

A preliminary attempt of direct methanol synthesis from biomass pyrolysis syngas over Cu/ZnO/Al₂O₃ catalysts

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25 **Abstract**

26 The possibility of direct methanol synthesis from biomass pyrolysis syngas (BPS) over
27 Cu/ZnO/Al₂O₃ catalysts was investigated using a fixed bed reactor. A commercial benchmark catalyst
28 and an in-house Cu/ZnO/Al₂O₃ catalyst prepared using the co-precipitation method, Cu/Zn/Al =
29 68/28/4 wt%, were tested for methanol synthesis from a model BPS containing 25% H₂, 25% CO,
30 20% CH₄, 20% CO₂, and 10% N₂. The experiments were performed under different conditions of
31 temperature (220 - 260 °C), pressure (2 - 4 MPa) and time on-stream (TOS, 0 - 100 h). Methanol was
32 successfully synthesised with the highest space-time yield of 0.185 g g_{cat}⁻¹ h⁻¹. Higher pressures and
33 lower temperatures favoured methanol production. The fresh and used catalyst samples were also
34 characterised using N₂-physisorption (BET), X-ray diffraction (XRD), and X-ray photoelectron
35 spectroscopy (XPS) to investigate the mechanisms of catalyst deactivation. While CH₄ present in the
36 BPS did not affect catalyst performance, the high concentration of CO₂ enhanced Cu oxidation,
37 leading to decreased catalyst performance with increasing TOS. After 100 h TOS, the methanol yield
38 obtained over the commercial and in-house catalysts decreased by around 9.2% and 4.3%,
39 respectively. This research has provided new insights into the challenges of producing methanol from
40 unconventional syngas and motivated future work to develop a robust catalyst that can serve syngas
41 with H₂-deficient and high concentrations of CO₂.

42 **Keywords:** Biomass pyrolysis syngas; Catalyst activity; Catalyst deactivation; Methanol synthesis.

43

44 **Highlights**

- 45 • Methanol was successfully synthesised from model biomass pyrolysis syngas (BPS)
- 46 • Excessive CO₂ in BPS oxidises Cu, leading to catalyst deactivation
- 47 • Presence of CH₄ in BPS does not affect catalyst performance
- 48 • Low temperature and high pressure favour methanol yield and selectivity
- 49 • High Cu⁰/Cu⁺ ratio significantly enhances catalytic activity

50

51 1. Introduction

52 Methanol is an important industrial chemical widely employed as a solvent, fuel and building block
53 for hydrocarbons [1–4]. Methanol synthesis is a well-developed industrial route that uses syngas from
54 coal gasification or natural gas steam reforming as feedstock. The current commercial methanol
55 synthesis is economically viable only at large-scale installations [5,6]. The gasified or reformed
56 syngas is usually cleaned and conditioned to achieve high H₂/CO (~2) and low CO₂ concentration (2
57 - 5 vol%) [7].

58 Syngas can be produced via pyrolysis of biomass, providing a renewable syngas route at a small and
59 flexible scale to accommodate the scattered biomass resources by its nature. Unlike gasification and
60 steam reforming, water is not required in pyrolysis. Biomass pyrolysis syngas (BPS) typically consists
61 of hydrogen, carbon monoxide, carbon dioxide, methane, and other low molecular weight
62 hydrocarbons [8,9], which can be directly used in gas engines after cleaning [10]. However, BPS
63 usually has a low H₂/CO ratio (≤ 1) and high CO₂ concentration ($\geq 15\%$) that can negatively affect
64 methanol productivity. To be most effective, the direct conversion of BPS into methanol would,
65 therefore, require a robust catalyst that can handle high CO₂ concentration and H₂-deficient syngas.

66 The Cu/ZnO/Al₂O₃ catalyst is an industrially proven catalyst for methanol synthesis from syngas
67 operating at the stoichiometric number (S_N) ≥ 2 (Eq. 1), under high H₂/CO and low CO₂
68 concentrations [7,11–13]. Likewise, for methanol production from CO₂ hydrogenation, the catalyst
69 usually works at a high concentration of H₂ with a molar ratio of H₂ and CO₂ ≥ 3 [14–16]. Excess
70 H₂ is preferable to increase the methanol yield [17].

$$71 \quad S_N = \frac{n_{H_2} - n_{CO_2}}{n_{CO} + n_{CO_2}} \geq 2.0 \quad (1)$$

72 Despite this, some effort has been made to investigate the application of Cu/ZnO/Al₂O₃ catalysts for
73 methanol synthesis from unconventional, H₂ deficient and CO₂-rich syngas. Tjandra et al. [18]
74 utilised a Cu/ZnO/Al₂O₃ catalyst to produce methanol at low H₂/(CO+CO₂) ratio between 0.5 and 2.0
75 when the CO₂/CO ratio was constant (0.11). It was found that methanol productivity increased as the

76 $\text{H}_2/(\text{CO}+\text{CO}_2)$ ratio increased, but the catalyst activity was reduced significantly during the first 100
77 h on stream due to deactivation. Yin et al. [19] examined methanol yield and selectivity for methanol
78 production from biomass syngas over a commercial Cu/ZnO/Al₂O₃ catalyst by varying the S_N from
79 0.36 to 2.11. It was found that a greater H_2 concentration favours methanol production, and the
80 selectivity of methanol from syngas is higher at low CO_2/CO ratios. Nonetheless, no prior work has
81 investigated how H_2 -deficient BPS that contains impurities, especially high CO_2 and CH_4 , affects the
82 activity and stability of Cu/ZnO/Al₂O₃ catalysts in direct methanol synthesis.

83 In this study, the potential of BPS as a feedstock for methanol synthesis was evaluated, taking into
84 consideration the presence of CH_4 in the syngas. A model BPS containing 25% H_2 , 25% CO , 20%
85 CH_4 , 20% CO_2 , and 10% N_2 was used in the experimentation. Benchmarking against a commercial
86 catalyst, an in-house Cu/ZnO/Al₂O₃ catalyst was also prepared by the co-precipitation method with
87 metal compositions tuned. The catalysts were tested for their catalytic activity under a range of
88 operating conditions. The longevity tests of the catalysts were performed to investigate deactivation
89 as a function of time on stream. Changes in structure and surface chemistry related to catalyst
90 deactivation were systematically explored by characterising calcined, reduced, and spent catalysts.

91 **2. Experimental**

92 **2.1 Materials**

93 Copper (II) nitrate hydrate (98.5%), zinc nitrate hexahydrate (99%), aluminium nitrate nonahydrate
94 ($\geq 98\%$), and sodium carbonate anhydrous were purchased from Chem Supply Australia. A pelletised
95 commercial methanol catalyst (HUC-98) was purchased from Hutong Global Co. Ltd (Tianjin,
96 China). Before use, the commercial catalyst was ground and sieved to pass 125 μm . Meanwhile, a
97 premixed model BPS gas with a composition of 25% H_2 , 25% CO , 20% CH_4 , 20% CO_2 , and 10% N_2
98 (volume ratio) was purchased from BOC Australia. The model BPS is a representation of syngas
99 produced from an industrial pyrolysis unit using wood chips as feedstock.

