

Catalytic Performance of Cu/ZnO/Al₂O₃/ZrO₂ for Slurry Methanol Synthesis from CO₂ Hydrogenation: Effect of Cu/Zn Molar Ratio

(Prestasi Pemangkinan Cu/ZnO/Al₂O₃/ZrO₂ untuk Sintesis Metanol Sluri daripada Penghidrogenan CO₂: Kesan Nisbah Molar Cu/Zn)

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ABSTRACT

Catalytic hydrogenation of carbon dioxide (CO₂) to methanol is an attractive way to recycle and utilize CO₂. A series of Cu/ZnO/Al₂O₃/ZrO₂ catalysts (CZAZ) containing different molar ratios of Cu/Zn were prepared by the co-precipitation method. The catalysts were characterized by temperature-programmed reduction (TPR), field emission scanning electron microscopy-energy dispersive x-ray analysis (FESEM-EDX) and X-ray diffraction (XRD). Higher surface area, SA_{BET} values (42.6-59.9 m²/g) were recorded at low (1) and high (5) Cu/Zn ratios with the minimum value of 35.71 m²/g was found for a Cu/Zn of 3. The reducibility of the metal oxides formed after calcination of catalyst samples was also affected due to change in metal-support interaction. At a reaction temperature of 443 K, total gas pressure of 3.0 MPa and 0.1 g/mL of the CZAZ catalyst, the selectivity to methanol decreased as the Cu/Zn molar ratio increased, and the maximum selectivity of 93.9 was achieved at Cu/Zn molar ratio of 0.33. With a reaction time of 3h, the best performing catalyst was CZAZ75 with Cu/Zn molar ratio of 5 giving methanol yield of 6.4%.

Keywords: Carbon dioxide; copper; hydrogenation; methanol synthesis; zinc; zirconia

ABSTRAK

Penghidrogenan pemangkin karbon dioksida (CO₂) kepada metanol adalah satu cara yang menarik untuk mengitar semula penggunaan CO₂. Satu siri pemangkin Cu/ZnO/Al₂O₃/ZrO₂ (CZAZ) yang mengandungi nisbah molar Cu/Zn yang berbeza disediakan melalui kaedah pemendakan bersama. Kaedah pencirian yang dijalankan untuk pemangkin adalah melalui kaedah program penurunan suhu berkala (TPR), analisis pengimbas mikroskop pemancaran medan-serakan tenaga sinar-x (FESEM-EDX) dan pembelauan sinar-X (XRD). Luas permukaan tertinggi telah direkodkan iaitu (42.6-59.9 m²/g) pada nisbah Cu/Zn rendah (1) dan tinggi (5) dengan nilai minimum 35.71 m²/g pada nisbah Cu/Zn adalah 3. Kebolehpenerunan oksida logam yang terbentuk selepas sampel pemangkin dikalsinasi juga memberi kesan yang disebabkan oleh penukaran interaksi logam sokongan. Pada suhu tindak balas 443 K, jumlah tekanan gas 3.0 MPa dan 0.1 g/mL pemangkin CZAZ, pemilihan terhadap metanol berkurangan dengan peningkatan nisbah molar Cu/Zn, dan nilai pemilihan maksimum adalah 93.9 terhasil pada nisbah molar 0.33. Dengan masa tindak balas 3 jam, pemangkin dengan prestasi terbaik adalah CZAZ75 dengan nisbah molar 5 memberi hasil metanol 6.4%.

Kata kunci: Karbon dioksida; penghidrogenan; sintesis metanol; tembaga; zink; zirkonia

INTRODUCTION

During the last decade, hydrogenation of carbon dioxide to bulk chemicals like methanol and dimethylether, has been considered as one of the most economical and effective ways to chemically fix huge amount of emitted CO₂. Methanol process typically uses Cu/ZnO/Al₂O₃ (CZA) catalysts and commonly, CO₂ is added with synthesis gas to provide the required stoichiometric conditions of the feed gas by consuming excess hydrogen (Speight 2002). It has been reported that CO behaves as a scavenger of oxygen atoms hampering active metal sites of the catalyst leading to decrease in the activity. At present the conventional CZA catalysts exhibit poor activity for CO₂ hydrogenation, because of water formation and strong hydrophilic character of alumina (Arena et al. 2007). Several authors

