



Enhancing the catalytic performance of Cu/ZnO/Al₂O₃ catalyst in methanol synthesis from biomass-derived syngas with CeO₂, MnO₂ and ZrO₂ as promoters

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Funding information

Australian Research Council, Grant/Award Numbers: DP210103766, DP220100116; Future Energy Export CRC, Grant/Award Number: 21.RP2.0059; Australian Renewable Energy Agency, Grant/Award Number: 2018/RND013; Australian Department of Foreign Affairs and Trade (DFAT); Australia Awards Indonesia

Abstract

The performance of Cu/ZnO/Al₂O₃ (CZA) catalysts promoted by addition of CeO₂, MnO₂ or ZrO₂ in direct methanol production from unconventional syngas was experimentally investigated. The unconventional syngas used in this study contain 25% H₂, 25% CO, 20% CH₄, 20% CO₂ and 10% N₂, representing biomass-derived syngas cultivated from an industrial wood chips pyrolysis plant. The catalysts were synthesised using co-precipitation technique and tested for methanol synthesis in a fixed-bed reactor. The activity test of the catalysts showed that the addition of CeO₂ or ZrO₂ to the CZA catalyst improved the methanol yield, albeit with lower selectivity, whereas adding MnO₂ enhanced methanol selectivity but decreased the methanol yield. ZrO₂-promoted catalyst showed the best-improved activity and stability. The calcined and spent catalysts were characterised using X-ray diffraction (XRD), N₂ physisorption, N₂O chemisorption, hydrogen temperature-programmed reduction (H₂-TPR) and X-ray photoelectron spectroscopy (XPS). The characterisation results indicate that the catalytic activity is dependent on Cu dispersion, Cu-active surface area, the catalyst reducibility, Brunauer–Emmett–Teller (BET) surface area and the Cu⁰/Cu⁺ ratio. In contrast, catalyst stability was related to the proportion of Cu⁺ among all surface Cu species.

KEYWORDS

biomass-derived syngas, catalyst deactivation, catalyst promoters, Cu/ZnO/Al₂O₃ catalyst, methanol synthesis

1 | INTRODUCTION

Methanol is one of the largest manufactured chemical commodities and potentially an effective biofuel because it is simple to store and transport as a liquid at ambient

temperature and has a high energy density per unit volume.¹ It can also be readily used as a primary material for synthesising various beneficial organic compounds with industrial significance.² Methanol is currently synthesised on a large scale using syngas derived from

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coal gasification or natural gas steam reforming as the primary feedstock. The methanol synthesis is performed exclusively using the Cu/ZnO/Al₂O₃ (CZA) catalyst at elevated pressures (4–10 MPa), temperatures (200–300°C), with syngas composition of H₂/CO ≥ 2 and low content of CO₂ (2–5%vol).^{3–7} There are more than 90 methanol plants worldwide, with a total production of about 110 million metric tons (Mt) per year.⁸ About 80% of this methanol production is synthesised from syngas-derived natural gas, followed by coal (17%) and renewable resources (3%).⁹

Exploring renewable sources for methanol production has garnered significant attention. Several renewable feedstocks for methanol production, such as municipal solid waste, biomass and CO₂, have been developed. In principle, using biomass-derived syngas as a feedstock for methanol synthesis presents challenges due to its low H₂ content, impurities like CH₄ and high CO₂/CO ratio.¹⁰ Consequently, biomass-derived syngas must be treated before use in methanol synthesis.^{5,6} Nevertheless, syngas conditioning leads to high energy consumption and significantly increases the capital cost of methanol synthesis.¹¹ Therefore, direct methanol synthesis from biomass-derived syngas scheme and the effect of the unconventional composition of biomass-derived syngas on the catalyst activity and stability need to be explored.

Despite the widely used CZA catalyst in commercial methanol plants from conventional syngas, the performance of the CZA catalyst is inadequate in the methanol synthesis process employing syngas containing high concentrations of CO₂.^{12,13} The deficient performance of the catalysts can be linked to several factors, including the oxidation effect of CO₂, the negative effect of water on the catalyst's active site stability associated with copper sintering and the high hydrophilic nature of alumina.^{14,15} Accordingly, the research on advancing CZA catalyst performance is ongoing. One of the approaches is using additional promoters, such as MnO₂, CeO₂, La₂O₃, MgO, Cr₂O₃ and ZrO₂, that play a significant role in the performance of CZA catalyst for methanol synthesis.^{16–19} It has been recommended that the incorporation of a promoter into the CZA catalyst enhances the activity of the catalyst by increasing the density of basic sites, improving copper dispersion and copper specific surface area, increasing the BET surface area and reducing the average crystallite size of copper.^{16–19} However, the feedstock utilised in these studies did not represent the typical unconventional syngas derived from biomass, as they did not consider the H₂ deficient, high concentration of CO₂ and the presence of CH₄ in the syngas.

In our previous research, in-house Al₂O₃-, CeO₂- and ZrO₂-promoted Cu/ZnO catalysts were prepared and

evaluated for their performance in direct synthesis of methanol from unconventional syngas, with characteristics H₂ deficient, containing high levels of CO₂ and impurity of CH₄.^{20,21} Methanol was successfully synthesised, yet the catalysts experienced deactivation as the time on stream (TOS) increased, a phenomenon ascribed to the agglomeration of Cu and ZnO and the oxidation of Cu due to high CO₂ content in the unconventional syngas. In addition, no evidence was found to indicate that CH₄ in the unconventional syngas impacts catalytic performance. The highest methanol yield and stability in the longevity test were obtained from the CZA catalyst.

Therefore, in the present work, CeO₂, MnO₂ and ZrO₂ were used as an additional promoter for the CZA catalyst. The catalysts were prepared and characterised using XRD, N₂O chemisorption, N₂ physisorption, H₂-TPR and XPS techniques. The catalysts were evaluated in methanol synthesis from unconventional syngas. The results were compared with available data of the reference CZA catalyst reported elsewhere.²⁰ This work aims to systematically study the influence of CeO₂, MnO₂ and ZrO₂ addition on the performance of CZA catalyst. In addition, the relationship between the deactivation, change in the structure and the physicochemical characteristics of the final catalysts were investigated.

2 | EXPERIMENTAL

2.1 | Materials

Copper nitrate hydrate (Cu(NO₃)₂·2.5H₂O, 98.5%), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 99%), aluminium nitrate nonahydrate (Al(NO₃)₃·9H₂O, ≥98%) and sodium carbonate (Na₂CO₃) were acquired from Chem Supply Australia. Cerium nitrate hexahydrate (Ce(NO₃)₃·6H₂O, 99%), manganese nitrate tetrahydrate (Mn(NO₃)₂·4H₂O, ≥97%) and zirconium oxynitrate hydrate (ZrO(NO₃)₂·xH₂O, 99%) were purchased from Sigma Aldrich Australia. A premixed unconventional syngas with a composition of H₂/CO/CH₄/CO₂/N₂ = 25/25/20/20/10 (volume ratio) was acquired from BOC Australia. The syngas configuration represents the syngas generated from an industrial wood chips pyrolysis plant.