101 **2.2 Catalyst preparation**

102 According to previous investigations of Cu/ZnO/Al₂O₃ catalyst for methanol synthesis, the ideal Cu
103 to Zn ratio was around 70:30, while the optimum Al concentration ranges from 1 – 4 wt% [20–22].
104 However, due to the unconventional composition of BPS as a feedstock for methanol synthesis, an
105 in-house Cu/ZnO/Al₂O₃ catalyst was designed with metal composition of Cu/Zn/Al= 68/28/4 wt% to
106 promote Cu dispersion and thermal stability. A higher Al concentration can also enhance the
107 homogeneous element distribution of the final catalyst [21,23]. The catalyst was prepared by the co-
108 precipitation method. Appropriate concentrations of metal nitrates were dissolved in deionised (DI)
109 water under magnetic stirring, and the temperature was kept at 65 °C. At the same time, Na₂CO₃ was
110 dissolved in DI water simultaneously to obtain a 1M solution. The mixed metal nitrates solution and
111 Na₂CO₃ precipitant were parallelly dropped into a magnetically stirred beaker containing 300 mL of
112 DI water by two peristaltic pumps. The temperature and pH of the mixed slurry were controlled to be
113 65 °C and 6.5, respectively. The obtained slurry was aged for 120 min under magnetic stirring.
114 Subsequently, the solid was filtered and washed with hot DI water (300 mL g_{cat}⁻¹). The suspension
115 was dried in an oven overnight at 90 °C. The dried precursor was crushed and sieved to pass 125 µm.
116 Finally, the powder precursor was calcined in a muffle furnace at 350 °C, with a heating rate of 2 °C
117 min⁻¹ for 5 h. The catalyst was labelled CZA.

118 **2.3 Catalysts characterisation**

119 The Cu, Zn and Al ratios in the catalysts were determined using a Thermo Scientific iCAP 7400 Duo
120 Inductively Coupled Plasma Optical Emission Spectrometer (ICP-OES). Approximately 0.05 g of the
121 catalyst was fused in 0.3 g of lithium metaborate/tetraborate flux in a platinum crucible at 1000 °C.
122 The fused bead was dissolved in 50 mL of 10% hydrochloric acid. Before analysis, an aliquot of the
123 sample was further diluted 10x using 5% HNO₃. Samples were analysed at RF power of 1250 Hz in
124 radial and axial view using a V-groove nebuliser and a cyclonic spray chamber at a nebulising flow
125 rate of 0.65 mL min⁻¹, with an online internal standard (Y and Lu 5ppm). Calibration standards were
126 prepared from synthetic stock in 5% HNO₃ and matrix-matched to the fused samples by adding an

equivalent of fusion blank. Certified reference materials OREAS 43p, NIST694 (Western phosphate rock), and NIST1633C (Fly ash) were used as the standard reference material to ensure analytical accuracy. The analysis included three replicate samples, three duplicate samples and a procedural blank to ensure reproducibility. Analytical precision was good, with relative standard deviations (RSD) on the duplicates typically <1%.

The surface area, pore volume and pore diameter of the catalysts were acquired using the Micromeritics Tristar II instrument at -196 °C. Before measurement, catalyst samples were degassed at 200 °C for 12 h under a vacuum. Multi-point BET analysis of the nitrogen adsorption isotherm was applied to calculate the specific surface area in the range of $p/p_0 = 0.2 - 0.5$, and the pore volume determined by adsorption at $p/p_0 = 0.995$.

X-ray diffraction (XRD) was carried out on a Malvern Panalytical Aeris XRD equipped with a Co $K\alpha$ ($\lambda=1.78901$ Å) radiation source at 40 kV and 15 mA to examine the crystallographic structure of the catalysts. The pattern was collected at a continuous scanning rate of $0.04^\circ \text{ s}^{-1}$ over a 2θ range of 20 to 79° . Xpert Highscore software was used to analyse the powder spectra and identify minerals. Without accounting for instrumental broadening effects and assuming isotropic crystallites, the average size of the crystallites of the catalyst samples was estimated using the full width at half maximum (FWHM) of peaks fit to the XRD spectrum from the Scherrer equation (Eq. 2).

$$D = 0.9\lambda/\beta\cos\theta \quad (2)$$

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

The nitrous oxide (N_2O) dissociative chemisorption technique [24–26] was used to determine the exposed copper surface area (SA_{Cu}) and copper dispersion (D_{Cu}). The chemisorption analysis was conducted using Quantachrome ChemBET PULSAR TPR/TPD equipped with a thermal conductivity detector (TCD). The catalysts (~ 0.1 g) were first reduced in 10 v/v% H_2/N_2 mixture (20 mL min^{-1}) for 60 minutes at 250°C (ramp: $10^\circ \text{C min}^{-1}$), and the moles of consumed H_2 were denoted as n_1 . The

152 samples were cooled to 50 °C under helium flow, and then exposed to 5 v/v% N₂O/He mixture (30
 153 mL min⁻¹) for 60 minutes at 50 °C before being purged with helium for 30 minutes. Similarly, the
 154 second reduction was applied to the catalyst samples in 10 v/v% H₂/N₂ mixture (20 mL min⁻¹) for 60
 155 minutes at 400 °C (ramp: 10 °C min⁻¹), and the moles of consumed H₂ were denoted as n₂. The
 156 exposed surface area (S_{Cu}) and dispersion (D_{Cu}) of Cu were calculated using Eq. (3) and (4).

$$157 \quad SA_{Cu}(m^2 g^{-1}) = (2 n_2 \times N) / (1.47 \times 10^{19} \times m) \quad (3)$$

$$158 \quad D_{Cu}(\%) = 100 \times 2 n_2 / n_1 \quad (4)$$

159 where N is Avogadro's constant (6.022×10²³ atoms mol⁻¹), 1.47×10¹⁹ is the number of metallic Cu
 160 atoms per square meter, and m is the amount of catalyst (g).

161 The specific surface area of Cu (S_{Cu}) was used to calculate the average particle size of Cu (d_{Cu}) with
 162 a spherical particle model according to Eq. (5) [27,28].

$$163 \quad d_{Cu}(m) = 6 / \rho_{Cu} \times S_{Cu} \quad (5)$$

164 where ρ_{Cu} is the density of metallic copper (8960 kg m⁻³) and S_{Cu} is the specific surface area of copper
 165 (m² g⁻¹).

166 Meanwhile, a laser diffraction particle size analyser (Malvern Panalytical, Mastersizer 3000E) was
 167 used to determine the particle size distributions (PSD) of the catalysts. The PSD analysis was
 168 performed in ultrapure water under ultrasound treatment with obscuration ≤ 5%.

169 The reducibility of the catalysts was obtained through a hydrogen temperature-programmed reduction
 170 (H₂-TPR) experiment using a Quantachrome ChemBET PULSAR TPR/TPD equipped with a thermal
 171 conductivity detector (TCD). Specifically, the sample (~0.1 g) was heated from room temperature to
 172 200 °C at 10 °C min⁻¹, held for 60 minutes to remove adsorbed water, and then cooled down to 50 °C
 173 in an N₂ flow (high purity, 19 mL min⁻¹). H₂ reduction was then performed in the gas environment of
 174 a 5 v/v% H₂/N₂ mixture (20 mL min⁻¹). The sample was heated to 380 °C at a heating rate of 10 °C

175 min⁻¹ and held for 60 min. Then, the catalyst bed was purged with an N₂ flow until it was cooled to
176 50 °C.