have established that copper based catalysts containing zirconia are active in the synthesis of methanol from CO₂ and H₂ (Samson et al. 2014; Ud Din et al. 2016; Witoon et al. 2016; Zhang et al. 2006). Arena (2008) investigated the reaction of CO₂ hydrogenation in a fixed bed reactor on Cu-ZnO/ZrO₂, (ZrO₂ loading, 43 wt. %; Zn/Cu (at/at), 0.0-2.8). Characterization data indicate that ZnO promotes the dispersion and reactivity of metal copper to oxygen, while both ZnO and ZrO₂ support markedly enhance the surface CO₂ adsorption. A synergism of metal Cu hydrogenation and oxide basic sites discloses the primary role of the metal/oxide interface on the functionality of Cu-ZnO/ZrO₂ catalysts in the CO₂ to CH₃OH hydrogenation reaction. da Silva et al. (2016) prepared a Cu/ZrO₂ catalyst series and investigated the influence of the preparation variables on

the catalytic behavior and high activity and selectivity for methanol synthesis from CO₂ hydrogenation have been obtained in their work. However, the zirconia bears the disadvantages of low surface area and poor thermal stability compared to the alumina counterparts. Zhang et al. (2006) addressed this issue by spreading the zirconia in supports with relative higher surface area, such as g-alumina. The effect of zirconia modification of g-Al₂O₃ supported Cu catalyst was tested in a fixed-bed reactor at temperature of 240°C. It was found that the methanol selectivity improved from 16.9 to 20.3% upon 10 wt. % addition of Zr.

Based on the thermodynamic analysis, the methanol production by CO₂ hydrogenation is favourable at low temperature due to the exothermic reaction. Sherwin and Frank (1976) introduced the idea of three-phase methanol synthesis. An inert and high boiling point liquid is utilized as a heat-carrier for the exothermic reactions (Zhang et al. 2016). The advantages of the three-phase reactor system are mild reaction conditions, higher methanol selectivity and higher catalytic activity (Graaf et al. 1996). Brookhaven National Laboratory showed that methanol was highly produced from CO/H₂ at low temperature of 373-403K using a NaH/ tertiary amyl alcohol/Ni(OAc)₂ catalyst (Xu et al. 2009). However, the catalyst is less active and selective in CO₂ hydrogenation to methanol due to the strong basic property of the catalyst which can easily deactivated by traces amount of CO₂ and water. Although numerous papers concerning methanol synthesis from CO₂ and H₂ have already been published, however, few reports on the low-temperature three-phase methanol synthesis. Neither reaction data nor any correlations between the composition of copper-based catalyst containing Cu, Zn Al and Zr and the activity of the hydrogenation of CO₂ in the three-phase reactor system are available in the literature. The specific objective of this study was to assess the effects of Cu/Zn molar ratio of the zirconia-promoted Cu/ZnO/Al₂O₃ catalyst on the physicochemical properties of the catalyst in terms of reducibility, surface area, particle size and their catalytic activities in the three-phase CO₂ hydrogenation process. Catalysts containing copper, zirconia and zinc oxide were chosen, due to the known synergistic effect of Cu and ZnO, and the ability of zirconia to act as a promoter of the methanol synthesis reaction. In addition, alumina has high surface area and we anticipated that it will increase the Cu⁰ active sites and thus improve the activity of Cu/Zn/ZrO₂ catalyst.

EXPERIMENTAL

PREPARATION OF CATALYST

Five catalysts, CZA45, CZAZ30, CZAZ45, CZAZ60 and CZAZ75 were prepared by using co-precipitation procedure reported in Shaharun et al. (2012). CZA was a Cu/Zn/Al (without Zr) catalyst. CZAZ catalysts were Cu/Zn/Al/Zr catalysts with added Zr present in different Cu/Zn molar ratios (*R*), in which the sum of the contents of Cu and Zn

was constant and equal to 90 mol %. The composition of CZA and CZAZ catalysts are shown in Table 1. The CuO/ZnO/Al₂O₃/ZrO₂ (CZAZ) catalyst precursors with various mole ratio of Cu were prepared by mixing an appropriate amount of aqueous solutions of copper, zinc, zirconium and aluminum nitrate (Sigma Aldrich 99.8%) and sodium carbonate (Merck 99.8%). The catalysts were assigned as (CZAZX) where X represent mol % of Cu in the formulation. A Cu/ZnO/Al₂O₃ (CZA45) methanol synthesis catalyst with Cu/Zn molar ratio of 1 was used as a reference system. For precursor CZA45, a solution of 1.2 M sodium carbonate was added drop wise into a mixed aqueous solution of copper nitrate, zinc nitrate and aluminium nitrate of 1 M at constant temperature and pH of 40°C and 6.5-7.0, respectively. After precipitation, the solids were digested and aged at room temperature (2 h), filtered and repeatedly washed with hot deionized water, then dried at 100°C (16 h) and further calcined in air at 350°C (4 h).

