



Research article

High dispersion by Cd incorporation leads to accelerate methanol synthesis rate in CO₂ hydrogenation over Cu-Zn/SiO₂ catalysts

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ABSTRACT

Green methanol fuel synthesis by CO₂ hydrogenation is regarded as one of the potential viable techniques for meeting future energy demands. Enhancing catalytic performance and process knowledge are crucial for the practicality of catalyzed CO₂ conversion pathways. Here, coprecipitation was utilized to prepare Cu-Zn bimetallic catalysts based on silica gel. To examine the stimulating function of Cd metal, the produced catalysts were doped with varying concentrations of the Cd metal. The nitrogen adsorption-desorption isotherm revealed mesoporous nature of catalysts. The X-ray diffraction (XRD) investigations as well as Field Emission Scanning Electron Microscopy (FESEM) studies concluded higher degree of metal oxides dispersion on surface of silica gel support. The study of Fourier-transform infrared (FTIR) spectroscopy revealed successful incorporation of metal oxides on surface of silica gel support by originating absorption band in metal oxides regions. The X-ray photoelectron spectroscopy (XPS) exposed surface chemical nature of the Cu-Zn/SiO₂ catalysts promoted by Cd metal. On the top of that, XPS investigations confirmed the results derived from XRD and FESEM investigations in terms of catalysts dispersion over silica gel support by Cd promotion. The methanol synthesis rate was accelerated from 167 to 197 g_{-meth}/kg_{-cat}.h by incorporating Cd to the parent Cu-Zn/SiO₂ catalyst. Furthermore, similar trend in terms of accelerating methanol synthesis rate was sustained with further addition of Cd content to Cd-promoted silica gel supported Cu-Zn catalysts. The activity data demonstrated active and selective profile of Cd for CO₂ reduction to methanol by taking into account methanol synthesis rate and selectivity. Structure-activity studied documented in promoting character of Cd metal as structural promoter in CO₂ hydrogenation to methanol.

1. Introduction

The vast industrialization not only resulted in enormous utilization of rapidly depleting fossil fuels but huge devastation in natural environment. Concerns over the depletion of fossil resources and rising emissions of greenhouse gases have grown among the international community. Global consumption of fossil fuels has increased since the beginning of Industrial Revolution in 18th century. A

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turning point in the history of energy will be reached if this trend is reversed. Data from World Energy Outlook 2022 published lately indicate that the impact of the energy crisis is unprecedented in its scale and complexity [1]. However, there has also been significant volatility in the oil markets, necessitating two unprecedented-scale oil stock releases by IEA member countries to avert even more serious disruptions. The natural gas, coal, and power markets have experienced the strongest shocks. According to the World Energy Outlook 2022 (WEO), the current geopolitically and economically precarious global energy system is fragile and unsustainable, making the energy markets in particular vulnerable. This scenario signifies the importance of finding new renewable, sustainable and green energy sources with better impact on the environment. On the other hand, in order to maintain average temperature of world below 1.5 °C by 2050, it is mandatory to reduce of CO₂ emissions to 15 where it was 35 Gt CO₂-eq/yr in year 2020 [2]. This goal can also be facilitated by executing catalytic CO₂ hydrogenation to methanol. Consequently, the proposed research route will provide win-win situation to both environmental and economic fronts.

Methanol, one of the important starting materials in several industrial sectors, including the pharmaceutical, cosmetic, perfume, and fine chemical industries is of vital importance. Methanol can be utilized as an alternative fossil fuel and is frequently employed in the creation of biodiesel [3,4] Methanol is regarded as an alternate fuel substitute due to its interaction with gasoline, its clean burning qualities, high biodegradability and capacity to undergo reformation to produce hydrogen. Iceland has emerged as the leading industrial example for environmentally friendly CO₂ and H₂ geothermal methanol production [5]. Methanol synthesis by pure CO₂ hydrogenation is considered as one of the potential directions in green and sustainable chemistry in producing green fuel. From the thermodynamic perspective, low temperatures and high pressures are necessary for the exothermic CO₂ hydrogenation reaction that produces methanol. Because to CO₂'s limited reactivity, however, temperatures higher than 200 °C are needed to achieve a successful conversion. A variety of metals have been investigated to study CO₂ hydrogenation to methanol. The active role of Cu metal has been univocally documented by studies related to mechanism of reaction over Cu based catalysts for the said reaction [6–10]. Likewise, the role of Zn has also been recognized as active metal pertaining to its role of enhancing Cu dispersion on one hand with facilitation of CO₂ adsorption on the other [11,12]. On the top of that, the interface of Cu-ZnO have been reported as amongst the most active areas for catalysts activity where intermediate products such as formates and carbonates are further undergoes hydrogenation to yield methanol [13–15].

Apart from these active metals, methanol production by CO₂ reduction has been further facilitated by the utilization of different promoters. Based on the mechanism by which promoters alter the catalysts activity could be classified into two main types such as structural and chemical promoters [16]. The main mechanism by which structural promoters raise the activity of a catalyst is by expanding the physical parameters such as dispersion of an active phase. Chemical promoters also called as electronic promoters alter the chemical environment of active metal and raise the rate of reaction per surface area in order to enhance catalytic activity. A variety of chemical and structural promoters have been utilized for CO₂ hydrogenation to methanol [17–19]. Our previous studies documented the promoting role of Nb₂O₅ by exemplifying higher degree of CuO crystallization leading to enhanced catalytic activity [20]. Similarly, very recently, Zaman et al. investigated Cd promoter in methanol production by hydrogenating CO₂ and recorded the promoting role of Cd by enhancing basicity profile of PdZn catalysts through creation of oxygen vacancies [2]. A very rare data have been reported for the prompting role of Cd in various catalytic reactions. Ma et al. [21] investigated cadmium as a promoter for Fischer-Tropsch synthesis over Co/Al₂O₃ catalysts. The activity data revealed that 1-olefin selectivity of Cd promoted cobalt catalyst was increased and its 2-olefin selectivity was reduced as a result of Cd enhancing electronic backdonation. Recently, Mohandessi et al. [22] investigated the promoting role of cadmium for dry methane reforming over Ni@γ-Al₂O₃ catalysts According to their results, cadmium enhanced the reducibility of catalysts and considerably enhanced their dispersion and basicity of the catalysts. These characteristics led to the Cd(5 %)/Ni(15 %)/Al₂O₃'s high activity and stability in the reaction at 600–750 °C. Wang et al. [23] revealed a Cd/TiO₂ catalyst with a 15.8 % CO₂ conversion and an 81 % methanol selectivity. Similarly, using microkinetic modeling and density functional theory calculations, the CO₂ hydrogenation to CH₃OH catalytic reaction pathways over a previously reported Cd₄/TiO₂ catalyst were investigated. The formate pathway yields more methanol than reverse water-gas shift (RWGS) route, according to calculations, metal-oxide contact plays the role of an active sites for CO₂ hydrogenation [24].

