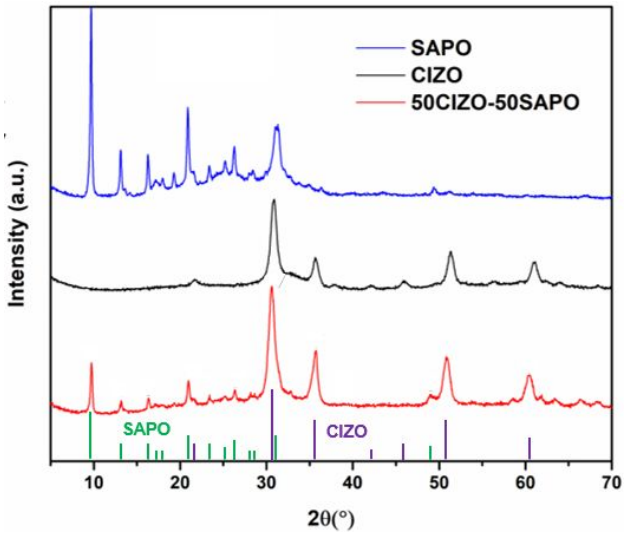

Fig. S1. XRD patterns of SAPO, CIZO and 50CIZO-50SAPO bifunctional catalysts.

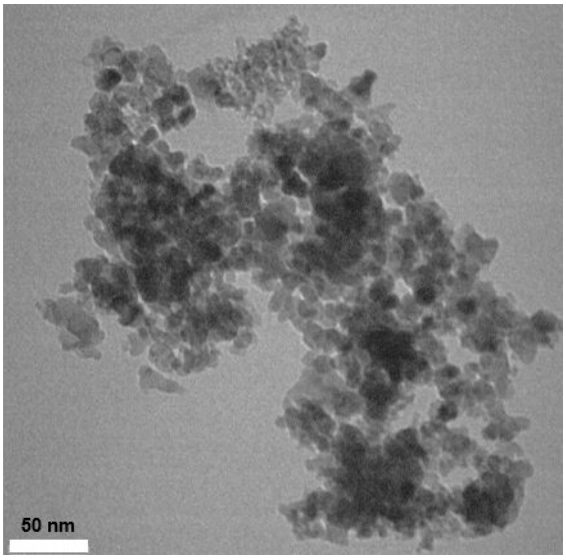

Fig. S2. TEM image of $Cu_{0.25}$-$In_{0.75}$-$Zr_{0.25}$-O (CIZO).

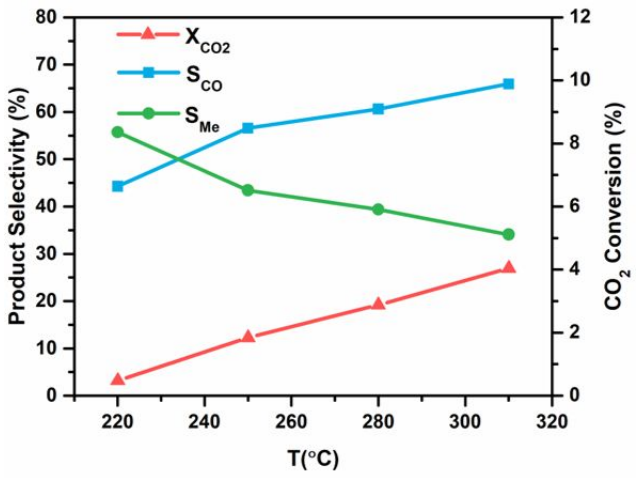

Fig. S3. Catalytic properties of CIZO catalyst. Reaction condition: P=30 bar, GHSV= 6000 ml/(g_{cat}·h).

