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CO₂ Hydrogenation to Methanol over Novel Melamine-Based Polyaminal Porous Polymer Coordinated to Cu-Based Catalyst

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Abstract

The catalytic conversion of carbon dioxide to methanol is significantly important both practically and scientifically for the reduction in CO₂ emissions. Furthermore, it can partially address the issue of human reliance on non-renewable resources. The main motivation of this study is to use a melamine polymer network to support a copper-based catalyst for CO₂ hydrogenation to methanol. Based on Schiff base chemistry, a facile catalyst-free process, a novel porous polyaminal polymer (MGPN) was prepared with nitrogen contents as high as 38%. MGPN was used as a support for Cu-based catalyst and applied in CO₂ hydrogenation to CH₃OH under mild conditions. A deep characterization of the MGPN@CuO/ZnO/Al₂O₃ catalyst was made through FTIR, N₂ adsorption–desorption, SEM-EDS, TEM, TGA, XRD, CO₂-TPD, and H₂-TPR techniques. The CO₂ hydrogenation study was performed in a fixed bed reactor with a residence time of 1.104 s on varying parameters such as the metal loading, catalyst amount, flow rate, pressure, calcination temperatures, reduction temperatures, and catalytic reaction temperature profile. The space-time yield (STY) of 145.43 mg_{methanol}·g_{catalyst}^{−1}·h^{−1}, a selectivity of 98.36%, and CO₂ conversion of 11.76% were obtained under an economically and energetically sustainable low-pressure (1 MPa) and 260 °C hydrogenation process.

Keywords: CO₂ hydrogenation; melamine based polymer; Cu-based catalyst; methanol; catalysis

1. Introduction

The swift rise in atmospheric CO₂ concentrations, chiefly caused by the widespread burning of fossil fuels, has resulted in considerable environmental issues, such as global warming, ocean acidification, and the melting of polar ice [1]. Therefore, converting CO₂ to value-added products is a very attractive method for using a non-toxic, renewable, and abundant carbon source [2]. Utilizing CO₂ as a plentiful and cost-effective C1 feedstock for value-added compounds is a promising approach within the realm of green chemistry [3,4]. The primary platform chemicals utilizing CO₂ as a feedstock comprise formic acid, methanol, methane, and hydrocarbons, alongside diverse CO₂ transformations [5,6].

Methanol, among platform chemicals, has attracted significant attention as an important fuel due to its status as a valuable commodity chemical with several industrial applications [7,8]. Currently, the hydrogenation of CO₂ to methanol has garnered significant



Academic Editor: Zhong-Wen Liu

Received: 2 April 2025

Revised: 11 June 2025

Accepted: 23 January 2026

Published: 5 February 2026

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interest in scientific research. The development of the synthesis of methanol catalysts employed copper (Cu) along with other metals such as nickel, silver, and iron to manufacture methanol under high-pressure circumstances.

Cu-based catalysts are used in the industry to convert CO₂ to methanol due to their low cost and high hydrogenation activity [9–12]. Copper is asserted to serve as the principal active site for the catalytic process. ZnO and Al₂O₃ serve not merely as inert supports; they assume more significant functions in the catalytic reaction [13]. Integrated microscopic and theoretical investigations have corroborated the synergistic impact of Cu/ZnO, demonstrating that Zn species are essential components of active sites in methanol synthesis, positioned atop highly active Cu metal and ZnO and various reaction mechanisms [14–16]. The Badische Anilin-und-Soda-Fabrik (BASF) pioneered the sector by introducing the Cr₂O₃-ZnO catalyst to produce methanol by utilizing carbon monoxide (CO) and hydrogen (H₂) at high-pressure settings (250 atm) and elevated temperature (320 °C) [17]. The initial catalysts displayed activity under high pressures and temperatures; nevertheless, they lacked stability and were highly prone to deactivation, requiring frequent replacement, which increased the production costs. Although the Korea Institute of Science and Technology developed the Cu/ZnO/Al₂O₃ catalyst with high activity and selectivity, the challenge of ensuring sufficient catalyst stability is still hindered for its industrial applications. In addition to conventional supports like ZnO, ZrO₂, CeO₂, and Al₂O₃ [1], recent advancements in catalyst design have concentrated on employing metal—organic frameworks (MOFs), such as MCM-41 and SBA-15, as supports for Cu-based catalytic systems. However, drawbacks of these types could arise from the production cost or the lower selectivity toward methanol [14,18]. Thus, the fundamental concern with conventional Cu-based catalysts for CO₂ conversion is the progressive agglomeration of copper nanoparticles (NPs) throughout the reaction, which reduces active Cu/ZnO surfaces [1]. Consequently, it is essential to concentrate on formulating strategies to stabilize these active surfaces and enhance the long-term efficacy of Cu-based catalysts.

In the past decade, there has been significant interest in porous organic polymers (POPs) due to their potential applications in drug release, gas storage, and heterogeneous catalysis [15,16,19]. The benefit of these POPs in heterogeneous catalysis is mostly evident due to the ability to engineer materials with functionalized building blocks under varying reaction conditions. POPs such as covalent organic frameworks (COFs) provide highly functionalized pore surfaces for various catalytic and photocatalytic activities [20].

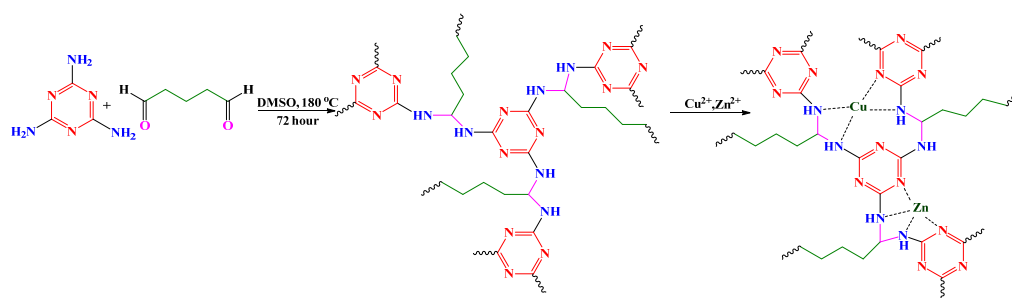
Melamine-based polymer networks, a category of POPs, garnered our interest due to their straightforward synthesis, adjustable fundamental properties, and comparatively low-cost precursors [21]. Moreover, melamine-based polymers have been employed for CO₂ adsorption [22–27] and the hydrogenation of CO₂ to produce formic acid [28–30]. Melamine (MA) is a cost-effective chemical compound utilized in the plastic and coating industries [31,32]. To our knowledge, melamine-based polymers have not been employed to hydrogenate CO₂ to methanol or methane.

Therefore, the main objective of this work is the synthesis of a novel Cu-based catalyst utilizing the melamine glutaraldehyde polymer network (MGPN) as an economical solid support, leveraging commercially available raw ingredients for polyaminal networks to facilitate straightforward and cost-efficient production. Several techniques are used to characterize the catalyst, as well as the evaluation of its performance toward the CO₂ conversion to methanol. The influence of critical parameters on catalytic performance is tested.

2. Results and Discussion

2.1. Materials Synthesis and Characterization

Successful production of melamine glutaraldehyde polymer networks (MGPNS) was demonstrated by using melamine (MA) as the A3-type cross-linker and glutaraldehyde (GA) as a difunctional aliphatic aldehyde. In this reaction, the amine groups of melamine react with glutaraldehyde to form Schiff bases, which are again attacked by melamine, resulting in the formation of amina ($-\text{NH}-\text{C}-\text{NH}-$), which essentially yields the desired MGPNS as described in Scheme 1. It is known that melamine amines have a dynamic structure between primary and secondary amines. Thus, imine formation may be limited [33]. For the first time, to our knowledge, this functional porous MGPNS used as a support is crosslinked with a CZA catalyst for CO_2 hydrogenation to CH_3OH .



Scheme 1. Synthesis of MGPNS and MGPNS@CZA catalyst.

The successful synthesis of MGPNS and MGPNS@CZA-2 was confirmed by Fourier transform infrared (FTIR). Figure 1a displays the FTIR spectra of MA, MGPNS, and MGPNS@CZA-2. The absorption bands at 3470 cm^{-1} and 3410 cm^{-1} (NH_2 stretching) and at 1645 cm^{-1} (NH_2 deformation) correspond to the primary amine groups of melamine. The peaks at 2870 cm^{-1} (C-H stretching of CHO) and 1690 cm^{-1} (C=O stretching) of glutaraldehyde are absent in the MGPNS and MGPNS@CZA spectra. In the MGPNS spectrum, the characteristic peak of aliphatic C-H at 2846 cm^{-1} appeared. Distinct bands appear for quadrant stretching at 1541 cm^{-1} in MGPNS and 1506 cm^{-1} in MGPNS@CZA-2 and for semicircle stretching at 1405 cm^{-1} in MGPNS and MGPNS@CZA-2 of the triazine moiety, which implies the successful incorporation of melamine into the network. New peaks at 2920 and 1278 cm^{-1} were assigned to the methylene C-H and C-N groups of the amina, respectively [32,34]. Furthermore, a wide band at 3367 cm^{-1} confirms the N-H stretching of a secondary amine, which is formed due to the condensation of the monomers. Additionally, in the spectrum of MGPNS@CZA-2, peaks at 492 and 1097 cm^{-1} correspond to N-M-N stretching vibrations that confirm the formation of a metal coordination complex in MGPNS@CZA-2 [35,36]. The composition of the MGPNS was confirmed through the CHN elemental analysis (Table S2). The elemental compositions were 51.27% for C, 6.12% for H, and 38.39% for N, which agrees with their theoretical values.