2.2 | Preparation of CZA-based catalysts

Catalysts were formulated utilising a Cu/Zn = 68/28 and fixed Al content of 4% weight, with the incorporation of 2% weight of an additional promoter resulting in a final metallic composition of Cu/Zn/Al/M = 66.6/27.4/4/2% weight (M represents Ce, Mn and Zr). The catalysts were



synthesised using the co-precipitation method. Metal nitrates were immersed in deionised (DI) water with appropriate concentrations while stirred magnetically at a temperature of 65°C. Simultaneously, a 1 M solution of Na_2CO_3 in DI water was prepared as a precipitant. Two peristaltic pumps were used in parallel to transfer the blended metal nitrates solution and the precipitant into a beaker that was magnetically stirred and contained 300 mL of DI water. The pH and temperature of the slurry mixture were regulated to 6.5°C and 65°C, respectively. At the same temperature, the slurry was stirred magnetically for 120 min. Subsequently, the slurry was repeatedly filtered and rinsed with hot DI water (300 mL $\text{g}_{\text{cat}}^{-1}$). Following the overnight drying of the suspension at 90°C in an oven, the dried precursor was pulverised and passed through a 125 μm sieve. The powder precursor was then subjected to calcination in a muffle furnace at a temperature of 350°C for 5 h, with a heating rate of 2°C min^{-1} . The synthesised catalysts were identified as CZA, CZA/Ce, CZA/Mn and CZA/Zr, which correspond to CZA, CZA-CeO₂, CZA-MnO₂ and CZA-ZrO₂, respectively.

2.3 | Characterisation of catalysts

The concentration of Cu, Zn and the promoters in the catalysts were measured using a Thermo Scientific iCAP 7400 Duo Inductively Coupled Plasma-Optical Emission Spectrometer. Micromeritics Tristar II instrument was used to perform N_2 physisorption analysis to assess the surface area, pore volume and pore diameter of the calcined and spent catalysts at -196°C. A Malvern Panalytical Aeris X-ray diffraction (XRD) apparatus with a $\text{Co K}\alpha$ ($\lambda = 1.78901 \text{ \AA}$) source of radiation at 40 kV and 15 mA was used to examine the crystalline structure of the calcined and spent catalysts. The powder spectra and identified minerals were evaluated using Xpert Highscore software. The Scherrer equation (Equation 2) was used to calculate the average crystallite size of catalyst samples using the full width at half maximum (FWHM) of XRD spectrum peaks. The hydrogen temperature-programmed reduction (H_2 -TPR) experiment and nitrous oxide (N_2O) chemisorption tests were performed using Quantachrome ChemBET PULSAR TPR/TPD equipped with a thermal conductivity detector (TCD). While the former was performed to determine catalyst reducibility, the latter was for measuring Cu surface area (SA_{Cu}), Cu dispersion (D_{Cu}) and average Cu particle size (d_{Cu}),^{22,23} as shown by Equations (3)–(5). X-ray photoelectron spectroscopy (XPS) tests were conducted on a Thermo Scientific Nexsa Surface Analysis System equipped with a hemispherical analyser to determine the oxidation state of Cu species

on the surface of reduced and used catalysts. Advantage software (V5.9931) was used for data processing. Characterisation procedure specifics are described elsewhere.^{20,21}

$$D = \frac{0.9\lambda}{\beta \cos \theta}, \quad (2)$$

where D (nm) represents crystallite size, λ (nm) wavelength, β (radian) FWHM and the Bragg angle denoted by θ .

$$SA_{\text{Cu}}(\text{m}^2 \text{g}^{-1}) = (2n_2 \times N) / (1.47 \times 10^{19} \times m), \quad (3)$$

$$D_{\text{Cu}}(\%) = 100 \times 2n_2 / n_1, \quad (4)$$

$$d_{\text{Cu}}(\text{m}) = 6 / \rho_{\text{Cu}} \times SA_{\text{Cu}}, \quad (5)$$

where N ($6.022 \times 10^{23} \text{ atoms mol}^{-1}$) is Avogadro's constant, 1.47×10^{19} is the number of metallic Cu atoms per square metre, m (g) is catalyst quantity, n_1 (mol) is moles of consumed H_2 in the first reduction, n_2 (mol) is moles of consumed H_2 in the second reduction and ρ_{Cu} ($8.96 \times 10^6 \text{ g m}^{-3}$) represents metallic copper density.

2.4 | Catalytic activity test

A high pressure fixed-bed reactor apparatus was used for catalyst evaluation. A detailed description can be found in our previous publication.²⁰ In brief, about 1.5 g of catalyst was introduced into the reactor tube (stainless steel, internal diameter = 10 mm, length = 600 mm). The catalyst samples were reduced prior to the reaction at 250°C with a heating rate of 5°C min^{-1} . The reduction took place for 4 h under atmospheric pressure, under 10%v/v H_2/N_2 mixture, with a flow rate of 50 mL min^{-1} . The reactor's temperature was subsequently lowered to <50°C after the reduction process. The gas atmosphere was then changed to unconventional syngas with 2000 h^{-1} of gas hourly space velocity (GHSV), and the reactor pressure was then increased to 4 MPa. The reactor pressure was regulated by an electronic back pressure regulator. The reactor temperature was subsequently elevated with a heating rate of 5°C min^{-1} to the target range of 220–260°C.

An online gas chromatograph (GC, Agilent 7890A) equipped with TCD and flame ionisation detector (FID) was used to analyse the effluent at different TOS. TCD was connected to a TDX-01 column and used for analysing H_2 , CO, CH_4 and CO_2 using N_2 as the internal standard. FID was linked to an HP-PLOT/Q column and

used to analyse CH₃OH and hydrocarbons. Equations (6)–(8) were used to calculate the conversion of feed (X_{Gas}), the space–time yield (STY) of methanol and methanol selectivity.

$$X_i = \frac{\frac{A_{i,in}}{A_{N_2,in}} - \frac{A_{i,out}}{A_{N_2,out}}}{\frac{A_{i,in}}{A_{N_2,in}}} \times 100\%, \quad (6)$$

$$STY = \frac{[\text{mass of CH}_3\text{OH}]}{[\text{mass of catalyst}] \times [\text{time}]}, \quad (7)$$

$$\text{Selectivity} = \frac{[\text{moles of CH}_3\text{OH}]}{[\text{moles of CO}_{\text{converted}}]} \times 100\%. \quad (8)$$

$A_{i,in}$ and $A_{i,out}$ represent H₂, CO, CO₂ and CH₄ peak areas in the TCD chromatograms before and after the reaction. In order to prevent condensation during analysis, the temperature of the effluent gas sampling line was controlled at 120°C.

