

Research Article

Reporting the Bismuth Promotion for Green Methanol Synthesis by CO₂ Hydrogenation over MgO-Supported Cu-Zn Catalysts

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Due to the effective exploitation of carbon resources and concurrent decrease in the concentration of atmospheric carbon dioxide (CO₂), the thermochemical conversion of CO₂ into high-value chemical compounds has emerged as a significant research field. In this article, we report on the effective thermochemical conversion of CO₂ for the synthesis of methanol by using Bi-promoted Cu-Zn/MgO catalysts. Cu-Zn bimetallic catalysts supported by MgO were created using the coprecipitation technique. The catalysts that were produced were subjected to varying concentrations of bismuth in order to examine their potential enhancing properties. Several analytical methods were applied to examine the physicochemical profile of the calcined catalysts. ICP-OES confirmed the actual bulk concentration of bismuth in each bismuth-supported Cu-Zn/MgO catalysts. X-ray diffraction studies revealed crystalline form of MgO catalysts support on one hand and high dispersion of Cu and Zn metal oxide on the MgO surface on the other. The study employed scanning electron microscopy (SEM) to examine the morphology of produced catalysts with uniform distribution, since this revealed their nanosize. The mesoporosity characteristic of Bi-promoted Cu-Zn/MgO catalysts was demonstrated by BET surface investigations. The catalytic performance of Bi-promoted Cu-Zn/MgO catalysts for methanol production by CO₂ hydrogenation was revealed by activity data in liquid phase slurry reactor. The active profile of Bi could be further justified by comparative studies conducted for the current work with literature.

1. Introduction

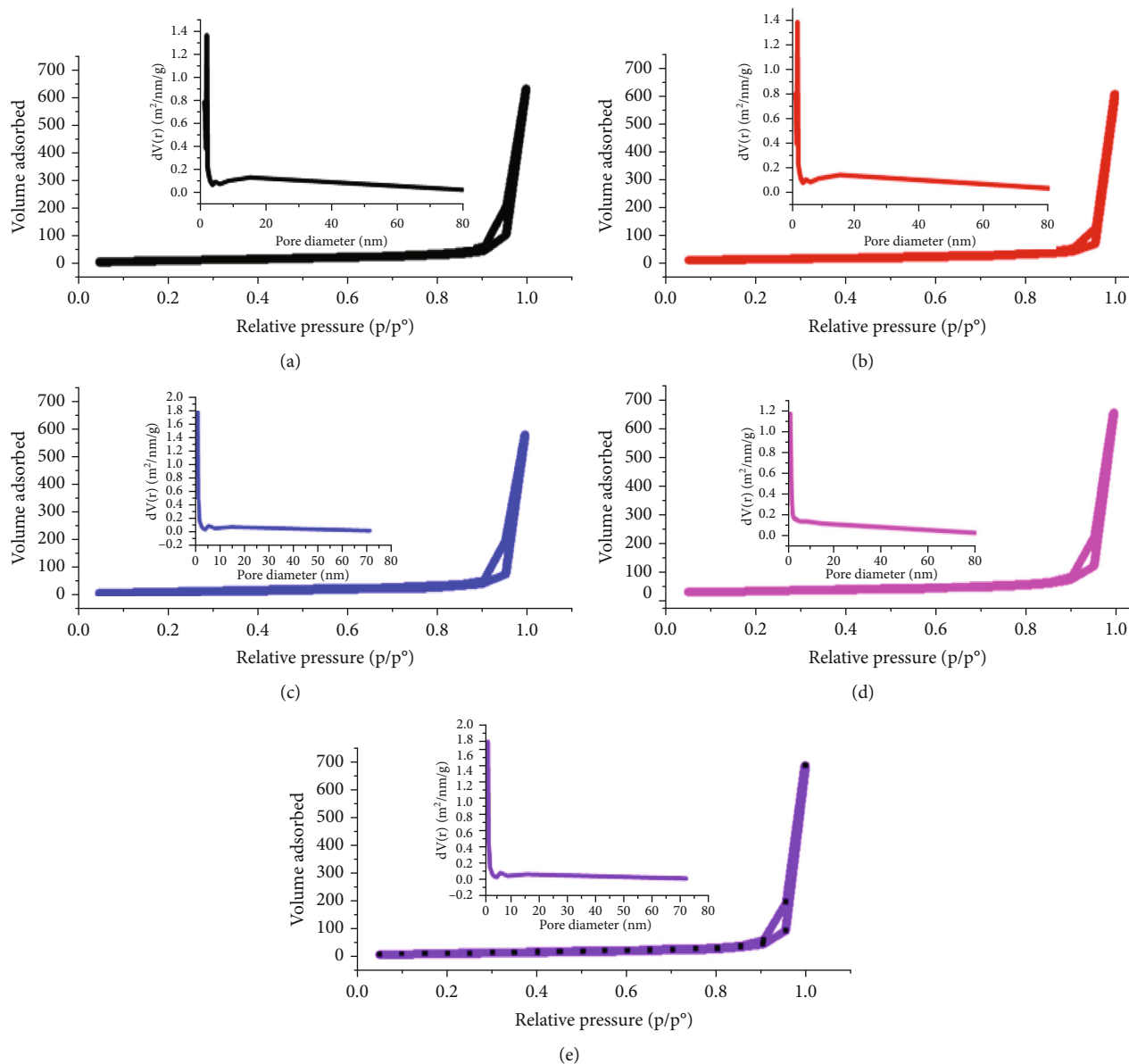
The objective of keeping the rise in the world average temperature below 1.5°C by 2050 is supported by the reduction of CO₂ emissions from 35 Gt CO₂-eq/yr (2020) to 15 Gt CO₂-eq/yr, creating a carbon-neutral earth environment. This continues to fuel research into methods that use CO₂ as an alternative carbon source and in carbon capture and utilization technologies. As a result, many ideas for a carbon economy with zero net emissions of greenhouse gases have surfaced [1, 2]. Heterogeneous hydrogenation, which transforms CO₂ into methanol, is one of the potential methods for CO₂ fixation [3–5]. Methanol is a well-known commodity that can be utilized as direct methanol fuel cells (DMFC) as well as a source of hydrogen and as a key feedstock in the chemical sector [4].