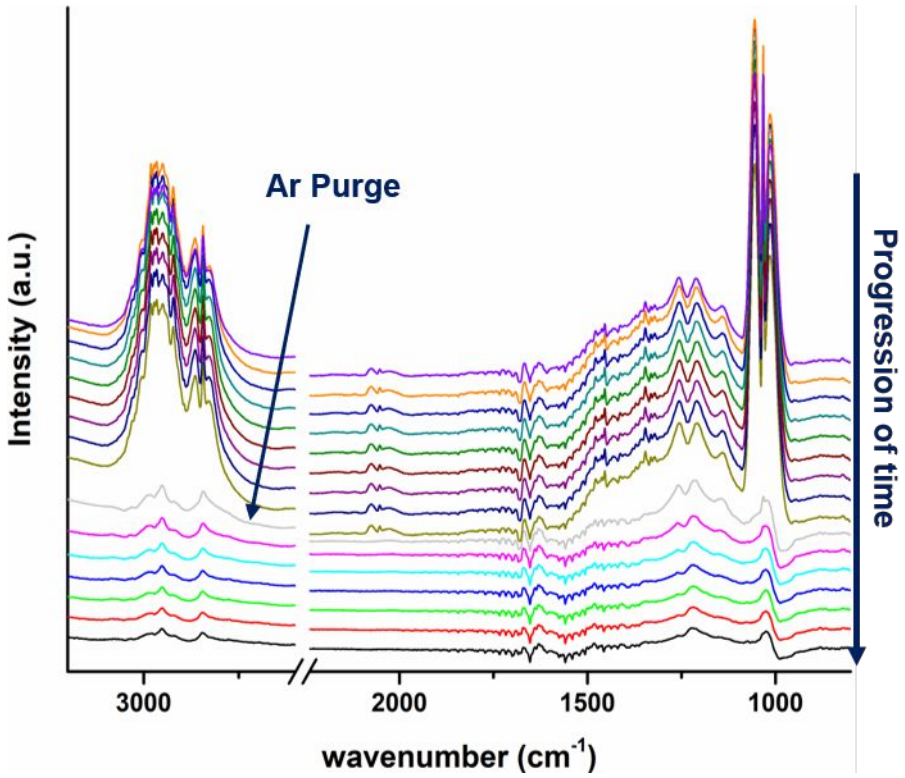

Fig. S4. Time-evolved DRIFTS spectra of gas methanol feeding followed by Ar purging over reduced 50CIZO-50SAPO bifunctional catalyst at 30 ℃.

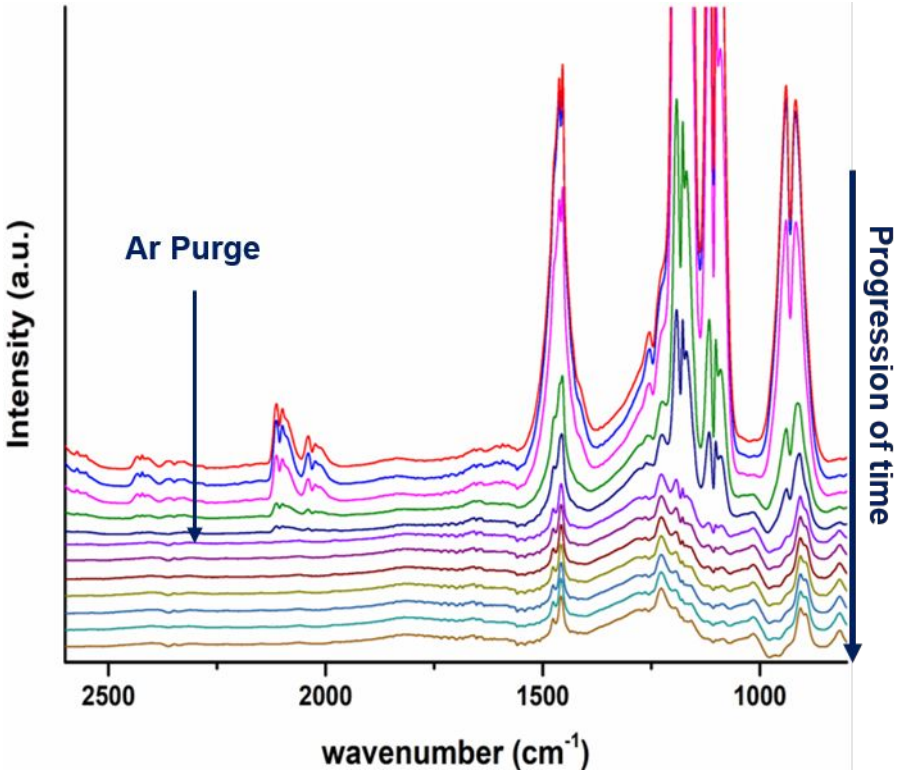

Fig. S5. Time-evolved DRIFTS spectra of DME feeding followed by Ar purging over reduced 50CIZO-50SAPO bifunctional catalyst at 30 ℃.

