

Supplementary information

Origin of MnO induced Cu⁰/Cu⁺ surface active centers for CO₂ containing syngas conversion to DME via tandem catalysis

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Detailed methodology of catalyst characterization

BET surface areas, pore volumes and pore sizes of catalyst samples were determined by multipoint measurements using Micromeritics 3Flex Version 5.00. All the calculations were made on the basis volume of test gas adsorbed on the surface of samples at liquid nitrogen boiling point of -196 °C. Pore volume was calculated at P/P₀ value of 0.98 of Nitrogen. (P/P₀ is the ratio of partial vapor pressure to saturated pressure of Nitrogen). Prior to Nitrogen physisorption measurements, samples were purified by degassing. A small amount (0.2 g) of calcined methanol component was taken in glass tube and degassing was done at 195±5 °C for 2 h in the presence of helium under vacuum at a ramp rate of 10 °C/min.

Diffraction patterns of precursors and calcined form of all the catalyst samples were recorded from Rigaku Miniflex 300 using Cu K-alpha radiations of wavelength 1.541 Å generated at 40kV and 15 mA as anode of X-ray source for analyzing crystallinity and phases. X-rays, scattered from the sample, are scanned at 4°/min with step size of 0.02° and recorded by the detector and the obtained spectra was identified as a function of detector angles 2θ and photon intensity. Diffraction peak positions were obtained in the range of 5°–80° 2θ. Crystallite size of CuO was evaluated using Scherrer equation ($L = k\lambda/\beta\cos\theta$), where L is the crystallite size, β is full width at half maximum, λ is the wavelength of X-ray source and k is the shape factor. Crystal phases were determined using database compiled by the JCPDS (Joint Committee on Powder Diffraction Standards).

Suitable temperature for the reducibility of metallic function, CuO to Cu⁰ has been studied in hydrogen atmosphere carried out on Micromeritics Chemisorb 2720 equipment with a thermal conductivity detector (TCD). 0.05 g of calcined catalyst sample was fed in U- shaped quartz reactor and subjected to pretreatment at 200 °C for 2 h in a flowing stream of high purity argon for removal of moisture, and other volatile impurities present in the sample. After cooling down to room

temperature, gas stream of diluted H₂ (10.2 vol% H₂ in Ar at 30 mL/min) was introduced, and the temperature was ramped from ambient to 700 °C at 10 °C/min. The TPR spectrum (change in the moles of H₂) was recorded by the response of thermal conductivity detector.

The acid properties viz. total surface acidity and acid strength distribution of the hybrid calcined catalyst was determined by NH₃-TPD on the same apparatus used for H₂-TPR. Catalyst sample was completely saturated with diluted NH₃ gas (5% NH₃ in He) at 50 °C after pretreatment as described for TPR. Afterwards, physically adsorbed NH₃ was removed by purging the examined sample with helium for 40 min at the same temperature. Following this, TPD experiments were performed by elevating the temperature from ambient to 600 °C under flowing helium at the rate of 30 mL/min. The chemically bound ammonia desorption was monitored by TCD signals, and quantitatively total acidity was calculated from the integrated peak area related to calibration curve which is obtained from known amount of NH₃ pulses.

Surface morphologies of the samples were analyzed using FESEM instrument of JEOL series (JSM-7800F Prime) equipped with tungsten filament. Sample was mounted on carbon tape and sputter coated with gold prior to analysis. Size of nanoparticles were verified by acquiring the HRTEM images of the calcined samples using FEI TecnaiTF20 microscope equipped with high resolution camera, operated at an accelerating voltage of 100 kV. For the analysis, a small droplet of the suspension of dispersed nanoparticles in ethanol under ultrasound irradiation was deposited on a holey carbon coated 400 mesh Cu grids and dried in air.