In the industrial methanol synthesis process, which operates at high reaction temperatures ranges between 200 and 300°C and high pressures (5.0–10.0 MPa), the traditional Cu/ZnO/Al₂O₃ catalysts have been frequently utilized [5]. It was discovered that their poor catalytic activity and stability for the CO₂ conversion was due to the strong hydrophilic nature of alumina, which also explained why water had a detrimental impact on the rate of methanol synthesis [6, 7]. Keeping this important factor in mind, this study was planned to apply MgO as a catalyst support for the title reaction.

The conversion of CO₂ into worthwhile and practical fuels and chemicals is one of the fundamental solutions for addressing and resolving the main energy and environmental challenges. However, due to carbon dioxide thermodynamic stability, it is highly difficult to convert it into useful products.

TABLE 1: ICP-OES and BET data of Bi-promoted Cu-Zn/MgO catalysts.

Catalysts	Bi targeted conc. (wt.%)	Bi ICP-OES conc. (wt.%)	BET SA (m^2/g)	Pore volume (cc/g)	Pore diameter (nm)
$\text{Bi}_0\text{Cu-Zn/MgO}$	0	0	49	0.98	2.15
$\text{Bi}_1\text{Cu-Zn/MgO}$	0.30	0.32	42	0.93	1.71
$\text{Bi}_2\text{Cu-Zn/MgO}$	0.50	0.47	48	0.88	1.70
$\text{Bi}_3\text{Cu-Zn/MgO}$	0.80	0.80	52	1.00	1.53
$\text{Bi}_4\text{Cu-Zn/MgO}$	1.00	1.10	46	1.06	1.70

FIGURE 1: Nitrogen adsorption-desorption isotherms and pore size distributions of (a) $\text{Bi}_0\text{Cu-Zn/MgO}$, (b) $\text{Bi}_1\text{Cu-Zn/MgO}$, (c) $\text{Bi}_2\text{Cu-Zn/MgO}$, (d) $\text{Bi}_3\text{Cu-Zn/MgO}$, and (e) $\text{Bi}_4\text{Cu-Zn/MgO}$ catalysts.

