

CO₂ hydrogenation to methanol using Cu-Zn catalyst supported on reduced graphene oxide nanosheets



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ABSTRACT

Supporting Cu-Zn catalyst on reduced graphene oxide nanosheets

Supported Cu-Zn/reduced graphene oxide (rGO) catalysts were synthesized via an incipient wetness impregnation and evaluated for a CO₂ hydrogenation to methanol. The structure, surface reactivity, and adsorption properties were investigated extensively by FE-SEM, TEM, XRD, Raman, FT-IR, N₂ sorption, TGA, TPR, and XPS techniques. The effects of Cu-Zn metal loading content and the reaction temperature were investigated toward the methanol production from the CO₂ hydrogenation. It was found that supported rGO nanosheets could greatly enhance the catalytic performance and help the dispersion of bimetallic compounds Cu-Zn particles. The 10 wt%CuZn/rGO catalyst yielded the highest space time yield (STY) of 424 mg_{MeOH} g_{cat}⁻¹ h⁻¹ at a reaction temperature and pressure of 250 °C and 15 bar, respectively.

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1. Introduction

Recently, global warming has become a serious problem affecting humanity due to a rapid increase of CO₂ emission which has consequently led to an increase in the average global temperature [1]. Therefore, various techniques have been proposed to reduce the atmospheric CO₂ accumulation, for example: carbon capture and storage (CCS) [2–4] that aims to capture and store large quantities of CO₂, and carbon capture and utilization (CCU) [5–7] that aims to convert CO₂ to fuels such as dimethyl ether (DME) dimethyl carbonate (DMC), and methanol (MeOH) [8–13]. Especially for the production in the latter case, DME, DMC, and MeOH are key feedstock for industrial chemicals, which can be converted into high molecular weight hydrocarbons and alternative fuels, where the CO₂ hydrogenation process is one of the most efficient and economical routes for CO₂ emission utilization [14–20]. However, the hydrogenation reaction is highly exothermic and it is difficult to activate CO₂ owing to its high stability [21,22]. Therefore, catalysts are employed to reduce the activation energy of the hydrogenation step and break the CO₂ bonds [23,24].

Cu-Zn oxide-based catalysts have been widely reported for the CO₂ hydrogenation to methanol process [25–30]. The role of Zn oxide is to improve the dispersion of metallic copper particles. Additionally, it has been found that Zn oxide exhibits an active site for hydrogen spillover. Moreover, the interaction between Cu and Zn oxide causes an electron transfer from Zn oxide to Cu metal that occurs as Cu⁰ and Cu⁺ species, which are crucial for CO₂ hydrogenation to methanol [31–36]. It has been confirmed by other studies that copper metal alone cannot be the sole active site for higher activities in methanol synthesis [37,38]. While Cu-Zn oxide-based catalysts have been well-researched for methanol synthesis, these catalysts are not prevalent because the metals have low active surface area and are prone to sintering.

Hence, catalyst supports are used as a metal receptor to increase surface area and improve metal dispersion [39–43]. Carbon materials such as carbon nanotubes (CNTs) and activated carbon (AC) have been commonly used as the catalyst supports due to their attractive physical and thermal properties such as high surface area (i.e., 180–200 m² g⁻¹ [44–47]), uniform and straight pores, inert graphitic surface, and high thermal stability, while also exhibiting good performance for adsorption of hydrogen [48–51]. However, CNTs and AC still have lower specific surface areas when compared with graphene [50].

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The unique physical, chemical, and mechanical properties of graphene make it an ideal support material for the catalysts such as high theoretical surface area of $2630\text{ m}^2\text{ g}^{-1}$, which provides an attractive platform for surface interactions and surface chemistry, tensile strength of 130 GPa, thermal conductivity of $4840\text{--}5300\text{ W m K}^{-1}$, and electron mobility of $15,000\text{ cm}^2\text{ V}^{-1}$ [52–57]. Beside, graphene has been used worldwide as a catalytic support material for various chemical reactions and used in photoelectric catalysis, lithium ion battery, and fuel cell.

In this work, supported Cu–Zn on reduced graphene oxide (rGO) catalysts were synthesized via incipient wetness impregnation and evaluated for CO₂ hydrogenation to methanol. The supporting materials were synthesized via an oxidation of graphite to graphene oxide, followed by a chemical reduction method. The reaction temperature and percent loading of the bimetallic Cu–Zn compounds on the graphene support were finely tuned to achieve the high performance of CO₂ hydrogenation to methanol.

2. Experimental

2.1. Chemicals and materials

The chemicals used in this study were graphite powder (20–40 μm , Sigma Aldrich), sodium nitrate (99.5% NaNO₃, Qrec),

potassium permanganate (99% KMnO₄, Ajax Finechem), sulfuric acid (98% H₂SO₄, Qrec), hydrogen peroxide (30% H₂O₂, Merck), hydrazine hydrate (80% N₂H₄, Merck), copper nitrate trihydrate (99.5% Cu(NO₃)₂·3H₂O, Qrec), zinc nitrate hexahydrate (98% Zn(NO₃)₂·6H₂O, Lobachemie), and water, which was purified via a Milli-Q system ($>18\text{ M}\Omega\text{ cm}$, Millipore).