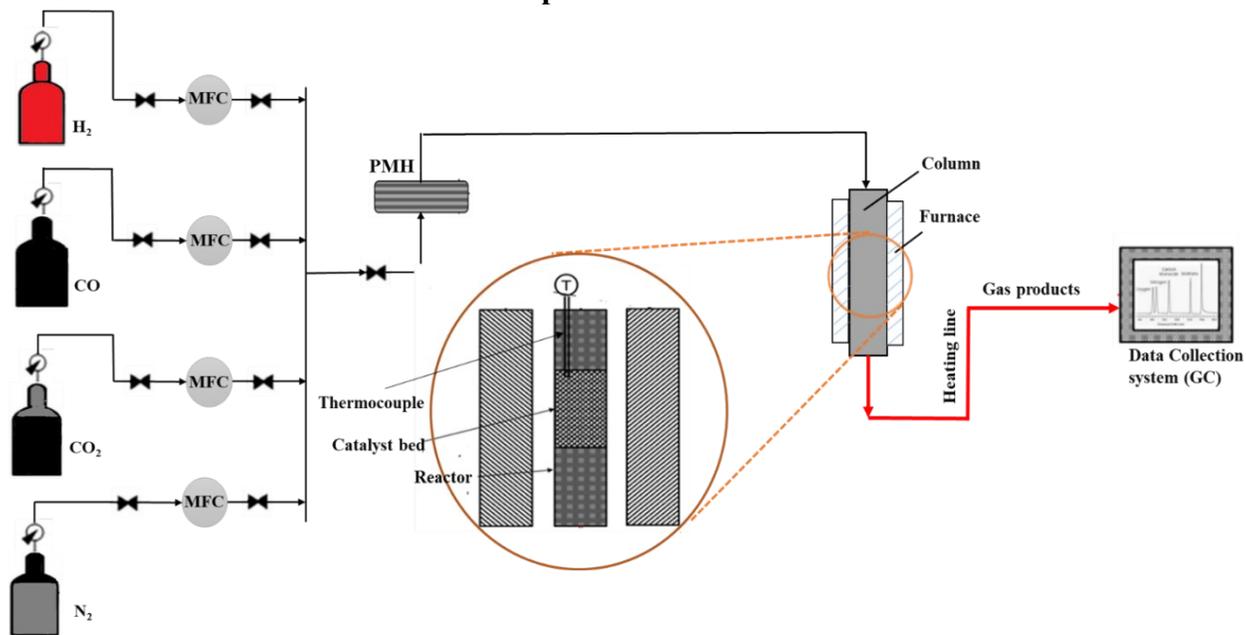
X-ray photo electron spectroscopy (XPS) measurements of calcined, reduced and spent catalysts were carried out to study the surface chemical states and surface compositions of different species (Cu, Zn, Mn), on Physical Electronics; PHI 5000 VersaProbe II high vacuum multi-technique surface analysis system equipped with a dual anode Al K α (h ν = 1486.6 eV, non-monochromatic) as an excitation source. The spectra of Cu 2p, Zn 2p, Mn 2p and O 1s were recorded and the reported binding energy values were calibrated by C 1s peak at 284.6 eV.

The metallic surface area (S_{Cu}), dispersion (D_{Cu}) and average particle size (d) of Cu on catalysts were obtained from an H₂ chemisorption study using Pulsar Automated Chemisorption Analyzer (Quantachrome Instruments). Prior to analysis, 0.3 g of sample was charged into the reactor and in-situ reduced at 300 °C under H₂ flow (20 mL/min, 99.99%) for 1 h. Then, the sample was flushed in a He stream until the temperature dropped down to 50 °C. After this, sample was exposed to H₂ gas stream for a minimum of 1 h to ensure complete saturation and then physically adsorbed H₂ was

flushed under the He flow. Finally, the process of desorption was performed by ramping temperature upto 350 °C at a heating rate of 5 °C/min using He as a carrier. Metallic properties were reported in Table 2.