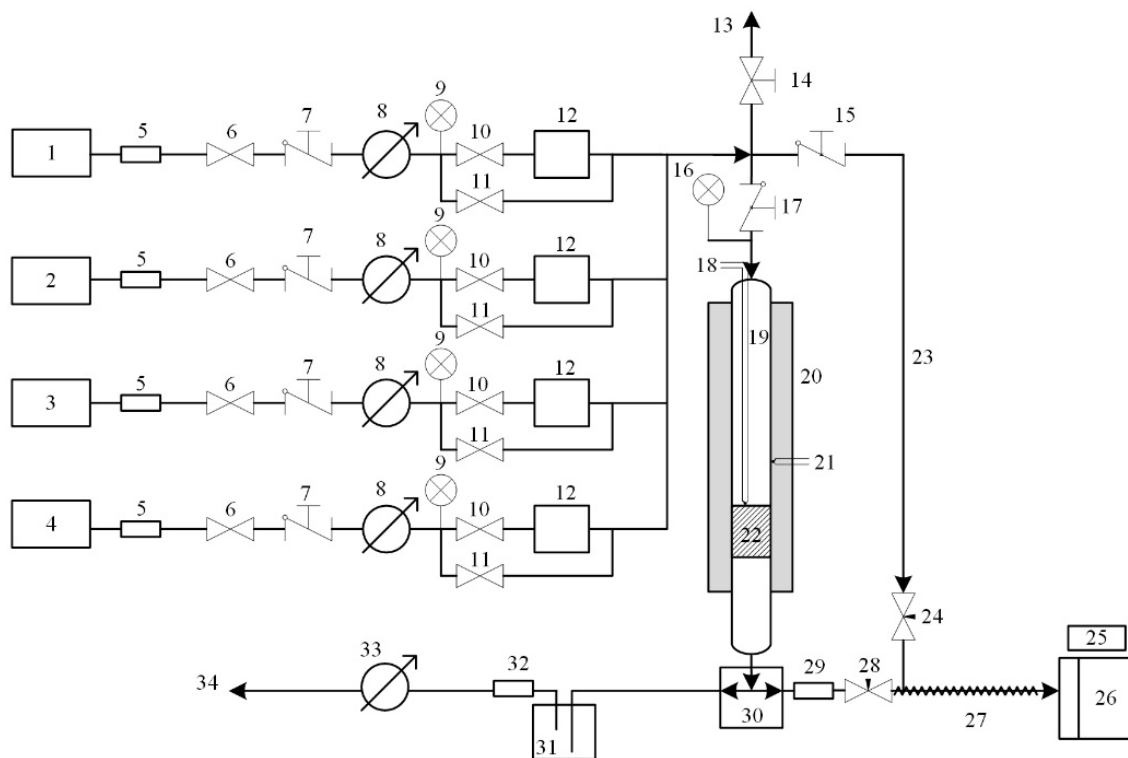
177 X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific Nexsa Surface
178 Analysis System equipped with a hemispherical analyser. The incident radiation was monochromatic
179 Al K α X-rays (1486.6 eV) at 72 W (6 mA and 12 kV, 400 $\times$ 800 μ m² spot). Survey (wide) and high-
180 resolution (narrow) scans were recorded at analyser pass energies of 150 and 50 eV and step sizes of
181 1.0 eV and 0.1 eV, respectively. The base pressure in the analysis chamber was less than 5.0×10^{-9}
182 mbar. A low-energy dual-beam (ion and electron) flood gun was used to compensate for surface
183 charging. Data processing was carried out using Avantage software (V5.9931), and the energy
184 calibration was referenced to the main line of C 1s at 284.8 eV. The background used for curve fitting
185 was Smart.

186 ***2.4 Evaluation of catalytic performance***

187 The catalyst activity tests were performed in a high-pressure fixed-bed reactor system (Figure 1).
188 Approximately 1.5 g of catalyst was placed into a stainless-steel reactor (10 mm internal diameter
189 and 600 mm length). Before the reaction, the catalyst was reduced at 250 °C with a heating rate of
190 5 °C min⁻¹ at atmospheric pressure for 4 h in a 50 mL min⁻¹ flow of 10% H₂ in N₂. After the reduction,
191 the reactor temperature was cooled to below 50 °C. The gas environment was then switched to model
192 BPS at gas hourly space velocity (GHSV) of 2000 h⁻¹, and the reactor pressure was elevated to the
193 desired value of 2 - 4 MPa, controlled by an electronic back pressure controller. The reactor
194 temperature was then increased to the targeted value of 220 - 260 °C at a heating rate of 5 °C min⁻¹.

195 The effluent was sampled at different times on stream and analysed using an online Agilent 7890A
196 Gas Chromatograph (GC), which is equipped with a thermal conductivity detector (TCD) connected
197 to a TDX-01 column and a flame ionisation detector (FID) connected to an HP-PLOT/Q column. The
198 effluent gas sampling line was maintained at 120 °C to prevent condensation during analysis. CH₃OH
199 and hydrocarbons were analysed on the HP-PLOT/Q column, whereas the TDX-01 column was used

200 to measure H₂, CO, CH₄, and CO₂ with N₂ as the internal standard. The conversion of feed (X_{Gas}),
 201 the mole fraction of gas containing effluent gas (mf_{Gas}), the methanol selectivity (S), and the space-
 202 time yield of methanol (STY) were computed according to the Eqs. (6) - (9).



204 Figure 1. A schematic of the catalytic activity test apparatus. 1. Gas cylinder 1%O₂ in N₂; 2. Gas
 205 cylinder H₂; 3. Gas cylinder N₂; 4. Gas cylinder premixed syngas; 5. Filter; 6. Ball
 206 valve; 7. One way valve; 8. Pressure regulator; 9. Pressure indicator; 10. Ball valve;
 207 11. Ball valve; 12. Mass flow controller; 13. To vent; 14. One way valve; 15. One way
 208 valve; 16. Pressure indicator; 17. One way valve; 18. Reactor's thermocouple; 19.
 209 Reactor; 20. Electric heater; 21. Heater's thermocouple; 22. Catalyst bed; 23. Bypass
 210 feed line; 24. Needle valve; 25. PC; 26. GC; 27. Heat trace line; 28. Needle valve; 29.
 211 Filter; 30. Heating box; 31. Condenser; 32. Filter; 33. Electronic back pressure; 34. To
 212 vent.

$$213 \quad X_{Gas} = \frac{\frac{Gas_{in}}{N2_{in}} - \frac{Gas_{out}}{N2_{out}}}{\frac{Gas_{in}}{N2_{in}}} \times 100\% \quad (6)$$

Gas_{in} and Gas_{out} are the peak area of H₂, CO, CO₂, and CH₄ in the TCD chromatograms before and after the reaction.

$$mf_{Gas(i)} = \frac{\text{mole of gas}_{(i)}}{\text{mole of effluent gas}} \times 100\% \quad (7)$$

The mole of gas is the mole of a particular gas (i)= H₂, CO, and CH₃OH, whereas the mole of the effluent gas is the total mole of all compounds detected by the TCD and FID detector.

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

$$STY = \frac{[\text{mass of CH}_3\text{OH}]}{[\text{mass of catalyst}] \times [\text{time}]} \quad (9)$$

Once the target time on stream (TOS) was reached, the reactor was returned to atmospheric temperature and pressure under an N₂ flow of 50 mL min⁻¹. Subsequently, the spent catalyst was passivated using 1% O₂ in N₂ at 50 mL min⁻¹ for 5 h to prevent rapid oxidation when exposed to the atmosphere (pyrophoric). The spent catalyst was safely discharged from the reactor and stored in a vacuumed desiccator.

3. Results and Discussion

3.1 Calcined catalysts characterisation

Table 1 Chemical compositions and physiochemical properties of Cu/ZnO/Al₂O₃ catalysts

Catalyst	Cu/Zn/Al (wt%)		N ₂ adsorption/desorption			N ₂ O chemisorption		
	Designed	ICP-OES	SA _{BET} ^a	V _p ^b	d _p ^c	SA _{Cu} ^d	D _{Cu} ^e	d _{Cu} ^f
			(m ² g ⁻¹)	(cm ³ g ⁻¹)	(nm)	(m ² g ⁻¹)	(%)	(nm)
HUC-98	-	65.3/26.2/8.5	89	0.2	9.5	42.1	30.9	15.9
CZA	68/28/4	70.9/25.1/4.0	84	0.3	15.1	48.0	34.4	13.9

^a Surface area BET from N₂ physisorption analysis.