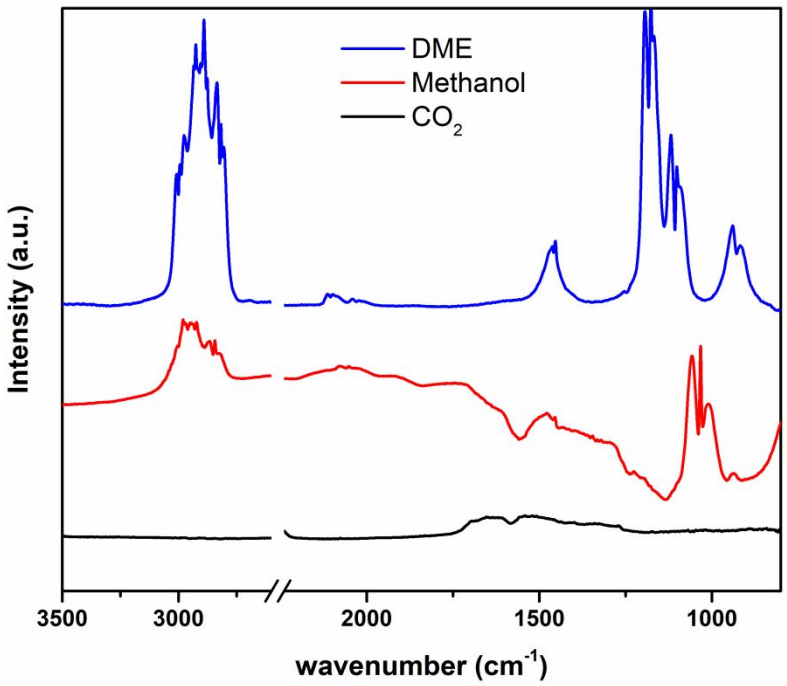

Fig. S6. DRIFTS spectra of CO_2, methanol and DME over reduced 50CIZO-50SAPO surface. T:250 ℃, flow rate: 20 mL/min.

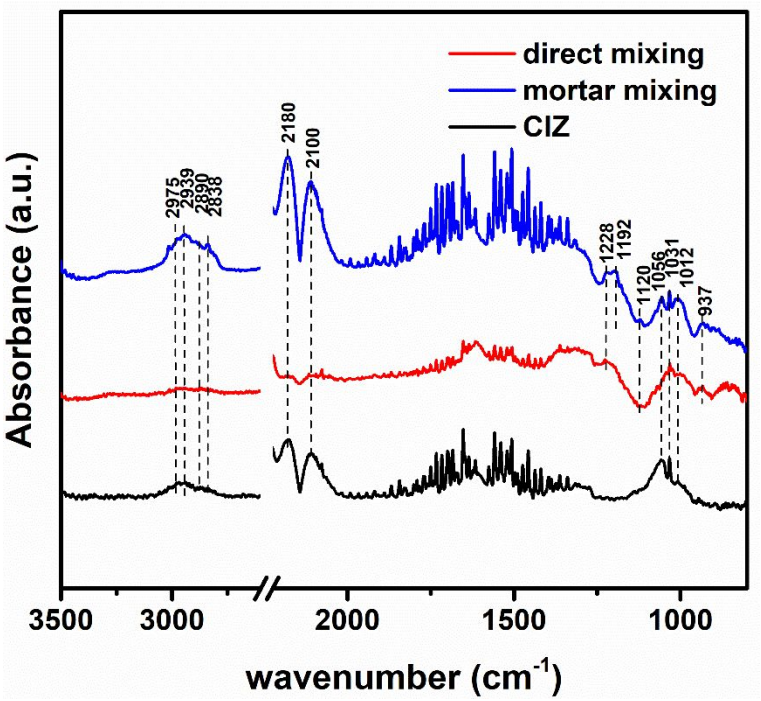

Fig. S7. Comparison of DRIFTS spectra among mortar and direct mixing CIZO-SAPO, and CIZO catalysts for CO_2 hydrogenation reaction. T:250 ℃, P= 7 bar, flow rate: 20 mL/min.