After reaching the targeted TOS, the temperature and pressure of the reactor were brought down to atmospheric conditions while being protected by N₂ at a flow rate of 50 mL min^{−1}. The spent catalyst was then passivated by treating it with a 1%v/v O₂ in N₂ mixture at a flow rate of 50 mL min^{−1} for 5 h. The passivation was carried out to prevent rapid oxidation of the catalyst upon exposure to the atmosphere, as it is pyrophoric. After being securely retrieved, the used catalyst was placed in a vacuumed desiccator.

3 | RESULTS AND DISCUSSION

3.1 | Calcined catalyst characterisation

Inductively coupled plasma–optical emission spectrometry (ICP-OES) was used to determine the ratios of Cu, Zn, Al, Ce, Mn and Zr in the calcined catalysts. The measured concentrations are shown in Table 1 and found to be within the expected range.

TABLE 1 Calcined CZA-based catalysts composition determined by ICP-OES technique.

Catalyst	Cu/Zn/Al/promoter (% weight)	
	Designed	ICP-OES
CZA	68/28/4	67/28.7/4.3
CZA/Ce	66.6/27.4/4/2	65.3/28.1/4.5/2.1
CZA/Mn	66.6/27.4/4/2	65.2/28.4/4.2/2.2
CZA/Zr	66.6/27.4/4/2	66.4/27.4/2.2/4

The XRD crystallinity of the catalysts, defined as the degree of long-range structural order comprising a crystal lattice, is depicted in Figure 1 for the calcined samples. The diffraction peaks observed at 2θ values of 41.2°, 45.05° and 57.1° are indicative of CuO, while the peak at 36.9° is a characteristic of ZnO. CuO and ZnO peaks are present in all prepared catalysts. No noticeable peaks associated with Al₂O₃, CeO₂, MnO₂ and ZrO₂ were observed due to the relatively low concentration of these elements, which may be present in an amorphous phase. Furthermore, no new distinct peaks were observed that could be attributed to the formation of new complex. There is no ZnO peak in the CZA/Mn spectra, which may suggest either (i) overlap with the broad CuO diffraction peak at 2θ values of 41.2° and/or (ii) incomplete decomposition of the catalyst precursor. Kikhtyanin et al.²⁴ have attributed the broad peak diffractions and low signal intensity of CuO and ZnO in CZA/Mn to the incomplete decomposition of the precursor catalyst and suggested increasing the calcination temperature. The crystallite size of CuO in the calcined catalysts was determined using XRD patterns through the Scherrer equation, as presented in Table 2.

BET surface areas and pore properties of calcined CZA-based catalysts are listed in Table 2. The presence of CeO₂ and ZrO₂ increased surface area BET, pore diameter and pore volume of the catalysts, yet the opposite trend with the addition of MnO₂. As illustrated in Figure 1, adding CeO₂ and ZrO₂ reduced the intensity of the CuO peak. These results demonstrate that the crystallisation degree of CuO and crystallite size of CuO decrease with the addition of CeO₂ and ZrO₂, resulting in a larger BET surface area. The N₂O chemisorption

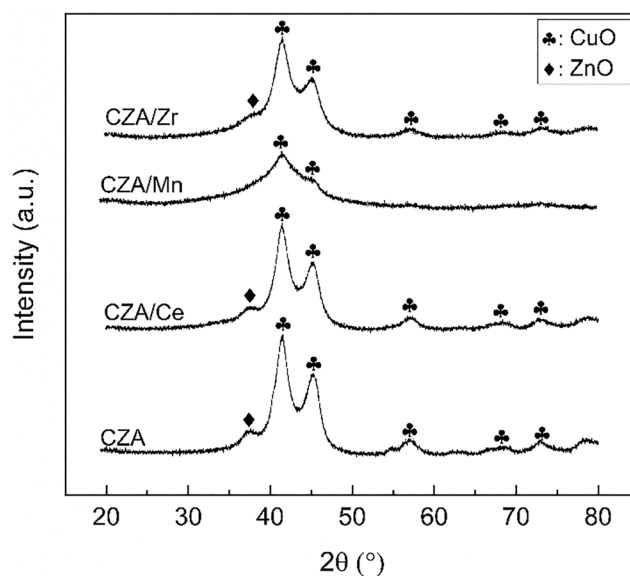


FIGURE 1 XRD patterns of calcined catalysts.



TABLE 2 Physiochemical properties of calcined catalysts.

Catalyst	XRD d_{CuO} (nm)	N ₂ physisorption			N ₂ O chemisorption		
		SA_{BET}^a (m ² g ⁻¹)	V_p^b (cm ³ g ⁻¹)	d_p^c (nm)	SA_{Cu}^d (m ² g ⁻¹)	D_{Cu}^e (%)	d_{Cu}^f (nm)
CZA	5.8	84	0.3	15.1	48.0	34.4	13.9
CZA/Ce	5.2	94	0.4	16.8	48.7	35.6	13.7
CZA/Mn	-	68	0.2	13.6	32.8	22.9	20.4
CZA/Zr	4.7	101	0.4	16.5	50.0	39.9	13.4

^aBET surface area from N₂ physisorption measurements.^bPore volume.^cPore diameter.^dSurface area of copper from N₂O chemisorption analysis.^eDispersion of copper.^fParticle size of copper.

technique was used to calculate surface area of copper (SA_{Cu}), dispersion of copper (D_{Cu}) and particle size of copper (d_{Cu}), as shown in Table 2. The highest metallic Cu surface area, Cu dispersion and the smallest Cu particle size were obtained from CZA/Zr catalyst. The improvement of the CZA catalyst with ZrO₂ addition is in accordance with the literature reported previously.^{25,26}

Figure 2 shows the reducibility of copper in calcined catalysts investigated with an H₂-TPR experiment. TPR profile of CZA exhibited a single and sharp reduction peak at 290°C. However, promoted CZA catalysts demonstrated a slightly broadened peak compared to the original CZA catalyst. The broad peaks can be attributed to the reduction of two distinct CuO phases: dispersed CuO reduced at low temperature and bulk CuO reduced at high temperature.^{27,28} Adding CeO₂ and ZrO₂ improves the reducibility of CZA catalysts. As depicted in Figure 2, the reduction peak of CZA/Ce and CZA/Zr shifted to lower temperatures of 285 and 281°C, respectively. However, the reduction peak of the MnO₂-promoted CZA catalyst shifted to a higher temperature of 318°C. The result suggests that the quantity of easily reducible well-dispersed CuO is in order of CZA/Zr > CZA/Ce > CZA > CZA/Mn; thus, well-aligned with D_{Cu} obtained from N₂O chemisorption. From the XRD and BET analysis results, the addition of CeO₂ and ZrO₂ improves the dispersion of CuO and reduces the crystallite sizes of CuO, which facilitates the reduction of CuO. In contrast, the reduction of MnO₂-promoted catalyst becomes more challenging and slower owing to the strong interaction between Cu and Mn ions during the reduction process that is opposite the Cu reduction.²⁹

3.2 | Catalytic performance

Blank control experiments were conducted and no CO₂ + H₂ and CH₄ + CO₂ reactions were evident.