^b Total pore diameter.

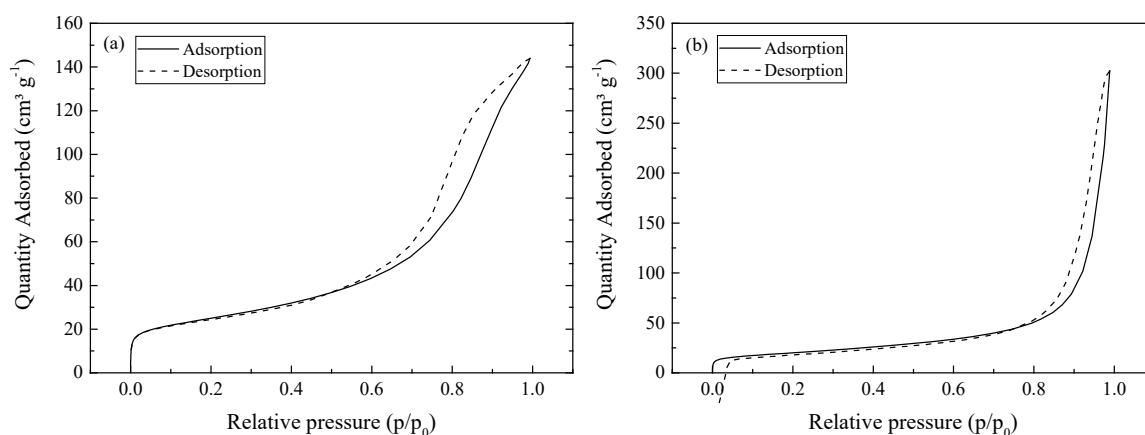
^c Average pore diameter.

^d Copper surface area from N₂O chemisorption measurements.

^e Copper dispersion.

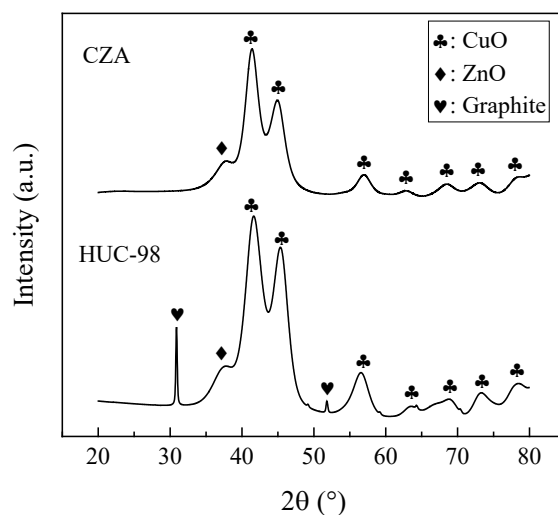
^f Average copper particle size.

235 The precise concentrations of Cu, Zn and Al-containing HUC-98 and CZA catalysts were examined
 236 by ICP-OES, as indicated in Table 1, and were found to be within the range of expected values. Figure
 237 2 depicts the N₂ adsorption-desorption isotherms of the calcined catalysts. Following the IUPAC
 238 classification, the isotherms of all samples are Type-IV with H3-type hysteresis loops, indicating
 239 mesoporous materials with slit-like pores that suggest homogeneous dispersion of metal oxides [29–
 240 31]. The physical characteristics of the calcined catalysts are detailed in Table 1. The analysis was
 241 conducted three times, and the standard deviation of the BET surface area was less than 3.0.



242
 243 Figure 2 N₂ adsorption-desorption isotherms of calcined catalysts: (a) HUC-98 and (b) CZA.

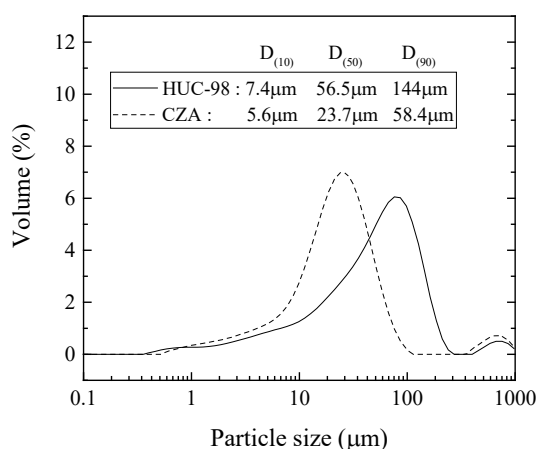
244 XRD was used to investigate the crystallinity of the catalysts, and the XRD pattern of the calcined
 245 catalysts is shown in Figure 3. The diffraction peaks at 2θ values of 41.2° , 45.05° , and 57.1°
 246 correspond to CuO, whereas the peak at 2θ value of 36.9° relates to ZnO. The centred peak at 31.1°
 247 in calcined catalyst HUC-98 was attributed to graphite, typically used as the catalyst binder [32].
 248 According to the Scherrer equation calculation, the CuO crystallite sizes of calcined HUC-98 and
 249 CZA were 6.27 and 5.77 nm, respectively. This result demonstrates that all the synthesised materials
 250 contain copper and zinc oxides. No peaks were associated with alumina, indicating that this low-
 251 concentration promoter was amorphous.



252

253 Figure 3 XRD patterns of calcined catalysts.

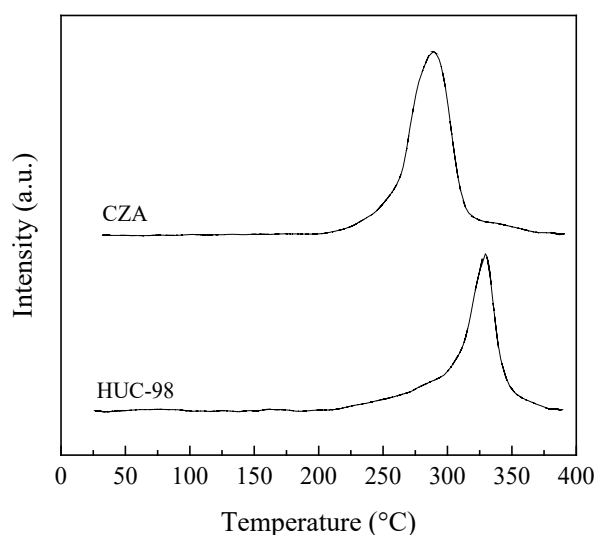
254 The metallic copper surface area (SA_{Cu}), dispersion (D_{Cu}), and particle size (d_{Cu}) were estimated
 255 using N_2O chemisorption data. The N_2O chemisorption data (Table 1) shows that the CZA catalyst
 256 has a larger copper surface area and copper dispersion but a smaller copper particle size than HUC-
 257 98. Therefore, it is expected that the CZA catalyst would be able to provide more catalytically active
 258 sites with high dispersion and high exposed copper surface area. Moreover, as depicted in Figure 4,
 259 the particle size distributions of the catalysts obtained from the Laser Diffraction Mastersizer particles
 260 size analysis show that the CZA catalyst has smaller aggregates than HUC-98 at all percentiles (D_{10} ,
 261 D_{50} , and D_{90}), where the mean diameters for catalysts CZA and HUC-98 are 23.7 μm and 56.5 μm ,
 262 respectively.