It is possible to convert CO_2 when a molecule with a large Gibbs free energy, such as H_2 , is present [8]. It is crucial to obtain H_2 from renewable feedstocks and energy sources (also known as “green H_2 ”) in order to make the reaction entirely sustainable. Exothermic CO_2 hydrogenation occurs at low

temperatures and high pressures, where it is thermodynamically preferred. One of the preferable thermodynamic parameters is the execution of such processes at liquid phase reaction medium. The application of slurry reactor provides the conducive reaction environment to absorb the generated heat during

the reaction to keep the catalytic system more active as compared to traditional fixed bed reactors.

Because of their low cost and relatively high efficiency, copper-based catalysts have [9] been considered as the most promising nonprecious metal-based catalytic systems for the industrial synthesis of methanol via the hydrogenation of carbon dioxide. Compared to supported copper materials, unsupported copper catalysts have inferior catalytic activity [9–11]. Similarly, zinc oxide has also been reported with greater efficiency in terms of catalyst activities for CO₂ hydrogenation to methanol. The presence of ZnO improves hydrogen spillover efficacy, which ultimately encourages CO₂ conversion [9, 12, 13]. It is suggested that Cu/ZnO's synergism will result in the production of defect sites as well as new active sites at the interface (metal support effect) of Cu/ZnO. Recently, it was demonstrated that bismuth may switch between various catalytic reactions in terms of reactant activation and product selections. Bi(III) in the form of Bi₂O₃, a Lewis acid, is the most common type of bismuth employed in catalysis which facilitates hydrogenation reaction. The transfer hydrogenation reaction was carried out by team of researchers from Max Planck Institute for Coal Research, Germany, by using a Bi(I) complex as the catalyst. The team used ammonia borane as a hydrogen source, a bismuthinidene complex as the catalyst, and tetrahydrofuran (THF) at 35°C to convert a variety of azoarenes to the matching hydrazines [14]. Similarly, the role of bismuth has rarely been investigated in methanol synthesis by CO₂ hydrogenation. Jia et al. studied titanium-based bismuth (Bi-TiO₂) for CO₂ hydrogenation to methanol [15]. The study concluded the vital role of Bi in CO₂ conversion as catalyst activity was dependent on the particle size of bismuth. Similarly, Bi-TiO₂ was observed with a strong tendency towards CO₂ adsorptions on one hand and suppressing the formation of CO and hydrogen on the other [16–18].

One of the common problems with catalysts in industrial processes is catalyst deactivation. Catalyst deactivation is caused by a variety of causes, including as poisoning, heat degradation, compound formation, chemical side reactions, fouling, and mechanical attrition/crushing [19]. Catalyst deactivation results from thermal deterioration, particularly when heat is generated throughout the reaction pathway. Methanol is produced through the exothermic hydrogenation of CO₂. Because the reaction is exothermic, heat created during the synthesis of methanol is said to deactivate catalysts involved in the process. In these situations, the amount of heat produced must be decreased to prevent catalyst deactivation. One option is to conduct the reaction in liquid phase, in which case the heat produced is absorbed by a reaction solvent with a large heat capacity. In addition to preventing catalyst deactivation, low temperature liquid phase CO₂ hydrogenation to methanol is thermodynamically preferred. Liquid phase reactions are carried out in slurry reactors. Kim et al. [20] carried out a comparison of fixed bed reactors and slurry reactors for CO₂ hydrogenation. When compared to fixed bed reactors, they found that the use of slurry reactors enhanced CO₂ conversion by more than two times.