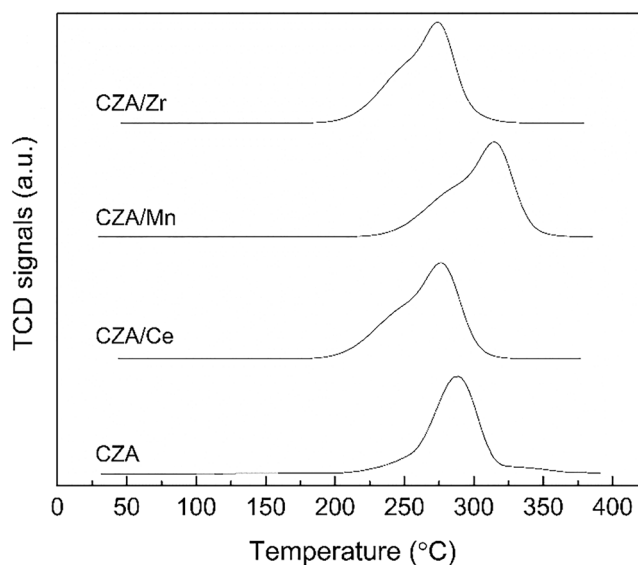
FIGURE 2 H₂-TPR profiles of the calcined catalysts.

Figure 3 illustrates the relationship between temperature and various parameters, including feed conversion, methanol STY and methanol selectivity. The data presented correspond to a 6 h TOS. Overall, the low temperature facilitated the conversion of H₂ and CO, in addition to the yield and selectivity of methanol for all catalysts. The conversion of H₂ and CO implied that CO was hydrogenated to produce methanol. Meanwhile, CO₂ and CH₄ were produced as the product of the water–gas shift reaction and a by-product of CO hydrogenation, respectively.^{30,31} These results align with a kinetic model promoted by Villa et al.,³² in which methanol is formed through CO hydrogenation, while a water–gas shift reaction takes place to produce CO₂. In addition, methanol synthesis from the hydrogenation of CO and CO₂ is an exothermic reaction that results in a molecular decrease. In accordance with Le Chatelier's principle, the equilibrium of the methanol synthesis reactions is advanced by lower temperatures and higher pressures.

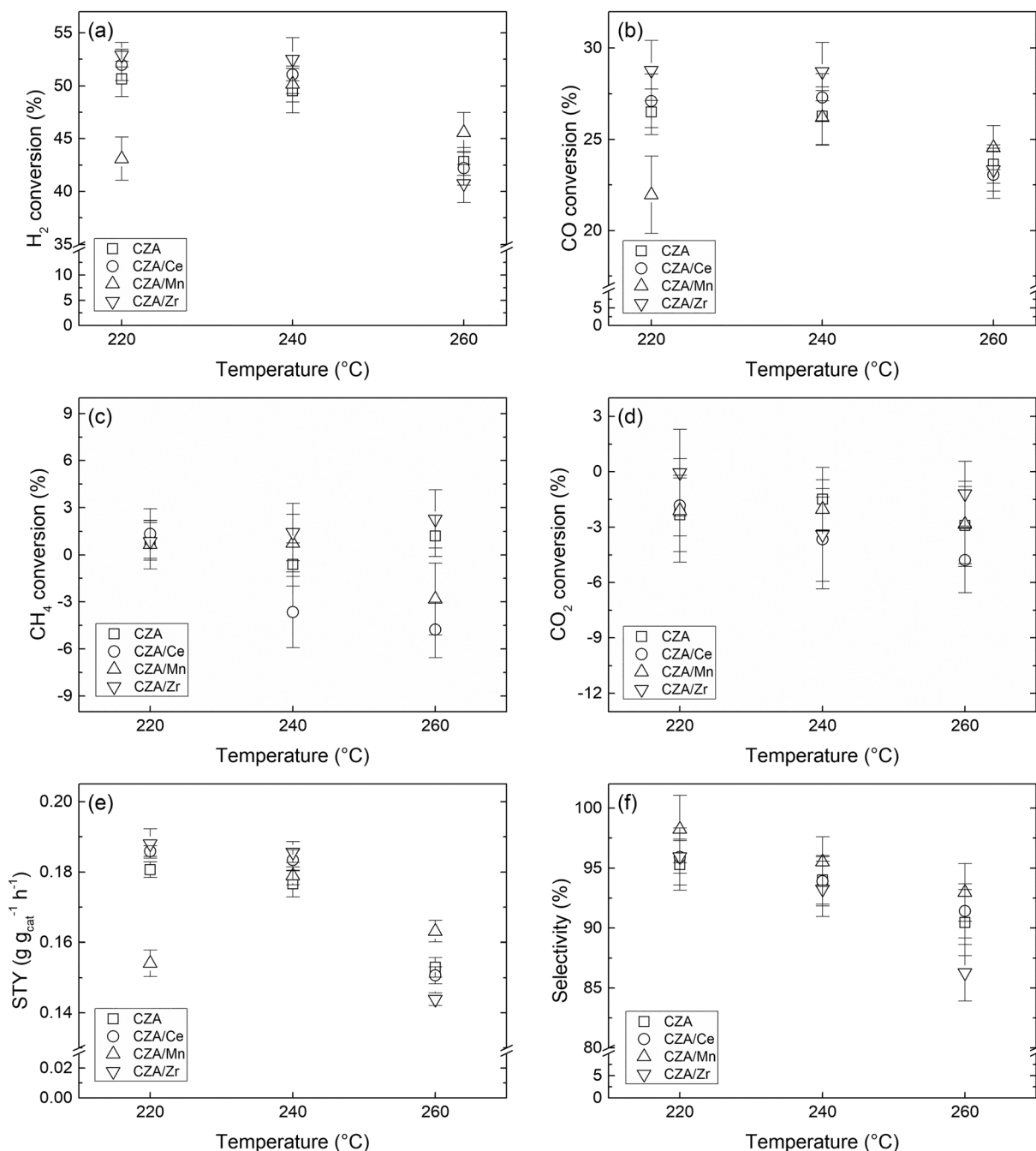


FIGURE 3 Feed conversion, methanol STY and selectivity as a function of temperature: $P = 4\text{ MPa}$, $GHSV = 2000\text{ h}^{-1}$. Error bars represent the standard deviation from experiments repeated three times.