263

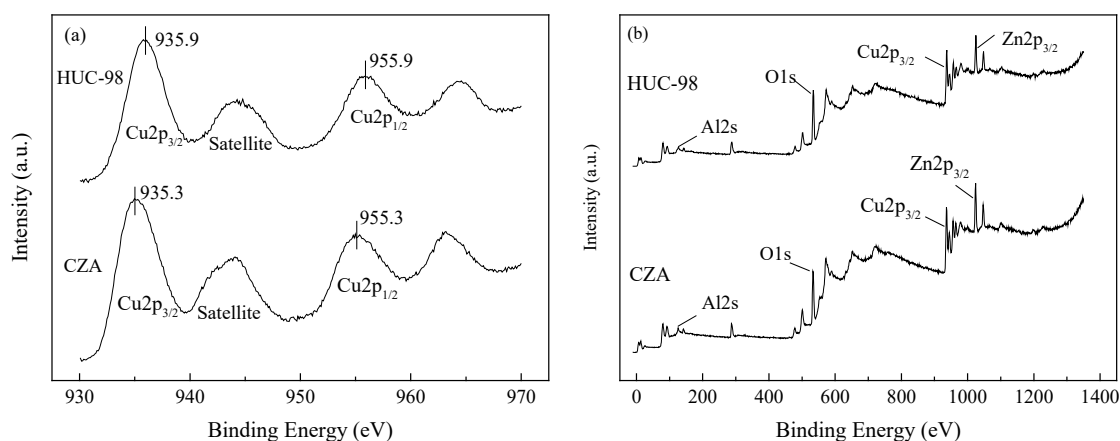
264 Figure 4. Particle size distribution of calcined catalysts.

265 The reducibility of copper in calcined catalysts HUC-98 and CZA was examined with an H₂-TPR
 266 experiment, shown in Figure 5. The reduction peak corresponds to copper oxides reduction ($\text{CuO} \rightarrow$
 267 $\text{Cu}_2\text{O} \rightarrow \text{Cu}$) [33]. The H₂-TPR peak temperature value of CZA (290 °C) was lower than the HUC-
 268 98 (330 °C), which can be associated with smaller copper particles of CZA compared to HUC-98
 269 [34,35]. This result agrees with those obtained by previous XRD and N₂O chemisorption (Table 1)
 270 techniques. All catalysts demonstrated H₂-TPR profiles with one single and clear reduction peak. It
 271 represents an evenly distributed microstructure of copper particles in all catalysts [36]. In addition,
 272 no further reduction beyond 390 °C was observed, which aligns with previous research reported
 273 elsewhere [37,38].



274
 275 Figure 5. H₂-TPR profiles of the calcined catalysts.

276 XPS profiles of the calcined catalysts were evaluated to determine the chemical state of the Cu
 277 species, and the spectra are shown in Figure 6(a). Peaks corresponding to the Cu2p_{3/2} and Cu2p_{1/2}
 278 located at 935 eV and 955 eV and satellite peaks at around 942 - 944 eV indicate the dominance of
 279 Cu²⁺ in the calcined samples [39,40]. As shown in Figure 6(b), the Zn2p_{3/2} for all catalysts had binding
 280 energy of approximately 1024 eV, demonstrating an oxidation state of +2 [41], as suggested by the
 281 XRD. Peaks at a binding energy of 114 eV and 534 eV also indicated the existence of Al2s and O1s
 282 in the calcined catalysts, agreeing with results from ICP-OES.



283

284 Figure 6. XPS Spectra of calcined catalysts: (a) Cu2p (b) Survey.

285 3.2 Effect of temperature and pressure on feed conversion and methanol productivity

286 Figure 7 depicts the feed conversion, its mole fraction at the effluent gas, and the selectivity and
 287 space-time yield (STY) of methanol as a function of temperature and pressure, after 6 h time on
 288 stream (TOS). It was found that low temperature and high pressure favoured H₂ and CO conversion,
 289 methanol selectivity, and methanol formation. All catalysts exhibited a decrease in H₂ and CO mole
 290 fraction in the effluent, suggesting that the production of methanol from the simulated BPS was likely
 291 through the hydrogenation of CO [42–44]. In contrast, CH₄ and CO₂ were produced under all reaction
 292 conditions, which is favoured at higher pressures. While methane and higher hydrocarbons are known
 293 by-products of methanol synthesis and CO hydrogenation, CO₂ production is most likely the result
 294 of the water-gas shift reaction [45–47].

295 Overall, the differences in methanol formation and conversions of H₂ and CO obtained over HUC-
 296 98, and CZA catalysts were insignificant (less than 2%). However, at 220 °C, the activity of the CZA
 297 catalyst was noticeably higher than HUC-98. Under reaction conditions of 220 °C and 3 MPa, the
 298 conversion of H₂, CO, and methanol yield obtained over CZA were 42.2%, 21.5%, and 0.139 g g_{cat}⁻¹
 299 h⁻¹, respectively. Under the same process conditions, the results obtained over HUC-98 were 13.4%
 300 H₂ conversion, 5.6% CO conversion, and 0.038 g g_{cat}⁻¹ h⁻¹ methanol STY. This observation may be
 301 associated with the easy reducibility of catalyst CZA compared to HUC-98, which is signified by
 302 smaller CuO particles and finely dispersed copper of CZA catalyst [35,48]. Nonetheless, the highest

methanol yield of $0.179 \text{ g g}_{\text{cat}}^{-1} \text{ h}^{-1}$ was obtained from the HUC-98 catalyst at 240°C and 4 MPa reaction conditions. Therefore, this condition was then used for the longevity test of the catalysts with a constant gas hourly space velocity (GHSV) of 2000 h^{-1} .