2.2. Preparation of rGO

Graphene oxide (GO) was synthesized according to the modified Hummers method [58], with additional modifications following Sawangphruk et al. [59]. First, graphite powder (5.0 g) and NaNO₃ (7.5 g) were mixed in H₂SO₄ (500 ml). Then, KMnO₄ (40.0 g) was slowly added under stirring at 200 rpm in an ice bath for 24 h. Water (500 ml) and H₂O₂ (150 ml) were added into mixture solution in an ice bath under stirring at 200 rpm for 24 h. The product was collected by centrifuge and washed with water several times until the pH was neutral. The as-synthesized product was dried at 50 °C for 24 h. Next, rGO was prepared via a chemical reduction of GO. First, the as-prepared GO (1.0 g) was dispersed in 300 ml of water under sonication for 1 h. Then, hydrazine (30 ml) was added into the suspension while stirring at 200 rpm at 98 °C for 24 h to eliminate oxygen functional groups. Finally, the as-synthesized product was collected via vacuum filtration and

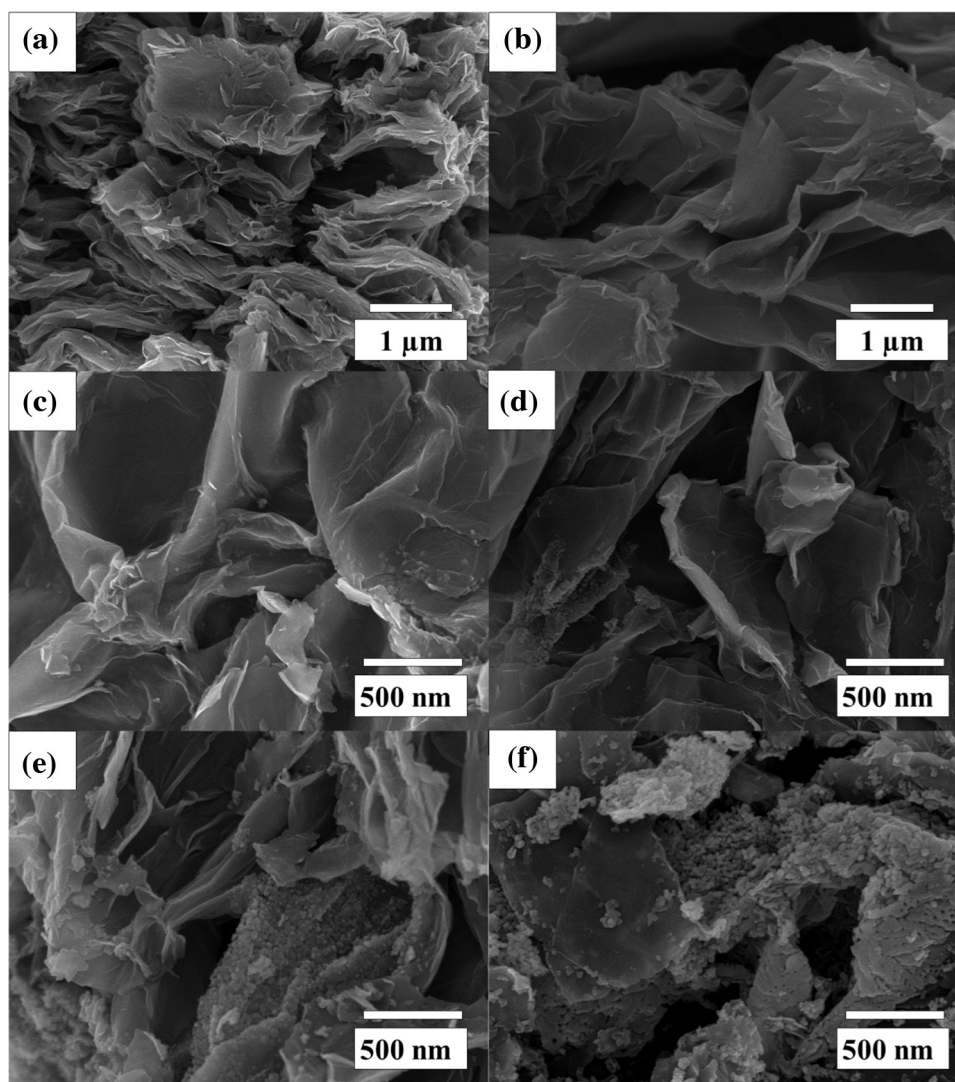


Fig. 1. SEM images of (a) rGO, (b) calcined rGO, (c) 5%CuZn/rGO, (d) 10%CuZn/rGO, (e) 20%CuZn/rGO, and (f) 30%CuZn/rGO.

washed with water to remove the residual reducing agent. The as-synthesized rGO was dried at 50 °C for 24 h.

2.3. Preparation of Cu-Zn/rGO

The catalysts were prepared with different weight percentages of 5, 10, 20, and 30 Cu-Zn metals, with equimolar of Cu-Zn with rGO support via an incipient wetness impregnation. Subsequently, the as-prepared catalysts were dried at 100 °C for 12 h and calcined in air at 350 °C for 2 h with a heating rate of 2 °C min⁻¹ to eliminate impurities and form surface metal oxides.

2.4. Catalyst characterization

The surface morphology of obtained catalysts was observed with a field emission scanning electron microscope (FE-SEM) and a transmission electron microscopy (TEM). X-ray diffraction (XRD) patterns were characterized by using an X-ray diffractometer (XRD, Philips X-Pert) with Cu K α radiation source ($\lambda_{K\alpha} = 1.54 \text{ \AA}$) at an angle in the 2θ range of 5–90°, 40 kV, 30 mA, with a scan rate of 2° min⁻¹. Raman spectra of graphene-based materials were analyzed with a Senterra Dispersive Raman Microscope (Bruker

Optics) with laser (532 nm). Fourier-transform infrared (FT-IR) spectra were measured with a spectrophotometer (Bruker Tensor 27) in the range of 400–4000 cm⁻¹, with a resolution of 4 cm⁻¹ to investigate the chemical bonds formed. The specimens were prepared by grinding the samples together with potassium bromide (KBr) and compressing them into thin pellets. The BET surface area (S_{BET}), nitrogen adsorption isotherms, pore size distribution, and pore volume (V_p) of as-synthesized catalysts were measured with the N₂-sorption measurement (Quantachrome Autosorp-1C instrument) at –196 °C.