Overall, the addition of CeO_2 and ZrO_2 into the CZA catalyst improved the conversion of H_2 and CO and methanol STY at a lower temperature. However, the activity of these catalysts decreased at a higher temperature, resulting in lower methanol STY compared to the original CZA at 260°C. The highest conversion of H_2 (54%) and CO (28%) and methanol STY ($0.187\text{ g}_{cat}^{-1}\text{ h}^{-1}$) were obtained from CZA/Zr catalyst at 220°C. According to the characterisation results in Table 2, the improvement in the catalytic performance of

the CZA/Zr catalyst can be attributed to the increase in Cu dispersion, Cu surface area and BET surface area. On the contrary, CZA/Mn catalyst showed better activity at the higher temperature of 260°C, where methanol STY ($0.165\text{ g}_{cat}^{-1}\text{ h}^{-1}$) was obtained. The highest methanol selectivity at all temperature ranges was also gained from MnO_2 -promoted catalyst: 98.2%, 95.5% and 93% at 220°C, 240°C and 260°C, respectively. Comparable results were also conveyed by Chen et al.,³³ albeit for conventional feedstock. The observation is an indication of a strong



interaction between Cu and Mn. The activity result in Figure 3 is consistent with the H₂-TPR experiments in Figure 2, which demonstrated that a higher temperature is needed to reduce the MnO₂-promoted catalyst.

Since the activity of all the catalysts is almost similar at the temperature of 240°C, this temperature value was used to examine the effect of TOS on the activity of the catalyst, shown in Figure A1. The conversion of H₂, CO, and methanol STY slightly decreased within 24 h of TOS for all catalysts. In contrast, the selectivity of methanol and the concentration of CH₄ and CO₂ showed no apparent trend. Among the catalysts, CZA/Mn was the most susceptible to catalyst deactivation as the catalyst's activity continuously decreased, decreasing methanol STY from 0.180 to 0.160 g g_{cat}⁻¹ h⁻¹ after 24 h on stream. However, the highest methanol selectivity was obtained from this catalyst. In the meantime, the CeO₂-promoted catalyst showed relatively higher activity than the original CZA. The most active and stable catalyst is CZA/Zr, where the methanol STY decreased by about 2.3% after 24 h TOS. With regard to its reactivity and notably enhanced stability, the CZA/Zr demonstrates the promising potential for applications in methanol synthesis from unconventional syngas. Therefore, CZA/Zr was used for the catalyst longevity test and deactivation study. The obtained results were compared to the reference CZA catalyst.

3.3 | Longevity test

Figure 4 displays the feed conversion, methanol STY and methanol selectivity achieved using CZA and CZA/Zr catalysts in the methanol production process, with a TOS of 100 h. In contrast to the CZA/Zr catalyst, the CZA catalyst exhibited a comparatively significant decline in H₂ and CO conversion after 50 h TOS (Figure 4a). The methanol STY for the CZA catalyst has been observed to decline from approximately 0.185 g g_{cat}⁻¹ h⁻¹ at 10 h TOS to 0.168 g g_{cat}⁻¹ h⁻¹ after 100 h TOS.

In the meantime, improved stability was shown by the CZA/Zr catalyst, where the activity of the catalyst started to decrease after 80 h TOS. The methanol STY decreased by ~8.3% from the maximum value of 0.196 g g_{cat}⁻¹ h⁻¹ to 0.180 g g_{cat}⁻¹ h⁻¹ after 100 h TOS (Figure 4b). These results demonstrate that the addition of a small quantity of ZrO₂ into the CZA catalyst significantly enhanced its long-term durability in the process of methanol synthesis from unconventional syngas. As shown in Figure 4c, the selectivity of methanol over the CZA catalyst is slightly higher than the CZA/Zr catalyst. The methanol selectivity obtained from the two catalysts exhibits no trend throughout 100 h TOS.

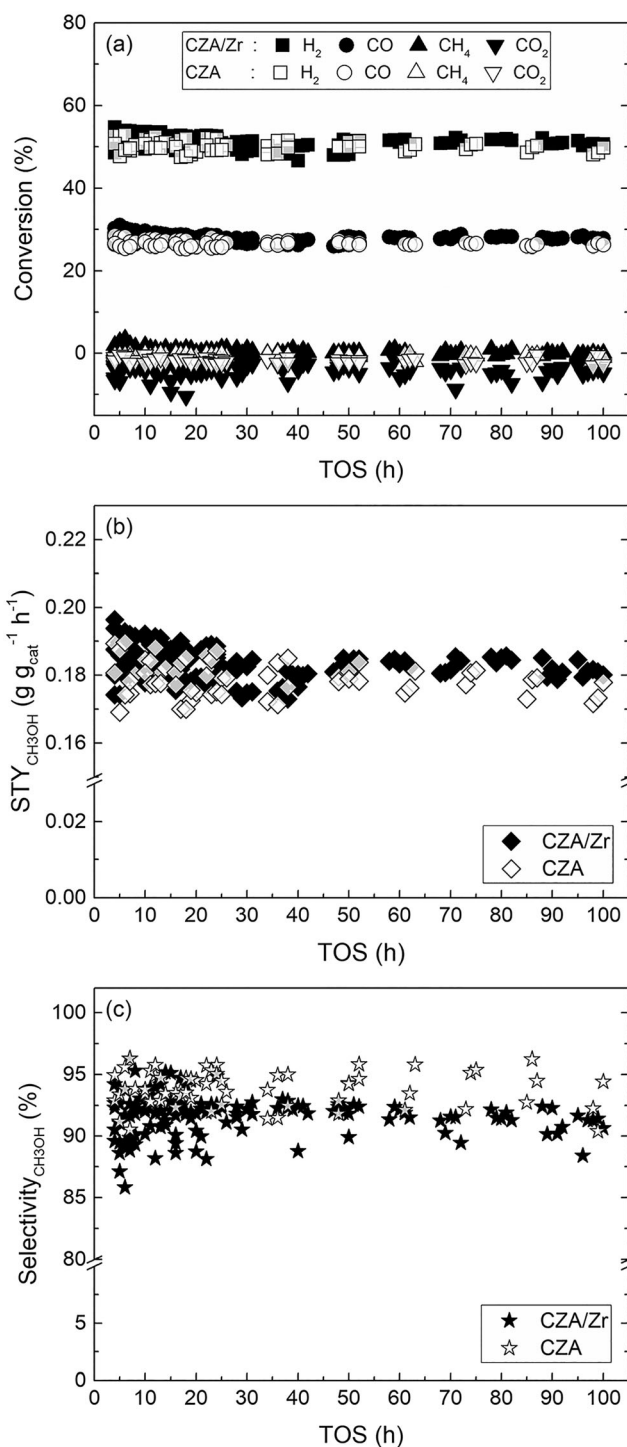


FIGURE 4 Effect of TOS on (a) feed conversion, (b) methanol STY and (c) methanol selectivity, with operating conditions of $T = 240^{\circ}\text{C}$, $P = 4\text{ MPa}$, $\text{GHSV} = 2000\text{ h}^{-1}$, TOS = 100 h.