Slurry reactions are more favorable in these types of reactions to use than traditional fixed bed reactors. Conventional gas phase synthesis is not preferable over slurry phase methanol production. This is a result of the rapid rate of reaction heat transfer, adjustable reaction temperature, cheap manufacturing costs, and low total investment cost. Different solvents have been employed to investigate liquid phase methanol synthesis [25,26]. Zeng et al. [27] employed several alcohol-based reaction solvents for the liquid phase synthesis of methanol. In their investigation, the reaction solvent ethanol produced the maximum activity for the synthesis of methanol. Tsubak et al.'s [28] research provided more evidence for the catalytic function of ethanol, showing that methanol synthesis was even prevented when cyclohexane was used in lieu of ethanol as a reaction medium at the reaction temperature of 150 °C. Based on such findings, ethanol was utilized as reaction solvent for the current work.

From the above discussions, the aim and objectives of the presented work could be easily inferred. The research hypothesis which reinvigorated the current work, is based on the versatile character of Cd metal in terms of its performance in variety of catalytic reaction. Considering Cd's catalytic role, the goal of the current work is to determine how it promotes the production of methanol by hydrogenating CO₂ in three phase slurry Parr reactor using Cu-Zn/SiO₂ catalysts.

2. Experimental

2.1. Materials

The silica gel powder was used as catalyst support to disperse Cd, Cu and Zn metals homogeneously. Nitrate precursor materials for

each Cu and Zn metals were used in the current work. Similarly, cadmium nitrate salt was utilized to deposit the Cd metal to investigate its promoting role. An alkaline medium was prepared with ammonium hydroxide to facilitate the synthesis of Cu-Zn/SiO₂ catalysts that are promoted by Cd metal. **2.2 Catalysts synthesis.**

A series of Cu-Zn/SiO₂ catalysts promoted by different loadings of Cd metal were produced via co-precipitation [29]. Zinc nitrate hexahydrate was added once copper nitrate hexahydrate had completely dissolved in the deionized water. The stirring solution was then supplemented with a specified amount of cadmium nitrate. A given amount of silica was put to mixture once all metal precursors salts had been dissolved completely. Ammonium hydroxide was utilized to create Cd-promoted silica gel supported Cu-Zn catalysts under slightly alkaline conditions. The solution temperature was increased to 85–90 °C and aggressively stirred by keeping constant pH magnitude of 8 for 1 h. Centrifugation was used for 10 min at 2000 rpm to separate the precipitates from the liquid supernatant. Thus synthesized catalysts were dried in an oven overnight. In a muffle furnace, the dried Cu-Zn/SiO₂ catalysts promoted by Cd were calcined for 4 h at 350 °C. The weight percentage of Cd metal varied during the catalyst's formation, but the quantities of each Zn as well as Cu metals in calcined Cd-promoted silica gel supported Cu-Zn catalysts were always 5 wt percent. Consequently, Cu-Zn/SiO₂ catalysts that were promoted by Cd at weight percentages of 0, 0.3, 0.5, 0.8, and 1 were prepared and designated as Gel₁, Gel₂, Gel₃, Gel₄, and Gel₅ catalysts, in that order.

2.2. Catalysts characterization

The phases of each Cd-promoted silica gel supported Cu-Zn catalysts were identified by powder X-ray diffraction (XRD) using Philips X-ray diffractometer equipped having wavelength of CuK radiation 0.15406 nm. Using infrared spectroscopy, the structure and the available functional groups of Cu-Zn/SiO₂ catalysts was investigated. Thermo Scientific model iD5 ATR was utilized for this purpose. Using N₂ adsorption-desorption isotherms, a number of surface parameters such as BET surface area, pore size and pore volume of each Cd-promoted silica gel supported Cu-Zn catalysts was examined. The morphological examinations were carried out using JEOL ASEM 6360A equipment, which is produced in Japan. Prior to FESEM investigations to study morphology of Cd-promoted silica gel supported Cu-Zn catalysts, all catalysts samples were coated with gold. The current study employed a quantachrome autosorb IQ model ASIQA3V600000-6 device for such assessments. The catalysts were vacuum-dried for 24 h at 373 K before analysis. The Brunauer-Emmet-Teller (BET) equation was used to compute specific surface area, and for this purpose, Gurvitch rule which is based on the adsorption of liquid volume of gas at $P/P_0 = 0.95$ was used to obtain the total pore volume. The Barrett-Joyner-Halenda (BJH) equation was utilized to determine average pore diameter. The X-ray photoelectron spectroscopy (XPS) was used to scan the catalysts' Cu, Cd, and Zn metal surfaces. Thermo Scientific X-ray Photoelectron Spectrometer K-ALPHA model and a monochromated, Al K-Alpha X-ray source were utilized to conduct XPS experiments in the current study. The binding energies of all studied components were calibrated using the C1s peak at 284.80 eV in order to remove the charge effect occurring for any XPS peak.

2.3. Activity studies

Activity investigations of Cd-promoted silica gel supported Cu-Zn catalysts by hydrogenating CO₂ to methanol fuel were conducted using Parr 5500 slurry, tank batch reactor. Following standard protocol, being reaction solvent, 50 ml of ethanol was added to a 100 ml reactor vessel. Before reaction studies each catalyst was reduced in pure hydrogen flow at 380 °C for 4 h. A fixed-bed quartz reactor with a length of 50 cm and internal diameter of 1.5 cm was employed for reduction of catalysts. In a typical protocol, a given amount of calcined catalyst held between ceramic fiber plugs was placed in the center of reaction tube. The reduction process was carried out of by 20 mL/min flow rate of H₂ feed gas with constant temperature of 380 °C for 4 h. After this, a 0.5 g of thus reduced catalysts were hung in 50 ml ethanol placed in reaction cell of Parr reactor. This was followed by closing the Parr reactor cell and purging it by using a 1:3 M ratio of CO₂/H₂. Subsequently, reactor pressure and temperature were adjusted to 30 bar and 230 °C, respectively by reactor controller. The reaction studies were continued for 3 h. Lastly, the reaction products were analyzed using Agilent GC Model 7890B gas chromatography (GC). A flame ionization detector (FID) was utilized to measure the amount of methanol produced in liquid form. Activity of all catalysts were conducted three times and average value was taken to ensure reproducibility of results.