Due to the poor solubility of MGPNS in common solvents, the solid-state ^{13}C NMR (^{13}C SS-NMR) spectrum is further utilized to characterize the molecular structure. As shown in Figure 1b, the strong signal at 168.1 ppm was assigned to carbons in the triazine rings. A signal at 165.95 ppm was assigned to the triazine ring carbons of the second ring, as each methylene group is attached to two melamine rings, and each one experiences a different environment depending on cross-linking. The broad signal at 57.7 ppm was assigned to the methylene group in amina linkages. The peaks that appear at 41.03 ppm , 27.17 ppm , and 17.81 ppm were attributed to the C-H aliphatic bond of GA. Additionally, a weak signal appears at 163.25 ppm , owing to the remaining imine bonds in the network. On the other hand, the absence of carbonyl signal at 194 ppm assures the absence of the GA

precursor in the final product, indicating the complete condensation between $-CHO$ and $-NH_2$ groups, which is in good agreement with the previous results of melamine-based polymers [21,33,34,37,38].

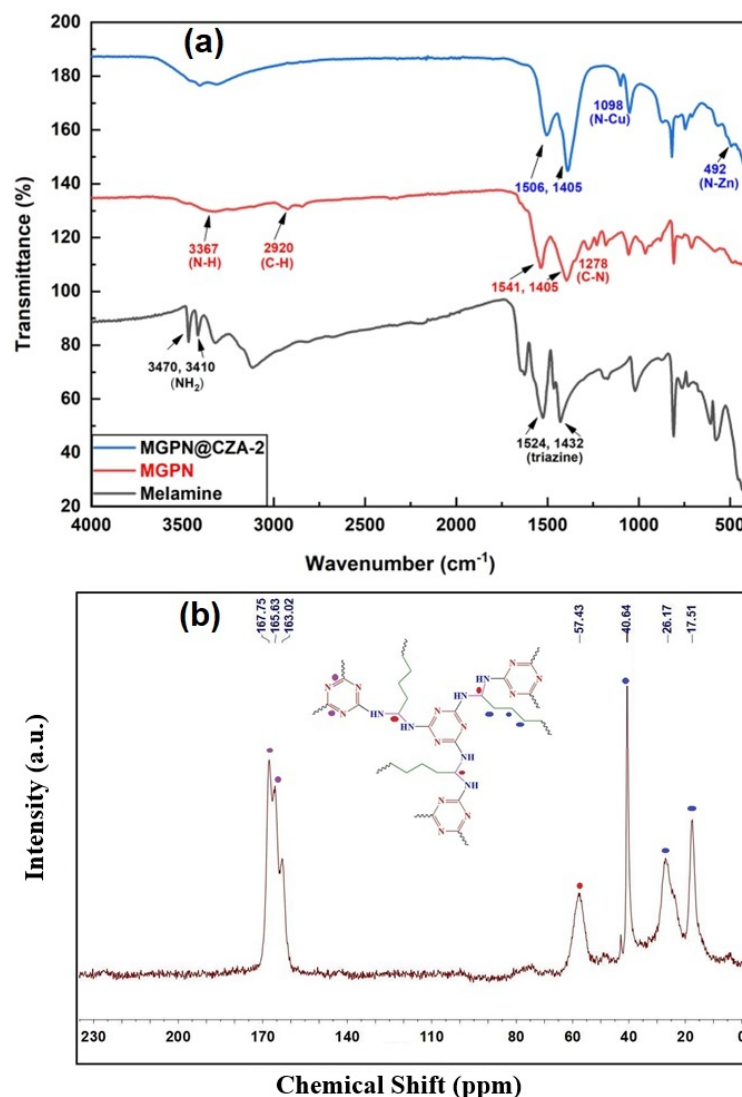


Figure 1. (a) FTIR spectra of melamine, MGPN, and MGPN@CZA-2, and (b) solid-state ^{13}C -NMR spectrum of MGPN.

The thermal stability of MGPN and MGPN@CZA-2 materials was investigated by TGA, and the obtained thermogram is presented in the Supplementary Information (Figure S1 and Table S3). In the TGA thermogram of MGPN, the main weight loss started at a temperature over $345\text{ }^{\circ}C$ due to the network breakdown, and the burning began gradually above $400\text{ }^{\circ}C$. Therefore, MGPN is stable up to $345\text{ }^{\circ}C$. On the other hand, the TGA thermogram of MGPN@CZA-2 shows a steep weight loss at ca. $468\text{ }^{\circ}C$ and a higher char residue of 63% at $807\text{ }^{\circ}C$ due to the presence of CZA moiety. This value was higher than the previously reported melamine-based Schiff base network, indicating that the synthesized MGPN@CZA-2 is more stable [29,34,37]. The surface area and pore size of the synthesized materials are important parameters for the study of the adsorption capacity of the catalyst; therefore, we studied the porosity features of the MGPN and MGPN@CZA-2 by performing the N_2 adsorption–desorption isothermal analysis at 77 K. According to IUPAC [39], both adsorption isotherms of MGPN and MGPN@CZA-2 show a modest gas uptake at relatively low pressures and increase slowly in the middle region as shown in

Figure 2a. This behaviour confirms the mesoporous nature of the synthesized MGPn and MGPn@CZA-2 catalysts. Also, these isotherms have a very marked hysteresis loop during desorption; this behaviour can be attributed to the deformation of the pores during the measurement due to a low rigidity of the network [34,38,40–42]. Moreover, we used the Brunauer–Emmett–Teller (BET) model to investigate the surface area and the pore volume of materials. The as-prepared MGPn was found to have a BET surface area of $62.72 \text{ m}^2 \cdot \text{g}^{-1}$ with a total pore volume of $0.062 \text{ cm}^3 \cdot \text{g}^{-1}$. After cross-linking with CZA-2 to form MGPn@CZA-2, the measured BET area was $50.36 \text{ m}^2 \cdot \text{g}^{-1}$ with a total pore volume of $0.374 \text{ cm}^3 \cdot \text{g}^{-1}$. The pore size distributions of the as-prepared catalysts were also estimated using the NLDFT method. The pore sizes observed were distributed in mesoporous ranges under the isothermal curves. Figure 2b shows that the MGPn revealed two mesoporous at 2.74 and 4.48 nm, while the MGPn@CZA-2 exhibited three mesoporous at 2.62, 5.34, and 9.06 nm. This BET surface area of MGPn@CZA-2 was higher than other Cu-based catalysts, which indicated that the crosslinking of MGPn with CZA enhanced the surface area of the catalyst. For example, the other Cu-based catalysts' BET surface areas were 27.00 and $25.38 \text{ m}^2 \cdot \text{g}^{-1}$ using $\text{CuZnO}/\text{Al}_2\text{O}_3$ and $\text{CuZnO}/\text{ZrO}_2$, respectively [43,44]. The porosity properties of these two MGPn and MGPn@CZA-2 are summarized in the Supplementary Information (Table S4).

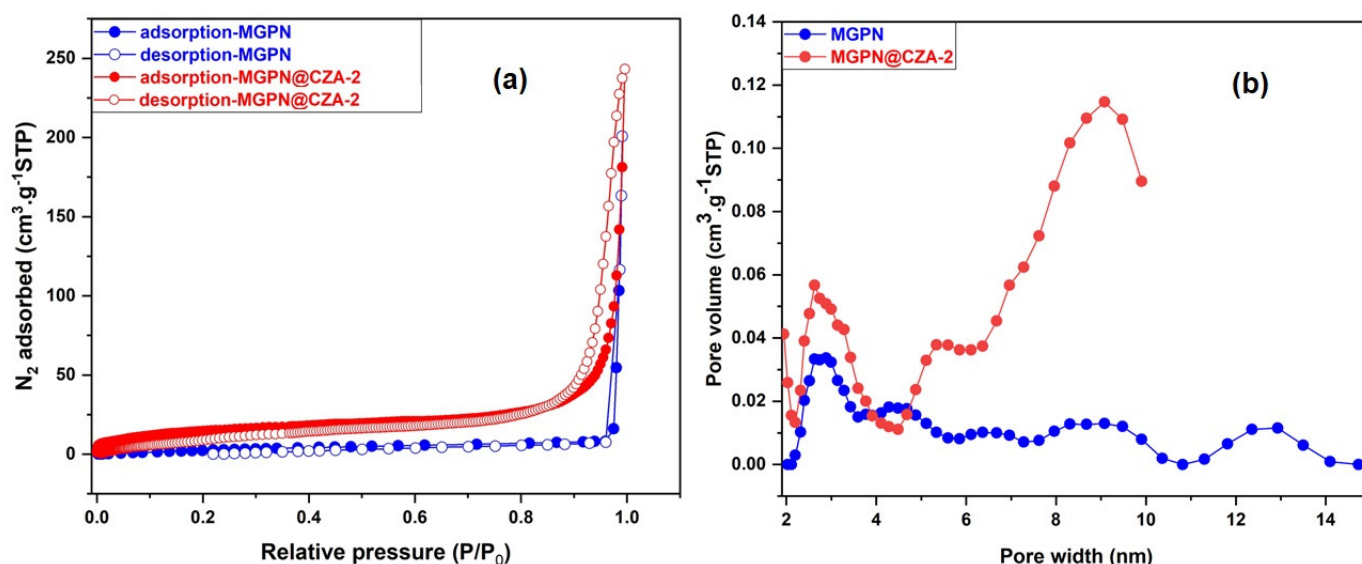


Figure 2. (a) Nitrogen adsorption/desorption isotherms of MGPn and MGPn@CZA-2, and (b) pore size distribution profile of MGPn and MGPn@CZA-2.