The thermogravimetric analyzer (TGA, Perkin Elmer STD 2960) measured the thermal decomposition of the as-synthesized catalysts. The samples were loaded into an alumina pan and heated in a flow of ambient air from 25 to 600 °C with a heating rate of 10 °C min⁻¹. The reduction temperature of as-synthesized catalysts was obtained by temperature-programmed reduction (TPR). Measurements were performed at 25–800 °C in a continuous flow apparatus using an Inconel-tube reactor (Inconel-600, O. D. 3/8 in.). For this experiment, the mixture of H₂ and Ar (9.6% H₂ balanced with Ar) was fed into the catalyst bed. H₂ consumption was monitored by using a Shimadzu gas chromatograph (GC-2014) equipped with a thermal conductivity detector (TCD). The surface

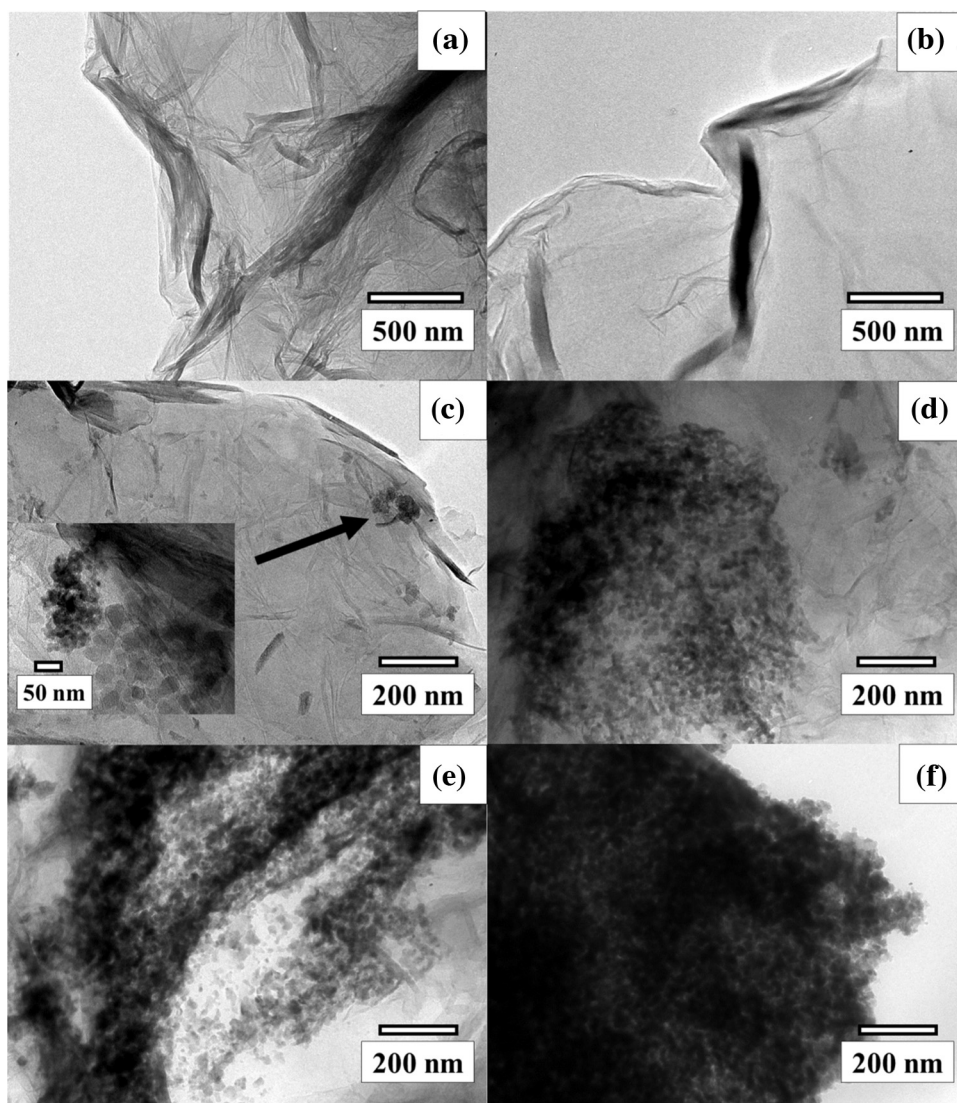


Fig. 2. TEM images of (a) rGO, (b) calcined rGO, (c) 5%CuZn/rGO, (d) 10%CuZn/rGO, (e) 20%CuZn/rGO and (f) 30%CuZn/rGO.

analysis was performed using X-ray photoelectron spectroscopy (XPS) for investigating the oxidation state of Cu-Zn, chemical bonding and chemical composition that compromise between the theoretical and actual metal loading composition.

2.5. Catalytic activity test

The catalytic testing in the CO₂ hydrogenation reaction was performed in a tubular stainless steel fixed-bed reactor. 0.25 g of the catalyst was in-situ reduced at 350 °C for 2 h with flowing H₂ (40 ml min⁻¹). Then, the temperature was cooled to the desired reaction temperature. After that, a gas mixture CO₂/H₂ = 1/3 (GHSV = 2400 h⁻¹) was fed to the reactor. The reaction pressure was raised to 15 bar and the gaseous products were analyzed with a gas chromatograph (Shimadzu, GC-14A equipped in a Unibead-C packed column with TCD and a Porapak Q column with FID).