Methanol synthesis rate was computed by the equation given below

$$\text{Rate of methanol yield} = \text{g of methanol produced} / \text{Kg of catalyst} \times \text{h}$$

Similarly, selectivity of methanol was calculated as

$$\text{Meth. selectivity} = \frac{\text{moles of methanol produced}}{\text{total moles of products}} \times 100$$

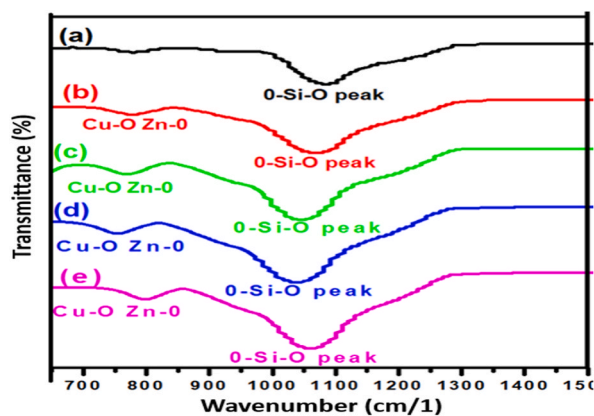
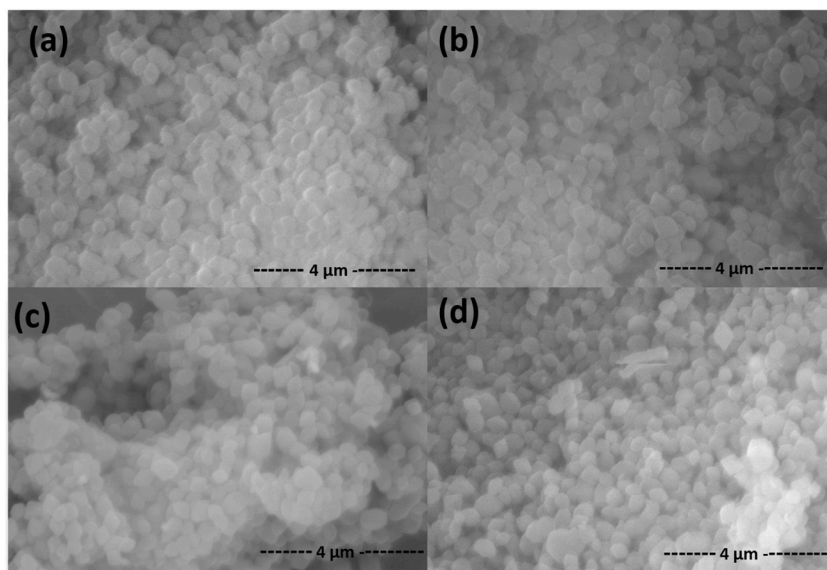
3. Results and discussions

3.1. ICP-OES data of Cd-promoted silica gel supported Cu-Zn catalysts

To quantify the exact concentration of each metal in Cd-promoted silica gel supported Cu-Zn catalysts, inductively coupled plasma–optical emission spectrometry (ICP-OES) was utilized. The results obtained by ICP-OES technique have been displayed in [Table 1](#). The ICP-OES results established successful incorporation of each metal in targeted amount by manifesting a good agreement between the measured value and formulated amount in terms of all three namely Cd, Cu and Zn metals.

Table 1Metal composition data obtained by ICP-OES for Cd incorporated Cu-Zn/SiO₂ catalysts.

Catalyst	Cd (wt.%) targeted	Cd (wt.%) by ICP-OES	Cu (wt.%) targeted	Cu (wt.%) by ICP-OES	Zn (wt.%) targeted	Zn (wt.%) by ICP-OES
Gel ₂	0.30	0.27	5	4.97	5	4.98
Gel ₃	0.50	0.45	5	4.91	5	4.95
Gel ₄	0.80	0.84	5	5.11	5	5.03
Gel ₅	1.00	0.98	5	4.95	5	4.89

Fig. 1. FTIR spectra of (a) silica, (b) Gel₁ (c) Gel₂, (d) Gel₃, and (e) Gel₄ catalysts.Fig. 2. FESEM images of (a) Gel₂, (b) Gel₃, (c) Gel₄ and (d) Gel₅ catalysts.

3.2. Functional group identification of Cd-promoted silica gel supported Cu-Zn catalysts

The FTIR transmittance spectra in the wavenumber range of 600–1500 cm⁻¹ for both bare silica gel and Cd-promoted silica gel supported Cu-Zn catalysts were displayed by Fig. 1. A strong and wide transmission band ranging from 1000 to 1100 cm⁻¹ was recorded for bare silica gel. This band was associated to the asymmetric Si-O-Si stretching vibration bonding as recorded in the literature [30]. Interestingly, when metal oxides were deposited on the surface of the silica gel the same transmission band was appeared as evident from the FTIR profile of each Cd-promoted silica gel supported Cu-Zn catalysts. The appearance silica gel transmission bands show that the structural features of silica gel were persisted by the incorporation of metal oxides. More importantly, besides the fundamental silica gel transmission band, another wide band with the wavenumber ranges of 700–850 was observed in each spectrum of Cd-promoted Cu-Zn/SiO₂ catalysts. This additional transmission band confirms the incorporation of Zn, Cu and Cd