3.4 | Catalyst deactivation

A range of characterisation techniques was employed to systematically investigate the relationship between catalyst deactivation and transformations in the structure and chemistry of the catalyst at various stages during the

methanol synthesis from unconventional syngas. Figure 5 depicts the XRD pattern of reduced and spent catalysts at different TOS, including 25, 50 and 100 h. The ZnO is denoted by peaks centred at 37.3° and 42.3° , whereas Cu is represented by peaks centred at 50.5° and 59.1° . The peaks of Cu and ZnO became sharper as the TOS increased, indicating an increase in the crystallite sizes of Cu and ZnO. The average crystallite diameters of Cu (d_{Cu}) and ZnO (d_{ZnO}) for reduced and spent catalysts determined using the Scherrer equation are shown in Table 3.

Table 3 showed that d_{Cu} and d_{ZnO} increased by extending reaction time. Aggregation of Cu and ZnO reduce the surface area of Cu and the number of active redox sites on ZnO, which could be one reason for the

catalyst deactivation.¹⁵ Interestingly, the d_{Cu} of CZA/Zr was decreased after TOS 50 h. The decrease was probably due to the reconstruction of Cu species during the initial reaction stage.¹⁵ As shown in Table 3, d_{Cu} and d_{ZnO} of the CZA/Zr catalyst are slightly lower than the CZA catalyst, also reflected in the catalyst activity. The observation suggests that the addition of ZrO into the CZA catalyst can prevent the aggregation of Cu and ZnO. These results agree with the reported literature.^{34,35}

The N_2 physisorption and N_2O chemisorption results of reduced and spent catalysts are also shown in Table 3. The N_2 physisorption analysis reveals that the BET surface area of the spent catalysts decreased as the TOS increased. However, the pore volume relatively levelled off, and the pore diameter fluctuated. Since the greater

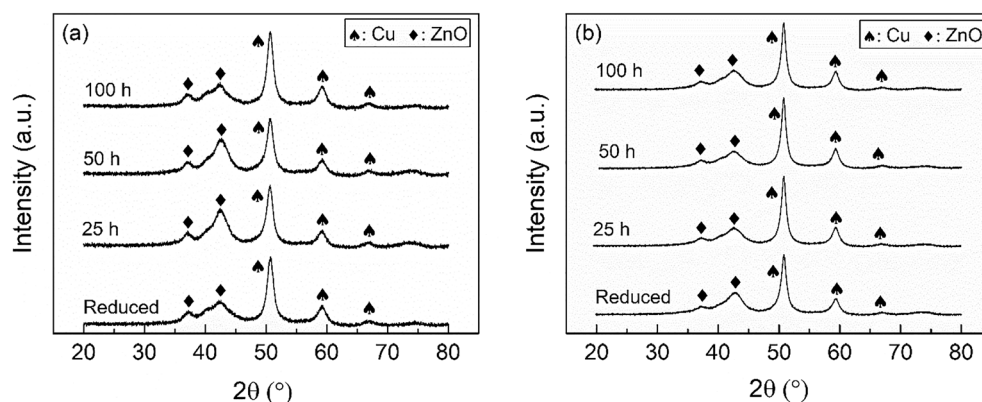


FIGURE 5 XRD patterns of reduced and spent catalysts: (a) CZA and (b) CZA/Zr.

TABLE 3 Physiochemical properties of reduced and spent Cu/ZnO/ Al_2O_3 -based catalysts.

Catalyst	XRD		N_2 physisorption			N_2O chemisorption		
	d_{Cu}^{a} (nm)	$d_{\text{ZnO}}^{\text{b}}$ (nm)	$SA_{\text{BET}}^{\text{c}}$ ($\text{m}^2 \text{g}^{-1}$)	V_{p}^{d} ($\text{cm}^3 \text{g}^{-1}$)	d_{p}^{e} (nm)	$SA_{\text{Cu}}^{\text{f}}$ ($\text{m}^2 \text{g}^{-1}$)	D_{Cu}^{g} (%)	d_{Cu}^{h} (nm)
CZA (reduced)	9.8	3.1	75	0.3	16.6	-	-	-
CZA (25 h)	9.9	3.3	69	0.3	16.2	22.7	18.8	21.4
CZA (50 h)	10.3	3.7	68	0.3	16.8	18.3	17.1	26.3
CZA (100 h)	10.5	3.6	60	0.2	16.6	10.5	12.2	36.9
CZA/Zr (reduced)	9.1	2.6	79	0.3	20.3	-	-	-
CZA/Zr (25 h)	9.5	2.4	69	0.3	18.0	28.5	20.0	23.5
CZA/Zr (50 h)	9.2	2.9	71	0.3	18.7	25.8	19.0	25.9
CZA/Zr (100 h)	9.2	3.2	68	0.3	18.3	19.6	16.5	34.8

^aAverage crystallite size of Cu calculated using the Scherrer equation from XRD results.

^bAverage crystallite size of ZnO.

^cBET surface area from N_2 physisorption measurements.

^dPore volume.

^ePore diameter.

^fSurface area of copper from N_2O chemisorption analysis.

^gDispersion of copper.

^hParticle size of copper.

specific surface area can provide a larger number of active sites, the reduction in BET surface area may contribute to catalyst deactivation. The reduction in the Cu surface area of the catalysts can be attributed to the growth of Cu crystallites,^{36,37} as revealed by the XRD results. The outcomes of the N₂O chemisorption of spent catalysts showed a strong correlation between the evolution of active phase (Cu) surface area and the activity of the catalyst.

As the increased of TOS from 25 to 100 h, the surface area of copper (SA_{Cu}) and dispersion of copper (D_{Cu}) decreased, whereas Cu particle size increased. The results aligned with the literature results.^{15,38} The reduction in SA_{Cu} and D_{Cu} can be attributed to the prolonged reaction time and high temperatures, leading to the agglomeration of Cu particles consistent with XRD and N₂ physisorption results. Therefore, the higher copper surface area and copper dispersion of CZA/Zr can be related to the superior stability of this catalyst compared to the CZA catalyst, which is consistent with the reported literature.^{39,40}

XPS measurements were conducted to investigate the oxidation state of the Cu species and the surface composition of the CZA and CZA/Zr catalysts at various stages.

The XPS spectra of Cu2p and CuLMM of the reduced and spent catalysts are displayed in Figure 6. The reduced catalysts displayed Cu2p_{3/2} and Cu2p_{1/2} peaks ranging from 930 to 940 eV and 950 to 960 eV, respectively (Figure 6a,c). The weakened or absent satellite peak observed at 942–944 eV suggests the existence of Cu⁰ and/or Cu⁺ due to Cu²⁺ reduction. The presence of the reduced Cu species is well-aligned with the XRD observations of the reduced and spent catalysts, as shown in Figure 5. In the interest of deconvoluting the overlapping binding energy of Cu2p_{3/2} between Cu⁰ and Cu⁰, it is necessary to use CuLMM Auger electron spectra to accurately determine the surface concentrations of Cu⁰ and Cu⁺.⁴¹ The spectra were subjected to deconvolution, resulting in the identification of three distinct peaks at energy levels of 914.2, 916.8 and 918.5 eV, representing Cu⁺, Cu²⁺ and Cu⁰, respectively^{42,43} (Figure 6b,d). The concentrations were expressed in terms of kinetic energy.