3. Results and discussion

3.1. Catalyst characterization results

Fig. 1 shows the apparent morphologies of the catalyst samples evaluated with FE-SEM measurements. The images reveal a large number of rGO nanosheets as anchoring sites from the catalyst support. Meanwhile, 5, 10, 20, and 30% of Cu-Zn/rGO catalyst samples exhibit Cu-Zn metals on rGO nanosheets. FE-SEM images of Fig. 1c–f clearly show that increasing the percent loading of bimetallic compounds of Cu-Zn leads to more aggregation of the active metals.

TEM images of the catalyst samples are shown in Fig. 2. From the TEM images of rGO and rGO after calcination (Fig. 2a and b, respectively), both rGO and calcined rGO have a wrinkled morphology caused by a few layers of rGO nanosheets having restacked. After calcination, the wrinkled morphology decreases, revealing the advantage for rGO structure. In the TEM images of 5, 10, 20, and 30% of CuZn/rGO catalyst samples, Cu-Zn particles were found to be coated on the surfaces of rGO. With increasing percent loading of bimetallic compounds of Cu-Zn, the particles appeared to form increasingly small aggregates, as shown in Fig. 2c–f.

The reduction of GO into rGO was also investigated with the X-ray diffraction (XRD) technique. The XRD patterns of the catalyst samples are shown in Fig. 3. The peak pattern of GO, which is similar to the standard reference peak [60], is shown in Fig. 3a. Under reduction conditions, the main peak for GO at ~10° is shifted to ~26°, which is assigned to the graphitic planes (002) of the graphene nanosheets, indicating that GO was reduced to graphene [61]. Following the loading of bimetallic compounds Cu-Zn, the

new peaks from the diffraction pattern correspond to the crystal phases of CuO and ZnO, which are clearly visible. The calcination and loading of bimetallic compounds Cu-Zn do not alter the structure of rGO as the peak patterns of rGO still remain, but the intensity is slightly reduced due to metal coverage, as expected (Fig. 3c–g). These results are also confirmed by the Raman spectrometer. Moreover, the size of the graphitic crystallites (L_a) and the stacking height (L_c) in the rGO support can be calculated from the (002) graphitic peak and the (100) planes, respectively using the Scherrer equation, and the d -spacing in the rGO support can be approximated by the Bragg's Law as described by the following equations [62–64]:

$$L_a = \frac{1.84\lambda_{K\alpha}}{\beta \cos \theta} \quad (1)$$

$$L_c = \frac{0.89\lambda_{K\alpha}}{\beta \cos \theta} \quad (2)$$

$$2d \sin \theta = n\lambda \quad (3)$$

where β is the full width at half-maximum (FWHM) of the (002) and (100) peaks. The graphitic crystallite size was determined to be 4.5 nm for rGO, 5.4 nm for rGO after calcination, and 4.9 nm for rGO after loading of Cu-Zn. The stacking height of rGO and rGO after calcination are 3.4 and 3.6 nm, respectively. Meanwhile, the stacking heights of 5, 10, 20, and 30% of Cu-Zn/rGO catalyst samples are 4.5, 5.3, 5.8, and 6.0 nm, respectively. This increase of height was attributed to the insertion of Cu-Zn particles between the rGO nanosheets. Additionally, the d -spacing of the rGO support was found to be about 2 Å.

Raman spectroscopy was utilized to identify the structure and degree of disorder in carbon-based materials of the graphitic support, both before and after metal impregnation. The Raman spectra of the catalyst samples are shown in Fig. 4. Typically, GO and rGO show a strong disorder in the lattice of the sp³-hybridized carbon atoms, a so-called D band, and an in-plane bond-stretching motion of pairs of sp² carbon atoms, namely G band [65], that occur at about 1350 cm⁻¹ and 1585 cm⁻¹, respectively [66]. After calcination and loading of bimetallic compounds Cu-Zn, the Raman spectra reveal similar D and G bands at about 1350 and 1585 cm⁻¹, respectively. The D/G intensity ratio of all catalysts is approximately 1, which is consistent with the previous study [67]. The intensity of the D band is slightly higher than the G band; therefore, it can be deduced that rGO has many smaller graphitic sheets [68]. Furthermore, the crystallite size (L_a) can be calculated

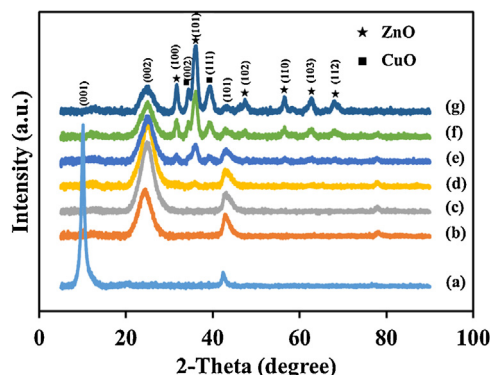


Fig. 3. XRD patterns of (a) GO, (b) rGO, (c) calcined rGO, (d) 5%CuZn/rGO, (e) 10% CuZn/rGO, (f) 20%CuZn/rGO and (g) 30%CuZn/rGO.

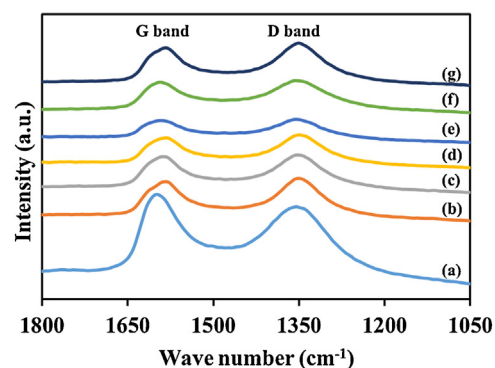


Fig. 4. Raman spectra of (a) GO, (b) rGO, (c) calcined rGO, (d) 5% CuZn/rGO, (e) 10% CuZn/rGO, (f) 20%CuZn/rGO and (g) 30%CuZn/rGO.