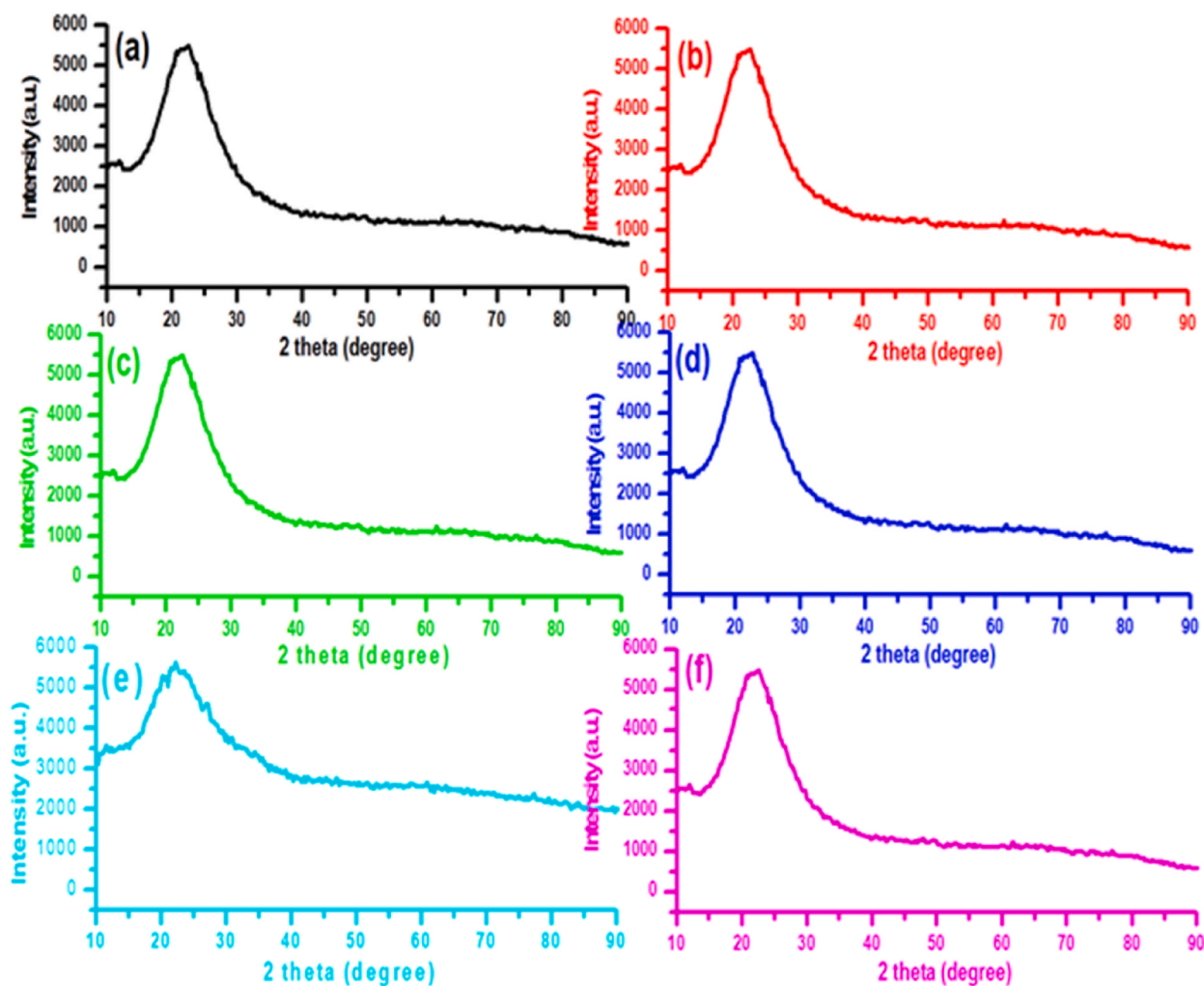


Fig. 3. XRD pattern of (a) silica, (b) Gel₁ (c) Gel₂, (d) Gel₃, (e) Gel₄ and (f) Gel₅ catalysts.

mixed metal oxides as documented in literature [31–33].

3.3. Morphology studies of Cd-promoted silica gel supported Cu-Zn catalysts

The FESEM images of Cd promoted silica gel based Cu-Zn catalysts have been displayed in Fig. 2. As demonstrated by FESEM images, the Cd promoted Cu-Zn particles were found well distributed over the silica gel support.

Furthermore, irrespective of the Cd the FESEM studies also confirmed the uniform morphology of Cd promoted Cu-Zn particles over the silica gel support. Consequently, the FESEM investigations resulted uniform and well distribution form of morphology in case of Cd-promoted silica gel supported Cu-Zn catalysts with high dispersion. The observation recorded by FESEM studies could be apprehended by visualizing the role of Cd as a structural promoter. This particular role could be probably explained that incorporation of Cd resulted in the creation of void gaps between the adjacent Cu and Zn metal oxide which ultimately resulted in high degree of dispersion of catalysts. The same trend in resulting dispersion by Cd promotion has been also supported by applying other analytical techniques discussed in later sections of the current work.

3.4. XRD pattern of Cd-promoted silica gel supported Cu-Zn catalysts

Fig. 3 shows the XRD spectra of pure silica gel and Cd promoted silica gel based Cu-Zn catalysts. As displayed by Fig. 3 (a), a broad XRD peak centered at $2\theta = 22^\circ$ is observed which can be assigned to the mesoporous SiO₂. In other words, the occurrence of a broad XRD peak at the said 2θ position correlates to the presence of amorphous silica with JCPDS-card 96-900-1582. Such interpretations of XRD peak by mesoporous silica were also reported by Pradip et al. [34] for mesoporous silica while investigating repositioning of mesoporous silica from waste hexafluorosilicic acid. Likewise, Purnawira et al. [35] also recorded similar XRD pattern for mesoporous