The morphology of the MGPn before and after its crosslinking with CZA-2 was investigated by SEM, TEM, and EDX-mapping techniques. In Figure 3a, some spherical particles are observed on the surface of MGPn or embedded into the internal voids of MGPn, which indicates the successful incorporation of melamine into the MGPn. The SEM image of CZA-2 shows interwoven star shapes, as seen in Figure 3b. Figure 3c showed that the copper-based catalyst was dispersed on the surface of the MGPn support, which indicated the crosslinking of the copper-based catalyst on MGPn. The TEM images indicate that CZA species are uniformly distributed over the melamine polymeric framework, as presented in Figure 3d–f. The EDX-mapping results that confirm this uniform distribution are presented in the Supplementary Information (Table S5, Figures S2–S6).

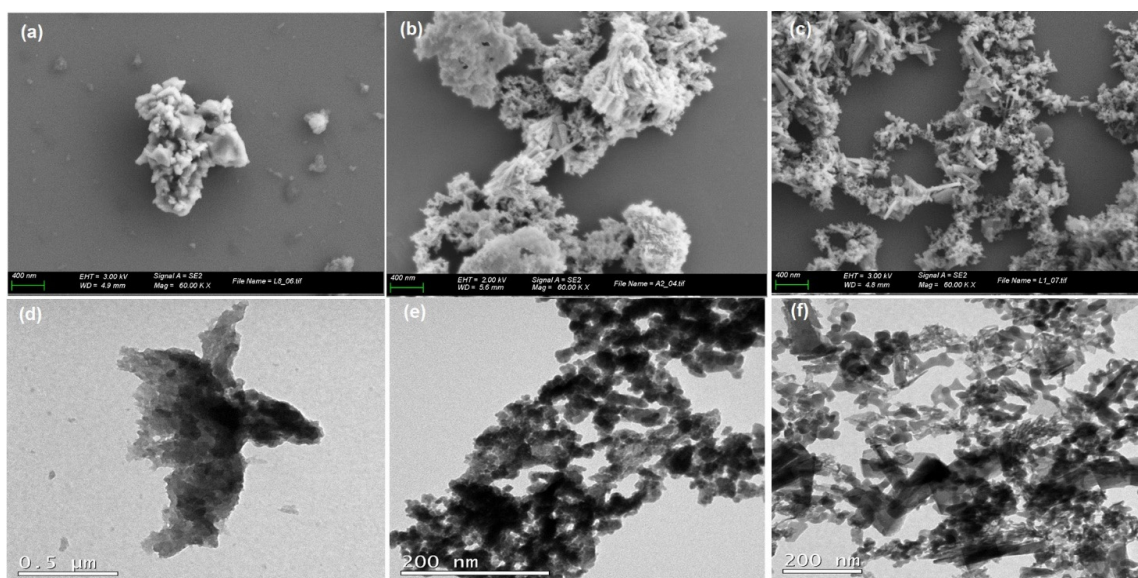


Figure 3. SEM images of (a) MGPn, (b) CZA-2, and (c) MGPn@CZA-2, and TEM images of (d) MGPn, (e) CZA-2, and (f) MGPn@CZA-2.

The XRD analysis is another local structural technique that can provide complementary information to the above data. As presented in the Supporting Information (Figure S7), the powder XRD pattern of the MGPn has a wide peak, positioned around $2\theta = 20^\circ$, corresponding to the most amorphous part. The lack of any sharp peaks may indicate the absence of melamine, meaning that all melamine has reacted. A similar behaviour was observed for the structurally related polyaminal porous polymers [32,37,45]. Figure 4a shows the XRD patterns of the MGPn@CZA-2 catalyst prepared before catalysis, characterized by the presence of two main peaks corresponding to the well-crystallized phase of CuO at $2\theta = 35.8^\circ$ and 38.9° [46,47]. Peaks at $2\theta = 31.6^\circ$ and 47.7° , indicative of zinc and aluminum phases, are detected with a weak intensity, which implies that aluminum and zinc phases are in an amorphous-like or a micro-crystallite state [48]. Moreover, another peak is observed at $2\theta = 29.3^\circ$ for the catalysts containing a high zinc content, which is ascribed to the $\text{Zn}(\text{OH})_2$ phase (JCPDS 20-1437) [49].

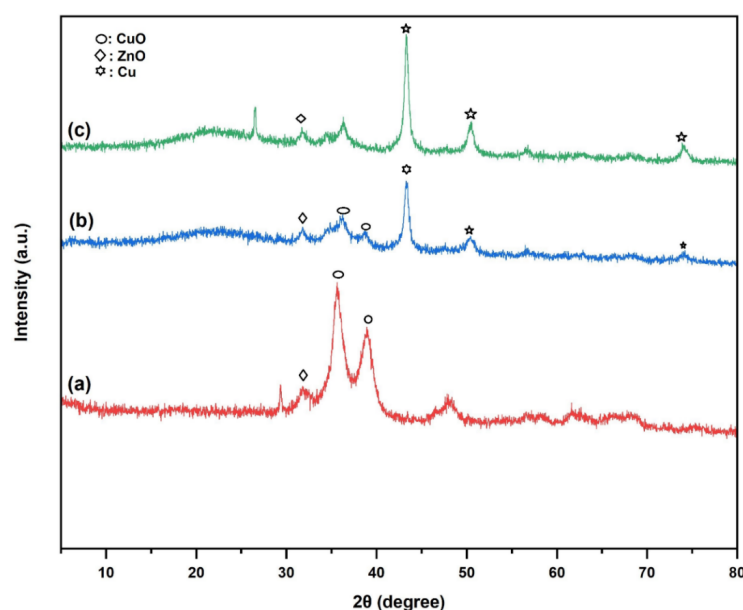


Figure 4. XRD images of MGPn@CZA-2: (a) before catalysis, (b) after catalysis, and (c) after stability.

The reducibility of the MGP@CZA-2 was investigated by hydrogen temperature-programmed reduction (H₂-TPR) in a 50–800 °C temperature range. The intensity of the reduction peaks is proportional to the amount of H₂ consumed during the reduction process. As shown in Figure 5a, the reduction profile exhibits two main bands, below and above 300 °C, related to H₂ consumption. To understand the TPR results, the broad band of H₂ consumption below 300 °C is divided into two peaks, which are signed to α and β peaks. The two peaks at 206 °C and 273 °C were attributed to the reduction in CuO. The low-temperature peak (α) is attributed to the reduction in highly dispersed CuO surface species, whereas the second peak (β) is related to the reduction in the bulk CuO [50,51]. The other peak (γ), appearing at temperatures higher than 300 °C, may be related to reducing zinc oxide [49].

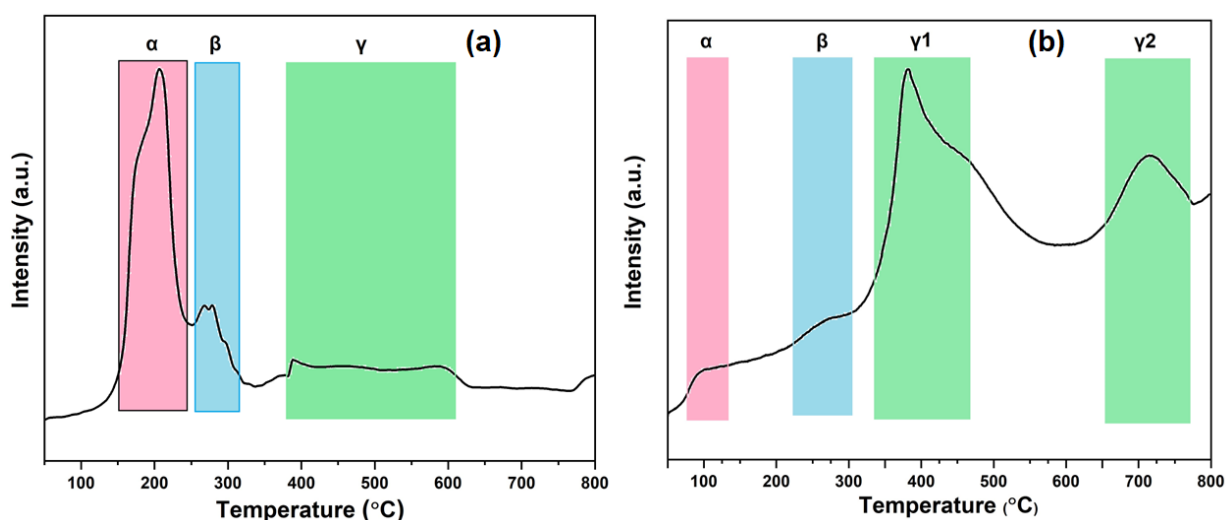


Figure 5. (a) H₂-TPR profile of MGP@CZA-2 and (b) CO₂-TPD profile of MGP@CZA-2.

As presented in Figure 5b, the CO₂-TPD profile of the catalyst was divided into four peaks (α , β , γ_1 , and γ_2). The first adsorbed peak of the weak basic site (α) could be attributed to the presence of nitrogen in the MGP structure that physisorbs CO₂ [52,53]. The second peak of weakly basic sites (β) is related to the metal–oxygen pairs. The third peak of the strongly basic site (γ_1) corresponds to unsaturated oxygen atoms. The fourth peak of the moderately basic site (γ_2) is due to CO₂ chemisorption on the CuO basic sites [44,54]. The basic sites of β seemed to be more correlated to the active sites for CO₂ hydrogenation than the other basic sites, considering that the reaction temperature was 180–300 °C.