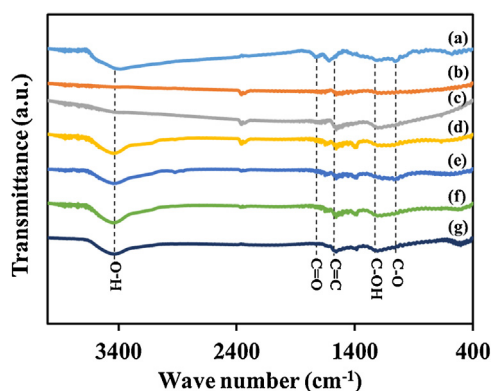


Fig. 5. FTIR spectra of (a) GO, (b) rGO, (c) calcined rGO, (d) 5% CuZn/rGO, (e) 10% CuZn/rGO, (f) 20% CuZn/rGO and (g) 30% CuZn/rGO.

according to the following equation:

$$L_a(\text{nm}) = \frac{560}{E_l^4} \left(\frac{I_D}{I_G} \right)^{-1} \quad (4)$$

where E_l , I_D , and I_G are the excitation laser energy in eV ($E_l = 2.33$ eV at $\lambda = 532$ nm), intensities of the D and G bands, respectively. The in-plane size L_a was calculated to be 17.1 nm for rGO, 18.1 nm for rGO after calcination, and 17.7 nm for rGO after loading of bimetallic compounds of Cu-Zn [69]. This is the same order of magnitude as the crystallite size accessed from the XRD analysis of the rGO, rGO after calcination, and after loading of bimetallic compounds of Cu-Zn ($L_a = 4.5$, 5.4, and 4.9 nm, respectively). In conclusion, the results from the Raman spectra confirm that the structure of rGO does not change after calcination and with the presence of bimetallic compounds of Cu-Zn.

Fig. 5 shows the FTIR spectra of the catalyst samples. The presence of the peak at $\sim 1560 \text{ cm}^{-1}$ is attributed to the skeletal vibration from the aromatic C=C stretching bands. Meanwhile, the vibration and deformation bands of O—H are found at $\sim 3420 \text{ cm}^{-1}$, the stretching vibration band of C=O at $\sim 1700 \text{ cm}^{-1}$, the stretching vibration band of C—OH at 1200 cm^{-1} and the stretching vibration band of C—O at 1040 cm^{-1} , which is in good agreement with the previous study [70]. These results confirm that the structures of both the calcined rGO and Cu-Zn loaded rGO do not change. It should be remarked that the two small peaks at 2358 and 2332 cm^{-1} were not generated from the analyzed samples, but they correspond to residual carbon dioxide from measurement conditions, and they should be ignored.

N₂ adsorption/desorption isotherms and the pore-size distributions of all samples were characterized, and the obtained results are shown in Fig. 6a and b, respectively. According to the IUPAC classification, the isotherm of all samples exhibited Type-IV behavior with a H3 hysteresis loop, indicating the presence of mesoporous structure and slit-shaped pores. The pore-size distribution shows predominant peak at 3.8 nm and another minor peak at 2.2 nm, denoting the presence of mesopores. BET surface area, pore volume and average pore diameter of the catalysts are shown in Table 1. The BET surface areas of rGO, rGO-calcined, 5% CuZn/rGO, 10% CuZn/rGO, 20% CuZn/rGO, and 30% CuZn/rGO are 57.9, 117.3, 65.6, 82.7, 41.2, and 41.8 m² g⁻¹, respectively. It should be remarked that the BET surface area of all samples is lower than the theoretical surface area (2630 m² g⁻¹), indicating that the rGO nanosheets consist of more than one layer as indeed found from XRD analysis. The BET surface area of rGO increases when it is calcined, due to a removal of impurities,

Table 1

BET surface area, pore volume, and average pore diameter of Cu-Zn/rGO catalysts.

Sample	BET Surface Area (m ² g ⁻¹)	Pore Volume (cm ³ g ⁻¹)	Average Pore Diameter (nm)
rGO	58	0.2589	4
rGO-calcined	117	0.5955	4
5%CuZn/rGO	66	0.2094	4
10%CuZn/rGO	83	0.2273	4
20%CuZn/rGO	41	0.1468	4
30%CuZn/rGO	42	0.1424	4

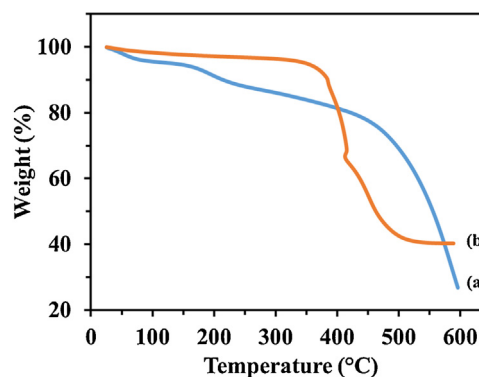


Fig. 7. TGA patterns of (a) rGO and (b) 30%CuZn/rGO.