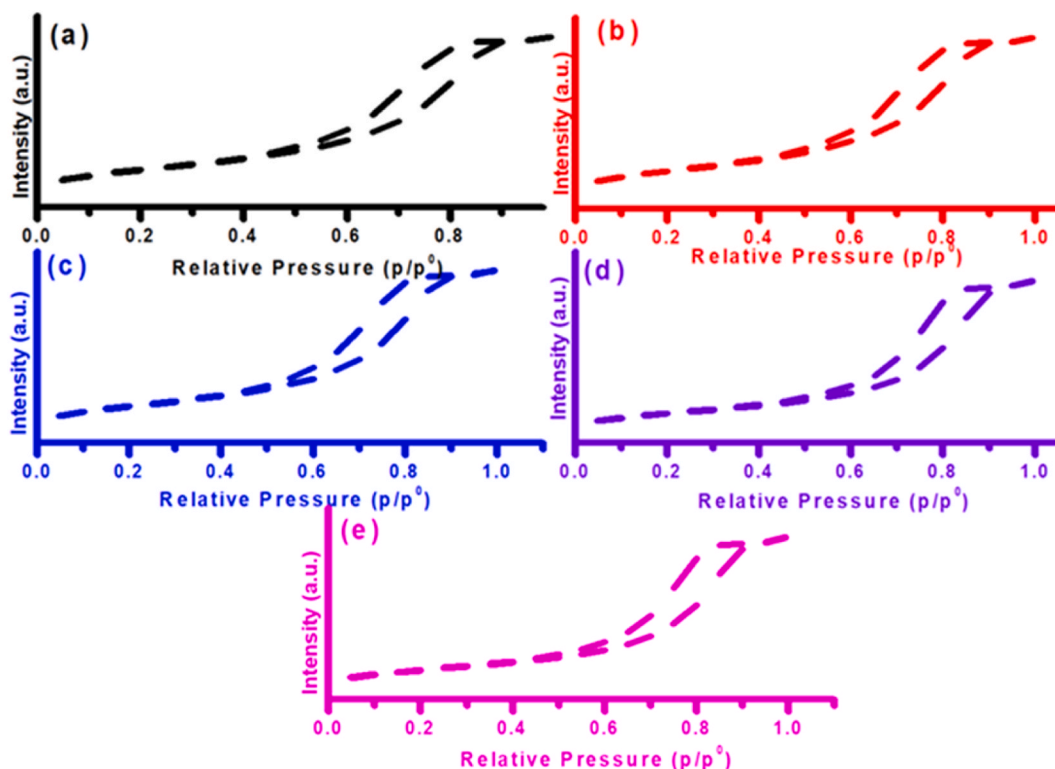


Fig. 4. N_2 adsorption-desorption isotherms of (a) Gel₁, (b) Gel₂, (c) Gel₃, (d) Gel₄ and (e) Gel₅ catalysts.

Table 2

BET parameters of Cd promoted Cu-Zn/SiO₂ catalysts.

Catalysts	BET surface area (m ² /g)	Pore Volume (cc/g)	Pore Size (nm)
Gel ₁	225	0.46	4.77
Gel ₂	215	0.47	4.79
Gel ₃	175	0.45	6.15
Gel ₄	170	0.46	7.12
Gel ₅	172	0.43	7.51

silica while reporting the synthesis of mesoporous silica from natural waste rice husk. Further observation revealed that XRD patterns of each Cd-promoted silica gel supported Cu-Zn catalysts displayed nearly the same diffraction pattern (Fig. (3b-f)). This indicates that despite the metal oxide loadings, the original silica gel structure was preserved. On top of that, no other identifiable diffraction line was visible in the XRD patterns of each Cd-promoted silica gel supported Cu-Zn catalysts. The resultant XRD patterns suggest that no further crystalline phase was revealed along silica gel phase that was detected. Another significant inference that can be drawn by missing metal oxide diffraction lines is the dispersion of catalysts components with higher degree on the silica gel surface. Similarly, another explanation for these observations could be the existence of these metal oxides in amorphous form. Thus, XRD data might be explained by supposing that metal oxides occur over the surface of the silica support in a highly distributed form.

3.5. BET analysis of Cd-promoted silica gel supported Cu-Zn catalysts

The technique of N_2 adsorption-desorption isotherms was employed to examine the porosity of Cu-Zn/SiO₂ catalysts promoted by Cd metal. The N_2 adsorption-desorption isotherms of silica gel as well as each Cd-promoted silica gel supported Cu-Zn catalysts is shown in Fig. 4.

Fig. 4 displays the representative silica gels' nitrogen adsorption isotherms. This substance exhibits mesoporous structures, as may be seen. The isotherms show that silica catalysts displayed mesoporosity by exhibiting an IUPAC Type IV form of isotherm associated with a hysteresis loops. This observed feature is consistent with evidences from silica-supported catalysts reported in the literature [36, 37]. The magnitude of BET surface area was slightly decreased by enhancing Cd addition to the support (Table 2). The BET results also revealed that the metal oxides were deposited exclusively on external surface of mesoporous silica rather than in the bulk. This can be interpreted from the fact that the pore volume of Cd promoted Cu-Zn/SiO₂ catalysts remained almost constant by adding Cd metal