Figures:

a. Schematic of the fixed bed reactor set up



MFC (Mass flow controllers), PMH (Pre-mixer heater), GC (Gas Chromatography)

Fig. S1: The schematic of the fixed bed reactor for direct syngas conversion to DME

b. Isotherms

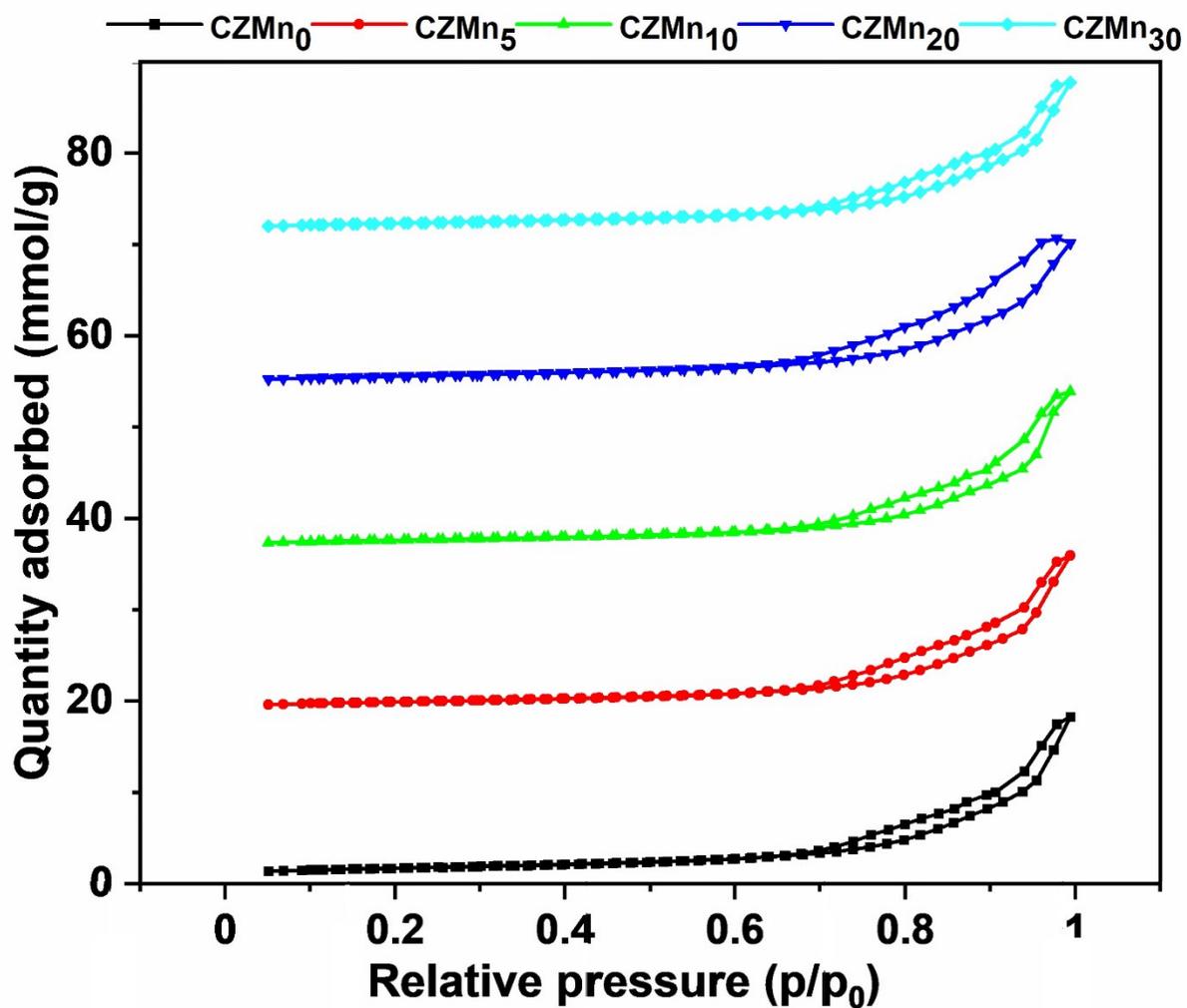


Fig. S2: N₂ adsorption-desorption isotherms for as synthesized CZMn_x catalysts (a) CZMn₀ (b) CZMn₅ (c) CZMn₁₀ (d) CZMn₂₀ (e) CZMn₃₀