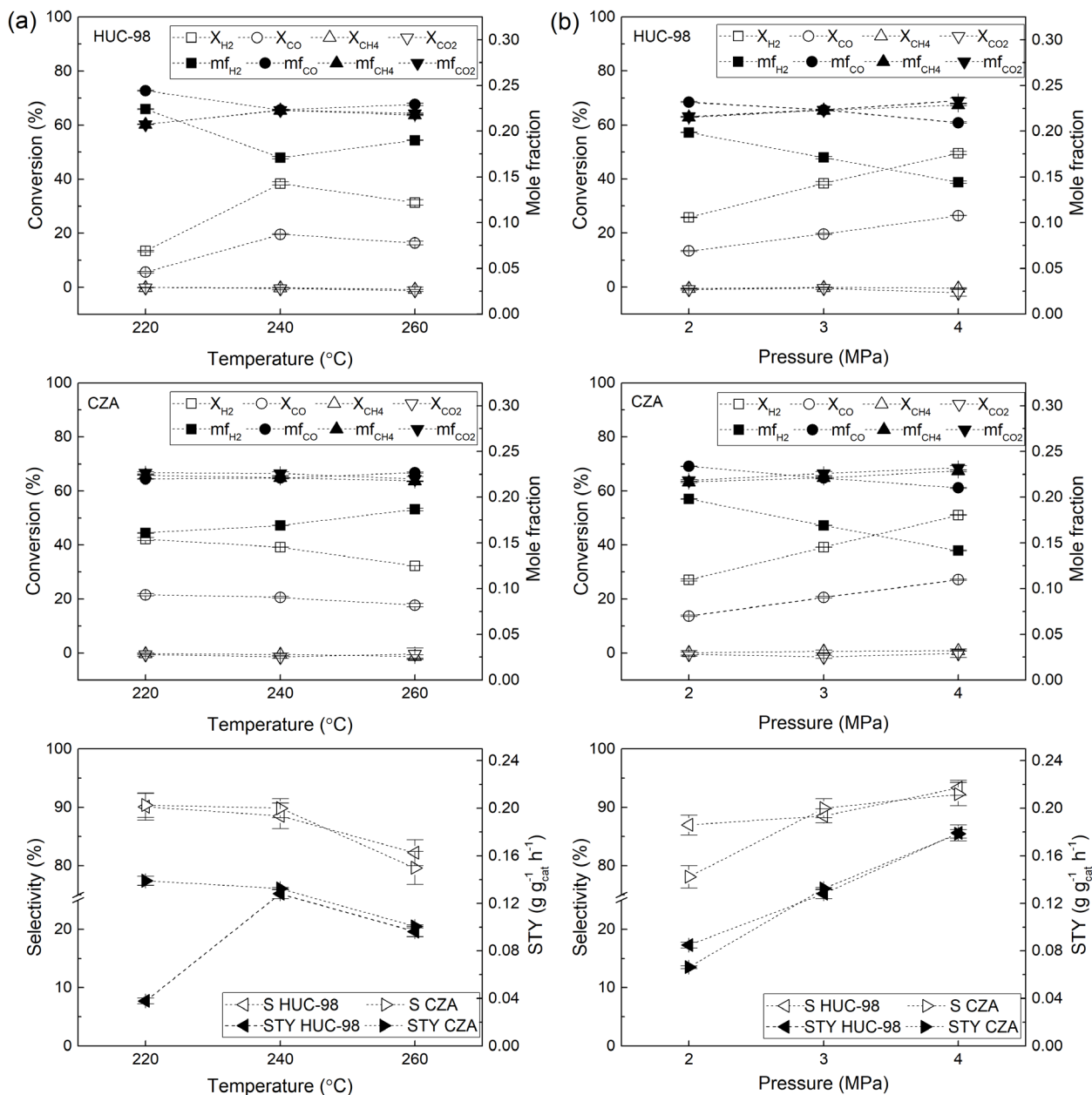


Figure 7. The effect of temperature and pressure on feed conversion and effluent-containing gases: (a) Effect of temperature, $P = 3 \text{ MPa}$ (b) Effect of pressure, $T = 240^\circ\text{C}$. Error bars represent the standard deviation from three times repeated measurements.

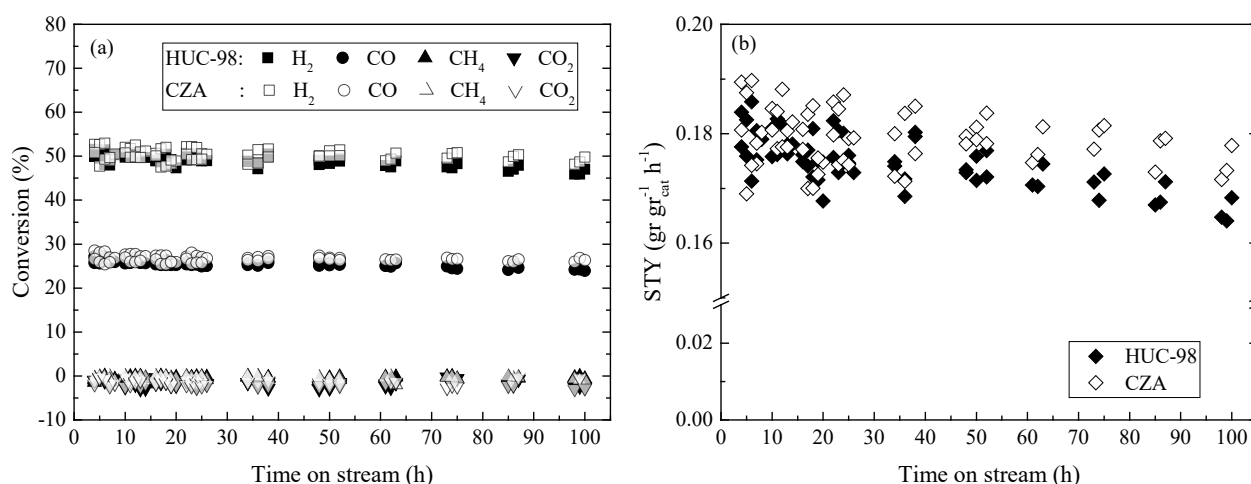


Figure 8. Feed conversion (a) and STY of methanol (b) with the TOS of 100 h. Reaction condition: T= 240 °C, P= 4 MPa, GHSV= 2000 h⁻¹.

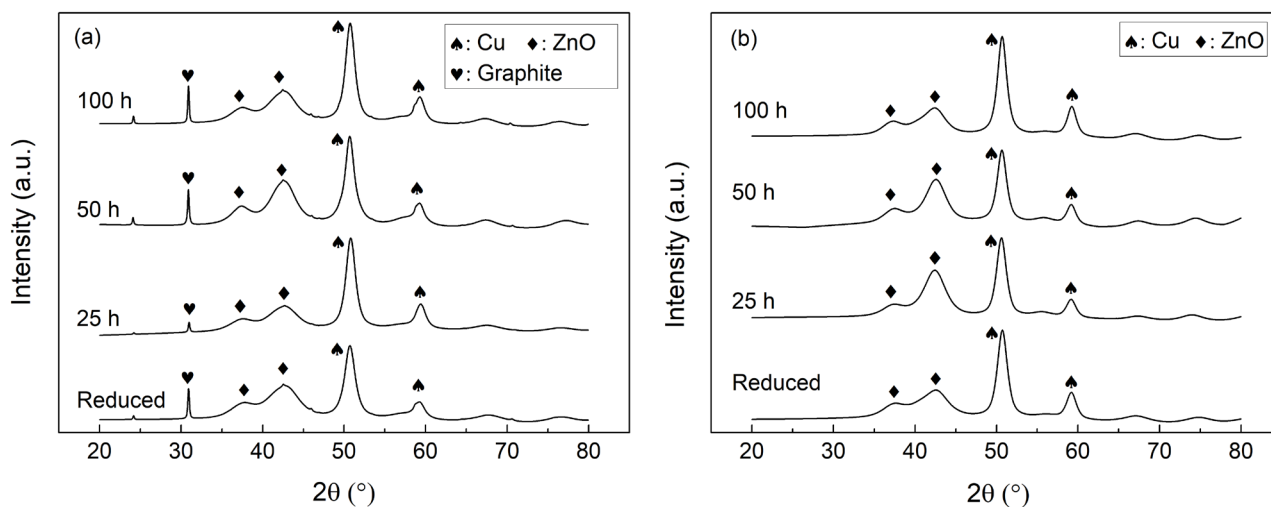
3.3 Longevity test

The feed conversion and the STY of methanol obtained over HUC-98 and CZA catalysts during methanol synthesis from BPS with a TOS of 100 h are presented in Figure 8. Overall, the conversion of H₂ and CO obtained over the two catalysts slightly decreased with the increase of TOS yet remained stable and showed no significant trend for CH₄ and CO₂ (Figure 8a). After 30 h on stream, the commercial catalyst of HUC-98 experienced a relatively rapid decrease in the conversion of H₂ and CO compared to the CZA catalyst. As a result, the initial STY of methanol at 10 h of TOS for the two catalysts, around 0.185 g g_{cat}⁻¹ h⁻¹, decreased to 0.168 and 0.177 g g_{cat}⁻¹ h⁻¹ after 100 h on stream for catalysts HUC-98 and CZA, respectively (Figure 8b). These results indicate that the deactivation of the catalysts occurred during the 100 h TOS.