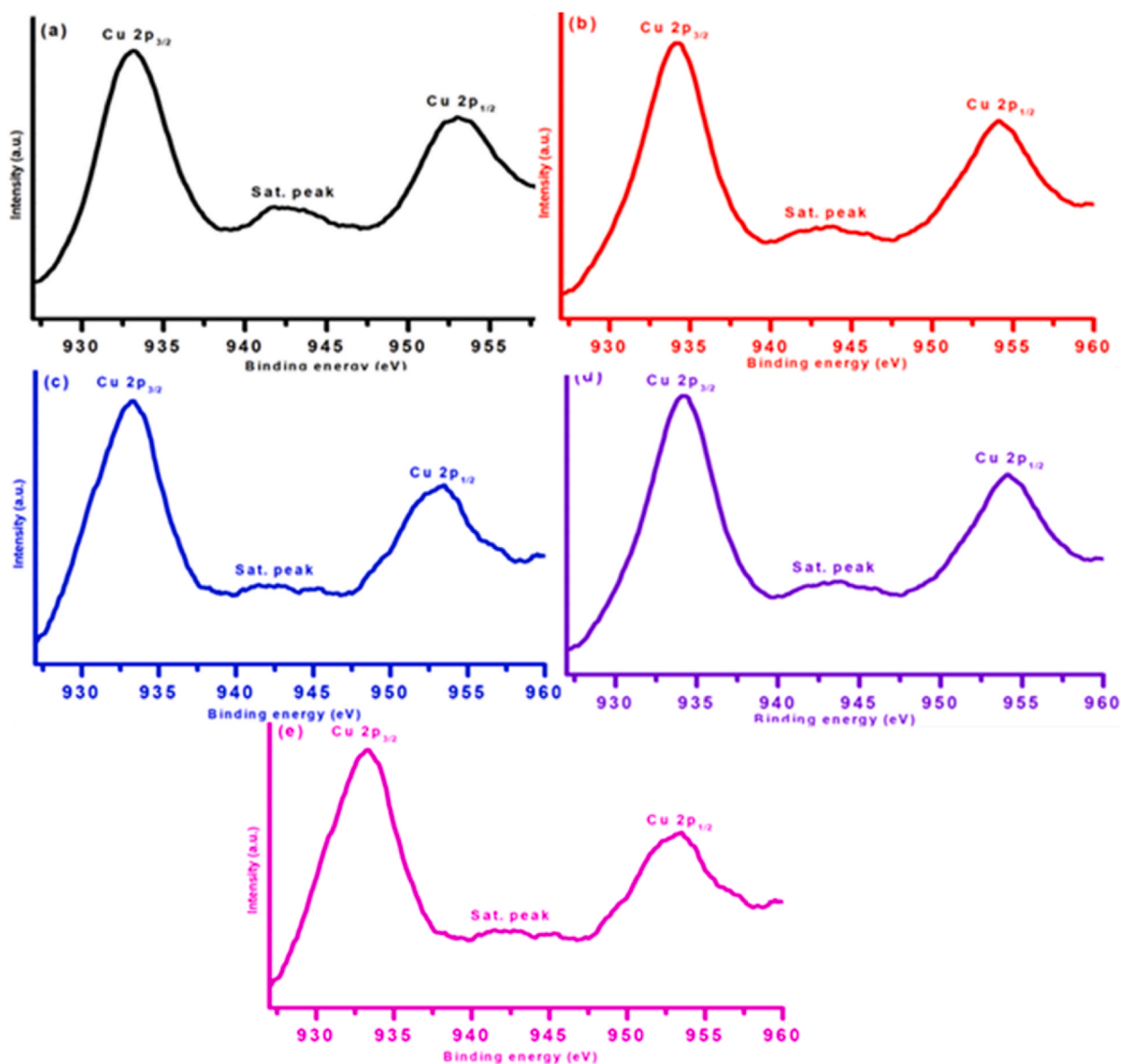


Fig. 5. XPS spectra of Cu2p for (a) Gel₁, (b) Gel₂, (c) Gel₃, (d) Gel₄ and (e) Gel₅ catalysts.

concentrations to Cu-Zn/SiO₂ catalysts. In addition, pore size of Cd-promoted silica gel supported Cu-Zn catalysts was recorded with pore size ranging from 4.77 to 7.51 nm, which confirms the mesoporosity of catalysts as exhibited by hysteresis loops of the isotherms. The current work figured out that pore size was slightly increased by Cd promotion.

This trend of increasing magnitude of pore size could be justified by decreasing magnitude in BET surface area. In summarizing the findings, the nitrogen adsorption-desorption investigations revealed no major changes in surface properties of each Cd promoted Cu-Zn/SiO₂ catalysts.

3.6. Surface chemistry of Cd-promoted silica gel supported Cu-Zn catalysts

Using XPS, the surface chemical nature and oxidation states of each Cd-promoted silica-supported Cu-Zn bimetallic catalysts was examined.

Fig. (5a-e) displays the XPS spectra of Cu2p in Cd-promoted silica-supported Cu-Zn bimetallic catalysts at different Cd concentrations. Cu2p_{3/2} and Cu2p_{1/2} are represented by the two Cu peaks in the Cu metal XPS spectra, which have binding energies with magnitudes of 932.8 and 952.9 eV, respectively. At higher binding energies of about 9 eV, the spectra showed a satellite peak in addition to these fundamental XPS peaks. The d⁹ structure of Cu in its ground state is associated with the satellite characteristic seen for

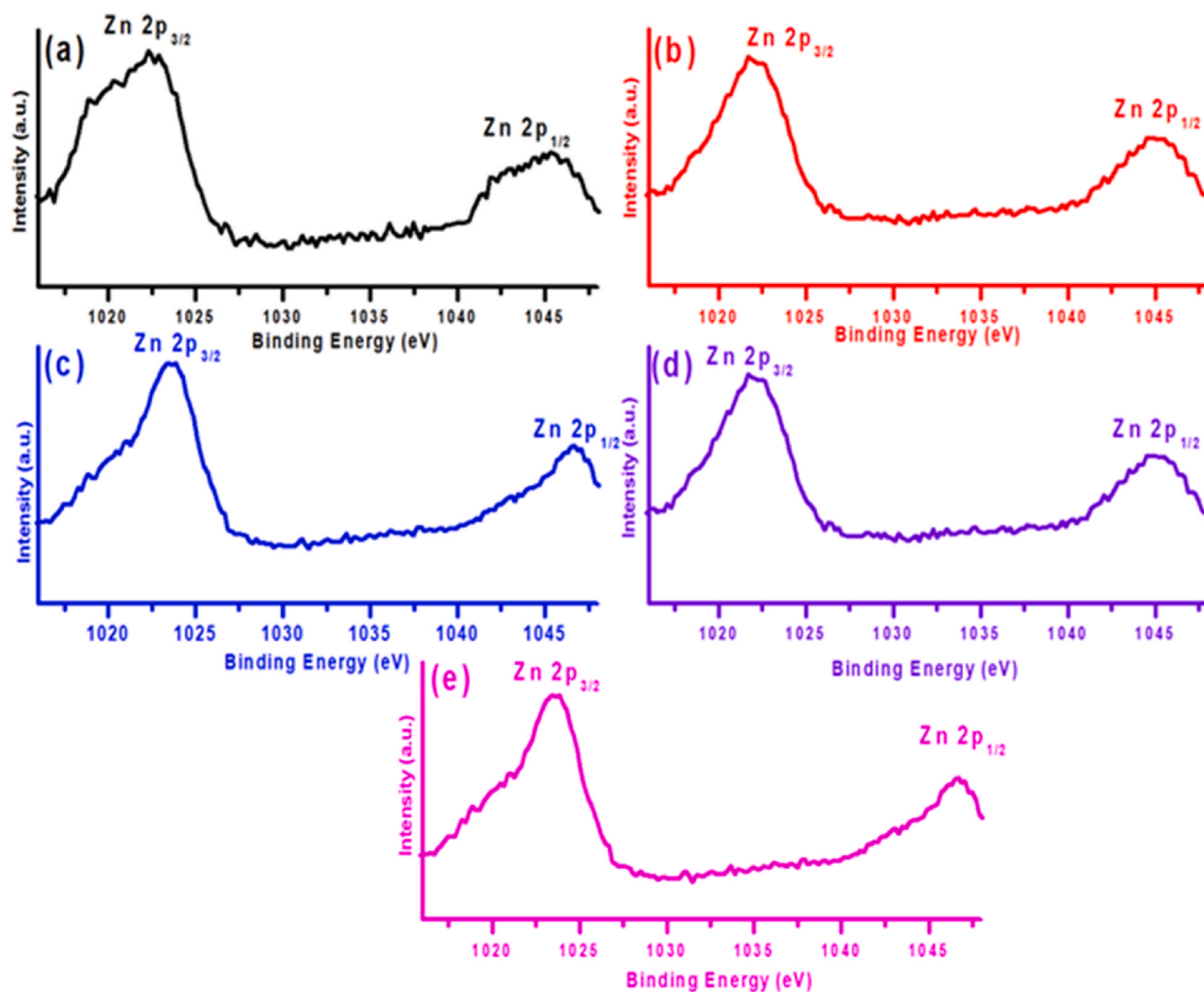


Fig. 6. XPS spectra of Zn2p for (a) Gel₁, (b) Gel₂, (c) Gel₃, (d) Gel₄ and (e) Gel₅ catalysts.