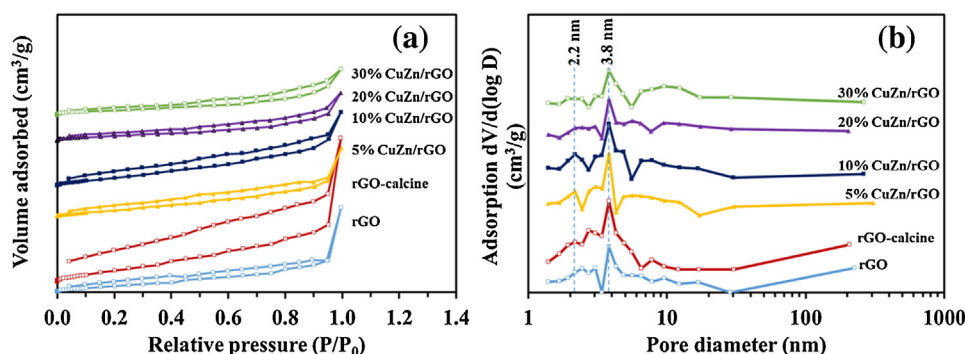


Fig. 6. N₂-adsorption/desorption isotherms (a) and pore size distributions (b) of catalysts.

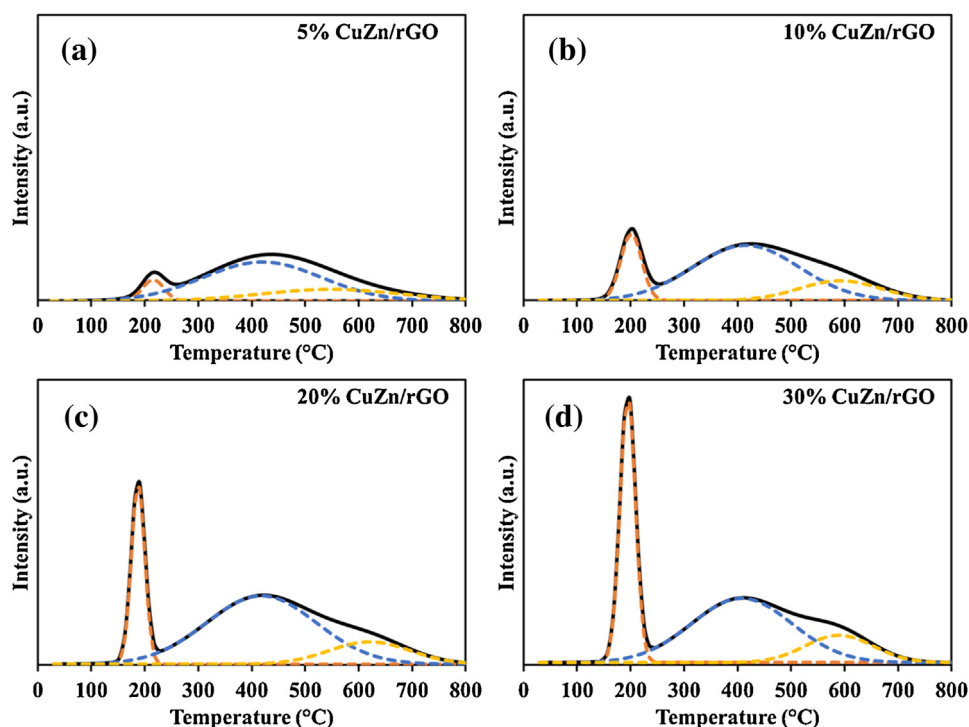


Fig. 8. H₂-TPR profiles of (a) 5%CuZn/rGO, (b) 10%CuZn/rGO, (c) 20%CuZn/rGO, and (d) 30%CuZn/rGO.

leaving some pores inside the rGO and resulting in higher porosity. The samples which are loaded with bimetallic compounds of Cu-Zn contain the active metals anchored on the surfaces of rGO nanosheets. These bimetallic metals are reported to be able to prevent restacking of the rGO nanosheets [71]. One explanation of the BET surface area of 5% CuZn/rGO lower than 10% CuZn/rGO is that the amounts of the metal particles are too low to resist restacking in rGO nanosheets. By increasing the percent loading of Cu-Zn (i.e. 10 wt% Cu-Zn), the surface is slightly increased. However, at higher loadings >10 wt%, the BET surface area was found to decrease, likely caused by the agglomeration of Cu-Zn, which obscures the surface of rGO nanosheets.

The TGA patterns of the catalyst samples are shown in Fig. 7. TGA profile of rGO (Fig. 7a) implies that the first weight loss step of rGO between 100 and 200 °C could result from the desorption of physisorbed water. The next major weight loss step is observed at 450 °C and then the rGO completely decomposes at ≥600 °C. Since the major weight loss is above the calcination temperature of 350 °C, TGA can confirm that rGO was not destroyed by the calcination step. Upon addition of the bimetallic Cu-Zn compounds, TGA revealed that the percent weight loss of 30% CuZn/rGO (Fig. 7b) is lower than that of rGO because it was protected by loaded metals on its surface. The onset of weight loss occurs at 400 °C, which is lower than that of rGO, but there was no loss observed up to the calcination temperature.

The reduced behavior of the catalysts was investigated by TPR measurement, as shown in Fig. 8. The first reduction peak is related to the reduction of CuO species having the one-step reduction, Cu(II) to Cu(0), and the temperature of the peak appears in the range of 150–250 °C. The reduction peaks of the CuO species increase in intensity, which corresponds to the increase of Cu-Zn loading. In this experiment, the reduced temperature was 350 °C, bringing about the complete reduction

of CuO and partial reduction of ZnO. Consequently, the catalysts were found as Cu(0), Zn(0), and ZnO.