c. XRD spectra for calcined methanol component

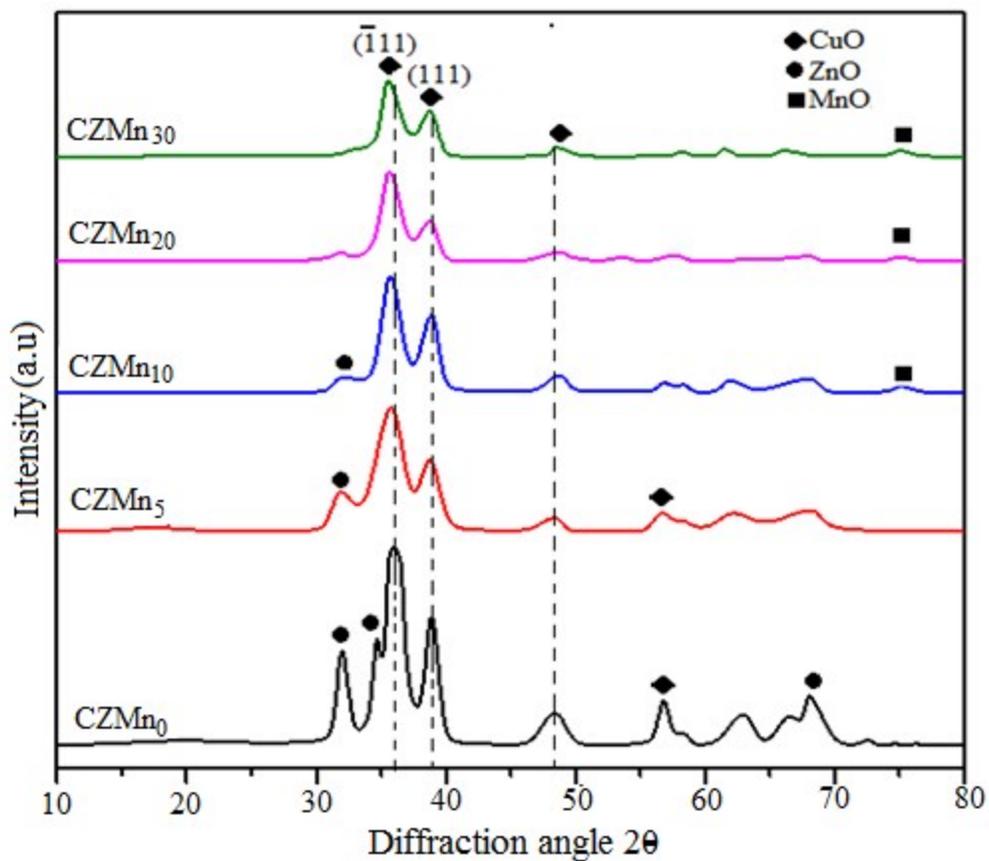


Fig. S3: XRD spectra of calcined methanol synthesis component

d. SEM images of as synthesized catalyst precursors

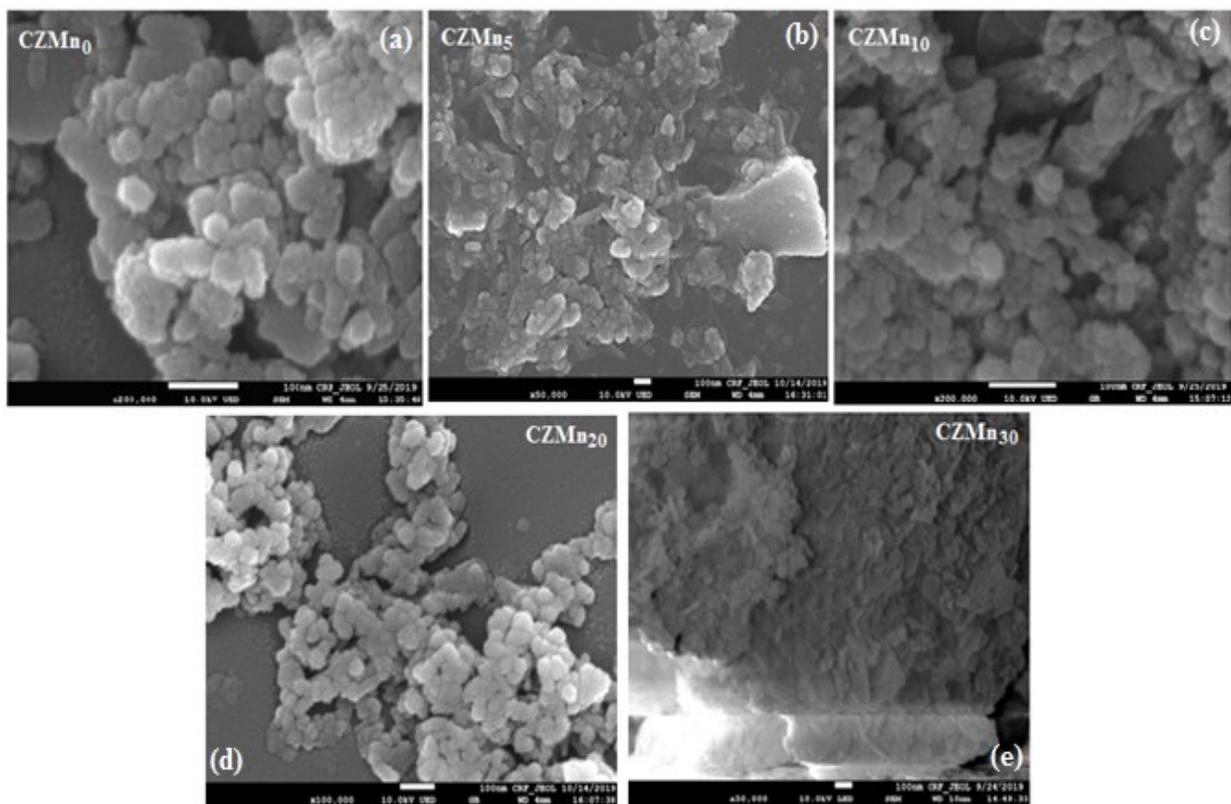


Fig. S4: SEM images of all the as-synthesized catalyst precursors: (a) CZMn₀ (b) CZMn₅ (c) CZMn₁₀ (d) CZMn₂₀ and (e) CZMn₃₀