TABLE 1. Composition of the CZA and CZAZ catalysts

Code	Chemical Composition (mol %)				<i>R</i> (Cu/Zn)
	Cu	Zn	Al	Zr	
CZA45	45	45	10	0	1
CZAZ30	30	60	5	5	0.33
CZAZ45	45	45	5	5	1
CZAZ60	60	30	5	5	3
CZAZ75	75	15	5	5	5

CHARACTERIZATION

The morphology, average particle size and elemental compositions of the catalyst were studied by field emission scanning electron microscope-energy dispersive X-ray (JEOL 6340). The thermogravimetric analysis (TGA) profiles were measured in a nitrogen flow at a heating rate of 20°C/min from room temperature to 500°C using a Perkin Elmer SPA 6000. Thermogravimetric Analyser (TGA) was used to measure weight changes of the sample when heated under a flow of N₂ (flow rate of 20 mL/min) at a constant heating ramp of 20°C/min. X-ray Diffraction (XRD) analyses were performed using a Bruker D8 Advanced diffractometer instrument equipped with a Cu K α radiation source, operated at 40 kV and 30 mA ($\lambda = 0.15418$ nm). The patterns were recorded for 10° < 2 θ < 90. Surface area (S_{BET}) and pore volume (PV) values were determined from N₂ adsorption-desorption isotherms at 77 K, using an ASAP 2020 (Micrometrics Instrument) gas adsorption device. The samples were degassed at 200°C for 2 h under 50 mTorr vacuum. The reduction behavior of the catalysts (0.5 g) was studied in the range 50-500°C with Thermo Scientific TPDRO1100 equipped with thermal conductivity detector. The catalyst samples were degassed in a flow of nitrogen at 200°C to remove traces of water and cooled down to room temperature. TPR was performed using 5% H₂/Ar mixture flowing at 20 mL/min and heated at the rate of 10°C/min (Ud Din et al. 2014).

CATALYTIC ACTIVITY

Experimental runs were conducted at fixed temperature (T), total gas pressure (P) and catalyst loading of 443 K, 3.0 MPa and 0.5 g, respectively. Prior to the activity studies, the catalyst was reduced at 623 K for 2 h in 20 mL/min of pure hydrogen (99.9%) under atmospheric pressure. After reduction, the activities of the catalysts in hydrogenation of CO_2 were carried out in a stirred high pressure micro reactor (model: Parr 4593). A schematic of the experimental set up is shown in Figure 1. The reactor was equipped with an automatic temperature control system, which consisted of an external electric heating jacket. A pressure transducer-monitor system with high precision was also connected to the reactor for on-line measurement of reactor pressure and temperature. The catalyst was reduced in a gas mixture of H_2/Ar (10/90 v/v) at 623 K with a gas flowrate of 20 mL/min. The feed mixture containing ethanol solvents (25 mL) and reduced catalyst was taken in the preheated reactor. The reactor was purged with nitrogen and H_2/CO_2 gas successively and then adjusted to the desired temperature. It was pressurized with mixture of CO and $\text{H}_2 = 3$ v/v to a desired total pressure which was maintained constant during the whole run. The stirrer was set at 450 rpm while the reaction continued. Liquid samples were withdrawn and analyzed at regular time intervals to follow the progress of the reaction. Gas and liquid samples were analyzed using gas chromatograph equipped with thermal conductivity detector (TCD, Shimadzu GC-17A) and flame ionization detector (FID, Shimadzu GC-2010), respectively. Helium was used as a carrier gas, and its flow rate was maintained at 20 mL/min. The gas chromatograph was calibrated by external standard calibration method, and a mass balance check was carried out to verify the results obtained in each run. The activities of the CZA and CZAZ catalysts were determined after passing the reactants over the catalyst for 3 h. Initial experiments were repeated two times to check for reproducibility. Measurements are in general reproducible within a maximum of 10% but mostly within a few percent. The CO_2 conversion, X_{CO_2} ,