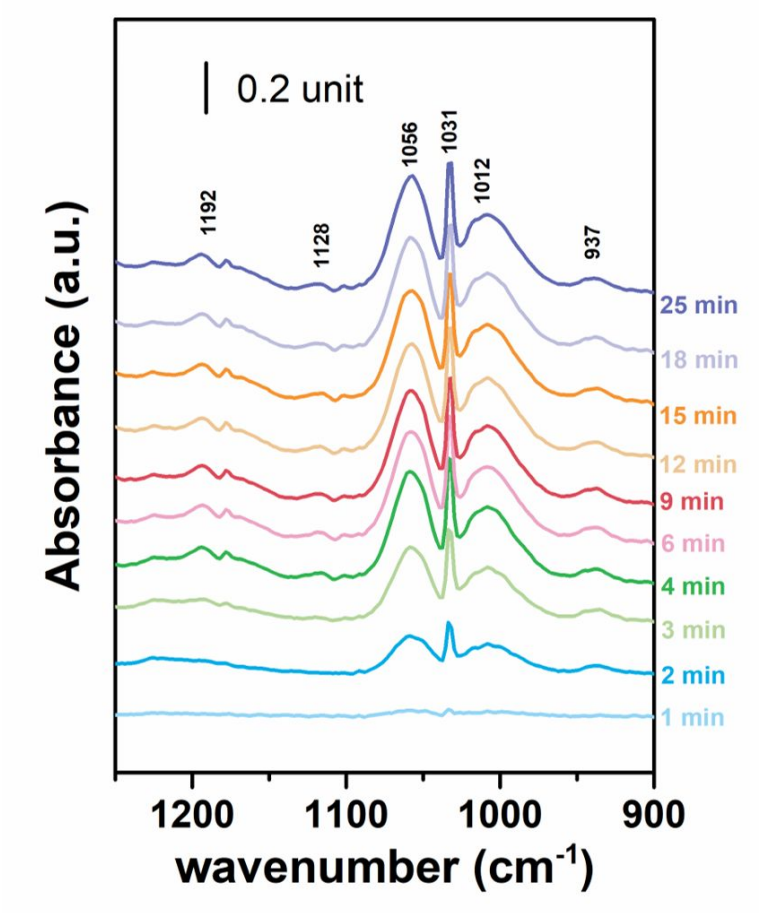

Fig. S8 Time-evolved DRIFTS spectra of methanol dehydration to DME on 50CIZO-50SAPO catalyst. T=250 ℃, flow rate: 20 ml/min, methanol composition: 17%. (Estimated by methanol saturated vapor pressure at 25 ℃) Methanol was fed starting from 0 min.

Table S1. Physical Properties of SAPO-34[a].

Properties	Values
Specific surface area (m^2/g)	≥550
Pore volume (cm^3/g)	≥0.27
Average particle size (μm)	2
Component content (%)	
SiO_2	10
Al_2O_3	42
Na_2O	0.1

a. Obtained from supplier.

Table S2. Assignment of CO_2 hydrogenation related intermediate species in DRIFTS spectra.

Species	Wavenumber (cm^{-1})	Assignment
$CO_{2(ads)}$	1616	$\nu_{as}(OCO)$
Methoxy	1028	$\nu(OCH_3)$
	2975	
	2939	$\nu(CH_x)$ +
	2890	$\delta(CH_x)$
	2838	

Table S3. Peak positions and assignments of gaseous and adsorbed methanol related species.

$CH_3OH_{(g)}$		$CH_3OH_{(ads)}$	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
2982	ν(OCO)	2975	ν(OCO)
2922	$\delta(CH_x)$	2939	$\delta(CH_x)$
2865	$\nu(CH_x)$	2890	$\nu(CH_x)$
2843	ν(CH)	2838	ν(CH)
2077	ν(C-O)	1670	ν(OCO)
2052		1628	
1666	ν(OCO)	1216	
1628		1028	$\nu(OCH_3)$
1256			
1210			
1141			
1056	$\nu(OCH_3)$		
1031			
1015			

Table S4. Peak position and assignment of gaseous and adsorbed DME related species.