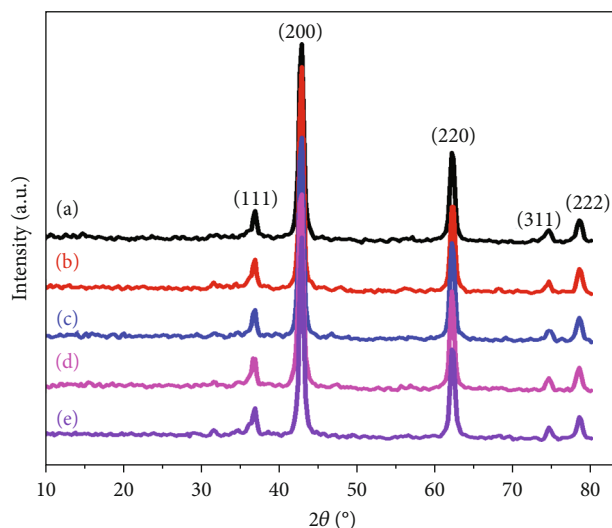


FIGURE 2: XRD patterns of (a) Bi₀Cu-Zn/MgO, (b) Bi₁Cu-Zn/MgO, (c) Bi₂Cu-Zn/MgO, (d) Bi₃Cu-Zn/MgO, and (e) Bi₄Cu-Zn/MgO catalysts.

The current study was designed to evaluate Bi's boosting role in the CO₂ hydrogenation process used to produce methanol in slurry reactors using Cu-Zn/MgO catalysts while keeping in mind the catalytic role of Bi as reported in the literature. A series of Cu-Zn/MgO catalysts with varying concentrations of Bi were synthesized. The synthesized Bi-promoted Cu-Zn/MgO catalysts were characterized by variety of analytical techniques, and each catalyst was evaluated for methanol synthesis by CO₂ hydrogenation in three phase slurry reactor.

2. Experimental

2.1. Materials. The precursor materials, bismuth nitrate, zinc nitrate nonahydrate, and copper nitrate hexahydrate, were used to synthesize Bi-promoted MgO-supported Cu-Zn catalysts. To create an alkaline environment for the production of Cu-Zn/MgO catalysts supported by Bi by using ammonium hydroxide was utilized.

2.2. Catalyst Synthesis. The Bi-promoted bimetallic Cu-Zn/MgO catalysts were prepared by using coprecipitation technique [9]. Zinc nitrate hexahydrate was added after copper nitrate hexahydrate had been thoroughly dissolved in distilled water. The solution was then given a specified dosage of bismuth nitrate. This was followed by addition of calculated dose of MgO once nitrate salts were dissolved. Ammonium hydroxide was used to synthesize Bi-promoted bimetallic Cu-Zn/MgO catalysts under basic medium. At a constant pH of 8, solution temperature was increased to 90°C and churned ferociously for a full hour. Centrifugation was then used to separate the precipitates for 30 minutes at 1800 rpm and dried in oven. Thus, synthesized Bi-promoted bimetallic Cu-Zn/MgO catalysts underwent a 4-hour calcination process at 350°C in furnace. The formulation of annealed Bi-promoted Cu-Zn/MgO catalysts contained constant amounts of 5 weight percent of Cu and Zn with varying concentrations of bismuth like