Surface composition in the reduced and spent catalysts of CZA and CZA/Zr at different stages are recorded in Table 4. The Cu²⁺/(Cu⁰ + Cu⁺) for CZA and CZA/Zr catalysts increased with increasing the TOS. Specifically, the ratio increased from 0.6 to 1.9 for the CZA catalyst and from 0.4 to 0.9 for the CZA/Zr catalyst after 100 h of

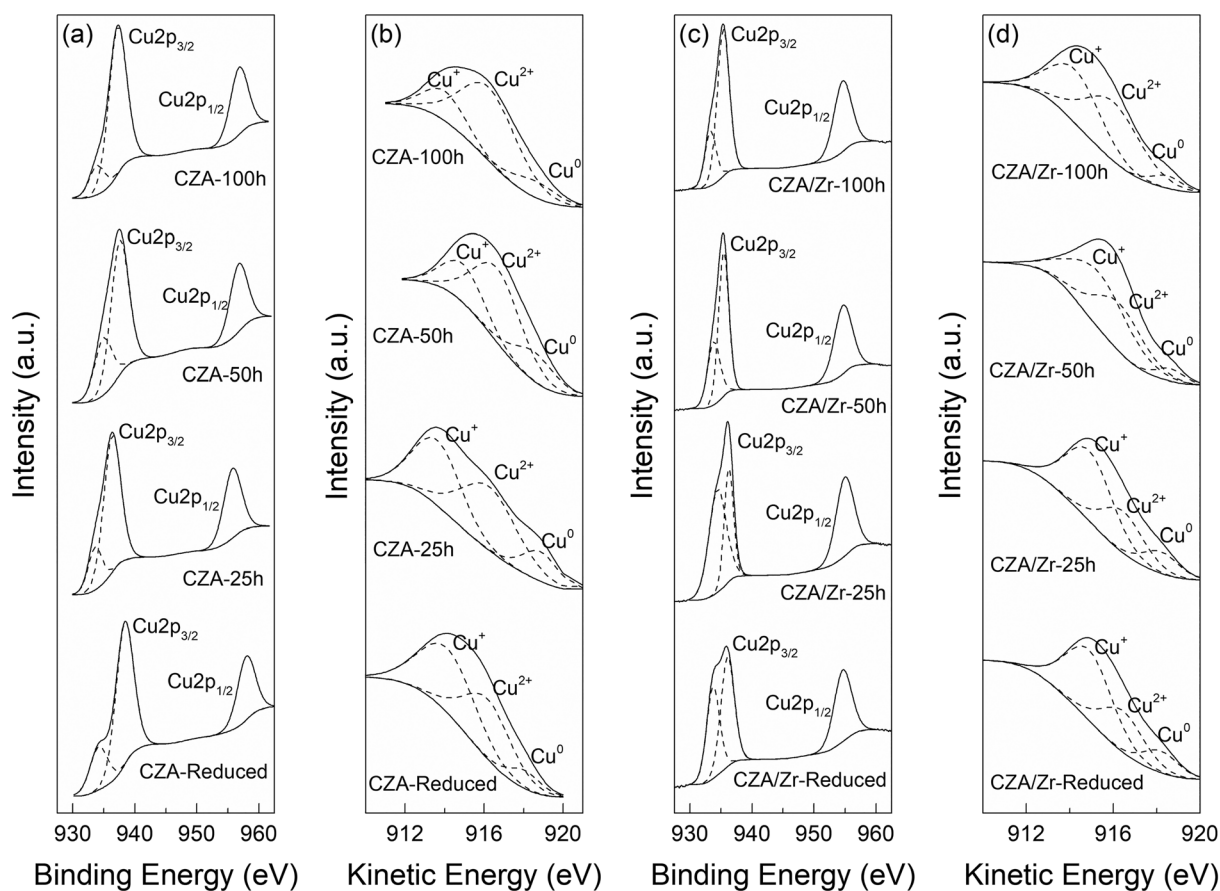


FIGURE 6 XPS spectra of the reduced and spent catalysts (a) Cu2p CZA, (b) CuLMM CZA, (c) Cu2p CZA/Zr and (d) CuLMM CZA/Zr.

TABLE 4 Curve fittings of Cu₂p_{3/2} and CuLMM of the reduced and spent catalysts.

Samples	Surface content ^a (%)			Surface content ^b (%)			
	Cu ²⁺	Cu ⁰ + Cu ⁺	Cu ²⁺ /(Cu ⁰ + Cu ⁺)	Cu ⁺	Cu ²⁺	Cu ⁰	Cu ⁰ /Cu ⁺
CZA (reduced)	38.1	61.9	0.6	40.6	36.5	22.9	0.56
CZA (25 h)	49.2	50.8	1.0	34.9	46.2	18.9	0.54
CZA (50 h)	61.3	38.7	1.6	24.3	63.3	12.4	0.51
CZA (100 h)	65.8	34.2	1.9	22.4	67.1	10.5	0.47
CZA/Zr (reduced)	29.2	70.8	0.4	46.8	30	23.2	0.50
CZA/Zr (25 h)	34.4	65.6	0.5	46.5	32	21.5	0.46
CZA/Zr (50 h)	36.3	63.7	0.6	44.2	35.1	20.7	0.47
CZA/Zr (100 h)	48.6	51.4	0.9	34	50.1	15.9	0.47

^aSurface content calculated from Cu₂p_{3/2}.^bSurface content calculated from CuLMM.

TOS. The result indicates that the Cu oxidation state was enhanced by prolonging the operating time due to the oxidation of Cu⁰ and Cu⁺ to form Cu²⁺. The oxidising atmosphere created by the high content of CO₂ in unconventional syngas might be the cause of Cu oxidation.⁴⁴ The impact of the re-oxidation process during the passivation of the catalyst is believed to be negligible as oxygen atoms do not penetrate the bulk of the copper particles.⁴⁵ Both Cu⁰ and Cu⁺ species are believed to contribute to the performance of the catalyst in methanol synthesis.^{46,47} The concentration of Cu⁰ and Cu⁺ in CZA/Zr is higher than CZA catalyst, which can be related to its superior activity after 100 h TOS. This observation might be attributed to the higher reducibility of the CZA/Zr catalyst, resulting in increased Cu dispersion⁴⁸ and exposure of metallic Cu on the catalyst surface.⁴⁹

However, there is no agreement on whether Cu⁰ or Cu⁺ is more active in the methanol synthesis reaction. Liu et al.⁵⁰ and Chen et al.⁵¹ suggested that catalysts with higher concentrations of Cu⁺-favoured methanol synthesis. In contrast, Chen et al.⁵² and Arena et al.⁵³ postulated that Cu⁰ exhibited higher activity than Cu⁺. In addition, it has been observed that higher Cu⁰/Cu⁺ leads to higher STY methanol.^{20,54,55} As shown in Table 4, the Cu⁰/Cu⁺ for both catalysts declined with prolonged TOS, which is aligned with the catalysts' evaluation results and suggests that the more Cu⁰, the more active the catalyst. The initial concentration of Cu⁺ in the CZA catalyst significantly decreased by about 40.1% after 50 h TOS, yet it declined only 5.5% for the CZA/Zr catalyst. The finding can be related to the stability of the catalysts throughout the longevity test, whereby the deactivation of CZA and CZA/Zr catalysts commenced after 50 h TOS and 80 h TOS, respectively. It suggests that Cu⁺ is responsible for the stability of the catalyst during the methanol synthesis from unconventional syngas.