3.4 Catalysts deactivation

The catalyst structure and chemistry were systematically examined at a different TOS to investigate the reasons behind catalyst deactivation during the methanol synthesis from BPS. XRD patterns of the reduced and spent catalysts at different TOS (25 h, 50 h, and 100 h) are shown in Figure 9, in which peaks centred at 37.3° and 42.3° were attributed to ZnO, whereas Cu was ascribed by the peak centred in 50.5° and 59.1°. Even though the graphite diffraction peak is shown in the HUC-98 XRD

329 pattern, graphite will not be discussed further since it is widely regarded as an inert component that
 330 has negligible contribution to catalytic activity [49].



331

332 Figure 9. XRD patterns of reduced and spent catalysts: (a) HUC-98 and (b) CZA.

333 Table 2 Average crystallite sizes of Cu and ZnO species of the reduced and spent catalysts

Samples	Crystallite Size (nm) ^a	
	Cu	ZnO
HUC98-reduced	9.1	2.9
HUC98-25 h	10.0	3.0
HUC98-50 h	10.3	3.5
HUC98-100 h	10.4	3.1
CZA-reduced	9.8	3.1
CZA-25 h	9.9	3.3
CZA-50 h	10.3	3.7
CZA-100 h	10.5	3.6

334

^a Calculated using Scherrer equation.

335 In the meantime, as shown in Table 2, the mean crystallite sizes of Cu and ZnO for HUC-98 and CZA
 336 catalysts increased by extending the reaction time, which might be one of the reasons for the catalyst
 337 deactivation. Generally, agglomeration of Cu and ZnO particles is strongly temperature dependent.

338 However, produced water during methanol synthesis from CO₂-rich syngas may enhance the
 339 crystallisation of Cu and ZnO in the catalyst [50]. The particle sintering decreases the Cu surface area
 340 and active redox sites on ZnO [51], which leads to catalyst deactivation.

341 Table 3 N₂ physisorption analysis of the reduced and spent catalysts

Catalyst	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore diameter (nm)
HUC-98 (reduced)	79	0.2	11.3
HUC-98 (25 h)	71	0.2	11.3
HUC-98 (50 h)	68	0.2	10.9
HUC-98 (100 h)	58	0.2	11.3
CZA (reduced)	75	0.3	16.6
CZA (25 h)	69	0.3	16.2
CZA (50 h)	68	0.3	16.8
CZA (100 h)	60	0.2	16.6

342 The N₂-physisorption analysis of reduced and spent catalysts, as depicted in Table 3, shows that the
 343 BET surface area and the pore volume of the spent catalysts decreased with TOS, while the pore
 344 diameter fluctuated. The decrease in BET surface area can be considered one of the reasons for the
 345 catalyst deactivation because it plays a vital role in determining the activity of the catalyst for
 346 methanol synthesis. A higher specific surface area may give more active sites for the reaction, and in
 347 turn increase catalytic activity [52–54]. The decreasing surface area of the catalysts can be associated
 348 with the increase of Cu crystallite size due to Hüttig temperature of copper, the temperature at which
 349 surface atoms become considerably mobile (134 °C), which is much lower than the reaction
 350 temperature (240 °C). Moreover, since methanol synthesis is an exothermic reaction, the high
 351 temperature generated as part of the reaction advances the mobility of Cu atoms, which leads to
 352 sintering [49,55].

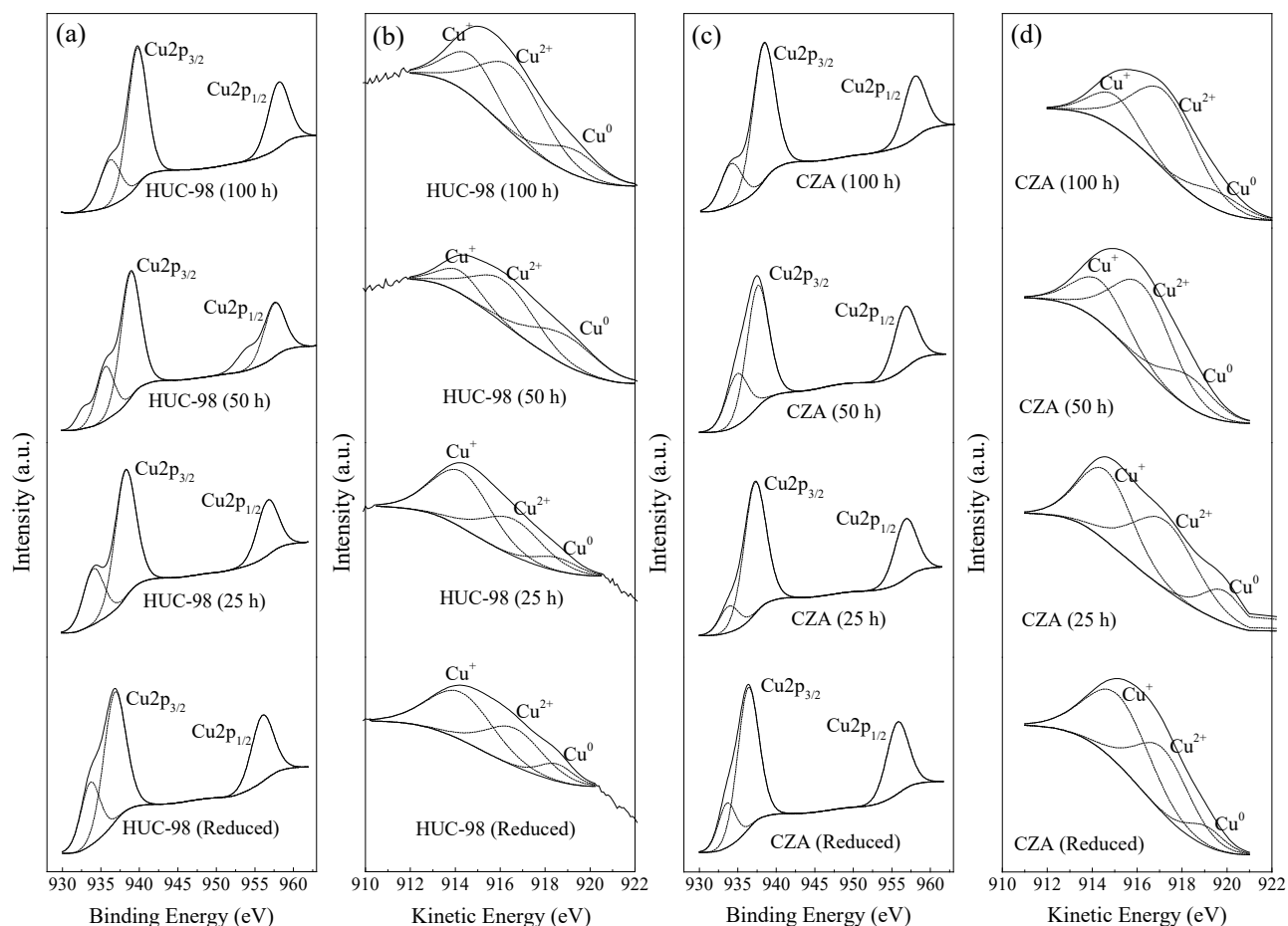


Figure 10. XPS spectra of the catalysts (a) Cu2p HUC-98 (b) Cu LMM HUC-98 (c) Cu2p CZA (d) Cu LMM CZA.