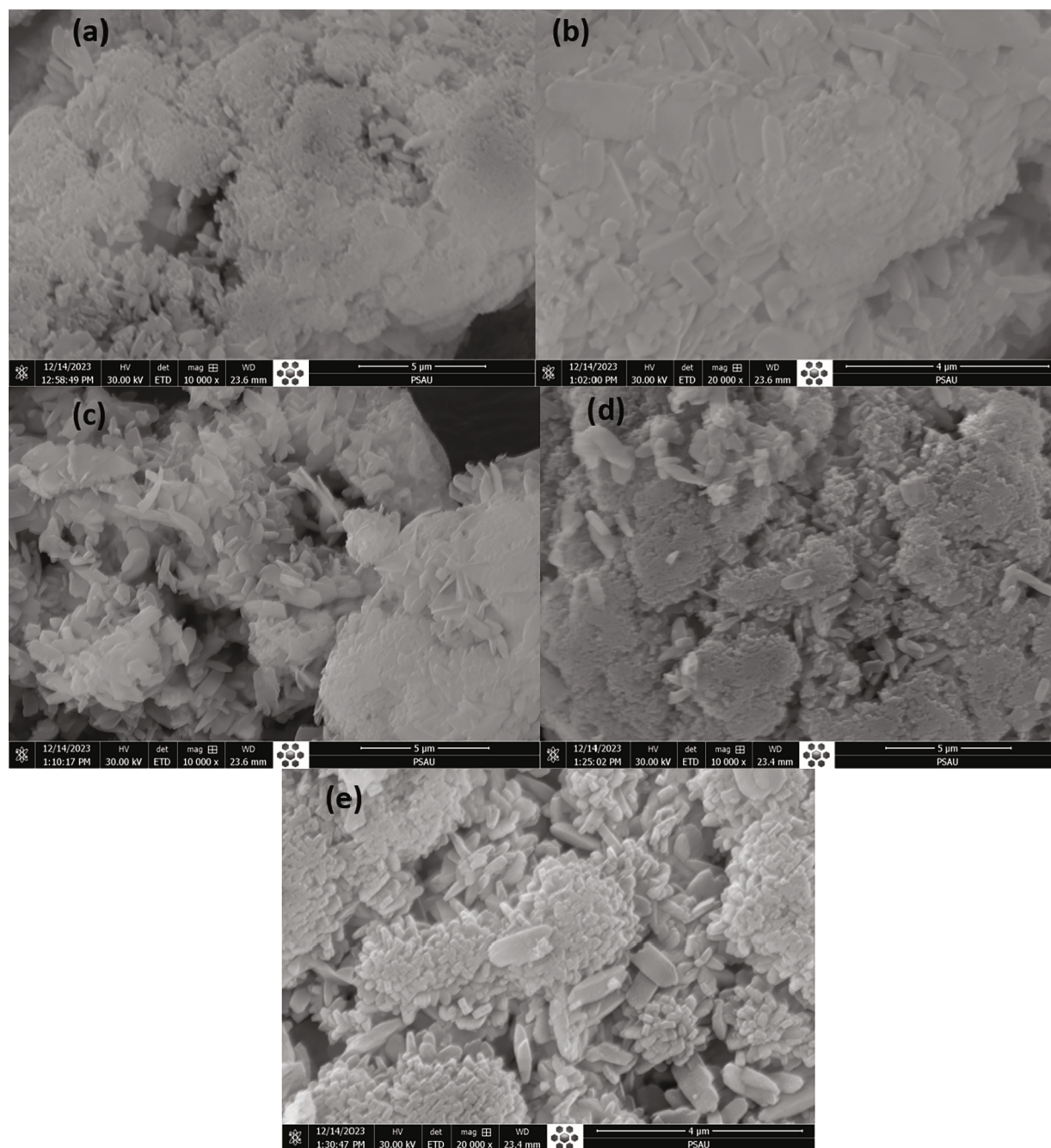


FIGURE 3: FESEM images of (a) $\text{Bi}_0\text{Cu-Zn/MgO}$, (b) $\text{Bi}_1\text{Cu-Zn/MgO}$, (c) $\text{Bi}_2\text{Cu-Zn/MgO}$, (d) $\text{Bi}_3\text{Cu-Zn/MgO}$, and (e) $\text{Bi}_4\text{Cu-Zn/MgO}$ catalysts.

0, 0.3, 0.5, 0.8, and 1 weight percent of Bi. Thus, synthesized catalysts were labelled as $\text{Bi}_0\text{Cu-Zn/MgO}$, $\text{Bi}_1\text{Cu-Zn/MgO}$, $\text{Bi}_2\text{Cu-Zn/MgO}$, $\text{Bi}_3\text{Cu-Zn/MgO}$, and $\text{Bi}_4\text{Cu-Zn/MgO}$ catalysts, respectively, in the current study.

2.3. Characterization of Catalysts. The actual concentration of bismuth over MgO-supported Cu-Zn catalysts was determined ICP-OES which stands for Inductively Coupled Plasma-Optical Emission Spectrometry. Thermo Scientific's iCAP 7000 series ICP spectrometer, model 7400, was employed in this instance.

The morphology of catalysts was examined using field emission scanning electron microscopy (FESEM) with equipment from JEOL Japan (ASEM 6360A model).