4 | CONCLUSIONS

The performance of CZA catalysts promoted by adding CeO₂, MnO₂ and ZrO₂ were evaluated for direct methanol synthesis from unconventional syngas. The yield and selectivity of methanol and feed conversion were analysed as a function of temperature and TOS. The results were compared with those of a reference CZA catalyst and showed a strong correlation between the performance of the catalyst and the introduction of additional promoter. Methanol selectivity was enhanced by adding MnO₂. The existence of ZrO₂ inhibits the agglomeration of Cu and ZnO and prevents the oxidation of Cu, hence improving the activity and stability of the catalyst.

ACKNOWLEDGEMENTS

This work has benefited from the financial and other supports from the Australian Research Council under the Discovery Projects Scheme (DP210103766 and DP220100116), the Future Energy Export CRC (FEnEX CRC Project # 21.RP2.0059) and the Australian Renewable Energy Agency (ARENA: Funding Agreement 2018/RND013). Sabar Pangihutan Simanungkalit acknowledges the Australian Department of Foreign Affairs and Trade (DFAT) and Australia Awards Indonesia for providing the Australia Awards Scholarships. Open access publishing facilitated by The University of Western Australia, as part of the Wiley - The University of Western Australia agreement via the Council of Australian University Librarians.

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How to cite this article: Simanungkalit SP, Okoye CO, Zhang Z, Wu J, Zhang D. Enhancing the catalytic performance of Cu/ZnO/Al₂O₃ catalyst in methanol synthesis from biomass-derived syngas with CeO₂, MnO₂ and ZrO₂ as promoters. *Asia-Pac J Chem Eng.* 2024; 19(5):e3121. doi:[10.1002/apj.3121](https://doi.org/10.1002/apj.3121)



APPENDIX A

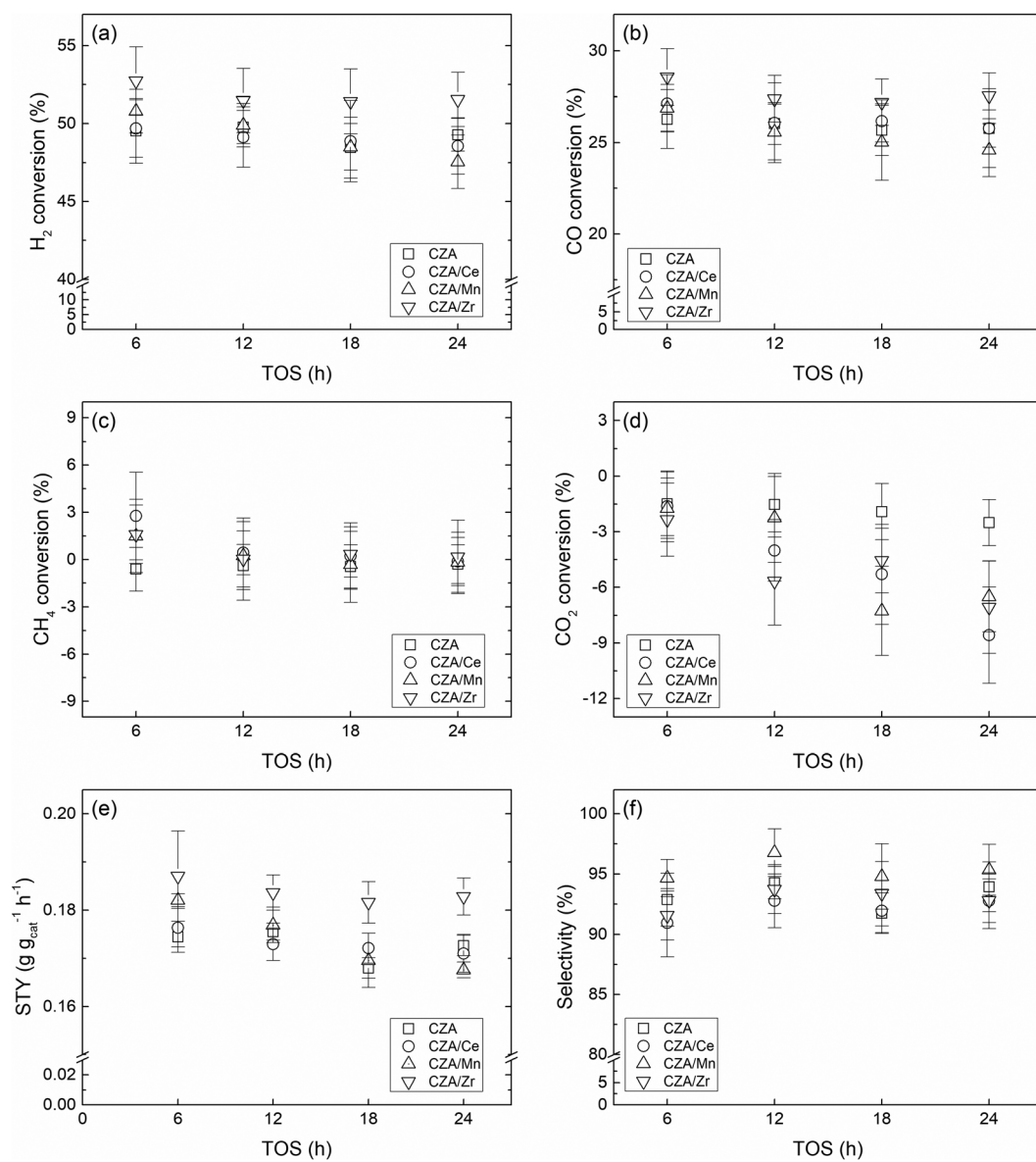


FIGURE A1 The effect of time on stream (TOS) on feed conversion and methanol productivity: $T = 240^\circ C$, $P = 4\ MPa$, $GHSV = 2000\ h^{-1}$. Error bars represent the standard deviation from experiments repeated three times.