2.2. Catalyst's Performance in Methanol Synthesis

Based on one of the interesting properties of MGP@CZA catalyst, as shown previously in the CO₂-TPD profile, it was noted that the strong basic sites in the catalyst are promoted due to the existence of metal oxide promoters. Consequently, the hydrogenation of CO₂ into methanol is preferable to its dissociation to CO compared to the adsorption of the intermediate species on the moderate basic sites [55]. Therefore, the hydrogenation of CO₂ to CH₃OH was performed firstly to assess the activity of the MGP@CZA catalyst using different copper loadings. Then, the catalyst with the amount of copper that allowed us to obtain the highest value of the STY was further used under different reaction conditions by varying the effect of (a) calcination temperature, (b) catalyst amount, (c) flow rate, (d) pressure, (e) reducing temperature, (f) catalytic reaction temperature profile, and the (g) reusability and stability of the catalyst. The time contact could be explained by studying the effect of copper loading and flow rate. The STY values of methanol ranged from

77.44 $\text{mg}_{\text{CH}_3\text{OH}} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ to 93.02 $\text{mg}_{\text{CH}_3\text{OH}} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ by using a range of copper loading from 48.77% to 62.36% under the following conditions (temperature 260 °C, pressure 10 bar and flow rate 10 $\text{mL} \cdot \text{min}^{-1}$) shown in Figure 6a. This could be attributed to the increase in the active sites with increasing copper amount and could be explained following the theory of the dual-site mechanism for the methanol production [12,49], where the dissociative adsorption of the hydrogen molecule is produced on the ZnO sites, while the carbon dioxide is adsorbed on copper active sites. Therefore, the mechanism is favoured when there are more active sites together. Hence, an increase in the metal loading favours the mechanism of the CH_3OH synthesis reaction. This behaviour can be explained by relating the metal loading amount with the basic nature of the MGPN support. In another way, the increase in STY with an increase in CZA content could be explained by the fact that more metal species are available in the basic centres of the polymer network, resulting in the enhanced conversion of readily available CO_2 . Additionally, it was observed that a slight increase in the value of STY was attained when the copper loading ranged from 56.87% to 62.36%. This could be referred to with the further addition of CZA. It is proposed that saturation of basic centres occurred with an accompanying decrease in the CO_2 adsorption sites, thereby causing a slight increase in STY. Moreover, control experiments at 10 $\text{mL} \cdot \text{min}^{-1}$, 10 bar, and 260 °C were performed to elucidate the role of MGPN support and unsupported CZA-2 in the hydrogenation reaction. The values of STY obtained using MGPN support (10 mg) and unsupported CZA-2 (10 mg) were 15.71 and 51.35 $\text{mg} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, respectively, as shown in Figure 6a. This agrees with the previous study, which used a melamine polymer network to support the hydrogenation of CO_2 to formates [29]. Therefore, it was speculated that MGPN@CZA-2 would exhibit the best CO_2 conversion and CH_3OH selectivity, consistent with the catalytic performance results. Many researchers [47] have reported that the activity of the CZA increases linearly with the increase in the metallic copper surface area. However, other reports [43] suggest that the yield of CH_3OH is not proportional to the copper surface area for Cu–ZnO and Cu–ZnO– Al_2O_3 and that other factors can be involved. In this study, the conversion of CO_2 increases with the increase in the copper content in the prepared catalysts, which is in agreement with the previous study [12]. Also, we see the selectivity of CH_3OH and CO increase with increasing copper amount, but CH_4 selectivity appears only with a low copper amount in MGPN@CZA-1 of 3.21%. We can see that the selectivity of CH_4 reached 26.03% using MGPN support alone, as presented in the Supporting Information (Table S6). After these results, MGPN was used as a support and to enhance the catalytic activity of CZA in the hydrogenation of CO_2 to CH_3OH . Thus, MGPN@CZA-2 was chosen as the optimum amount of CZA for this catalytic reaction in economic terms.

The performance of the MGPN@CZA-2 catalyst prepared under different calcination temperatures for CH_3OH synthesis from CO_2 hydrogenation is summarized in Figure 6b. The CH_3OH yield increases with calcination temperature, with a maximum of 350 °C, then decreases at higher temperatures. Consequently, a continued decline of catalytic activity from MGPN@CZA-2-400 to MGPN@CZA-2-500 is observed. Although the polymer exhibited higher stability at higher temperatures, as demonstrated in TGA, the decrease in STY at higher calcination temperatures (>400 °C) could be attributed to the presence of large particles, as reported by Ramirez et al. [19]. CH_3OH synthesis is an exothermic reversible reaction whose equilibrium constant decreases when temperature increases. Therefore, an increase in the reaction temperature is disadvantageous to CH_3OH synthesis. On the other hand, CH_3OH selectivity increased slightly when the calcination temperature was increased from 300 to 500 °C (95.67 to 96.73%). As is well known, for copper-based catalysts, higher dispersion of Cu usually results in a higher catalytic activity [56,57]; the variation trend could be explained in terms of the dispersion of Cu in CZA catalysts. Furthermore, it is noteworthy that a maximum value of CH_3OH selectivity (99.26%) can be observed

for MGP@CZA-2 at a calcination temperature of 350 °C. Also, a very small difference in CH₃OH selectivity (95.76–96.73%) is observed for the other calcination temperature from 400 to 500 °C, as shown in Supporting Information (Table S6), which agrees with the previous studies [58]. After studying the effect of copper amount and calcination temperature parameters, three different amounts of the MGP@CZA-2 catalyst were tested (10 mg, 20 mg, and 40 mg), and the optimum amount of catalyst is presented in Figure 6c. As observed, the final STY was relatively higher when 10 mg of the catalyst was used for the catalytic test. The reason could be attributed to the fact that in the case of using a low amount of catalyst, more active sites are in contact with the carbon dioxide, which enhances the catalytic conversion of carbon dioxide to methanol. Thus, 10 mg of the catalyst was chosen as the best amount for this catalytic reaction. Additionally, CH₃OH selectivity decreased from 97.56% to 94.46% with the increase in the catalyst amount, as presented in the Supporting Information (Table S6).

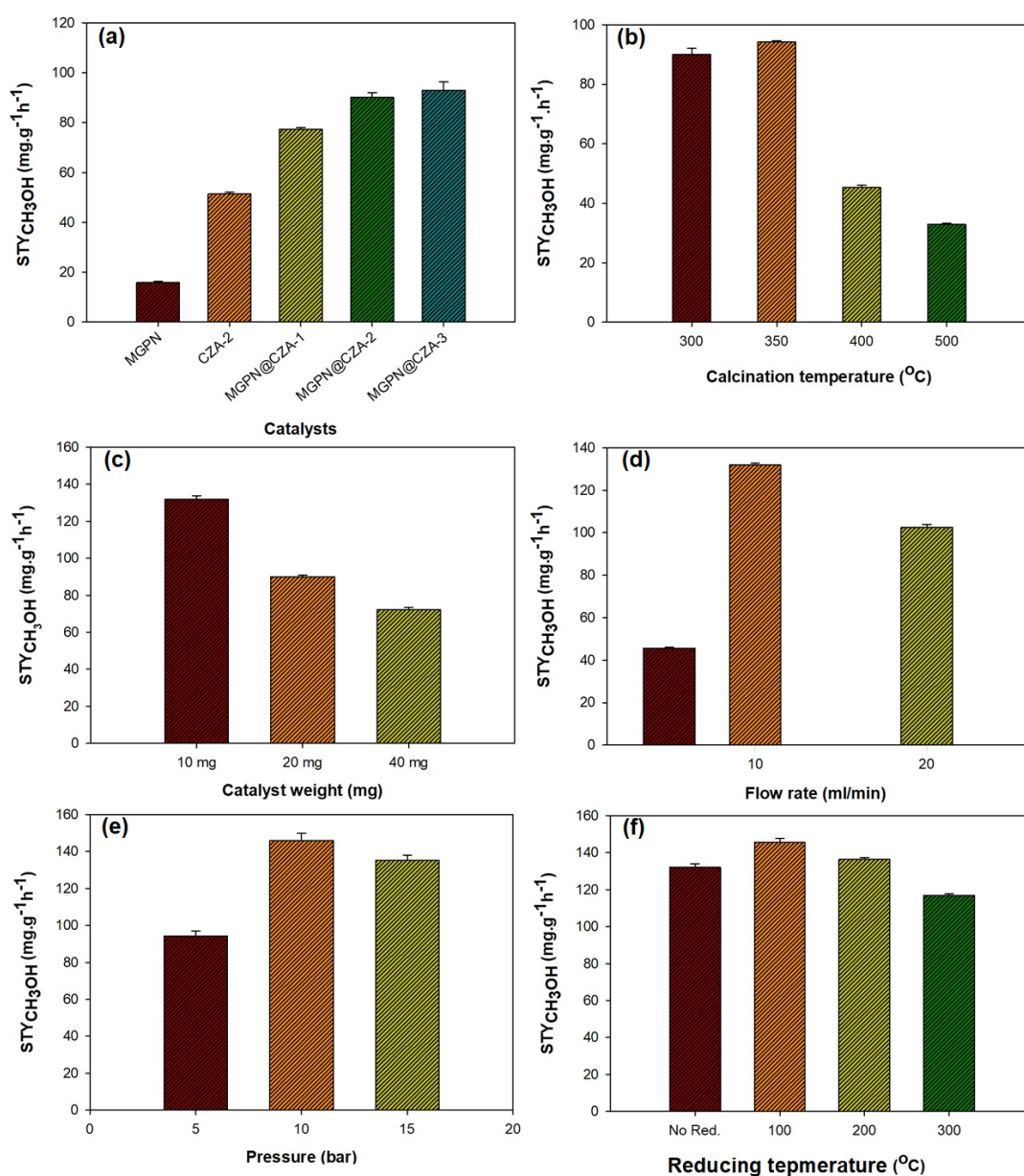


Figure 6. Effects of (a) copper loading, (b) calcination temperature (°C), (c) catalyst amount, (d) flow rate, (e) pressure, and (f) reducing temperature (°C) in the catalytic hydrogenation of CO₂ to CH₃OH.