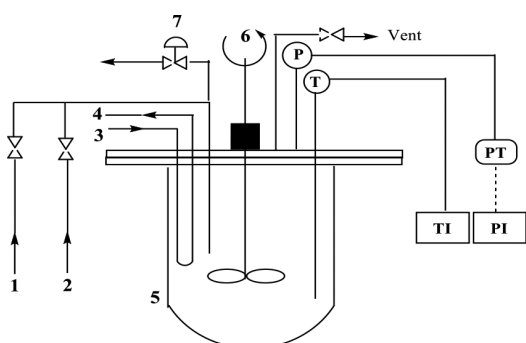


FIGURE 1. Schematic of the experimental setup: (1) nitrogen; (2) syngas (CO/H_2); (3) cooling water in; (4) cooling water out; (5) high pressure reactor; (6) stirrer; (7) sampling valve; (T) thermocouple; (P) pressure gauge; (PT) pressure transducer; (PI) pressure indicator; (TI) temperature indicator

and methanol selectivity, S were calculated using (1) and (2), respectively.

$$X_{\text{CO}_2} (\%) = \frac{(n_{\text{CO}_2})_0 - (n_{\text{CO}_2})_t}{(n_{\text{CO}_2})_0} \times 100 \quad (1)$$

$$S (\%) = \frac{Y_{\text{CH}_3\text{OH}}}{X_{\text{CO}_2}} \times 100 \quad (2)$$

where $(n_{\text{CO}_2})_0$ is the mole fraction of CO_2 in the feed gas; and $(n_{\text{CO}_2})_t$ is the mole fraction of CO_2 at time; t (3 h) and $Y_{\text{CH}_3\text{OH}}$ is the yield of methanol.

RESULTS AND DISCUSSION

TGA was used to investigate the presence of any decomposable materials in the uncalcined catalyst. Figure 2 shows that a small weight loss of approximately 5% started at 50°C was attributed to moisture and continued up to a temperature of 200°C. Increasing the temperature led to an additional weight loss of 25% in the temperature range between 200 and 350°C, corresponding to the decarboxylation of MCO_3 ($\text{M} = \text{Cu}, \text{Zn}, \text{Zr}$) to form $\text{MO}_2 + \text{CO}_2$, as reported by Cai et al. (2012). The CuCO_3 formed in the co-precipitation procedure as follows:

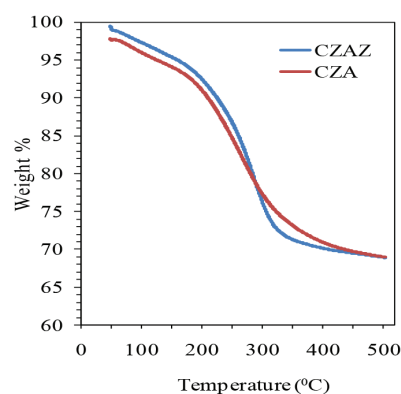
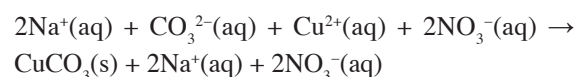


FIGURE 2. Thermogravimetric analysis of uncalcined CZA45 and CZAZ45

Calcination of the catalyst at 350°C for 4 h was expected to remove all the displaceable water, metal carbonates and counter ions present in the catalyst. Table 2 shows the characteristics of the catalysts. A marked decrease in BET specific surface area, SA_{BET} was observed from 59.87 m^2/g of CZA45 to 42.62 m^2/g of CZAZ45. The results showed that the incorporation of 0.5 mol% of Zr reduced the surface area of the catalyst, although the ZnO content has a significant influence on the catalyst texture (Figure 3). This result is in accordance with the results regarding the crystallite size, as determined from XRD.

Broader diffraction peaks were observed for CZA than CZAZ which indicates that the crystallite sizes of CuO observed in CZA are smaller than CZAZ catalyst. A maximum of 51.22 m²/g was obtained over CZAZ30, whereas CZAZ60 catalyst showed the lowest surface area. Higher SA_{BET} values (42.6-59.9 m²/g) are recorded at low (1) and high (5) Cu/Zn ratios with the minimum value of 35.71 m²/g found for a Cu/Zn of 3. Among the CZAZ catalyst, the catalyst with Cu/Zn molar ratio of 3 resulted in a much greater cumulative volume (ca. 0.305 cm³/g).