The porosity of Bi-promoted Cu-Zn/MgO catalysts was investigated using the nitrogen adsorption-desorption isotherm technique. For these kinds of evaluations, the Quantachrome autosorb IQ model ASIQA3V600000-6 instrument was used in the current study.

Powder X-ray diffraction (XRD) was used to analyze Bi-promoted Cu-Zn/MgO catalysts. A Philips X-ray diffractometer with CuK radiation ($\lambda = 0.15406 \text{ nm}$) was used to identify each

catalyst's phase. The Debye-Scherrer equation, $D = K\lambda/\beta\cos\theta$, is used to determine the crystalline size of the nanoparticles. Here, D stands for the crystalline size of the nanoparticles, and K stands for the Scherrer constant (0.98), is the wavelength (1.54), and is the full width at half maximum (FWHM).

2.4. Activity Studies. The Parr 5500 slurry reactor was utilized to perform activity studies of Bi-promoted Cu-Zn/MgO catalysts for methanol production by CO₂ hydrogenation [1, 10, 11]. As the reaction solvent, 50 milliliters of ethanol was typically supplied to a 100-milliliter reactor vessel. Within the reaction vessel, 0.5 g of prereduced samples was placed in the reaction cell. The reaction cell containing catalyst contents was purged using a 1:3 molar ratio of feed gases CO₂/H₂. Finally, the pressure of reactor was enhanced to 30 bar while temperature of the cell was heated to 190°C. GC analysis was performed on the products using Agilent made GC having model number 7890B. The amount of methanol was quantified by flame ionization detector (FID).

Methanol production rate was formulated by the following equation:

$$\text{Rate of methanol yield} = \frac{\text{g of methanol produced}}{\text{kg of catalyst}} \times \text{h.} \quad (1)$$

3. Results and Discussions

3.1. ICP-OES Measurements. The Bi promotion studies were designed with Bi formulation range of 0.3 to 1.0 weight % over MgO-supported Cu-Zn catalysts. The actual bulk concentration was determined by ICP-OES investigations, and the results are reported in Table 1. As evident from the tabulated data, a good agreement between the targeted magnitude of Bi and measured value of Bi was found in each Bi-promoted Cu-Zn/MgO catalysts. The ICP-OES results confirmed the appropriate choice of the catalyst synthesis method by demonstrating the formulation of the catalysts in terms of Bi concentrations.

3.2. BET Analysis. Figure 1 shows nitrogen adsorption-desorption isotherms of Cu-Zn/MgO and Bi-promoted Cu-Zn/MgO catalysts. According to IUPAC categorization, the nitrogen adsorption-desorption isotherm displayed a type III isotherm curve.

The appearance of such kind of isotherm indicates the presence of both mesopore and macropore pore size. This observation was further supported by BJH pore size distribution as shown in the subset of each figure by manifesting a wide range of pore size between 2 and 80 nm.

Table 1 shows magnitude of BET surface area, pore volume, and pore size of Bi-promoted Cu-Zn/MgO catalysts. As demonstrated by the tabulated data, the surface parameters of Bi-promoted Cu-Zn/MgO catalysts were less influenced by variation in Bi promotion to the parent Cu-Zn/MgO catalysts. A slight variation was recorded in BET surface area that could be justified by the relevant variation in magnitude of pore volume and pore size, respectively. Generally, metal doping affects the surface parameters of the support. However, there are no fixed or definite rules regard-

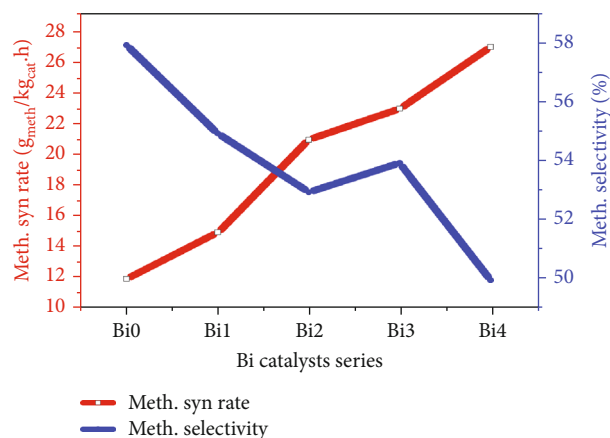


FIGURE 4: Activity and selectivity patterns of Bi-promoted Cu-Zn/MgO catalysts.