Regarding the second parameter related to the contact time effects, the effect of flow rate on the CO₂ conversion and methanol selectivity over the most active MGPNCZA-2-300 °C catalyst was studied. Three different flow rates, including 5 mL·min^{−1}, 10 mL·min^{−1} and 20 mL·min^{−1}, were tested, as presented in Figure 6d. As observed, the final STY was relatively higher when 10 mL·min^{−1} flow was used for the catalytic test. The reason is that the higher the flow rate, the shorter the contact time between the feed gas and the active components on the surface of catalysts. However, the CH₃OH selectivity increased with the increase in flow rate, as shown in the Supporting Information (Table S6), indicating that the decrease in the rate of reverse water-gas shift (RWGS) reaction is larger than that of the CH₃OH synthesis reaction with the increase in flow rate, which is in agreement with the previous studies carried out so far [59], while the lower value of STY at 5 mL·min^{−1} could be attributed to mass transfer problems. Also, CH₃OH selectivity reached 95.43% when the flow rate increased, but CO selectivity decreased when the flow rate increased, as shown in the Supporting Information (Table S6). Thus, 10 mL·min^{−1} flow was chosen as the best amount for this catalytic reaction. Three different pressures, including 5 bar, 10 bar, and 15 bar, were tested, as presented in Figure 6e. As observed, the final STY was relatively higher when 10 bars were used for the catalytic test, and then a slight decrease in the STY of CH₃OH was observed at 15 bars. The obtained results could be attributed to the saturation of the STY value of CH₃OH or as a result of catalyst deactivation, changes in the reaction kinetics, and by-product formation by increasing the pressure [60]. Thus, 10 bar as a lower pressure was chosen as the best pressure for this catalytic reaction, which is better in operational and economic terms. We can see the selectivity of CH₃OH increasing with increasing pressure. Also, CH₃OH and CO selectivity decreases slightly with increasing pressure. On the other hand, CH₄ selectivity increased, as shown in the Supporting Information (Table S6). As presented in Figure 6f, three different reduction temperatures (100, 200, and 300 °C) were tested for the catalyst MGPNCZA-2 calcined at the best temperature (300 °C). With increasing the reducing temperature, the STY of CH₃OH decreased, accompanied by a decrease in CH₃OH selectivity, as shown in the Supporting Information (Table S6). Moreover, the CO₂ conversion was calculated under the best conditions of flow (10 mL·min^{−1}), pressure (10 bar), catalyst amount (10 mg), calcination temperature of the catalyst (300 °C), reducing the temperature of the catalyst (100 °C) and was found to be 11.76%. The variation in the catalytic activity for CH₃OH synthesis with different temperatures for the reaction is plotted in Figure 7a. We can see that the CO₂ conversion and the yield of CH₃OH increase with the elevation of reaction temperature. In contrast, CH₃OH yield reaches a maximum at 280 °C and then slightly decreases. It is well known that the reaction rate increases with the increase in temperature, and more CO₂ is converted to CH₃OH [47]. However, the yield of CH₃OH declines with the increase in temperature, which can be due to the formation of CO. It is noticed that only a fraction of CO₂ was converted to CO, while the rest was converted to CH₃OH. The CH₃OH synthesis is an exothermic reversible reaction whose equation constant decreases when temperature increases. Therefore, an increase in reaction temperature is disadvantageous to methanol synthesis. We also noted that the CH₃OH synthesis was more sensitive than the RWGS according to the reaction temperature. This trend agreed with previous studies [61,62]. Also, the selectivity of methanol increases slightly with increasing temperature, reaching the maximum of 97.60% at 280 °C and then slightly decreasing to 95.32% at 300 °C. Additionally, the selectivity of CO has a small value of 2.51% at 300 °C, and CH₄ selectivity decreases with increasing temperature, as shown in Figure 7b. Moreover, the CO₂ conversion was found to be based on the temperature reaction. For instance, it was found that, by increasing the temperature to 260 °C, an increase in the CO₂ conversion was observed to reach 11.76%. Increasing the temperature to 300 °C decreases the conversion

value to 9.1%. This result could be explained in terms of thermodynamics due to the exothermic reaction of the methanol synthesis and the endothermic reaction of the reverse water-gas shift [14]. Moreover, the highest values of the STY and selectivity of methanol, as well as the conversion, could be attributed to the fact that the catalyst shifts the equilibrium conversion of CO₂ reactions to the right, which mainly enhances the formation of methanol by water adsorption produced from the catalytic hydrogenation of CO₂ [63]. Also, the removal of the by-product water could be attributed to the hydrophobicity properties of the catalyst, which is assessed by the determination of the water contact angle before (81.41°) and after calcination (86.08°), as described in detail in the Supplementary File (Section S8) [64].

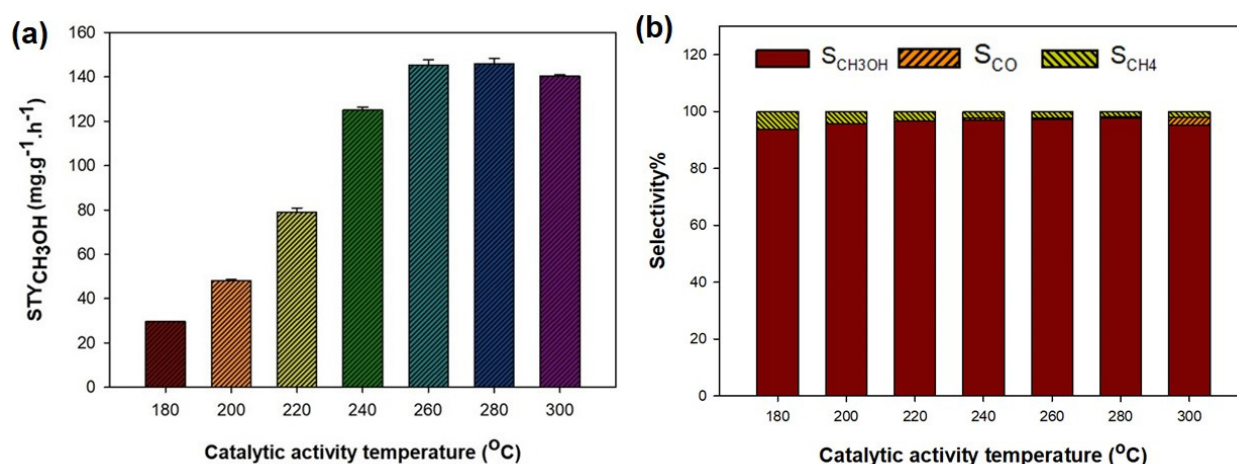


Figure 7. Effect of catalytic reaction temperature (a) in the catalytic hydrogenation and (b) selectivity of CO₂ to CH₃OH.

2.3. The Stability and Reusability of the Catalyst

To assess the stability of the MGP@CZA-2-300 °C catalyst, the synthesis of CH₃OH by CO₂ hydrogenation was measured over 30 h, and the results are presented in Figure 8a,b. As observed, after 30 h of continuous reaction, the catalytic performance of the catalyst decreased by only 27%. Meanwhile, the CH₃OH selectivity decreased slightly from ~98% (at 1 h) to ~97% (at 30 h). Additionally, the CO selectivity increased slightly from ~1.43% (at 1 h) to ~2.31% (at 30 h), and traces of CH₄ can be neglected as shown in Table 1. These results suggest that the MGP@CZA-2 catalyst prepared by the ex situ method exhibits a stable catalytic performance for CO₂ hydrogenation. To evaluate the reusability of the catalyst, after the catalytic reaction was finished, it was recalcined at 300 °C and used again. The reusability test was carried out eight times; the results are presented in Figure 8b. As shown, after the recalcination of the used catalyst, it showed the same catalytic activity as the fresh catalyst. For instance, the STY of CH₃OH decreased slightly from 145.43 to 126.64 mg·g⁻¹·h⁻¹ after cycle 8. Also, the CH₃OH selectivity decreased from 98.36 to 96.01 after eight cycles, accompanied by a slight increase in the selectivity of CH₄ and CO, as shown in Table 1. As can be observed in Figure 9a,b, the catalyst maintained its porous structure after the catalytic reaction, which confirms the catalyst's sustainable performance and follows the stability test results presented in Figure 8a. However, as seen in Figure 9c,g, as the catalytic reaction progresses for a longer time, the surface pores of the catalysts are aggregated, which can explain the decrease in STY during the stability process, as shown in Figure 8a. Thus, the irreversible structure changes are attributed to the segregation of the Cu-based catalyst, which hinders its catalytic activity [65].

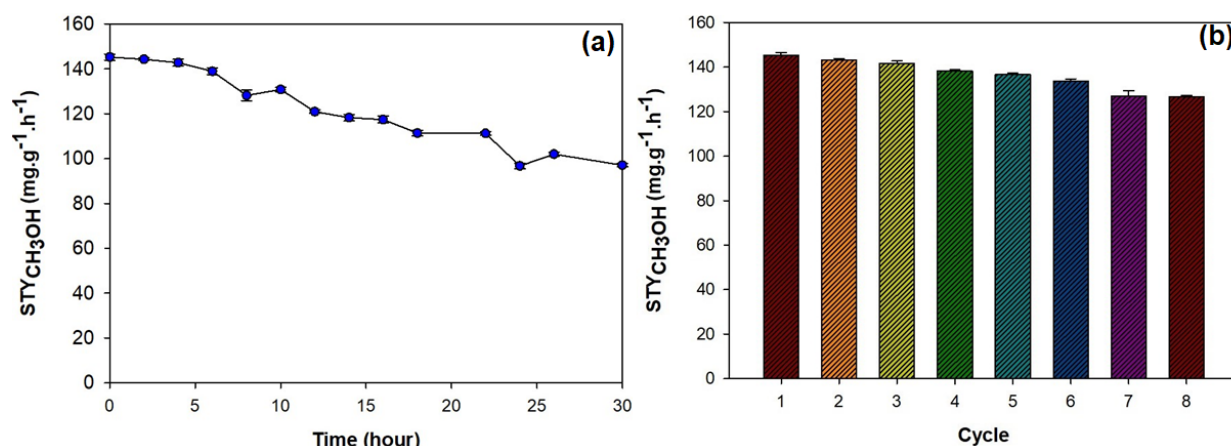


Figure 8. (a) Stability and (b) reusability results of the MGPn@CZA-2 catalyst.