Morphological changes of the catalyst can be vividly observed with field emission scanning electron microscope (FESEM). It can be seen in Figure 4 that the catalyst morphology changed along with the variation of the Cu/Zn molar ratio. The morphology of the CZAZ catalysts is in the form of homogeneous flake-like sheet at low CuO content (0.33 molar ratio of Cu/Zn) and it is transformed to the agglomerated block-like crystal morphology at high CuO content. Smaller particle, uniform size distribution, relatively lower crystallization degree and more particles agglomerated to form cluster-like crystal can be observed from the catalyst CZA (Figure 5(A)). However, comparing with the catalyst CZA, the catalyst CZAZ exhibited larger particle in the range of 17.32 to 33.46 nm (Figure 4(C)-4(E)). The particle size of CZAZ catalyst increased with increase of Cu/Zn molar ratio. However, CZAZ75 which contained the highest Cu/Zn molar ratio exhibited relatively smaller average particle size compared to the CZAZ45 and CZAZ60. These findings suggest that the molar ratio of Cu/Zn in CZAZ catalyst significantly affects and contributes

in favor of forming a suitable morphological material and beneficial to the catalytic reaction. This observation is similar to that of XRD and TPR studies as discussed in the forthcoming sections.

Figure 5 summarizes the FESEM mapping and EDX of the CZAZ catalyst, showing the metal distribution on the surface of support. Each element present in the catalyst structure is represented by dots with specific colour. It can be seen from the figures that Cu species are homogeneously distributed without any aggregation. Such behavior is reasonably related to the incorporation of ZrO₂, which can prevent the growth and agglomeration of Cu particles due to the barrier effect of surrounding ZrO₂, as well as the enhanced interactions between metal and supports. Similarly, such a phenomenon also was found in other supported copper-based catalysts on Zr-containing supports previously reported (Li et al. 2017). The EDX analysis demonstrated that Cu, Zn, Al and Zr were the only 4 elements observed at the surface of catalyst and the elements were evenly dispersed within the catalyst matrix.

The XRD patterns that characterized the structure of the catalysts synthesized are shown in Figure 6. The poor crystallinity of the CZA catalyst is shown by the low signal-noise ratio. Only a few peaks can be seen above the baseline. Two well-defined peaks visible at 2θ = 35.5° and 38.9° were ascribed to a typical structure of the tenorite, a monoclinic structure of CuO with the active crystal planes of (1 1 1) and (2 0 0) of JCPDS card files No. 48-1548 (a = 4.62°Å, b = 3.43°Å and c = 5.06°Å) (Guo et al. 2011; Pung et al. 2014). Thus, it can be deduced that the

TABLE 2. Characteristics of CZA and CZAZ catalyst

Catalyst	SA _{BET} (m ² /g)	PV (cm ³ /g)	Average diameter of pore (nm)	Average particle size (nm)
CZA45	59.87	0.449	27.3	18.40
CZAZ30	51.22	0.238	45.6	17.32
CZAZ45	42.62	0.275	29.8	21.25
CZAZ60	35.71	0.305	43.1	33.46
CZAZ75	48.69	0.291	22.3	19.76

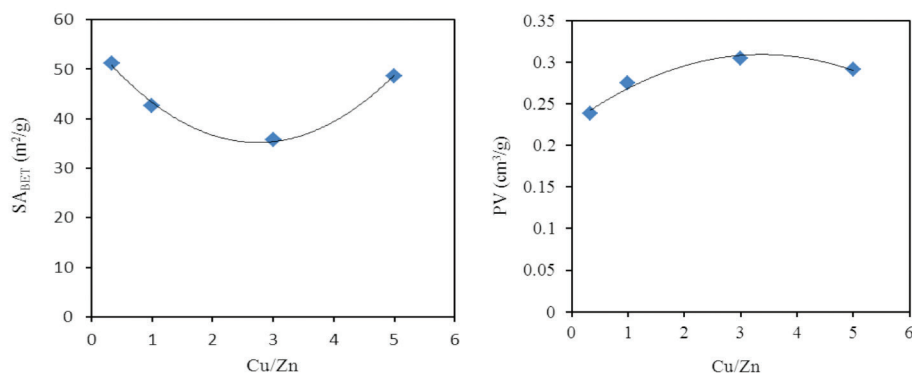


FIGURE 3. Effect of Cu/Zn molar ratio on the (A) SA_{BET} and (B) pore volume of the CZAZ catalyst