The surface chemical compositions of the catalysts were evaluated via XPS technique as shown in Fig. 9. The survey XPS spectrum of 10% CuZn/rGO (see Fig. 9a) shows the predominant peak of carbon (C1s) at 284.4 eV, a minor oxygen (O1s) peak at 532.4 eV, a nitrogen (N1s) peak at 400.4 eV, a copper (Cu2p) peak, and zinc (Zn2p, Zn3s, Zn3p) peak [72]. The C1s peak in the XPS spectra of 10% CuZn/rGO (Fig. 9b) can be further deconvoluted into five peaks at 284.9, 285.2, 286.4, 287.5, and 289.1 eV, which are assigned to C—C, C—N, C—O, C=O, and O—C=O groups, respectively [73,74]. This result confirms that the functional groups of GO were mostly reduced by hydrazine, and the sp³ carbons in GO were converted to sp² carbons. Additionally, with the addition of bimetal, Cu-Zn, the structure of rGO (C—C) remains unchanged. From Fig. 9c, it is also observed that the Zn2p has two fitting peaks found at about 1022 and 1045 eV, corresponding to Zn2p_{3/2}, and Zn2p_{1/2}, respectively [75]. The spin energy separation between the Zn2p_{3/2} and the Zn2p_{1/2} is 23 eV. It can be indicated that the Zn atoms are in a completely oxidized state [76]. The two fitting peaks observed in the O1s region with binding energies of 531.4 and 532.8 eV are attributed to the oxidized metal ions in the nanoparticles (Fig. 9d) [77]. Fig. 9e exhibits the Cu2p XPS spectrum. The peaks appear at 934 eV and 962.9 eV, together with two peaks overlapping at 942 and 944.3 eV, which are assigned to the peak of Cu2p_{3/2}. On the other hand, the peak occurs at 954.2 eV, corresponding to the peak of Cu2p_{1/2}. These are attributed to the fully oxidized CuO surface [78]. The N1s spectra consist of three group peaks (Fig. 9f), which are assigned to the stretches of pyridinic-N, pyrrolic-N, graphitic-N, at binding energies of 399.2, 400.4, and 401.8 eV, respectively [79]. These nitrogen atoms can provide the lone pair electrons that can create polarity. Subsequently, the created polarity enhanced the insertion

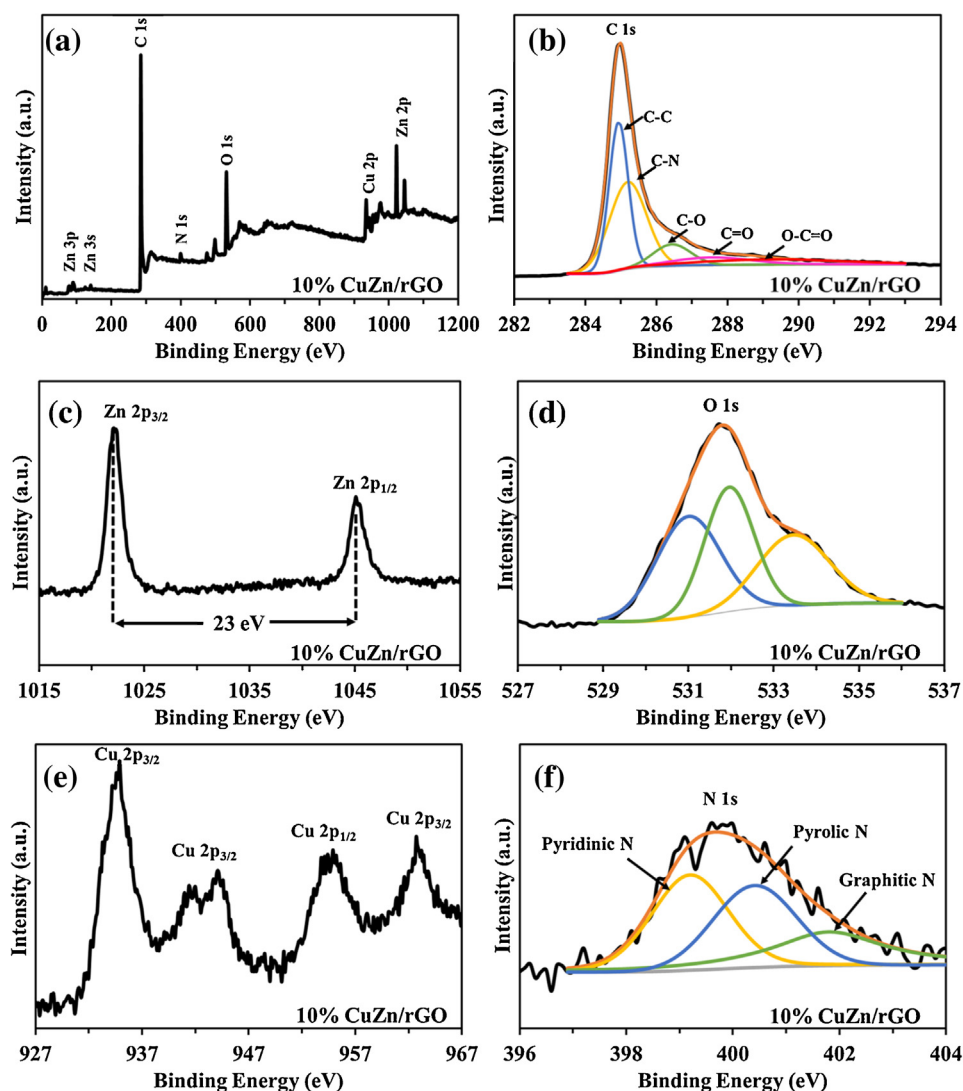


Fig. 9. XPS spectra for (a) survey spectra, (b) C 1s, (c) Zn 2p, (d) O 1s, (e) Cu 2p, and (f) N 1s of 10% CuZn/rGO.

of the copper and zinc ions in the rGO nanosheets [80,81] and formed metal complex [82].