the CuO. There is no satellite peak in Cu₂O spectra because screening by charge transfer into the d states is not feasible due to the completion of the d shell of Cu₂O. Hence, XPS profiles of Cd promoted Cu-Zn/SiO₂ catalysts has figured out Cu²⁺ oxidation state of Cu metal in all studied catalysts. In contrast, the XPS spectra of reduced catalysts showed only fundamental XPS peaks with no satellite peak (Fig. S1) indicating the presence of metallic copper.

Fig. (6a-e) displays the Zn2p XPS spectra in Cu-Zn/SiO₂ catalysts that are promoted by Cd at different Cd doses. At BE scales of 1021 and 1044 eV, two typical doublets for Zn2p_{3/2} and Zn2p_{1/2} were observed, regardless of the quantity of Cd metal. Thus, Zn in Cu-Zn/SiO₂ catalysts was shown to be in the Zn²⁺ oxidation state according to XPS measurements. Therefore, XPS analyses verified presence of zinc in ZnO form.

The XPS spectra of Cd metal in Cd-promoted silica gel supported Cu-Zn catalysts are displayed in Fig. (7a-d). The picture clearly shows that, in accordance with reports in the literature [27], two observed XPS peaks at 405.3 eV and 412.1 eV are recognized as the electronic excitations of Cd 3d_{5/2} and Cd 3d_{3/2}, respectively [38]. These XPS results showed that cadmium was in its Cd²⁺ oxidation state, which suggests that CdO form of cadmium exists in Cd-promoted silica gel supported Cu-Zn catalysts. Moreover, the alteration in Cd content in C Cd-promoted silica gel supported Cu-Zn catalysts did not change positions of the Cd XPS peaks on the binding energy scale.

X-ray photoelectron spectroscopy (XPS) is a widely used technique for analyzing metal dispersion in case of metal supported catalysts [39–41]. Especially, the estimation of dispersion of different components on surface of catalyst support by taking into account the XPS peak intensity ratio of metal-support have been reported in the literature [42] As displayed by Fig. 8, the Cd content in Cd-promoted silica gel based Cu-Zn catalysts was increased, so did the XPS intensity ratio of Cd and silica (I_{Cd}/I_{silica}). A key sign of metal dispersion of catalysts components over support surface is the increasing trend in I_{Cd}/I_{silica} magnitude with corresponding Cd loading. Davis and Tatarchuk also made similar observations for TiO₂ supported silver catalysts [42]. More significantly, the XPS research results corroborate the XRD pattern's findings, which linked the dispersion of catalysts components over support's surface to

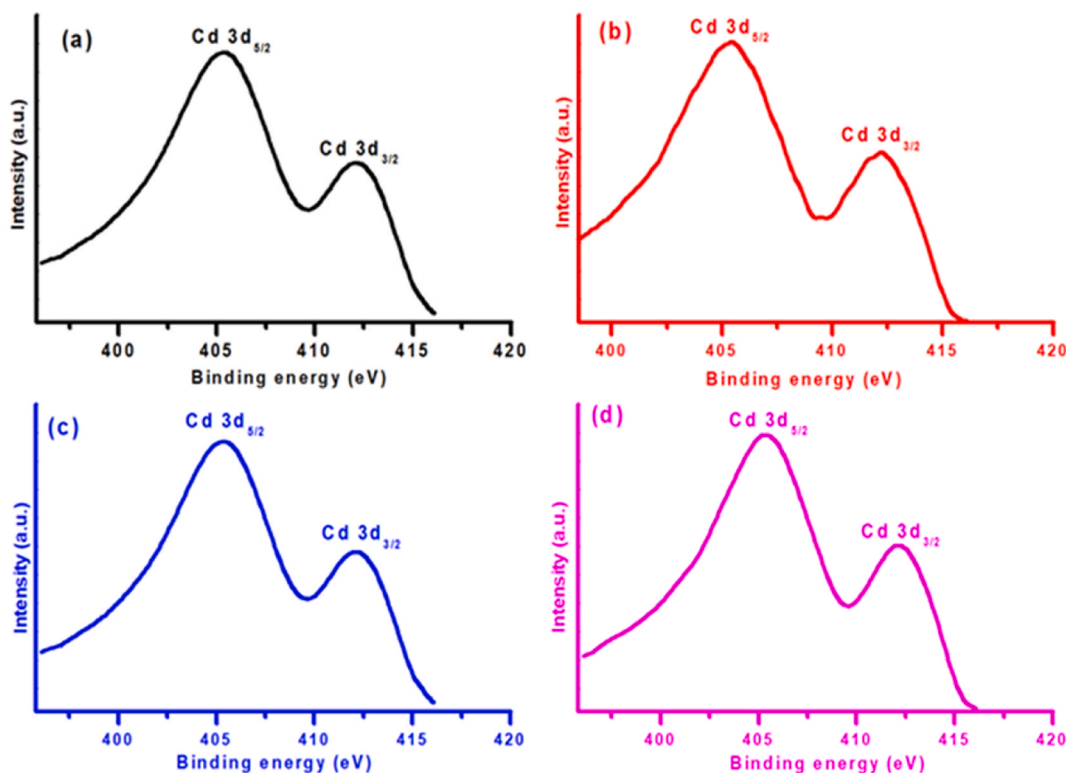


Fig. 7. XPS spectra of Cd_{3d} for (a) Gel_2 , (b) Gel_3 , (c) Gel_4 and (d) Gel_5 catalysts.