ing metal doping and variation in surface area. The quantity of metal dopant strongly affects on the specific surface area of the samples. The doping of metal ion within suitable concentration range may lead to the larger surface areas or the lower surface areas. In contrast, in some cases, metal doping does not take up much space, and it may not be the cause of the change in surface area. This gives us the clear indication that metal doping did not result in clogging the pores of the support as observed in the current study. The less variation in magnitudes of pore volume and pore diameters also advocates this trend.

3.3. XRD Studies. X-ray diffraction studies were carried out to get information regarding the phase of MgO-supported Cu-Zn catalysts and Bi-promoted Cu-Zn/MgO catalysts. The diffraction pattern of each catalyst has been displayed by Figure 2. As evident from the figure, five distinct diffraction peaks were observed in 2 theta range of 10-80 degrees. The resulted five distinctive reflection peaks were indexed to the (1 1 1), (2 0 0), (2 2 0), and (3 1 1) diffraction planes, representing the cubic form of MgO [21].

More importantly, all these diffraction lines were recorded with almost same intensity in all studied catalysts which indicates the stability of MgO support as there is no distortion in the crystalline structure. Using the Debye-Scherrer formula, the average crystallite size of MgO was determined to be 8 nm for the peak with the greatest peak (2 0 0). Interestingly, no diffraction line was observed for either Cu, Zn, and Bi metal oxides in all studied catalysts. The nonexistence of such diffraction lines could be due to many reasons as reported in the literature [22–24]. One of the possible reasons includes the presence of such metal oxides in amorphous form. However, this point could be negated by the fact that both Cu and Zn metal oxides calcined at such high temperature generally found in well crystalline form. Another possible reason could be the occurrence of Zn and Cu metal oxides with a degree of high dispersion over the surface of the support. In that scenario, the resulted XRD patterns advocate the deposition of metal oxides over the MgO surface with higher magnitude of catalyst dispersion. The disappearance of Bi diffraction line

TABLE 2: Performance of Bi-promoted Cu-Zn/MgO catalysts in hydrogenating CO₂ to methanol with reported data.

Catalysts	CO ₂ /H ₂ ratio	Pressure (bar)	Temperature (°C)	Meth. syn. rate (g/kg-h)	Reactor type	Reference
BiCu-Zn/MgO	1:3	30	190	28	Slurry	Current work
Cu/CNT	1:3	30	230	75	Slurry	[22]
Cu-Mg/CeO ₂	1:3	30	230	71	Slurry	[25]
Co-Cu/zeolite	1:3	30	190	27	Slurry	[23]
CoFe ₂ O ₄	1:3	30	230	35	Slurry	[26]
AgCu/zeolite	1:3	30	230	72	Slurry	[27]
10Cu-ZnO/SiO ₂	1:3	30	220	26	Slurry	[28]
50Cu-ZnO/SiO ₂	1:3	30	220	55	Slurry	[28]
CZAZ-0Al	1:3	50	250	218	Slurry	[29]
CZAZ-20Al	1:3	50	250	168	Slurry	[29]
1Mn-Cu/MoO ₃	1:3	30	190	28	Fixed bed	[30]
Cu/ZnO/Al ₂ O ₃ /ZrO ₂	1:3	30	230	32	Fixed bed	[31]
Cu-ZnO/SiO ₂	1:3	30	230	26	Fixed bed	[32]
2ZCZ	1:3	30	250	68	Fixed bed	[13]
1.5ZCZ	1:3	30	250	90	Fixed bed	[13]
1Mn-Cu/MoO ₃	1:3	30	230	28	Slurry	[33]
Cu-Mg/zeolite	1:3	30	230	32	Fixed bed	[34]
Cu-ZnO/SiO ₂	1:3	30	230	26	Slurry	[28]
Cu/ZnO/Al ₂ O ₃ /ZrO ₂	1:3	30	220	32	Slurry	[29]
4PdSiO ₂	1:3	30	220	134	Slurry	[24]

could also be justified by its lower concentration in each catalysts. This is because of the fact that more likely the lower intensity reflections due to low concentrations become indistinguishable from noise.