$CH_3OCH_{3(g)}$		$CH_3OCH_{3(ads)}$	
Wavenumber (cm^{-1})	Assignment	Wavenumber (cm^{-1})	Assignment
2113	ν(C-O)	1475	$\delta(CH_x)$
2100	$\nu_{as}(OCO)$	1457	
2040		1228	ν(OCO)
2023	$\nu(OCH_3)$	1192	$\nu(OCH_3)$
1454	$\delta(CH_x)$	1015	
1191	$\nu(OCH_3)$	937	-
1163		895	-
1120		815	-
1100			
1090			
917	-		
907	-		

Table S5. Comparison of CO formation rate between CIZO and CIZO-SAPO catalyst.

Catalyst	CIZO	50CIZO-50SAPO
CO yield ($mg/g_{cat}/h$)	62.4	96.3

Table S6. Comparison of CO_2 to DME performance among state-of-the-art catalysts.

Catalysts	Reaction conditions	CO_2 conversion (%)	DME selectivity (%)	Ref
CuInZr/SAPO-34	250 ℃, 30 bar, 6000 ml/(g_{cat} h)	4.3	60.6	Present work
CuZnZr/FER	260 ℃, 50 bar, 8000 ml/(g_{cat} h)	13.6	38.3	1
CuZnZr/ZSM-5	220 ℃, 30 bar, 9000 ml/(g_{cat} h)	9.0	48.4	2
CuZnZr/MFI	240 ℃, 30 bar, 10000 ml/(g_{cat} h)	15.3	38.1	3
Pd-CuZnZr/HZSM-5	200 ℃, 30 bar, 1000 h^{-1}	8.91	32.2	4
PdZn/Al_2O_3	220 ℃	4.9	59.8	5
La-CuZnAl/HZSM-5	250 ℃, 30 bar, 3000 h^{-1}	25.1	17.3	6

Reference

(1) Bonura, G.; Cannilla, C.; Frusteri, L.; Mezzapica, A.; Frusteri, F. DME production by CO_2 hydrogenation: Key factors affecting the behaviour of CuZnZr/ferrierite catalysts. *Catal. Today.* **2017,** 281, 337-344.

(2) Bonura, G.; Cordaro, M.; Cannilla, C.; Mezzapica, A.; Spadaro, L.; Arena, F.; Frusteri, F. Catalytic behaviour of a bifunctional system for the one step synthesis of DME by CO_2 hydrogenation. *Catal. Today.* **2014,** 228, 51-57.

(3) Frusteri, F.; Bonura, G.; Cannilla, C.; Ferrante, G. D.; Aloise, A.; Catizzone, E.; Migliori, M.; Giordano, G. Stepwise tuning of metal-oxide and acid sites of CuZnZr-MFI hybrid catalysts for the direct DME synthesis by CO_2 hydrogenation. *Appl. Catal. B-Environ.* **2015,** 176, 522-531.

(4) Sun, K.; Lu, W.; Wang, M.; Xu, X. Low-temperature synthesis of DME from CO_2/H_2 over Pd-modified CuO-ZnO-Al_2O_3-ZrO_2/HZSM-5 catalysts. *Catal. Commun.* **2004,** 5, 367-370.

(5) Bahruji, H.; Armstrong, R. D.; Ruiz Esquius, J.; Jones, W.; Bowker, M.; Hutchings, G. J. Hydrogenation of CO_2 to Dimethyl Ether over Brønsted Acidic PdZn Catalysts. *Ind. Eng. Chem. Res.* **2018,** 57, 6821-6829.

(6) Wengui, G.; Hua, W.; Yuhao, W.; Wei, G.; Miaoyao, J. Dimethyl ether synthesis from CO_2 hydrogenation on La-modified CuO-ZnO-Al_2O_3/HZSM-5 bifunctional catalysts. *J. of Rare. Earth.* **2013,** 31, 470-476.