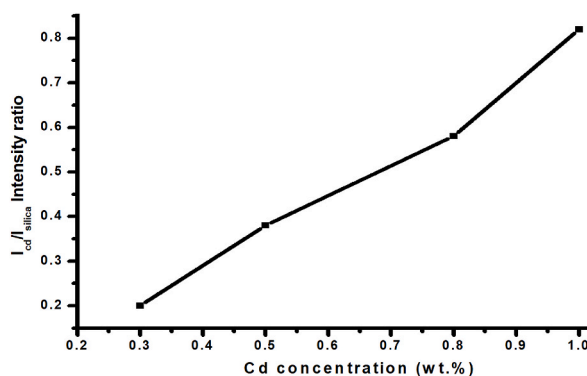


Fig. 8. Relationship between Cd concentration and I_{Cd}/I_{silica} .

the absence of metal diffraction lines. The increase in catalysts dispersion by Cd incorporation has also been reported by Mohandessi et al. [22] while investigating the promoting role of cadmium for dry methane reforming over $Ni@-\gamma-Al_2O_3$ catalysts.

In the current work, almost linear relationship was found between increasing Cd promoter concentration and I_{Cd}/I_{silica} , which reveals the dispersion of catalysts components on surface of silica support. A slight deviation in this linear trend was observed by increasing Cd concentration to 0.8 wt% as evident from the graph. This slight deviation could be due to the growth of catalysts particles with Cd promotion to that extent. By concluding the XPS investigation, the XPS results further elaborated and endorsed the findings obtained from XRD and FESEM techniques documented in the former sections.

4. Activity studies of Cd-promoted silica gel supported Cu-Zn catalysts

The catalytic activity as well as selectivity profile of each Cd-promoted silica gel supported Cu-Zn catalysts was carried out in a slurry phase tank reactor. The synthesis rate and methanol selectivity of Cu-Zn/ SiO_2 catalysts boosted by Cd are displayed in Fig. 9. By adding Cd to the parent Cu-Zn/ SiO_2 catalyst, the rate of methanol synthesis increased from 144 to 167 g.meth./Kg.cat.h. Additionally,

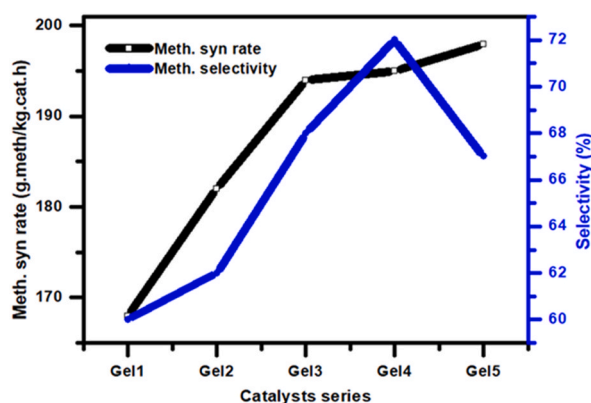


Fig. 9. Activity and selectivity trend of Cd promoted Cu-Zn/SiO₂ catalysts.

adding additional Cd to the Cd-promoted silica gel supported Cu-Zn catalysts continued the same pattern of increasing the rate of methanol synthesis as seen in Fig. 9. It is also worth to note that, improvement in methanol synthesis rate was also documented with the same pace with the Cd concentration was increased from 0.3 to 0.5 wt percent. Although, methanol synthesis rate of consistently enhanced by Cd promotion throughout the range of Cd concentration however, the intensity was slightly declined as recorded for the first two spiking of Cd metal to parental Cu-Zn/SiO₂ catalysts. On the other hand, methanol selectivity also recorded the same trend of increasing selectivity with Cd promotion. However, contradictory to the methanol synthesis rate, the selectivity of methanol was improved with Cd promotion until 0.8 wt percent however, it was declined with further rise in Cd promotion. The incorporation of highest concentration of Cd to the resulted in decline in methanol selectivity. This could be due to the strong interactions with H₂O molecules generated during the methanol synthesis reaction, which likely prevented it from improving the methanol selectivity and instead encouraged the reverse water gas shift (RWGS) reaction to produce CO. Such observations were also reported by Kourtelesis et al. [21] while reporting kinetics and thermodynamics investigation of methanol synthesis by CO₂ hydrogenation over La₂O₃-promoted CuO/ZnO/Al₂O₃ catalysts. Similarly this point could be further supported by the findings of another study conducted by Wang et al., [43]. The study concluded that although the rate of methanol production was enhanced by addition of suitable amount of water however, methanol selectivity was adversely affected by addition of water.

To summarize the activity studies, the current research work verified the pivotal promoting function of the Cd promoter in silica based Cu-Zn catalysts for CO₂ hydrogenation in terms of both catalysts activity and selectivity.

The structure-activity correlation is an important factor for understanding the mechanism and background of catalysts pertaining to the efficiency of catalysts in particular reactions. In the current case, the substantial evidence was observed leading the physical interaction of Cd metal with the parental silica based Cu-Zn catalysts. This could be inferred from the XPS and FTIR findings where no chemical shift was observed in Cd metal promoted silica based Cu-Zn catalysts having different Cd loadings. However, the promoting role of Cd could be justified based on the XRD and BET studies, where high dispersion of active metals was recorded with Cd promotion. Consequently, Cd behaved as a structural promoter in the current case rather than a chemical promoter. The current findings, elaborate the application of structural supports in methanol synthesis catalysts. Similar observation were also recorded by Koppen et al. [44] for Fischer-Tropsch synthesis where adding manganese oxide to silica based cobalt catalysts improved the metallic cobalt's dispersion in reduced catalysts. On the other hand, a larger tendency of cobalt silicate formation resulted from this increased dispersion of cobalt.

5. Conclusion

The Cd metal promoted Cu-Zn/SiO₂ catalysts were produced using co-precipitation approach in the current study. The produced catalyst was evaluated using several analytical techniques. FESEM and XRD studies revealed amorphous nature of silica support with higher dispersion of active metals on surface of support. Such, findings were further endorsed by XPS investigations. No significant chemical interaction was recorded by XPS findings. The activity data established stimulating role of Cd both in terms of synthesis rate and methanol selectivity. Structure-activity studies figured out the role of Cd as structural promoter in CO₂ hydrogenation to methanol.

CRedit authorship contribution statement

Mshari A. Alotaibi: Concept, Data curation, Funding acquisition, Writing – original draft, Writing – review & editing. **Israf Ud Din:** Data curation, Writing – review & editing, Writing – original draft, Formal analysis, Conceptualization. **Abdulrahman I. Alharthi:** Concept, Data analysis, Methodology, Writing – original draft, Writing – review & editing. **Tooba Saeed:** Concept, Writing – review & editing. **Maizatul S. Shaharun:** Concept, Formal analysis. **A. Naeem:** Concept, Supervision.

Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.heliyon.2024.e40545>.

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