3.4. FESEM Analysis. FESEM studies revealed the sponge type of morphology of Bi-promoted bimetallic Cu-Zn/MgO catalysts in Figure 3. As demonstrated in Figure 3, the FESEM picture revealed well-dispersed Bi-promoted Cu-Zn/MgO catalysts. The homogeneous and fine particles of Cu-Zn/MgO catalysts were observed with the first two spikes of Bi promoter. However, a slight agglomeration of metal oxides could be observed with further rise in Bi concentration to the Cu-Zn/MgO catalysts.

3.5. Activity Studies. Figure 4 shows the activity statistics for the CO₂ hydrogenation process that produces methanol in slurry-based tank reactor. The catalytic profile of Bi-promoted bimetallic Cu-Zn/MgO was evaluated in terms of methanol production rate as well as methanol selectivity. As portrayed by the figure, methanol production rate of Cu-Zn/MgO was increased from 12 to 15 g_{meth}/kg_{cat}·h when Bi was incorporated to parent catalysts. Furthermore, the same trend in increasing methanol synthesis rate with Bi addition indicates promoting character of Bi in the process of methanol production by CO₂ reduction. Furthermore, the same trend of accelerating methanol production rate was observed with further rise in Bi concentration to parent Cu-Zn/MgO catalyst. The rate of methanol production was somewhat improved by the maximal Bi promoter resulting the

pivotal position of Bi promotion. Interestingly, contrary to the methanol production rate, the methanol selectivity was progressively declined by Bi promotion to Cu-Zn/MgO catalyst.

The better activity of Bi-promoted Cu-Zn/MgO catalyst could be justified by the fact that bismuth oxide has been considered as a basic oxide. Therefore, adding bismuth oxide to the parent Cu-Zn/MgO catalyst actually results in the development of more basic sites for the catalysts. On the other hand, keeping the acidic nature of CO₂, more basic sites are needed to speed up the reaction. Yan et al. investigated the role of bismuth oxide for photocatalytic methanol synthesis by CO₂ reduction and documented the similar observation in terms of improving catalyst activity [17]. Moreover, the high activity of Bi-promoted catalysts has been explained by the abundance of defective bismuth sites that stabilize the *OCHO intermediate using calculations from density functional theory, resulting in improved catalyst activity [17]. Likewise, the Bi promoter behaved differently in different catalytic systems. Apart from *OCHO intermediate stabilization, Bi promotion also reported to increase rate of CO formation, one of the common byproducts as documented in the literature [17]. Hence, the decline in methanol selectivity could be justified in the current work.

The catalytic performance of Bi-promoted Cu-Zn/MgO catalysts was equated with literature related to methanol synthesis by CO₂ hydrogenation. The comparative studies have been illustrated in Table 2. The results displayed in the table showed good methanol synthesis rate for methanol production by CO₂ hydrogenation despite lower reaction temperature in the current study.

4. Conclusion

In the current work, coprecipitation was used to create Cu-Zn bimetallic catalysts supported by MgO. To research the stimulating role of bismuth, varied concentrations of Bi were added to the produced catalysts. Various analytical techniques were applied to examine physicochemical characteristics of catalysts. Crystalline MgO catalyst support was discovered using X-ray diffraction examinations, and high Cu and Zn metal oxide dispersion was found on the MgO surface. An investigation of the morphology using scanning electron microscopy (SEM) revealed that the produced catalysts were uniformly distributed at nanoscale sizes. Through BET surface research, the mesoporous nature of the Bi-promoted Cu-Zn/MgO catalysts was found. Activity results showed an active profile for the Cu-Zn/MgO catalysts used in liquid phase slurry reactors to hydrogenate CO₂ to methanol.

Data Availability

Data will be available on request.

Conflicts of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported.

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