Table 1. The selectivity data for CO₂ hydrogenation to CH₃OH using MGPn@CZA-2.

Test	Time (Hour)/ Cycle Number	Selectivity (%)		
		CH ₃ OH	CH ₄	CO
Stability	1	98.57	1.43	N.D. *
	2	98.40	1.45	0.15
	4	98.54	1.45	N.D.
	6	98.73	1.26	N.D.
	8	98.51	1.48	N.D.
	10	98.20	1.79	N.D.
	12	98.32	1.67	N.D.
	14	97.97	2.02	N.D.
	16	98.32	1.67	N.D.
	18	98.15	1.84	N.D.
	22	97.68	2.14	0.17
	23	97.97	2.02	N.D.
	25	98.10	1.89	N.D.
	30	97.68	2.31	N.D.
Reusability	1	98.36	0.89	0.76
	2	98.35	0.85	0.85
	3	98.10	0.86	0.86
	4	97.83	0.86	0.86
	5	96.42	2.25	2.25
	6	96.19	2.48	2.48
	7	95.23	3.22	3.22
	8	96.01	2.60	2.60

* N.D.: Not detected. Reaction conditions: weight of catalyst = 10 mg, calcination temperature = 300 °C, flow = 10 mL min⁻¹, pressure = 10 bar, and H₂: CO₂ = 3:1.

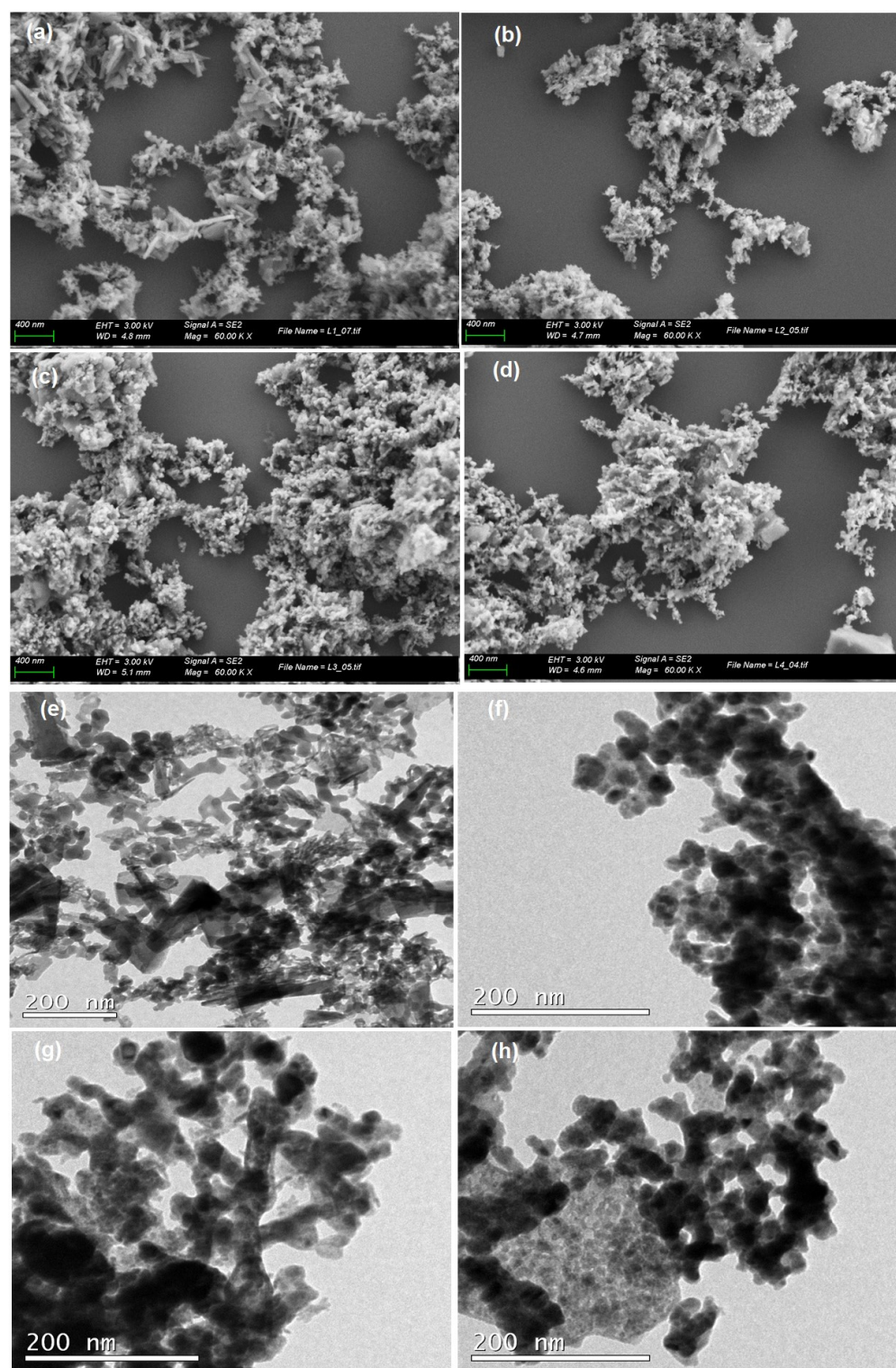


Figure 9. SEM and TEM images of the catalyst MGPn@CZA-2: SEM; (a) before catalysis, (b) after catalysis, (c) after the stability, (d) after reusability, and TEM; (e) before catalysis, (f) after catalysis, (g) TEM after stability, and (h) TEM after reusability.

The elemental composition of the catalyst obtained from EDS is presented in Table 2. The comparison of the atomic ratio of the copper and oxygen for the catalyst before and after catalysis and stability are in good agreement with the XRD results presented in Figure 4. As shown in Figure 4b, for the catalyst after the reaction, the emergence of new peaks corresponding to Cu and the disappearance of the CuO phase are in accordance

with the decrease in oxygen atomic ratio and increase in Cu ratio in elemental composition presented in Table 2. The strong diffraction peaks at $2\theta = 43.45^\circ$, and the weak ones at $2\theta = 50.62^\circ$ and 74.23° (JCPDS 01-089-2838) are attributed to the Cu phase [11,43]. The weak peak at $2\theta = 31.6^\circ$ is identified to belong to the ZnO phase. Additionally, as presented in Figure 4c, after stability tests, the peaks for the Cu phase become sharper and stronger and a decrease in the catalytic activity is observed. Consequently, only the CuO phase changes without affecting the ZnO phase. We also observed that the peak assigned to $\text{Zn}(\text{OH})_2$ disappears after catalysis due to the decomposition of zinc hydroxide with temperatures higher than 150°C [66]. As presented in Figure 9e–h, there are slight differences in the aggregation of catalyst material after catalysis and reusability tests, but after stability tests, it becomes more aggregated, which may cause the decrease in STY. The average sizes of MGPNCZA-2 were measured roughly using TEM and were found to be 23 ± 6.9 nm, 22.1 ± 6.9 nm, 19.8 ± 7.1 nm, and 21.1 ± 6.3 nm before and after catalysis, stability, and reusability, respectively.

Table 2. EDS results of the catalyst before catalysis, after catalysis, after the stability, and after the reusability test.

Element	Before Catalysis		After Catalysis		After Stability		After Reusability	
	Wt%	At.%	Wt%	At.%	Wt%	At.%	Wt%	At.%
C	32.05	40.47	32.64	38.39	30.31	36.79	31.70	40.27
N	18.78	22.09	13.51	20.00	20.32	21.34	15.52	16.18
O	15.35	16.46	11.84	13.40	18.00	9.46	18.37	8.26
Al	2.24	1.18	3.16	2.20	1.97	2.11	4.09	3.13
Cu	30.41	19.54	28.95	18.09	20.17	21.81	21.77	24.82
Zn	1.17	0.26	8.91	7.92	9.23	8.49	8.55	7.34

Using the MGPNCZA catalyst in CO_2 hydrogenation, methane was obtained in a small yield, as shown in the Supplementary File (Figures S8–S10).

2.4. Comparison with Alternative Catalysts

To further evaluate the catalytic activity of the catalyst MGPNCZA-2, a comparison is made in terms of methanol yield (STY) and selectivity between the catalyst MGPNCZA-2 obtained under optimum conditions in this study and other Cu-based catalysts for CO_2 hydrogenation for methanol synthesis, as presented in Table 3. The MGPNCZA-2 catalyst described in this work shows an improved catalytic hydrogenation of CO_2 . The remarkable affinity for methanol synthesis of MGPNCZA-2, compared to the other catalysts described in the literature, is highlighted by its increased ability to perform the hydrogenation reaction in a range of approximately 47–59% more than other catalysts based on $\text{CuO-ZnO-Al}_2\text{O}_3$.

Table 3. Catalytic performance comparison of different Cu-based catalysts.