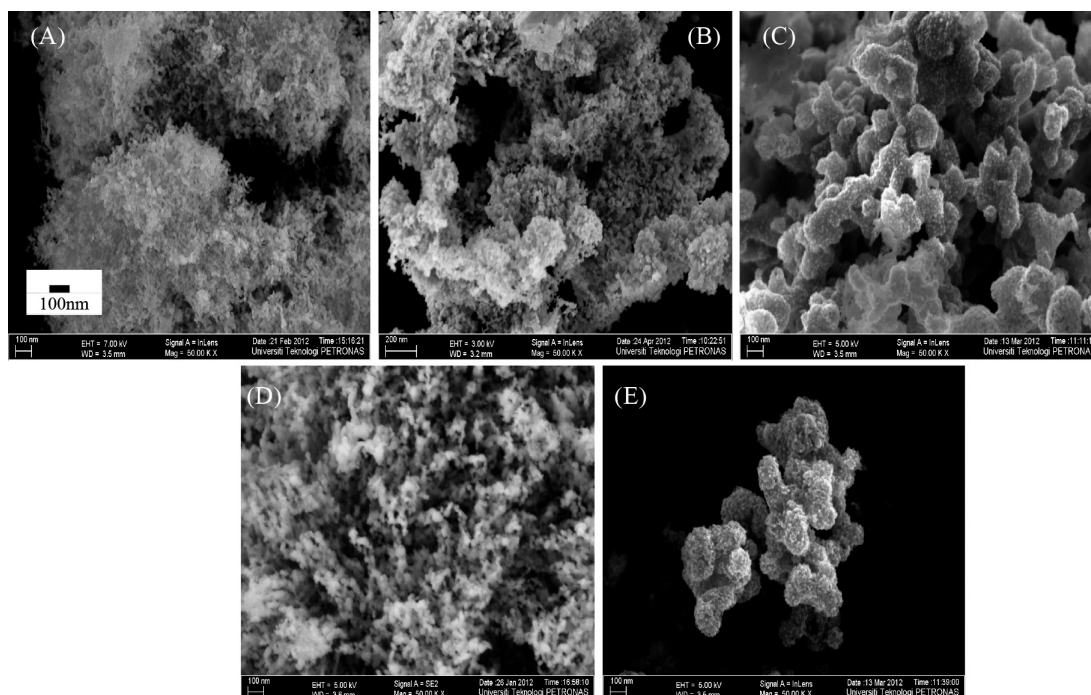


FIGURE 4. FESEM images of (a) CZA45, (b) CZAZ30, (c) CZAZ45, (d) CZAZ60, (e) CZAZ75

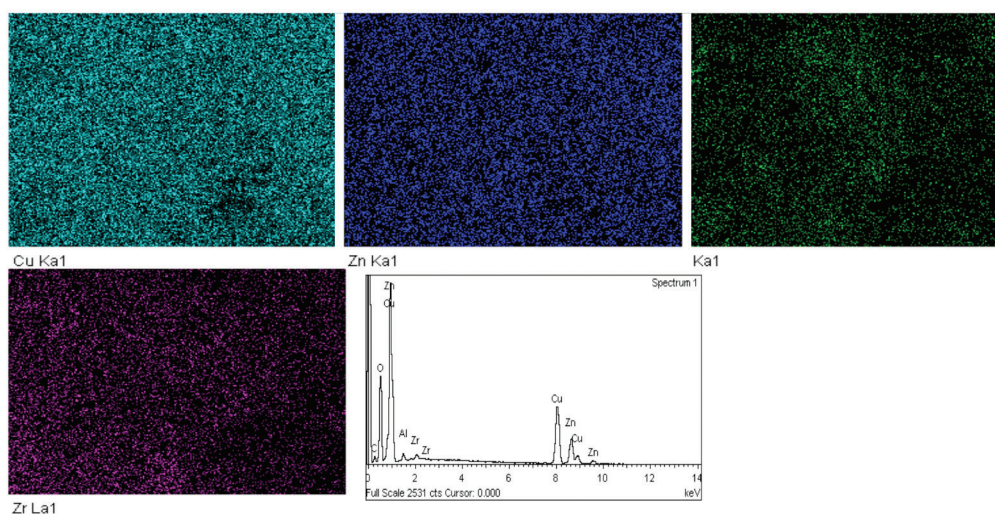


FIGURE 5. Representative elemental mapping for CZAZ45 catalyst

copper species in the precursors calcined at 623 K have been converted to CuO. Furthermore, the diffraction peaks of ZnO and CuO overlap at $35^\circ < 2\theta < 37^\circ$ for all samples, suggesting less ordered structure whereby the fine particles of CuO and ZnO are well-mixed and part of CuO would be incorporated into the structure of ZnO. This is consistent with the XRD results observed usually in Cu/Zn/Al ternary oxides (An et al. 2007; Xiao et al. 2017). The intensity of both peaks reduces at lower copper loading (CZAZ30 and CZAZ45), while they become much sharper with much higher intensities at higher copper loadings (CZAZ60 and CZAZ75). The dramatic increase in peak intensity with increasing Cu metal content may reflect the growth in

crystal size. With the addition of Zr, the diffraction peak width for CuO decreased slightly. This indicates that the crystallization degree of CuO, as well as the particle sizes of CuO crystallites though it cannot be determined accurately with the Scherrer equation since the CuO XRD reflection is weak, increase with the presence of Zr. There were no peaks that can be assigned to ZrO_2 and Al_2O_3 , indicating that both metal oxides existed in an amorphous or microcrystalline state, which could not be detected by XRD technique due to the low degree of crystallization (Bangbai et al. 2013).