XPS spectra results of the reduced and spent catalysts, as shown in Figures 10a and c, further highlight the Cu species transition of the catalysts during the methanol synthesis. All the reduced catalysts exhibited Cu2p_{3/2} peaks at 930 – 940 eV and Cu2p_{1/2} at 950-960 eV. The decreasing intensity/absence of the satellite peak at 942 – 944 eV implies that the Cu²⁺ species were reduced to Cu⁰ and/or Cu⁺. The existence of the reduced Cu species is in good agreement with the XRD measurements of the reduced and spent catalysts (Figure 9). Due to the high degree of overlap between the binding energy of Cu⁺ and Cu⁰ in the deconvolution of Cu2p_{3/2} [56], the auger electron spectra of Cu LMM was used to determine the relative surface concentrations of Cu⁺ and Cu⁰, and reported as kinetic energy. The spectra were deconvoluted into three overlapping peaks at 914.2, 916.8 and 918.5 eV (Figure 10b and d), which correspond to Cu⁺, Cu²⁺, and Cu⁰ [57–59].

367 Table 4 Curve-fittings of Cu₂p_{3/2} and Cu LMM of the catalysts

Samples	Surface content, ^a (%)		$\text{Cu}^{2+} / (\text{Cu}^0 + \text{Cu}^+)$	Surface content, ^b (%)			$\text{Cu}^0 / \text{Cu}^+$
	Cu^{2+}	$\text{Cu}^0 + \text{Cu}^+$		Cu^+	Cu^{2+}	Cu^0	
HUC98-reduced	25.7	74.3	0.4	51.9	28.9	19.2	0.4
HUC98-25 h	32.4	67.6	0.5	50.1	33.2	16.7	0.3
HUC98-50 h	60.7	39.3	1.6	29.0	61.8	9.2	0.3
HUC98-100 h	65.4	34.6	1.8	27.4	64.5	8.1	0.3
CZA-reduced	38.1	61.9	0.6	40.6	36.5	22.9	0.6
CZA-25 h	49.2	50.8	0.9	34.9	46.2	18.9	0.5
CZA-50 h	61.3	38.7	1.7	24.3	63.3	12.4	0.5
CZA-100 h	65.8	34.2	2.0	22.4	67.1	10.5	0.5

368 ^a Surface content calculated from Cu₂p_{3/2}, ^b Surface content calculated from Cu LMM.

369 The calculated and deconvoluted Cu species oxidation state on the catalyst's surface is shown in
 370 Table 4. The value of $\text{Cu}^{2+}/(\text{Cu}^0 + \text{Cu}^+)$ increased significantly from 0.4 and 0.6 at the reduced
 371 condition to 1.8 and 2.0 after 100 h reaction for catalysts of HUC-98 and CZA, respectively. In other
 372 words, the oxidation degree of the Cu species was increased by prolonging the reaction time, where
 373 Cu^0 and Cu^+ were oxidised and formed Cu^{2+} during the reaction. It is most probably due to the high
 374 concentration of CO₂ in the syngas, which creates an oxidising atmosphere [60]. The amount of Cu^{2+}
 375 might be affected by the re-oxidation through passivation treatment that creates thin and protective
 376 oxide layer. However, the effect of re-oxidation is considered insignificant since oxygen atoms do
 377 not migrate into the bulk of the copper particles [61,62].

378 The Cu^0/Cu^+ continuously decreased with extended TOS, which is consistent with the activity results
 379 of the catalysts. The Cu^0/Cu^+ was higher in CZA than the HUC-98 commercial catalyst, which was
 380 probably explained by why the activity of catalyst CZA is more stable than HUC-98 during the
 381 longevity test. Higher Cu^0/Cu^+ in the CZA catalyst might be associated with easier reducibility in the
 382 TPR experiment, indicating that more metallic Cu are exposed on the surface of the catalyst [63] and

383 fined Cu dispersion [41]. Metallic copper (Cu^0) is considered the active component in the Cu-based
384 catalyst for methanol synthesis [64,65]. These results suggest that the oxidation of the Cu species was
385 the main factor for the deactivation of catalysts in methanol synthesis from BPS.

386 4. Conclusions

387 A commercial and an in-house prepared Cu/ZnO/Al₂O₃ catalysts were tested for direct synthesis of
388 methanol from a model biomass pyrolysis syngas (BPS). Methanol yield, feed conversion, selectivity
389 and catalyst deactivation were examined as a function of temperature, pressure and time on stream
390 (TOS). Methanol was successfully synthesised over the Cu/ZnO/Al₂O₃ catalysts at a maximum STY
391 of 0.185 g g_{cat}⁻¹ h⁻¹. CO hydrogenation was the main route for methanol synthesis. High pressure and
392 low temperature favoured CO and H₂ conversion and methanol formation. Inevitably the catalysts
393 became deactivated as the TOS increased, which is attributed to the high CO₂ concentration in the
394 BPS causing Cu oxidation. While there was no evidence suggesting that CH₄ in the BPS affects the
395 catalytic performance, Cu oxidation and the agglomeration of Cu and ZnO were identified as the main
396 reasons for the catalyst deactivation.

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614 **Figure Captions**

615 Figure 1. A schematic of the catalytic activity test apparatus. 1. Gas cylinder 1%O₂ in N₂; 2. Gas
616 cylinder H₂; 3. Gas cylinder N₂; 4. Gas cylinder premixed syngas; 5. Filter; 6. Ball valve;
617 7. One way valve; 8. Pressure regulator; 9. Pressure indicator; 10. Ball valve; 11. Ball
618 valve; 12. Mass flow controller; 13. To vent; 14. One way valve; 15. One way valve; 16.
619 Pressure indicator; 17. One way valve; 18. Reactor's thermocouple; 19. Reactor; 20.
620 Electric heater; 21. Heater's thermocouple; 22. Catalyst bed; 23. Bypass feed line; 24.
621 Needle valve; 25. PC; 26. GC; 27. Heat trace line; 28. Needle valve; 29. Filter; 30. Heating
622 box; 31. Condenser; 32. Filter; 33. Electronic back pressure; 34. To vent.

623 Figure 2. N₂ adsorption-desorption isotherms of calcined catalysts: (a) HUC-98 and (b) CZA.

624 Figure 3 XRD patterns of calcined catalysts.

625 Figure 4 Particle size distribution of calcined catalysts.

626 Figure 5. H₂-TPR profiles of the calcined catalysts.

627 Figure 6. XPS Spectra of calcined catalysts: (a) Cu2p (b) Survey.

628 Figure 7. The effect of temperature and pressure on feed conversion and effluent-containing
629 gases: (a) Effect of temperature, P= 3 MPa (b) Effect of pressure, T= 240 °C. Error bars
630 represent the standard deviation from three times repeated measurements.

631 Figure 8. Feed conversion (a) and STY of methanol (b) with the TOS of 100 h. Reaction
632 condition: T= 240 °C, P= 4 MPa, GHSV= 2000 h⁻¹.

633 Figure 9. XRD patterns of reduced and spent catalysts: (a) HUC-98 and (b) CZA.

634 Figure 10. XPS spectra of the catalysts (a) Cu2p HUC-98 (b) Cu LMM HUC-98 (c) Cu2p CZA (d)
635 Cu LMM CZA.

636

637 **List of Tables**

638 Table 1 Chemical compositions and physiochemical properties of Cu/ZnO/Al₂O₃ catalysts

639 Table 2 Average crystallite sizes of Cu and ZnO species of the reduced and spent catalysts

640 Table 3 N₂ physisorption analysis of the reduced and spent catalysts

641 Table 4 Curve-fittings of Cu2p_{3/2} and Cu LMM of the catalysts

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A preliminary attempt of direct methanol synthesis from biomass pyrolysis syngas over Cu/ZnO/Al₂O₃ catalysts

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