Catalyst	T ^a (°C)	P ^b (Bar)	STY _{CH₃OH} (mg·g _{cat} ^{−1} ·h ^{−1})	S _{CH₃OH} (%)	Reference
TiO ₂ /CuO-ZnO-Al ₂ O ₃	260	26	97.7	30.98	[67]
CuO-ZnO-ZrO ₂	240	30	4.9	54.1	[68]
Cu/ZnO/ZrO ₂	270	50	213.0	56.8	[69]
CuO-ZnO-ZrO ₂ -Al ₂ O ₃	240	20	262.7	74.2	[70]

Table 3. Cont.

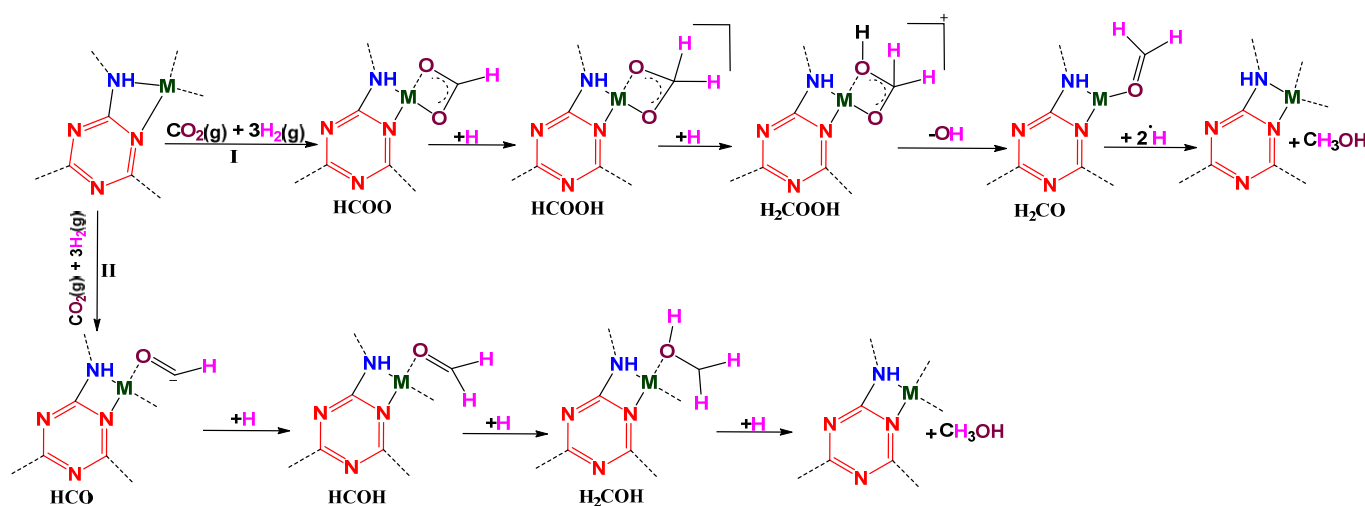
Catalyst	T ^a (°C)	P ^b (Bar)	STY _{CH₃OH} (mg·g _{cat} ^{−1} ·h ^{−1})	S _{CH₃OH} (%)	Reference
Cu-ZnO/ZrO ₂	240	30	225.5	75.0	[71]
CuO-ZnO-ZrO ₂ -Al ₂ O ₃ /rGO	240	20	310.7	78.9	[70]
[CuCs@FeBTC] _{aa} @rGO) _{H2}	260	10	86	92	[72]
CuO/ZnO/Al ₂ O ₃ @chitosan	260	10	92.44	90	[11]
MGPN@CZA-2	260	10	145.43	98.36	This work
NU-1000-NH ₂ /PrS-Cu	280	10	100	100	[73]

^a and ^b are the temperature and pressure conditions for the results.

2.5. CO₂ Hydrogenation Proposed Mechanism

From the experimental results shown in Figure 6a, we can conclude that the MGPN alone has a low value of methanol STY 15.71 mg·g^{−1}·h^{−1}, which increases to 145.43 mg·g^{−1}·h^{−1} when it is crosslinked to CZA. The reason for this is the presence of the electron-donating basic sites on MGPN (−N= and −NH−), which stabilize CZA and provide high activity for CH₃OH formation. It indicates that the triazine of the outer parts of MGPN can be used to complex CZA, as shown in Scheme 1.

The mechanism of CO₂ hydrogenation on Cu/ZnO catalysts occurred through two mostly accepted pathways: a) formate route, in which CO₂ hydrogenation produces formate intermediates (HCOO), and (b) reverse water-gas-shift (RWGS) and CO hydrogenation route, where CO₂ is converted to CO, followed by CO hydrogenation to methanol via formyl (HCO) and formaldehyde (HCHO) intermediates [8,74]. Scheme 2 shows a plausible reaction mechanism for the hydrogenation of CO₂ to CH₃OH over the MGPN@CZA catalyst. Further studies are needed to confirm which route is the predominant path for the CO₂ hydrogenation to CH₃OH using MGPN@CZA.



Scheme 2. Plausible reaction mechanism of CO₂ hydrogenation over MGPN crosslinked CZA catalyst.

3. Materials and Methods

3.1. Materials

Melamine, glutaraldehyde (GA), anhydrous dimethyl sulfoxide (DMSO), zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O), aluminum oxide (Al₂O₃) and sodium carbonate (Na₂CO₃), tetrahydrofuran, methylene chloride,

ethanol, methanol, and acetone were purchased from Merck (Madrid, Spain). The purity of all reagents is higher than 99.0%, and they were used as received. The carbon dioxide and hydrogen mixture with a molar ratio of 1:3, respectively, was provided by Carburos Metalicos, S.A (Barcelona, Spain).

3.2. Catalyst Preparation

3.2.1. Synthesis of Melamine Glutaraldehyde Polymer Network (MGPN)

In a typical reaction procedure, melamine (313.41 mg, 2.485 mmol) and glutaraldehyde (704 μ L, 3.728 mmol) were dissolved in dimethyl sulfoxide (15 mL) in a dry 50 mL 2-neck round-bottom flask fitted with a condenser and nitrogen gas line. The mixture was heated to 180 °C for 72 h and continuously stirred at 400 rpm. The solid MGPN was separated via vacuum filtration and washed with excess acetone, methanol, ethanol, tetrahydrofuran, and dichloromethane, respectively. The sample was dried under a vacuum at 105 °C for 24 h to obtain the final product, a brown powder with an 84% yield.

3.2.2. Synthesis of MGPN@CZA Catalyst

A commercial-like Cu-based CZA catalyst was synthesized using a co-precipitation method because it is reported as the most common catalyst, Cu/ZnO/Al₂O₃, used for methanol synthesis. However, this commercial catalyst easily agglomerates [1]. To overcome this disadvantage, the support of MGPN was used to enhance the dispersion of the metal on the surface of the support. Three catalyst samples (MGPN@CZA-1, MGPN@CZA-2, and MGPN@CZA-3) were prepared by a simple ex situ method by varying the amount of CZA to obtain different metal loadings on the polymeric support, as shown in the Supplementary Information (Table S1). Briefly, 0.1 g of the as-prepared MGPN was dispersed in 100 mL Milli-Q water using an ultrasonic bath for 30 min, and then copper nitrate trihydrate (0.6178 g), zinc nitrate hexahydrate (0.2444 g), and aluminum oxide (0.0725 g) were added to the MGPN suspension and left under stirring at 400 rpm and room temperature for 2 h. Next, 26.5 g of Na₂CO₃ (1M) were dissolved in 250 mL of Milli-Q water and were added to the metal salt solutions containing MGPN to keep the pH value constant (pH = 7) and the resultant solution was stirred at 400 rpm and 70 °C for 2 h. Finally, the suspension was centrifuged 3 times (15 min and 6500 rpm), washed with DI water, and dried at 105 °C overnight. The synthesized catalyst was coded as MGPN@CZA-1. The same procedure was followed to prepare the MGPN@CZA-2 and MGPN@CZA-3 catalysts.

3.2.3. Synthesis of CZA Catalyst

The best concentration of Cu-based catalyst coordinated with the MGPN was prepared as a control. The same procedure of MGPN@CZA was followed as described in Section 3.2.2 but without the MGPN.

3.3. Materials Characterization

The functional groups were identified using the Fourier transform infrared spectroscopy (FTIR, Bruker Tensor 27, Billerica, MA, USA). The number of carbon atoms was ascertained using the ¹³C cross-polarization magic-angle spinning (CPMAS) Nuclear magnetic resonance (NMR, Bruker-400NMR, Rheinstetten, Germany) spectrometer, spectra operating at 12 KHz. The morphology of the surface, size distribution, and composition of the synthesized materials were determined using the Field emission Scanning electron microscopy (FE-SEM, Merlin, Baden-Württemberg, Germany), equipped with an energy dispersive spectroscopy (EDS) detector (EDS Oxford LINCA X-Max). Transmission electron microscopy (TEM, Hitachi H-7000, Tokyo, Japan) was used to analyze the size and morphology of the produced materials. The crystallographic examination and the structural analysis of the synthesized compounds were conducted by X-ray diffraction (XRD). The

XRD patterns were recorded in a diffractometer (Panalytical X'Pert, Almelo, The Netherlands) using Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) equipped with a secondary monochromator. The XRD analysis was performed at a range of $10\text{--}80^\circ$ on 2θ with a step size of 0.026° at room temperature. Confirmation of the crystallinity phases of the synthesized compounds was performed by comparing them with the database of the HighScore Plus software, version 3.0e (3.0.5). The CHN analysis (Thermo Scientific Flash 2000, Waltham, MA, USA) was employed to determine the elemental composition of the MGPn sample.

Thermogravimetric analysis (TGA) was performed on a TGA-Q500 thermobalance using 2.8 mg of sample at a constant heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$ in an interval of $25\text{--}810^\circ\text{C}$ under a nitrogen atmosphere with a flow of $60 \text{ mL}\cdot\text{min}^{-1}$.