e. HRTEM images of reduced CZMn₂₀ catalyst

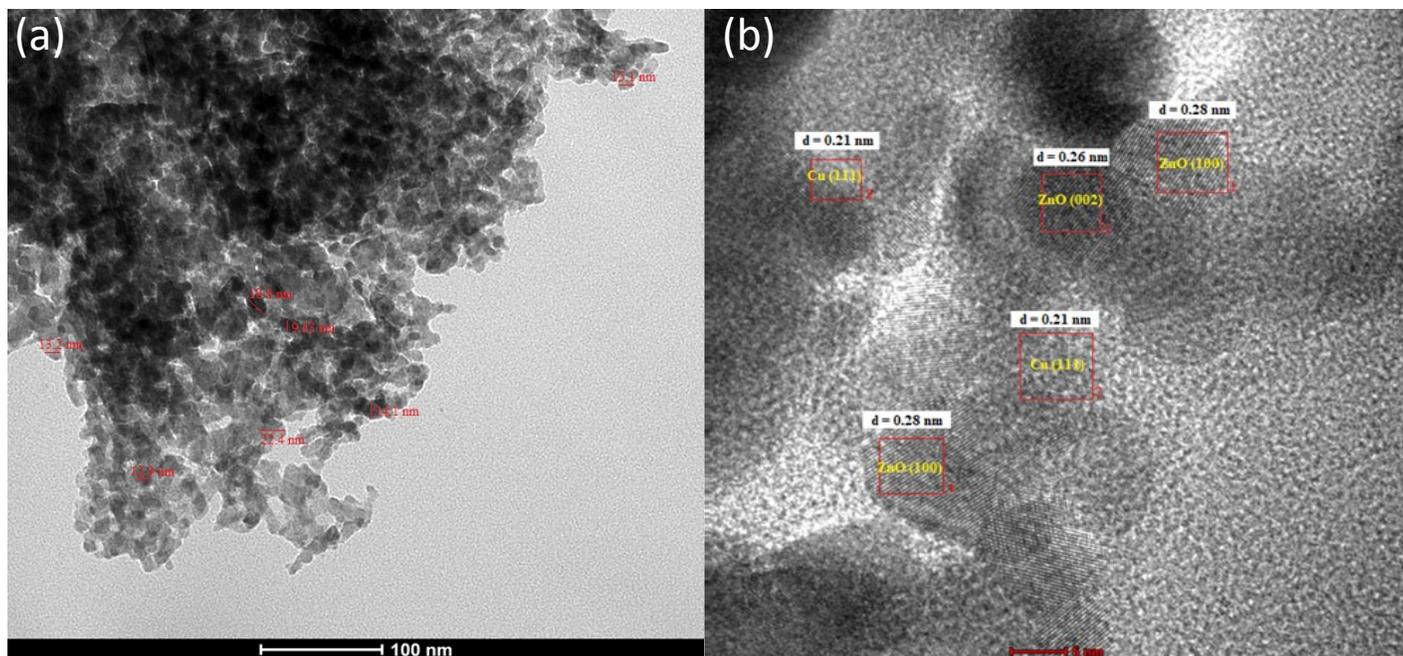


Fig. S5: (a) HRTEM image of reduced CZMn₂₀ catalyst (b) Lattice fringes of reduced CZMn₂₀ catalyst

Table S1: Crystallite size of Cu and ZnO for different reduced catalysts

Catalyst	Cu size (nm)*	ZnO size (nm)*
CZMn ₀	28.9	18.7
CZMn ₅	26.4	18.6
CZMn ₁₀	24.1	18.2
CZMn ₂₀	21.1	17.9
CZMn ₃₀	30.6	18.9

^a The full width at half maximum (FWHM) of Cu (111) peak and ZnO (101) peak are used in size calculation by Scherrer equation.

Annexure 1:

Calculations for determining S_{Cu}

$$S_{Cu} = [100 (Mol H_2)(SF)(N_0)] / [(SD_{Cu})(W_{Cu})]$$

Where Mol H_2 = amount of H_2 consumed per unit mass of the catalyst, SF= stoichiometric factor=2, N_0 = Avogadro constant, SD_{Cu} = copper surface density= 1.47×10^{19} atoms/ m^2 , W_{Cu} = Cu content of the catalyst (wt%) [S1]

For CZMn₂₀

Mol of H_2 consumed = 0.0116 mmol

$$N_0 = 6.023 \times 10^{23}$$

$$W_{Cu} (\%) = 0.552 \times 63.54 = 35.07$$

Putting all the values in above equation:

$$S_{Cu} = \frac{100 \times 0.0000116 \times 2 \times 6.023 \times 10^{23}}{1.47 \times 10^{19} \times 35.07}$$

$$S_{Cu} = 2.72 \frac{m^2}{g_{Cu}}$$