Figure 7 shows the H_2 -TPR profiles of the CZA and CZAZ catalysts. The H_2 -TPR profile showed a single peak

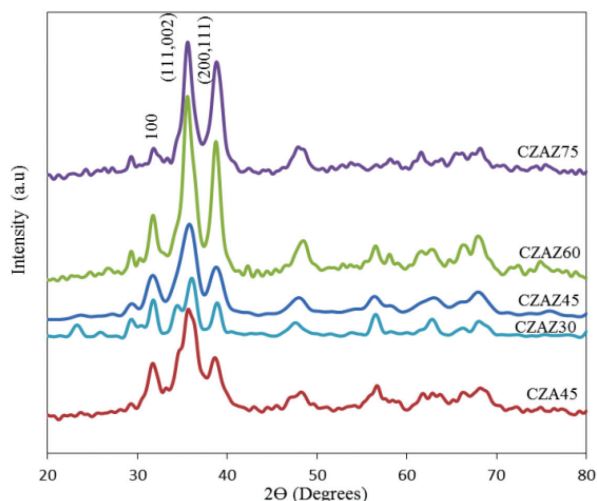


FIGURE 6. XRD patterns of CZA45 and CZAZ catalysts with different Cu/Zn molar ratio

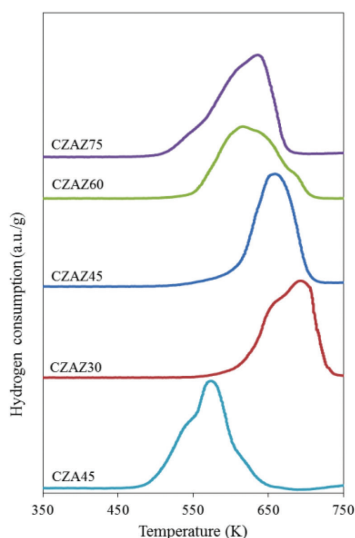


FIGURE 7. H₂-TPR profiles of the CZA and CZAZ catalysts

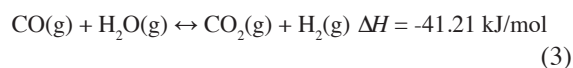
attributed to the reduction of CuO: $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$. The hydrogen consumption during TPR occurred at approximately 568–685 K, which is typical for the reduction of supported copper oxide to metallic copper (Witton et al. 2016). The CZA45 samples displayed the reduction temperature peak maxima at approximately 568 K. The maximum was shifted to 650 K for the CZAZ45, indicating comparatively strong metal-support interaction as compared to CZA. Thus, the incorporation of 0.5 mol% of ZrO₂ causes increase in the metal-support interaction, hence increase in the reduction temperature maxima and reduction in the reducibility of copper oxide. According to Velu and Suzuki (2003), the binding energies of Cu 3d bands for Cu/ZnO/Al₂O₃/ZrO₂ is higher (4.4 ± 0.1 eV) compared to that of Cu/ZnO/Al₂O₃ (around 3.7 eV) and suggest a significant modification in the electronic structure of copper species at the catalyst surface with respect to the

chemical composition. In addition, the higher reduction temperature is justified by the much larger CuO crystallite size in CZAZ. These TPR results correlated well with the study by Melian-Cabrera (2002) on Cu/ZnO/Al₂O₃ and Arena et al. (2008) on Cu-Zn/ZrO₂ catalysts. The TPR profiles revealed reduction temperature of 568–685 K and the highest amount of H₂ adsorbed per gram sample was achieved by the CZAZ30 catalyst with the lowest Cu/Zn molar ratio.