The textural properties of the catalysts were determined by nitrogen adsorption/desorption experiments at -196°C using an ASAP 2020 Micrometrics Inc., Norcross, GA, USA. Before the analysis, samples were degassed at 80°C for 20 h. The surface area (S_a) was calculated with the Brunauer–EmmettTeller (BET) equation for p/p_0 values to be between 0.002 and 0.99. Pore size distributions of the samples were determined from the sorption data using the non-local density functional theory (NLDFT) method. An AutoChem (Micromeritics, Norcross, GA, USA) instrument using 12 vol% H_2/Ar at a flow of $50 \text{ N mL}\cdot\text{min}^{-1}$ in a temperature range of $35\text{--}800^\circ\text{C}$ with a heating ramp of $10^\circ\text{C}\cdot\text{min}^{-1}$ was used for temperature-programmed reduction (H_2 -TPR) measurements. The same equipment was used for the CO_2 -temperature-programmed desorption (CO_2 -TPD) measurements, with a feed of CO_2/He (10% vol/vol) at a flow of $50 \text{ N mL}\cdot\text{min}^{-1}$ in a temperature range of $35\text{--}800^\circ\text{C}$ with a heating ramp of $5^\circ\text{C}\cdot\text{min}^{-1}$.

3.4. Catalytic Experiments

To evaluate the catalytic efficacy of the materials for carbon dioxide hydrogenation, the catalysts were arranged in a fixed bed reactor with an internal diameter of 5.25 mm and a height of 8.90 cm, yielding a volume of 1.92 cm^3 , utilizing a specific quantity of catalyst (10 mg, 8.5 mm bed height), which produces a residence time of 1.104 s. For reduction, the catalyst underwent pretreatment with hydrogen gas at a $20 \text{ mL}/\text{min}$ flow rate under ambient pressure at 300°C for two hours. Glass wool was used to seal each reactor end to avert potential material leakage. The catalytic efficacy of the MGPn@CZA catalysts in the CO_2 hydrogenation reaction was assessed in a fixed bed reactor at a temperature of 260°C , with a flow rate of $10 \text{ mL}/\text{min}$ and a pressure of 10 bar. The catalytic reaction studies utilized the reaction gas with a volumetric ratio of H_2 to CO_2 of 3:1. The results for STY and selectivity are presented for a reaction temperature of 260°C and a pressure of 10 bar throughout the paper. The samples were obtained using SKC FlexFoil PLUS sampling bags (SKC Inc., Blandford Forum, UK), and the gas mixture was analyzed using a Shimadzu 2010 gas chromatograph (Shimadzu, Kyoto, Japan) equipped with a flame ionization detector and helium as the carrier gas to quantify methanol and methane. The software employed was Chromeleon (version 6.80 SR 15b); the inlet temperature was 260°C , the flow rate was $50 \text{ mL}/\text{min}$, the column was Stabilwax-DA (Restek, Bellefonte, PA, USA, with dimensions of $15 \text{ m} \times 0.53 \text{ mm ID} \times 1 \mu\text{m}$ film thickness), and the detector temperature was 280°C . Carbon monoxide and carbon dioxide concentrations were quantified using a GC System (Agilent 7890B, Agilent Technologies, Inc., Santa Clara, CA, USA) equipped with a thermal conductivity detector (TCD, Agilent Technologies, Inc., Santa Clara, CA, USA), employing helium as the carrier gas, an input temperature of 120°C , an intake flow rate of $20 \text{ mL}/\text{min}$, the column was CarboPLOT (Agilent, Agilent Technologies Netherlands B.V., Middelburg, The Netherlands, with dimensions of $25 \text{ m} \times 0.53 \text{ mm ID} \times 25 \mu\text{m}$ film thickness), and a detection temperature of 150°C . The software utilized was Agilent OpenLAB CDS ChemStation (Version A.01.04). The selectivity and STY of methanol were

assessed to evaluate the catalytic activity of each substance. In the selectivity calculations, only methanol, carbon monoxide, and methane were considered as possible products. The selectivity, STY, and conversion of methanol were determined using Equations (1)–(3) [41,61]:

$$STY_{CH_3OH}(\frac{mg}{g} \cdot h) = (\frac{Mass\ of\ methanol(mg)formed}{W_{catalyst}(g) \times hour}) \quad (1)$$

$$Selectivity_{CH_3OH}(\%) = 100 \times (\frac{moles\ of\ methanol\ formed}{n[CO_2]_{in} - n[CO_2]_{out}}) \quad (2)$$

$$Conversion_{CO_2}(\%) = 100 \times (\frac{A[CO_2]_{in} - A[CO_2]_{out}}{A[CO_2]_{in}}) \quad (3)$$

where $n[CO_2]_{in}$ is the moles of CO_2 at the reactor inlet, $n[CO_2]_{out}$ stands for the moles of CO_2 at the reactor outlet, W_{cat} is the weight of the catalyst used (g), $A[CO_2]_{in}$ is the chromatography peak area of CO_2 at the reactor inlet, and $A[CO_2]_{out}$ is the peak area of CO_2 at the reactor outlet.

4. Conclusions

A novel mesoporous MGP@CZA catalyst was successfully synthesized by crosslinking MGP with $CuO/ZnO/Al_2O_3$ via a simple ex situ method. The MGP@CZA catalyst was satisfactorily applied in the catalytic CO_2 hydrogenation to CH_3OH . The results indicate that using MGP with electron-donating sites as support for $CuO/ZnO/Al_2O_3$ catalyst increased the activity of CO_2 hydrogenation to CH_3OH , and, therefore, the STY increased. High activity and selectivity toward CH_3OH were obtained when the catalyst was calcined at $350\ ^\circ C$, flow rate of $10\ mL \cdot min^{-1}$, and pressure of 10 bar, with a maximum STY of $145.43\ mg_{CH_3OH} \cdot g_{cat}^{-1} \cdot h^{-1}$, and selectivity of CH_3OH 98.36%. Additionally, utilizing MGP as a support for the catalyst CZA will obviate the necessity for alternative supports, such as metal oxides like CeO_2 , ZrO_2 , or metal–organic frameworks (MOFs), which, although beneficial, entail increased prices, energy consumption, and environmental toxicity. On the other hand, the metal loading study agrees with the theory of the dual-site nature of the main reaction path, confirming the role of the ZnO and metallic copper in the hydrogenation of CO_2 to CH_3OH in the Cu/ZnO catalyst. The emergence of the peaks attributed to the Cu phase was in complete accordance with the elemental composition of the catalyst obtained from the EDS analysis, demonstrating the important role that the CuO phase plays in the reaction. Additionally, the porous structure of the catalyst was maintained after stability and reusability tests, which certifies its sustainable catalytic ability. Further characterizations are needed as future studies to confirm the species of metals in the catalyst via the XPS analysis and the determination of copper surface area as well as the identification of the properties of the catalyst after reduction. Also, subsequent tests are needed to identify other by-products and, hence, complete mass balances of carbon for the yield results and to determine the performance of the catalyst in the catalytic conversion of CO_2 without and with its calcination at lower temperatures before the reduction.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16020170/s1>. Figure S1: TGA curves of (a) MGP and (b) MGP@CZA-2; Figure S2: EDX mapping for the synthesized MGP; Figure S3: EDX mapping for the CZA-2, Figure S4: EDX mapping for the MGP@CZA-2 before catalysis; Figure S5: EDX mapping for the MGP@CZA-2 after catalysis; Figure S6: EDX mapping for the MGP@CZA-2 after stability, Figure S7: XRD pattern of the synthesized MGP; Figure S8: Effects of (a) copper loading, (b) calcination temperature ($^\circ C$), catalyst amount (c), flow rate (d), pressure (e) and reducing temperature ($^\circ C$) in the catalytic hydrogenation of CO_2 to CH_4 ; Figure S9: Effect of catalytic reaction temperature in the catalytic hydrogenation of CO_2 to CH_4 ; Figure S10: Stability and reusability

results of the MGP@CZA-2 catalyst; Figure S11: Optical image of the water contact angle of MGP@CZA catalyst before (a) and after calcination (b); Table S1. Weights of Cu-based catalyst; Table S2: CHN Elemental analysis of MGP; Table S3: $T_{d5\%}$, $T_{d10\%}$, and Char yield of MGP and (b) MGP@CZA-2; Table S4: Porosity properties of MGP and (b) MGP@CZA-2; Table S5: EDS results of the as-prepared MGP, CZA-2, and MGP@CZA-2; Table S6: The selectivity data for the CO₂ hydrogenation; Table S7: The conversion data for CO₂ hydrogenation.

Author Contributions: Conceptualization, A.A.M.; Methodology, L.S.A.A. and A.A.M.; Software, L.S.A.A. and A.A.M.; Validation, A.A.M.; Formal analysis, A.A.M.; Investigation, L.S.A.A.; Resources, J.M.-V., X.F. and A.A.; Data curation, L.S.A.A.; Writing—original draft, L.S.A.A.; Writing—review and editing, A.A.M., J.M.-V., X.F. and A.A.; Supervision, J.M.-V. and A.A.; Funding acquisition, X.F. All authors have read and agreed to the published version of the manuscript.

Funding: This study was financially supported by the Spanish Ministerio de Ciencia e Innovación in the call Proyectos de Transición Ecológica y Transición Digital 2022, Squeezer project, ref. TED2021-130407B-I00. Ahmad Abo Markeb thanks the Spanish Ministry of Universities for his Maria Zambrano scholarship, ID 715364.

Data Availability Statement: The data presented in this study are available upon request.

Conflicts of Interest: The authors declare no conflicts of interest.

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