3.2. Catalytic activity results

3.2.1. Effect of reaction temperature

The effect of hydrogenation temperature over 30%CuZn/rGO was investigated. From Fig. 10, it shows that the space-time yield of methanol (STY_{MeOH}) increases at reaction temperatures up to 250 °C, and then decreases above 250 °C. It can be explained that although a higher reaction temperature is preferred for CO₂ hydrogenation, it is possible that active metal particles agglomerated to form a larger cluster at a temperature above 250 °C. Consequently, the reaction temperature of 250 °C, which gave the highest space-time yield of methanol, was chosen for the activity testing of other catalysts.

3.2.2. Catalytic performance

The catalytic performance of the catalysts for CO₂ hydrogenation to methanol is summarized in Table 2. The 10 wt%CuZn/rGO catalyst exhibits the highest activity for the hydrogenation of CO₂ with a 26% CO₂ conversion, 5.1% MeOH selectivity, and 424 ± 18

$mg_{MeOH} g_{cat}^{-1} h^{-1} STY_{MeOH}$ at 250 °C and 15 bar after 5 h on stream of CO₂ and H₂. When the reaction was over, the spent catalyst was re-examined its structure with an XRD, in order to assess the stability of rGO. The obtained XRD pattern (not shown here) reveals that the catalyst still has the same structure as that of the

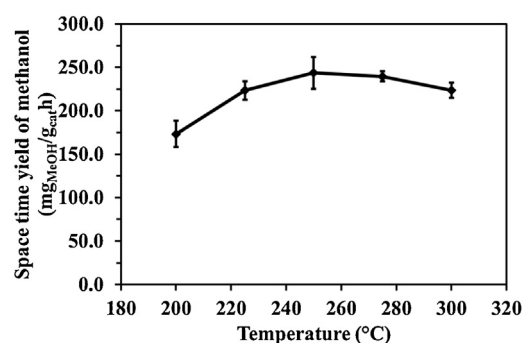


Fig. 10. Space time yield of methanol as a function of temperature, using 30%Cu-Zn/rGO catalyst.

Table 2The catalytic performance of CO₂ hydrogenation to methanol at 250 °C and 15 bar (average over 5 h).

Sample	CO ₂ conversion (%)	CH ₃ OH selectivity (%)	CO selectivity (%)	CH ₄ selectivity (%)	STY of CH ₃ OH (mg/g _{cat} h))
5%CuZn/rGO	14	2.8	69.2	11.1	220
10%CuZn/rGO	26	5.1	33.9	7.1	424
20%CuZn/rGO	19	8.5	55.9	15.0	244
30%CuZn/rGO	20	15.6	62.4	16.0	244

Table 3Comparison of the obtained performance on CO₂ hydrogenation to methanol with previous published works.

Catalysts	CO ₂ Conv. (%)	STY _{CH₃OH} (mg/g _{cat} h)	Condition T (°C)/P (bar)	Reference
CuZnGa	15.8	135	270/30	[17]
Cu-ZnO/Al ₂ O ₃	9.4	11	250/20	[31]
Cu-Zn/SiO ₂	2.0	66	250/20	[37]
16%Pd _{0.1} Zn ₁ /CNTs	6.2	37	220/80	[50]
Cu-ZnO	11.2	9	250/30	[83]
Cu/ZnO/ZrO ₂	24.6	210	270/50	[84]
10Cu60Zn30	21.0	274	250/15	[85]
10%CuZn/rGO	26.0	424	250/15	This work

fresh catalyst. When increasing the loading beyond 10 wt%, the CO₂ conversion and STY_{MeOH} decreased because the agglomeration of active metals led to reduced copper oxides to metallic Cu⁰, which is a crucial active metal for methanol synthesis.

Regarding the other works, the achieved performance by this work was compared to those of previous published works [17,31,37,50,83–85] as shown in Table 3. It is clearly seen that this work gives the highest STY_{MeOH} under the lowest operating pressure. As the matter of fact, the rGO, reduced by hydrazine, plays very important role in the enhanced performance of the CuZn/rGO catalyst. Refer to the XPS analysis as described earlier, the nitrogen atoms that linked with the rGO can reduce the energy barrier of H₂ dissociation [86,87]. It was reported that pyridinic-N is a favorable site for hydrogen bond interaction, which can attract hydrogen donor molecule to increase the STY_{MeOH} [88]. In addition, nitrogen groups can transfer multiple electrons, which involve in the conversion of CO₂ to methanol [89,90]. As a comparison, only a bulk Cu-ZnO catalyst gives a STY_{MeOH} less than 9 mg_{MeOH} g_{cat}^{−1} h^{−1} [83,91].

4. Conclusions

rGO nanosheets with diluted oxygen-containing groups were for the first time used as the support of the bimetallic Cu-Zn catalysts. The catalytic performances of the as-synthesized catalysts on the rGO support were investigated toward the CO₂ hydrogenation reaction to methanol fuel. The effects of the quantity of Cu-Zn loaded onto rGO support and the reaction temperature for converting CO₂ to methanol were studied using a tubular stainless steel fixed-bed reactor. The gas products were subsequently investigated by the gas chromatography technique. The investigation showed that increasing the reaction temperature over 250 °C can obstruct the methanol synthesis by decreasing the space time yield of methanol. Increasing the loading content of bimetallic compounds Cu and Zn over 10 wt% can lead to the undesired aggregation, less dispersion, and low specific surface area, eventually exhibiting poor catalytic activity with low space-time yield of methanol. After finely tuned, the rGO-supported Cu-Zn catalyst can provide the highest catalytic performance toward the CO₂ hydrogenation to methanol at a reaction temperature of 250 °C and a loading content of 10 wt% Cu and Zn metals on the rGO support. The catalyst provides the highest methanol productivity

of 424 mg_{MeOH} g_{cat}^{−1} h^{−1}, which may lead to the practical CO₂ conversion to methanol.

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