TABLE 3. TPR data of CZA and CZAZ catalysts

Catalyst	$T_{0,\text{red}}$ (K)	T_m , (K)	mmol H _{2,tot} /g _{cat}
CZA45	470	568	5.965
CZAZ30	568	687	6.582
CZAZ45	557	650	5.012
CZAZ60	530	610	6.413
CZAZ75	490	638	5.957

All catalysts were active in the methanol synthesis using CO₂ and hydrogen as reactants, and the only products detected were methanol, carbon monoxide and water. Table 4 summarizes the performance of CZA and CZAZ in the hydrogenation of CO₂. A comparative study of the activity data of CZAZ catalyst with the reported literature showed that the CZAZ catalysts showed higher activity for methanol yield and CO₂ conversion at lower temperature (443 K and 30 bar) as compared to that recorded by Zhang et al. (2016) over Cu/ZnO/Al₂O₃/ZrO₂ (523 K and 50 bar) and da Silva et al. (2016) over Cu/ZnO/Al₂O₃ catalysts (523 K and 50 bar). The gas analysis confirmed that reverse water gas shift reaction (3) occurred during the test due to the formation of lower concentration of water compared to methanol.



Using CZAZ catalysts, the CO₂ conversion values rising from 6.3 to 15.8%, counterbalanced by a drop in methanol selectivity from 93.9 to 40.3%. The highest CO₂ conversion and methanol yield was obtained over the CZAZ75 with Cu/Zn molar ratio of 5. In addition, it produced lowest yield of undesired product H₂O. Hence, the CZAZ75 was concluded as the best performance catalyst amongst the catalysts tested in this study. The greater pore volume and large surface area at high CuO content may be responsible to the observed high activity of the CZAZ75 catalyst. Smaller pore may lead to feed gas diffusion limitations inside the pores. The results are in comparable with other CO₂ hydrogenation studies carried out on Cu/ZnO/ZrO₂ catalysts. For instance, Raudaskoski et al. (2007) have obtained CO₂ conversions of 3.7–16.7% and 22.0–35.1% selectivity to methanol at 230°C and 30 bar on Cu/ZnO/ZrO₂ catalysts prepared by precipitation method with different ageing time. As depicted above, the CO₂ conversion over the CZAZ catalyst increased progressively

TABLE 4. Comparison of catalyst performance for hydrogenation of CO₂ to methanol in stirred reactor

Catalyst	CO ₂ conversion (%)	CH ₃ OH selectivity (%)	CH ₃ OH yield (%)	H ₂ O yield (%)	Reference
CZA45	5.80	39.50	2.29	1.30	} Present work
CZAZ30	6.31	93.93	5.93	1.22	
CZAZ45	7.93	67.73	4.42	0.94	
CZAZ60	10.23	55.44	5.87	1.04	
CZAZ75	15.81	40.27	6.36	0.91	
Cu/ZnO/Al ₂ O ₃	9.00	36.00	-	-	da Silva et al. (2016)
Cu/ZnO/Al ₂ O ₃ /ZrO ₂	14.20	62.00	-	-	Zhang et al. (2016)

with the increase of Cu/Zn molar ratio and it is consistent with the change of the specific surface area, SA_{BET} (Table 1). Several studies have demonstrated that there are two active centers involved in the catalytic process of CO₂ hydrogenation over the Cu/ZrO₂-based catalysts (Lin et al. 2009; Raudaskoski et al. 2007; Sloczynski et al. 2004; Xiao et al. 2015). One is the Cu component, and the other is the so-called 'support' ZrO₂. The Cu serves to dissociatively adsorb H₂ and to provide a source of atomic hydrogen by spillover and the ZrO₂ serves to adsorb CO₂ as bicarbonate species which then undergo stepwise hydrogenation to methanol. However, the selectivity of methanol over CZAZ catalysts decreases with the increase of Cu/Zn molar ratio which may be due to the reverse water-gas shift (RWGS) reaction. High activity of the CZAZ75 catalyst can be explained by the characterization results, i.e. the high metallic copper surface area, S_{Cu} , easier reduction of copper oxide to metallic copper and smaller average particle sizes relative to the other samples.

CONCLUSION

CZA and CZAZ catalysts with various molar ratio of Cu/Zn were synthesized via co-precipitation method for methanol synthesis from CO₂ hydrogenation. The influences of Cu/Zn molar ratio on the physicochemical and catalytic properties of the CZA and CZAZ catalysts were investigated. The effect of Cu/Zn molar ratio on CZAZ catalyst reduced the BET surface area and increased the average pore size of the catalyst. The surface area for CZA was 59.87 m²/g and it decreased to 42.62 m²/g with incorporation of 0.5 mol% of Zr. The TPR results showed that the addition of Zr affected the reduction of copper oxides. The FESEM mapping and EDX of the both catalyst showed that the active metal was well dispersed on the surface of support material. A suitable molar ratio of Cu/Zn is beneficial for the catalytic activity of CZAZ catalyst and a maximum methanol yield is obtained at the Cu/Zn molar ratio of 5.

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