Similarly, the surface area values were calculated for other catalysts also.

Formula for Cu dispersion and average Cu particle size

The Cu dispersion was calculated using the following formula [S1]:

$$\%D_{Cu} = [10^4 (Mol H_2)(SF)(At.Wt.Cu)] / W_{Cu}$$

Where Mol H_2 = amount of H_2 consumed per unit mass of catalyst

SF= stoichiometric factor=2

At.Wt._{Cu}= atomic weight of Cu=63.54

W_{Cu} = Cu content of the catalyst (wt%)

Average Cu particle size was calculated using the following formula [S2]

$$d = 6 (At.Wt_{Cu}) / (D_{Cu} \rho \sigma N_0)$$

Where ρ = Cu metal density (8.94 g/cm³)

σ = area occupied by surface Cu atoms (6.85 Å² per atom)

N_0 = Avogadro constant

References

[S1] S. Natesakhawat, J. W. Lekse, J. P. Baltrus, P. R. Ohodnicki, B. H. Howard, X. Deng, C. Matranga, Active Sites and Structure–Activity Relationships of Copper-Based Catalysts for Carbon Dioxide Hydrogenation to Methanol, *ACS Catal.* 2 (2012) 1667-1676. <https://doi.org/10.1021/cs300008g>

[S2] A. Karelovic, G. Galdames, J. C. Medina, C. Yévenes, Y. Barra, R. Jiménez, Mechanism and structure sensitivity of methanol synthesis from CO₂ over SiO₂-supported Cu nanoparticles, *J. Catal.* 369 (2019) 415-426. <https://doi.org/10.1016/j.jcat.2018.11.012>